Rhombohedral C$_{60}$ polymer: A semiconducting solid carbon structure

Susumu Okada and Susumu Saito

Department of Physics, Tokyo Institute of Technology, 2-12-1 Oh-okayama, Meguro-ku, Tokyo 152, Japan
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We study the two-dimensionally polymerized rhombohedral phase of C$_{60}$ by using the local-density approximation in the density-functional theory. The electronic structure of this hybrid solid carbon of sp^2 and sp^3 C atoms is found to be essentially three dimensional with a narrow fundamental gap due to a strong interlayer interaction, which also stabilizes the system considerably. Possible modifications of this elemental semiconductor are also discussed. [S0163-1829(97)04407-X]

Ever since solid C$_{60}$, the third form of carbon, was discovered,[1] this phase of crystalline carbon has been studied intensively, and many interesting physical properties have been discovered. Solid C$_{60}$ is electronically different from metallic graphite and insulating diamond and is a moderate-gap semiconductor. Many doped materials including the alkali-metal-doped high-transition temperature superconductors have been produced.[2–4] Furthermore, the external pressure applied to solid C$_{60}$ at high temperatures is found to induce polymerization of C$_{60}$ to give three distinct phases,[5–8] which can be classified as another form of crystalline carbon consisting of both sp^2-like (threefold coordinated) and sp^3-like (fourfold coordinated) C atoms and deserving intensive studies. Among the three phases, the two-dimensionally polymerized rhombohedral phase is found to be the majority phase[6] and is of particular interest due to its layered structure like graphite, which is well known to be a host material for a large variety of intercalated systems showing interesting physical properties.

In this paper, we report the electronic structure of this rhombohedral phase obtained by using the local-density approximation (LDA) within the density-functional theory under the reported geometry giving excellent agreement with the x-ray diffraction pattern.[6] While the material has been transformed from solid C$_{60}$, its electronic structure is found to be considerably different from solid C$_{60}$. The system is an elemental semiconductor in which the fundamental-gap is indirect. Although the polymerization transforms as much as one-fifth of C atoms from sp^2-like to sp^3-like, the fundamental-gap value does not approach the diamond value but rather becomes smaller by 0.7 eV. We have also optimized the geometry under the observed lattice constants in the LDA (Fig. 1). The relaxation from the reported geometry is found to be small, confirming the stability of the rhombohedral phase. The total energy of rhombohedral C$_{60}$ is found to be very close to that of solid C$_{60}$.

As is shown in Fig. 1, C$_{60}$ clusters form a triangular lattice in each layer, and the space group of this system is $R\bar{3}m$. It is convenient to express the lattice parameters of the rhombohedral system by using the hexagonal-system parameters. Then, the lattice parameters of this system are $a=9.19$ Å and $c=24.5$ Å.[6] The interlayer distance is $c/3$. Each C$_{60}$ cluster now contains 12 sp^3-like C atoms having an interfullerene bond. As a result of this polymerization, each C$_{60}$ is deformed from a truncated icosahedron and the diameter along the c-axis direction becomes shorter. Intercluster distances not only within the layer (9.19 Å) but also between adjacent layers (9.73 Å) are definitely smaller than that of fcc C$_{60}$
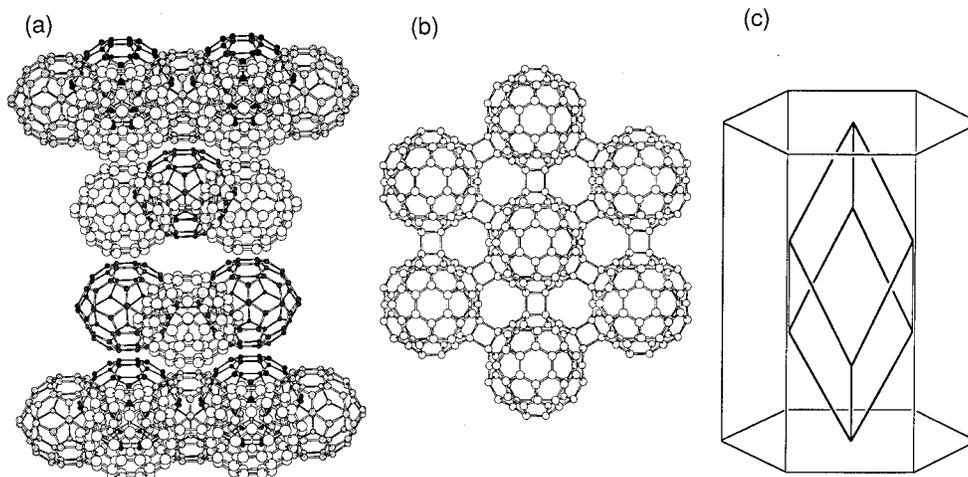

FIG. 1. (a) Geometry of the two-dimensionally polymerized rhombohedral C$_{60}$ optimized in the density-functional theory. (b) Its top view along the c axis. (c) Conventional hexagonal-lattice expresion. The primitive cell of the rhombohedral lattice with six parallelogram faces is also shown.
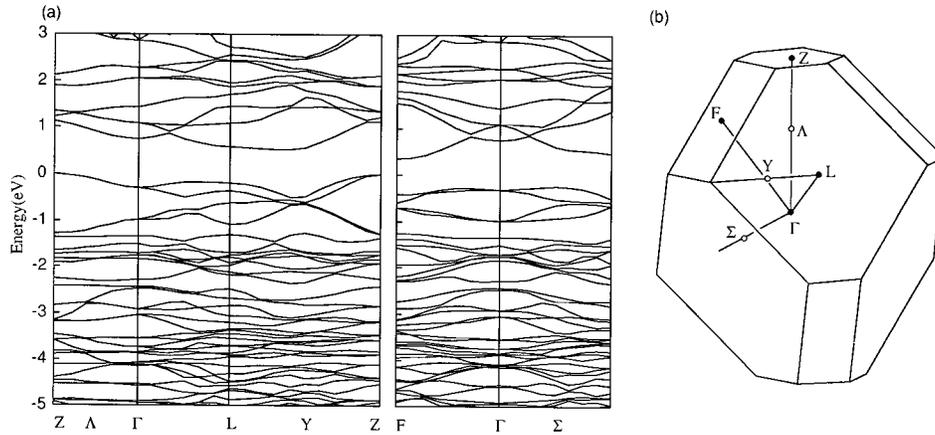
FIG. 2. (a) Band structure of the two-dimensionally polymerized rhombohedral C_{60}. Energy is measured from the top of the valence band at the Z point. (b) Symmetry points and lines in the first Brillouin zone of the rhombohedral lattice.

(10.04 Å). Hence, the interlayer interaction to be taken into account in the LDA should be important.

As for the exchange-correlation potential in the LDA, the Ceperley-Alder potential[9] is adopted. The conjugate-gradient procedure both for the self-consistent electronic-structure calculation and for the geometry optimization is adopted.[10] The norm-conserving pseudopotential is used with a separable approximation.[11] The plane-wave basis set with the cutoff energy of 50 Ry is used.

In Fig. 2, the band structure of the C_{60} rhombohedral phase is shown. The top of the valence band is found to be at the Z point, and the bottom of the conduction band is at the F point. The fundamental energy gap between these band extremes is 0.35 eV. Although the system is a mixture of sp^2-like and sp^3-like C atoms, this value is considerably smaller than those of diamond, the sp^3 system, and solid C_{60}, the sp^2-like system. The fundamental-gap energy of the face-centered cubic (fcc) C_{60} obtained by the same computational procedure is 1.06 eV. Although the LDA generally underestimates the energy gap, the difference between the rhombohedral and fcc C_{60}, about 0.7 eV, should be more reliable. Also several important features of the band structure are different from those of fcc C_{60}.[12] In the case of fcc C_{60} the threefold-degenerate lowest-unoccupied t_{1u} state of the C_{60} cluster forms the isolated conduction band. However, in the case of the rhombohedral C_{60}, the lowest branch of the conduction band is rather separated from higher states. Furthermore, band dispersions are generally larger than those of fcc C_{60} and all the unoccupied states form one continuous conduction band.

In the case of the rhombohedral C_{60} polymer, only 48 C atoms out of 60 atoms in each C_{60} possess the π state. In addition, these 48 carbon atoms are divided into two equivalent 24-atom groups below and above the polymerization plane. Hence, as far as the π-derived bands are concerned, the constituent unit of this system is considered to be not the C_{60} molecule but rather the 24-atom bowl-shape cluster. Since the important states around the fundamental gap are π states, it is natural that the band structure around the gap shows considerably different features from those of the fcc C_{60}.

Rather clear band dispersions along the Λ line show that the rhombohedral C_{60} is electronically a three-dimensional system. As a matter of fact, the inverse effective-mass tensor values for directions parallel and perpendicular to the polymerization plane are of the same order for both holes and electrons. The effective masses at the bottom of the conduction band (electron masses) obtained by the diagonalization of the effective-mass tensor are $0.2m_e$, $0.7m_e$, and $0.9m_e$ (m_e is the bare electron mass). Also the effective masses of the top of the valence band (hole masses) are $0.5m_e$, $0.6m_e$, and $1.8m_e$.

Since the rhombohedral phase has a stacking structure, one can consider various kinds of doped phases with atoms or molecules in the interlayer spaces, as in the case of graphite intercalation compounds. In fact, several metal-doped rhombohedral C_{60} compounds, such as NaC_{60}, have been recently synthesized.[13] It is now well known that fcc C_{60} has three interstitial sites per unit cell, i.e., one octahedral site and two tetrahedral sites. The rhombohedral C_{60} also has three interstitial sites originating from them. The maximum radii of spheres fitting into these sites are 1.90 and 1.02 Å for octahedral and tetrahedral sites, respectively. (Two tetrahedral sites are still equivalent in the rhombohedral phase.) These rather large values suggest that one can dope even the largest alkali and alkaline-earth metal atoms, including Cs and Ba, into an octahedral site. On the other hand, one can dope only Li, Na, Mg, and Ca into the smaller tetrahedral site unless the interlayer distance is enlarged by doping. The electronic density of states (DOS) of the rhombohedral C_{60} is shown in Fig. 3. For this calculation, we used 128 k points in the first Brillouin zone and 0.01-eV Gaussian broadening. Although the doping may cause a modification of the energy bands,[14] one can estimate roughly the relative height of the Fermi-level density of states $N(E_F)$ of the doped materials from the conduction-band DOS of the pristine phase by simply filling it from the bottom if the charge transfer from metal atoms to carbon cages is to take place. The obtained values for $N(E_F)$ for the n-electron doped cases are 8.5, 1.0, 6.7, 7.5, 7.4, and 8.1 (states/eV) for $n=1$, 2, 3, 4, 5, and 6, respectively. Hence, the two-electron doped system may be a poor metal. Otherwise, electron-doped systems have considerable $N(E_F)$ and may be metallic.

Finally, we have checked the structural parameters of this rhombohedral phase given by the tight-binding (TB) model.[6,8] The structural optimization has been performed by
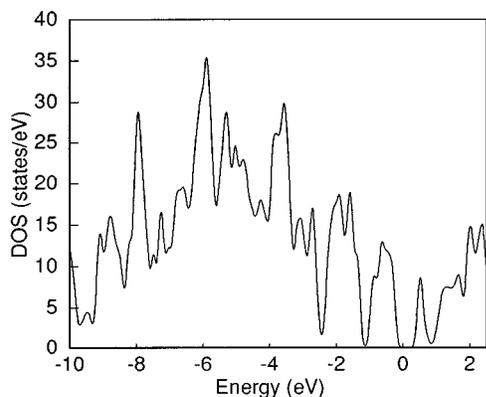
FIG. 3. Density of states of the rhombohedral C_{60}.

TABLE I. Total energies per atom of fcc C_{60} and the polymerized rhombohedral C_{60} obtained in the LDA. Energies are measured from the total energy per atom of graphite. In each case, the geometry is fully optimized under the measured lattice constant. In addition, the LDA total energy of the rhombohedral C_{60} under the previously reported geometry based on the TB model (Ref. 6) is also given.

	Total energy (eV)
fcc	0.762
rhombohedral	0.763
rhombohedral (TB geometry)	0.775

using the conjugate-gradient method in the LDA. The total energy per atom for the optimized geometry is listed in Table I together with the LDA value for TB geometry as well as that of fcc C_{60}. The difference between energies of the optimized and the TB geometries is very small and the geometrical parameters reported previously are considered to be accurate. The small differences from the TB geometry are the compression of the C_{60} units along the c axis and the extension along other axes. The decrease of the C_{60}-unit diameter along the c axis is only 0.08 Å, while the extension along other axes is even smaller. More importantly, the LDA total energy of the rhombohedral phase is found to be very close to that of fcc C_{60}. Their difference is only 0.001 eV per atom, being consistent with the observed reversible transformation between the two phases.[5] This high stability of the rhombohedral phase should be due to a strong interlayer interaction.

In summary, we have studied the electronic structure of the two-dimensionally polymerized rhombohedral C_{60} phase by using the local-density functional theory. Due to the short C_{60}-C_{60} distances both within and between layers, the material is found to be electronically three dimensional, and to be an elemental semiconductor having an indirect gap between Z and F points. The gap value is considerably smaller than that of fcc C_{60}. A structural optimization has also been performed and the reported geometry is confirmed to be stable. This layered solid carbon is of high interest not only as a semiconductor but also as a host material to be doped with various kinds of atoms and molecules as in the case of graphite. The conduction-band density of states indicates that electron-doped phases can be metallic. Synthesizing polymerized C_{60} and its doped phases should extend further the field of science and technology of fullerenes.

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