

New Metallic Crystalline Carbon: Three Dimensionally Polymerized C₆₀ Fullerite

Susumu Okada,¹ Susumu Saito,² and Atsushi Oshiyama³

¹*Institute of Material Science, University of Tsukuba, Tennodai, Tsukuba 305-8573, Japan*

²*Department of Physics, Tokyo Institute of Technology, 2-12-1 Oh-okayama, Meguro-ku, Tokyo 152-8551, Japan*

³*Institute of Physics, University of Tsukuba, Tennodai, Tsukuba 305-8571, Japan*

(Received 8 February 1999)

We explore new polymerized C₆₀ fullerite phases by using the total-energy calculations in the density-functional theory. Starting from the two dimensionally polymerized tetragonal phase, we find a new stable three dimensionally polymerized structure to be synthesized under uniaxial pressure of about 20 GPa. In sharp contrast to other polymerized C₆₀ phases and to solid C₆₀, the new polymer possesses metallic electronic structure with a relatively large Fermi-level density of states. Its conduction-electron distribution and the energetics are studied in detail.

PACS numbers: 61.48.+c, 71.20.-b

Behavior of C₆₀ fullerites under pressure is of great interest due to the possibility of not only their structural transformations into diamond but also syntheses of new crystalline carbon networks [1–7]. In the last five years, several polymerized fullerites have been synthesized from the face-centered-cubic (fcc) C₆₀ by applying moderate pressure at elevated temperature [8–10]. Three different phases possessing one- or two-dimensional C-C networks have been identified so far, i.e., the one-dimensional orthorhombic [9], the two-dimensional tetragonal [9], and the two-dimensional rhombohedral phases [8–10]. The polymerization is attained via formation of four-membered rings (so-called [2 + 2] cycloaddition mechanism) among fullerenes [11–13] with the rehybridization from sp^2 to sp^3 . Hence, the polymerized fullerites consist of hybrid networks of sp^2 (threefold coordinated) and sp^3 (fourfold coordinated) atoms and are classified as a new family of crystalline carbon, which is different from the phases consisting of sp^2 , i.e., fcc C₆₀ [14], nanotube [15], and graphite, and also different from the sp^3 phase, i.e., diamond. In addition to the characteristics of network topology, the electronic structure of the two dimensionally polymerized phases is quite different from that of other crystalline carbon phases [16]. Therefore, synthesis of other crystalline phases consisting of sp^2 and sp^3 atoms with novel physical properties is a fascinating challenge in condensed matter science. In particular, the synthesis of three dimensionally polymerized phases is a promising target.

In this Letter, we explore the possibility of three dimensionally polymerized fullerites as novel crystalline phases of carbon using the density-functional theory. We predict that a *three dimensionally polymerized metallic fullerite* is realized by applying uniaxial pressure on a two dimensionally polymerized fullerite. We start with the tetragonal phase of the two dimensionally polymerized fullerite, since the phase is lower in energy than the rhombohedral phase. The tetragonal phase is known to have the square-lattice polymerized layers which are stacked along the c axis. At-

taining the polymerization between the adjacent layers, we reduce the lattice constant c , which mimics application of uniaxial pressure along the axis. Under the lattice constant of $c = 10.70$ Å, we find a novel stable three dimensionally polymerized structure with 24 sp^3 and 36 sp^2 hybridized C atoms per C₆₀. Surprisingly, the electronic structure of the system is metallic in sharp contrast to not only that of polymerized fullerites [16] but also that of the fcc C₆₀ [17] which are all known to be semiconducting.

As for the study of the electronic and geometric structures, we use local-density approximation (LDA) in the density-functional theory [18]. To express the exchange-correlation potential of electrons, we use the functional form fitted to the Ceperley-Alder result [19]. Norm-conserving pseudopotentials generated by using the Troullier-Martins scheme are adopted to describe the electron-ion interaction [20]. In constructing the pseudopotentials, core radii adopted for C $2s$ and $2p$ states are both 1.5 bohrs. The valence wave functions are expanded by the plane-wave basis set with a sufficient cutoff energy of 50 Ry. We adopt the conjugate-gradient minimization scheme both for the self-consistent electronic-structure calculation and for the geometric optimization [21].

To explore the possibility of the three dimensionally polymerized fullerite phase, we perform the geometry optimization under a number of reduced lattice constants c . In this calculation, we keep an *Immm* space group symmetry with lattice parameter values of $a = b = 9.09$ Å in the ab plane as in the case of the initial tetragonal phase. In Fig. 1, we show the total energy for the optimized structure as a function of c . Total energy increases monotonically at first with decreasing c . A new phase emerges, however, with the lattice constant less than about 11 Å: The total energy of the new phase has the minimum at $c = 10.70$ Å. This phase is stable under ambient pressure and is of three dimensionally polymerized character as clarified in detail below. It is clear from Fig. 1 that the two-dimensional tetragonal phase undergoes structural transformation to the novel three-dimensional polymer phase under uniaxial

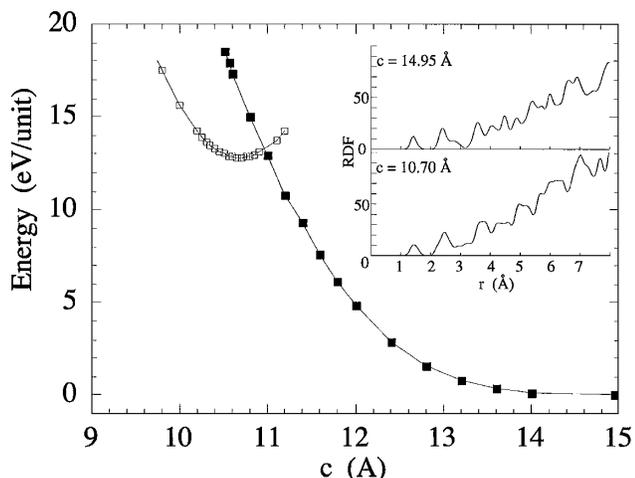


FIG. 1. Total energy per unit cell of the tetragonal C_{60} polymer as a function of the lattice constant c . Energy is measured from the two dimensionally polymerized phase under the experimental lattice constant ($c = 14.95 \text{ \AA}$). Inset: Radial distribution function for the two-dimensional tetragonal ($c = 14.95 \text{ \AA}$) and three dimensionally polymerized phase ($c = 10.70 \text{ \AA}$).

pressure. Using the relation $P = -\frac{\partial E}{\partial V}$ and the common tangent of the two total energy curvature in Fig. 1, the critical pressure is found to be $P_c = 20.2 \text{ GPa}$.

As mentioned above, the lattice constants in the ab plane are fixed in this calculation. Hence, their relaxation at ambient pressure after the three-dimensional polymerization is certainly expected. The optimal values of a and b estimated from the elastic constants are both 9.4 \AA which are about 0.3 \AA longer than the initial values. Although the decomposition of polymerization in the ab plane would take place under much enlarged a and b values, we have confirmed by using the model potential [22] that 9.4 \AA is well shorter than the critical decomposition length. In addition, the stability of the three-dimensional polymer phase can be also seen in the absolute values of force components of each atom at $c = 10.70 \text{ \AA}$. The maximum value is as small as 0.06 eV/\AA . Especially, the force acting on C1 and C3 atoms is less than 0.04 eV/\AA .

The three-dimensional picture for the obtained new phase is given in Fig. 2 [23]. The number of sp^3 atoms is 24 per C_{60} , increasing by 16 compared with the two-dimensional phase. In contrast to the other pressure-induced polymerized phases, the new intercluster bonds connecting adjacent layers are formed not via a $[2 + 2]$ cycloaddition mechanism but via a new bonding mechanism in which each protruding atom (C4 or C7 in Fig. 2) of the bent hexagons in a fullerene forms a bond with its partner atom (C7 or C4) of the fullerene in the adjacent layers. The length of the additional intercluster bonds (C4–C7) is 1.60 \AA , which is closer to the typical sp^3 bond length. The remaining bonds of C4 and C7 atoms have lengths of $1.42, 1.50, 1.56, 1.51, 1.44,$ and 1.53 \AA for C4–C6, C4–C2, C4–C1, C7–C7, C7–C8, and C7–C5, respectively. The stretched bonds give rise to a broadening

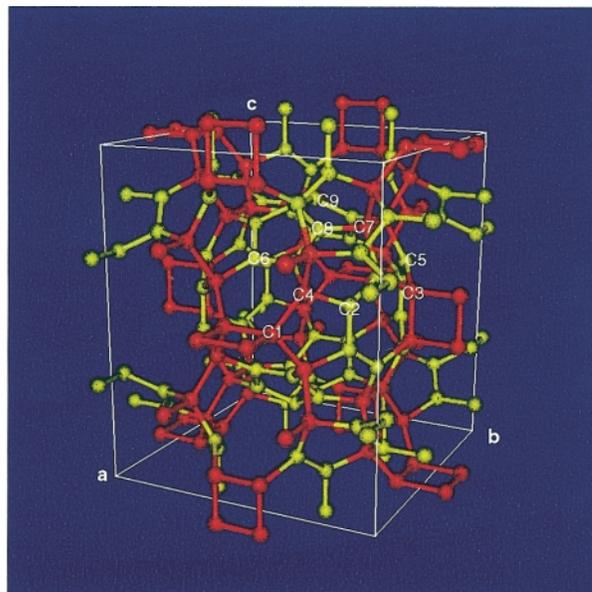


FIG. 2 (color). Optimized geometry of the three dimensionally polymerized C_{60} fullerite. The sp^3 (fourfold-coordinated) atoms are denoted by the red spheres. Atom index is the same as in our previous paper [16].

of peaks in a spectrum for the radial distribution function (RDF) (Fig. 1 inset). In spite of the hybrid network of both sp^2 and sp^3 atoms, the RDF spectrum of the new three-dimensional phase is quite different from that of the diamond but rather similar to that of graphite [6]. Furthermore, bond angles related to the atoms connecting the C_{60} units are $\theta_{C1C4C7'} = 126.22^\circ$, $\theta_{C6C4C7'} = 98.22^\circ$, $\theta_{C2C4C7'} = 108.98^\circ$, $\theta_{C1C4C2} = 109.46^\circ$, $\theta_{C1C4C6} = 111.43^\circ$, $\theta_{C2C4C6} = 98.69^\circ$, $\theta_{C7C7C4'} = 116.53^\circ$, $\theta_{C8C7C4'} = 102.54^\circ$, $\theta_{C5C7C4'} = 119.71^\circ$, $\theta_{C5C7C8} = 103.63^\circ$, $\theta_{C5C7C7} = 103.91^\circ$, and $\theta_{C7C7C8} = 109.59^\circ$, where prime denotes atoms in the adjacent C_{60} unit. The present results reflect that the atoms which are responsible for polymerization possess the character of sp^3 (109.5°) hybridization rather than sp^2 (120.0°).

Since the three dimensionally polymerized phase has covalent bonds between the layers, the system is expected to possess remarkable stiffness. We calculate a bulk modulus of the system. The obtained value is 47 GPa which is smaller than that of diamond so that the phase is not a candidate for the superhard material [5]. The strength of the intercluster bonds in the two dimensionally polymerized phases estimated by the LDA as the energy gain upon the bond formation is about 1.6 eV per bond which is smaller than that of the ideal sp^3 value estimated for diamond by about 2 eV per bond [16]. Hence, the strength of sp^3 bonds in the new phase is also considered to be weaker than that of the ideal sp^3 bond. In addition, the strength of the sp^2 bonds in the phase is also expected to be weaker than that of ideal sp^2 , owing to the distortion of the C_{60} unit. These may be the reasons for the small bulk modulus in spite of the hybrid network of sp^2 and sp^3 carbon atoms.

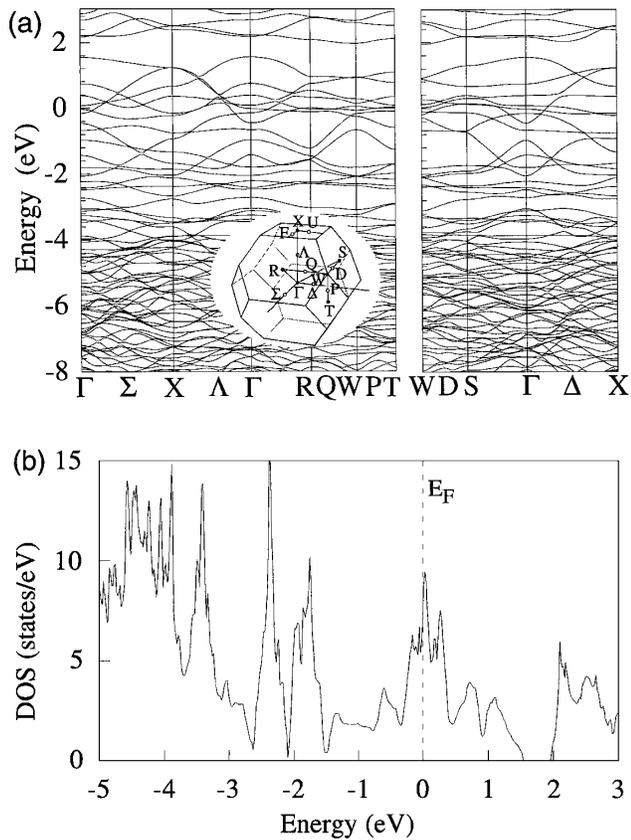


FIG. 3. (a) Band structure of the three dimensionally polymerized C_{60} fullerite. Energy is measured from the Fermi energy E_F . (b) Density of states of the phase.

The electronic band structure of the three-dimensional polymer under optimized geometry ($a = b = 9.09$ and $c = 10.70$ Å) is shown in Fig. 3(a). It is evident that the new phase has metallic electronic structure completely different not only from the pressure-induced two dimen-

sionally polymerized fullerites which have been presently identified but also from the fcc C_{60} fullerite. The structural phase transition at the pressure of about 20 GPa, which we predict, is therefore electronically an insulator-metal transition. Each electron state of the new phase does not always correspond to the energy level in an isolated C_{60} cluster. Several characteristics [16] of the band structure observed in the two-dimensional polymer phases are absent. The origin of the metallic electronic structure of the system is partly due to an enhanced dangling-bond character, i.e., distorted π -electron distribution, of the three-fold coordinated atoms owing to distortion of the C_{60} unit. For instance, the bond angles of the hexagon at the C9 is $\theta_{C9C9C8} = 113.80^\circ$ so that the sp^3 character of the atoms is stronger than that in the $I_h C_{60}$ (120°). However, energy bands near the Fermi level are dispersive. Accordingly, these states are not usual dangling-bond states but states consisting of overlapping π -like states on the three-fold coordinated atoms which are considerably distorted from the ideal sp^2 geometry. This circumstance is clearer in later analysis for the local density of states at the Fermi level.

We show the density of states (DOS) near the Fermi level in Fig. 3(b). For integration over the Brillouin zone (BZ), we use 512 k points in the first BZ. Owing to the relatively flat bands along the Q and P lines, the system has large DOS at Fermi level [$N(E_F)$]. The estimated value of $N(E_F)$ is 7.7 states/ C_{60} for each spin. Hence the system is a candidate for a superconducting material consisting entirely of carbon atoms, as is similar to solid C_{36} [24]. Synthesis of new elemental superconductors is one of great important challenges in condensed matter physics. Our result provides a new target for those materials.

In Fig. 4, the local density of states near the Fermi level $\rho_{E_F}(\mathbf{r})$ in the three-dimensional polymer is shown. It is defined by $\rho_{E_F}(\mathbf{r}) = -\frac{1}{\pi} \text{Im} \sum_{n,\mathbf{k}} \int_{E_F-\Delta}^{E_F+\Delta} dE \frac{|\phi_{n\mathbf{k}}(\mathbf{r})|^2}{E - \epsilon_{n\mathbf{k}} + i\delta}$,

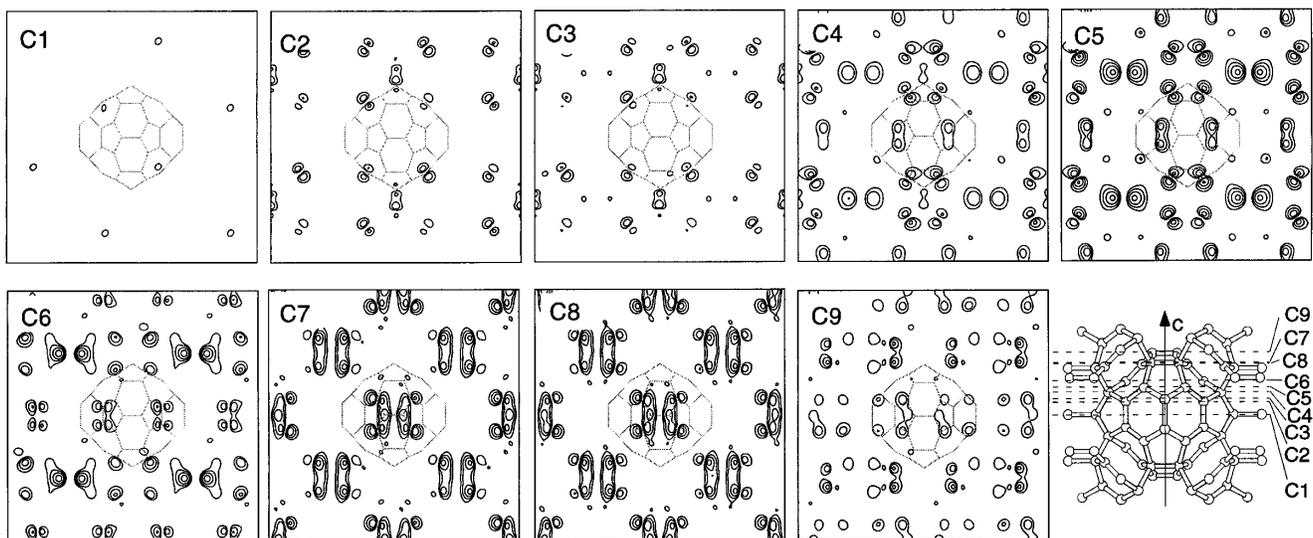


FIG. 4. Local density of states near the Fermi level of the three dimensionally polymerized C_{60} on nine inequivalent C-atom planes. Location of planes is also illustrated. Each contour represents twice (or half) the density of the neighboring contour.

where $\Delta = 0.1$ eV and 27 k points in the first BZ are taken for the k summation. Almost all states are localized on the atoms possessing threefold coordination and π -like electronic states. Hence, as far as the π -like states are concerned, we should take notice of the network topology of threefold-coordinated atom sites. Then, the constituent units of the conducting system are considered to be two pentagon dimers (C_5-C_5) and four C_4 chains [25]. Via π - π overlap, the former units form the undulated two-dimensional π network being parallel to the ab plane, and the latter form a one-dimensional zigzag network along the c direction. Consequently the carrier of the system has the three-dimensional character which is quite different from that of graphite. In particular, a rather large amplitude of ρ_{E_F} is observed on the C6, C8, and C9 atoms which are forming a pentagon dimer. In contrast to these sp^2 atoms, there is no carrier on the fourfold-coordinated atoms except C3. In particular, we cannot observe any carrier around the C1 atom (xy plane). Hence these atoms possess the σ -like electronic states. On the other hand, the small but sizable amplitude on the C3 atoms indicates that the states around C3 atoms still have bonding π character. Since the atom has an angle of 90° which is quite different from the ideal sp^3 , the electronic structure is not simply classified as sp^3 but an interesting combination of sp^2 and sp^3 .

Numerical calculations were performed on the VPP500 at ISSP, and SX3/34R at IMS. This work is supported in part by JSPS under Contract No. RFTF96P00203, The Nissan Science Foundation, and The Grant-in-Aid for Scientific Research on the Priority Area "Fullerenes and Nanotubes" by the Ministry of Education, Science, and Culture of Japan.

[1] S. J. Duclos *et al.*, Nature (London) **351**, 380 (1991).

[2] M. Núñez-Regueiro *et al.*, Nature (London) **354**, 289 (1991).

- [3] M. Núñez-Regueiro, P. Monceau, and J.-L. Hodeau, Nature (London) **355**, 237 (1992).
- [4] D. W. Snoke, Y. S. Raptis, and K. Syassen, Phys. Rev. B **45**, 14419 (1992).
- [5] F. Moshary, N. H. Chen, and I. F. Silvera, Phys. Rev. Lett. **69**, 466 (1992).
- [6] J. L. Hodeau *et al.*, Phys. Rev. B **50**, 10311 (1994).
- [7] M. E. Kozlov *et al.*, Appl. Phys. Lett. **66**, 1199 (1994).
- [8] Y. Iwasa *et al.*, Science **264**, 1570 (1995).
- [9] M. Núñez-Regueiro *et al.*, Phys. Rev. Lett. **74**, 278 (1995).
- [10] G. Oszlanyi and L. Forro, Solid State Commun. **93**, 265 (1995).
- [11] C. Goze *et al.*, Phys. Rev. B. **54**, R3676 (1996).
- [12] Y. Maniwa *et al.*, Carbon **34**, 1287 (1996).
- [13] A. M. Rao *et al.*, Phys. Rev. B **55**, 4766 (1997).
- [14] W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Hoffman, Nature (London) **347**, 354 (1990).
- [15] S. Iijima, Nature (London) **354**, 56 (1991).
- [16] S. Okada and S. Saito, Phys. Rev. B **59**, 1930 (1999).
- [17] S. Saito and A. Oshiyama, Phys. Rev. Lett. **66**, 2637 (1991).
- [18] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- [19] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- [20] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991); L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
- [21] O. Sugino and A. Oshiyama, Phys. Rev. Lett. **68**, 1858 (1992).
- [22] J. Tersoff, Phys. Rev. Lett. **61**, 2879 (1988).
- [23] Atomic coordinate is available via the following Email address: sokada@swift.mf.ims.tsukuba.ac.jp.
- [24] M. Côté, J. C. Grossman, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **81**, 697 (1998); C. Piskoti, J. Yarger, and A. Zettl, Nature (London) **393**, 771 (1998).
- [25] S. Saito, S. Okada, S. Sawada, and N. Hamada, Phys. Rev. Lett. **75**, 685 (1995).