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11 February 1991; accepted 30 April 1991

Light-Transparent Phase Formed by Room-Temperature Compression of Graphite

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Single-crystal graphite has been compressed at room temperature and found to undergo a transformation at 18 gigapascals as indicated by a drastic increase in the optical transmittance. This high-pressure phase is unquenchable; a more transparent phase formed by the heating of this phase can be quenched at ambient conditions. This latter phase is probably "hexagonal diamond," and the present observations suggest that the structure of the transparent phase obtained by the room-temperature compression is different from the hexagonal diamond structure.

ALTHOUGH EXTENSIVE STUDIES have been carried out on diamond made by the catalyst-solvent process, little is known about the direct transformation from graphite to diamond under high pressure. More than 20 years ago, Aust and Drickamer (*1*) and Bundy and Kasper (*2*) found a sudden increase in the electrical resistivity of graphite when it was compressed above 15 GPa at room temperature. This change was reversible on release of pressure. When the sample was heated under pressure, however, a permanent increase in resistivity was observed, even after the complete release of pressure, and the "hexagonal diamond" phase was the phase in the recovered sample.

Recently, experiments have been carried out to investigate the behavior of natural single crystals of graphite at high pressure and room temperature. Hanfland *et al.* (*3, 4*) obtained Raman and reflectivity data and reported that the broadening of the high-frequency E_{2g} Raman line and the decrease in optical reflectivity started at about 9 GPa, which indicated the onset of the transformation. This transformation was fully achieved at about 17 GPa. They stated that this transformation at room temperature may be related to the formation of an sp^3 bonded structure. On the other hand, Goncharov *et al.* (*5*) observed in the pressure range between 15 and 35 GPa a sharp decrease in the reflectivity and a simultaneous broadening of the intralayer Raman spectral band. They also reported that, with increasing pressure, the sample became transparent gradually from 35 GPa and eventually became light-transparent (bleaching effect) at about 55 GPa. They attributed these changes to the phase transformation into an amorphous phase. Moreover, Zhao and Spain (*6*) carried out powder x-ray diffraction experiments and reported that some new diffraction peaks appeared above 11 GPa but they could not identify the structure.

These experimental results indicate the possibility of a pressure-induced transformation in graphite at room temperature, but the nature and the pressure of this transformation remain unclear. In order to clarify these points, we carried out optical observations with single-crystal synthetic graphite.

A single crystal of kish graphite (Toshiba Ceramics Co.), which was formed by the supersaturation of carbon in molten iron, was used as a starting material. This sample was easily cleaved with a razor edge, and we prepared a very thin hexagonal-shaped single crystal (~1 μm thickness and 150 μm edge length). The experiments were carried out with a modified Mao-Bell–type diamond anvil cell, and the pressure was determined by the ruby fluorescence method. A mixture of methanol and ethanol (4:1) was used as the pressure medium.

Before the compression (Fig. 1A), because the sample was very thin, it was not completely opaque even at atmospheric pressure. When the pressure was increased at room temperature, visual observation in the pressure range below 18 GPa revealed no noticeable change. However, at 18 GPa, several light-transparent spots suddenly appeared in the sample (Fig. 1B), and they spread over the whole sample area while the pressure was kept constant. Figure 1C was taken 30 min and Fig. 1D 2 hours after the transformation had started. In each spot, the color change was not gradual but was discontinuous and drastic. On release of the pressure, the transparent phase reversed suddenly to the original dark-color phase at 2.5 GPa; thus, the high-pressure phase could not be quenched at ambient conditions.

Absorption spectra of the sample were measured under various conditions, and no noticeable structure was found in the visible light spectra. The pressure variation of the optical density at 580 nm is plotted in Fig. 2 for both increasing and decreasing pressure. This transition is reversible with large hysteresis. The optical density of the recovered sample is slightly higher than that of the starting material, probably because of the polycrystalline nature of the recovered material.

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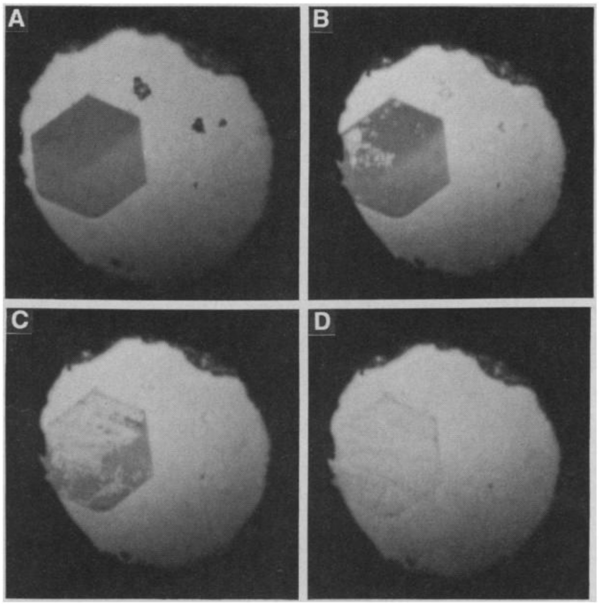

Fig. 1. In situ observation of a single crystal of graphite during the phase transformation at 18 GPa and room temperature. (**A**) Atmospheric pressure. (**B**) Pressure-induced phase transformation begins at 18 GPa and is accompanied by a drastic decrease in the optical density. (**C**) Thirty minutes after the start of the transformation. Pressure is held at 18 GPa. (**D**) Two hours after the start of the transformation. The whole sample was transformed to the high-pressure phase, which has high light transmissivity.

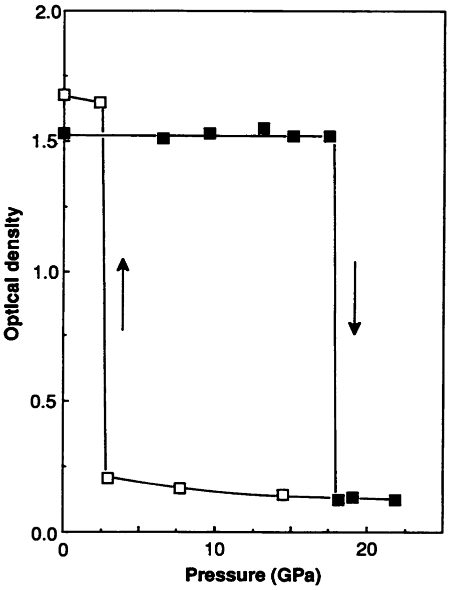

Fig. 2. Pressure variation of the optical density of graphite at 580 nm (sample thickness, ~1 μm) for both increasing and decreasing pressure.

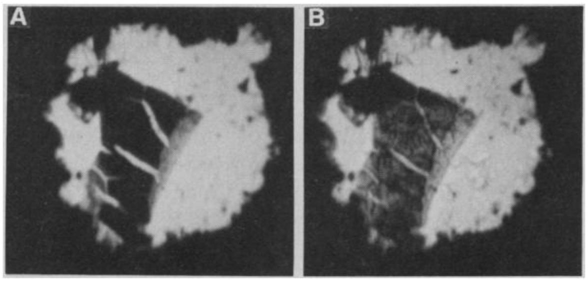

Fig. 3. Effect of heating on the high-pressure, room-temperature phase. (**A**) Before the heating (20 GPa). Although the whole sample has already transformed to the high-pressure phase, the sample is too thick to allow us to observe the transmissivity of light except the thin edges. (**B**) After heating by a YAG laser. The transmissivity of light increased drastically.

We repeated the same experiments with graphite of different thicknesses. In every case, we observed the discontinuous color bleaching at 18 GPa. When much thicker samples (10 μm) were used, however, the transformation became less obvious because the optical density of the sample became too large to allow us to observe the transmitted light even after the transition. As the pressure was increased further above 18 GPa, the transmissivity of this high-pressure phase increased gradually and even the thick samples became transparent at about 50 GPa.

Our results are in fair agreement with the report by Hanfland *et al.* (*4*), except that in some cases they observed the initiation of the transition at pressures lower than 10 GPa. We thought this disagreement might be caused by the local stress concentrations around the sample because they used KCl as a pressure medium. When we repeated our observation using KCl as a pressure medium, the result was unchanged. We could not find any change until the pressure was increased to 18 GPa. Their other evidence of the onset of the transformation near 9 GPa was the broadening of the E_{2g} Raman mode. However, this pressure is close to the freezing pressure of the methanol-ethanol mixture used in their Raman mode measurement. Thus, there is a possibility that this broadening was caused by the sudden change of the stress in the sample.

On the other hand, Goncharov *et al.* (*5*) reported that a noticeable change in color was observed at pressures above 35 GPa. This result is probably due to the fact that they used a sample so thick that they missed the beginning of the bleaching at 18 GPa. The onset of the anomalies in the other measurements (reflectivity and the Raman signal) are in harmony with our present results. Recently, Takano and Wakatsuki observed a discontinuous volume change of graphite at 18 GPa by measuring the applied load and the pressure generated in the diamond anvil cell (*7*).

Some of the x-ray observations (*3, 6*) indicate the onset of the transition at lower pressures than 18 GPa. These experiments were carried out on compressed powdered samples under nonhydrostatic condition. A large uniaxial component of pressure and the orientation of each crystal to the compression axis might be responsible for these discrepancies. We can conclude that, when a single crystal of graphite is compressed in a quasi-hydrostatic environment, a phase transformation occurs at 18 GPa and room temperature that accompanies the sudden increase in the light transmissivity.

Our next question was whether this high-pressure phase was hexagonal diamond. We heated the high-pressure phase at 20 GPa using a yttrium-aluminum-garnet (YAG) laser. Because of the very large temperature gradient of the laser heating, it is difficult to measure the temperature accurately. From the incandescent light, however, it is expected that a large portion of the sample was heated to 1000°C or more. Figure 3A shows the sample before the heating. The thin edges are colorless, and the thick central portion is still dark brown. After the laser heating, the sample became much more transparent than before (Fig. 3B). This transparent phase was retained even when the applied pressure was released completely. The fact that this phase is quenchable and the resemblance of the pressure-temperature condition of the present experiments with those reported by Bundy and Kasper (*2*) suggest that graphite has transformed into hexagonal diamond (lonsdalite) after the heating. The high-pressure phase formed at room temperature became almost as transparent as the heated phase when it was compressed above 50 GPa. However, this high-pressure phase without heating was unquenchable at ambient conditions even if it had very high transmissivity in the high-pressure range. This result strongly suggests that the high-pressure phase achieved at room temperature has a different structure from the hexagonal diamond.

In order to study the structure and the nature of bonding of this new high-pressure phase, it will be necessary to make high-pressure in situ x-ray and Raman observations. Unfortunately, data from earlier studies are not of sufficient quality for this purpose. Very high-quality x-ray observations with synchrotron radiation and Raman observations free from the effect of the surrounding diamond anvils are the important next step.

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17 December 1990; accepted 2 April 1991

Monolayer Crystallization of Flagellar L-P Rings by Sequential Addition and Depletion of Lipid

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The L-P ring complex is thought to be a molecular bushing that supports flagellar motor rotation at about 10,000 revolutions per minute with presumably very little friction. Structural studies of this complex have been limited because only very small amount of samples are available. Therefore devising an efficient method of crystallization was essential. The addition of a phospholipid and its subsequent slow depletion by phospholipase A_2 have been used to successfully grow well-ordered monolayer crystals that extend up to about 10 micrometers. The interaction of the L-P ring complex with lipid membranes was also visualized during this process.

BACTERIA SWIM BY ROTATING ONE OR more flagellar filaments driven by rotary motors at the base of each flagellum. The hook–basal body (HBB) complex is a part of the flagellar motor that can be easily detached from the cell membrane and consists of four ring structures and a rod connected to a hook (Fig. 1) (*1*). The L-P ring complex is composed of the outer two of the four rings and is thought to be a bushing that supports the flagellar motor, bearing its rapid rotation in both the clockwise and counterclockwise direction. Its structure, particularly at its inner surface, is interesting from a microtribiological aspect. The outermost ring, which sits in the outer membrane, is designated the L ring and is composed of 27-kD protein subunits; the other ring, which is thought to be associated with the peptidoglycan layer, is called the P ring and consists of 38-kD protein subunits (*2*). Although the overall shape of the L-P ring complex has been revealed by cylindrically averaged image reconstruction of the basal body from electron micrographs with the use of single particle averaging (*3*), more detailed structure, including organization of the subunits in the ring complex, remains to be elucidated. Three-dimensional image reconstruction from electron micrographs is especially useful for analysis of such intrinsic membrane proteins because of their potential tendency to form monolayer crystals. However, this method has so far been applied only to proteins available in large amounts, which are necessary for screening conditions to obtain well-ordered crystals large enough for analysis. A large-scale preparation of the L-P ring complexes has been hindered by the fact that each bacterium has only about ten of them. Therefore, it was essential to devise an efficient method of crystallization.

In order to maximize the limited amount of the sample available, the procedure for the purification of the L-P ring complex was improved (*4*) from the one developed by Aizawa *et al.* (*2*) in two respects. First, a high concentration of urea was used instead of acid degradation for more reproducible partial degradation of HBB complex. Second, contaminants such as outer membrane components and DNA fragments were removed by enzymatic digestion. In Fig. 2A, axial views are shown of the purified L-P ring complex, and Fig. 2B shows lateral views, which have been called "staples" (*2*). The open side of this staple has been assigned to the L ring and the closed side to the P ring (*3*, *5*).

After the removal of urea by centrifugation and resuspension, it was impossible to keep the L-P ring complexes dispersed even in the presence of 2% Triton X-100. Various kinds and concentrations of other detergents, ionic and non-ionic, gave no improvement. However, when a small amount of a phospholipid, dimyristoylphosphatidylcholine (DMPC), was added to the L-P ring aggregates, there appeared small patches of ring arrays apparently embedded in phospholipid membrane sheets or vesicles (Fig. 2C). The rings were packed closely in a well-ordered hexagonal lattice. Besides these patches, there were also single L-P rings with flaps or vesicles attached (Fig. 2D). Comparison between Fig. 2B and Fig. 2D shows that these extra structures, which are presumably lipid membranes, are attached to the L ring portion of the complex. This observation shows directly that the L ring has a high affinity for phospholipid and that the L-P ring complex can be effectively incorporated and concentrated in membranes through this property.

Overnight incubation at 30° to 37°C following the addition of the phospholipid favored the growth of well-ordered arrays of submicrometer size. Longer incubation, however, induced the formation of random aggregates of L-P ring complexes rather than larger arrays. In order to find better crystallization conditions, the effect of the ratio of Triton X-100 and DMPC on array formation was examined (Fig. 3, A to C). When the detergent:phospholipid ratio was high, the resulting arrays were planar, well ordered, and tightly packed, but also contained large cracks that separated ordered areas and limiting their size (Fig. 3A). When the ratio was low, there were large continuous vesicular membranes in which L-P ring complexes were embedded and arrayed loosely (Fig. 3C). Since no ratio we tried was entirely satisfactory, we used a strategy of first incubating the above mixture at a high DMPC concentration to facilitate incorporation of the L-P ring complexes into large and continuous proteomembranes and then slowly depleting the DMPC to pack the L-P rings into well-ordered arrays. We hypothesized that

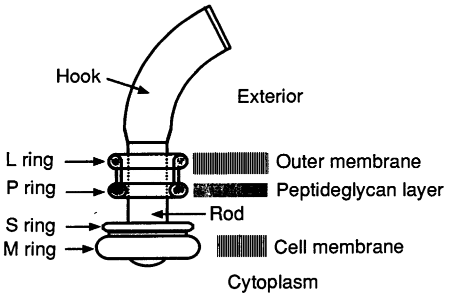

Fig. 1. Schematic diagram of the HBB complex of *Salmonella typhimurium,* showing the configurations and the locations of four rings: L, P, S, and M. The cross section of the L-P ring complex is hatched.

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