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Development of a Flux Stabilizer for Solid-state Nuclear Magnetic Resonance with a Hybrid Magnet

Kenjiro Hashi,*[1] Tadashi Shimizu,[1] Teruaki Fujito,[2] Atsushi Goto,[1] Shinobu Ohki,[1]
Toshihisa Asano,[1] Shigeki Nimori,[1] Giyuu Kido,[1] and Jun Kida[3]
[1]*National Institute for Materials Science (NIMS), 3-13 Sakura, Tsukuba, Ibaraki 305-0003*
[2]*Probe Laboratory Inc., 3-13 Sakura, Tsukuba, Ibaraki 305-0003*
[3]*JEOL Ltd., 3-1-2 Musashino, Akishima, Tokyo 196-8558*

(Received September 21, 2010; CL-100807; E-mail: HASHI.Kenjiro@nims.go.jp)

A flux stabilizer has been developed for solid-state NMR measurements with a hybrid magnet installed at the National Institute for Materials Science. The stabilizer consists of an electric circuit, a pickup, and a feedback coils to cancel out the fluctuating magnetic field at a sample by inductive field regulation. Stability of the magnetic field was improved from 6.3 $\mathrm{ppm_{rms}}$ to 1.4 $\mathrm{ppm_{rms}}$ by the flux stabilizer. Advantages of the flux stabilizer are demonstrated by ^{79}Br magic-angle-spinning NMR measurements of KBr at 28 T.

Nuclear magnetic resonance (NMR) is one of the most powerful analytical tools to investigate structures and properties of materials from a microscopic point of view. NMR systems require high magnetic fields, because sensitivity and resolution of NMR spectra increase with the external magnetic field.

A superconducting magnet is used for a conventional NMR system. The magnetic field achievable by a superconducting magnet, however, is approaching its upper limit unless new materials with higher critical fields become available. At present, steady magnetic fields over 25 T are available only with the help of a resistive magnet. A hybrid magnet consisting of a superconducting magnet and a resistive magnet provides magnetic fields over 25 T. A hybrid magnet, however, has disadvantages in field stability. Trial NMR measurements with a hybrid magnet installed at the National Institute for Materials Science (NIMS) indicated that the hybrid magnet has a potential for a practical solid-state NMR measurements.[1] There are some efforts to cancel out the field fluctuation by a signal manipulation.[2] The performance of the hybrid magnet has also been improved by a reconstruction of a power source and an improved resistive insert magnet.[3,4] In spite of these improvements, further stabilization of the magnetic field is required for solid-state NMR measurements.

A flux stabilizer was reported for NMR measurement with a resistive magnet installed at the National High Magnetic Field Laboratory (NHMFL).[5] They achieved field stability of 2 ppm with the stabilizer. In this study, we have developed a flux stabilizer for solid-state NMR measurements with a hybrid magnet installed at NIMS. Advantages of the flux stabilizer are demonstrated by ^{79}Br magic-angle-spinning (MAS) NMR measurements of KBr at 28 T. A flux stabilizer cancels the fluctuating magnetic field at a sample by inductive field regulation. Figure 1 shows an electric circuit diagram of the stabilizer. The stabilizer consists of a pickup PU, a compensation BO coils, and a feedback electric circuit. A 3740-turn pickup coil was placed close to the MAS housing. A 130-turn compensation coil was placed centered at the sample. The pickup and compensation coils are concentric, and their major axes parallel to the *z* direction of the magnetic field. The compensation coil covers both the sample and the pickup coil. The feedback electric circuit generates the magnetic field with the compensation coil to cancel out the external fluctuating magnetic field at the pickup coil and the sample.

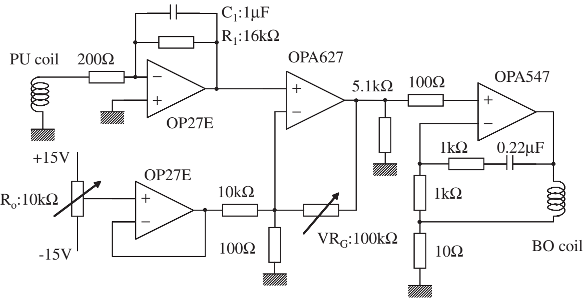

Figure 1. Electric circuit diagram of the flux stabilizer. A high output current operational amplifier OPA547 feeds current to the compensation BO coil to minimize the field fluctuation detected by the PU coil.

Fourier transform (FT) MAS-NMR measurements of ^{79}Br of KBr was performed at 28 T. A single shot FT power NMR spectrum was obtained from a free-induction-decay (FID) signal. The FID signal was digitized with a sampling rate of 390.625 kHz for 4096 points. The resolution of the FT spectrum was 95.4 Hz, i.e., 0.3 ppm. A 2 mm in diameter spherical sample holder was used in a 4-mm sample tube of zirconia. The MAS speed was 10 kHz.

The fluctuation of the magnetic field affects NMR spectra. Figure 2 shows the time dependence of ^{79}Br-MAS-NMR spectra acquired with 1-s intervals at 28 T without the field stabilization. The spectral shape changes in every measurement, and wiggles appear due to the fast fluctuation. The peak position also changes in every measurement due to the slow fluctuations between signal acquisitions.

These extrinsic changes due to the fluctuation are reduced by using the flux stabilizer. The effect of the stabilization on the time dependence of the FT spectra can be clearly seen in Figure 3. The full width at half-maximum (FWHM) of each spectrum with the stabilization is reduced to about 800 Hz (2.6 ppm), which is about five times smaller than that without the stabilization. The fluctuation of the peak position is also reduced by the stabilizer from 1900 (6.3 $\mathrm{ppm_{rms}}$) to about 420 $\mathrm{Hz_{rms}}$ (1.4 $\mathrm{ppm_{rms}}$). The achieved field stability of 1.4 $\mathrm{ppm_{rms}}$ is almost comparable to that achieved at NHMFL of 2 ppm.

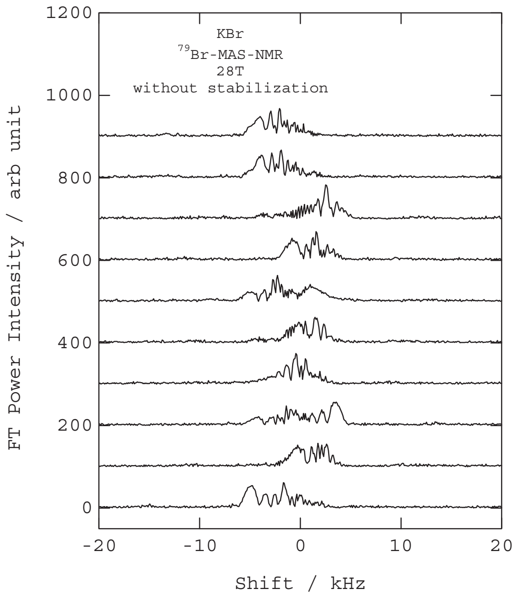

Figure 2. Time dependence of a single shot ^{79}Br-MAS-NMR spectrum of KBr at 28 T without the stabilization.

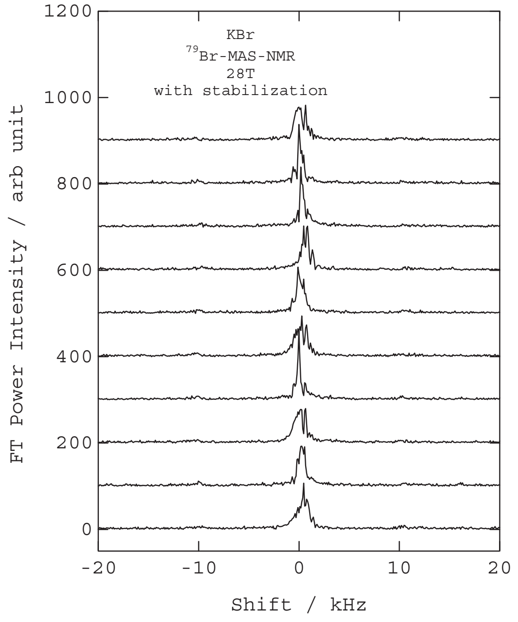

Figure 3. Time dependence of a single shot ^{79}Br-MAS-NMR spectrum of KBr at 28 T with the stabilization.

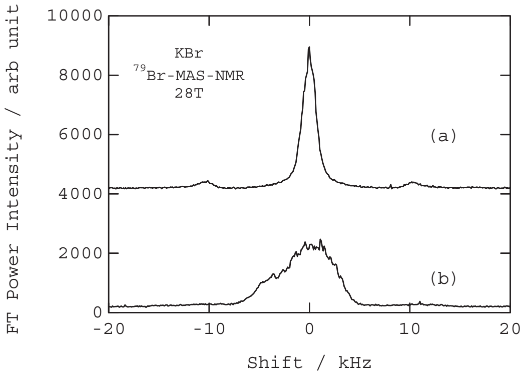

Figure 4. ^{79}Br-MAS-NMR spectra of KBr at 28 T obtained by averaging 40 times (a) with and (b) without the stabilization, respectively.

The advantage of the improvements in field stability is also confirmed by averaging NMR signals. Figure 4 shows ^{79}Br-MAS-NMR spectra of KBr obtained by averaging 40 times (a) with and (b) without the stabilization, respectively. The FWHM of the averaged spectrum is improved from 6600 (22 ppm) to 1700 Hz (5.6 ppm) by the stabilization. The FWHM of the averaged spectrum with the stabilization originates from both the field inhomogeneity and the field fluctuation. As mentioned above, the peak position of a single shot spectrum still fluctuates with 1.4 ppm_{rms} in spite of the stabilization. This remaining fluctuation may cause the FWHM of the averaged spectrum of about 3.3 ppm by assuming the Gaussian distribution of the fluctuation, because a Gaussian distribution with a standard deviation of σ gives a FWHM of $2\sigma(2\ln 2)^{1/2}$. Thus, the FWHM of the averaged spectrum with the stabilization is expected to be 5.9 ppm together with a FWHM of a single shot spectrum of 2.6 ppm, which agrees well with the experimental value of 5.6 ppm.

In summary, we have obtained MAS-NMR spectra of KBr at 28 T. The FWHM of 5.6 ppm was achieved for the spectrum obtained by averaging 40 times. The achieved FWHM of 5.6 ppm, however, is not enough for a practical solid-state NMR measurement. The spectral resolution of about 1 ppm is required for a practical solid-state NMR measurement of quadrupolar nuclei such as ^{27}Al. In order to obtain an averaged NMR spectrum with a spectral resolution of 1 ppm, further improvements will be needed for both the field stability and homogeneity. The larger feedback gain of the stabilizer would reduce the remaining field fluctuation. The FWHM due to the field inhomogeneity would be reduced by using a smaller sample. The sample size, however, has a lower limit because the signal-to-noise ratio become worse with reducing the sample size. Development of a room-temperature shim will be required to improve field inhomogeneity.

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