A new magnet configuration for a solution NMR spectrometer

T Suzuki¹, M Okada¹, T Wakuda², S Kido², H Tsukamoto², K Takeuchi² and H Kitaguchi³

¹ Materials Research Laboratory, Hitachi Ltd., 7-1-1, Omika, Hitachi-shi Ibaraki 319-1292, Japan
² Hitachi Works, Hitachi Ltd., 3-1-1, Saiwai, Hitachi-shi Ibaraki 317-8511, Japan
³ National Institute for Materials Science, 1-2-1 Sengen, Tsukuba-shi Ibaraki, 305-0047, Japan

Abstract. We have developed a new configuration for a high-sensitivity NMR spectrometer, using a superconducting split magnet and a room temperature cross-bore. To achieve higher sensitivity, we selected a solenoid-shaped probe coil; the split-magnet system was adopted to get around the complex probe in the structure. The superconducting split magnet is divided into two multilayer coils, and the vertical bore is located between them. A sample tube is inserted into the vertical bore and a probe system is inserted into the horizontal bore. We have already fabricated these magnet systems in the 300MHz and 600MHz resonance frequency-classes. The systems are composed of a superconducting split magnet for the main field, with superconducting shim coils located inside and outside the split magnet. The 600MHz system has run for more than 13 months with less than 1Hz/h field drift. Recent results showed that the signal to noise ratio of a correlation sample (0.1% ethyl benzene) was 4523 for the 600MHz system with a cryogenic probe system.

1. Introduction

Nuclear magnetic resonance (NMR) spectrometers used to obtain information about the structure and dynamics of proteins have a high field-strength superconducting magnet to increase mass sensitivity. In addition, a cryogenic probe system is combined with the NMR magnet system for higher sensitivity. Increasing the strength of the magnetic field improves the sensitivity of the NMR, but now the performance of magnets up to 20T has reached the limit of Nb₃Sn superconductors. Another way of improving the sensitivity is to adopt a solenoid-shaped probe detector (antenna) in place of a saddle- or birdcage-shaped antenna for the conventional NMR. The solenoid-shaped probe antenna is expected to produce about twice the sensitivity of the saddle-shaped one [1]. However, the use of a solenoid-shaped antenna in a conventional NMR system is restricted to researching solids. Because the direction of the magnetic field intersects with the aperture of a solenoid-shaped antenna, it is difficult to measure liquid solutions, such as proteins, in standard sample tubes using the conventional solenoid-shape superconducting-magnet. Therefore, we have designed an NMR magnet system in a new configuration using a superconducting split magnet. Figure 1(a) is a schematic illustration of a conventional NMR with a superconducting solenoid-magnet and saddle-shaped probe antenna. Figure 1(b) schematically depicts our novel NMR

¹ Address all correspondence to: takayuki.suzuki.qj@hitachi.com
with a split magnet and a solenoid-shaped RF antenna. The tube containing the liquid sample is inserted at the top of the NMR system.

In this paper, we present the specifications and describe the performance of our new NMR magnet system, and show the results of test NMR measurements.

Figure 1. Schematic illustration of the NMR systems.

2. High-sensitivity NMR spectrometer

We have developed a new configuration for a high-sensitivity NMR spectrometer with a superconducting split magnet and a room temperature cross-bore [2]. Figure 2 shows a cross-sectional view of the new NMR magnet system and the positional relationship of the NMR magnet system, sample tube, and NMR probe. The split-magnet system was adopted to get around the complex probe in the structure. The cross-bore consists of a vertical and a horizontal bore. The horizontal bore is a concentric arrangement of the split-magnet bore. The superconducting split magnet is divided into two multilayer coils, and the vertical bore is located between them. The magnet system is composed of superconducting main coils for a global magnetic field and superconducting shim coils for high homogeneity [3]. To achieve a sufficiently homogeneous magnetic field, we have designed the shim coils by numerical analysis to incorporate three novel design concepts [4]. The sample tube is inserted into the vertical bore and the probe system is inserted into the horizontal bore. The sample tube and the probe meet at the centre of the cross-bore. A solenoid-shaped RF antenna is located in the tip of the NMR probe, and the sample tube is inserted in the solenoid-shaped RF antenna. Each bore passes completely through to the other side, so this configuration can be utilized in many novel experimental applications.

Figure 2. Schematic illustration of NMR magnet system with sample tube and NMR probe.
3. Magnet specifications and performance

We have already fabricated three magnet systems in the resonance frequency-classes of 300MHz and 600MHz [4]. The strengths of the magnetic fields of the 300MHz and 600MHz systems are 7 teslas and 14 teslas, respectively. Table 1 lists the specifications of these magnet systems. Each system is composed of a superconducting split magnet for the main field, with superconducting shim coils located inside and outside the split magnet. The 300MHz magnet systems consist of 10 NbTi main coils and 2 NbTi self-shielded coils with 15 superconducting joints and a stored energy of 0.7MJ; the 600MHz magnet system consists of 12 Nb3Sn main coils, 6 NbTi main coils and 2 NbTi self-shielded coils with 53 superconducting joints and a stored energy of 10MJ. To create the homogeneous magnetic field, our NMR magnet systems have dozens of superconducting shim coils placed inside the main coils as well as outside them. The 300GHz#2 magnet system is compact and its volume is one-third that of the 600GHz system, because the 300GHz#2 magnet system has an effective thermal shield system that is liquid nitrogen free and a low consumption of liquid helium.

Table 1. Specifications of 300GHz and 600GHz superconducting split magnets.

|                     | 300GHz#1 (prototype) | 300GHz #2 | 600GHz |
|---------------------|----------------------|-----------|--------|
| Number of main-coils | 10 (NbTi)            | 10 (NbTi) | 12 (Nb3Sn), 6 (NbTi) |
| Number of shield-coils | 2 (NbTi)            | 2 (NbTi)  | 2 (NbTi)  |
| Number of superconducting shim-coils | 26 (inner) | 14 (inner) | 28 (inner) |
| Operating Current   | 205.1A               | 205.1A    | 297A   |
| Stored Energy       | 0.7MJ                | 0.7MJ     | 10MJ   |
| Cryostat size       | 2.5m x 2.2m x 2.0m   | 1.7m x 1.1m x 1.3m | 2.6m x 2.2m x 2.0m |
| Weight              | 8 ton                | 4.3 ton   | 12 ton |
| Superconducting Joints | 15 (main)         | 15(main)  | 56 (main) |
|                     | 79 (shim)            | 72 (shim) | 134 (shim) |

Figure 3 is a schematic illustration of the cross-bore. The cross-bore consists of three tubes, each of which is used at one of three temperatures. The outermost bore is connected to a liquid helium vessel at 4.2K, the middle bore is a thermal shield, and the innermost bore is used for NMR measurements at room temperature. To avoid contact between the bores caused by deformation due to thermal contraction, the fabrication tolerances are severe. The cross-bore is made of aluminium to retain the homogeneous magnetic field in the centre of the cross-bore before shimming.

![Cross-bore diagram](image)

**Figure 3.** Schematic illustration of cross-bore.

To improve the reliability of the superconducting magnet by restricting excessive deformation, we adopted the coil-support system shown in Figure 4. An outer frame is supported by the large hoop stress of the superconducting coil. A support located between the split magnets is a part of base frame,
and it counterbalances the attraction force. Furthermore, we restricted a magnetization of this support not to exceed the ability of shimming system, and selected a lower-magnetization material to keep the homogeneity of the magnetic field.

![Figure 4. Configuration of coil-support system for split-magnet.](image)

In December 2005, we started the 600MHz split-magnet system. Figure 5 shows its quench history. Before the split coils were put into the vacuum vessel, excitation tests were performed in a top-access cryostat. The quench current was gradually increased with the test number. After the quench current reached 90% of the rated current, the split coils were warmed up to room temperature and installed in the vacuum vessel. We followed with tests of the NMR magnet system. Finally, in May 2006, the 600MHz split-magnet system reached the rated current after 14 quench training times, and we verified its persistent current mode operation. Throughout the quench training, the magnet system exhibited no serious deterioration behaviour. To protect the system against failure in case of a quench, our split-magnet system is equipped with a passive quench protection system, shown in Figure 6. The resistance heaters are connected in parallel with the superconducting main coils, and one resistance heater of one main coil is placed against neighbouring main coils. Once a quench has occurred in one coil, the resistance heater raises the temperature of neighbouring coils, and the neighbouring coils lead to quench. The protection system makes the quench from one coil to the next and the magnet-stored energies are consumed from all coils. In consequence, the temperature elevation of each coil is suppressed. This test demonstrated that our system is useful for quench protection against a stored energy of 10MJ.

![Figure 5. Quench training in the 600MHz split-magnet system.](image)

![Figure 6. Quench protection system in the split-magnet system.](image)

Table 2 shows the measurement results for the 300MHz and 600MHz superconducting split magnets. The field drift of all magnets is less than 1Hz/h, which is an acceptable value for an NMR magnet. In
addition, the 600MHz and 300MHz magnet systems have run for more than 13 months and 10 months respectively with less than 1Hz/h field drift. The initial inhomogeneous magnetic field before shimming by the superconducting shim system is a few dozen ppm. After shimming, the inhomogeneity is less than 0.1ppm over a 20mm DSV. These measurement results show that the tolerances of the magnet structures are very strictly controlled, all of the joints perform normally, and the shim system is good enough to create a homogeneous field.

Table 2. Measurement results of 300MHz and 600MHz superconducting split magnets.

|                      | 300MHz#1 | 300MHz #2 | 600MHz |
|----------------------|-----------|-----------|---------|
| Magnetic field stability | < 1Hz     | < 1Hz     | < 1Hz   |
| Initial magnetic homogeneity over a 20mm DSV | 20 ppm    | 25 ppm    | 60 ppm  |
| Magnetic homogeneity over a 20mm DSV after shimming by superconducting shim system | < 0.1 ppm | < 0.1 ppm | < 0.1 ppm |

4. NMR spectrum acquisition in the 600MHz split-magnet system

We have measured the NMR spectrum and evaluated the line shape and signal to noise ratio (S/N) in a correlation sample. Table 3 shows the summary of line shape and signal to noise in the 600MHz system. We have the appreciable result that the line shape is narrow after room temperature shimming, and the signal to noise ratio is higher than in a conventional 600MHz system. The recent measurement of the signal to noise ratio of a correlation sample (0.1% ethyl benzene) was 4523 for the 600MHz system with a cryogenic probe system [2]. The room-temperature shim system affords excellent field homogeneity and contributes to the good performance of this split-magnet system.

Table 3. Summary of line shape and signal to noise ratio at 600MHz.

|                      | 600MHz magnet with cryogenic probe | 600MHz magnet with standard probe |
|----------------------|------------------------------------|----------------------------------|
| Temperature of receiver coil | 12K                                | RT                               |
| Target nuclei        | H                                  | H                                |
| Line shape (non-spin) | 0.7 (the width at half-height of CHCl₃ proton peak) | 0.4 (the width at half-height of CHCl₃ proton peak) |
| Line shape (non-spin) | 19 (0.11% of CHCl₃ proton peak)     | 17 (0.11% of CHCl₃ proton peak)  |
| Signal to noise ratio | 4523                               | 1486                             |

5. Conclusion

We have successfully developed a high-sensitivity NMR spectrometer, using a superconducting split-magnet and a cross-bore. The 600MHz split-magnet system has been rated as operational after 14 quench training times, and has run more than 13 months in persistent current mode with less than 1Hz/h field drift. Throughout the quench training, the magnet system exhibited no serious deterioration behaviour, and the quench protection system performed effectively. Furthermore, the superconducting shim coils located inside and outside the split magnet controlled the inhomogeneity of the magnetic field to less than 0.1ppm over a 20mm DSV. The recent measurement of the signal to
noise ratio of a correlation sample (0.1% ethyl benzene) was 4523 for the 600MHz system with a cryogenic probe system.

Acknowledgement
The authors would like to thank Professors E. Masada, Y. Kimura, T. Kohzuma, D. Kohda, and H. Morita for stimulating discussions. This work is supported in part by the Research Promotion Bureau, Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, under contract Nos. 17-260 and 18-489.

References
[1] D. L. Hoult and R. E. Richards 1976 J. Magnetic Resonance 24 71-85
[2] M. Okada and H. Kitaguchi 2007 Proc. 20th Int. Conf. on magnet technology (IEEE).
[3] K. Maki, T. Wakuda, M. Tsuchiya, S. Kido, H. Tsukamoto, K. Takeuchi, M. Okada, and H. Kitaguchi 2007 Proc. 20th Int. Conf. on magnet technology (IEEE).
[4] M. Tsuchiya, T. Wakuda, K. Maki, T. Shiino, H. Tanaka, N. Saho, H. Tsukamoto, S. Kido, K. Takeuchi, M. Okada, and H. Kitaguchi 2007 Proc. 20th Int. Conf. on magnet technology (IEEE).