Achievement of 1020 MHz NMR

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Abstract

We have successfully developed a 1020 MHz (24.0 T) NMR magnet, establishing the world's highest magnetic field in high resolution NMR superconducting magnets. The magnet is a series connection of LTS (low- T_c superconductors NbTi and Nb₃Sn) outer coils and an HTS (high- T_c superconductor, Bi-2223) innermost coil, being operated at superfluid liquid helium temperature such as around 1.8 K and in a driven-mode by an external DC power supply. The drift of the magnetic field was initially ± 0.8 ppm/10 h without the ²H lock operation; it was then stabilized to be less than 1 ppb/10 h by using an NMR internal lock operation. The full-width at half maximum of a ¹H spectrum taken for 1 % CHCl₃ in acetone-d₆ was as low as 0.7 Hz (0.7 ppb), which was sufficient for solution NMR. On the contrary, the temporal field stability under the external lock operation for solid-state NMR was 170 ppb/10 h, sufficient for NMR measurements for quadrupolar nuclei such as ¹⁷O; a ¹⁷O NMR measurement for labeled tri-peptide clearly demonstrated the effect of high magnetic field on solid-state NMR spectra.

Keywords: magnet development, 1020 MHz, high- T_c superconducting magnet, Bi-2223, driven mode magnet

1. Introduction

Extensive efforts have been made continuously to develop a higher field NMR magnet[1, 2, 3, 4], because higher magnetic fields can improve the NMR resolution and sensitivity. An example of the benefit can be seen for half-integer quadrupolar nuclei in solid-state NMR, because the line width due to the 2nd order quadrupole interactions becomes narrower with increasing the magnetic field.[5] A hybrid magnet can be a promising method to exceed the limit of magnetic field strength available from the current superconducting magnet technology.[6, 7, 8]. Since the hybrid magnet has still the disadvantage in its magnetic field stability, homogeneity and running costs compared to superconducting NMR magnets, the hybrid magnet does not seem to come into general use right now. For superconducting NMR magnets, a break through in the magnetic field intensity was achieved for 920 MHz in 2001 [1, 2], and 1 GHz (i.e. 1000 MHz) was reached in 2009[4]. For LTS (low- T_c superconductors) magnets, there are very small margins in the critical field, critical temperature and critical current density above 900 MHz. Thus, it seems that LTS magnets have an upper limit of magnetic field strength around 1 GHz. An LTS/HTS (high- T_c superconductors) magnet

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system is now a leading candidate to exceed 1 GHz, as there still remains sufficient margin in the critical field for HTS conductors above 1 GHz.

Thus, we started in 2006 a project to develop an NMR magnet which comprises an HTS innermost coil and LTS outer coils[9]. For the project, we modified the 920 MHz NMR magnet which had been installed in the National Institute for Materials Science since 2002[2]. The innermost coil of the 920 MHz magnet was replaced by a Bi-2223 HTS coil intended to nominally enhance the magnetic field up to 1030 MHz[10]. In March 11, 2011, the first day after the magnet was filled with liquid helium, we had an unprecedentedly huge earthquake, the Great East Japan Earthquake, and the magnet was seriously damaged. It took more than two years to complete repair of the magnet. About three years behind the initial schedule, we have exceeded 1000 MHz and finally achieved 1020 MHz (24.0 T) in October, 2014. In the present paper, we will show a magnet design and fabrication, the magnet test result and an initial example of NMR spectra taken by the 1020 MHz NMR magnet. More details of the magnet repair and the magnet performance will be published elsewhere[11].

2. 1020 MHz magnet system

The magnet of the 920 MHz NMR system consisted of concentric LTS coils (NbTi and Nb₃Sn). The innermost Nb₃Sn coil of the NMR magnet was replaced by a Bi-2223 HTS coil, while outer LTS coils remain the same. The magnetic field of 24.0 T (1020 MHz) was achieved with a combination of 3.6 T by the new innermost Bi-2223 HTS coil and 20.4T by the outer LTS coils. Figure 1 shows a schematic cross-sectional view of the magnet. The size of the advanced NMR magnet is the same as the 920 MHz magnet.[2] The cryostat of the magnet consists of a liquid helium reservoir at 4.2 K and a pressurized superfluid liquid helium below 1.8 K. The LTS/HTS coils of the magnet was placed in the pressurized superfluid liquid helium. To achieve sufficient persistent current operation for NMR measurement, there are two major problems for LTS/Bi-2223 HTS coils. Firstly, there is a small residual resistance in a HTS conductor due to a gentle normal transition, i.e. a smaller n -index value. Secondly, a superconducting joint technique has not been developed sufficient for stable persistent current operation. Thus, the magnet has been designed to operate in an external current mode, or a driven mode. The basic principle of the magnetic field stabilization, field correction, and the NMR measurement has already been shown for a driven mode 500 MHz LTS/HTS NMR magnet in Ref. [12].

For a driven mode operation of the 1020 MHz NMR magnet, a safety system was newly developed. Figure 2 shows a schematic view of the 1020 MHz NMR system. An ultra-stabilized DC power supply (Danfysik, MPS 854) is connected to the magnet top flange with copper bus bars to reduce electric resistance between the power supply and the magnet. A newly developed gas-cooled current lead is used to connect the bus bars to the magnet. The DC power supply is energized by a commercial AC power source, which is equipped with a standby generator. The DC power supply is also supported by an uninterruptible power supply for unexpected input power source failure and/or momentary reduction of power source voltage. For a case of the DC power supply failure, a protecting circuit for the magnet is installed between the DC power supply and the magnet. More details of the safety system will be published elsewhere[13].

3. Experimental

NMR measurements were performed with a JEOL ECA spectrometer. The spectrometer is equipped with a ²H lock system, sufficient to stabilize the magnetic field fluctuation caused by the DC power supply for solution NMR. A laboratory made external lock is used for solid-state NMR; a ²H frequency detection coil was installed beside the NMR sample, connected to the lock system of the spectrometer[14]. Z₀ coil of a room-Temperature (RT) shim was used for the lock operation. The inhomogeneity of the magnetic field was corrected by superconducting (SC) shim coils, RT shim coils and ferromagnetic shims. The SC shim coils are operated in a persistent mode, whereas the main coil of the magnet was operated in a driven mode. It is difficult to achieve an axisymmetric cylindrical configuration by spirally winding the Bi-2223 thin tape conductor around a coil form; additionally, end windings become thicker and asymmetric due to joining tape

Figure 1: Schematic cross-section view of the 1020 MHz NMR magnet.

Figure 2: Schematic view of the 1020 MHz NMR magnet system. The electric circuit for the main current consists of an uninterruptible power supply (UPS), an ultra-stabilized DC power supply and a protecting circuit.

Figure 3: Long term drift of the 1020 MHz NMR magnet without NMR lock for 70 h.

conductors. Thus, field errors for the 1020 MHz NMR magnet were much larger than those for the 920 MHz NMR Magnet. For this reason, several type of ferromagnetic shims were installed in the magnet system.

4. Magnetic field drift and spatial homogeneity

Long term magnetic field drift, without the NMR lock operation was measured as shown in Fig. 3. The shift in ^2H resonance frequency for D_2O was recorded with a time interval of 10 min for 70 h. The field fluctuation comprised both a long-term component and a short-term component. The former component was $< \pm 0.6$ ppm, which was affected by room temperature, the performance deviation of the power source and the relaxation of the screen current induced magnetic field[15]. On the contrary, the latter component is due to short-term current ripples $< \pm 0.15$ ppm. By controlling the room temperature, the total fluctuation of the magnet without the NMR lock operation has been reduced to be $< \pm 0.7$ ppm for 70 hours, which enables NMR lock operation installed in the spectrometer.

Thus, an internal lock with ^2H was applied to a solution NMR probe. Figure 4 shows drift of a single shot ^1H spectrum of 1% CHCl_3 in acetone- d_6 under the internal lock operation. The spectrum was recorded with a time interval of 5 min for 10 h. The temporal stability with the internal lock operation is less than 1 ppb/10 h.

An external lock by using ^2H of a D_2O micro probe was applied for a MAS probe. Figure 5 shows a drift of ^{81}Br of KBr under the external lock operation. The peak positions of a single shot ^{81}Br spectrum were plotted with a time interval of 5 min for 10 h. The external lock detection signal was weaker than that of the internal lock, as the sample volume of D_2O for the external lock micro coil was extremely limited, and furthermore the magnetic field at the point where the D_2O sample was placed was not sufficiently homogeneous. Thus, the temporal stability with the external lock (< 170 ppb/10 h) was much inferior to that of the internal lock (1 ppb/10 h) for a solution probe. The stability of the external lock is, however, sufficient for solid-state NMR measurements of quadrupolar nuclei.

The homogeneity of the magnetic field was sequentially adjusted by SC, ferromagnetic shims[16] and RT shims, based on the magnetic field data collected along a spiral locus. As some error components were extremely large, it was improbable to achieve sufficient magnetic field homogeneity without using ferromagnetic shims. More details will be published elsewhere[17]. Figure 6 shows a ^1H spectrum of CHCl_3 in acetone- d_6 ; it is shown that the full-width at half maximum, i.e. magnetic field homogeneity, of 0.7 Hz (0.7 ppb) is successfully achieved after field corrections.

5. An example of NMR spectra.

As an example of NMR spectra with the 1020 MHz NMR magnet, a MAS measurement of quadrupole nuclei is demonstrated by ^{17}O of a tri-peptide. Figure 7 shows a ^{17}O MAS spectrum of labeled L-tryptophanyl-glycyl-glycine dihydrate (WGG)[18] measured with the 1020 MHz (24.0 T) magnet at a MAS speed of 20

Figure 4: Stability of a single shot ¹H spectrum of 1% CHCl₃ in acetone-d₆ with the internal lock for 10 h.

Figure 5: Drift of ⁸¹Br in KBr with the external lock.

Figure 6: ^1H spectrum of CHCl_3 in acetone- d_6 .

Figure 7: ^{17}O MAS spectra of labeled L-tryptophanyl-glycyl-glycine dihydrate (WGG) at 14.1 T and 24.0 T. Simulation for 24.0 T is also plotted.

kHz. A ^{17}O MAS spectrum on the same sample with a 600 MHz (14.1 T) NMR magnet at a MAS speed of 19 kHz is also shown in Fig. 7. The averaging scan numbers were 19800 and 11400 for the 14.1 T and 24.0 T measurements, respectively. The line width of the spectrum with the 1020 MHz magnet is much narrower than that with the 600 MHz NMR magnet indicating the efficiency of the high magnetic fields for solid-state NMR measurements. The spectrum with the 1020 MHz magnet is simulated by a calculation as shown in Fig. 7. The parameters obtained by the calculation ($\delta_{\text{iso}} = 297$ ppm, $C_Q = 8.4$ MHz, $\eta_Q = 0.25$) are consistent with the previous study[18].

6. Summary

In summary, we have achieved the 1020 MHz NMR system successfully. It is confirmed that temporal field stability and spatial field homogeneity of the magnet are sufficient for solution and solid-state NMR measurements. Other NMR measurements with this magnet are being in progress[19].

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