Trial Measurement of NMR in a Bitter Magnet of NIMS

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Magnetic field homogeneity and stability of a Bitter type resistive magnet of National Institute for Materials Science (NIMS) have been examined at fields up to 23.5 T by means of NMR. The field homogeneity is 100 ± 10 ppm over a 5 mm DSV (diameter of spherical volume), being independent of field strength. The field instability observed at 23.5 T contains, at least, two contributions; 1) a periodic oscillation of frequency 50 ± 1 Hz and amplitude 100 ± 25 ppm, and 2) a drift at a typical rate of 50 ± 20 ppm/h. The magnet power supply seems to be primarily responsible for both instabilities.

High magnetic fields are required to improve NMR sensitivity and resolution especially for low-γ_N (γ_N nuclear gyromagnetic ratio) and/or large-Q (Q quadrupole moment) nuclei. Despite of successive progress of superconducting magnets (SCM) toward higher fields,[1] the uppermost field has been approaching its technological limit. Then, a hybrid or resistive magnet has recently been expected to be an alternative method to provide high fields up to 25–45 T.[2]

The aim of the present work is to examine the specifications of a Bitter type resistive magnet installed in our Institute (NIMS)[3] from the view point of NMR. A hybrid magnet is a combination of a Bitter magnet and SCM. Possible field fluctuations in the hybrid magnet can be attributed mostly to the Bitter magnet, due to the electrical specifications of the power supply and also to the low inductance of the Bitter magnet. Therefore we need to inspect the Bitter magnet first.

Figure 1 shows a schematic view of the Bitter magnet in NIMS. Although the magnet can be energized up to 28 T, the uppermost field guaranteed for a long time operation like NMR measurements is 25 T. We carried out the present work at a field of 23.5 T to intend simulating a milestone field corresponding to 1 GHz for proton. The power supply is 15 MW of 430 V and 35 kA. Cooling water flows in a rate of 700 $\mathrm{m^3/h}$, and its temperature regulated to be 9 ± 1 °C at the inlet. The outlet temperature is raised up to 28 °C at 23.5 T.

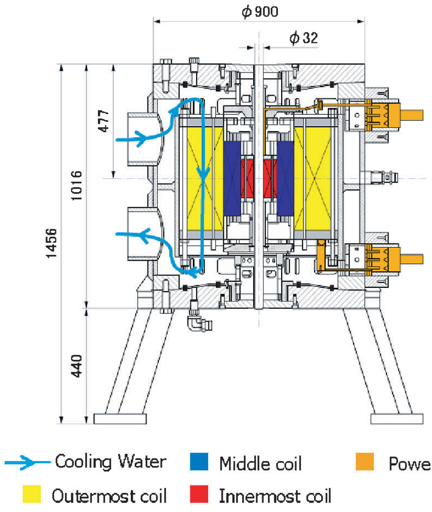

Figure 1. Schematic view of the Bitter magnet in NIMS. The three coils are made of stacking the Bitter plates.

The field distribution measured at 23.5 T along the axial direction (z-axis) can be fitted by a quadratic function, as shown in Figure 2. We can find from the fitting that (1) a maximum field is located at $z = 477 \pm 1$ mm, (2) the axial homogeneity is 100 ± 10 ppm over the length of 5 mm. We have found the same results as those from the measurement at 13.35 T. The NMR line width is also plotted as a function of z in Figure 2. The full width at the half maximum (FWHM) observed at the field center and 23.5 T is 30 ± 2 kHz, which corresponds to 27 ± 2 G (113 ± 10 ppm). The line broadening observed here may arise from possible inhomogeneity within the cylindrical sample volume which has a length of 5 mm in the xy plane and a diameter of 2 mm. The homogeneity seems approximately the same for both within the x–y plane and in the z-direction.

The field drift measured by the FID (free induction decay) signal of ^{2}D NMR in D_2O at 23.5 T during 1 h has been estimated to be 50 ± 20 ppm/h. This is a little bit better than the nominal specification of 100 ppm/h of the power supply stability.

Figure 3 shows fluctuations of the magnetic field at 23.5 T and the Fourier transform of the time dependence. There is a sharp peak at 50 ± 1 Hz in the FT spectrum. The amplitude of this oscillation is 20 ± 5 G, i.e., 100 ± 25 ppm. The AC ripple left behind in the power supply seems responsible for that. This is reasonable, considering the nominal specification of the rectifier, 100 ppm, in its root mean square amplitude for the AC ripple. We need an improvement of the power supply system to achieve a high resolution NMR measurement which may require

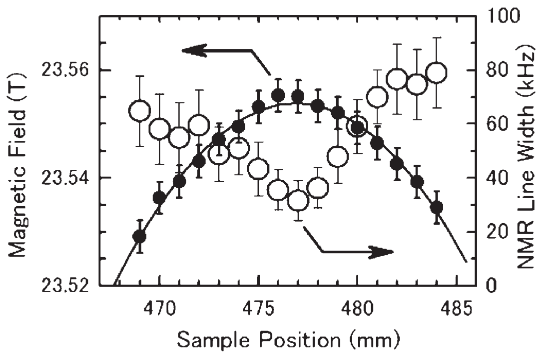

Figure 2. The closed symbols show the magnetic field evaluated by the spin echo signal of ^{63}Cu NMR in Cu metal at the sample position measured along the z-axis direction from the top of the magnet. The open symbols show the line width.

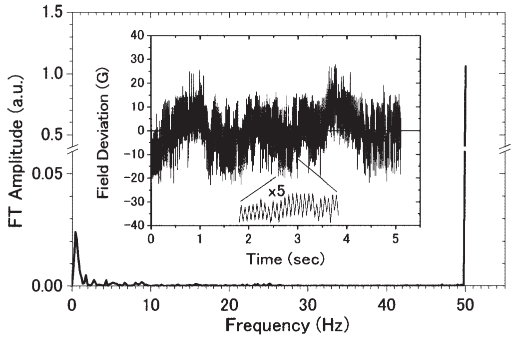

Figure 3. Fluctuations of the magnetic field monitored by the spin echo signal of ^{63}Cu NMR in Cu metal at 23.5 T. The time dependence is shown in the inset where the vertical axis represents the field deviation from 23.5 T. The main panel shows the Fourier transform of the fluctuation.

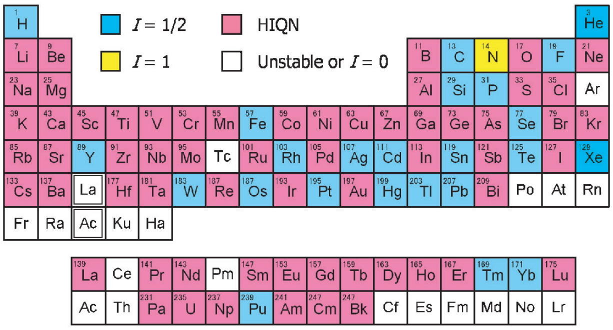

Figure 4. Periodic chart of the 4 types of nuclear spin. Most abundant isotopes are only shown. HIQN indicates the spin half-integer quadrupole nuclei. Colored elements (blue, red and yellow) are the NMR available ones.

a stability of 1 ppm/h or better.

Possible applications of such a high field NMR may cover a wide range of quadrupolar nuclei like Al, B, Ca, Cu, O, Ti, etc., which are very often essential ingredients especially in inorganic materials. About 75% among the NMR available elements are spin half-integer quadrupolar nuclei (HIQN), as shown in Figure 4. Many HIQN can be seen in practically important materials. HIQN located at non-cubic sites gives a poor resolution, because a possible 2nd order quadrupole effect giving rise to a line broadening cannot completely be resolved by a conventional high resolution technique such as magic angle spinning (MAS). Applying high field may be the best straightforward solution to improve the resolution of HIQN, because the 2nd order quadrupole effect is reduced in inverse proportion to the field.[4]

We plot the typical examples of HIQN in Figure 5. The vertical axis in Figure 5 is the square of the nuclear perceptivity relative to that of proton, Γ/Γ_0, being proportional to the time taken to accumulate the signal.[5] The lower the nucleus is plotted, the weaker the NMR signal is in a common experimental condition. The horizontal axis in Figure 5 is the coupling constant of the 2nd order quadrupole interaction in the central transition

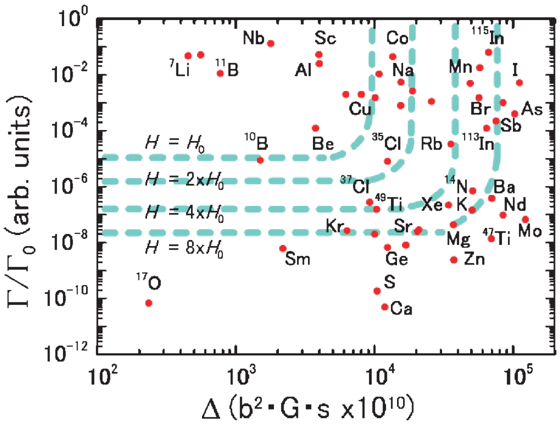

Figure 5. Magnetic field dependence of signal intensity and resolution of typical quadrupole nuclei. Δ is plotted in the units of barn^2·Gauss·second × 10^{10}.

(+1/2 ↔ −1/2),[4] defined by

$$\Delta = \left[\frac{Q}{2I(2I-1)}\right]^2\left[\frac{I(I+1)-\frac{3}{4}}{\gamma_N}\right] \quad (1)$$

The definition of Δ is only dependent on the nuclear constants, so that it represents "resolution susceptibility" how much the nucleus is sensitive to the 2nd order quadrupole interaction in a common environment. The more right the nucleus is plotted, the poorer the spectrum resolution is. The contours drawn in Figure 5 illustrate how high fields work for both signal intensity and resolution for HIQN. We have obtained the field dependence of the contours in a qualitative manner by considering the field dependences of the signal intensity[5] and 2nd order quadrupole effect[4] relative to a unit field H_0. The higher the field is, the more elements can be resolved in a better signal intensity.

In conclusion, for a high resolution measurement, magnet shims will be needed and the AC ripple of 50 ± 1 Hz should be reduced to a tenth or less. High fields can provide a new opportunity to upgrade NMR of quadrupolar nuclei in inorganic materials.

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