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COMMUNICATIONS

Achievement of a 920-MHz High Resolution NMR

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We have developed a 920-MHz NMR system and performed the proton NMR measurement of H_2O and ethylbenzene using the superconducting magnet operating at 21.6 T (920 MHz for proton), which is the highest field produced by a superconducting NMR magnet in the persistent mode. From the NMR measurements, it is verified that both homogeneity and stability of the magnet have a specification sufficient for a high resolution NMR.

Key Words: **high field; superconducting magnet; 920 MHz; ethylbenzene.**

1. INTRODUCTION

As NMR sensitivity and resolution increase with the external magnetic field, an NMR system in a higher magnetic field is required (*1, 2*). In particular, the NMR measurement of a proton around the NMR frequency of 1 GHz is desired for structural biology, because the NMR linewidth in proteins becomes narrower around 1 GHz using the TROSY pulse sequence (*3*). An NMR system for high magnetic fields is also desired for an MQ-MAS spectroscopy of solid-state materials such as a catalyst which consists of low-γ, large-Q nuclei, or both. Furthermore, a high field NMR may improve one of the challenging problems in the realization of an NMR quantum computer about how to prepare enough *qubits*[2] for practical use. Since chemical shift differences are utilized to make the current best achievement of 5 qubits (*4*) in a solution NMR quantum computer (*5, 6*), higher fields would be favored for providing more *qubits.* For a solid-state NMR quantum computer (*7*), a high field NMR has a gain such that a small number of nuclei can be used for a *qubit* due to higher sensitivity.

Recently, a superconducting (SC) magnet operating at 21.6 T (920 MHz for proton) in the persistent mode was developed by the National Institute for Materials Science (NIMS) (*8*). We have also developed a prototype of a 920-MHz NMR spectrometer to examine the performance of the magnet by NMR measurements (*9*). In this paper, we describe the details of the 920-MHz NMR magnet and spectrometer system we have developed so far and specify the results of the proton NMR measurements of H_2O and ethylbenzene.

2. APPARATUS

2.1. Superconducting Magnet

NIMS has been working toward developing a 1-GHz NMR magnet for structural biology and other studies since 1995. The magnet is designed to consist of two separate sections: first, an outer magnet to ensure a 900-MHz achievement even in the worst case and second, an inner magnet that aims for an additional 100 MHz. The outer magnet consists of the low temperature superconducting coils (three Nb_3Sn and five NbTi coils) designed to generate a field of 21.1 T (900 MHz) in persistent mode. In our future plan, an inner magnet made of an oxide high-temperature superconductor (Bi-2212) may be used to generate an additional field of 2.4 T, resulting in a central field of 23.5 T, corresponding to 1 GHz for proton NMR.

The present magnet, in fact, employs a Nb_3Sn coil for an inner magnet, instead of the Bi-2212 coil still under development. Consequently, the magnet consists of four Nb_3Sn solenoid coils, three NbTi solenoid coils, and two split-paired NbTi coils, as shown in Fig. 1. The magnet is operated at 1.6 K by pressurized superfluid helium.

The magnet is about 15,000 kg in weight and 5 m in height including the legs. The initial tests of the magnet's operation have been made for about 2 years in a steelworks for manufacturing ship crankshafts at Kobe Steel Ltd., because a 30,000-kg crane mounted at a height greater than 12 m was needed for assembling the magnet. The present NMR measurement was also made there

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[2] A *qubit* is an abbreviation of a *quantum bit*, which is a unit of information in a quantum computer (*4–6*).

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for about 2 weeks by shipping the NMR spectrometer to Kobe from NIMS in Tsukuba. During the present NMR measurement, the crane worked mostly far from the magnet, but occasionally it got close to the magnet in minutes within the magnetic area of about 10 m in radius, causing a temporal shift of the magnetic field easily observed from the NMR signal fluctuations. It was found from our NMR measurement that, immediately after the crane leaves the magnetic area, the magnetic field returns to exactly the same as that before the temporal shift occurs. The temporal shift was so obvious that we easily skipped the bad data. We believe that the essence of the results presented here does not involve any effect from the temporal shift at all.

We achieved a persistent-mode operation at 21.17 T (901.3 MHz) in December 1999 and at 21.62 T (920.3 MHz) in April 2001. The magnetic field of 21.62 T is the highest field produced by an SC NMR magnet. The field distribution is adjusted with the nine-channel SC shim, giving the field homogeneity better than ± 0.1 ppm in a volume of 10 mm in diameter and 20 mm in height. The room temperature (RT) bore is 54 mm in diameter.

2.2. *NMR Spectrometer*

Although the goal of our development is a complete set of a 920-MHz high resolution NMR spectrometer system, we have still only prepared the prototype. The NMR power amplifier and spectrometer up to 1 GHz are custom-made by Thamway Ltd. The power amplifier is 50 W. The spectrometer is designed for a phase coherent pulsed method and is stabilized in the accuracy of ± 0.1 ppm /°C. The resolution of AD converter is up to 1.2 Hz. No NMR-lock is used during all the measurements in this work.

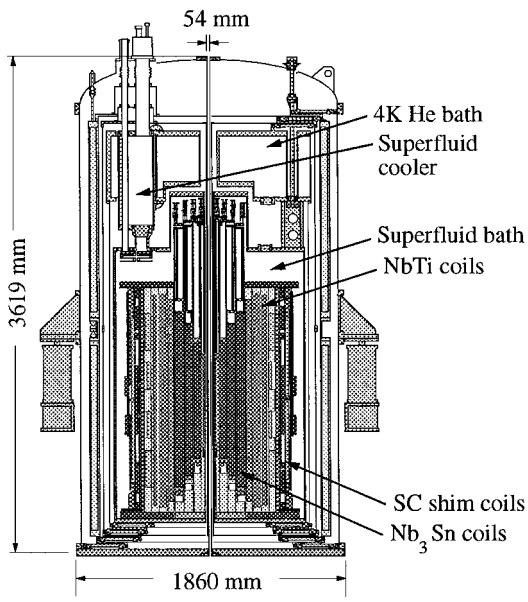

FIG. 1. The schematic view of the magnet system.

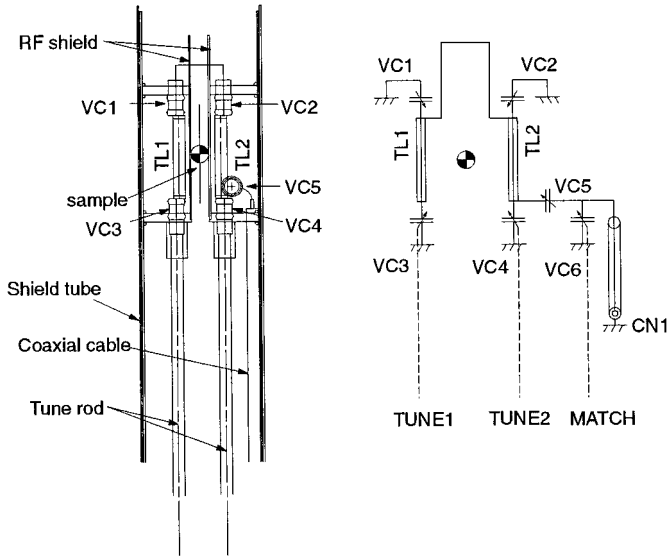

FIG. 2. The schematic view of the probe and its electric circuit diagram. VC1–VC6 are variable capacitors, and TL1 and TL2 are transmission lines.

The probe was also developed. The schematic view of the probe and its electric circuit diagram are shown in Fig. 2. A pair of parallel transmission lines TL 1 and TL 2 works as both transmitting and receiving "coil." The probe has a frequency range between 900 MHz and 1 GHz. The RF shield has a sample window of 13 mm in height. The detail of the probe is patent pending (*10*). The 19-channel RT matrix shim was incorporated with the probe to reduce the space. The present probe does not have sample-spinning gear. The total resolution of the probe may be comparable to or better than commercially available solid state probes.

3. NMR MEASUREMENTS AND DISCUSSION

The samples of $CDCl_3$ diluted ethylbenzene and 100% H_2O were sealed in glass tubes of 5 mm in diameter. The NMR spectrum measurement was performed at 920.2208 MHz without averaging signal or spinning sample. The FT spectra were obtained by Fourier transforming a free induction decay (FID) signal.

Figure 3 shows the proton FT-NMR spectrum of H_2O. The FID signal obtained by applying a 90° pulse of 8-μs width was digitized with a sampling rate of 2.5 kHz for 4096 points. The full linewidth at half maximum (FWHM) of the spectrum reaches about 4 Hz. The FWHM may be reasonable for the probe used here because of no sample spinning and because the LC resonator materials are suspected of a small but finite magnetic susceptibility (*11, 12*). A relatively poor signal-to-noise ratio is ascribed to the parallel transmission lines which have a quite low filling factor because of the shape.

We have measured the stability of the SC magnet from the proton resonance frequency of water for a week by the probe with RT shim. Figure 4 shows the time dependence of the resonance

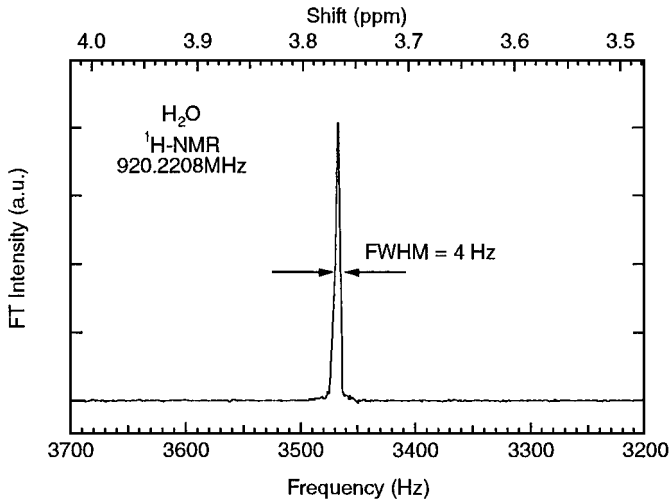

FIG. 3. The proton FT-NMR spectrum of H_2O measured at 920.2208 MHz.

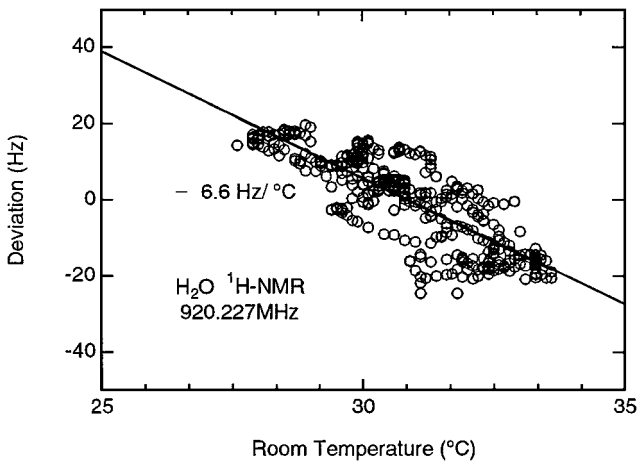

FIG. 5. The correlation between the room temperature and the deviation of the resonance frequency from the linear fit shown in Fig. 4. The straight line shows a linear fit through the points.

frequency measured at 920.227 MHz and room temperature. The room temperature had been monitored but not controlled during the measurement. The oscillation of the resonance frequency found in Fig. 4 can be explained mostly by the temperature dependence of the resonance frequency of water. Figure 5 shows the correlation between the room temperature and the deviation of the resonance frequency from the linear trend due to the drift of the magnet. We find from Fig. 5 that the resonance frequency depends on the temperature with the rate of -6.6 ± 0.2 Hz/°C, consistent with the reported value of -7.3 Hz/°C (*13*). The discrepancy between the temperature dependences may be ascribed to a possible difference between the temperature of the sample mounted inside the magnet bore and the room temperature monitored outside the magnet.

The stability of the magnet was also measured for more than 30 days by another probe which has poorer sensitivity and no RT shim. The long-term stability of the magnet is shown in Fig. 6, together with the data measured by the probe with RT shim. The data by the probe without RT shim show large noise level and no oscillation due to the room temperature variation because of its low sensitivity. It can be seen from Fig. 6 that the drift decays to a smaller value. The drift data taken by the probe with RT shim 90 days after the 920-MHz persistent operation started are more reliable. We get the magnet drift of -2.44 ± 0.02 Hz/h by a linear fit through the data in Fig. 4.

Figure 7 shows the proton FT-NMR spectrum of ethylbenzene measured at 920.2208 MHz. The spectrum shows clear splittings

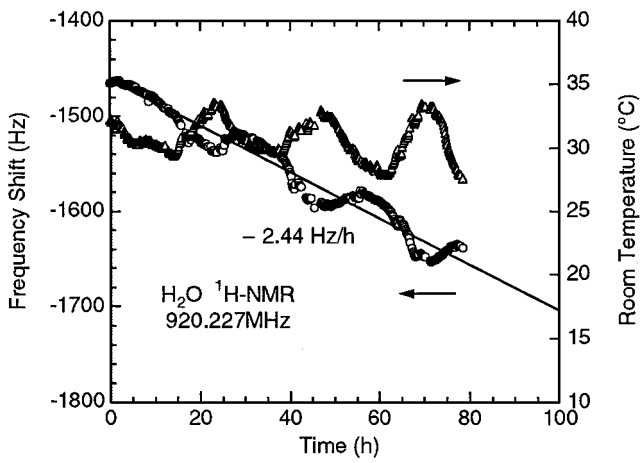

FIG. 4. The time dependence of the proton resonance frequency (circles) and the room temperature (triangles). The frequency shift is measured from the operating frequency 920.227 MHz. The straight line shows a linear fit through the frequency shift data, which is the magnet drift (see text).

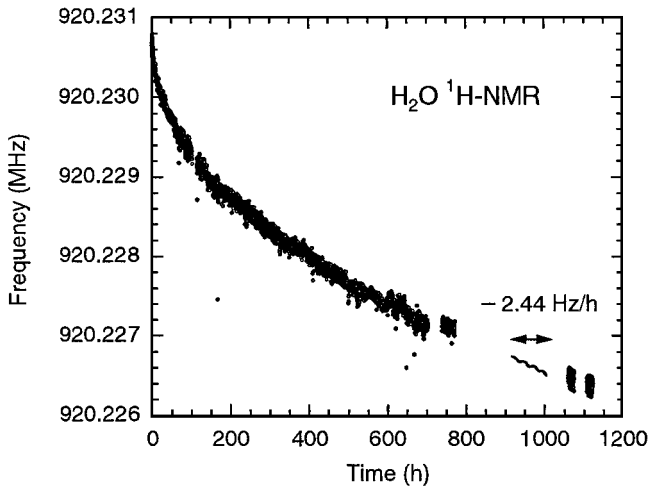

FIG. 6. The long-term stability of the magnet measured by a probe with no RT shim. The data during the period indicated by arrows are taken from the plot in Fig. 4. The data of Fig. 4 are shifted vertically for the comparison, because the operating frequency was a little bit different.

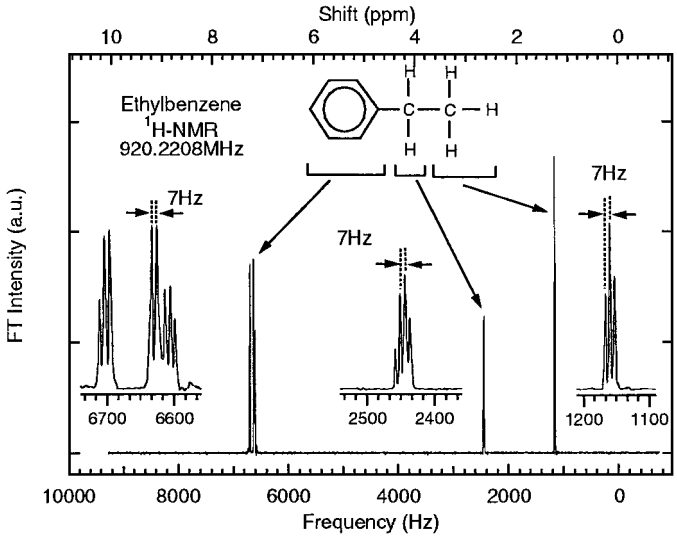

FIG. 7. The proton FT-NMR spectrum of ethylbenzene measured at 920.2208 MHz. Insets show the spectra expanding the each peak.

as can be expected in such a high field as 920 MHz. The FID signal obtained by a single pulse of 50-μs width was digitized with a sampling rate of 5 kHz for 4096 points. Three peaks were observed corresponding to phenyl, methylene, and methyl groups, consistent with the data taken by a 800-MHz spectrometer. The peaks corresponding to methylene and methyl groups have quartet and triplet fine structures due to the J couplings, respectively. The value of J (7 ± 2 Hz) obtained here is consistent with the reported value, within the resolution of the present AD converter 1.2 Hz. The spectrum of the phenyl group has a relatively complicated fine structure, at least eight peaks, due to the existences of the chemically nonequivalent sites therein, which is also the same feature as the spectrum taken by a 800-MHz spectrometer.

4. SUMMARY

We have developed a 920-MHz NMR system and performed high field proton NMR measurements of H_2O and ethylbenzene. The resolution of 4 Hz for H_2O is achieved with SC shim, RT shim, and no sample spinning. We also have measured the stability of the SC magnet for a week from the proton NMR, which shows -2.44 ± 0.02 Hz/h. These results indicate that the SC magnet and SC shim have the specifications sufficient for high resolution NMR measurements of liquid. It is desired that an RT Lagrangé shim and a high resolution probe especially designed for solution and solid NMR such as a CP-MQMAS be developed for further applications of the magnet. The probe materials are required to have magnetic susceptibility lower than $\pm 0.1 \times 10^{-6}$ cgs/cm^3 to improve a resolution up to 0.01 ppm (*12*).

The 920-MHz SC magnet will be used for a collaborative study with the Genomic Sciences Center of RIKEN. There is also another plan to develop a solid state NMR for the magnet. The 920-MHz NMR system may play an important role in improving NMR quantum computer performance by providing a large number of qubits utilizing the improved resolution.

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