High-pressure *in situ* x-ray-diffraction study of the phase transformation from graphite to hexagonal diamond at room temperature

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High-pressure *in situ* x-ray diffraction was carried out to clarify the nature of the pressure-induced phase transformation in graphite at room temperature. The combined use of a Drickamer-type high-pressure apparatus with sintered diamond as an anvil material and very intense x rays from synchrotron radiation made it possible to obtain high-quality x-ray-diffraction data, as well as information on the orientation relation, for this phase transformation. It was found that the transition starts at 14 GPa at room temperature, although this onset pressure is sensitive to the nature of the sample and of the applied pressure. X-ray-diffraction profiles obtained on the high-pressure phase are well explained by the hexagonal diamond structure, but the observed c/a ratio is slightly larger than that of ideal packing. The observed orientation relation satisfies the previously proposed martensitic transition mechanism from graphite to hexagonal diamond. But this hexagonal diamond formed at room temperature is unquenchable upon the release of pressure, and how it differs from the quenched phase formed under high pressure and temperature remains to be clarified.

I. INTRODUCTION

Conversion of graphite into diamond by static pressure using catalyst or solvent methods has been a subject of intensive study for more than 30 years. In contrast, only very limited studies have been carried out on the direct conversion of graphite into diamond. Aust and Drickamer[1] and Bundy and Kasper[2] observed a rapid increase of the electrical resistivity of well-crystallized graphite when it was compressed to above 15 GPa. At room temperature, this change was reversible upon the release of pressure. However, when the sample was heated above 1000 °C under pressure, Bundy and Kasper[2] observed an irreversible increase of the electrical resistivity. In the recovered sample they observed some additional diffraction lines which could be indexed as a "hexagonal diamond" structure. A mineral which gives a similar powder x-ray-diffraction pattern was found in meteorites and was named Lonsdaleite.[3,4] In spite of these findings, the nature of this hexagonal diamond remains unclear because its existence has been studied by low-resolution powder x-ray-diffraction patterns or by electron microscope observations, and no single crystal of this structure has ever been obtained.

Recently, due to the development of the diamond anvil apparatus, many high-pressure studies on graphite have been carried out using optical methods, which clearly indicate the existence of a pressure-induced phase transfor-

mation at room temperature. Hanfland *et al.*[5,6] observed a sudden drop of optical reflectivity and a broadening of the high-frequency E_{2g} Raman line above 9 GPa, which indicated the onset of the transformation. This transformation was fully achieved at about 17 GPa. Goncharov, Makarenko, and Stishov,[7] in a Raman and reflectivity study, observed a sharp decrease in the reflectivity and a simultaneous broadening of the intralayer Raman spectra between 15 and 35 GPa. Utsumi and Yagi[8] made an optical observation on a very thin (about 1 μm thick) single crystal of graphite and found that it turned into a light transparent phase above 18 GPa. Takano, Harashima, and Wakatsuki[9] reported the existence of several discontinuous volume changes at 18 and 25 GPa. Although various speculations, such as the formation of an sp^3-bonded structure,[2,5] an amorphous phase,[7] or an intermediate phase between graphite and hexagonal diamond,[9] were made, the nature of this high-pressure phase or its relation with the hexagonal diamond is still not clear.

Several attempts to determine the crystal structure of this high-pressure phase by x-ray diffraction were made using the diamond anvil apparatus.[5,10,11] However, in the diamond anvil apparatus, the thickness of the sample becomes less than 100 μm above 10 GPa and, consequently, light element materials such as graphite give very poor diffraction patterns. Moreover, graphite has a layered structure and it is difficult to make a fine powder. Even

when a single crystal is crushed into fine particles, they have flakelike shapes, and when such a sample is compressed uniaxially, they develop a strong preferred orientation. All these situations have made it difficult to obtain high-quality x-ray-diffraction data on graphite under pressure, and, consequently, the structure of the high-pressure phase has remained unsolved.

The purpose of the present study is to overcome these difficulties and clarify the crystal structure of the high-pressure phase formed by the room-temperature compression of graphite. Preliminary experiments indicate that this phase transformation is sensitive to the nature of the applied pressure as well as to the type of starting material used. In order to see these effects, three different types of high-pressure apparatus and two different starting materials were used. The combined use of a Drickamer-type high-pressure apparatus with sintered diamond as an anvil material and very intense x rays from synchrontron radiation made it possible to get high-quality *in situ* x-ray-diffraction data on this high-pressure phase.

II. EXPERIMENT

Three different types of high-pressure apparatus (Drickamer-type anvil, cubic anvil, and diamond anvil) were used. In the ordinary Drickamer-type apparatus, a WC alloy is used as an anvil material. With this material, however, it is difficult to generate pressures high enough to induce the phase transition of graphite at room temperature, mainly because of the limited hardness of the WC alloy. Therefore, in the present study, we developed a Drickamer-type high-pressure apparatus using sintered diamond anvils. A schematic drawing of the Drickamer-type apparatus used in the present study is shown in Fig. 1. The anvil is made of a cylindrically-shaped sintered diamond (De Beers SYNDIE No. 15151, 15 mm in cross-sectional diameter and 15 mm high), which is made of 70-μm-size diamond powder and a metal binder. Eight facets were made on one end of this cylinder so that an octagonal-shaped top face is formed. The cross-sectional diameter of this octagonal-shaped anvil top is 3 mm and the angles between this top face and the facets surrounding the top face are 30°. We have tested several different angles and found that this is the optimum angle to get a large sample volume without

sacrificing the efficiency of pressure generation. A mixture of amorphous boron and epoxy resin (2:1 by weight) is used as a pressure-transmitting medium. The medium is made of three parts as shown in Fig. 1. The two end parts are made by compacting the boron-epoxy mixture using the anvil as a pattern. The central disk is made of the same material by compacting it in a piston cylinder-type jig. The sample chamber is a small hole drilled at the center of the disk and its initial size is 1 mm (cross-sectional diameter)$\times$1 mm high, which is deformed into approximately 1.2 mm (cross-sectional diameter)$\times$0.6 mm high after the compression. This hole is filled with the sample and gold pressure marker. The x-ray-diffraction volume of the sample in the Drickamer cell is more than ten times that of the diamond anvil cell.

The x rays pass into the sample chamber through a small hole [1 mm (cross-sectional diameter)] drilled in the cylinder and through a pressure-transmitting medium. In the present study, diffracted x rays were detected in two different orientations. One was in the plane containing the compression axis of the anvils ("*V*" in Fig. 2) and the other was in the plane perpendicular to it ("*H*" in Fig. 2), and the diffraction angle (2θ) was set at 10° in both cases. In the *V* (vertical) direction, part of the diffracted x ray passed through the anvil, but in the energy range above 30 keV, the effect of the absorption by the anvil was negligibly small, and high-quality x-ray-diffraction patterns were obtained. By applying a force of about 40 tons to this apparatus, samples were pressurized to 30 GPa. So far, we have made more than 20 runs up to 30 GPa and no fracture of the anvils has occurred yet.

The advantage of this apparatus over the diamond anvil apparatus is as follows: (1) Because of the much larger size of the sample chamber, diffracted x rays from samples with a low atomic number such as graphite are much stronger and high-quality x-ray-diffraction profiles can be obtained. (2) The x-ray beam enters the sample chamber from the direction perpendicular to the compression axis of the opposed anvils and the diffracted x ray can be observed in two different orientations relative to the compression axis (*V* and *H* in Fig. 2). Consequently, it is possible to get various information on the crystal structures of highly oriented samples.

All the x-ray experiments were carried out using the synchrotron radiation facility at the National Institute for High Energy Physics (KEK), Tsukuba. The x-ray source used for this Drickamer-type apparatus was a
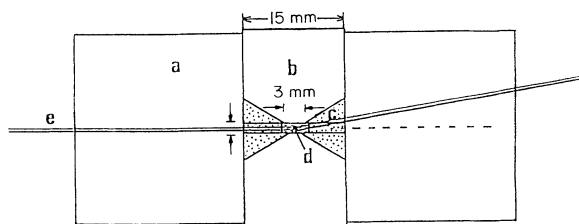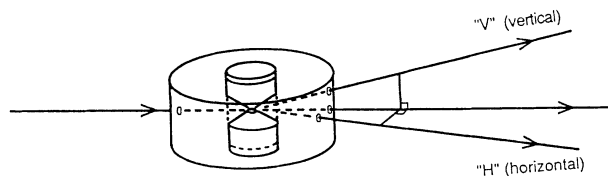

FIG. 1. Cross section of the Drickamer-type high-pressure apparatus using sintered diamond anvils. (a) Cylinder, (b) sintered diamond anvil (c) pressure medium made of a mixture of amorphous boron and epoxy resin, (d) sample, and (e) x-ray beam.

FIG. 2. Two observational directions for the powder x-ray-diffraction study using a Drickamer-type apparatus. In the vertical method "*V*," the solid-state detector is placed in the vertical plane which contains the compression axis. In the horizontal method "*H*," it is placed in the horizontal plane perpendicular to the compression axis.

white beam from the bending magnet of the Accumulation Ring, which was operated at 6.5 GeV with a ring current of 15–30 mA. The energy dispersive technique was employed and x rays in the energy range from 20 to 80 keV were used for the measurement. The incident beam was collimated to 0.1 mm×0.3 mm using 10-mm-thick slits made of tungsten carbide. Powdered gold was placed at the bottom of the sample chamber and, by changing the position of the incident beam, x-ray-diffraction patterns from the sample and the gold pressure standard were obtained separately. A pure germanium detector was adopted and a typical exposure time for the sample was 300–1000 sec, while a 200-sec exposure was long enough to get high-quality patterns for gold. The pressure was determined using the equation of state of gold calculated by Jamieson, Fritz, and Manghnani.[12]

A second type of high-pressure apparatus is a cubic anvil which can compress the samples isotropically.[13] Two systems named "MAX80" and "MAX90" were used. Both systems consist of a hydraulic press and a cubic-anvil-type high-pressure vessel. A cube-shaped pressure-transmitting medium is squeezed isotropically by six anvils with a truncation of 3 mm. The sample is embedded in a cube-shaped pressure-transmitting medium made of a mixture of amorphous boron and epoxy resin. Details of these systems and experimental techniques have been described previously.[14–16] "MAX90" uses sintered diamond as an anvil material, and, consequently, the pressure range has been extended, so far, to 18 GPa, while "MAX80" uses tungsten carbide anvils and the maximum attainable pressure is about 12 GPa.

"MAX80" was combined with the Accumulation Ring (the same source used for the Drickamer-type apparatus), while "MAX90" was operated at the vertical wiggler port of the Photon Factory in KEK. This ring was operated at 2.5 GeV and 150 mA and the energy range used for the measurement was from 20 to 70 keV. The incident beam was collimated to 0.1 mm×0.1 mm and a typical exposure time was 1000 sec.

The third high-pressure apparatus is a lever-and-spring-type diamond anvil apparatus.[17] A monochromatized x ray from the bending magnet of the Photon Factory was focused on the sample through a pin hole collimator with a diameter of 120 μm. An imaging plate was used for recording the diffracted x ray and the distance between the sample and the imaging plate was 153 mm. The energy of the x ray used for the experiment was 18 keV and a typical exposure time was 6 h. Data recorded on the imaging plate was measured and digitized by a two-dimensional optical reader and the intensity of the diffracted x ray was calculated as a function of 2 θ by integrating the observed intensity along the polar coordinates. The origin of the coordinates is adjusted to the recorded position of the direct x-ray beam. Two-dimensional intensity data are converted into one-dimensional data through this integration, and the data can be further analyzed by the same techniques used for angle-dispersive x-ray patterns from conventional diffractometers. Details of this analysis are reported elsewhere.[18]

All the quantitative x-ray-diffraction data were ob-

tained using either the Drickamer-type or cubic-type apparatus and the analysis was made as follows: x-ray-diffraction data collected by the detector were accumulated in the 2048-channel memory of a multichannel pulse-height analyzer and then sent to a computer for analysis. The background was then subtracted and the peak position of the diffraction profiles were determined by a least-squares fitting of a Gaussian curve to the diffraction peaks. Accuracy of the *d* values determined by these systems in KEK is usually about 0.05%. In the present study, however, various factors such as a low signal-to-noise ratio, the broad nature of the diffraction lines, coexistence of two phases, and the frequent overlapping of diffraction lines, reduced the accuracy considerably. Because of all these factors, the accuracy of the *d* values reported in this paper is approximately 0.2%.

The starting material for most of the present experiments is a kish graphite made by the oversaturation of carbon in molten iron. It is a very well-crystallized type of graphite and is the same material used for the previously reported optical observation.[8] This well-crystallized single-crystal graphite was crushed into powder by grinding it in a mortar and then fine powder was selected by gravity separation after dispersing it in acetone. The fine powder (the typical particle size was a few μm) thus collected was then compacted into a small cylindrical shape and inserted in the sample chamber. Starting materials thus prepared already had strong preferred orientation because, in spite of the small grain size, each particle has a flakelike shape. In order to see the effect of the starting material on the transition pressure, fine carbon powder for chemical analysis was also used in a different run and the details will be described later.

III. RESULTS

Diffraction profiles obtained in the *V* (vertical) direction using the Drickamer-type cell are summarized in Figs. 3(a) and 3(b) for increasing and decreasing pressure paths, respectively. The compacted starting material was placed in the sample chamber so the *c* axis of the graphite was preferentially aligned parallel to the incident x-ray beam. Consequently, before the compression, the (002) diffraction line of graphite was very weak while the (100) and (110) diffractions were strong. As soon as the pressure was applied, deformation of the sample chamber and rotation of the crystals occurred and the *c* axis was aligned preferentially to the compression axis. Thus, the (002) line became stronger with pressure. When the pressure was increased to around 14 GPa, an additional diffraction peak began to appear which has a slightly larger *d* spacing than (100) of graphite. By increasing the pressure further, the intensity of this peak increased, and we could observe three more diffraction lines of the high-pressure phase, although one of them was broad and overlapped with (101) of graphite. Even at the highest pressure achieved in this experiment (28.7 GPa), the graphite peaks were still observed clearly and we could not get a pure diffraction profile of the high-pressure phase.

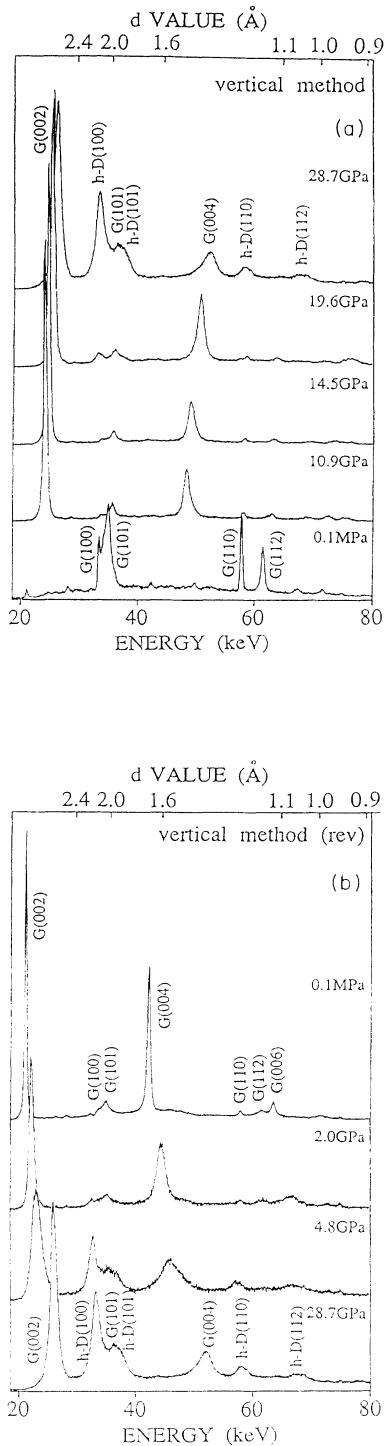By decreasing the pressure, we could observe the

FIG. 3. The variation of the x-ray-diffraction profiles of graphite with pressure observed in the vertical direction using a Drickamer-type apparatus. In the pressure-increasing process (a), the (002) line of graphite becomes strong as soon as the pressure is applied because of preferred orientation. New diffraction lines indexed by a hexagonal unit cell appear at about 14 GPa, and they become stronger as the pressure is increased. In the pressure-decreasing process (b), the diffraction lines of the high-pressure phase remain until the pressure is released to below about 3 GPa, but they are completely converted to graphite at ambient pressure.

diffraction lines of the high-pressure phase until the pressure was released to below about 3 GPa. After the pressure was released completely, strong (002) and (004) diffractions of graphite were observed, which means that the low-pressure phase has preferred orientation similar to that before the transition. From these observations, it becomes clear that the transition starts at around 14 GPa in the pressure-increasing process. The transition is reversible but has a very large hysteresis and the high-pressure phase is not quenched to 1 atm pressure.

Results of observations in the H (horizontal) direction are shown in Fig. 4. In this case, strong (100) and (101) diffraction lines of graphite were observed during compression, as opposed to the (002) line seen in the vertical direction. This is quite reasonable since the c axis of graphite was preferentially aligned parallel to the compression axis. At about 14 GPa, additional lines of the high-pressure phase appeared. The position of the most intense line of the high-pressure phase was between the (100) and (101) peaks of graphite, which contrasted strongly with the pattern observed in the vertical direction. These additional lines became stronger with pressure but the diffractions from graphite did not disappear completely. The behavior in the pressure-decreasing process was also the same as that observed in the vertical direction. Combining the information obtained from both the vertical and the horizontal directions, we could observe six and five diffraction lines for graphite and the high-pressure phase, respectively. The variations of the d values of these diffraction lines with pressure are summarized in Fig. 5. Five diffraction lines for the high-pressure phase can be successfully indexed by a hexago-
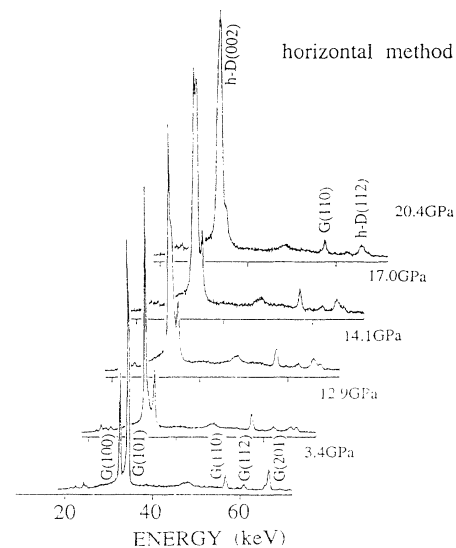

FIG. 4. The variation of the x-ray-diffraction profiles of graphite with pressure obtained in the horizontal direction using the Drickamer-type apparatus. Before the phase transformation, the (100) line of graphite is strong. The phase transformation occurs at around 14 GPa and the most intense line of the high-pressure phase, indexed as h-D(002), is observed at a position between the (100) and (101) lines of graphite, which is in remarkable contrast to the vertical observation.
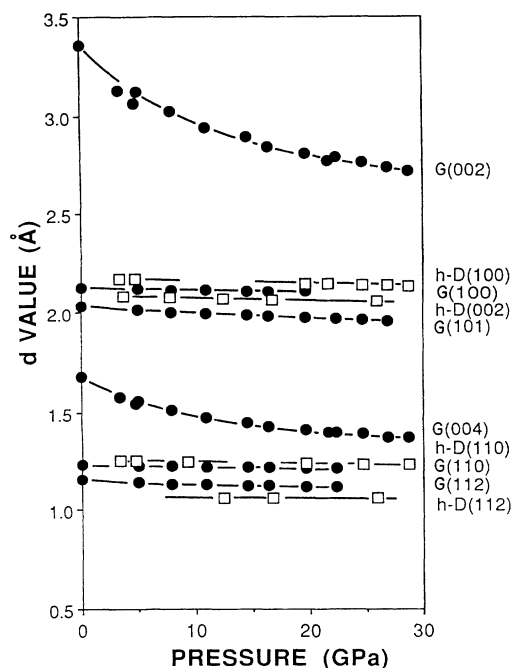
FIG. 5. Variation of the *d* spacing values of graphite and hexagonal diamond as function of pressure obtained by the Drickamer-type apparatus. Solid circles and open squares represent graphite and hexagonal diamond, respectively.
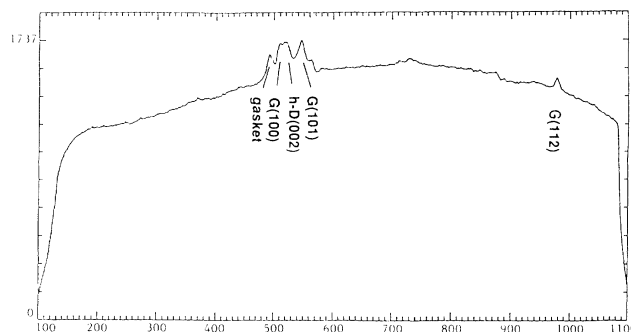

FIG. 6. Typical x-ray-diffraction profile of graphite under high pressure obtained by the diamond anvil cell and imaging plate. The pressure is 20 GPa, and the exposure time is 6 h. Although the diffraction line of the high-pressure phase can be observed slightly, the signal-to-noise ratio is very low and detailed analysis is difficult.

nal unit cell. Since the line indexed as $h(101)$ overlaps with a graphite line, its *d* value has a large uncertainty and is not included in Fig. 5.

An example of the diffraction profile obtained using the diamond anvil apparatus at 20 GPa is shown in Fig. 6. Although the best combination of an x-ray source and a detector currently available for this apparatus were used and the exposure time was quite long (6 h), the signal-to-noise ratio of the obtained diffraction profile was very low. This is because only a very small amount of the sample could be contained in the diamond anvil cell. Only a few strong lines can be observed and detailed analysis is impossible. Also, a small portion of the incident x-ray beam was hitting the gasket in this particular run and the diffraction from the gasket was also observed. In spite of the poor quality, the diffraction profile obtained by this method is clearly similar to that obtained by the horizontal observation in the Drickamer cell. That is, the (100) and (101) lines of graphite are strong and the strongest line of the high-pressure phase appears between them. In the diamond anvil apparatus, the incident x ray enters the sample chamber parallel to the compression axis of the opposed anvils. Therefore, the crystal planes almost parallel to the compression axis contribute to the diffraction and it is quite reasonable that the diffraction lines observed using the diamond anvil cell are very similar to those observed in the horizontal direction in the Drickamer-type cell. Most of the previous x-ray observations on the high-pressure phase of graphite[10,11] were made employing this diamond anvil technique and, consequently, the information obtained by them was very limited.

An example of the observation using the cubic anvil apparatus is shown in Fig. 7. The nature of the pressure in the cubic anvil apparatus is expected to be much more isotropic compared to the diamond anvil or Drickamer-type anvil apparatus. However, in the present study, the starting material installed in the sample chamber was compacted in advance and had a strong preferred orientation from the beginning. Consequently, the observed
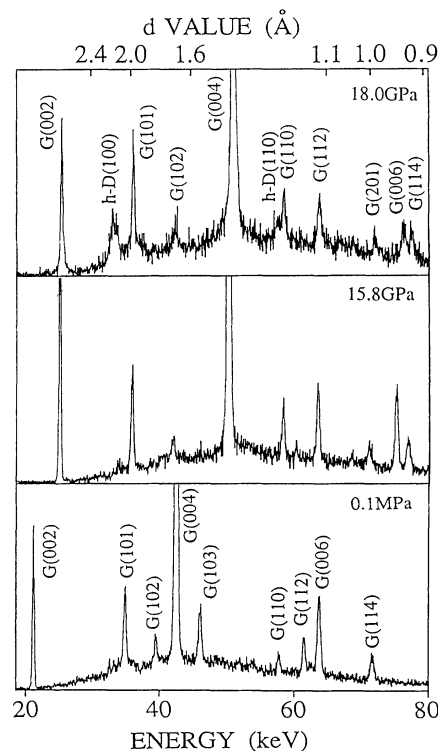

FIG. 7. Variation of the x-ray-diffraction profile of graphite with pressure obtained by the cubic anvil apparatus. The transition does not occur until the pressure is raised to 18 GPa. This indicates that the graphite to hexagonal diamond transition is strongly affected by the nature of the applied pressure.

TABLE I. Graphite-hexagonal diamond transition pressure at room temperature. All measurements are in units of GPa.

	Drickamer anvil	Cubic anvil	Diamond anvil (single-crystal sample)	Diamond anvil (powder sample)
Kish graphite	14	18	18	15
Graphite for chemical analysis	23	> 18		

diffraction profile was very similar to that observed in the vertical direction of the Drickamer-type anvil. In this case, however, the onset of the transition was delayed until the pressure was raised to 18 GPa, even though the starting material was identical. This means that the transition pressure is sensitive to the nature of the pressure.

The transition pressure in the pressure-increasing process varied depending not only on the nature of the applied pressure, but also on the nature of the starting material. In order to see this effect, a fine carbon powder for chemical analysis (Tokai Carbon Co.), which has high purity but is poorly crystallized, was compressed by the Drickamer-type anvil and the cubic anvil apparatus. In both cases, the occurrence of the transition was shifted to higher pressures. In the experiment using the Drickamer anvil, the diffraction peaks of the high-pressure phase appeared at about 23 GPa. In the cubic anvil experiment, no peaks of the high-pressure phase were observed at all even when the sample was compressed up to 18 GPa, which was the maximum pressure generated by this apparatus. The variation of the transition pressure in all the experiments is summarized in Table I.

IV. DISCUSSION

A. Compression of the graphite phase

Figure 8 shows the variation of the lattice parameters a/a_0 and c/c_0 of graphite phase obtained by the cubic anvil apparatus. As described before, in this apparatus, graphite did not transform to the high-pressure phase until 18 GPa. Because of the large size of the sample, high-quality x-ray-diffraction patterns were obtained and a precise compression curve of the lattice parameters was determined from the six diffraction lines. For comparison, the previously reported data is also plotted in the same figure. The compression along the c axis reported by Hanfland et al.[5] (open triangles in Fig. 8) is in fairly good agreement with our present data, though their results were derived from only two diffraction lines [(002) and (101)] obtained using the diamond anvil cell. They also reported that, above 14 GPa, these diffraction lines of graphite disappeared and a high-pressure phase was formed, though its structure could not be identified because of the poor quality of the diffraction pattern. This transition pressure (14 GPa) is the same as that obtained in the present experiment using the Drickamer-type anvil. On the other hand, Zhao and Spain[10] reported that, at around 11 GPa, a softening of the interlayer spacing occurred and additional diffraction lines appeared. Thus,

the compression curve of the c axis has an anomaly (open circles in Fig. 8) if the very weakly observed diffraction line near 3 Å gives the c-axis spacing. Below 10 GPa, the compressibility of the c axis derived by Zhao and Spain[10] is considerably smaller than that of our present data. In the pressure region above 11 GPa, however, all the data are consistent with our compression curve. In their experiment, a diamond anvil cell and fixed-anode x-ray source were used. As mentioned before, in the graphite experiment using a diamond anvil cell, it is difficult to get a high-quality diffraction pattern, and, because of the preferred orientation, the intensity of the (002) line diminishes under high pressure. Therefore, it may be possible that they miss-indexed the graphite peaks as those of the high-pressure phase. Lynch and Drickamer[19] also gave a low compressibility, but this is probably due to the use of an old and different pressure scale. The compression data
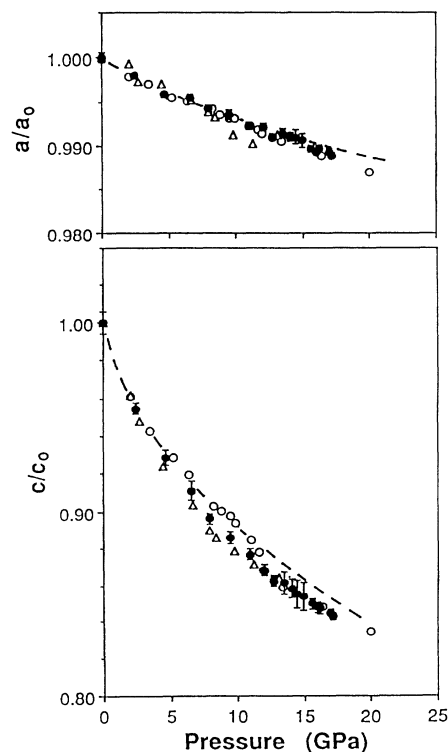
FIG. 8. Relative lattice parameters a/a_0 and c/c_0 of graphite as a function of pressure. The solid circles correspond to the present results obtained by the cubic anvil apparatus. For comparison, previously reported data are also plotted. ●, present work; ○, Ref. 10; △, Ref. 5; — — —, Ref. 19.

along the *a* axis obtained by the present observation is in fairly good agreement with the previous data, although they are slightly scattered.

B. Structure of the high-pressure phase

All the additional diffraction lines of the high-pressure phase obtained by the present study are successfully indexed by a hexagonal unit cell. Observed and calculated *d* values and the unit-cell parameters at 25 and 5 GPa are summarized in Table II, together with the data on hexagonal diamond reported by Bundy and Kasper.[2] The present high-pressure phase is unquenchable and it is impossible to make a direct comparison with the quenched hexagonal diamond, which was observed at atmospheric pressure. Therefore, straight lines were fitted to the *d* values of the high-pressure phase observed between 5 and 25 GPa in Fig. 8. The *d* values at ambient condition were obtained by the extrapolation of these straight lines, and the until cell was calculated using these extrapolated *d* values. This high-pressure phase was so incompressible that fitting by a higher-order line would be meaningless in this pressure range. The obtained *d* values and unit cell are summarized in Table II. The unit cell thus obtained is very close to that of hexagonal diamond (Lonsdaleite), which suggests that the high-pressure phase observed in the present study has the same structure as hexagonal diamond, although the present high-pressure phase is unquenchable on release of pressure.

In order to get a definite conclusion, it is necessary to compare the intensity of the diffraction lines. In the present experiment, however, the occurrence of preferred orientation made it difficult to analyze the crystal structure from the peak intensities. Actually, as is clear from Figs. 3 and 4, the observed intensity for the high-pressure phase differs a lot depending on the direction of observation. However, intensities in the vertical and the horizontal observations are reproducible, which means a certain orientation relation exists between graphite and the high-pressure phase. Our observation can be summarized
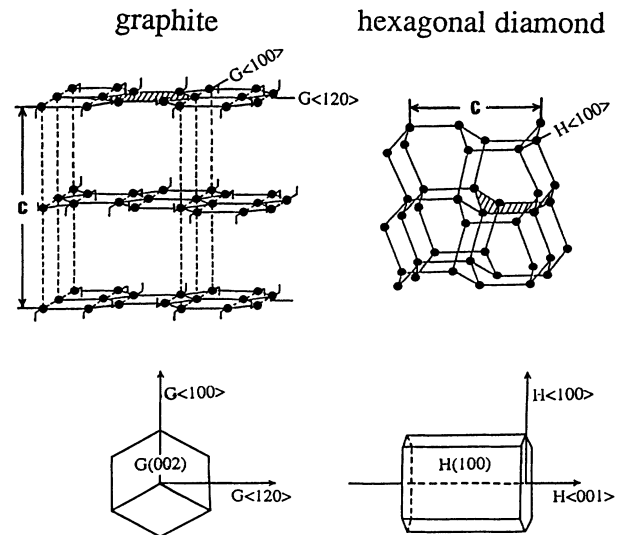

FIG. 9. Structures and orientation relations of graphite and hexagonal diamond.

as follows: (1) When the (002) line of graphite is strong, the (100) line of the high-pressure phase is strong. (2) When the (100) line of graphite is strong, the (002) line of the high-pressure phase is strong. Mechanisms and orientation relations of the phase transformation from graphite to hexagonal diamond were proposed by Bundy and Kasper[2] and Lonsdale.[20] They proposed that the mechanism is martensitic and the orientation relationship is as follows: $H(100)$ is parallel to $G(002)$, and $H\langle 001\rangle$ and $H\langle 100\rangle$ are parallel to $G\langle 120\rangle$ and $G\langle 100\rangle$, respectively. Here, H and G represent hexagonal diamond and graphite, respectively. These orientation relations and the structure of graphite and hexagonal diamond are summarized in Fig. 9. It is clear that our present observation in two different directions is completely in harmony with this proposed orientation relationship.

In order to confirm the reliability of the present observation of the orientation relationship, we have studied the

TABLE II. *d*-spacing parameter of the hexagonal diamond.

					d (Å)		
	25 GPa		5 GPa		0.1 Mpa		
hkl	Obs.	Calc.[a]	Obs.	Calc.[a]	Obs.[b]	Calc.[a]	Obs (Bundy and Kasper)[c]
100	2.139	2.137	2.170	2.165	2.180	2.176	2.19
002	2.055	2.053	2.079	2.079	2.086	2.086	2.06
101	(1.9)[d]	1.895	(1.9)[d]	1.920		1.929	1.92
101		1.480		1.499		1.506	1.50
110	1.234	1.234	1.249	1.250	1.256	1.257	1.26
103		1.152		1.167		1.172	1.17
112	1.057	1.057	1.169	1.071	1.074	1.076	1.075
201		1.034		1.048		1.053	1.055
	$a=2.467(3)$ Å		$a=2.500(6)$ Å		$a=2.513(6)$ Å		$a=2.52$ Å
	$c=4.105(5)$ Å		$c=4.158(6)$ Å		$c=4.171(5)$ Å		$c=4.12$ Å

[a]Calculated value based on the lattice constants derived from the observed diffraction peaks.
[b]Extrapolated value (see text).
[c]Quenched sample from high-pressure and high-temperature conditions (Ref. 2).
[d]Overlapped with the (101) peak of graphite.

phase transformation in boron nitride using the same method. The details of the experimental result on boron nitride are reported elsewhere.[21] This material is known to undergo a pressure-induced phase transformation from a hexagonal graphitelike structure to a hexagonal wurtzite-type structure at about 10 GPa. The structures of both low- and high-pressure phases have close similarities to those of graphite and hexagonal diamond, respectively. However, because of a slight difference in the stacking sequence of basal planes in the graphitelike structures, the orientation relationship between the low- and high-pressure phases is different. In boron nitride, the transformation occurs with h-$BN(002)$ parallel to w-$BN(002)$. Here, h and w represent low- and high-pressure phases, respectively. Our experimental results clearly showed that, in contrast to the results on graphite, very strong diffraction from the (002) line of the high-pressure phase was observed in the vertical direction, while the (100) line was very strong in the horizontal direction (Fig. 3 in Ref. 21). This means that the orientation of the c axis remains unchanged before and after the transition. This result is in good agreement with the orientation relationship described above and confirms the reliability of the present observations.

Based on these analyses, we can conclude that the crystal structure of the phase formed by the room-temperature compression of graphite is identical to that of hexagonal diamond. In diamond, there are many other possible structures which have a similar framework with slightly different stacking sequences. To check these possibilities, we have examined the diffraction patterns carefully but we could not find any other meaningful lines in the d-value range between 3.5 and 1.0 Å. This means that, even though it is impossible to exclude all the possibilities of slightly modified structure, the basic framework of this high-pressure phase cannot be so different from hexagonal diamond. The present observation also supports the orientation relationship proposed by Bundy and Kasper.[2] However, they could not get good enough diffraction patterns to determine the unit cell precisely. They assumed that the bond length in hexagonal diamond is identical to that in cubic diamond and, consequently, obtained the same density for both phases. In the present analysis, however, we could determine the unit cell without any assumption and found that the unit cell is slightly, but meaningfully, larger than that reported by them. The a axis is almost the same but the c axis is about 1% larger. Fahy and Louie[22] calculated the structural properties of hexagonal diamond using an *ab initio* pseudopotential local-orbital method and obtained slightly a larger c axis also (4.14 Å, conferred to 4.12 Å in Ref. 2). This expansion of the c axis is probably due to the repulsion between the carbon atoms which are aligned along the c axis. Because of this slight expansion, the c/a ratio becomes 1.66, which is slightly larger than 1.63, the ideal value of this hexagonal structure. This c/a ratio remains unchanged up to at least 30 GPa and the bulk modulus of this hexagonal diamond calculated from the present data is 425±25 GPa, which is indistinguishable from that of cubic diamond with the experimental error.

C. Difference of the transition pressure

As shown in Table I, the transition pressure varies greatly depending on many factors such as the nature of the starting material and the way of compression. The existence of an orientation relation between the low- and high-pressure phases suggests that the nature of this transition is not a diffusion type but a martensitic type. Graphite has a layered structure and carbon atoms within the layers are connected by sp^2-type covalent bonds while the bond between layers has the nature of a van der Waals force. Consequently, as shown in Fig. 5, compressibility along the c axis is much larger than that along the a axis. At about 18 GPa, where the transformation starts in a quasihydrostatic environment, the bond length between layers is approximately 2.8 Å. Since this transition has a martensitic nature, the condition of the adjacent layer is very important. When the distance between two layers became smaller than the above-mentioned value, and two layers are properly positioned, then the transition is expected to occur.

These hypotheses can explain the observed differences of the transition pressure well. As reported before,[8] when a very thin single crystal is compressed in a quasihydrostatic environment, the transition starts and is completed in a very narrow pressure interval between 18 and 19 GPa. In this case, since the sample is very thin, it is expected to be nearly a perfect crystal and the distance between layers is reduced homogeneously. On the other hand, when a powdered sample is compressed directly in a solid pressure-transmitting medium, a very heterogeneous compression occurs and some portion of the sample may be compressed more than the average. Besides, because of the random orientation, some portions of the sample may have difficulty finding a proper neighboring layer to accomplish the transition even when the nominal pressure is much higher than the transition pressure. Since the most important factor for the onset of the transition is the compression along the c axis, the transition starts at a lower nominal pressure when the sample is compressed uniaxially. This may be the reason why the transition pressure is low in the Drickamer-type cell.

The difference of the transition pressures in different starting materials can be explained in a similar manner. In the very well crystallized graphite sample we used, the transition occurs easily. On the other hand, high-purity carbon for chemical analysis is not so well crystallized and the transition occurs with more difficulty.

So far, many high-pressure studies have been done on graphite but the transition pressures reported are scattered. This is quite reasonable because the high-pressure apparatus and the nature of the starting materials used for each study have varied widely. Reproducible results can probably be obtained only when a high-quality single crystal is compressed in a highly hydrostatic environment.

D. Behavior under high temperature

It became clear in the present study that the crystal structure of the high-pressure phase formed by the

room-temperature compression of graphite is indistinguishable from that of hexagonal diamond. However, the hexagonal diamond so far reported was quenchable to atmospheric pressure while the present high-pressure phase is unquenchable. The reason for this difference remains unclear. Bundy and Kasper[2] made a speculation that, when the high-pressure phase formed at room temperature in heated above a critical temperature, this crystal structure is "set" and can be quenched. However, the physical meaning of "set" is not clear at all. It is known that in some materials the grain size and the presence of impurities affects the quenchability of high-pressure phases. In the case of hexagonal diamond, further studies using electron microscope observation will be required to clarify the physical processes during heating.

In a previous paper,[8] we have reported that, when the graphite was heated by a YAG laser under high pressure, a more light transparent phase than that formed by room-temperature compression was obtained. In a quenched product we have observed cubic diamond instead of hexagonal diamond. In laser heating, a very large temperature gradient is formed and some portion of the sample may be heated to a very high temperature. Therefore, it is likely that, when hexagonal diamond is heated above a certain temperature, it may transform directly into cubic diamond. In the case of boron nitride, the conversation from a wurtzite-type structure to a cubic-diamond-type structure is known to occur when the wurtzite-type phase is heated under pressure. For diamond, further study using high-pressure and high-temperature *in situ* x-ray observation will be required to clarify the relations among graphite, hexagonal diamond, and cubic diamond.

V. CONCLUSION

High-pressure *in situ* x-ray-diffraction studies on graphite were carried out up to 30 GPa at room temperature. The following results were obtained from these observations. (1) Phase transformation from graphite to a high-pressure phase occurs at about 14 GPa when well-crystallized single-crystal graphite is squeezed using a Drickamer-type high-pressure apparatus. (2) Diffraction profiles obtained on this high-pressure phase are well explained by the hexagonal diamond structure. (3) The transition pressure in the increasing and decreasing pressure process has a large hysteresis and the high-pressure phase formed at room temperature was unquenchable upon the release of pressure. (4) Hexagonal diamond formed at room temperature has a c/a ratio of 1.66 which is slightly larger than that reported before. (5) The transition pressure is very sensitive to the nature of the starting material as well as to the nature of the pressure applied to the sample. (6) The transition has a martensitic nature and the diffraction from two different orientations satisfies the orientation relationship proposed previously.

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