

# Amorphization of fullerite (C<sub>60</sub>) at high pressures

V. V. Brazhkin,<sup>1)</sup> A. G. Lyapin, Yu. V. Antonov, and S. V. Popova

*Institute of High-Pressure Physics, Russian Academy of Sciences, 142092 Troitsk, Moscow Region, Russia*

Yu. A. Klyuev and A. M. Naletov

*All-Union Scientific-Research Institute of Diamonds, 119110, Moscow, Russia*

N. N. Mel'nik

*Physics Institute, Russian Academy of Sciences, 117924 Moscow, Russia*

(Submitted 18 July 1995)

*Pis'ma Zh. Éksp. Teor. Fiz.* **62**, No. 4, 328–333 (25 August 1995)

A number of carbon phases, which are metastable under normal conditions and which include amorphous “phases,” were synthesized from fullerite crystals (C<sub>60</sub>) by heating to different temperatures (from 20 to 700°C) under a pressure of 12.5 GPa. The structure, Raman spectra, density, and mechanical properties of the samples obtained were studied. It was found that amorphization of fullerite occurs in a wide temperature range and includes the following: 1) at the initial stages — partial amorphization with preservation of C<sub>60</sub> molecules and formation of intermediate crystalline phases and 2) at the final stages — complete amorphization in the system of atoms with destruction of C<sub>60</sub> molecules and formation of a disordered network with a large fraction of *sp*<sup>3</sup> bonds. The mechanical properties of the intermediate phases are approximately half as good as those of diamond and the mechanical properties of the amorphous “phases” are close to those of “diamond.” © 1995 American Institute of Physics.

Several dozen studies on the behavior of fullerite under pressure have been published. Phase transitions associated with orientational transformations or with partial polymerization of the molecules have been investigated at relatively low pressures (up to 3 GPa).<sup>1,2</sup> At higher pressures (up to 55 GPa) transitions of fullerite into diamond, graphite, or an amorphous state of carbon have been observed.<sup>3–9</sup> It has been reported that formation of covalent bonds between molecules (one-, two-, and three-dimensional polymerization) is possible at intermediate stages of transformation.<sup>10,11</sup> An amorphous phase consisting of carbon atoms in the *sp*<sup>3</sup> state (“amorphous diamond”) with high hardness and density not less than 90% of the density of diamond has been obtained by impact (55 GPa, 2000 K).<sup>8</sup> In a number of studies it was concluded on the basis of empirical estimates<sup>12,13</sup> and by means of indirect experiments<sup>14</sup> that the elastic moduli and the hardness of the high-pressure phases of fullerite can even be higher than for diamond. Despite the fact that such sensational announcements appeared a long time ago, unequivocal experimental proofs of the existence of an ultrasuperhard modification of fullerite have still not been presented. Most experiments were performed using diamond

anvils, the experimental samples were very small, and there are hardly any studies of the properties of the obtained metastable modifications of fullerite under normal conditions.

Solid-phase amorphization of fullerite at high pressure is not a unique phenomenon. There are numerous examples of crystal–amorphous state transformations with increasing and decreasing pressure (see, for example, the review in Ref. 15). The stable phase of carbon graphite can also transform, under increasing pressure at room temperature, into an amorphous state at a pressure of 30–40 GPa.<sup>16</sup>

Our objective in the present work was to study the solid-phase amorphization processes in fullerite at high pressures and temperatures and to investigate the properties of the obtained metastable phases of carbon.

The samples were synthesized from fullerite powder, prepared in the Russian Science Center “Kurchatov Institute,” with  $C_{60}$  content not less than 99.9% and  $\sim 100\text{-}\mu\text{m}$  crystalline grains. A “Iolita” chamber (modification of the “toroid” chamber with an altered profile) was used to produce the high pressure. This chamber makes it possible to generate pressures of up to 13 GPa in volumes up to  $50\text{ mm}^3$ . Heating was performed by passing a current through a heater into which a Pd container with the fullerite sample was inserted (the sample consisted of  $C_{60}$  powder pressed into a 2-mm high and 2 mm-diameter cylinder). The structure of the samples obtained was investigated by the method of x-ray diffraction ( $\text{Cu K}\alpha$ ). The density of the samples was determined by the pycnometric method. The Raman spectra were obtained on an U1000 spectrometer (Jobin-Ivon) with a resolution of  $2\text{ cm}^{-1}$  in the back-scattering geometry with unpolarized light. Young’s modulus was measured by the ultrasonic method (measurement of the longitudinal velocity of ultrasound at 5 MHz by the method of Papadakis). The mechanical properties were investigated by the method of pressing-in diamond Vickers pyramids under loads of 5.5, 9.8, and 19.6 N. The magnitude of the load was varied, depending on the pattern of crack formation around the indentations. The Vickers hardness  $H_V$ , the critical coefficient of stress intensity (crack resistance)  $K_{Ic}$ , and the yield stress were calculated by the procedure proposed in Ref. 17 and successfully used for investigating superhard materials. The process of combustion of the metastable phases of carbon in air was studied with a Derivatograf–C (MOM) derivative thermogravimetric apparatus (the rate of heating was equal to 20 K/min).

The experimental samples were obtained under a pressure of 12.5 GPa with a holding time of 30 s at different temperatures. The structural data and the Raman spectra of the phases obtained are shown in Fig. 1. Some properties of the experimental samples are presented in Table I. It can be concluded from the data presented that the amorphization of fullerite at  $P = 12.5\text{ GPa}$  occurs in the range 300–500°C. Amorphization precedes and accompanies a number of transformations in the crystalline state. Crystalline peaks in the x-ray diffraction pattern were indexed according to a fcc structure with a smaller parameter ( $a = 12.1\text{--}12.3\text{ \AA}$ , x-ray density  $\rho = 2.6\text{ g/cm}^3$ , samples 3 and 4) —  $\beta$  phase, and a distorted monoclinic variant ( $a = 11.8\text{ \AA}$ ,  $c = 13.6\text{ \AA}$ , x-ray density  $2.6\text{ g/cm}^3$ , sample 5) —  $\gamma$  phase. The parameters of the  $\beta$  and  $\gamma$  modifications correspond to a distance of 1.5–1.6 Å between the closest atoms in neighboring  $C_{60}$  molecules (under the assumption that the molecules are preserved); this is an argument in favor of the hypothesis of three-dimensional polymerization of fullerite molecules under pressure. We note that at atmospheric pressure the distance between the  $C_{60}$  molecules in the fcc phase of fullerite

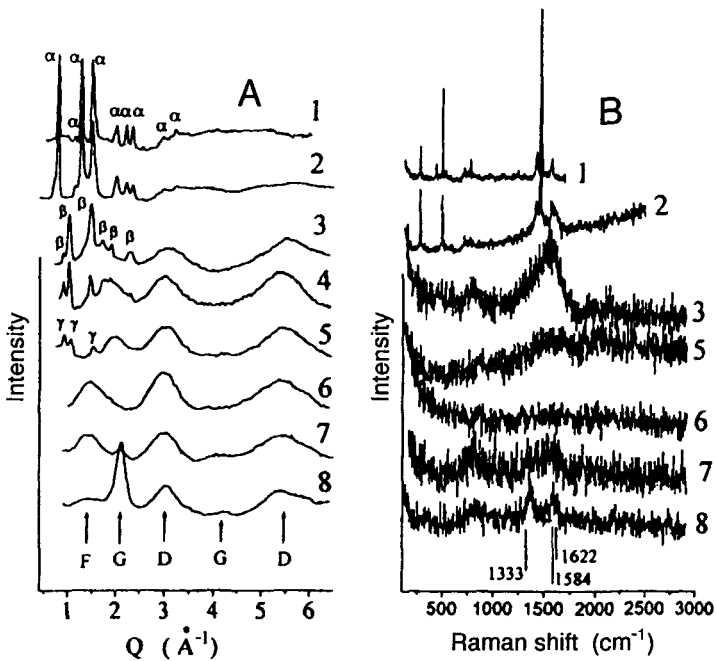


FIG. 1. Structure factors for x-ray scattering (a) and Raman scattering spectra (b) for samples obtained by heat and pressure treatment of  $C_{60}$  at  $P = 12.5$  GPa. The numbers on the curves correspond to the numbers of the samples in Table I (1 — initial fullerite). The crystalline reflections of the  $\alpha$ - ( $C_{60}$ ),  $\beta$ -, and  $\gamma$  phases of fullerite are marked by the corresponding letters. The amorphous halos of the disordered fullerite (F), diamond (D), and graphite (G) are marked by arrows. The positions of the Raman peaks of diamond ( $1333\text{ cm}^{-1}$ ) and polycrystalline graphite ( $1584$  and  $1622\text{ cm}^{-1}$ ) are also indicated in the figure.<sup>19</sup>

is equal to  $3\text{ \AA}$  (the lattice constant  $a = 14.2\text{ \AA}$ ),  $2\text{ \AA}$  ( $a = 12.7\text{ \AA}$ ) at  $12.5\text{ GPa}$ , and  $1.6\text{ \AA}$  ( $a = 12.2\text{ \AA}$ ) at  $25\text{ GPa}$ .<sup>5,18</sup> The  $\beta$  and  $\gamma$  phases do not exist in the “pure” form — a large fraction (not less than 40%) of the carbon atoms is in the amorphous phase (see the diffuse maxima in Fig. 1a for samples 3–5). The Raman spectra from the mixture of  $\beta$  and  $\gamma$  phases with an amorphous modification consist of a wide asymmetric peak in the high-frequency region and several weak peaks in the low-frequency region of the spectrum. In Refs. 4 and 6 similar Raman spectra were apparently incorrectly assigned to the purely amorphous state of carbon. Further heating at high pressures leads to a state which, according to the x-ray data, can be described as “amorphous diamond” (Fig. 1a, sample 6). The absence of appreciable peaks in the Raman spectrum (Fig. 1b) indicates that both  $sp^3$  and  $sp^2$  states of the carbon atoms are present in the amorphous network. As the synthesis temperature increases, a mixture of disordered diamond and compacted graphite (samples 7 and 8) forms.

The data on the pycnometric density (see Table I) agree well with the estimates of the density from the x-ray data. The density of the amorphous phase  $3.15\text{ g/cm}^3$  is less than the value  $3.4\text{ g/cm}^3$  obtained for “amorphous diamond” at  $55\text{ GPa}$ .<sup>8</sup> This difference is probably due to the large fraction of remaining  $sp^2$  states of carbon atoms (correspond-

TABLE I. Density  $\rho$ , Young's modulus  $E$ , hardness  $H_V$ , and yield stress  $\sigma_y$  for carbon samples obtained from  $C_{60}$  under pressure at various synthesis temperatures  $T_{syn}$ .

Sample	$T_{syn} (^{\circ}C)$	$\rho(g/cm^3)$	$E(GPa)$	$H_V(GPa)$	$\sigma_y(GPa)$
1	Initial	1,67 <sup>2)</sup>	-	-	-
2	20	1,7	-	-	-
3	300	2,5	350	23, 3 $\pm$ 1, 5	11,6
4	400	2,8	400	27, 6 $\pm$ 1, 5	11,6
5	450	3,0	-	50 $\pm$ 9	12,6
6	500	3,15	700	73, 4 $\pm$ 1	40,7
7	600	3,0	-	-	-
8	700	3,2	-	-	-
Error	$\pm 30$	$\pm 0, 15$	$\pm 100$	-	$\pm 0, 5$

ing to triple coordination) in the amorphous phase obtained at lower pressures.

The amorphous state is quite stable at atmospheric pressure. Combustion of the samples by heating in air occurs in the temperature range 600–900°C. No changes are observed in the structure or the phase composition.

The hardness characteristics of the obtained phases are of great interest (see Table I). The samples consisting of a mixture of  $\beta$  and  $\gamma$  phases with an amorphous modification have high Young's moduli  $E \sim 300$ –400 GPa and hardness  $H_V \sim 25$ –50 GPa. These values are higher than the corresponding values for corundum, whose characteristics are comparable to those of cubic boron nitride, and approximately half the corresponding values for diamond ( $E \sim 1100$  GPa,  $H_V \sim 70$ –130 GPa).<sup>19</sup> The samples 3–5 are characterized by high plasticity. This could be attributed to the polymer structure of the phases. The amorphous state obtained from fullerite is characterized by even higher Young's modulus  $E \sim 700$  GPa and hardness  $H_V \sim 75$  GPa, only slightly less than the values for diamond.

The coefficient of crack resistance  $K_{1c}$  for the obtained superhard phases falls in the range 8–16 MN/m<sup>3/2</sup> [for comparison,  $K_{1c}$  for diamond falls in the range 5–12 MN/m<sup>3/2</sup> and for cubic boron nitride  $K_{1c}$  falls in the range 8–15 MN/m<sup>3/2</sup> (Ref. 19)].

The assumption that it is possible to produce phases, based on  $C_{60}$  molecules, which are harder than diamond, thus has not been confirmed. As far as the amorphous phases of carbon with a high fraction of  $sp^3$  states are concerned, they can indeed have mechanical properties, including hardness, which are comparable to those of diamond (besides the present work, see Refs. 20 and 21). A detailed discussion of the mechanical properties and other moduli of different modifications of carbon will be given in future papers.

It is interesting that the amorphization of fullerite under pressure is attributable simultaneously to disordering of the positions of the  $C_{60}$  molecules (see the small-angle halos  $Q \sim 1.5$ –2 Å<sup>-1</sup> in Fig. 1a, curves 3–5) and to the formation of a disordered network of atoms (diffuse peaks with  $Q \sim 3$  Å<sup>-1</sup> and  $Q \sim 5.3$  Å<sup>-1</sup>, samples 3–6). In contrast to the solid-phase amorphization of other molecular compounds of the  $SiO_2$  type, the disordering processes on different scales in the case of fullerite can be easily separated because of the large size of  $C_{60}$  molecules. The appearance of defects in the fcc

structure of fullerite in the form of groups of  $C_{60}$  molecules bound by  $sp^3$  states at 12.5 GPa already occurs at room temperature (sample 2, see also Ref. 18). Such an “adhesion” of the molecules is easily explained on the basis of the large rms displacements of the atoms during thermal vibrations ( $\sim 0.3 \text{ \AA}$  at  $T \sim 300 \text{ K}$  and  $0.5 \text{ \AA}$  at  $T \sim 600 \text{ K}$ ), since for an average distance between the molecules  $L \sim 2.0 \text{ \AA}$  a significant fraction of the molecules during vibrations may “turn out to be” sufficiently close to one another ( $1.5\text{--}1.6 \text{ \AA}$ ) for  $sp^3$  states, which bind the  $C_{60}$  molecules, to appear. At the locations where the  $C_{60}$  molecules are in “contact” the atomic structure of fullerenes is distorted and nano-sections of an amorphous network are formed. Further heating leads to complete destruction of the molecules and to the formation of an amorphous network of carbon from  $sp^3$  and  $sp^2$  configurations. The large fraction of  $sp^2$  configurations in the amorphous phase is indicated by data on the density and the Raman spectra. Moreover, as the temperature of synthesis under pressure increases further, disordered graphite precipitates (sample 7–8,  $Q \sim 4.1 \text{ \AA}^{-1}$ ). The reason that a high fraction of  $sp^2$  configurations remains at  $P = 12.5 \text{ GPa}$  is that the energy required for distorting a structure consisting of  $sp^2$  bonds is lower than for “diamond-like” structure consisting of  $sp^3$  bonds.<sup>20</sup>

The position of the amorphization region in the  $P\text{--}T$  plane ( $300\text{--}500^\circ\text{C}$ , 12.5 GPa) agrees well with the line of transformations into the insulator state, as determined in Ref. 7. This line is probably the line of the onset of amorphization. The amorphization pressure of fullerite is approximately 10–15 GPa lower than the pressure of disordering in graphite.<sup>16</sup> The virtual magnitudes of the pressures of equilibrium of fullerite with diamond ( $-7$  to  $-8 \text{ GPa}$ ) and with amorphous diamond ( $2\text{--}3 \text{ GPa}$ ) can be estimated from the thermodynamic data presented in Refs. 20 and 22. These pressures are also 10–15 GPa lower than the pressures of equilibrium of graphite with diamond ( $\sim 2 \text{ GPa}$ ) and graphite with amorphous diamond ( $\sim 16 \text{ GPa}$ ). The pressure of the fullerite–amorphous diamond transformation decreases, because the chemical potential of the fcc phase of  $C_{60}$  is much greater than the chemical potential for graphite.

In summary, we conclude that the amorphization of fullerite at high pressures occurs simultaneously in the subsystem of molecules and in the network of atoms. The fact that the amorphization pressure in fullerite is lower than in graphite because of the high metastability of  $C_{60}$  crystals makes it possible to use large, high-pressure chambers to obtain bulk samples of amorphous carbon with a high fraction of  $sp^3$  configurations up to “amorphous diamond.” These amorphous phases, just as the intermediate modifications based on  $C_{60}$  molecules, have strong mechanical properties. The optical and electrical properties of the phases which we obtained are the subject of our next investigations.

We are grateful to S. M. Stishov for discussions and helpful remarks and to P. A. Sadykov, E. V. Kvitck, O. V. Stal'gorova, E. V. Chernysheva, N. V. Kalyaeva, P. I. Artemov, N. I. Epishina, and T. I. Bulygina for assistance with the experiments.

This work was supported by the Russian Fund for Fundamental Research (project 95-02-03677), the Ministry of Science and Technology Policy of the Russian Federation, and the Soros International Science Foundation (project MTK300).

<sup>1</sup>e-mail: paskal@adonis.jasnet.com

<sup>2</sup>See Ref. 22.

- 
- <sup>1</sup>I. B. Bashkin, V. I. Rashchupkin, A. F. Gurov *et al.*, *J. Phys. Condens. Matter* **6**, 7491 (1994).  
<sup>2</sup>A. P. Jephcoat, J. A. Hriljac, L. W. Finger, and D. E. Cox, *Europhys. Lett.* **25**(6), 429 (1994).  
<sup>3</sup>M. N. Regueiro, P. Monceau, and J. L. Hodeau, *Nature* **355**, 237 (1992).  
<sup>4</sup>M. N. Regueiro, L. Abello, G. Luitz, and J. L. Hodeau, *Phys. Rev. B* **46**, 9903 (1992).  
<sup>5</sup>S. J. Duclos, K. Brister, R. C. Haddon *et al.*, *Nature* **351**, 380 (1991).  
<sup>6</sup>D. W. Snoko, Y. S. Raptis, and K. Syassen, *Phys. Rev. B* **45**, 14419 (1992).  
<sup>7</sup>M. N. Regueiro, P. Monceau, A. Rassat *et al.*, *Nature* **354**, 289 (1991).  
<sup>8</sup>H. Hirai and K. Kondo, *Appl. Phys. Lett.* **64**, 1797 (1994).  
<sup>9</sup>C. S. Yoo and W. J. Nellis, *Science* **254**, 1489 (1991).  
<sup>10</sup>C. S. Yoo and W. J. Nellis, *Chem. Phys. Lett.* **198**, 379 (1992).  
<sup>11</sup>H. Yamawaki, M. Yoshida, Y. Kakudate *et al.*, *J. Phys. Chem.* **97**, 11161 (1993).  
<sup>12</sup>R. S. Ruoff and A. L. Ruoff, *Appl. Phys. Lett.* **59**, 1553 (1991).  
<sup>13</sup>R. S. Ruoff and A. L. Ruoff, *Nature* **350**, 663 (1991).  
<sup>14</sup>V. D. Blank, S. G. Buga, M. Yu. Popov *et al.*, *Zh. Tekh. Fiz.* **64**, 153 (1994) [*Tech. Phys.* **39**, 828 (1994)].  
<sup>15</sup>E. G. Pobnyatovsky and O. I. Barcalov, *Mat. Sci. Rep.* **8**, 147 (1992).  
<sup>16</sup>A. F. Goncharov, *JETP Lett.* **51**, 418 (1990).  
<sup>17</sup>A. R. Evans and T. R. Wilshaw, *Acta Metall.* **24**, 939 (1976).  
<sup>18</sup>J. Haines and J. M. Leger, *Solid State Commun.* **90**(6), 361 (1994).  
<sup>19</sup>A. V. Kurdyumov, V. G. Malogovets, N. V. Novikov *et al.*, *Polymorphic Modifications of Carbon and Boron Nitride* [in Russian], *Metallurgiya*, Moscow, 1994.  
<sup>20</sup>P. C. Kelires, *Phys. Rev. B* **47**, 1829 (1993).  
<sup>21</sup>P. J. Martin S. W. Filipczuk, R. P. Netterfield *et al.*, *J. Mater. Sci. Lett.* **7**, 410 (1988).  
<sup>22</sup>E. N. Yakovlev and O. A. Voronov, *High Temp.-High Press.* (1995) (to be published).

Translated by M. E. Alferieff