Solid State NMR of ^{11}B and ^{13}C in Boron Carbide, $B_{12}C_3$ and ^{11}B Enriched $B_{12}C_3$

Toshie Harazono,* Yukiyo Hiroyama,† and Tokuko Watanabe††

Research Center, Mitsubishi Chemical Co., Ltd., 1000, Kamoshida, Aoba-ku, Yokohama 227

†Bruker Japan, 3-21-5, Ninomiya, Tsukuba, Ibaraki 305

††Tokyo University of Marine Sciences, 4-5-7, Kounan, Minato-ku, Tokyo 108

(Received February 8, 1996)

^{11}B- and ^{13}C-solid state NMR of boron carbide with different isotope ratios, $B_4C(^{11}B/^{10}B = 80.42/19.58$; natural abundance isotope) and $^{11}B_4C(^{11}B/^{10}B = 99.5/0.5$; ^{11}B enriched sample), has been investigated. The linewidth of the icosahedral B ($6h_1$ and $6h_2$) in ^{11}B-static NMR signal in $^{11}B_4C$ was greater in $^{11}B_4C$ than in B_4C, which indicates that the B–B dipole–dipole interaction is the main mechanism for the broadening of the ^{11}B-static NMR signal. The quadrupole coupling constant calculated from the signal position of ($\pm 1/2 \leftrightarrow \pm 3/2$) transition was about 0.1 MHz. ^{11}B-MAS spectra revealed the presence of at least two additional B sites (37 ppm and near -60 ppm) besides the icosahedral B sites (-6 ppm).

Recently, boron carbide, B_4C ($=B_{12}C_3$) has attracted considerable attention as the dopant of graphite–B_4C composites which have useful properties, such as high strengths in tensile, bending or impact, and high heat- or acid-resistances. In spite of the usefulness of B_4C, few physical and chemical analyses of their properties have employed the method of solid state NMR.

The crystal structure of boron carbide has been known to be the rhombohedral unit cell ($B_{12}C_3$) which is composed of the icosahedral subunit (B_{12}) and the three-atom chain of carbon atoms (C_3), as shown in Fig. 1.[1] Boron atoms occupy two nonequivalent sites of $6h_1$ (bonded to carbon atom; closed small circle) and $6h_2$ (bonded to boron atom; open small circle) while carbon atoms are present in 1b (atom at the center of the chain; closed large circle) and 2c (atoms at ends of the chain; open large circle). Concerning the structure of B_4C, several investigations on the basis of ^{11}B and ^{13}C NMR have been reported,[2—8] but there still exist controversial subjects in the assignment of signals and in the substitution between B and C in B_4C.

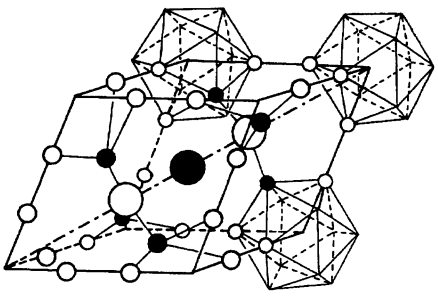

Fig. 1. Crystal structure of boron carbide. •: Boron-$6h_1$, ○: Boron-$6h_2$, ●: Carbon-1b, ○: Carbon-2c.

Thus far, the signal due to two types of B in the icosahedron (near 0 ppm) and the signal due to B substituted in the central C of three-atom chain (near 130 ppm) were detected by ^{11}B NMR.[2—4] Such data suggest the presence of $(B_{11}C)(CBC)$ or $B_{10}C_2(CBB)$ in $B_{12}C_3$.[4] The presence of icosahedral C in B sites in icosahedron such as $B_{11}C(CBC)$ or $B_{10}C_2(CBB)$ besides $B_{12}(CCC)$ was strongly emphasized from ^{13}C- MAS NMR for ^{13}C-enriched boron carbide, and ^{11}B-MAS and -static NMR spectra by Kirkpatrick et al.[4] Conard et al. also supported the presence of icosahedral C site by ^{13}C and ^{11}B NMR.[5] On the other hand, Duncan reported that the carbon was only present as C_3 chains on the basis of ^{13}C–^{11}B heteronuclear dipole couplings determined from the results of spin-echo experiments.[6,7] Therefore, the assignment of the ^{13}C signal at 79 ppm does not agree between Kirkpatrick et al. and Duncan, i.e., icosahedral C in the former and central C of chain in the latter.

It was reported that the quadrupole coupling constant, e^2qQ/h, of the icosahedral B ($6h_1$ and $6h_2$) was (0.2—1.3) MHz in the single crystal[2] and (0.06—1) MHz in the powder[3] by ^{11}B–CW NMR. On the other hand, e^2qQ/h of B in the chain was reported as 5.55 MHz[2] and 5.4 MHz[3] by Silver and Bray, and Hynes and Alexander, respectively.

On the other hand, very few investigations on the interpretations of ^{11}B-static lineshape have been reported.[2—5,8] The earlier investigations of ^{11}B spectra in boron carbide were based on the analysis of second-order quadrupolar effects.[2,3] Conard et al. indicated that the ^{11}B-static spectrum was composed of a central line and an asymmetrical doublet due to a second-order quadrupolar effect.[5] Further, Saraswati et al. mentioned that the peak separation was based on a mixture

of phases.[8] Kirkpatrick et al. suggested that the linebroadening of ^{11}B-static signal was due to unaveraged second-order quadrupole effects and a large homonuclear dipole–dipole interaction.[4] The interpretation of ^{11}B linebroadening is thus controversial.

In this paper, we aim to elucidate the structure of boron carbide (B_4C) and the interpretation of ^{11}B-static lineshape. For this purpose we measured the ^{11}B-static and -MAS NMR and ^{13}C-MAS NMR spectra on boron carbide with different isotope ratios, i.e., B_4C ($^{11}B/^{10}B = 80.42/19.58$) and ^{11}B-enriched $^{11}B_4C$ ($^{11}B/^{10}B = 99.5/0.5$). The isotope-enriched ^{11}B spectrum is new data on boron carbide.

Experimental

Materials. B_4C and $^{11}B_4C$ were purchased from Hermann C. Starck Berlin Co., Ltd. and Eagle Pitcher Co., Ltd., respectively. As impurities, a few % of graphite and 0.7 % of Si in B_4C, and a slight amount of B_2O_3 and 0.3 % of Ca in $^{11}B_4C$ were detected by X-ray powder diffraction and an atomic emission spectrometry.

Apparatus and Measurements. X-Ray powder diffraction with monochromated Cu $K\alpha$ was carried out using a Philips PW1700 diffractometer. The amount of impurity was determined by Shimadzu GE-170 atomic emission spectrometer. The measurements of ^{11}B NMR spectra were carried out at 96.258 MHz on a Bruker MSL-300 spectrometer. The MAS spectra were measured with a 4 mm probe at spinning rates in the range of 7.5 to 15 kHz, and the static spectra with a static probe (dir. 10 mm). A 90° pulse was 1.1 μs and chemical shifts were recorded relative to $(C_2H_5)_2O{\cdot}BF_3$. A quadrupolar-echo pulse sequence was used for MAS and static measurement. The ^{13}C-MAS NMR spectra were measured at 75.468 MHz on a Bruker MSL-300 spectrometer equipped with a 4 mm probe at a spinning rate of 15 kHz. A 90° pulse was 4.2 μs and glycine was used as an external reference, where the ^{13}C chemical shift of carbonyl peak was assigned to be 176.03 ppm. All measurements were performed at room temperature.

Results and Discussion

^{11}B-MAS NMR Spectra. The ^{11}B-MAS NMR spectrum of B_4C is indicated in Fig. 2. The spectrum of $^{11}B_4C$ was identical with that of B_4C. A strong signal was appeared at −6 ppm, and this was assigned as B in the icosahedron (◆: main peak; ◇: sideband). This result agrees with that by Kirkpatrick et al.[4] The chemical shifts of two boron sites, i.e., $6h_1$ and $6h_2$ sites, in the icosahedron are not distinguished in the main peak in the spectrum.

As seen in Fig. 2, small peaks appeared besides the main peak (◆) and the sidebands (◇). The signal positions marked by △ and ○ syncronistically shifted with the spinning rates such as 7500, 10000, 12500, and 15000 rps. The positions marked by ▲ (37 ppm) and ● (−60 ppm) in the spectrum were unchanged regardless of the spinning frequency. These two peaks revealed the presence of at least two additional B sites. Signals with these chemical shifts have not been reported before. Since the intensities of these peaks are much weaker than that of main peak, by a factor of about 1/100, these signals might be the B substituted at the disorderd sites, such as CBB, BBB chain as well as 4B cluster.[2,4,10] More detailed experiments will be needed for the assignment of these peaks.

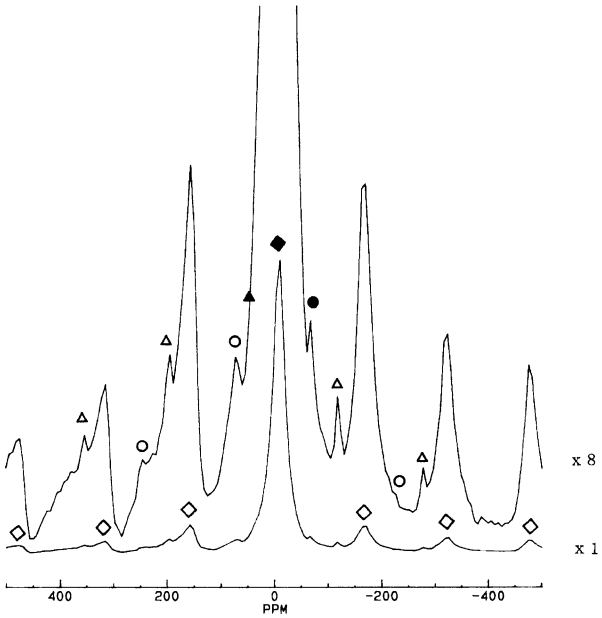

Fig. 2. ^{11}B-MAS NMR spectrum of B_4C. specral width: 1.0 MHz, data point: 8 K, 90° pulse: 1.1 μs, acquisition number: 100 times, recycle time: 2s, spinning rate: 15000 rps. The two signals exist in the positions marked by an ▲ and ●, and the spinning sidebands due to the signals marked by the △ and ○, respectively.

Silver and Bray[2] distinguished three crystallographically nonequivalent B positions, $6h_1$, $6h_2$, and CBC using a single crystal sample by continuous wave (CW) NMR. Kirkpatrick et al.[4] observed a very small prominent peak near 130 and 85 ppm in ^{11}B-MAS NMR spectra and a shoulder near 180 ppm in static NMR spectrum in addition to the main peak at near 0 ppm when they used powdered samples. They assigned the peak at 130 ppm to B of CBC, which was based in part on the previously published data.[2,3,9] In the present work, however, our powdered samples did not show any peaks at 130 and 85 ppm in all MAS NMR spectra investigated so far. These peaks must be very small and burried in sidebands, if they even exist. According to the result obtained from the crystal sample,[2] that is, the measured intensity of the CBC signal is about 5% of that of the 0 ppm line, at least 60% of the 1b positions are occupied by B atoms. In powdered samples, however, the calculated relative intensities of the intermixture of $(B_{12})(CCC)$ and $(B_{11}C)(CBC)$ were not consistent with the experimental data,[3,4,9] Therefore, it is quite difficult to decide from the signal intensity of ^{11}B-MAS NMR of powdered samples whether $(B_{11}C)(CBC)$ species is intermixed in the B_4C used in the present investigation or not.

^{13}C-MAS NMR Spectra. The ^{13}C-MAS NMR spectrum of B_4C is shown in Fig. 3. Two peaks were observed at 79 ppm and −0.6 ppm. The larger peak at −0.6 ppm was assigned to carbon atoms (2c) at the end of the chain.[4–7] As for the peak at 79 ppm, two assignment has been reported: one is CCC in the C_3 chain,[5,6] and the order is the icosahedral C replaced to B ($6h_1$).[4,9,10]

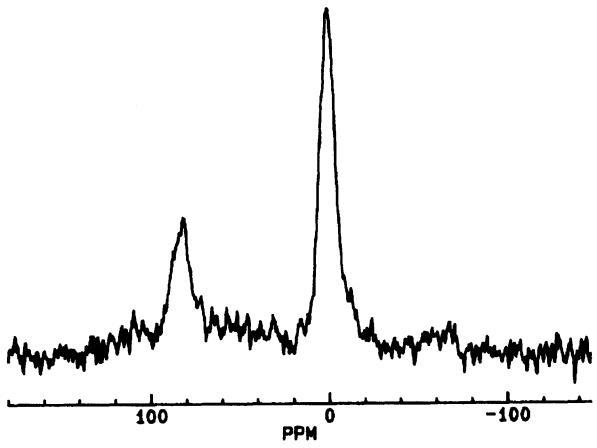

Fig. 3. ^{13}C-MAS NMR spectrum of B_4C. specral width: 30000 Hz, data point: 8 K, 90° pulse: 4.2 μs, acquisition number: 3000 times, recycle time: 20 s, spinning rate: 15000 rps.

Although both assignments were done based on the data of the chemical shift and its anisotropy of the analogous organic compounds, both lack direct evidence. Therefore, one can not say which assignment is correct at present. The relative intensity of the end C atom (2c) of the chain to icosahedral C atom ($6h_1$) in ($B_{11}C$)(CBC) or to center C atom (1b) in B_{12}(CCC) should be 2 in both cases, if all nuclei were observed. Actually, the observed ratio was 3.13 in this work, 2.11 (66.4/31.4) in Kirkpatrick work[4] and 2 to 3.3 in the estimation[9] from the data by Hynes and Alexander.[3] As already mentioned in the previous papers, it is reasonable that boron carbide, B_4C, comprises B_{12}(CCC) and ($B_{11}C$)(CBC). If this is true, three ^{13}C peaks corresponding to C atoms in 2c, 1b, and $6h_1$ sites should be observed in MAS NMR spectra. Nevertheless, nobody has been able to observe the third peak. Possibly, the third peak might be missed because of the relaxation mechanism, or two peaks of the three might have the same chemical shift. If we assume B_4C as $(B_{12})_{1-x}(CCC)_{1-x}(B_{11}C)_x(CBC)_x$, the ratio of the three peaks, corresponding to C atoms in 2c, 1b, and $6h_1$ sites, should be $2:1-x:x$, respectively. Therefore, we can evaluate what percentage of B in icosahedral is replaced by C in B_4C from the observed signal ratio (=3.13) under the various assignments. The evaluated values are shown in Table 1.

^{11}B-Static NMR Spectra. It is generally accepted that the linebroadening of the central transition of a quadrupole nuclei such as ^{11}B with nuclear spin 3/2 is dominated by second-order quadrupole interaction. Reports concerning the linebroadening of ^{11}B-static signal of boron carbide are rather scarce and are controversial, as mentioned in the introduction.[2—5,8] The linebroadening based on the quadrupole interaction and the dipole–dipole interaction is proportional to $(e^2qQ/h)^2/\nu_0$ and γ/r^3, respectively, where e^2qQ/h is the quadrupole coupling constant (Hz), ν_0 the Larmor frequency (Hz), γ the gyromagnetic ratio (rad/gauss·sec), r the distance between B and B (m), Q the quadrupole moment (m^2·A). γ and Q of ^{11}B and ^{10}B are as follows:

$$^{11}\text{B}: {}^{11}\gamma = 8579.4,\ {}^{11}\text{Q} = 0.036 \times 10^{-28},$$
$$^{10}\text{B}: {}^{10}\gamma = 2874.0,\ {}^{10}\text{Q} = 0.074 \times 10^{-28}.$$

The static NMR spectra of ^{11}B in B_4C and $^{11}B_4C$ are shown in Fig. 4. The linewidth of the signal is broader in $^{11}B_4C$ than in B_4C. We assumed that the linebroadening of the observed signal is solely dominated by the second-order quadrupole interaction, then we estimated e^2qQ/h as about 5 MHz. This value is extremely large compared with the previously reported data (0.2—1.3) MHz in the literature and our data (0.1 MHz) estimated from the side peaks. Considering such small quadrupole coupling constant, consequently, we assumed that the contribution of the second-order quadrupole interaction to the linebroadening is negligibly small. According to Saraswati et al.,[8] the separation between the asymmetric peaks in the ^{11}B in B_4C spectra remained constant, (16—20) kHz, in the field range of 12.5 to 25.35 MHz. This result also indicates that the line shape of ^{11}B is not affected by the second-order quadrupole effect and is not the addition of peaks of several species. Furthermore, as the maximum range of ^{11}B chemical shift is about 200 ppm, and e^2qQ/h is as small as (0.2—1.3) MHz, so the contribution of the chemical shift anisotropy to the linebroadening can be negligible. Further, J coupling is also negligible because the icosahedral one boron is bonded to

Table 1. Percentage of the Substituted C in the Icosahedral B site ($6h_1$) Estimated from the Signal Intensity Ratio in ^{13}C-MAS NMR Spectrum Shown in Fig. 3

Signal	−0.6 ppm	79 ppm	Not obsd	x in B_4C
Assignment	2c	1b	$6h_1$	0.36
	2c	$6h_1$	1b	0.64
	2c	1b+$6h_1$		a)
	2c+1b	$6h_1$		0.73
	2c+$6h_1$	1b		0.27

a) The ratio equals 2 in this assignment. Therefore, x was not calculated.

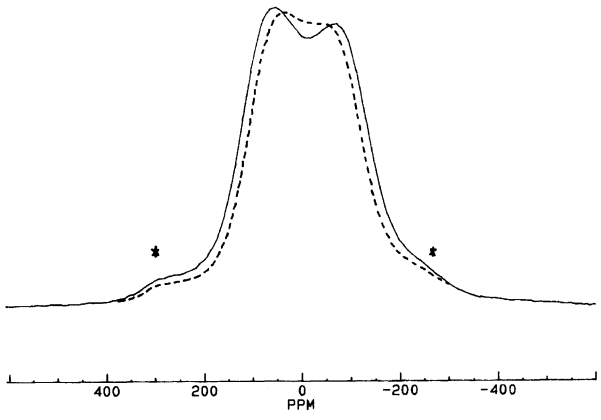

Fig. 4. ^{11}B-static NMR spectra of $^{11}B_4C$ (—) and B_4C (····). The signal marked by * is due to (±1/2↔±3/2) transitions. spectral width: 1.0 MHz, data points: 8 K, 90° plse: 1.1 μs, recycle time: 2 s, acquisition numbers: 200—300 pulse times.

the neighboring 5 or 6 boron atoms.

The X-ray powder diffraction pattern of $^{11}B_4C$, for which ^{10}B was replaced with ^{11}B, was the same as that of B_4C; this means that the crystal structure has not changed, i.e., the environment of electric field around B nuclei is not changed by replacing ^{10}B with ^{11}B. Therefore, we conclude that the linebroadening of ^{11}B-static spectra is not because of the second-order quadrupole effect, but because of the dipole–dipole interaction.

If the linebroadening is solely via the dipole–dipole interaction, the linewidth is represented by the second-order moment, M_2, which was presented by Van Vleck:[11]

$$M_2 = 3/5 \cdot P(^{11}B\text{–}^{11}B) \cdot N \cdot {}^{11}\gamma^2 h^2 I(I+1) \sum r^{-6} + 4/15 \cdot P(^{11}B\text{–}^{10}B) \cdot N \cdot {}^{10}\gamma^2 h^2 I'(I'+1) \sum r^{-6}.$$

Here I and I' are the nuclear spin of ^{11}B and ^{10}B, i.e., 3/2 and 3, respectively. h is the Planck constant in radians. $P(^{11}B\text{–}^{11}B)$ and $P(^{11}B\text{–}^{10}B)$ are the probabilities of ^{11}B and ^{10}B nuclei being bonded to an observed ^{11}B nucleus, respectively, and these are equal to the abundance ratio of ^{11}B and ^{10}B, i.e., $P(^{11}B\text{–}^{11}B)$=0.8042, $P(^{11}B\text{–}^{10}B)$=0.1958 for B_4C; $P(^{11}B\text{–}^{11}B)$=0.995, $P(^{11}B\text{–}^{10}B)$=0.005 for $^{11}B_4C$. N is the sum of $N(6h_1)$ and $N(6h_2)$, where $N(6h_1)$ and $N(6h_2)$ are the number of the bonds by which one boron in $6h_1$ site and $6h_2$ site is binding to another boron, that is, 5 and 6, respectively. N is therefore equal to 11.

The ratio of the square roots of M_2 in $^{11}B_4C$ to that in B_4C is calculated as 1.09, whereas the ratio of the observed half-linewidth in $^{11}B_4C$ to that in B_4C is 1.12. The ^{11}B-linebroadening in boron carbide is thus explained well by assuming that ^{11}B nuclei only relax through B–B dipole–dipole interactions.

We believe that the signals marked by the * in Fig. 4 are assigned to a $(\pm 1/2 \leftrightarrow \pm 3/2)$ transition based on a first-order quadrupole interaction, because the ^{11}B-MAS NMR signals does not appear at the positions marked by *, as mentioned above in the previous section. According to this relation, the magnitude of the separation between peaks = $e^2qQ/2h$, e^2qQ/h was calculated as 0.1 MHz. This value is consistent with the quadrupole coupling constants reported for the boron in the icosahedron in the previous papers.[2,3] Therefore, it is considered that boron atoms are present in a highly symmetric electric field.

Conclusions

In this paper, ^{11}B-static and -MAS NMR spectra of ^{11}B-enriched boron carbide, $^{11}B_4C$, were presented for the first time. The half-linewidth of ^{11}B-static signal of boron in the icosahedral site was broader in $^{11}B_4C$ by a factor of 1.12 compared to that in B_4C. The quadrupole splitting of the ^{11}B spectrum of boron carbide has been determined from the second-order shift in the central transition.[2] The quadrupole coupling constant (e^2qQ/h) for both icosahedral sites is very small (in the range 0.2—0.7 MHz for $6h_1$ site and 1.3 ± 0.1 MHz for $6h_2$ site)[2] and the quadrupole effect to the observed linewidth is negligibly small. Therefore, we applied the Van Vleck equation for the linewidth analysis of the static NMR, because ^{11}B nuclei are in Zeeman states in the field used (96.3 MHz, 7.05 T). The square root of the ratio of the second moments calculated for $^{11}B_4C$ and B_4C agreed with the ratio of the linewidths within the experimental error. Therefore, it is concluded that the ^{11}B–^{11}B and ^{11}B–^{10}B dipole–dipole interactions are the main mechanism for the broadening of the ^{11}B-static NMR signal.

Only the signal (−6 ppm) due to B nuclei in the icosahedral sites was detected and no signal was obtained at 130 ppm for B in the center of the chain (CBC) in ^{11}B-MAS NMR. If about 30 to 70 % of B_4C is $(B_{11}C)$(CBC), as estimated in Table 1, why was the B in CBC not detected in ^{11}B-MAS NMR? According to Silver and Bray,[2] the quadrupole coupling constant of B in CBC is large (5.58±0.02 MHz), corresponding to the frequency shift over 250 ppm and the linewidth of more than 35 kHz in static NMR. Therefore, the quadrupole effect was not enough averaged by the magic angle spinning used in this investigation. Furthermore, spinning side bands from the large main peak coexist in the position looked for, which caused the signal from B in CBC to be nondetectable in ^{11}B-MAS NMR. Besides the main peak due to icosahedral B, two small peaks were additionally observed at 37 and −60 ppm. This indicates the existence of minor B sites in B_4C. The center of these two peaks (−11.5 ppm) does not match the position of the main peak (−6 ppm). Therefore, the possibility of the peaks being due to the $(\pm 1/2 \leftrightarrow \pm 3/2)$ transition is denied.

In ^{13}C-MAS NMR, only two peaks at −0.6 and 79 ppm were detected and one signal is missing. The assignment of the 79 ppm signal is still controversial. From the data we can not say anything about the assignment of the peak, i.e., icosahedral C or center chain (CCC). Clear evidence of icosahedral carbon was presented for ^{13}C-enriched boron carbide such as B_4C, $B_{13}C_2$, and B_9C,[4] where the integrated intensities did not agree with the icosahedral carbon concentration expected from the sample model in this experiment. It is suggested that $B_{12}C_3$ exists as a solid solution that ranges in local composition between B_{12}(CBC) and B_6C_6(CBC).[12] To further understanding of the structure of boron carbide and ^{13}C- and ^{11}B-MAS NMR spectra, it would be necessary to investigate spectral variation among samples with the same nominal composition and with different boron to carbon ratios.

References

1) H. K. Clark and J. L. Hoard, *J. Am. Chem. Soc.*, **65**, 2115 (1943).
2) A. H. Silver and P. J. Bray, *J. Chem. Phys.*, **31**, 247 (1959).
3) T. V. Hynes and M. N. Alexander, *J. Chem. Phys.*, **54**, 5296 (1971).
4) R. J. Kirkpatrick, T. Aselage, B. L. Philips, and B. Montez, *AIP Conf. Proc.*, **231**, 261 (1991).
5) J. Conard, M. Bouchacourt, F. Thevenot, and M. Hermann, *J. Less-Common Met.*, **117**, 51 (1986).
6) T. M. Duncan, *J. Am. Chem. Soc.*, **106**, 2270 (1984).
7) T. M. Duncan, *AIP Conf. Proc.*, **140**, 177 (1986).

8) V. Saraswati and P. L. Paulose, *J. Less-Common Met.*, **128**, 85 (1987).
9) M. N. Alexander, *AIP Conf. Proc.*, **140**, 168 (1986).
10) T. L. Aselage and D. Emin, *AIP Conf. Proc.*, **231**, 177 (1991).
11) J. H. Van Vleck, *Phys. Rev.*, **174**, 168 (1948).
12) V. I. Matkovich and J. Economy, in "Boron and Refractory Bodies," ed by V. I. Matkovich, Springer-Verlage, New York (1977), Chap. VII.