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$^{10}B/^{11}B$ 1D/2D solid-state high-resolution NMR studies on boron-doped diamond

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ABSTRACT

In this work, three boron-doped diamond samples prepared from a high-pressure high-temperature synthesis method with the same starting materials but with different initial ratios for boron are studied. Magnetic susceptibility measurement shows that the increment of the initial amount of boron does not straightforwardly bring lower superconducting transition temperature. In accordance with our previous ^{11}B high-resolution magic-angle spinning (MAS) NMR results, we show that there are at least four boron signal components and the one at 28.5 ppm is ascribed to the substitutional boron in the diamond structure providing the carriers responsible for conductivity. From observed relative intensities of the four signal components, it is suggested that the excess boron, which does not contribute to the conductivity appears as a broad signal at around 65.5 ppm. We apply two-dimensional (2D) NMR to examine ^{1}H dipolar broadening and ^{11}B–^{11}B boron spin diffusion, and candidates purported so far for the excess boron, that is, a boron + hydrogen complex and –B–B– and/or –B–C–B– clusters are negated. From its chemical-shift value, it is suggested that the excess boron exists as trigonally coordinated boron. We further apply 2D nutation NMR to examine the size of its quadrupolar coupling and show that it is not very large. As for a structure that compromises the trigonal coordination invoked from the chemical-shift value and the small quadrupolar coupling, we postulate boron locally in a graphite-like structure but the symmetry of the electric field gradient around it is high. Furthermore, we show that ^{10}B MAS NMR is useful to selectively observe the substitutional boron in the diamond structure appearing at 28.5 ppm, whose quadrupolar coupling is much smaller than that of the excess boron at 65.5 ppm.

1. Introduction

Recently, we showed that ^{11}B solid-state NMR is useful for the characterization of boron-doped diamonds prepared by either high-pressure and high-temperature (HPHT) or chemical vapour deposition (CVD) methods with various starting materials [1,2]. Boron-doped diamond is an interesting material as it shows superconductivity [3]. The boron atom included into the diamond structure offers the effective carriers responsible for the superconductivity; therefore assignment of the boron NMR signal of the substituted boron at the carbon site was of importance.

From the comparison among the ^{11}B high-resolution solid-state NMR spectra achieved by using magic-angle spinning (MAS), and also their dependences on the magnetic field as well as the pulse-flip angle, we suggested that at least four kinds of boron including two impurities exist in boron-doped diamond [2]. In the two major signal components, we further suggested that one boron signal, whose quadrupolar coupling constant is small and its spin-lattice relaxation time (T_1) is short, is ascribed to boron that provides effective carriers for conduction [2]. In this work, we investigated three samples, whose starting materials used for the HPHT synthesis were the same (naphthalene and amorphous boron) but with different initial ratios, B/(B + C), to discuss the relation between the spectral feature and conductivity. To examine the complex boron NMR signals, we further applied ^{10}B solid-state NMR and several two-dimensional (2D) ^{11}B NMR techniques.

2. Experimental

2.1. Samples

Three boron-doped diamond samples (N1, N2, and N3) prepared by the HPHT method using naphthalene and amorphous boron with the initial boron concentration B/(B + C) = 0.75%, 2.4%, and 5.0% for N1, N2, and N3, respectively [4], were examined. The N3 sample is the one examined in our previous work (HPHT-1 in Ref. [2]). The magnetization

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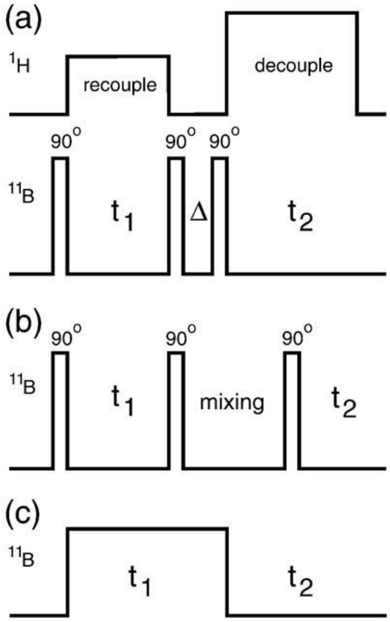

Fig. 1. Pulse sequences of 2D ^{1}H on/off experiment under MAS (a), 2D exchange NMR (b), and 2D nutation NMR (c).

properties were measured by a superconducting quantum interference device magnetometer down to 1.78 K. Borax (sodium tetraborate decahydrate; $Na_2[B_4O_5(OH)_4]\cdot8H_20$) was purchased from Kanto Chemical Co. Inc. and used without further purification.

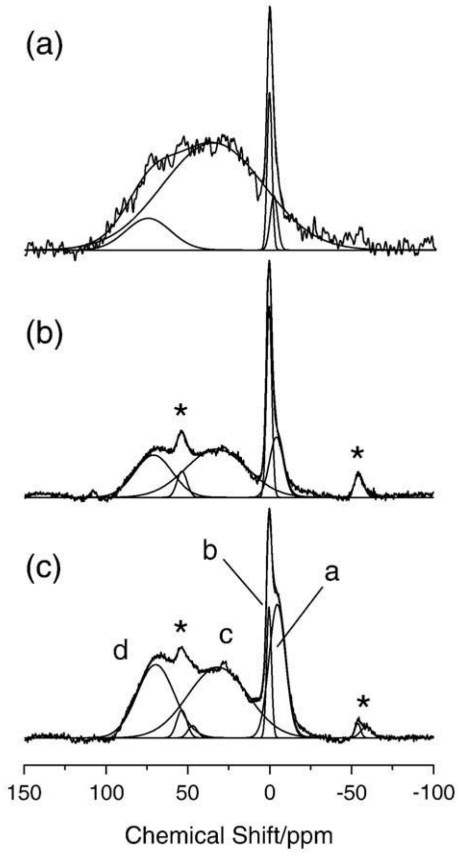

Fig. 2. ^{11}B MAS NMR spectra observed at 21.8 T for N1 (a), N2 (b), and N3 (c). The Gaussian lineshapes used for fitting to estimate the intensities of the four signal components are also shown. The peaks marked with * are spinning-side bands. The MAS frequency was 16 kHz.

2.2. NMR experiments

^{11}B and ^{10}B MAS NMR spectra were recorded at 21.8 T on a JEOL ECA 930 spectrometer with a JEOL 4 mm MAS probe and at 11.7 T on a JEOL ECA 500 spectrometer with a Chemagnetics 3.2 mm MAS probe. All experiments were done at room temperature. The ^{11}B resonant frequency at 21.8 was 298.4 and 160.5 MHz at 11.7 T. The ^{10}B resonant frequency at 11.7 T was 53.7 MHz. The MAS frequency was 16 kHz at 21.8 T and 20 kHz at 11.7 T. The ^{11}B and ^{10}B chemical shifts are referenced to those of saturated H_3BO_3 solution at 19.49 ppm, respectively. All one dimensional (1D) ^{10}B/^{11}B NMR spectra were observed by using a single 30° pulse calibrated using the ^{11}B or ^{10}B signals of saturated H_3BO_3 solution. The ^{11}B rf strength at 21.8 T was ca. 139 kHz and at 11.7 T ca. 167 kHz. The ^{10}B rf strength at 11.7 T was ca. 139 kHz. Fig. 1 shows the pulse sequences for the 2D experiments used in this work. Further details of NMR experiments are given in Section 5.

3. Results

3.1. ^{11}B MAS spectra and diamagnetic measurements

Fig. 2 shows the ^{11}B MAS NMR spectra of N1, N2, and N3 observed at 21.8 T, which consist mainly of four signals (signal-a to signal-d as indicated in the figure) with a few spinning-side bands designated by asterisks. According to the previous work [2], we fit each spectrum to a sum of Gaussian lineshapes. The absolute area intensities for the four signals in N1 to N3 obtained by fitting were scaled by taking the different number of signal accumulation into account and further divided by the weight of the corresponding sample to deduce relative concentration of the four kinds of boron. The concentrations in N1–N3 thus obtained are collated in Table 1. The concentration of signal-a, which was attributed to B_4C [2], increases monotonically with the increase of the initial amount of boron, while that of the other impurity (boron cluster; signal-b) decreases from N2 to N3.

Examination of Table 1 shows that, when the initial amount of boron is small, boron associated with signal-c (hereafter, boron-c), which we assigned [2] to the substitutional boron in the diamond structure, increases. Further increase of the initial amount of boron, however, does not straightforwardly contribute to the increase of boron-c but boron-d does also increase. Here we refer boron associated with signal-d to as boron-d. To examine how this observation is related with conductivity, the temperature dependence of the magnetization for each sample is observed (Fig. 3). Diamagnetic signals corresponding to superconductivity appeared for N2 and N3 below 4 K. Further the transition temperature for N2 is slightly lower than that for N3, indicating that excess boron does not contribute to conductivity. These results support our previous assignment of boron-c being boron contributing to conductivity. Further, the excess boron becomes boron-d.

3.2. ^{11}B chemical shifts

From the accumulated ^{11}B chemical-shift data of organo-boron compounds [5], it has been well established that ^{11}B shifts of tetrahedrally coordinated borons appear at lower frequencies; for a few examples, −16 to −20 ppm for $[BR_4^-]$, −6 ppm for $[BPh_4^-]$, and 3 ppm for $[B(OR)_4^-]$. The observed chemical shift of signal-c (ca. 28.5 ppm), which we assigned to the tetrahedrally coordinated

Table 1
Relative concentrations (g^{-1}) of the borons associated with the signals a–d.

	a	b	c	d
N1	11.1	2.6	31.7	6.2
N2	28.8	38.3	102.3	60.7
N3	36.3	16.5	112.6	71.6