Field-Swept NMR Spectra of ^{11}B in Pyrex Glass and ^{93}Nb in NbN Perturbed by Quadrupole Interaction*

H. Yoshida, H. Nishihara, S. Yokota, M. Ohyanagi, and T. Nakaoki

Faculty of Science and Technology, Ryukoku University, Seta-oecho 1, Otsu 520-21, Japan

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NMR experiments of ^{11}B by both field-swept and high-resolution NMR are reported to probe the electric field gradient at boron sites and its distribution in Pyrex glass. Both spectra are successfully interpreted with the same set of parameters. It is stressed that field-swept NMR experiments to observe total powder spectrum can be helpful to get information on electric field gradients and asymmetry parameters if there exist many nonequivalent sites of atoms, since satellite transitions are affected by the larger first-order quadrupole effect. Field-swept NMR of ^{93}Nb in superconducting NbN powder, prepared by self-propagating high-temperature synthesis, is also reported. A very broad field-swept spectrum disturbed by quadrupole interaction has been observed. The spectrum is simulated by assuming distributions in electric field gradient and Knight shift at Nb sites. It is stressed that a combination of experiments at separated frequencies is important

Key words: NMR; Pyrex; Glass; ^{11}B; NbN; Superconductor; ^{93}Nb.

1. Introduction

Modern Fourier-transform high-resolution NMR techniques with increased magnetic fields have been applied to solid state glasses. However, magic angle spinning (MAS) methods have been most successful for spin-1/2 nuclei since powder spectra of central transition of quadrupolar nuclei suffer from the residual broadenings of second-order quadrupole effects and distributions of both chemical shift and electric field gradient. In order to overcome this problem, more sophisticated methods of double rotation, dynamic angle spinning and multiple-quantum angle spinning have been proposed and studied [1]. However, these sophisticated high-resolution NMR methods are not simple and mainly focused on central transitions except the case which uses extremely short pulses to excite a spectral range which involves a part of the satellite transitions [1]. We report here a rather simple experiment of field-swept NMR, which is familiar in solid state physics, to observe total powder spectra of ^{11}B in Pyrex glass including satellite transitions. The satellite transitions are affected by the larger first-order quadrupole effect. Simulations for the total powder spectrum are reported and discussed together with usual high-resolution NMR data.

We also report another case of the field-swept NMR experiment of ^{93}Nb in a superconductor NbN prepared by self-propagating high-temperature synthesis. A very broad field-swept spectrum, disturbed by quadrupole interaction, has been observed, where no satellite peak has been apparent. The spectrum is simulated by assuming distributions in the electric field gradient and Knight shift at Nb sites. It is stressed that a combination of experiments at well-separated frequencies is important.

2. ^{11}B NMR in a Pyrex Glass

A Fourier-transformed high-resolution NMR spectrum of ^{11}B in Pyrex glass at 64.167 MHz has been taken with a Bruker MSL 200 and shown in Figure 1(a). The sharp peak at the center comes from tetrahedral BO_4 sites (12% of the total) and the residual double peak comes from trigonal BO_3 sites. It is quite different from that reported in a Japanese textbook [2] where only two peaks were observed and interpreted as overlapped spectrum from three sites with quadrupole frequency $\nu_Q = 3e^2qQ/2I(2I-1)h$ of 1.25, 2.50 and 2.55 MHz. NMR experiments in swept fields have been performed with a home-built, phase coherent pulsed NMR spectrometer. A field-swept NMR spectrum of ^{11}B in our sample of Pyrex glass at

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Reprint requests to Dr. H. Nishihara;
e-mail address, nisihara@rins.ryukoku.ac.jp.

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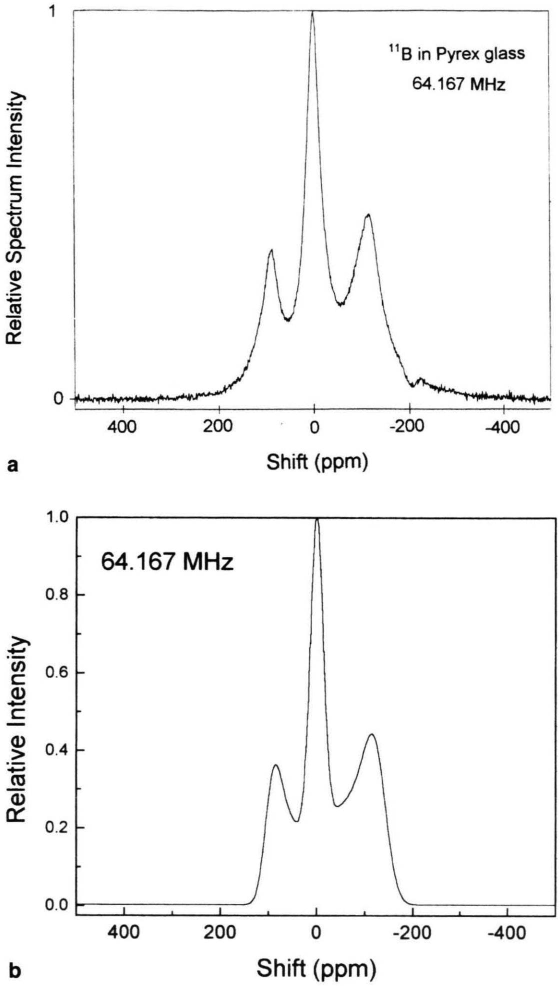


Fig. 1. (a) A Fourier-transformed high-resolution NMR spectrum of ^{11}B in a sample of Pyrex glass at 64.167 MHz with Bruker MSL200. (b) A simulated spectrum (see text).

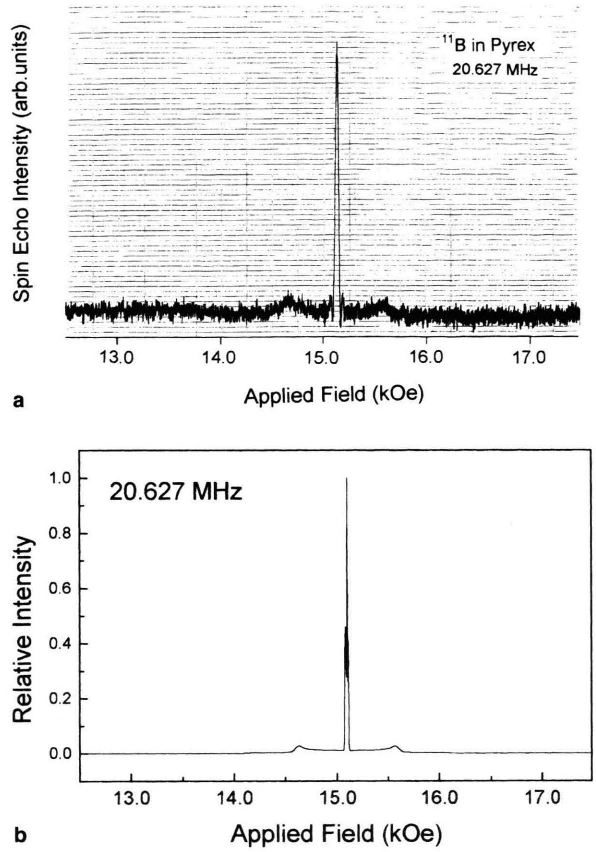


Fig. 2. (a) A boxcar trace of a field-swept NMR spectrum of ^{11}B in a sample of Pyrex glass at 20.627 MHz. (b) A simulated spectrum with the same set of parameters as in Figure 1(b).

20.62705 MHz is shown in Figure 2(a). Broad satellite transitions in the powder spectrum with nearly axial symmetry are seen together with a sharp central line. It is to be noted that a very sharp line suffers from instrumental broadening in this method due to spectral width of exciting rf pulses with an order of 10 kOe together with wiggles caused by the free decay signal after the second rf pulse. Two samples from different companies were tried but essentially the same spectra have been obtained. A Fourier-transformed NMR spectrum of ^{11}B at an applied field of 15.100 kOe with an electromagnet was also taken and is shown in Figure 3(a). In this kind of experiment, a very sharp line suffers from the broadening due to inhomogeneity of the static field created by the electromagnet.

Simulations of the spectra have been done by assuming Gaussian distributions in quadrupole frequency and Knight shift. Considering the instrumental width described above, all three experimental spectra can be explained reasonably well with the following same set of parameters: ν_Q= 1.35 [MHz], a standard deviation of the distribution in ν_Q of 0.06 ν_Q, and a standard deviation of the distribution in shift of 12 ppm for the trigonal BO_3 sites with 88% population, and ν_Q=1 [kHz], a standard deviation of the distribution in ν_Q of 0.03 ν_Q, and a standard deviation of the distribution in shift of 12.5 ppm for the tetrahedral BO_4 sites with 12% population, as are demonstrated in Figs. 1(b), 2(b) and 3(b).

Although the efficiency of the high-resolution NMR at high fields is apparent, it is stressed that the field-swept NMR experiment can be helpful to get information on electric field gradients and asymmetry parameters if there are many nonequivalent sites, since satellite transitions are affected by the larger first-order quadrupole effect.

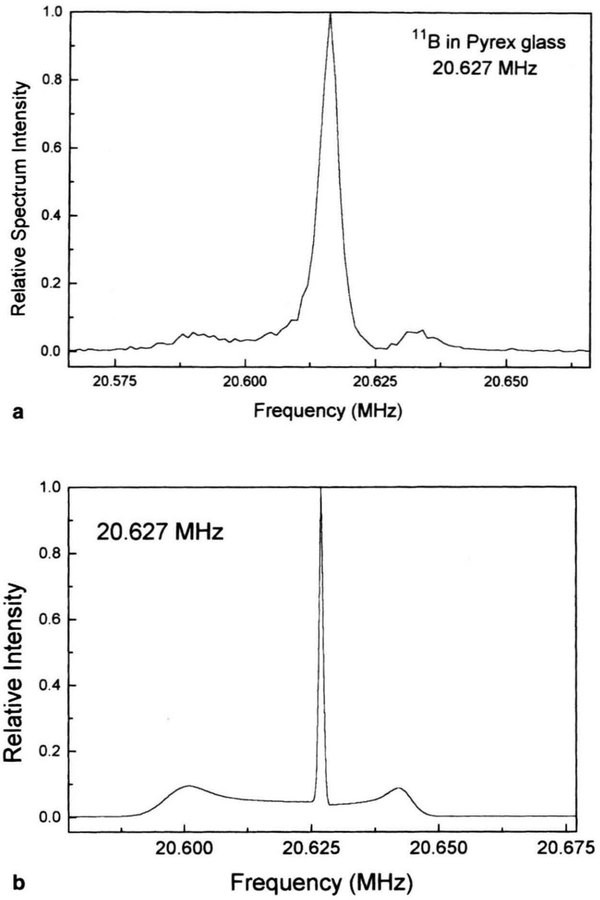


Fig. 3. (a) A Fourier-transformed NMR spectrum of ^{11}B at an applied field of 15.100 kOe with an electromagnet. (b) A simulated spectrum with the same set of parameters as in Figure 1(b).

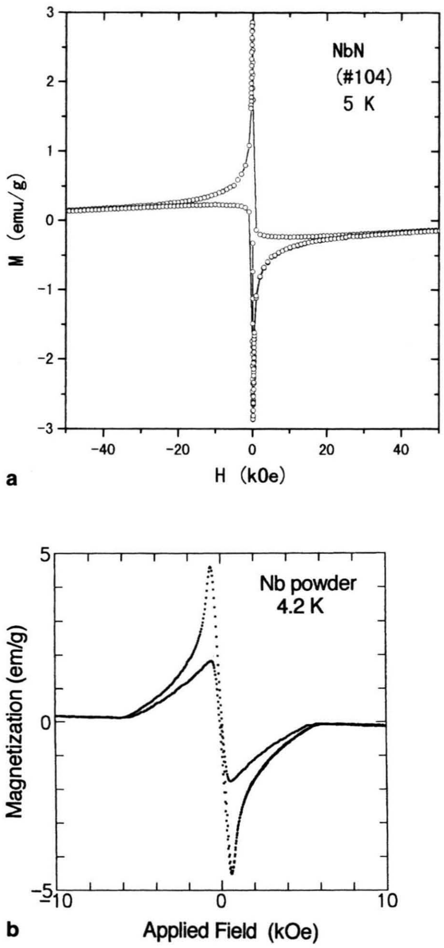


Fig. 4. (a) A hysteresis loop of the magnetization of NbN powder at 5 K synthesized by HTS (see text). (b) A hysteresis of the magnetization of Nb powder at 4.2 K.

For example, it is possible to decide whether an interpretation like in [2] is true or not by doing field-swept NMR, where two first-order satellite transitions with ν_Q of 1.25 and 2.50 (2.55) MHz must be separately observed.

3. ^{93}Nb NMR in NbN

Mononitrides of early transition metals are hard, resistant to chemical attack, stable at high temperatures, and used as protective coatings. A high-temperature phase of NbN with cubic B1 structure shows superconductivity below T_c of about 16 K with rather high critical field. The materials were originally synthesized by direct reaction of the metals in a nitrogen atmosphere at high temperature for extended periods of time. Chemical vapor deposition or reactive magnetron sputtering is also possible. The production of NbN is not easy since it is necessary to quench the high-temperature phase. The method of self-propagating high-temperature synthesis (SHS) has been also tried to take advantages of the short reaction times, the higher-purity of the products, the low-energy requirements and the relative simplicity of the method [3, 4]. Although the combustion process is often incomplete, and unreacted metal or lower nitrides are left in the product, we rather expect in the case of superconduction that such defects make the flux-pinning force even stronger and make the critical current higher. We demonstrate here that the field-swept NMR experiment of ^{93}Nb is powerful to characterize the product from a microscopic viewpoint, since quadrupole interaction for ^{93}Nb ($I=9/2$, $Q=-0.2$ barn) strongly disturbs a field-

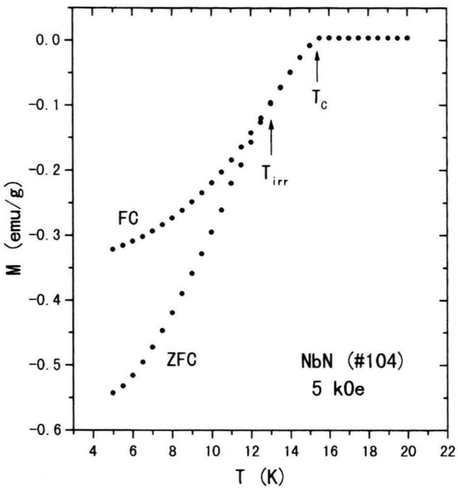


Fig. 5. An example of the temperature dependence of the magnetization under zero-field cooled (ZFC) and field-cooled (FC) conditions at an applied field of 5 kOe for a powder of NbN synthesized by SHS.

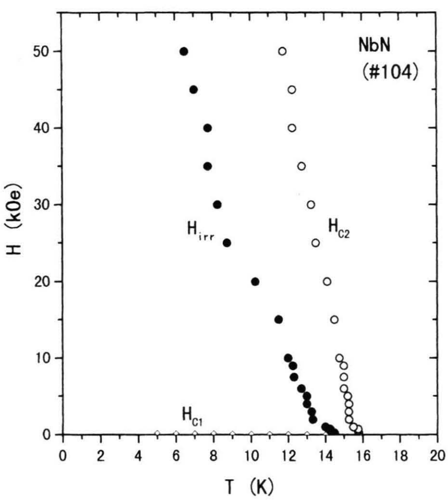
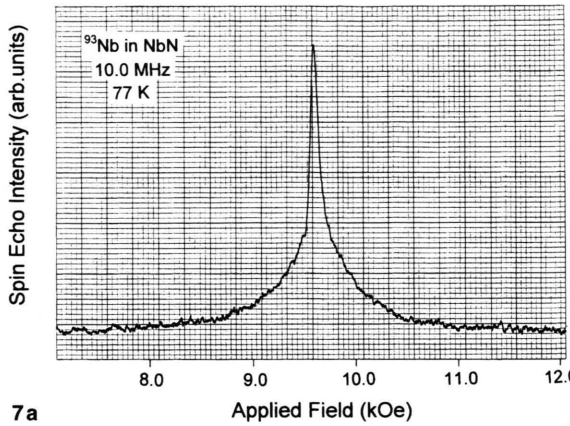


Fig. 6. The critical fields H_{C1} and H_{C2} and the irreversibility field H_{irr} as function of temperature for a powder of NbN synthesized by SHS.



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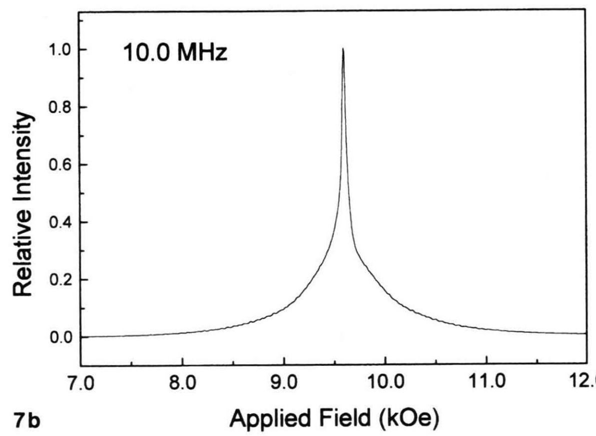
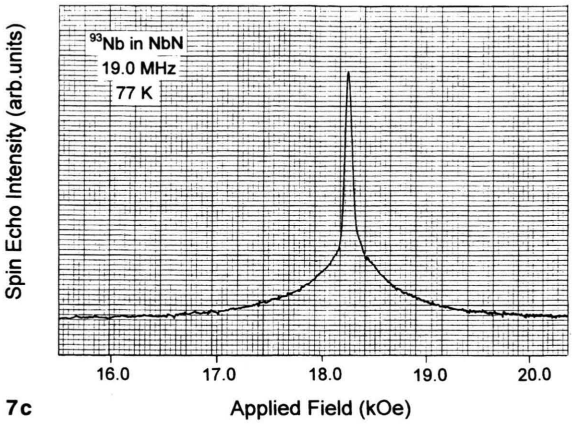


7b

swept NMR spectrum if the local symmetry around Nb deviates from the cubic symmetry in the high-temperature phase of NbN which is superconducting at low temperature.

The method of sample preparation has been described in [3]. The magnetization of the powder of NbN synthesized by SHS as a function of an applied field or temperature has been measured by a commercial SQUID magnetometer (Quantum Design MPMS-5S). The magnetization process of a sample #104 at 5 K, synthesized from a starting material of Nb +20 mol% NbN at a nitrogen pressure of 8 MPa, is shown in Fig. 4(a) which is compared to a typical data for Nb powder shown in Figure 4(b). An example of the temperature dependence of the magnetization in zero-field cooled (ZFC) and field-cooled (FC) conditions at 5 kOe for the same sample is shown in Figure 5. The critical fields H_{C1} and H_{C2} and the irreversibility field H_{irr} determined are shown in Fig. 6 as a functions of temperature. The volume fraction of the superconductor in the sample is estimated to be about 100% by assuming the demagnetizing factor for the spherical sample. The amount of the hysteresis of the magnetization is larger than in the case of Nb powder. Although it is apparently smaller than in the cases of NbTi or Nb_3Sn, where H_{C1} and H_{C2} are nearly the same.

NMR experiments have been performed with a home-built, phase coherent pulsed NMR spectrometer. Figures 7(a) and (c) show examples of field-swept NMR spectra of ^{93}Nb at 77 K taken at 10 and 19 MHz, respectively, in the same powder of NbN. No clear quadrupole satellite



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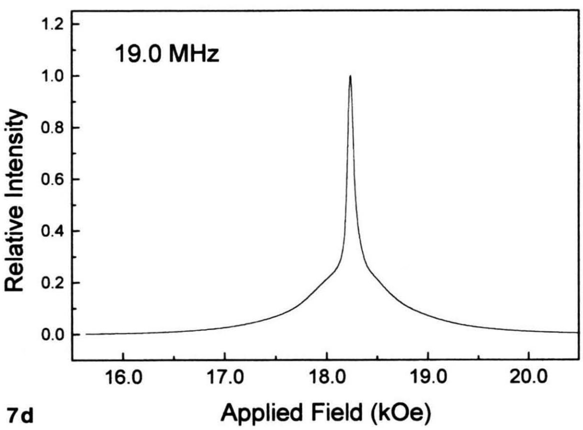

7d

Fig. 7 (a) A boxcar trace of a field-swept spin-echo spectrum of ^{93}Nb in NbN synthesized by SHS taken at 10 MHz and 77 K. (b) A simulated spectrum for 10 MHz. (c) A boxcar trace of a field-swept spin-echo spectrum of ^{93}Nb in the same sample of NbN taken at 19 MHz and 77 K. (d) A simulated spectrum for 19 MHz with the same set of parameters (see text).

lines are observed, and this shows that the local symmetry around Nb atoms deviats from cubic symmetry and the field gradient has a large distribution. A simulation of the spectra has been done by assuming Gaussian distributions in both quadrupole frequency ν_Q and Knight shift K. The experimental spectra could be reproduced reasonably well with the same set of parameters of $\nu_Q = 3e^2qQ/2I(2I-1)\,h = 0.60$ [MHz], a standard deviation of the distribution in ν_Q of 0.55 ν_Q, the isotropic part of the shift K_{iso}=0.015%, a standard deviation of the distribution in K_{iso} of 0.05%, the axially-symmetric part of the shift K_{ax} = 0.5%, and a standard deviation of the distribution in K_{ax} of 0.25%, as is demonstrated in Fig. 7(b) and (d). It is important to compare experiments with well-separated frequency to determine the distributions in the shift and the quadrupole frequency, since the width of the central transition is proportional to the frequency if it is dominated by the distribution in shift, while the width is inversely proportional to the frequency if it is dominated by the second order quadrupole effect.

In conclusion, the large randomness in the local environments at Nb sites due to quick reactions in SHS has been clearly seen by the present NMR experiments. It might be related to the relatively large flux-pinning force observed without special heat treatment after the reaction.

Acknowledgements

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[1] See, e.g., Proceeding of XIIIth International Symposium on NQI, Brown University, 1995 (Z. Naturforsch. **51a,** (1996) and references therein.
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