1 **High resolution NMR measurements using a 400 MHz NMR with an**
2 **(RE)Ba₂Cu₃O_{7-x} high-temperature superconducting inner coil:**
3 **towards a compact super-high-field NMR**

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Abstract

Use of high-temperature superconducting (HTS) inner coils in combination with conventional low-temperature superconducting (LTS) outer coils for a NMR magnet, i.e. a LTS/HTS NMR magnet, is a suitable option to realize a high-resolution NMR spectrometer with operating frequency > 1 GHz. From the standpoint of creating a compact magnet, (RE: Rare earth) $\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ (REBCO) HTS inner coils which can tolerate a strong hoop stress caused by a Lorentz force are preferred. However, in our previous work on a first-generation 400 MHz LTS/REBCO NMR magnet, the NMR resolution and sensitivity were about ten times worse than that of a conventional LTS NMR magnet. The result was caused by a large field inhomogeneity in the REBCO coil itself and the shielding effect of a screening current induced in that coil. In the present paper, we describe the operation of a modified 400 MHz LTS/REBCO NMR magnet with an advanced field compensation technology using a combination of novel ferromagnetic shimming and an appropriate procedure for NMR spectrum line shape optimization. We succeeded in obtaining a good NMR line shape and 2D NOESY spectrum for a lysozyme aqueous sample. We believe that this technology is indispensable for the realization of a compact super-high-field high-resolution NMR.

1 **Keywords:**
2 Compact super-high-field NMR
3 High-resolution NMR measurement
4 REBCO high-temperature superconducting (HTS) coil
5 Ferromagnetic shim
6 NMR line shape optimization
7 NOESY
8
9

1. Introduction

Although higher magnetic fields are required for the improvement of sensitivity and resolution of NMR measurements, the attainable magnetic field for conventional high-resolution NMR magnets using low temperature superconductors (LTS) is ~1 GHz (a magnetic field intensity of 23.5 T) [1,2]. One solution to obtain a magnetic field higher than 1 GHz is to use a resistive magnet or a resistive-and-superconducting (i.e. hybrid) magnet [3,4]. The 1.53 GHz (36 T) hybrid magnet [5] is being developed and will be operated at the National High Magnetic Field Laboratory (NHMFL) in the near future. The drawback of such a magnet is instability of the magnetic field as the resistive magnet is charged with a very-high current power supply having a large current ripple; i.e. basically it is not easy to make high-resolution NMR measurements except for quadrupole nuclei.

Another solution is to use a superconducting inner magnet with high-temperature superconductors (HTS). There are three types of HTS; a $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-x}$ (Bi-2223) multi-filamentary tape conductor [6,7], a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-x}$ (Bi-2212) multi-filamentary round wire [1,8], and a (RE; rare earth) $\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ (REBCO or RE-123) coated tape conductor [9,10,11]. These conductors provide a sufficiently high engineering current density at a high magnetic field > 23.5 T [1], enabling an NMR magnet to exceed an operating frequency of 1 GHz. Such a beyond 1 GHz NMR magnet can be effectively made if we employ LTS low field outer coils and HTS high field inner coils. Such an arrangement was firstly proposed by workers at the Massachusetts Institute of Technology (MIT) and was called a LTS/HTS NMR magnet [12,13]. The Japanese team that includes the present authors made a basic study for a 500 MHz LTS/Bi-2223 NMR magnet [14,15] and then succeeded in developing a 1.02 GHz LTS/Bi-2223 NMR magnet [16,17]. Thus, the new era of beyond 1 GHz high-resolution NMR spectroscopy has begun.

From the viewpoint of the size of an NMR magnet, the REBCO coated tape conductors are preferred over the Bi-2223 multi-filamentary tape conductors. This is because the REBCO coils show a higher tolerance against a hoop stress generated by a Lorentz force [18], which enables the coils to be operated at high current density in a high magnetic field. If we employ multiple HTS inner coils operated at high current density $\gg 100 \text{ A/mm}^2$, a >1 GHz NMR magnet can be made

possible having a much smaller size than the 1.02 GHz LTS/Bi-2223 NMR magnet [19]. Note that it was only possible to construct the innermost coil from the Bi-2223 tapes in the 1.02 GHz magnet and the current density of that coil was limited to $\sim 130 \text{ A/mm}^2$ due to the relatively low hoop stress tolerance. In this light, we have started development of a medium field LTS/REBCO NMR magnet towards the development of a compact super-high-field high-resolution NMR.

As described in our previous paper [19], the first LTS/REBCO NMR magnet with an REBCO inner coil was developed and operated at 400 MHz. However, the REBCO coil produced some notable difficulties in generating the stable and homogeneous magnetic field required for high-resolution NMR measurements as follows; (1) a substantial magnetic field drift with time, $\sim 1000 \text{ ppm}$ field change in $\sim 100 \text{ h}$ after the magnet charge, due to a relaxation of a screening current [20] induced in the REBCO coil, (2) a notable Z^2 field error harmonic, several tens of ppm for the space within $z = \pm 1 \text{ cm}$, due to a shielding effect of the screening current on the field correction coil, (3) large tesseral harmonics [21,22], typically several to ten ppm for the space within $z = \pm 1 \text{ cm}$, originating from the screening current and a slight non-axisymmetric shape of the REBCO coil, and (4) substantial reduction in the performance of the cryoshim (superconducting shim) coils due to the shielding effect of the screening current. The first problem was suppressed by a current sweep reversal method [14,19,23] and the second was compensated with ferromagnetic passive shims using steel wires [19]. However, the third problem, i.e. the large tesseral harmonics, could not be compensated due to the fourth problem, i.e. the reduction in the cryoshim coil performance. Due to those residual tesseral harmonics, a half-height width for a one-dimensional (1D) NMR line shape for a 1% chloroform solution and a signal to noise (S/N) ratio for a 0.1% ethylbenzene solution were 15 Hz and 28, respectively. This represents a resolution and sensitivity that are more than 10-fold worse compared to a conventional LTS NMR magnet. Eventually we had to give up high-resolution NMR measurements, such as NOESY on a protein sample.

Thus, to realize a compact super-high-field LTS/REBCO NMR magnet which can be used for high-resolution NMR measurements, finding effective remedies against the screening current in the REBCO coil is essential. Use of a multi-filamentary REBCO coated tape conductor [24,25,26] is one

possible method to reduce the effects of the screening current itself, although the fabrication of those conductors in long lengths still needs considerably more development. Furthermore, advancement in a more powerful shimming technology to compensate for the tesseral field error harmonics, even under the influence of the screening current, is particularly important.

In work described in the present paper, we modified the previous 400 MHz LTS/REBCO NMR magnet by installing a ferromagnetic passive shim for the large tesseral harmonics and an inner active cryoshim coil for the large Z₂ harmonic in combination with the conventional cryoshim coils and room temperature (RT) shim coils. These new systems were installed inside the REBCO coil to effectively compensate the large field error harmonics by avoiding the shielding effect of the screening current. In addition, the currents for the RT shim coils were optimized to obtain a sufficiently narrow NMR spectrum line shape, which considers a higher-order field error harmonics generated as a side effect of the ferromagnetic shim. Based on these operations, a multi-dimensional high-resolution NMR spectrum for a protein sample is demonstrated.

2. Experimental

2.1 The 400 MHz LTS/REBCO NMR magnet #2

The 400 MHz LTS/REBCO NMR magnet is composed of a REBCO inner coil and LTS outer coils; the details of the previously operated magnet #1 are described in ref. [19]. As shown in **Fig. 1**, for the present LTS/REBCO NMR magnet #2, an additional cryoshim (superconducting shim) coil wound with a Nb₃Sn LTS conductor was installed inside the REBCO coil to effectively compensate the large Z₂ error harmonic. The winding of the REBCO coil for the present magnet is thinner than that of the previous coil due to the space required for this inner-Z₂ cryoshim coil. In addition, a ferromagnetic shim composed of several steel sheets to compensate the tesseral harmonics was installed outside the RT shim coil unit (see **Fig. 1**). The detailed configuration of the ferromagnetic shim has been described elsewhere [27]. The magnet was connected to a highly stabilized DC power supply (Model 854, Danfysik); the current fluctuation amplitude is < 1 ppm. For a continuous operation without liquid helium refilling, evaporated helium gas was recondensed using a 4 K

pulse-tube cryocooler.

2.2 Compensation procedure of the large field inhomogeneity of the magnet

After the magnet was charged and a temporal drift of the magnetic field was suppressed by a current sweep reversal method [19], the large Z2 harmonic [19] was compensated with the inner-Z2 cryoshim coil. Then, ≤ 2 nd-order field error harmonics were compensated using a newly developed simple ferromagnetic shim composed of several arc-shaped steel sheets [27] and the conventional cryoshim coils placed outside the LTS coils. Finally, the field harmonics from the 1st to the 7th order were compensated with the RT shim coils. In these operations, inhomogeneity of the magnetic field was evaluated using a field mapping system (Resonance Research, FMU1200). A small NMR sample was moved along a helical path, 8.5 mm in radius and 30 mm in height, with a rotational pitch of 2.5 mm. The axial component of the magnetic field, i.e. B_z , was measured at each point on the helical path. Field distributions within $z = \pm 15$ mm were expanded with the Legendre spherical harmonics up to the 4th order [22]. The field inhomogeneity was evaluated for each harmonic such as zonal harmonics (Z1, Z2, Z3, ...) and tesseral harmonics (X, Y, ZX, ZY, ...).

After the compensation of the field inhomogeneity, the water chiller which was cooling the DC power supply and the compressor of the pulse-tube cryocooler was halted unexpectedly. As a result, the magnet entered a current dump mode and fully discharged. The magnet was charged again and the same procedure for the compensation of the field inhomogeneity was made; the experimental results shown in the present paper were obtained for this second operation.

2.3 NMR spectrum line shape optimization and NMR measurements

After the compensation of the large field inhomogeneity of the magnet, a NMR line shape optimization for 1% chloroform in acetone- d_6 was made by manually adjusting the currents of the RT shim coils while observing the field-frequency lock signal [28]. The optimization procedure for the currents, which considers higher-order field error harmonics generated by the ferromagnetic shim, will be described in the following section. Then, a NMR sensitivity test was made for 0.1%

ethyl benzene in CDCl₃ solution. Finally a 2D NOESY measurement using WATERGATE was made for 2 mM lysozyme in 90% H₂O and 10% D₂O.

3. Experimental results

3.1 Initial temporal drift of the field harmonics

The magnet was charged to 115.6 A with a current sweep rate of 0.01 A/s generating a central magnetic field of 9.396 T, i.e. 400.1 MHz. To suppress a drift of the magnetic field, a current sweep reversal method [19] was applied to the magnet; the magnet was first charged to 127.1 A which is 110 % of the operating current and then it was discharged immediately to the operating current, 115.6 A.

After these operations, temporal drifts of the field harmonics were measured with the field mapping system from $t = 362.8$ h to 671.7 h. Note that t is the elapsed time after the current sweep reversal. The lower-order field harmonics, such as Z1, X, and Y showed larger drifts than the other harmonics, as shown in **Fig. 2**. This is caused by the slight relaxation of the screening current in the REBCO inner coil. Due to these drifts of the field harmonics, a slight modification of the ferromagnetic shim design was required during the following shimming process.

3.2 Compensation of the large field inhomogeneity originating from the REBCO inner coil

Inner-Z2 cryoshim coil

Field distributions along the z -axis (the coil axis) were measured using the NMR Tesla-meter to coarsely estimate the Z2 error harmonic. The amplitude of the Z2 harmonic was -19807 Hz/cm² (see **Table 1(a)**). The inner-Z2 cryoshim coil was charged to 15 A and the Z2 harmonic was reduced to 167 Hz/cm² as shown in **Table 1(b)**.

Outer-cryoshim coils

After the compensation of the large Z2 harmonic, the field error harmonics were measured using the field mapping system. The tesseral harmonics originating from the REBCO inner coil notably appeared, as shown by **Table 1(b)**; the amplitudes for ZX, ZY, C2 and S2 were -5212

Hz/cm², -6887 Hz/cm², -663 Hz/cm², and 1199 Hz/cm², respectively. The performance of the outer cryoshim coils were substantially reduced, especially for the tesseral harmonics [19], and those for the ZX, ZY, C2 and S2 shim coils were only <500 Hz/cm². Therefore, the Z1, Z2, X, and Y harmonics were effectively reduced to -31 Hz/cm, 53 Hz/cm², 10 Hz/cm, and -132 Hz/cm, respectively, while the ZX, ZY, and S2 were uncompensated and remained respectively -6277 Hz/cm², -7668 Hz/cm², and 1153 Hz/cm² as shown in **Table 1(c)**.

Ferromagnetic passive shims

The residual tesseral harmonics, ZX, ZY and S2 were compensated by the ferromagnetic shim. The shim was designed to generate the 1st order and the 2nd order tesseral harmonics (i.e. X, Y, ZX, ZY, C2, and S2) [27] and several modifications of the configuration were made. After the determination of the ferromagnetic shim configuration, currents for the outer SC shim coils for the tesseral harmonics were finely adjusted. As a result, these tesseral harmonics were successfully compensated and the ZX, ZY, and S2 harmonics were reduced to 35 Hz/cm², 22 Hz/cm², and 2 Hz/cm², respectively (see **Table 1(d)**). However, the present ferromagnetic shim generates not only the target 1st and 2nd order tesseral harmonics but also undesired higher-order tesseral harmonics [21]. As shown in **Table 1(c) and 1(d)**, the 3rd order and the 4th order tesseral harmonics were increased as follows; Z2Y: 242 Hz/cm³ → 334 Hz/cm³, ZS2: 139 Hz/cm³ → 886 Hz/cm³, Z3X: 140 Hz/cm⁴ → 411 Hz/cm⁴, Z3Y: -134 Hz/cm⁴ → 336 Hz/cm⁴, and Z2S2: -222 Hz/cm⁴ → -703 Hz/cm⁴.

RT shim coils

After determining the configuration of the ferromagnetic shim and associated correction of the cryoshim coils, all the residual harmonics except C4 and S4 were compensated with the RT shim coils. After repetition of the operations, eventually, all the harmonics were decreased to <38 Hz/cmⁿ, i.e. 0.15 ppm/cmⁿ, as shown in **Table 1(e)**. Considering the reduced field error harmonics, a NMR spectrum line shape optimization appeared to be easy to achieve and the results will be described in the following section.

3.3 Line shape test and sensitivity test

^1H NMR spectra after a spectrum line shape optimization are shown in **Fig. 3**. First, the optimization was started from the magnetic field distribution corresponding to **Table 1(e)** as an initial condition. All the 34 field harmonics were changed interactively [28] from the lower-order to the higher-order harmonics to increase the field-frequency lock signal intensity. However, as shown in **Fig. 3(a)**, the spectrum widths at the 50%, 0.55% and 0.11 % heights were 5.3 Hz, 74.8 Hz and 85.2 Hz, respectively. They are much worse than the desired line shape [28]. Secondly, the optimization was restarted for all the 34 harmonics from an initial condition in which all the RT shim coil currents are zero. However, as shown in **Fig. 3(b)**, the obtained spectrum widths were 1.7 Hz, 81.1 Hz, and 105.8 Hz, which are still worse. Then, we retried the optimization started from an initial condition in which the RT shim coil currents for the ≥ 3 rd order harmonics are the values described in **Table 1(e)**, and the currents for other lower degree harmonics are zero. Under the condition, only the lower order harmonics were corrected first, and then all the 34 harmonics were optimized. As a result, a much better line shape was obtained, as shown in **Fig. 3(c)**; i.e. the ^{13}C satellite peaks are clearly observed and the spectrum widths are 0.5 Hz, 15.9 Hz, and 36.3 Hz, respectively. The reason for the difficulties encountered in the former optimization methods will be discussed later.

Figure 4 shows the ^1H sensitivity test result for 0.1% ethylbenzene in CDCl_3 obtained after the line shape optimization. The ^1H sensitivity, determined by the ratio of the central peak height of the quartet at 2.7 ppm to the base line noise over 0.4 ppm, was 318. The value is 11.4 times higher than the ratio of 28 obtained for the previous magnet #1 [19]. Comparison of the resolution and the sensitivity to other conventional NMR magnets will be described later.

3.4 NOESY for a protein sample

For the previous 400 MHz LTS/REBCO NMR magnet-#1, we could not make a precise NOESY measurement for a protein sample due to the residual field inhomogeneity [19]; the line

shape was so broad that the water signal could not sufficiently suppressed and the protein signals were buried. To the contrary, **Fig. 5** shows a 2D NOESY spectrum of a lysozyme sample obtained for the present magnet-#2. The water signal was well suppressed and the NOESY peak positions are nearly the same as those achieved by the 500 MHz LTS NMR magnet [15].

4. Discussion

4.1 Comparison with other NMR magnets

The NMR resolution and sensitivity are compared in **Table 2** between (a) the present 400 MHz LTS/REBCO NMR magnet #2, (b) the previous 400 MHz LTS/REBCO NMR magnet #1 [19], (c) the 500 MHz LTS/Bi-2223 NMR magnet [14], and (d) a conventional 500 MHz LTS NMR magnet [29]. For the present NMR magnet #2, both resolution (spectrum half-height width without sample rotation) and sensitivity are improved by >10 times compared to the previous NMR magnet #1 (see **Tables 2(a)** and **2(b)**). Considering the NMR sensitivity is proportional to the 1.75th power of the magnetic field intensity [30], the S/N ratio of 318 at 400 MHz corresponds to 470 at 500 MHz, which is comparable to the S/N ratio 512 for the 500 MHz LTS/Bi-2223 NMR magnet which showed much smaller effects of the screening current [14]. Thus, we have demonstrated that sufficient resolution and sensitivity can be obtained even under the strong influence of the screening current of the REBCO coil by introducing the new combination of the shimming technology including the ferromagnetic shim. Although those values are slightly worse compared to the LTS NMR magnet (see **Table 2(d)**), we believe that further optimization will give better results.

4.2 Combination of the ferromagnetic shim and the RT shim for high-resolution NMR

As described above, we encountered unexpected difficulty in optimizing the NMR spectrum line shape, even though the field error harmonics were fully compensated with the advanced method, including the ferromagnetic shim as shown in **Table 1(e)**. Here the reason of the difficulty and a method for a line shape optimization procedure for a LTS/REBCO NMR magnet with large field inhomogeneity are discussed.

Tables 3(a) and 3(b) show the electric currents for the RT shim coils corresponding to **Table 1(e)** and those corresponding to the successful NMR spectrum line shape shown in **Fig. 3(c)**, respectively. Note that the current values are represented by the field gradient, Hz/cm². For the present magnet #2, the ferromagnetic shim generated undesired higher-order tesseral harmonics [27] such as Z2X, Z2Y, ZC2, ZS2, Z3X, Z3Y, Z2C2, and ZC3. Therefore, larger number of harmonics must be controlled with the RT shim coils compared to a usual NMR spectrum line shape optimization for a LTS NMR magnet. However, obviously only the lower-order harmonics, such as Z, Z2, Z4, X, Y, ZX, and ZY, had been changed in the comparison shown in **Tables 3(a) and 3(b)** (see the bold figures in the fifth column of the table). This indicates that only the lower-order harmonics were changed and the other higher-order harmonics were preserved before and after the replacement of the field mapping unit by the NMR probe. Therefore, as demonstrated in the present experiment, the required procedure for the line shape optimization for the LTS/REBCO NMR magnet is as follows: (i) Setting the current values of the RT shim coils for the ≥ 3 rd order harmonics according to the harmonics obtained by the field mapping unit. (ii) Optimizing the current values only for the < 3 rd order harmonics. (iii) Optimizing all the harmonics in fine adjustment. If all the harmonics are adjusted interactively from the beginning, the combination of the RT shim coil currents tends to deviate from the optimized values, resulting in a bad line shape (see the spectra for **Fig. 3(a) and 3(b)**).

A gradient shimming [28] technique was tried, but however it could not be operated. This may be due to the field instability in the external current mode and very large field error harmonics in the LTS/REBCO NMR magnet. This has to be further investigated.

4.3 Instability of the field-frequency lock signal

In the NMR spectrum line shape optimization process, a temporal instability of the field-frequency lock signal was observed. As shown in **Fig. 6(a)**, the signal fluctuated with ~100 s cycles. Although instability of the signal is also observed for a conventional LTS NMR magnet operated in persistent current mode, the amplitude of the fluctuation for the present magnet was more noticeable. The fluctuation interfered with the optimization process as the operator could not judge whether the change in the signal level is due to the change of the RT shim current or not.

Figure 6(b) shows the fluctuation of the central magnetic field intensity which was obtained by picking the peak frequencies of the NMR spectra without field-frequency lock operation. This fluctuation originated from the current fluctuation of the DC power supply [14,29]. Considering the fact that the cycle of the fluctuation of ~100 s is comparable to that of the lock signal shown in **Fig. 6(a)**, the instability of the lock signal should be caused by the fluctuation of the magnetic field intensity. The present magnet intrinsically has a large Z2 error harmonic and this might fluctuate in accompaniment with the current fed from the DC power supply. This instability causes a degradation of the NMR spectrum line shape during the measurements. Therefore, an auto shimming operation of Z2 is required during measurements to keep the line shape as sharp as those shown in **Fig. 3(c)**

4.4 Significance of the present work towards the development of a compact super-high-field NMR

As described in the introduction, finding remedies for the deleterious effect of the screening current are essential to realize a compact super-high field NMR magnet. One potential solution is to use conductors that exhibit a reduced effect of the screening current, such as multi-filamentary REBCO coated-conductors [24,25,26], and another is the use of an advanced shimming technology to compensate the field inhomogeneity.

A design of a compact 1.2 GHz LTS/REBCO NMR magnet [19] shows that the total radial thickness of the multiple REBCO coils is several times larger than that for the present 400 MHz

1 magnet. This implies that the effect of the screening current would be still a problem even if we
2 could use conductors that reduce the effect of the screening current. The problem is that types and
3 magnitude of the tesseral harmonics that will appear in such a magnet are not predictable. In this
4 light, the present ferromagnetic shim has a great significance. It can be prepared on-site for
5 unpredictable large tesseral harmonics and used like “active” shim coils, as its configuration can be
6 quickly modified on-demand based on the measured field harmonics, as described in ref. [27]. The
7 RT shim coils are also required to support the ferromagnetic shim by compensating the higher-order
8 tesseral harmonics generated by the ferromagnetic shim as a side effect.

9 The application of this technique to a compact super-high-field NMR magnet has potential
10 problems such as the strong electromagnetic force generated during the inserting operation and
11 temporal changes of the field harmonics due to room temperature changes [27]. Therefore, they have
12 to be further investigated in conjunction with the magnet design.

14 **5. Conclusions**

15 A compensation of the large field inhomogeneity, an NMR spectrum line shape optimization, an
16 NMR sensitivity test, and a NOESY measurement for a protein sample were made for a 400 MHz
17 LTS/REBCO NMR magnet which has difficulties in generating a homogeneous magnetic field due
18 to the effects of a screening current. It was demonstrated that good line shape and sensitivity, and a
19 2D NOESY spectrum for a protein sample, i.e. high-resolution NMR measurements, can be achieved
20 with a combination of (a) advanced field compensation technology, including an on-site constructed
21 ferromagnetic shim for the unpredictable tesseral harmonics and (b) an appropriate procedure for the
22 NMR spectrum line shape optimization considering the existence of the higher-order field error
23 harmonics due to the ferromagnetic shim. We believe that these are key technologies for
24 high-resolution NMR measurements with a compact super-high-field NMR magnet using HTS inner
25 coils.

Acknowledgement

This work was supported by the Japan Science and Technology Agency (JST), under the Strategic Promotion of Innovative Research and Development Program. Part of the work was carried out in the RIKEN Junior Research Associate Program and Special Postdoctoral Researcher Program.

References

- [1] D. Larbalestier, J. Jiang, U. Trociewitz, F. Kametani, C. Scheuerlein, M. Dalban-Canassy, M. Matras, P. Chen, N. C. Craig, P. J. Lee, and E. E. Hellstrom, Isotropic round-wire multifilament cuprate superconductor for generation of magnetic fields above 30 T, *Nat. Mat.*, **13**, 1-7, 2014.
- [2] Bruker home page,
<https://www.bruker.com/products/mr/nmr/magnets/magnets/avance-1000/technical-details.html>
- [3] Z. Gan, H. Kwak, M. Bird, T. Cross, P. Gor'kov, W. Brey, and K. Shetty, High-field NMR using resistive and hybrid magnets, *J. Mag. Res.*, **191**, 135-140, 2008.
- [4] Y. Y. Lin, S. Ahn, N. Murali, W. Brey, C. R. Bowers, and W. S. Warren, High-resolution, >1 GHz NMR in unstable magnetic fields, *Phys. Rev. Lett.*, **85**, 3732- 3735, 2000.
- [5] M. D. Bird, H. Bai, S. Bole, J. Chen, I. R. Dixon, H. Ehmler, A. V. Gavrilin, T. A. Painter, P. Smeibidl, J. Toth, H. Weijers, T. Xu, and Y. Zhai, The NHMFL hybrid magnet projects, *IEEE Trans. Appl. Supercond.*, **19**, 1612-1616, 2009.
- [6] N. Ayai, S. Kobayashi, M. Kikuchi, T. Ishida, J. Fujikami, K. Yamazaki, S. Yamade, K. Tatamidani, K. Hayashi, K. Sato, H. Kitaguchi, H. Kumakura, K. Osamura, J. Shimoyama, H. Kamijyo, Y. Fukumoto, Progress in performance of DI-BSCCO family, *Physica C*, **468**, 1747-1752, 2008.
- [7] T. Nakashima, S. Kobayashi, T. Kagiya, K. Yamazaki, M. Kikuchi, S. Yamade, K. Hayashi, K. Sato, J. Shimoyama, H. Kitaguchi, H. Kumakura, Recent R&D progress on DI-BSCCO wires with high critical current properties, *Physica C*, **471**, 1086-1089, 2011.
- [8] F. Kametani, J. Jiang, M. Matras, D. Abaimov, E. E. Hellstrom, and D. C. Larbalestier, Comparison of growth texture in round wire Bi2212 and flat Bi2223 wires and its relation to high critical current density development, *Scientific Reports*, **5**, 8285, 2015.
- [9] D. W. Hazelton, V. Selvamanickam, J. M. Duval, D. C. Larbalestier, W. D. Markiewicz, H. W. Weijers, and R. L. Holtz, Recent development in 2G HTS coil technology, *IEEE Trans. Appl. Supercond.*, **19**, 2218-2222, 2009.
- [10] H. Maeda and Y. Yanagisawa, Recent developments in high-temperature superconducting magnet technology (Review), *IEEE Trans. Appl. Supercond.*, **24**, 4602412, 2014.
- [11] C. Senatore, M. Alessandrini, A. Lucarelli, R. Tediosi, D. Uglietti, and Y. Iwasa, Progresses and challenges in the development of high-field solenoidal magnets based on RE123 coated conductors, *Supercond. Sci. Technol.*, **27**, 103001 (26 pp), 2014.

- [12] Y. Iwasa, HTS and NMR/MRI magnets: Unique features, opportunities, and challenges, *Physica C*, **445-448**, 1088-1094, 2006.
- [13] S. Hahn, J. Bascunan, H. Lee, E. S. Bovrov, W. Kim, M. C. Ahn, and Y. Iwasa, Operation and performance analyses of 350 and 700 MHz low-/high-temperature superconductor nuclear magnetic resonance magnets: A march toward operating frequencies above 1 GHz, *J. Appl. Phy.*, **105**, 024501, 2009.
- [14] Y. Yanagisawa, H. Nakagome, K. Tennmei, M. Hamada, M. Yoshikawa, A. Otsuka, M. Hosono, T. Kiyoshi, M. Takahashi, T. Yamazaki, and H. Maeda, Operation of a 500 MHz high temperature superconducting NMR: Towards an NMR spectrometer operating beyond 1 GHz, *J. Mag. Res.*, **203**, 274-282, 2010.
- [15] T. Kiyoshi, S. Choi, S. Matsumoto, K. Zaitse, T. Hase, T. Miyazaki, M. Hamada, M. Hosono, Y. Yanagisawa, H. Nakagome, M. Takahashi, T. Yamazaki, and H. Maeda, HTS-NMR: Present Status and Future Plan, *IEEE Trans. Appl. Supercond.*, **20**, 714-717, 2010.
- [16] K. Hashi, S. Ohki, S. Matsumoto, G. Nishijima, A. Goto, K. Deguchi, K. Yamada, T. Noguchi, S. Sakai, M. Takahashi, Y. Yanagisawa, S. Iguchi, T. Yamazaki, H. Maeda, R. Tanaka, T. Nemoto, H. Suematsu, T. Miki, K. Saito, T. Shimizu, Achievement of 1020 MHz NMR, *J. Mag. Res.*, **256**, 30-33, 2015.
- [17] G. Nishijima, S. Matsumoto, K. Hashi, S. Ohki, A. Goto, T. Noguchi, S. Iguchi, Y. Yanagisawa, M. Takahashi, H. Maeda, T. Miki, K. Saito, R. Tanaka, and T. Shimizu, Development of Beyond-1 GHz NMR system – Successful Upgrade of 920 MHz NMR magnet to 1020 MHz Using Bi-2223 Innermost Coil –, *Submitted to IEEE Trans. Appl. Supercond.*
- [18] S. Matsumoto, T. Kiyoshi, A. Otsuka, M. Hamada, H. Maeda, Y. Yanagisawa, H. Nakagome and H. Suematsu, Generation of 24T at 4.2K using a layer-wound GdBCO insert coil with Nb₃Sn and Nb-Ti coils, *Supercond. Sci. Technol.*, **25**, 025017, 2012.
- [19] Y. Yanagisawa, R. Piao, S. Iguchi, H. Nakagome, T. Takao, K. Kominato, M. Hamada, S. Matsumoto, H. Suematsu, X. Jin, M. Takahashi, T. Yamazaki, and H. Maeda, Operation of a 400 MHz NMR magnet using a (RE:Rare Earth)Ba₂Cu₃O_{7-x} high-temperature superconducting coil: Towards an ultra-compact super-high field NMR spectrometer operated beyond 1 GHz, *J. Mag. Res.*, **249**, 38-48, 2014.
- [20] Y. Koyama, T. Takao, Y. Yanagisawa, H. Nakagome, M. Hamada, T. Kiyoshi, M. Takahashi, and H. Maeda, Towards beyond 1GHz NMR: Mechanism of the long-term drift of screening current-induced magnetic field in a Bi-2223 coil, *Physica C*, **469**, 694-701, 2009.
- [21] F. Romeo and D. I. Hoult, Magnetic field profiling: Analysis and correcting coil design, *Magnetic Resonance in Medicine*, **1**, 44-65, 1984.
- [22] D. F. Hillenbrand, K. M. Lo, W. F. B. Puncard, T. G. Reese, P. M. Starewicz, High-order MR shimming: a simulation study of the effectiveness of competing methods, using an established

- 1 susceptibility model of the human head, *Applied Magnetic Resonance*, **29**, 39-64, 2005.
- 2 [23] Y. Yanagisawa, H. Nakagome, Y. Koyama, R. Hu, T. Takao, M. Hamada, T. Kiyoshi, M.
3 Takahashi, and H. Maeda, Effect of current sweep reversal on the magnetic field stability for a
4 Bi-2223 superconducting solenoid, *Physica C*, **469**, 1996–1999, 2009.
- 5 [24] T. Machi, K. Nakao, T. Kato, T. Hirayama, and K. Tanabe, Reliable fabrication process for
6 long-length multi-filamentary coated conductors by a laser scribing method for reduction of AC
7 loss, *Supercond. Sci. Technol.*, **26**, 105016 (15pp), 2013.
- 8 [25] J. Souc, F. Gomory, J. Kovac, R. Nast, A. Jung, M. Vojenaciak, F. Grilli, and W. Goldacker,
9 Low AC loss cable produced from transposed striated CC tapes, *Supercond. Sci. Technol.*, **26**,
10 075020 (5pp), 2013.
- 11 [26] Y. Yanagisawa, Y. Xu, X. Jin, H. Nakagome, and H. Maeda, Reduction of screening
12 current-induced magnetic field of REBCO coils by the use of multi-filamentary tapes, *IEEE*
13 *Trans. Appl. Supercond.*, **25**, 6603705, 2015.
- 14 [27] S. Iguchi et al., To be submitted to *Supercond. Sci. Technol.*
- 15 [28] T. D. W. Claridge, High resolution NMR Techniques in Organic Chemistry, Elsevier, Oxford,
16 1999.
- 17 [29] Y. Yanagisawa, H. Nakagome, M. Hosono, M. Hamada, T. Kiyoshi, F. Hobo, M. Takahashi, T.
18 Yamazaki, and H. Maeda, Towards beyond-1 GHz solution NMR: Internal ^2H lock operation in
19 an external current mode, *J. Mag. Res.*, **192**, 329–337, 2008.
- 20 [30] R. Freeman, A hand book of nuclear magnetic resonance, Longman Group United Kingdom;
21 2nd edition (April 1997).
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- 23

Table captions:

Table 1. Magnetic field harmonics (a) after the magnet charging, (b) after the operation of the inner-Z2 cryoshim coil, (c) after the operation of the outer cryoshim coils, (d) after the operation of the ferromagnetic shim and (e) after the operation of the RT shim coils. The harmonics for (a) was obtained using the NMR Tesla-meter. Those for (b), (c), (d) and (e) were obtained using the field mapping system.

Table 2. Comparison of the NMR spectrum resolution and sensitivity for the present magnet with other magnets.

Table 3. Values of the RT shim coils current (a) after the compensation of the field inhomogeneity and those (b) after the succeeded NMR spectrum line shape optimization. The 5th column shows the ratio of (b) to (a). The current values are represented in Hz/cmⁿ.

Figure captions:

Figure 1. Cross sectional view of the 400 MHz LTS/REBCO NMR magnet #2.

Figure 2. Temporal drifts of the magnetic field harmonics after the 10 % current sweep reversal operation.

Figure 3. ^1H NMR spectra for 1% chloroform in acetone- d_6 for the present 400 MHz LTS/REBCO NMR magnet #2 obtained after the line shape optimization with the initial conditions in which (a) the RT shim coil currents corresponding to **Table 1(e)**, (b) all the RT shim coil currents were zero, and (c) the RT shim coil currents for the $>2\text{nd}$ degree harmonics were the values corresponding to **Table 1(e)**, and those for the other lower-order harmonics were zero. The spectra were obtained without sample spinning.

Figure 4. A sensitivity test result for the present 400 MHz LTS/REBCO NMR magnet-#2. The sample was 0.1% ethyl benzene in CDCl_3 . The spectrum was obtained from a single scan with sample rotation of 20 Hz.

Figure 5. A 2D NOESY spectrum for 2 mM lysozyme in 90% H_2O and 10% D_2O obtained using the present 400 MHz LTS/REBCO NMR magnet #2. The water signal was suppressed by WATERGATE. The number of scans was 16 and the measurement time interval was ~ 3 h. Auto RT shimming for Z, Z2, X and Y was in operation during the measurement.

Figure 6. (a) Temporal change of the signal level of the field-frequency lock for the final stage of the line shape optimization corresponding to the spectrum shown in **Fig. 3(c)**. The sample was 1% chloroform in acetone- d_6 . The signal fluctuated with a ~ 100 s cycle. (b) Instability of the magnetic field intensity obtained from peak frequencies of the NMR spectra for 1% chloroform in acetone- d_6 without field-frequency lock operation. The intensity fluctuated with ~ 100 s cycle and the peak-to-peak amplitude of 0.05 – 0.2 ppm. Note that the data for (a) and (b) were obtained separately.

Table 1

Harmonics		Order, <i>n</i>	Amplitude (Hz/cm ⁿ)				
			(a)After the magnet charging	(b) After the operation of the inner-Z2 cryoshim coil	(c) After the operation of the outer cryoshim coils	(d) After the operation of the ferro. shim	(e) After the operation of the RT shim coils
Zonal	Z1	1	-1068	-14745	-31	-52	13
	Z2	2	-19807	167	53	7	29
	Z3	3	-767	-873	-811	-688	17
	Z4	4	357	451	417	-491	-29
Tesseral	X	1	-	-283	10	83	-6
	Y	1	-	-10143	-132	0	-2
	ZX	2	-	-5212	-6277	35	-5
	ZY	2	-	-6687	-7668	22	2
	C2	2	-	-663	39	17	0
	S2	2	-	1199	1153	2	0
	Z2X	3	-	766	959	874	-4
	Z2Y	3	-	-77	242	334	4
	ZC2	3	-	542	623	518	-3
	ZS2	3	-	327	139	886	-6
	C3	3	-	118	42	121	1
	S3	3	-	248	232	177	2
	Z3X	4	-	124	140	411	-2
	Z3Y	4	-	23	-134	336	8
	Z2C2	4	-	-206	-304	-128	-4
	Z2S2	4	-	-235	-222	-703	3
	ZC3	4	-	157	135	290	8
	ZS3	4	-	50	110	65	-11
	C4	4	-	77	167	-4	19
	S4	4	-	8	-69	-33	-38

Table 2

		(a) 400 MHz LTS/REBCO NMR #2	(b) 400 MHz LTS/REBCO NMR #1 [19]	(c) 500 MHz LTS/Bi-2223 NMR [14]	(d) 500 MHz LTS NMR [29]
		(present)	(previous)		
Spectrum width (Hz) ¹⁾	Height				
	50%	0.2 [*] (0.5 [†])	0.3 [*] (15 [†])	0.61 [*] (-)	0.53 [*] (-)
	055%	7.0 [*] (15.9 [†])	10 [*] (235 [†])	8.7 [*] (-)	8 [*] (-)
	0.11%	19.2 [*] (36.3 [†])	40 [*] (286 [†])	<30 [*] (-)	11 [*] (-)
S/N ratio ²⁾		318	28	512	599

¹⁾ Sample: 1% chloroform in acetone-d₆.
^{*}Sample spinning frequency: 20 Hz.
[†]Without sample spinning.
²⁾ Sample: 0.1% ethyl benzene in CDCl₃. Sample spinning frequency: 20 Hz.

Table 3

Field harmonics	Order, <i>n</i>	Current for the RT shim coils (Hz/cm ⁿ)		Ratio (b)/(a)
		(a) After the field correction corresponding to Table 1(e)	(b) After the line shape optimization described in Fig. 2(c)	
Z1	1	218	753	3.5
Z2	2	202	646	3.2
Z3	3	1200	1273	1.1
Z4	4	449	820	1.8
X	1	497	1581	3.2
Y	1	-69	-348	5.1
ZX	2	-454	-930	2.0
ZY	2	-91	147	-1.6
C2	2	-133	-139	1.0
S2	2	-94	-53	0.6
Z2X	3	-1140	-1240	1.1
Z2Y	3	-500	-507	1.0
ZC2	3	-740	-635	0.9
ZS2	3	-531	-415	0.8
C3	3	-251	-263	1.1
S3	3	-171	-159	0.9
Z3X	4	-541	-680	1.3
Z3Y	4	-294	-404	1.4
C4	4	0	0	-
S4	4	0	0	-

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6