Table V. Tolerance Factors for Several $A_2^{3+}CuB^{4+}O_6$ Compounds for Which A_2CuO_4, $A_2B'_2O_7$, and CuO Compounds Also Exist

compd	t	sym	ref
$La_2CuTiO6$	0.950	pseudocubic	35
$La_2CuIrO6$	0.945	monoclinic	36
$La_2CuSnO6$	0.930	monoclinic	this work
"La_2CuZrO_6"[a]	0.923		this work
"$La_{1.5}Nd_{0.5}CuSnO_6$"[b]	0.922		this work
"La_2CuPbO_6"[a]	0.911		this work
"Nd_2CuSnO_6"[a]	0.899		this work

[a] Mixture of A_2CuO_4, $A_2B'_2O_7$, and CuO. [b] Mixture of La_2CuSnO_6, Nd_2CuO_4, $Nd_2Sn_2O_7$, and CuO.

where r_A, r_O, r_B, and $r_{B'}$ are the ionic radii[30] of the ions. The tolerance factor for La_2CuSnO_6 is 0.930. Attempts to decrease t by the substitution of the slightly smaller Nd^{3+} ion (1.27 Å) for the La^{3+} ion (1.36 Å) or the slightly larger Zr^{4+} ion (0.73 Å) or Pb^{4+} ion (0.78 Å) for Sn^{4+} ion 0.69 Å) result in the formation of $A_2B'_2O_7$, A_2CuO_4, and CuO. The lower limit of the tolerance factor for these types of systems seems to be between 0.930 and 0.923. The tolerance factors for these and two other compounds are listed in Table V. It appears that when $t < 0.930$, it is energetically unfavorable to further compress the $CuO_{4/2}$ and $B'O_{2/4}$ layers to bring oxygen atoms within A–O bonding distances and that the reactants form the three competing phases.

Conclusions

The synthesis of layered cuprates is an important goal because of their relationship to high-temperature cuprate superconductors. The synthesis of layered cuprates that are stoichiometric in oxygen is limited by several factors, however, which include the energetic favorability of ordering B cations between AO_3 layers and strong competition from phases that are energetically similar. La_2CuSnO_6 is an example of a compound in which these factors have been overcome.

Acknowledgment. This work benefitted from the use of the Intense Pulsed Neutron Source at Argonne National Laboratory with funding provided by the National Science Foundation and the Science and Technology Center for Superconductivity (NSF-DMR-8809854). We thank R. Hitterman, J. Jorgenson, and F. Rotella for their assistance with the neutron diffraction experiment. We gratefully acknowledge J. P. Thiel for his assistance with the refinement programs and helpful discussions and J. T. Vaughey for his helpful discussions. We also acknowledge the Northwestern Materials Research Center for support of the X-ray Diffraction Facility (MRL-DMR-8821571).

High-Field ^{11}B Magic-Angle Spinning NMR Characterization of Boron Nitrides

Paul S. Marchetti,[†] Daekeun Kwon,[‡] Wayde R. Schmidt,[§] Leonard V. Interrante,[‡]
and Gary E. Maciel*,[†]

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523;
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590; and
Department of Materials Engineering, Rensselaer Polytechnic Institute,
Troy, New York 12180-3590

Received November 16, 1990. Revised Manuscript Received March 25, 1991

High-field (14.0 T) ^{11}B magic-angle spinning NMR characterization of the major forms of boron nitride reveals differences between the cubic (c-BN) and hexagonal (h-BN) forms, in terms of both isotropic chemical shifts and magnitude of the second-order quadrupole contribution to observed NMR line shapes. ^{11}B NMR spectra of the pure turbostratic (t-BN) form and of t-BN in the form of an AlN/BN composite are indistinguishable from those of crystalline h-BN. This observation is in accord with the weak nature of the interplanar bonding interaction in t-BN. The results presented herein involving the structural characterization of boron nitrides by solid-state NMR should serve as a foundation for future studies involving pyrolytic conversion of organometallic and polymeric precursors to boron nitride.

Introduction

High-field solid-state NMR spectroscopy with magic-angle spinning (MAS) has proven to be a highly useful technique for the direct, yet nondestructive, characterization of crystalline inorganic oxides, including various silicates,[1] aluminosilicates[1-7] (especially zeolites), SiAlONs,[8,9] and oxynitrides.[3,10] Moreover, considerable progress has been made recently in applying this technique to the identification of high-performance non-oxide ceramic materials such as SiC,[3,11] Si_3N_4,[3,11,12] and AlN,[13,14] as well as to the study of pyrolytic conversion of organometallic precursors to these materials.[15-17] Among the

---

[†] Colorado State University.

[‡] Department of Chemistry, Rensselaer Polytechnic Institute.

[§] Department of Materials Engineering, Rensselaer Polytechnic Institute.

(1) Magi, M.; Lippmaa, E.; Samoson, A.; Engelhardt, G.; Grimmer, A. R. *J. Phys. Chem.* **1984**, *88*, 1518–1522.

(2) Fyfe, C. A.; Gies, H.; Feng, Y. *J. Am. Chem. Soc.* **1989**, *111*, 7702–7707.

(3) Turner, G. L.; Kirkpatrick, R. J.; Risbud, S. H.; Oldfield, E. *Am. Ceram. Soc. Bull.* **1987**, *66*, 656–663.

(4) Fyfe, C. A.; Gobbi, G. C.; Hartmann, J. S.; Lenkinski, R. E.; O'-Brien, J. H.; Beange, E. R.; Smith, M. A. R. *J. Magn. Reson.* **1982**, *47*, 168–173.

(5) Lippmaa, E.; Magi, M.; Samoson, A.; Engelhardt, G.; Grimmer, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 4889–4893.

(6) Thomas, J. M.; Bursill, L. A.; Lodge, E. A.; Cheetham, A. K.; Fyfe, C. A. *J. Chem. Soc., Chem. Commun.* **1981**, 276–277.

(7) Klinowski, J.; Thomas, J. M.; Audier, M.; Vasudevan, S.; Fyfe, C. A.; Hartman, J. S. *J. Chem. Soc., Chem. Commun.* **1981**, 570–571.

non-oxide ceramics, boron nitride is unique due to its high compressive strength, excellent thermal shock resistance, high thermal conductivity, and dielectric strength.[18] Despite the technological importance of BN and the increasing efforts to obtain BN in special forms (coatings, fibers, etc.) by precursor pyrolysis,[19-25] the characterization of BN by high-field MAS NMR has not yet been reported, although prior low-field ^{11}B studies of both cubic- and hexagonal-BN employing continuous-wave techniques have appeared in the literature.[26-29]

The application of liquid-state ^{11}B NMR spectroscopy to a wide variety of soluble organoboron compounds including boranes, carboranes, and related metalloboranes and metallocarboranes has been extensively pursued.[30,31] In contrast, the application of ^{11}B NMR to solid-state boron compounds has been relatively more limited. Most of the solid-state ^{11}B NMR characterizations have involved borates and boron-containing glasses in an attempt to probe coordination and symmetry of boron as it relates to the structures of glassy materials.[4,32-36] Boron has been also observed in solid-state NMR studies at low field in carboranes,[37-41] borides,[26,42-44] chalcogenides,[45] carbides,[46-50] phosphides,[27] and nitrides.[26-29]

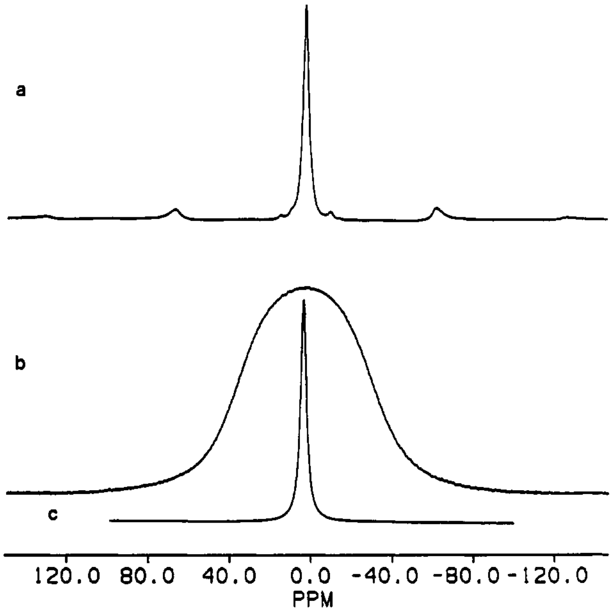

Figure 1. 192.55-MHz ^{11}B NMR spectra of cubic boron nitride: (a) 12.5 kHz MAS, 128 scans, 1.0-s recycle delay; (b) static powder spectrum, 128 scans, 1.0-s recycle delay; (c) theoretical simulation based on QCC = 0 and a 650-Hz Gaussian broadening.

The advantage of fast MAS in the NMR of quadrupolar nuclei at high field has previously been demonstrated in terms of reduction of second-order quadrupolar broadening of the central transition of an odd-half-integer spin[51] and improved resolution between resonances arising from sites of differing coordination (e.g., differing symmetry).[52] It should be noted, however, that for boron sites having the same coordination number, high field may in some cases be disadvantageous to the extent that quadrupole-induced peak shifts may increase resolution between peaks that lie within the same chemical shift region and such second-order quadrupole shifts are reduced at higher field. In such cases some lower-field strategy, e.g., variable-angle sam-

---

(8) Klinowski, J.; Thomas, J. M.; Thompson, D. P.; Korgul, P.; Jack, K. H.; Fyfe, C. A.; Gobbi, G. C. *Polyhedron* **1984**, *3*, 1267–1269.

(9) Dupree, R.; Lewis, M. H.; Smith, M. E. *J. Am. Chem. Soc.* **1989**, *111*, 5125–5132.

(10) Dupree, R.; Lewis, M. H.; Leng-Ward, G.; Williams, D. S. *J. Mater. Sci. Lett.* **1985**, *4*, 393–395.

(11) Hatfield, G. R.; Carduner, K. R. *J. Mater. Sci.* **1989**, *24*, 4209–4219.

(12) Carduner, K. R.; Carter, R. O., III; Milberg, M. E.; Crosbie, G. M. *Anal. Chem* **1987**, *59*, 2794–2797.

(13) Dupree, R.; Lewis, M. H.; Smith, M. E. *J. Appl. Crystallogr.* **1988**, *21*, 109–116.

(14) Hayashi, S.; Hayamizu, K.; Yamamoto, O. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 761–762.

(15) Taki, T.; Inue, M.; Okamura, K.; Sato, M. *J. Mater. Sci. Lett.* **1989**, *8*, 918–920.

(16) Taki, T.; Okamura, K.; Sato, M. *J. Mater. Sci* **1989**, *24*, 1263–1267.

(17) Schmidt, W. R.; Interrante, L. V.; Doremus, R. H.; Trout, T. K.; Marchetti, P. S.; Maciel, G. E. *Chem. Mater.* **1991**, *3*, 257.

(18) Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73–91.

(19) Bender, B. A.; Rice, R. W.; Spann, J. R. *Ceram. Eng. Sci. Proc.* **1985**, *6*, 1171–1183.

(20) Narula, C. K.; Paine, R. T.; Schaeffer, R. In *Better Ceramics Through Chemistry II*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; MRS Symplsia Proceedings 73; Materials Research Society: Pittsburgh, PA, 1986; pp 383–388.

(21) Narula, C. K.; Paine, R. T.; Schaeffer, R. In *Inorganic and Organometallic Polymers*; Zeldin, M, Wynne, K. J., Allcock, H. R., Eds.; ACS Symposia Series 360; American Chemical Society: Washington. D.C., 1988; pp 378–384.

(22) Shaw, S. Y.; Dubois, D. A.; Neilson, R. H. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposia Seriews 360; American Chemical Society: Washington, D.C., 1988; pp 385–391.

(23) Paciorek, K. J. L.; Krone-Schmidt, W.; Harris, D. H.; Kratzer, R. H.; Wynne, K. J. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds., ACS Symposia Series 360; American Chemical Society: Washington, D.C., 1988; pp 392–406.

(24) Seyferth, D.; Rees, W. S. Jr. in *Better Ceramics Through Chemistry III*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; MRS Symposia Proceedings 121; Materials Research Society: Pittsburgh, PA 1988; pp 449–454.

(25) Maya, L. In *Better Ceramics Through Chemistry III*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; MRS Symposia Proceedings 121; Materials Research Society: Pittsburgh, PA, 1988; pp 455–460.

(26) Silver, A. H.; Bray, P. J. *J. Chem. Phys.* **1960**, *32*, 288–292.

(27) Sears, R. E. *J. Phys. Rev. B.* **1981**, *24*, 4072–4074.

(28) Kurdyumov, A. V.; Pilyankevich, A. N., Tikhonenko, K. A.; Shul'man, L. A. *Sov. Phys. Solid State* **1974**, *16*, 1170–1171.

(29) Khusidman, M. B.; Neshpor, V. S. *J. Struct. Chem.* **1971**, *12*, 1008–1009.

(30) Wrackmeyer, B. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press; New York 1988; Vol. 20, pp 61–203.

(31) Siedle, A. R. *In Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press; New York 1988; Vol. 20, pp 205–314.

(32) Schramm, S.; Oldfield, E. *J. Chem. Soc., Chem. Commun.* **1982**, 980–981.

(33) Silver, A. H.; Bray, P. J. *J. Chem. Phys.* **1958**, *29*, 984–990.

(34) Jellison, G. E.; Bray, P. J. In *Borate Glasses: Structure, Properties, Applications*; Pye, L. D., Ed.; Plenum Press: New York, 1977; pp 353–367.

(35) Bray, P. J. In *Borate Glasses: Structure, Properties, Applications*; Pye, L. D., Ed.; Plenum Press: New York 1977; pp 321–351.

(36) Bray, P. J. *J. Non-Cryst. Solids* **1987** *95/96*, 45–60.

(37) Reynhardt, E. C. *J. Magn. Reson.* **1986**, *69*, 337–343.

(38) Reynhardt, E. C.; Watton, A.; Petch, H. E. *J. Magn. Reson.* **1982**, *46*, 453–468.

(39) Beckman, P.; Leffler, A. J. *J. Chem. Phys.* **1980**, *72*, 4600–4607.

(40) Leffler, A. J.; Alexander, M. N.; Sagalyn, P. L. *J. Chem. Phys.* **1977**, *67*, 844–845.

(41) Leffler, A. J.; Alexander, M. N.; Sagalyn, P. L.; Walker, N. *J. Chem. Phys.* **1975**, *63*, 3971–3986.

(42) Sears, R. E. J. *J. Chem. Phys.* **1982**, *76*, 5651–5652.

(43) Creel, R. B.; Barnes, R. G. *J. Chem. Phys.* **1972**, *56*, 1549–1562.

(44) Creel, R. B.; Segel, S. L.; Schoenberger, R. J.; Barnes, R. G.; Torgeson, D. R. *J. Chem. Phys.* **1974**, *60*, 2310–2322.

(45) Hurter, H. H.; Krebs, B.; Eckert, H.; Muller-Warmuth, W. *Inorg. Chem.* **1985**, *24*, 1288–1292.

(46) Duncan, T. M. *J. Am. Chem. Soc.* **1984**, *106*, 2270–2275.

(47) Silver, A. H.; Bray, P. J. *J. Chem. Phys.* **1959**, *31*, 247–253.

(48) Hynes, T. V.; Alexander, M. N. *J. Chem. Phys.* **1971**, *54*, 5296–5310.

(49) Hynes, T. V.; Alexander, M. N. *J. Chem. Phys.* **1972**, *56*, 681.

(50) Conard, J.; Bouchacourt, M.; Thevenot, F.; Herman, G. *J. Less-Common Met.* **1986**, *817*, 51–60.

(51) Ganapathy, S.; Schramm, S.; Oldfield, E. *J. Chem. Phys.* **1982**, *77*, 4360–4365.

(52) Dec, S. F.; Maciel, G. E. *J. Magn. Reson.* **1990**, *87*, 153–159.

pling spinning (VASS), may be preferential.[32]

Efforts in our laboratories are in part directed toward understanding the pyrolysis chemistry of organometallic precursors to ceramics, including ceramic composites containing boron nitride. In this context, solid-state NMR has proven to be an exceedingly powerful technique, since it can provide compositional and structural information on noncrystalline materials during the conversion from a polymeric precursor to a ceramic end product.[15-17] As a preliminary step in our effort to apply this technique to the study of the pyrolytic conversion of BN precursors and in an effort to characterize BN phases in ceramic composites, we present here the results of our investigation of three main forms of boron nitride by high-field solid-state ^{11}B NMR spectroscopy.

Experimental Section

Crystalline hexagonal boron nitride was obtained as a white powder from CERAC, Inc. The cubic form of boron nitride was obtained as a black powder from General Electric Co. (courtesy of F. R. Corrigan). Turbostratic boron nitride was prepared as either a single phase or in the form of an AlN/BN composite by pyrolysis (1000 °C, NH_3) of tris(ethylamino)borane or the polymer synthesized from a 3:1 mixture of tris(ethylamino)borane and diethylaluminum amide.[53]

High-speed MAS ^{11}B NMR spectroscopy was carried out at 14.0 T on a Bruker AM-600 spectrometer using a high-speed MAS probe built in-house and tuned to 192.55 MHz.[52,54,55] Samples were spun in 4.5-mm o.d. cylindrical Torlon rotors at speeds of 12–15 kHz. The sample size for this rotor system is typically ~40 mg. Similar experiments were also carried out at lower field on a heavily modified Nicolet NT-360 spectrometer (observed frequency 115.5 MHz).

Single-pulse excitation using a 90° (3.5 μs) solids pulse was employed.[56,57] Relaxation delays ranged from 1.0 to 10.0 s, depending upon the spin–lattice relaxation efficiency of a particular sample. Data blocks of 1K were obtained, using a 100-kHz spectral width and zero filled to 4K before Fourier transformation with no applied line broadening. All ^{11}B chemical shifts were determined relative to the highest-shielding resonance of borax, $Na_2B_4O_7{\cdot}10H_2O$, for which the chemical shift is 2.0 ppm relative to $Et_2O{\cdot}BF_3$, and are reported here relative to $Et_2O{\cdot}BF_3$.[58] Quadrupole coupling constants (QCC), asymmetry parameters (η), and isotropic chemical shifts (σ) were obtained by numerical simulation of experimental line shapes, using the FT NMR software package from Hare Research, Inc.

Results and Discussion

Boron nitride exists as three polytypes.[18] The cubic phase (c-BN), the high-temperature and high-pressure form, has the zincblende structure with local BN_4 tetrahedra. The hexagonal phase (h-BN), the most common form, has the graphitic structure with nearly planar networks of B_3N_3 hexagons, with each layer stacked in such a way that a boron atom in one layer is placed over a nitrogen atom in the next layer. In the turbostratic phase (t-BN), these layers are disordered and stacked with random translation and rotation.

The 192.55-MHz ^{11}B MAS (12.5 kHz) spectrum of c-BN (Figure 1a), shows mainly a symmetrical resonance at 1.6 ppm, along with minor first- and second-order spinning sidebands. The relatively small line width of 629 Hz (full width at half-maximum, fwhm) and the absence of any splitting or asymmetry in the shape of the main peak are indicative of a small quadrupole coupling constant (QCC), as might be expected for boron in a cubic crystal environment.[59-63] The observed line shape in Figure 1a may be simulated satisfactorily by using any QCC value as large as 1.4 MHz, irrespective of η, if the resulting second-order quadrupole line shape is convoluted with a Lorentzian function of sufficient width (roughly 500–650 Hz) to match the experimental spectrum. Any quadrupole coupling constant greater than 1.4 MHz (upper limit) results in an asymmetric line shape that is easily seen to disagree with the experimental result. Figure 1c shows a MAS spectrum simulated for QCC = 0, a Gaussian broadening of 650 Hz, and an isotropic chemical shift of 1.6 ppm. Considering the high symmetry of boron in c-BN and reported values for quadrupole coupling constants of tetrahedral boron in mineral and related systems,[58] most of which lie in the range 0.2–0.5 MHz, it is expected that the quadrupole coupling constant would be near zero in c-BN. In the case of near zero quadrupole coupling constant, the observed peak position of 1.6 ppm for boron in c-BN would correspond to the isotropic chemical shift. Sears[27] also reported no observable quadrupole effect for c-BN at 20 MHz, where even a small quadrupole coupling constant should make a relatively larger contribution to the total boron line width and line shape. The measured peak position, attributed solely to the chemical shift interaction, was reported in that study to be 28 ppm relative to triethyl borate (~10 ppm relative to $Et_2O{\cdot}BF_3$). Also apparent in Figure 1a are some very minor peaks on either side of the center band; the origin of these peaks is under investigation.

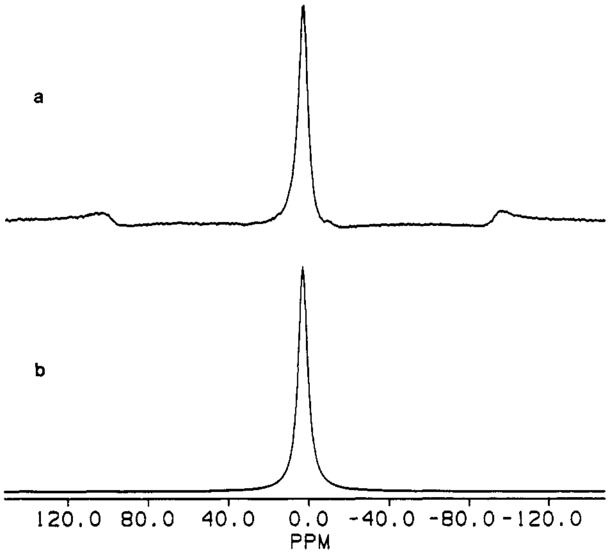

Figure 2. 115.5-MHz ^{11}B MAS NMR spectra of cubic boron nitride: (a) experimental (13-kHz MAS, 131 scans, 1.0-s recycle delay) and (b) simulation based on QCC = 0 = η and 630-Hz Gaussian line broadening.

Residual B–B and B–N dipolar couplings must be considered as possible sources of the 629-Hz MAS line width observed in the c-BN spectrum. From the known structure of c-BN, nearest-neighbor ^{11}B–^{11}B and ^{11}B–^{14}N dipolar

---

(53) Kwon, D.; Schmidt, W. R.; Interrante, L. V.; Marchetti, P.; Maciel, G. *IUPAC Symp. Proc.*, in press.

(54) Dec, S. F.; Wind, R. A.; Maciel, G. E.; Anthonio, F. E. *J. Magn. Reson.* **1986**, *70*, 355–359.

(55) Wind, R. A.; Anthonio, F. E.; Duijvestijn, M. J.; Smidt, J.; Trommel, J.; De Vette, G. M. C. *J. Magn. Reson.* **1983**, *52*, 424–434.

(56) Fukushima, E.; Roeder, S. B. W. *Experimental Pulse NMR—A Nuts and Bolts Approach*; Addison-Wesley: Reading PA, 1981; pp 106–112.

(57) Woessner, D. E. *Z. Phys. Chem. (Munich)* **1987**, *152*, 51–58.

(58) Turner, G. L.; Smith, K. A.; Kirkpatrick, R. J.; Oldfield, E. *J. Magn. Reson.* **1986**, *67*, 544–550.

(59) Cohen, M. H.; Reif, F. In *Solid State Physics*; Seitz, F., Trumbull, D., Eds.; Academic Press; New York, 1957; pp 321–438.

(60) Wentorf, R. H. *J. Chem. Phys.* **1957**, *26*, 956–957.

(61) Bundy, F. P.; Wentorf, R. H. *J. Chem. Phys.* **1963**, *38*, 1144–1149.

(62) Milledge, H. J.; Nave, F.; Weller, F. H. *Nature* **1959**, *184*, 715.

(63) Wentorf, R. H. *J. Chem. Phys.* **1961**, *34*, 809–812.

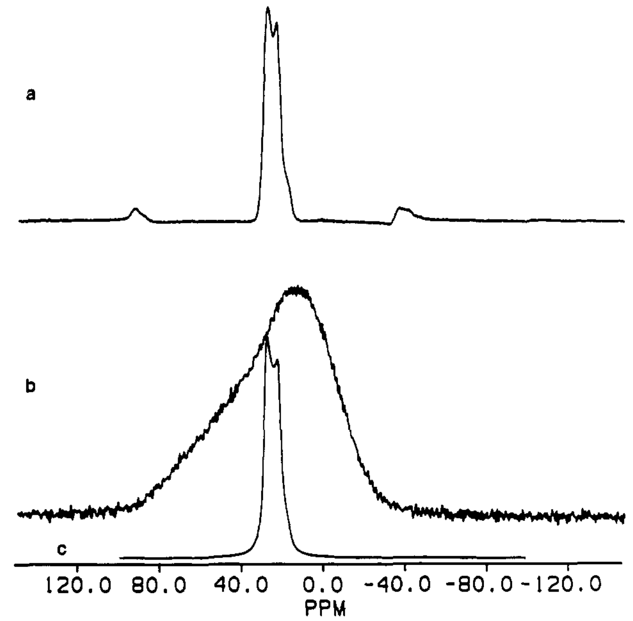

Figure 3. 192.55-MHz ^{11}B NMR spectra of hexagonal boron nitride: (a) 12.6-kHz MAS, 1024 scans, 10.0-s recycle delay; (b) static powder spectrum, 3811 scans, 10.0-s recycle delay; (c) theoretical simulation based on QCC = 2.9 MHz, $\eta = 0$, Gaussian broadening of 500 Hz, and an isotropic chemical shift of 30 ppm.

couplings are calculated to be 4.50 and 4.59 kHz, respectively. Dipolar couplings of this magnitude should easily be averaged by MAS at a speed of 12.5 kHz, *if such couplings were to behave inhomogeneously*. However, imperfect quantization along B_0 (because of the quadrupolar interactions) and sufficiently rapid relaxation can interfere with MAS averaging; such interferences should, in most scenarios, be less effective at higher field. Another possible source of the 629-Hz line width is the dispersion of isotropic chemical shifts; this effect should scale linearly (in hertz) with B_0. The second-order quadrupole effect would yield a smaller line width at higher field. In the present case, the residual MAS linewidth observed at 115.5 MHz (Figure 2a) is almost the same (627 Hz) as the value observed at 14 T. Figure 2 shows that a simulation with QCC = 0 = η and a Gaussian line broadening of 630 Hz (Figure 2b) yields a satisfactory agreement with the experimental spectrum (Figure 2a). It would appear that the line width in this case is not dominated by any one of the three effects mentioned above and may be substantially due to intrinsic T_2 effects.

Figure 1b shows the static ^{11}B powder spectrum of c-BN. The observed Gaussian line shape (fwhm = 13.49 kHz) is mainly the result of ^{11}B–^{14}N and ^{11}B–^{11}B direct dipolar couplings. As noted above, these interactions should be largely removed by fast (12–15 kHz) MAS (Figure 1a). A second-moment analysis[64] of the Gaussian static line shape obtained for c-BN, neglecting any line-shape contributions due to chemical shift anisotropy, yields an estimate of 1.56 Å for the B–N bond distance when both ^{11}B–^{14}N and ^{11}B–^{11}B nearest-neighbor dipolar couplings are taken into account, in excellent agreement with the literature value (1.57 Å) for c-BN.[60] The second-moment analysis shows that because the gyromagnetic ratio of ^{11}B is 4.44 times greater than that of ^{14}N, the nearest-neighbor ^{11}B couplings to ^{11}B make a greater contribution (66%) to the second moment than the shorter range couplings of directly bonded ^{14}N nuclei.

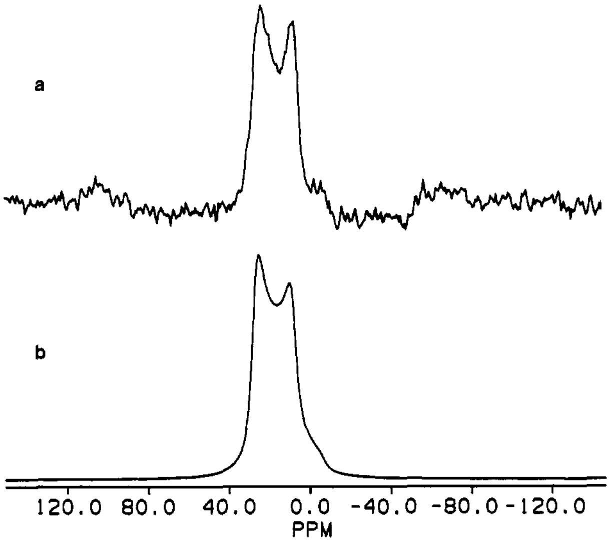

Figure 4. 115.5-MHz ^{11}B MAS NMR spectra of hexagonal boron nitride: (a) experimental (13-kHz MAS, 1285 scans, 10 s recycle delay) and (b) simulation based on QCC = 2.9 MHz, $\eta = 0$, and 600-Hz Gaussian line broadening.

Figure 3a presents the 192.55-MHz ^{11}B MAS (12.6 kHz) spectrum of h-BN, which shows first-order spinning sidebands.[65,66] The isotropic chemical shift was determined by simulation (Figure 3c) of the center-band pattern to be 30 ppm. The center-band pattern of this spectrum is typical of a second-order quadrupole line shape in the fast spinning limit for an $I = {}^{3}/_{2}$ nuclide of less than cubic symmetry. Simulation of this line shape (Figure 3c) yields values of 2.9 MHz and 0 for QCC and the asymmetry parameter, η, respectively. These values are in agreement with the low-field result of Silver and Bray[26] (QCC = 2.9 MHz) and with the known 3-fold boron site symmetry of h-BN, which should constrain the electric field gradient tensor to axial symmetry. Figure 4a shows the 115.5-MHz MAS (13 kHz) spectrum of h-BN. Figure 4b shows the corresponding simulation, obtained with QCC = 2.9 MHz, $\eta = 0$, and 600-Hz line broadening; the agreement is satisfactory.

The static powder spectrum of h-BN (Figure 3b), in contrast to that of the cubic form, shows a non-Gaussian line shape (fwhm = 10.64 kHz). Consistent with the 3-fold boron site symmetry, there is, in addition to the second-order quadrupole interaction and the dipolar coupling of boron to nearest-neighbor nuclei, a significant contribution of chemical shift anisotropy (axially symmetric tensor) to the observed static powder line shape.

The ^{11}B MAS (12.6 kHz) spectrum of synthetic boron nitride that has been identified as turbostatic according to XRD analysis is shown in Figure 5a.[67] Figure 5b is the corresponding static powder spectrum. The ^{11}B spectra of this form are very similar to those of h-BN. Spectra (not shown) taken on synthetic t-BN in the form of an AlN/BN composite are indistinguishable from those presented in Figure 5 for the single-phase t-BN. Figure 5c, identical with Figure 3c, is the theoretically simulated spectrum for the MAS spectrum.

The results of the ^{11}B NMR characterization of the major forms of boron nitride reported herein are entirely consistent with the primary effect of nitrogen coordination

---

[64] Slichter, C. P. *Principles of Magnetic Resonance*, 2nd ed.; Springer-Verlag: New York, 1978; pp 56–76.

[65] Pease, R. S. *Acta Crystallogr.* **1952**, *5*, 356–361.

[66] Hall, H. T.; Compton, L. A. *Inorg. Chem.* **1965**, *4*, 1213–1216.

[67] Thomas, J.; Weston, N. E.; O'Connor, T. E. *J. Am. Chem. Soc.* **1963**, *84*, 4619–4622.

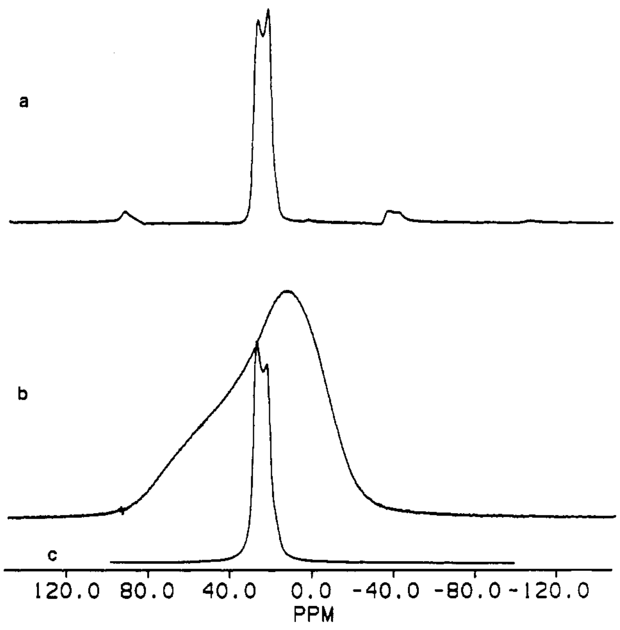

Figure 5. 192.55-MHz ^{11}B NMR spectra of turbostratic boron nitride: (a) 12.6-kHz MAS, 256 scans, 1.0-s recycle delay; (b) static powder spectrum, 2048 scans, 1.0-s recycle delay; (c) theoretical simulation based on QCC = 2.9 MHz, $\eta = 0$, a Gaussian broadening of 500 Hz, and an isotropic chemical shift of 30 ppm.

number (3 versus 4) and the corresponding boron site symmetry (trigonal versus tetrahedral) on boron chemical shielding as reported from solid-state NMR studies of both borates and glasses and from the extensive liquid-state NMR literature.[68]

Chemical shielding differences between trigonal and tetrahedral boron are readily explained on the basis of the predominant local paramagnetic contribution to ^{11}B chemical shielding.[68,69] The observed chemical shift ranges for 3-coordinate boron (90 to −10 ppm) and 4-coordinate boron (10 to −130 ppm) are apparently determined by the nature of hybridization (sp^2 versus sp^3) and the correspondingly larger electron density at the boron atom in the tetrahedral geometry relative to that in the trigonal geometry. This difference corresponds to a reduced $\langle 1/r^3 \rangle$ factor in the σ_p term for 4-coordinate boron relative to the 3-coordinate boron.

The effect of ligand heteroatom type on boron chemical shielding in 3-coordinate boron compounds correlates empirically with the extent of heteroatom-to-boron π-bonding, which varies in the order $C \ll N < O < F$. The π-donor strength of the σ-bonded heteroatom and the corresponding contribution to boron p_π orbital electron density accounts in terms of the $\langle 1/r^3 \rangle$ factor for the relatively lower shielding of boron in h-BN and t-BN (σ 30 ppm) compared to 3-coordinate boron in borax (σ 19 ppm) and in other boron–oxygen complexes.

The observed ^{11}B shielding for 4-coordinate boron is much less sensitive to ligand substitution effects, due to the absence of an empty p_π orbital capable of acquiring electron density from the σ-bonded heteroatom. Variations in the paramagnetic contribution (lower shielding effect) are therefore intrinsically much less for 4-coordinate boron compared to 3-coordinate boron. Comparison of the isotropic shift of c-BN (1.6 ppm) with that of the tetrahedral boron in borax (2.0 ppm)[58] shows that the two isotropic shifts are nearly the same.

Of particular interest is the fact that the spectra of the synthetic t-BN as the pure phase (Figure 5) and in the AlN/BN composite (spectrum not shown) are nearly identical with those of h-BN. This is not unexpected for pure-phase t-BN, since the disorder characteristic of the turbostratic form has no effect on the local boron environment but affects only the relative translational and rotational orientation of consecutive layers, which have a separation of 3.33 Å.[67] Here, bonding interactions between layers are of the weak (van der Waals) type and should have little consequence with regard to ^{11}B chemical shielding in boron nitride. The observation that spectra obtained on a composite mixture of BN with AlN are indistinguishable from that of pure t-BN suggests that the boron occurs as a distinct phase in the composite rather than in the form of a homogeneous solid solution. This conclusion is consistent with the observation of the characteristic XRD patterns for both AlN and BN upon crystallization of this composite at 1600 °C and the presence of uniformly dispersed AlN grains demonstrated by examination with TEM.[53]

Since this appears to be the first report on the structural characterization of boron nitride by high-field pulsed NMR spectroscopy, these data should serve as a basis for comparison in future studies of the pyrolytic conversion of organometallic precursors to boron nitrides.

Acknowledgment. The work at RPI was partially supported by grants from the General Eelectric Co. Superabrasives Division, the National Science Foundation under the Materials Initiative Chemistry Program, and the U.S. Air Force Office of Scientific Research. We acknowledge use of the Colorado State University Regional NMR Center, funded by NSF Grant No. CHE-8616437.

Registry No. BN, 10043-11-5; AlN, 24304-00-5.

---

[68] Kidd, R. G. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, pp 49–77.

[69] Karplus, M. P.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803–2807.