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High-resolution NMR with resistive and hybrid magnets: Deconvolution using a field-fluctuation signal

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Abstract

A method for compensating effect of field fluctuation is examined to attain high-resolution NMR spectra with resistive and hybrid magnets. In this method, time dependence of electromotive force induced for a pickup coil attached near a sample is measured synchronously with acquisition of NMR. Observed voltage across the pickup coil is converted to field fluctuation data, which is used to deconvolute NMR signals. The feasibility of the method is studied by ^{79}Br MAS NMR of KBr under a 30 T magnetic field of a hybrid magnet. Twenty single-scan NMR signals were accumulated after the manipulation, resulting in a high-resolution NMR spectrum.

Keywords: High-field NMR; Field fluctuation; Hybrid magnet

1. Introduction

A higher magnetic field is beneficial for increase of sensitivity and resolution in NMR, because equilibrium magnetization and chemical shift are proportional to an applied magnetic-field strength. So far, superconducting magnets that can provide a considerably stable field have been used for the most of high-resolution NMR measurements but the maximum field achieved is 21.9 T [1]. Pulsed magnets for NMR-use offer a very high-field of up to 58 T [2] but duration of the field is of the order of millisecond being too short for various NMR experiments. Furthermore, field reproducibility is insufficient for signal accumulation and homogeneity of the field is considerably poor. Thus the pulsed magnet is not suitable for high-resolution NMR at this time. Resistive and hybrid magnets of which their fields sustain more than 1 h are promising as a high-field magnet for high-resolution NMR. Indeed, Gan et al. have reported a ^{27}Al MAS NMR spectrum measured under a 40 T magnetic field using a hybrid magnet placed at National High Magnetic Field Laboratory in Florida [3]. High-resolution NMR experiments using resistive and hybrid magnets, however, have not yet been very popular, because of insufficient stability of magnetic fields in general. For example, a hybrid magnet at National Institute for Materials Science (NIMS) in Japan exhibits amplitude fluctuation of ca. ±1.5 mT with frequencies spreading around several tens of hertz [4]. Removing this fluctuation is indispensable for observation of a high-resolution NMR spectrum with this magnet.

Fluctuation of a magnetic field does exist in superconducting magnets, which is often called as drift [5]. The drift can be generally compensated by using the NMR lock. The fluctuation that can be removed, however, is limited for slow and small drift with a drift rate less than 1 Hz and a strength less than 1 mT. Thus the NMR lock is inapplicable to the resistive and hybrid magnets, because the large and fast fluctuation in these magnets is far beyond the limitation.

Several techniques for measuring high-resolution NMR spectra using the resistive and hybrid magnets have been examined [6–9]. These may be categorized into two groups;

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one is a method utilizing difference of signals (I) and the other method removes the fluctuating field mechanically (II). The NMR lock is in the group II.

For an example of the group-I method, an intermolecular zero-quantum coherence (iZQC) technique realizes high-resolution NMR through a two dimensional measurement, where difference of two signals for homonuclear dipolar-coupled spins is taken by creating ZQC [6]. Another group-I method detects two NMR signals simultaneously, where one is for observed nuclei and the other is for reference nuclei [7,10]. Effects of fluctuation on the target NMR signals are deconvoluted using the reference signal (a reference-deconvolution method).

As for the group-II method, Sigmund et al. placed a highly conducting metal tube around a sample to reduce NMR phase noise [8]. A feedback method using two different coils, a pickup coil and a compensation coil, wound around the NMR probe has also been reported [7,9]. A fluctuating field detected by the former coil is used to create a compensation field with the latter coil.

In the NMR measurements with the pulsed magnet [2,11,12], the time-dependent magnetic field $B(t)$ with duration of the order of millisecond has been measured by split pickup coils located above and below a sample, and used as a reference signal for deconvoluting the observed NMR signal. This deconvolution technique that may be categorized into the group I is applicable to NMR with resistive and hybrid magnets in principle. However, some modifications are required for such application, because it is difficult for a pickup coil to detect probable slow fluctuation of resistive and hybrid magnets with a cycle time much longer than several milliseconds.

In the present work, the compensation technique that has been employed in NMR with the pulsed magnet is adapted to realize high-resolution NMR in resistive and hybrid magnets. An induced electromotive force (IEF) signal that can be utilized to remove effect of field fluctuation from the NMR signal is measured synchronously with NMR by using a pickup coil wound near a sample. Conversion from IEF data to field-fluctuation data is performed with a numerical fitting. We demonstrate this method for ^{79}Br MAS NMR of KBr using the hybrid magnet of NIMS excited at 30 T.

2. Principles

A magnetic field $B(t)$ provided by a bitter or hybrid magnet can be expressed as

$$B(t) = B_0 + B_f(t), \tag{1}$$

where B_0 is a "static" high-field of several tens of tesla and $B_f(t)$ is a time-dependent fluctuating field with an amplitude of the order of millitesla. A single-scan signal of free induction decay (FID), $g(t)$, for n Lorentzian curves under the magnetic field of Eq. (1) may be written as

$$g(t) = \sum_{j=1}^{n} a_j \exp[-\mathrm{i}(\Delta\omega_j t + \phi_f(t) + \phi_{0j}) - t/T_{2j}], \tag{2}$$

where a_j, $\Delta\omega_j$, ϕ_{0j} and T_{2j} are, respectively, a signal intensity, an NMR frequency at B_0, an initial phase, and a spin–spin relaxation time for the jth spectral component. $\phi_f(t)$ is a time-dependent phase angle caused by the field fluctuation $B_f(t)$ that is expressed as

$$\phi_f(t) = \gamma \int_{-\tau_d}^{t} B_f(t')\mathrm{d}t', \tag{3}$$

where γ is the gyromagnetic ratio of an observed nuclei. τ_d is a sum of a width of an rf pulse for signal excitation and an acquisition delay time. An origin of time coincides with the start of an acquisition of the FID signal.

In the present work, we obtain $B_f(t)$ by measuring an induced electromotive force (IEF) signal, $V(t)$, that arises in a pickup coil attached near a sample. Since the magnetic field $B(t)$ is sustainable over 1 h, it is impractical to measure the IEF signal $V(t)$ for a whole process of an experiment. Then, the measurement of $V(t)$ is performed synchronously with each acquisition of the FID signal $g(t)$. In this case, $B_f(t)$ can be estimated from $V(t)$ using the following equation,

$$B_f(t) = B_{f0} - \frac{c}{mS}\int_{-t_{ini}}^{t} V(t')\mathrm{d}t'. \tag{4}$$

Here, m and S are the number of turns and the cross sectional area of the pickup coil, respectively. c is a parameter expressing the magnetic permeability of materials existing inside the pickup coil. The acquisition of $V(t)$ starts at $-t_{ini}$ which satisfies an condition of $t_{ini} \geqslant \tau_d$. B_{f0}, an offset value of the fluctuating field of the resistive or hybrid magnet, appears because of the following duplicate reasons. One is that the detectable fluctuation field at $t = -t_{ini}$ is probably not zero. The other more important reason is that slow fluctuation with a period much longer than several milliseconds is likely to occur, which cannot be detected correctly with the pickup coil. We assume here that such slow fluctuation can be treated as a constant in a time scale on the FID measurement of the order of millisecond. c and B_{f0} are therefore treated as fitting parameters in deconvolution and determined numerically (*vide infra*). The compensation of the effect of field fluctuation on the NMR signal is conducted by calculating $\exp[\mathrm{i}\phi_f(t)]$ using Eqs. (3) and (4) from the observed IEF signal $V(t)$ and deconvoluting the FID data as follows:

$$\begin{aligned} g'(t) &= g(t) \times \exp[\mathrm{i}\phi_f(t)] \\ &= \sum_{j=1}^{n} a_j \exp[-\mathrm{i}(\Delta\omega_j t + \phi_{0j}) - t/T_{2j}]. \end{aligned} \tag{5}$$

The processed signal, $g'(t)$, that does not include $\phi_f(t)$, corresponds to the FID signal under the "static" field B_0.

Here, we describe the procedure to obtain the two parameters, c and B_{f0}, which is necessary for compensation of fluctuation as well as accumulation of NMR signals. The

phase angle, $\phi_f(t)$, in Eq. (3) can be rewritten using Eq. (4) as

$$\phi_f(t) = \phi_{f0} + \omega_{f0}t - \frac{c\gamma}{mS}\int_{-\tau_d}^{t}\int_{-t_{ini}}^{t'} V(t'')dt''\ dt', \qquad (6)$$

where $\phi_{f0} = \omega_{f0}\tau_d$ and $\omega_{f0} = \gamma B_{f0}$. The parameter B_{f0} is included only in the first two terms on the right-hand side of Eq. (6). The first and second terms affect the NMR signal as an additional phase and a resonance shift, respectively. On the other hand, the parameter c in the last term affects the spectral structure such as the linewidth in addition to variation of the phase and shift. Since the parameter c is common to the signals in an accumulation experiment, we determine it at first by minimizing the average linewidth of the manipulated spectra. B_{f0} is then adjusted for each data so that the peak position of all spectra shifts to the same position that should be close to the average peak position of the uncorrected spectra. When the intensity of the NMR signal of a sample is insufficient to perform the compensation, a material having strong signal intensities may be measured together with the sample for compensation.

3. Experimental

The measurements of NMR and IEF signals were performed with using the hybrid magnet placed at NIMS. The magnet operated at a field of 30 T consists of a Bitter-type resistive magnet (16 T) and a superconducting magnet (14 T). Details about the magnet are given in Ref. [4].

A narrow-bore single-tuned NMR probe with a JEOL 4 mmϕ MAS unit was used. A head of the probe was covered with a 40 mmϕ tin-coated copper tube of 0.5 mm thickness. A pickup coil made of a 0.435 mmϕ Cu wire was wound around this tube. The coil spread to 100 mm length with ca. 200 turns and its inductance was 120 μH. The covered probe-head was further shielded by an aluminum tube of 3 mm thickness. The IEF signal was measured by a digital oscilloscope with the dwell time of 0.4 μs.

The MAS NMR signal of ^{79}Br in KBr was acquired using a Tecmag APOLLO spectrometer at a resonant frequency of 324.0 MHz. Powder KBr was packed to a 2.4 mmϕ sphere cell, which is fit into a JEOL 4 mmϕ zirconia rotor. The MAS frequency of $\nu_r = 15.23$ kHz was stabilized within ±10 Hz. The single excitation pulse of 5 μs and the acquisition delay of 6 μs were followed by the acquisition of the FID signal with the dwell time of 0.8 μs. The spectrometer sent a signal to the above mentioned oscilloscope before irradiating the rf pulse for synchronous measurements of the FID and IEF signals. The start of the IEF measurement was $t_{ini} = 50$ ms.

The cancellation of field fluctuation was performed with Eqs. (3)–(5) using a home-written FORTRAN program. An apodization with the Lorentzian line broadening of 10 Hz was employed for the FID data prior to Fourier transform.

4. Results and discussion

We measured the FID signal of ^{79}Br MAS NMR of the powder sample of KBr and the IEF signal synchronously for 20 times under the 30 T magnetic field of the hybrid magnet. Figs. 1a and b show four FID data of them and the corresponding Fourier-transformed (FT) spectra, respectively. A ^{79}Br MAS NMR spectrum of KBr consists of a main peak at ν' and its spinning sidebands that appear at positions separated from ν' by integer multiples of the MAS frequency ($\nu' \pm n\nu_r$). For example, the spectrum of No. 1 exhibits such a structure with $\nu' = -13$ ppm and the spinning sidebands with $n \sim 3$. The full width at half maximum (FWHM) of the main peak was estimated after phase corrections to be 4.4, 4.7, 5.3 and 2.9 ppm for the data in No. 1–4, respectively. The average FWHM was 4.4 ± 1.6 ppm for the 20 data. Note that the peak position and phase of these spectra vary for each spectrum and ripples appear on either side of the peaks. This is because the magnetic field is unstable in time. For the 20 data, the peak position spread out about 206 ppm (−183 to 23 ppm)

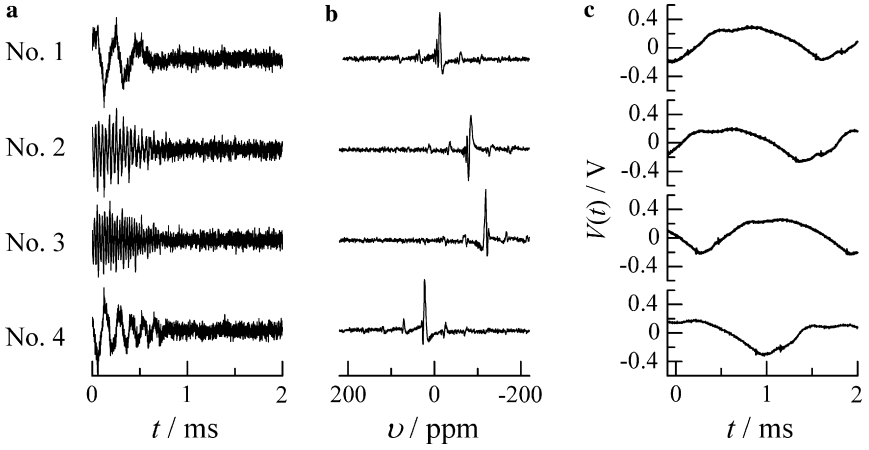

Fig. 1. Four examples of the single-scan data. (a) the FID signals of ^{79}Br MAS NMR of KBr acquired with the 30 T hybrid magnet, (b) the corresponding FT spectra, (c) the IEF signals measured synchronously with the FID signals shown in (a).

which corresponds to 6.3 mT. Hence, straightforward accumulation without compensation results in an undesirable spectrum (Fig. 3e-ii). The spreading of 6.3 mT is quite larger than the value of 3.0 mT obtained previously with this magnet [4]. This can be ascribed partially to instrumental differences and partially to a way of estimation; in the previous study the probe was inserted in an cryostat and a root-mean-square value of fluctuation was calculated.

Fig. 1c represents time dependence of the IEF signal, $V(t)$, measured synchronously with the FID signal in Fig. 1a by the pickup coil wound around the shielding tube of the NMR probe. It is found that field fluctuation observed by the pickup coil was not completely random but almost periodic with a cycle time of ca. 1.65 ms, but the starting point changes in each measurement. The amplitude of $V(t)$ was almost the same with the value of ca. 0.46 V peak-to-peak for all of our data.

Fig. 2a shows time dependence of the IEF signal, $V(t)$, which is the same data of No. 2 in Fig. 1c, and Fig. 2b is the corresponding fluctuation field, $B_f(t)$, converted using Eq. (4). Determination of the two parameters, c and B_{f0}, was carried out according to the scheme described in Section 2. The value of c was estimated as 5.0×10^4 T m^2 V^{-1} s^{-1}. B_{f0} spread within the range of −3.0–2.7 mT and was different for each data. For example, the B_{f0} value for the data in Fig. 2 was 0.4 mT. Fig. 2c shows time dependence of the phase angle, $\phi_f(t)$, obtained from the $B_f(t)$ in Fig. 2b with using Eq. (3).

We now show the step-by-step removing process of the fluctuating components from the NMR signal in Fig. 3. Fig. 3a-i and 3a-ii represent the raw FID signal of ^{79}Br MAS NMR and the corresponding FT spectrum, respectively. These are the data of No. 2 in Fig. 1. Fig. 3b shows the compensation signal, $\exp[i\phi_f(t)]$, generated with $\phi_f(t)$ obtained in Fig. 2c. Fig. 3c-i shows the deconvoluted signal, $g'(t)$, generated according to Eq. (5) by multiplying $g(t)$ (Fig. 3a-i) and $\exp[i\phi_f(t)]$ (Fig. 3b-i). Fig. 3c-ii shows that, as the result of the present compensation, the main peak of the spectrum shifted from ca. −82 ppm to −60 ppm, the phase changed from out-of-phase to in-phase, and the FWHM was reduced from 4.7 ppm to 3.2 ppm. Moreover, the ripples on the high-frequency side of the peak found in Fig. 3a-ii were removed. The spinning sideband also shifted to the position of integer multiples of the corrected main peak.

Fig. 3e shows the accumulated signal of the 20 single-scan raw data. The spectrum in Fig. 3e-ii has the spectral components distributing from ca. −183 to 23 ppm caused by field fluctuation of the hybrid magnet as denoted above. The superimposed data after deconvolution is shown in Fig. 3d. The signal-to-noise ratio of the spectrum in Fig. 3d-ii increases compared with that in Fig. 3c-ii because

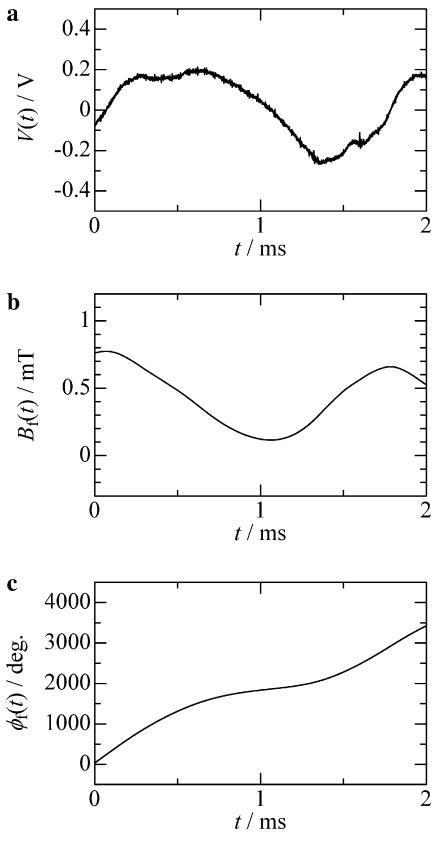

Fig. 2. Time dependence of (a) the IEF signal $V(t)$ measured synchronously with the FID siganl, (b) the corresponding field fluctuation $B_f(t)$ calculated by Eq. (4), and (c) the phase angle $\phi_f(t)$ by Eq. (3). The IEF data in (a) is the same data of No. 2 in Fig. 1(c).

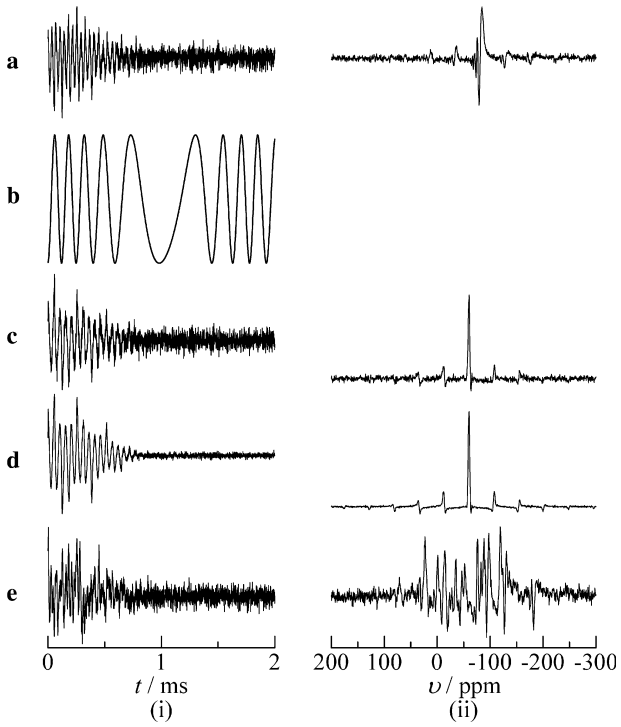

Fig. 3. (a) and (c–e): FID signals of MAS NMR of ^{79}Br in KBr measured with the hybrid magnet at 30 T (i) and the corresponding FT spectra (ii). (a) Shows the single-scan raw signal which is the same data of No. 2 in Fig. 1. (b-i) Represents the compensation signal for (a), $\cos\phi_f(t)$, fabricated from the IEF data shown in Fig. 2. (c-i) Shows the deconvoluted signal obtained by multiplying the raw signal (a-i) and the compensation signal (b-i) (see Eq. (5)). (d) and (e) Show the accumulated data of 20 deconvoluted and raw signals, respectively.

of proper accumulation. The spinning sidebands of the order of four ($\nu' \pm 4\nu_r$) or more become discernable after deconvolution and accumulation. The FWHM of 3.3 ppm obtained for the spectrum in Fig. 3d-ii is much smaller than the average FWHM of 4.4 ppm for the raw data. This is ascribed to the removal of the spectral distortion. The residual linewidth even after compensation is attributed to inhomogeneity of the magnet.

5. Conclusion

In the present work, we developed a method using a pickup coil for compensating effects of field fluctuation on an NMR signal observed under an unstable magnetic field. The method uses the IEF signal measured synchronously with FID for deconvolution calculation, and was demonstrated for ^{79}Br MAS NMR of KBr measured at the 30 T magnetic field of the hybrid magnet of NIMS by using an NMR probe attaching a pickup coil. Twenty single-scan NMR signals each of which has originally a different peak position and phase were deconvoluted and accumulated to generate a spectrum consisting of the single main peak and the spinning sidebands. The present method demands less for a sample as compared to the ZQC methods and the reference-deconvolution method.

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References

[1] K. Hashi, T. Shimizu, A. Goto, T. Kiyoshi, S. Matsumoto, H. Wada, T. Fujito, K. Hasegawa, M. Yoshikawa, T. Miki, S. Ito, M. Hamada, S. Hayashi, Achievement of a 920-MHz high resolution NMR, J. Magn. Reson. 156 (2002) 318.
[2] J. Haase, First ^{2}H NMR at 58 T, Appl. Magn. Reson. 27 (2004) 297.
[3] Z. Gan, P. Gorkov, T.A. Cross, A. Samoson, D. Massiot, Seeking higher resolution and sensitivity for NMR of quadrupolar nuclei at ultrahigh magnetic fields, J. Am. Chem. Soc. 124 (2002) 5634.
[4] K. Hashi, T. Shimizu, A. Goto, T. Iijima, S. Ohki, High-field NMR up to 30 T, Jpn. J. Appl. Phys. 44 (2005) 4194.
[5] C. Brevard, P. Granger, Handbook of High Resolution Multinuclear NMR, A Wiley-Interscience Publication, New York, 1981.
[6] Y.Y. Lin, S. Ahn, N. Murali, W. Brey, C.R. Bowers, W.S. Warren, High-resolution, >1 GHz NMR in unstable magnetic fields, Phys. Rev. Lett. 85 (2000) 3732.
[7] P.J.M. van Bentum, J.C. Maan, J.W.M. van Os, A.P.M. Kentgens, Strategies for solid-state NMR in high-field Bitter and hybrid magnets, Chem. Phys. Lett. 376 (2003) 338.
[8] E.E. Sigmund, V.F. Mitrovic, E.S. Calder, G.W. Thomas, H.N. Bachman, W.P. Halperin, P.L. Kuhns, A.P. Reyes, Inductive shielding of NMR phase noise, J. Magn. Reson. 159 (2002) 190.
[9] V. Soghomonian, M. Sabo, A. Powell, P. Murphy, R. Rosanske, T.A. Cross, H.J. Schneider-Muntau, Identification and minimization of sources of temporal instabilities in high field (>23 T) resistive magnets, Rev. Sci. Inst. 71 (2000) 2882.
[10] G.A. Morris, H. Barjat, T.J. Horne, Reference deconvolution methods, Prog. Nucl. Magn. Reson. Spectr. 31 (1997) 197.
[11] J. Haase, D. Eckert, H. Siegel, H. Eschrig, K.-H. Müller, A. Simon, F. Steglich, NMR at the frontier of pulsed high field magnets, Physica B 346-347 (2004) 514.
[12] M.B. Kozlov, J. Haase, C. Baumann, A.G. Webb, 56 T ^{1}H NMR at 2.4 GHz in a pulsed high-field magnet, Solid State Nucl. Magn. Reson. 28 (2005) 64.