Three-dimensional crystalline carbon: Stable polymers of C20 fullerene

著者	Okada Susumu, Miyamoto Yoshiyuki, Saito Mineo
journal or publication title	Physical review B
volume	64
number	24
page range	245405
year	2001-11
権利	(C)2001 The American Physical Society
URL	http://hdl.handle.net/2241/89415

doi: 10.1103/PhysRevB.64.245405

Three-dimensional crystalline carbon: Stable polymers of C_{20} fullerene

Susumu Okada,[1] Yoshiyuki Miyamoto,[2] and Mineo Saito[2,3]
[1]*Institute of Physics, University of Tsukuba, Tennodai, Tsukuba 305-8571, Japan*
and Center for Computational Physics, University of Tsukuba, Tennodai, Tsukuba 305-8577, Japan
[2]*Fundamental Research Laboratory, NEC Corporation, 34 Miyukigaoka, Tsukuba 305-8501, Japan*
[3]*NEC Informatec Systems, Ltd., 34 Miyukigaoka, Tsukuba 305-8501, Japan*
(Received 28 June 2001; published 28 November 2001)

We report on a first-principles total-energy calculation that provides the energetics and electronic structure of stable polymerized fullerites consisting of the smallest fullerene C_{20}. We find that the C_{20} fullerene has periodic three-dimensional covalent networks with orthorhombic and tetragonal symmetries. Both are found to be energetically stable and to be elemental semiconductors with a moderate energy gap of about 1.5 eV. Substantially high peaks of the density of states are found to appear below the top of the valence band, suggesting that these materials under hole-doped conditions are candidates for superconductors.

DOI: 10.1103/PhysRevB.64.245405 PACS number(s): 61.48.+c, 71.20.Tx, 74.70.Wz

Macroscopic production of the hollow-cage carbon cluster C_{60}, together with its crystalline form,[1] has triggered a great expansion of both theoretical and experimental research on the materials.[2] Although carbon atoms in solid C_{60} have sp^2 bonds with three adjacent atoms as in the case of graphite, the global bonding network is entirely different from that of the graphite: The fullerene has a closed network with zero dimension, whereas the graphite has a two-dimensional hexagonal network. This peculiar network topology decisively affects electronic properties of the fullerenes, such as superconductivity under a certain condition.[3] In a solid, C_{60} clusters behave as weakly interacting spheres and play an atom-like role to form a face-centered cubic lattice (fcc). In addition to the fcc C_{60}, C_{60} polymers in which the C_{60}'s are strongly bound via inter-C_{60} covalent bond have been also synthesized.[4–7] After the discovery of C_{60}, larger fullerenes such as C_{70} and C_{84} were synthesized,[8–10] and are known to be a structural constituent unit for their solid phases.[11,12] Therefore, fullerenes may be regarded as natural superatoms which could be self-organized, and which become a unique class of solids with a structural hierarchy.

Recently, the dodecahedral-cage cluster of 20 C atoms was chemically synthesized.[13,14] This cluster, C_{20}, is the smallest possible fullerenes cage, with 12 pentagons and no hexagon.[15] In analogy with C_{60} and large fullerenes, similar condensed phases of C_{20} are also expected to be synthesized. In sharp contrast to solid C_{60}, however, C_{20} is highly reactive owing to the pentagonal network, so C_{20} may be spontaneously polymerized and have a clathrate network as in the case of the silicon clathrate Si_{46} consisting of Si_{20} fullerenes.[16] Thus the condensed phases of C_{20} are expected to have a hybrid network of threefold- and fourfold-coordinated carbon atoms, which causes a form of solid carbon. Since the electron-phonon coupling of C_{20} is much stronger than that of C_{60},[17,18] the condensed phases synthesized from the C_{20} are candidates for superconductors.[17,19] Indeed, one and three dimensionally polymerized phases were theoretically examined, and one-dimensional phases were found to have a high density of states (DOS), suggesting the possibility of superconductivity. However, they have a higher total energy than the three-dimensional phase, and therefore are metastable.[19]

To realistically design crystalline carbon consisting of C_{20}, this work focuses on three-dimensionally polymerized phases, and determines the most stable structure among the C_{20} solids. In addition to a simple cubic (SC) structure studied previously,[19] we examine two initial geometries which have orthorhombic (body-centered-orthorhombic) and tetragonal structures transferred from the hexagonally closed-packed geometry (fcc) as adequate candidates for the ground-state structure of C_{20} solids. It is found that these two phases are much more energetically stable than the SC phase, and that the orthorhombic phase is the most stable. We confirm that there is no energy barrier for the polymerization process of these two phases: Thus it is likely that the materials are really synthesized. The optimized geometries have a three-dimensionally bonding network of both threefold- and fourfold-coordinated C atoms, whose network topology is similar to that of the Si clathrate, e.g., the Si_{46} network. The electronic structure of the phases is found to be semiconducting with moderate energy gap of about 1.5 eV. We also find that substantial peaks of the DOS appear around the energy gap, so the doped C_{20} solid is a candidate for the material exhibiting superconductivity.

All calculations have been performed using the local-density approximation (LDA) within the density-functional theory.[20,21] To express the exchange-correlation potential of electrons, we use a functional form fitted to the Ceperley-Alder result.[22,23] Norm-conserving pseudopotentials generated by using the Troullier-Martins scheme are adopted to describe the electron-ion interaction.[24,25] In constructing the pseudopotentials, core radii adopted for C $2s$ and $2p$ states are both 1.5 bohr. The valence wave functions are expanded by the plane-wave basis set with the cutoff energy of 40 Ry, which is known to give enough convergence of total energy to discuss the relative stability of various carbon phases.[24] We adopt the conjugate-gradient minimization scheme, both for the self-consistent electronic-structure calculation and for the geometric optimization.[26] A structural optimization is carried out not only on the internal atomic coordinates of C_{20} but also on each lattice parameter. Integration over the Brillouin zone is carried out using a 27-k-point sampling.

TABLE I. Cohesive energies of condensed phases of C_{20} fullerenes, obtained by the LDA total-energy calculation. Each value, in unit of eV per C_{20}, was obtained by subtracting a total energy of a condensed phases from that of an isolated cage.

Structure	Cohesive energy
Orthorhombic	14.90
Tetragonal	14.21
SC	8.56

Starting from the structure in which C_{20}'s are separated from each other, we find that the C_{20}'s form covalent intercluster bonds without any reaction barrier, and that the polymerized structure is energetically favorable. This energetic stability of condensed phases is totally due to the electron structure of C_{20} molecules: Because of the pentagonal network of the cage, the bonds have a small angle (108°) which is close to that of the ideal sp^3(109.5°) but is smaller than that of sp^2(120°). As a result, threefold-coordinated atoms have a dangling bond instead of a π bond. Since these dangling bonds induce instability, they are terminated as a consequence of the formation of interfullerene bonds in the polymerized phases. Optimized lattice parameters are $a = 5.95$ Å, $b = 5.96$ Å, and $c = 7.50$ Å for the orthorhombic phase, and $a = 5.96$ Å and $c = 7.60$ Å for the tetragonal phase. The calculated binding energies of these two phases are listed in Table I together with the SC phase.[19] Since the number of intercluster bonds is larger than that of the SC phase, both the tetragonal and orthorhombic phases are more energetically favorable than the SC phase. Among the two isomers studied here, the orthorhombic phase has a lower total energy than the tetragonal one.

Fully optimized structures of the orthorhombic and tetragonal phases of three-dimensionally polymerized C_{20} are shown in Figs. 1(a) and 1(b), respectively. In each structure, C_{20} is connected with four adjacent C_{20}'s via four-membered rings in a plane perpendicular to the *c* axis, whereas they are connected via eight single bonds with eight neighboring atoms along the direction parallel to the *c* axis. Thus the resulting materials have a three-dimensionally polymerized structure with a hybrid network of threefold- and fourfold-

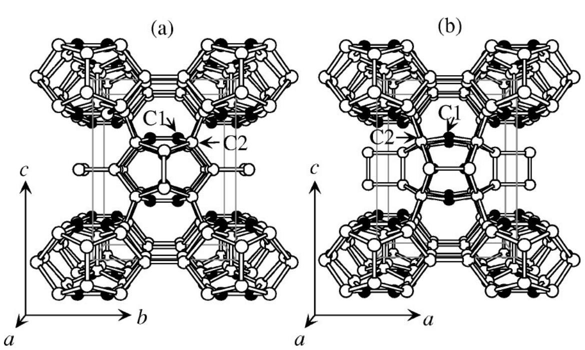

FIG. 1. Optimized geometries of (a) the orthorhombic and (b) tetragonal phases of condensed C_{20} fullerene. Solid and empty circles denote threefold-coordinated atoms and the fourfold-coordinated atoms, respectively.

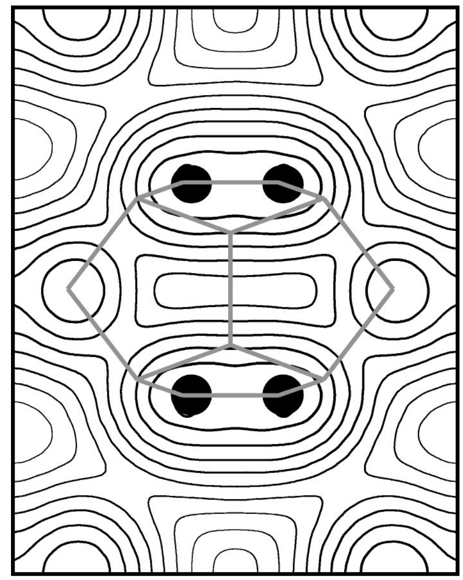

FIG. 2. The contour plot of the total valence-electron density of the (a) the orthorhombic and (b) tetragonal phases of C_{20} polymers. The solid circles denote the threefold-coordinated C atoms. The lowest-density contour represents $0.02e/\text{a.u.}^3$. Difference between each contour is $3.333\times10^{-3}e/\text{a.u.}^3$.

coordinated C atoms, as in the case of polymerized phases of C_{60}.[27] In both cases, the number of the threefold-coordinated C atoms is only four per C_{20}. The atoms form two C dimers located at the top and bottom of the C_{20}. On the other hand, the number of fourfold-coordinated C atoms is 16. The length of the intercluster bonds belonging to the four-membered ring is about 1.6 Å, which is longer than the typical sp^3 bond length (1.54 Å), but the intercluster bond along the *c*-axis direction is 1.49 or 1.51 Å for the orthorhombic and tetragonal phases. Remaining bonds related to the fourfold-coordinated C atoms range between 1.58 and 1.67 Å. Thus the fourfold-coordinated C atoms have an sp^3-like character rather than an sp^2 character. On the other hand, threefold-coordinated atoms tend to have shorter bond lengths than fourfold-coordinated atoms. In particular, the bond length between the dimerized carbon atoms is 1.29 Å, which is much shorter than the typical threefold bond length of 1.42 Å (sp^2 hybridization). The result suggests that the C atoms on the dimers have sp-like charge distributions although they have threefold coordination. The distribution of the total valence charge of the dimer unequivocally exhibits the sp character of the triple bonds (Fig. 2); i.e., double peaks of the charge distribution along the bond axis, which commonly appear in sp^2 π bond systems, are not seen, and the distribution is similar to that of acetylene. The bond angle related to the atom is $\theta_{C2C1C2} = 127.3°$, which is wider than the ideal sp^2 bond angle. This peculiar charge distribution is due to the large structural deformation of the C_{20} clusters: The threefold-coordinated atomic sites, i.e., the C dimers at the top and bottom of the C_{20} cage in Fig 1(a), are depressed inward, and the atoms form a flat structure with four neighboring atoms. This structural deformation suppresses dangling bond character of the threefold-coordinated

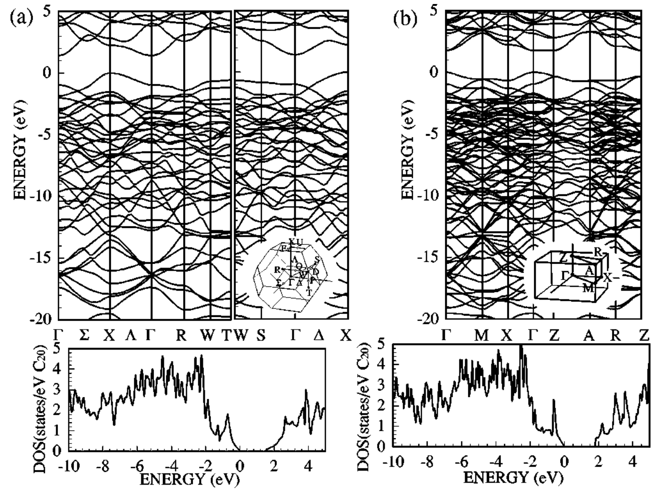

FIG. 3. The electronic band structure and DOS of (a) the orthorhombic and (b) tetragonal phases of C_{20}. The energy is measured from the top of the valence band. Symmetry points and lines in the first Brillouin zone of both phases are also given.

atomic sites without formation of additional interfullerene bonds.

For the fourfold-coordinated atomic sites, the bond length is slightly longer than that of the diamond. However, their bond angles are considerably distorted from that of the diamond (109.5°). The smallest bond angle at the singly bonded site is about 96° whereas the largest angle is about 123°. In particular, the four-membered ring has an angle of 90°, so that the bond angle related to the fourfold-coordinated atoms is highly deviating. Owing to this large distortion, it is unlikely that the system has a remarkable stiffness and is composed of an ultrahard material, even if it has a three-dimensional covalent bonding network as in the case of three-dimensionally polymerized C_{60}.[27]

The electronic band structure of the orthorhombic phase is shown in Fig. 3(a). A fundamental gap between the top of the valence band (X) and the bottom of the conduction band (Γ) is found to be 1.40 eV, which is similar to the gap value of the fcc C_{60}.[28] Thus the ground state of the condensed phase of C_{20} is found to be an elemental semiconductor with the moderate energy gap, which consists of both threefold and fourfold-coordinated carbon atoms. Here we focus on the character of the lowest unoccupied (LU) and highest occupied (HO) bands to discuss the origin of the band gap. As shown in Fig. 4, the HO and LU bands clearly exhibit bonding and antibonding π characters of the C1-C1 dimers, respectively. Thus the HO-LU band energy splitting is attributed to the anomalously strong π bonds of the dimer atoms. Since the other atoms are fourfold coordinated, they have only σ bonds. Bonds having the bonding (antibonding) character of σ bonds are located far below (above) the valence (conduction) band top (bottom), so the wave function of the LU and HO bands is localized around the dimer atoms. The width of the LU and HO bands is around 1.8 eV. The large band dispersion is mainly caused by the small interdimer distances, which induce a large overlap between π orbitals of the dimers.

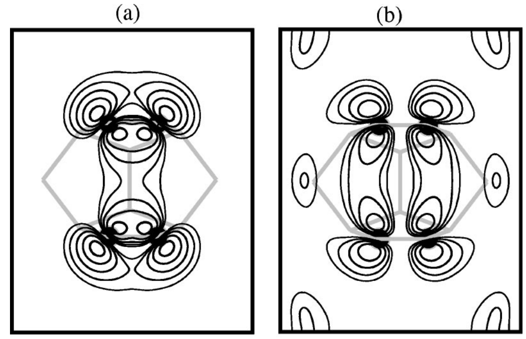

FIG. 4. Contour plot of the squared wave function of the (a) HO state and (b) LU state of the orthorhombic phase at the Γ point. The solid circles denote the threefold-coordinated C atoms. Each contour represent twice (or half) the density of the adjacent contour lines. The lowest-density contour represents $0.003e/\mathrm{a.u.}^3$.

Since the LU and HO states are separated from other conduction and valence bands to some degree, these states give DOS peaks around the gap. The calculated DOS of the orthorhombic phase is also shown in Fig. 3(a). For this calculation, we take 1400k points in the first Brillouin zone. It is thus expected that the polymeric phases of C_{20} exhibit a metallic character by means of carrier injection into the conduction or valence bands. Although the doping may cause a modification of the energy band, we can roughly estimate the relative height of the Fermi level density of states $N(E_F)$ of the doped materials from the valence-band (conduction-band) DOS of the pristine phase by simply filling the top (bottom) of valence (conduction) band. Calculated values of $N(E_F)$ for the n-hole-doped cases are 1.57, 1.25, 1.67, 1.56, and 4.49 (states/eV C_{20}) for $n=1$, 2, 3, 4, and 5, respectively. In particular, $N(E_F)$ for $n=5$ is comparable to that of the representative fullerene-based superconductor, K_3C_{60}.[29] Furthermore, a large electron-phonon coupling is expected to take place due to the strongly localized character of the π states in C1 dimers even though the condensed phases have clathrate networks which are completely different from the molecular crystals of fullerenes. Therefore, the condensed phase of C_{20} with doped carriers is a feasible candidate for the material exhibiting superconductivity at moderate transition temperature.

Figure 3(b) shows the electronic band structure of the tetragonal phase of polymerized C_{20}. Both the top of the valence band (HO) and the bottom of the conduction band (LU) are located at the Γ points: therefore, this material is a direct gap semiconductor. The calculated value of the fundamental energy gap is of 1.76 eV, which is larger than those of the orthorhombic phase and the solid C_{60}.[28] The characteristics of the band structure near the energy gap is similar to that of the orthorhombic phase: The highest branch of the valence band and the lowest branch of the conduction band have the π character of the C dimers on the polar region of the C_{20} cage. Thus for the electron states concerned with π electrons, both systems can be regarded as networks consisting of π electrons on the C_2 unit (acetylenes). The DOS for the tetragonal phase exhibits a character similar to that of the orthorhombic phase. The HO (LU) state causes moderate

DOS peaks below (above) the energy gap, and their heights are comparable with those of the orthorhombic phase; therefore, the tetragonal phase is also a candidate for the superconductor.

In summary, we have studied the geometric and electronic structures of condensed phases of a C_{20} fullerene based on a first-principles total-energy calculation. We have found that the C_{20} molecules form interfullerene covalent bonds without any energy barrier, and that the polymerized structure is energetically favorable. We have obtained two stable phases possessing orthorhombic and tetragonal symmetries, and the orthorhombic phase was found to be the most stable structures. Both phases were found to be interesting elemental semiconductors with moderate energy gaps of 1.4 and 1.7 eV for the orthorhombic and tetragonal phases, respectively. The DOS spikes were found to appear around the energy gap. It is thus plausible that carrier injections tuned to these spikes cause superconductivity.

We benefited from a conversation with T. Kawai. Numerical calculations were performed on the NEC SX5 Supercomputer at the Research Center of the Computational Science, Okazaki National Institute, and the NEC SX4 Supercomputer at the NEC Tsukuba Laboratory. This work was supported in part by JSPS under Contract No. RFTF96P00203, a Grant-in-Aid for Scientific Research on the Priority Area ‘‘Fullerenes and Nanotubes’’ by the Ministry of Education, Science, and Culture of Japan, and Frontier Carbon Technology by NEDO.

[1] W. Krätschmer, L.D. Lamb, K. Fostiropoulous, and D.R. Hoffman, Nature (London) **347**, 354 (1990).
[2] For a review of earlier works on fullerenes, see A. Oshiyama, S. Saito, N. Hamada, and Y. Miyamoto, J. Phys. Chem. Solids **53**, 1457 (1992).
[3] A.F. Hebard, M.J. Rosseinsky, R.C. Haddon, D.W. Murphy, S.H. Glarum, T.T.M. Palstra, A.P. Ramirez, and A.R. Kortan, Nature (London) **350**, 600 (1991).
[4] Y. Iwasa, T. Arima, R.M. Fleming, T. Siegrist, O. Zhou, R.C. Haddon, L.J. Rothberg, K.B. Lyons, H.L. Carter Jr., A.F. Hebard, R. Tycko, G. Dabbagh, J.J. Krajewski, G.A. Thomas, and T. Yagi, Science **264**, 1570 (1995).
[5] M. Núñez-Regueiro L. Marques, J-L. Hodeau, O. Béthoux, and M. Perroux, Phys. Rev. Lett. **74**, 278 (1995).
[6] G. Oszlanyi and L. Forro, Solid State Commun. **93**, 265 (1995).
[7] S. Okada and S. Saito, Phys. Rev. B **59**, 1930 (1999)
[8] F. Diederich, R.L. Whetten, C. Thilgen, R. Ettl, I. Chao, and M.M. Alvarez, Science **254**, 1768 (1991).
[9] K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, and Y. Achiba, Nature (London) **357**, 142 (1992).
[10] K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, and Y. Achiba, Nature (London) **357**, 142 (1992). M. Kainosho, in *Science and Technology of Fullerene Materials*, edited by P. Bernier *et al.*, MRS Symposia Proceedings No. 359, (Materials Research Society, Pittsburgh, 1995), p. 3.
[11] M. Kobayashi, Y. Akahama, H. Kawamura, H. Shinohara, H. Sato, and Y. Saito, Phys. Rev. B **48**, 16 877 (1993).
[12] S. Saito and M.L. Cohen, Solid State Commun. **99**, 891 (1996).
[13] H. Prinzbach, A. Weller, P. Landenberger, F. Wahl, J. Wörth, L.T. Scot, M. Gelmont, D. Olevano, and B.v. Issendorff, Nature (London) **407**, 60 (2000).
[14] M. Saito and Y. Miyamoto, Phys. Rev. Lett. **87**, 035503 (2001).
[15] D.J. Klein, W.A. Seitz and T.G. Schmalz, Nature (London) **323**, 703 (1986)
[16] C. Cros, M. Pouchard, and E.P. Hagenmuller, J. Solid State Chem. **2**, 570 (1970).
[17] G.B. Adams, O.F. Sankey, J.B. Page, and M. O'Keeffe, Chem. Phys. **176**, 61 (1993).
[18] A. Devos and M. Lannoo, Phys. Rev. B **58**, 8236 (1998).
[19] Y. Miyamoto and M. Saito, Phys. Rev. B **63**, 161401 (2001).
[20] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[21] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
[22] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[23] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[24] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).
[25] L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[26] O. Sugino and A. Oshiyama, Phys. Rev. Lett. **68**, 1858 (1992).
[27] S. Okada, S. Saito, and A. Oshiyama, Phys. Rev. Lett. **83**, 1986 (1999).
[28] S. Saito and A. Oshiyama, Phys. Rev. Lett. **66**, 2637 (1991).
[29] S. Saito and A. Oshiyama, Phys. Rev. B **44**, 11 536 (1991).