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Room-temperature transition of rhombohedral-type boron nitride under high static pressure

M. Ueno, K. Hasegawa,* R. Oshima, and A. Onodera
Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

O. Shimomura and K. Takemura
National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan

H. Nakae
Furukawa Electric Company, Chiyoda, Tokyo 100, Japan

T. Matsuda
Japan Metals and Chemical Company, Sakata, Yamagata 998, Japan

T. Hirai
Institute for Materials Research, Tohoku University, Sendai, Miyagi 980, Japan

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Rhombohedral-type boron nitride (*r*BN) has been studied to pressures of 61 GPa at room temperature in a diamond-anvil cell by *in situ* x-ray diffraction. Synchrotron radiation was employed as an x-ray source. A precursory structural change occurs at ~5 GPa. A transition to the cubic zinc-blende form (*c*BN) takes place at ~8 GPa and is completed above 20 GPa. For pressurization above 55 GPa, the cubic phase can be quenched to the ambient pressure.

I. INTRODUCTION

The rhombohedral form of boron nitride (*r*BN) is similar to the graphitelike modification (*h*BN) in that hexagonal networks are stacked parallel to each other. The stacking sequence is different; in *r*BN it is threefold ($ABCABC \cdots$), whereas twofold ($ABAB \cdots$) stacking is constructed in *h*BN. This difference leads to an expectation that, when compressed, the two forms would undergo transitions into different dense modifications, zinc-blende form (*c*BN) and wurtzitic form (*w*BN), respectively, by keeping those stacking sequences. Figure 1 demonstrates that the transitions could be achieved by approaches of the hexagonal networks followed by movement of atoms along the arrowed directions. The transitions are basically of the diffusionless type.

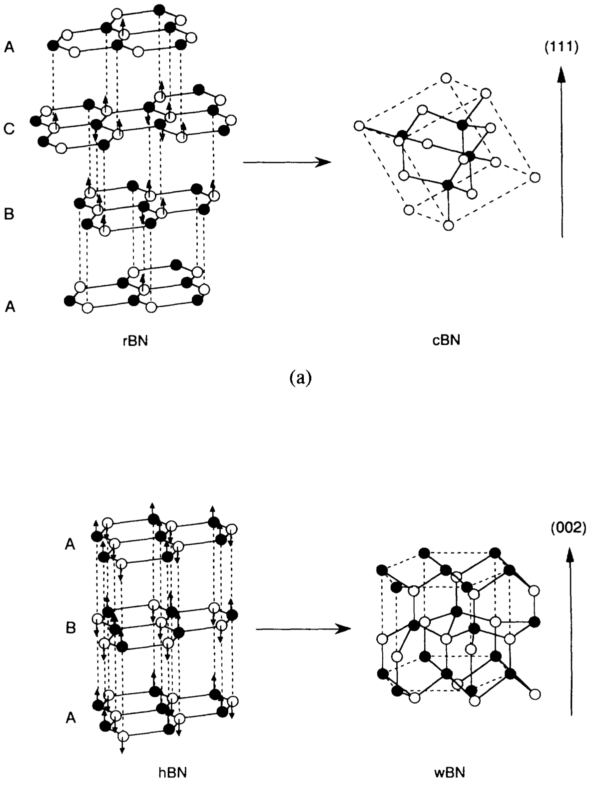
Some relevant results have been obtained from retrieval experiments. Shocked *r*BN transforms into *c*BN,[1] whereas static pressure in combination with high temperature converts *r*BN into either *c*BN or *w*BN.[2] Likewise, transition of *h*BN into *w*BN has been observed both under dynamic[3] and static[4] pressures. Specifically, the static compression studies have revealed that the *h*BN-to-*w*BN transition takes place at room temperature,[4] keeping the crystallographic orientation between the two phases,[5] implying that the diffusionless mechanism operates in this transition. The suggested room-temperature transition of *r*BN into *c*BN has not been reported previously to our knowledge. This paper describes an x-ray-diffraction study of *r*BN in a diamond-anvil cell up to 61 GPa at room temperature.

II. EXPERIMENTAL

Our *r*BN sample was prepared by chemical vapor deposition (CVD),[6] and the sample was the same as that used in the retrieval experiment.[2] X-ray-diffraction analysis showed that the lattice parameters of the present *r*BN were $a = 2.506 \pm 0.004$ Å and $c = 10.03 \pm 0.02$ Å, in agreement with earlier reports.[7,8]

The sample was pressurized at room temperature in a gasketed diamond-anvil cell. Two different culet sizes were employed for the diamond anvil, 0.6 mm below 23 GPa and 0.4 mm up to 61 GPa. A Ni-based alloy, U-700, was used for the gasket. A hole with diameter 0.28 or 0.12 mm, depending on the culet size, was drilled in the gasket for the sample chamber. Ruby chips to monitor the pressure[9] were incorporated into the gasket hole. A mixture of methanol and ethanol was used as the pressure-transmitting medium.

The sample in the diamond-anvil cell was x-rayed *in situ* under pressure using synchrotron radiation from the Photon Factory (PF) at the National Institute of High Energy Physics with collimation to 0.08 mm in diameter. The wavelength of the incident x rays was 0.6888 Å. An imaging plate (IP) (Ref. 10) was employed as the detector. The exposure time was typically about 5 h. Diffraction profiles were obtained by laser scanning of the Debye-Scherrer patterns recorded on IP's. In some cases the sample could be retrieved after release of pressure. The retrieved samples were subjected to transmission electron microscopy (TEM).



(a)

(b)

FIG. 1. Structures of boron nitride and modes of transitions. (a) *r*BN and *c*BN with a three-layered stacking sequence (*ABCABC* · · ·); (b) *h*BN and *w*BN having a two-layered stacking sequence (*ABAB* · · ·).

III. RESULTS

A. X-ray data

Figure 2 shows a typical example of x-ray-diffraction patterns. Three characteristic reflections from *r*BN appear in the pattern taken at 5.21 GPa. An unidentifiable peak also appears in this pattern. The *r*BN(003) reflection becomes significantly weakened at 14.2 GPa and, instead, the (111) reflection from *c*BN appears. The (101) and ($\bar{1}$02) reflections of *r*BN merge into the *c*BN(111) reflection. At 35.4 GPa and higher, no reflections from *r*BN can be observed. The *c*BN(111) reflection is slightly intensified with increasing pressure. The diffraction pattern at the top in Fig. 2 was obtained at 0.1 MPa but inside the diamond-anvil cell after release of pressure from 61 GPa. The *d* value obtained from the strongest peak is 2.090 Å, in fair agreement with the standard data for *c*BN at the ambient conditions.[11]

Figure 3 shows the relative intensity of the *r*BN(003) reflection plotted against pressure. The intensity decreases rapidly with increasing pressure to 8 GPa. Above 8 GPa, the *r*BN(003) reflection is quite weakened and virtually unaltered with pressure.

Figure 4 shows *d* spacings obtained from Fig. 2 and from additional experimental data. The *d* spacing of the *r*BN(003) reflection drastically decreases with increasing pressure, while those of *r*BN(101) and *r*BN($\bar{1}$02) reflections exhibit decreases by amounts less than half. Evidently the *r*BN(003) reflection disappears at about 20 GPa. On the other hand, the *c*BN(111) reflection appears

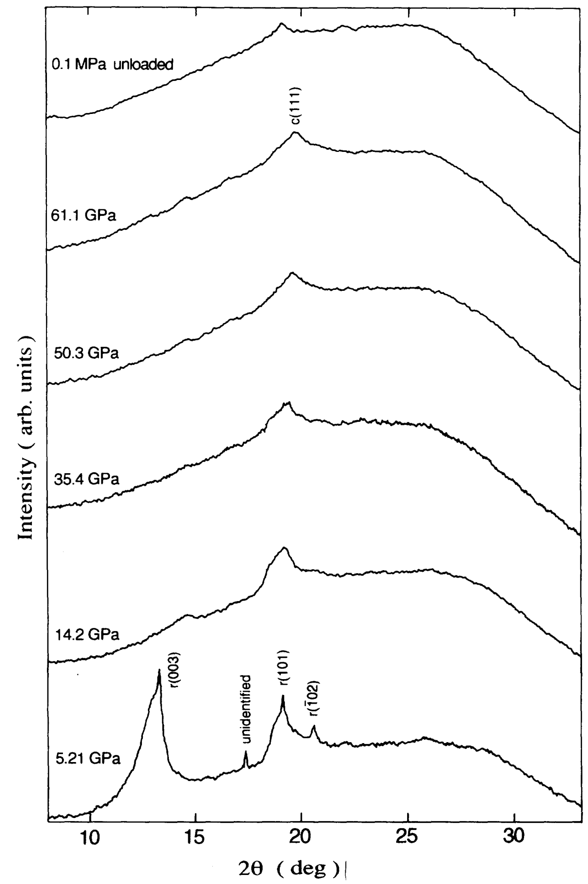


FIG. 2. Representative x-ray-diffraction patterns taken for the *r*BN sample. Each pattern was obtained by laser scanning of the Debye-Scherrer rings recorded on imaging plates. X-rays from synchrotron radiation were employed at a wavelength of 0.6888 Å. The small letters *r* and *c* denote *r*BN and *c*BN, respectively.

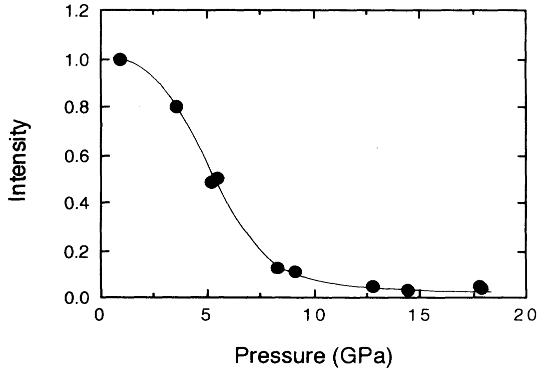


FIG. 3. Change of relative intensity of *r*BN(003) reflection with increasing pressure. Each intensity was calculated from the x-ray-diffraction pattern recorded on imaging plates and normalized to the value at 1 GPa.

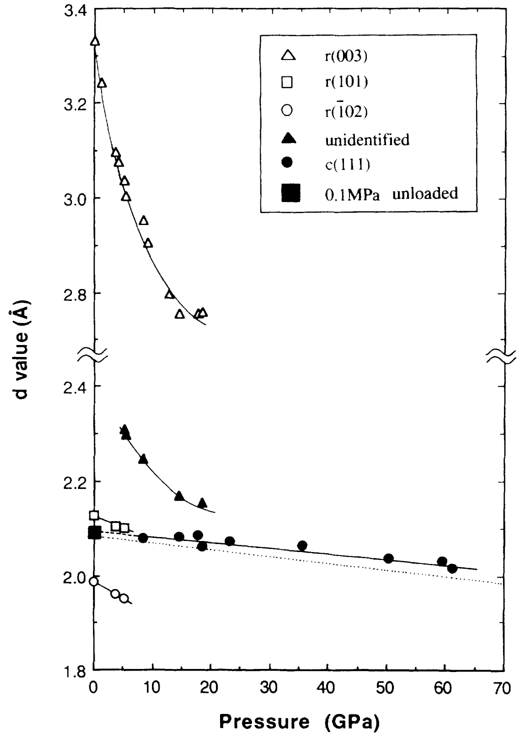
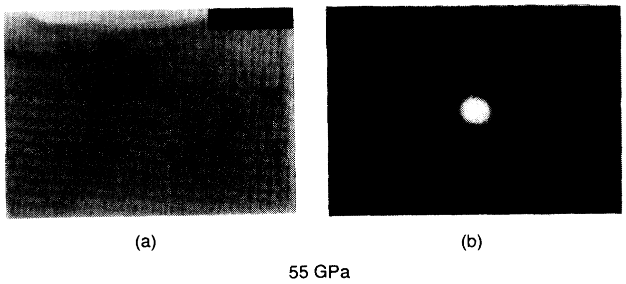


FIG. 4. Change of *d* values with pressure. The solid line is to guide the reader's eye. The dotted line is after Knittle *et al.* (Ref. 12) for the compression of *c*BN(111). Each point was taken on the loading process unless otherwise stated. In the inset, the small letters *r* and *c* denote *r*BN and *c*BN, respectively.



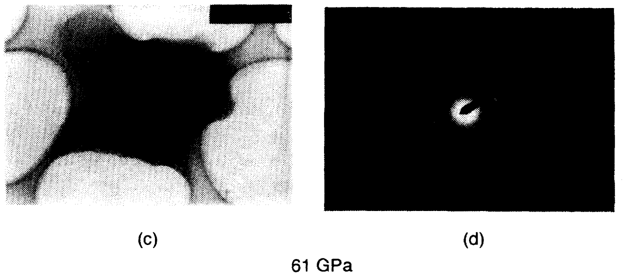


FIG. 5. TEM photographs and electron-diffraction patterns of samples retrieved from 55 and 61 GPa. (a) and (b) 55-GPa sample; (c) and (d) 61-GPa sample.

TABLE I. Comparison of the *d* values and lattice parameter obtained from the electron-diffraction patterns in Figs. 5(b) and 5(d).

	d_{obs} (Å)		JCPDS(25-1033)[a]	
h k l	Fig. 5(b)	Fig. 5(d)	*d* (Å)[a]	Relative int.[a]
1 1 1	2.10	2.08	2.09	100
2 0 0	1.84		1.81	20
2 2 0	1.28	1.26	1.28	60
3 1 1	1.10	1.09	1.086	40
	$a = 3.65$ Å	$a = 3.60$ Å	$a = 3.62$ Å	

[a] Reference 11.

at 8 GPa. The *d* value of *c*BN(111) is in fair agreement (within 1%) with data of Knittle *et al.*[12] throughout the pressure range covered in this study.

We note that the *d* value of unidentifiable peak in Fig. 2 is as compressible as the *r*BN(003) reflection (Fig. 4). Also, this peak disappears at a pressure similar to that of the disappearance of the *r*BN(003) reflection. These similarities suggest that the unidentifiable reflection presumably arises from the hexagonal network planes like *r*BN(003).

B. TEM observation

Figure 5 shows TEM photographs and electron-diffraction patterns of samples retrieved from pressures of 55 and 61 GPa. Figure 5(a) shows that the sample retrieved from 55 GPa is made up of very small particles with sizes about 300 Å in diameter. The electron-diffraction pattern of this sample, Fig. 5(b), exhibits reflections from the fcc lattice. Figure 5(c) shows that the sample retrieved from 61 GPa consists of two parts, one with fine grains and the other with a blocky grain. From the blocky grain an electron-diffraction pattern was obtained as shown in Fig. 5(d). The pattern can be indexed on the basis of *c*BN. Table I compares the *d* spacings and lattice constant of the two samples with the standard data.[11] The lattice constants from the two samples bracket the standard value.

IV. DISCUSSION

The present *in situ* x-ray-diffraction measurements have unequivocally shown that *c*BN appears at room temperature at ~8 GPa. In our previous retrieval experiment on *r*BN,[2] the samples pressurized to 15 GPa at room temperature did not contain any trace of *c*BN; however, the present study has shown that *c*BN can be retrieved when the samples are compressed beyond 55 GPa. Thus the *r*BN-to-*c*BN transition at room temperature is reversible below 15 GPa and irreversible, at least, above 55 GPa. There may of course be a threshold pressure for the irreversible change between 15 and 55 GPa.

The disagreements in the pressures for the disappearance of the *r*BN reflections and for the appearance of the *c*BN(111) reflection need some remarks. In Fig. 4, the *r*BN(101) and *r*BN($\bar{1}$02) reflections disappear at about 5

GPa, while the *r*BN(003) reflection persists up to 20 GPa. An appearance of the *c*BN(111) reflection takes place at about 8 GPa. In this connection, our preliminary Raman-scattering study of *r*BN (Ref. 13) has shown that a band assigned similar to the E_{2g} mode in *h*BN exhibits a change at 3–4 GPa, which corresponds to the pressure where the *r*BN(101) and *r*BN($\bar{1}$02) reflections vanish. From these observations it is likely that at 5 GPa, formation of a three-dimensional sp^3 bond is not yet achieved. The transition of *r*BN to *c*BN can be completed after the disappearance of the *r*BN(003) reflection above 20–25 GPa.

A recent first-principles calculation within the local-density-functional theory has simulated the mechanism of the *r*BN-to-*c*BN transition.[14] The simulation suggests that the *r*BN-to-*c*BN transition occurs with buckling of the layered networks and stretching of the intralayer bond length. The calculation demonstrates that when the interlayer distance of *r*BN (R) reaches a critical value, the buckling angle (θ) and the intralayer bond length (r) rapidly increase. This buckling takes place in our study and it may start at pressures of 3–5 GPa at which *r*BN(101) and *r*BN($\bar{1}$02) reflections disappear and the Raman mode of *r*BN changes.

The room-temperature transition pressure and a reaction boundary from the retrieval experiment are summarized in the phase diagram of BN in Fig. 6. The reaction boundary has a negative slope relative to the pressure ordinate at temperatures below 1300 °C and can be extrapolated to 20–30 GPa at room temperature. The present result at room temperature (20–25 GPa) eventually falls on this extrapolation.

No transformation to *w*BN has been observed in this study. However, our previous study[2] has shown that, at high temperature but above 10 GPa, *w*BN can be obtained from *r*BN and the *r*BN-*w*BN boundary has a small negative slope. Because of the smaller slope, the *r*BN-*w*BN boundary meets the room-temperature axis at pressures higher than 30 GPa. Then, in principle, the *r*BN-to-*w*BN transition could take place above 30 GPa at room temperature; however, the *r*BN-to-*c*BN transition has been already completed around this pressure, and, in view of the fact that *c*BN is more stable than *w*BN, *c*BN cannot be converted into *w*BN. Consequently, *w*BN will not appear from our *r*BN at room temperature.

A recent study in a cubic press has shown that above 7 GPa, *w*BN can be formed from *r*BN at room temperature.[15] Their samples were prepared from a solid-state reaction of $NaBH_4$ and NH_4Cl in N_2 gas, whereas ours were prepared by CVD. A comparison of the powder x-ray-diffraction patterns indicated that the (101) and ($\bar{1}$02) reflections were a little less well defined in our sample. At high pressure, most of the reflections in our sample became asymmetric as exemplified by the 5.21-GPa pattern in Fig. 2. This suggests that *r*BN becomes partly turbostratic[16] upon compression. In the cubic press experiment, the x-ray-diffraction pattern of the samples has been degraded to a greater extent.[15] The degradation can presumably be caused by the pressurization with a solid pressure-transmitting medium in the cubic press. Since the degradation of the diffraction pattern concerns the stacking sequence, this will prevent the formation of *c*BN and, instead, the *w*BN formation will prevail. Thus the difference in the modes of pressurization governs the transition paths in a much more effective manner than does the difference in the starting material.

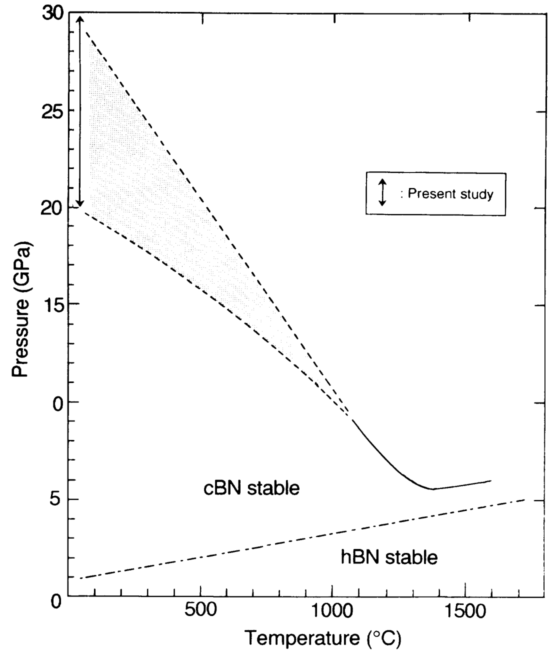


FIG. 6. Phase and reaction diagram of boron nitride. The solid line is a reaction boundary for the transition from *r*BN to *c*BN (Ref. 2). The shaded band surrounded by the broken lines is an extrapolation of the solid line. The dash-dotted line is after a thermodynamic calculation for equilibrium between *h*BN and *c*BN (Ref. 17). The solid line with arrows represents the result of the room-temperature transition of *r*BN to *c*BN obtained in this study.

V. CONCLUSION

In situ x-ray diffraction at high pressures along with post-compression electron-diffraction studies have revealed that *r*BN transforms at room temperature into *c*BN at pressures higher than 8 GPa. Prior to the transition, a structural change of *r*BN takes place at about 5 GPa, as evidenced by the disappearance of the *r*BN(101) and *r*BN($\bar{1}$02) reflections. The hexagonal network of *r*BN persists up to 20 GPa, above which the transformation is achieved.

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[*] Present address: Sumitomo Electric Co., Osaka 554, Japan.

[1] T. Sato, T. Ishii, and N. Setaka, J. Am. Ceram. Soc. **65**, C-162 (1982).

[2] A. Onodera, K. Inoue, H. Yoshihara, H. Nakae, T. Matsuda, and T. Hirai, J. Mater. Sci. **25**, 4279 (1990).

[3] A. Sawaoka, T. Sôma, and S. Saito, Jpn. J. Appl. Phys. **13**, 891 (1974).

[4] M. Wakatsuki and K. Ichinose, in *Proceedings of the 4th AIRAPT Conference,* edited by J. Osugi (Physicochemical Society of Japan, Kyoto, 1974), p. 441.

[5] M. Wakatsuki, K. J. Takano, and G. Fujita, Physica B+C **139&140B**, 256 (1986).

[6] T. Matsuda, N. Uno, H. Nakai, and T. Hirai, J. Mater. Sci. **21**, 649 (1986).

[7] A. Herold, B. Marzluf, and P. Perio, C. R. Acad. Sci. **246**, 1866 (1958).

[8] T. Ishii, T. Sato, Y. Sekikawa, and M. Iwata, J. Cryst. Growth **52**, 285 (1981).

[9] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[10] O. Shimomura, K. Takemura, H. Fujihisa, Y. Fujii, Y. Ohishi, T. Kikegawa, Y. Amemiya, and T. Matsushita, Rev. Sci. Instrum. **63**, 967 (1992).

[11] ASTM card 15-500, after F. P. Bundy and R. H. Wentorf, Jr., J. Chem. Phys. **38**, 1144 (1963).

[12] E. Knittle, R. M. Wentzcovitch, R. Jeanloz, and M. L. Cohen, Nature **337**, 349 (1989).

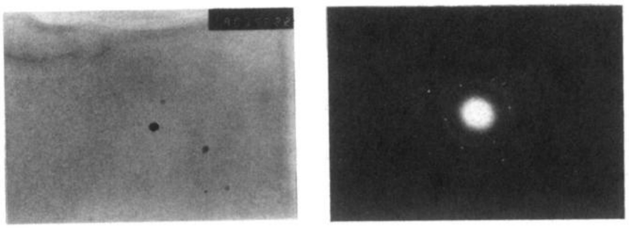
[13] M. Ueno, A. Onodera, I. Tanaka, and Y. Miyamoto (unpublished).

[14] R. M. Wentzcovitch, S. Fahy, M. L. Cohen, and S. G. Louie, Phys. Rev. B **38**, 6191 (1988).

[15] T. Taniguchi, O. Shimomura, T. Sato, T. Ohsawa, S. Yamaoka, W. Utsumi, and T. Kikegawa (unpublished).

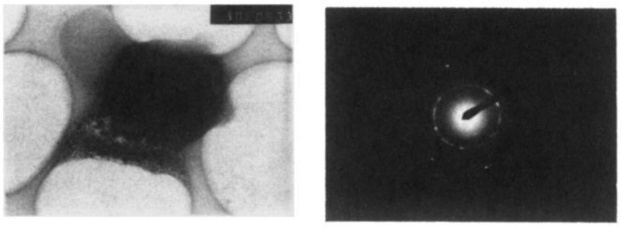
[16] J. Thomas, Jr., N. E. Weston, and T. E. O'Connor, J. Am. Chem. Soc. **84**, 4691 (1963).

[17] N. Shirota and N. A. Kofman, Dokl. Akad. Nauk SSSR **249**, 1346 (1979) [Sov. Phys. Dokl. **24**, 1001 (1979)].



(a) (b)

55 GPa



(c) (d)

61 GPa

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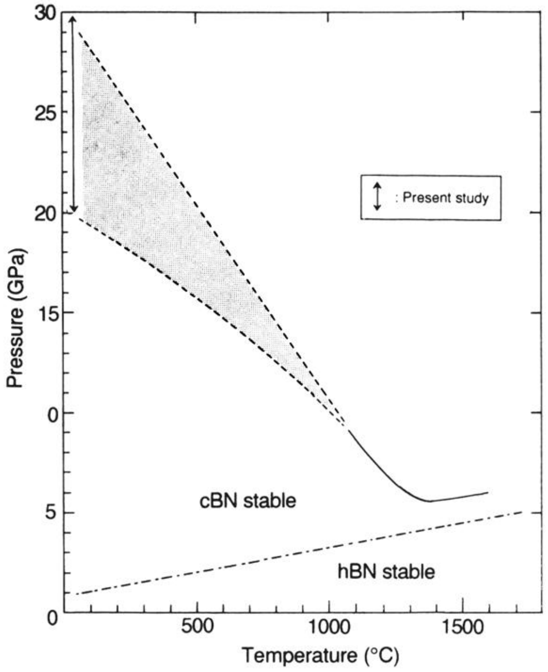

FIG. 6. Phase and reaction diagram of boron nitride. The solid line is a reaction boundary for the transition from *r*BN to *c*BN (Ref. 2). The shaded band surrounded by the broken lines is an extrapolation of the solid line. The dash-dotted line is after a thermodynamic calculation for equilibrium between *h*BN and *c*BN (Ref. 17). The solid line with arrows represents the result of the room-temperature transition of *r*BN to *c*BN obtained in this study.