電子構造: ルモヘドラデヒドロカプト120多核化合物の電子構造

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<td>年</td>
<td>2003-12</td>
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<td>DOI</td>
<td>10.1103/PhysRevB.68.235402</td>
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Electronic structure of metallic rhombohedral C$_{60}$ polymers

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(Received 15 June 2003; published 2 December 2003)

We report electronic structures and stabilities of rhombohedral C$_{60}$ polymers by using the local spin-density approximation in the framework of the density-functional theory. Owing to hybrid networks of $sp^2$-like (threefold coordinated) and $sp^3$-like (fourfold coordinated) carbon atoms, the electronic structures of these polymers are considerably different from that of a face-centered cubic (fcc) C$_{60}$. We find that polymerized structures attained at the double bonds are semiconducting whereas polymerized structures attained at single bonds are metallic. Significant overlap of the wave function in the space among three adjacent C$_{60}$ causes the metallic behavior on the latter polymers. We also find that the stacking ordering strongly affects the conducting properties of the metallic polymers. Despite substantial density of states at Fermi level, the C$_{60}$ polymers do not exhibit any magnetic ordering. Total energy calculations show that the metallic C$_{60}$ polymers have higher total energy than the semiconducting C$_{60}$ polymer phases.

I. INTRODUCTION

Polymerized phases of C$_{60}$ belong to a class of the crystalline fullerites. Each C$_{60}$ in the polymerized phases has covalent bonds between adjacent C$_{60}$ and consists of both $sp^2$-like (threefold coordinated) and $sp^3$-like (fourfold coordinated) carbon atoms. The $sp^3$-like carbon atoms, connecting C$_{60}$ units, result in infinite one-, two-, or three-dimensional covalent networks and drastically modulate electron states of the C$_{60}$ unit. These are the reason why the polymerized C$_{60}$ phases are classified as the class of the crystalline fullerites. In the last decade, several polymerized phases of C$_{60}$ have been synthesized by using photo-induced, alkaline-atom-induced, and pressure-induced polymerization procedures. Among these procedures, pressure-induced polymerization is known to be able to control network geometries and dimensionality by varying the pressure and temperature. Three different types of the polymerized phases have been experimentally synthesized under moderate hydrostatic pressure at elevated temperature. The x-ray diffraction experiments have clarified structures of one-dimensionally polymerized orthorhombic and two-dimensionally polymerized tetragonal and also rhombohedral phases. First-principle electronic structure calculations for the experimentally determined atomic structures of these polymerized phases have revealed that they are semiconducting with a narrow fundamental energy gap. Furthermore, the electronic structures of these phases are considerably different from that of a face-centered cubic phase of C$_{60}$ fullerite due to the presence of the $sp^3$-like carbon atoms which modulate network topologies of $\pi$-electron system.

Recently, anisotropic metallic properties were reported on highly oriented rhombohedral C$_{60}$ polymer. Furthermore, possible ferromagnetic spin ordering was also reported on the rhombohedral C$_{60}$ polymers. These results are obviously inconsistent with the previous electronic structure calculations. Thus, it is imperative to clarify the mechanism of the anisotropic conduction properties and the possible ferromagnetic ordering. In particular, the atomic structures, energetics, and detailed electronic structures of the rhombohedral C$_{60}$ polymers are desired.

Here, based on the first-principle total-energy calculation, we study the energetics and electronic structures of the rhombohedral C$_{60}$ polymer to explore the possibility of the anisotropic metallic property. There are two possibilities as to the intermolecular bond formation. In one configuration, the two C atoms shared by the two adjacent hexagons in a C$_{60}$ are covalently bonded to the C atoms which are shared by the two hexagons in the adjacent C$_{60}$ (66 structure); in another, the two C atoms shared by a hexagon and a pentagon in a C$_{60}$ are bonded to the adjacent C$_{60}$ (65 structure). Relative stability between the two configurations is unknown. Further, the two-dimensionally polymerized C$_{60}$ network is stacked along the $c$ axis of the hexagonal lattice in the rhombohedral phase. We thus need to clarify their stacking effects on the electronic structure and the energetics of the polymer. Our calculation clarifies the possibility of an anisotropic conduction property in the rhombohedral C$_{60}$ polymer in which the intermolecular covalent-bond structure is different from that in the rhombohedral polymer previously studied.

II. CALCULATION METHODS

All calculations have been performed by density-functional theory (DFT). To explore the possibility of polarization of the electron spin, exchange-correlation energy of interacting electrons is treated in the local spin-density approximation (LSDA) with a functional form fitted to the Ceperley-Alder result. Norm-conserving pseudo-potentials generated by using the Troullier-Martins scheme both for the electronic structure calculation and for the wave function basis set with a cutoff energy of 50 Ry which gives enough convergence of relative total energies of carbon-related materials. We adopt the conjugate-gradient minimization scheme both for the electronic structure calculation and for
the geometry optimization. For the geometry optimization, we assume the lattice parameters \( a = 9.19 \) Å and \( c = 24.5 \) Å which are obtained by the x-ray diffraction pattern analysis. Structural optimization has been performed until the remaining forces for each atom are less than 5 mRy/Å under the above lattice parameters. Integration over Brillouin zone is carried out using the 27-point sampling.

III. RESULTS AND DISCUSSIONS

As shown in Fig. 1, \( \text{C}_{60} \) clusters form a triangular lattice in each polymerized layer which is stacked along the direction perpendicular to the polymerized layers in rhombohedral symmetry. In the polymerized layer, each \( \text{C}_{60} \) molecule possesses 12 \( sp^3 \)-like carbon atoms which form covalent bond between adjacent \( \text{C}_{60} \) molecules. As stated above, we consider two different polymerized structures. In a \( \text{C}_{60} \) polymer reported by Núñez-Regueiro [Fig. 1(a)], polymerization is attained via formation of the four-membered ring from two

FIG. 1. Optimized geometries of each polymerized layer of (a) \( \text{C}_{66}(66) \) polymer and (b) \( \text{C}_{65}(65) \) polymer. Bottom of left in each figure shows the atomic structure at the interfullerene covalent bonds. Bottom right in each figure shows network geometries of \( sp^3 \)-like (threefold coordinated) carbon atoms.

FIG. 2. Schematic side and top views of the rhombohedral polymers with (a) the ABC-stacking and (b) the ACB-stacking structures. Dark shaded, pale shaded, and white circles denote the \( \text{C}_{60} \) molecules belonging in A, B, and C polymerized layers, respectively.

TABLE I. Total energies per atom of rhombohedral \( \text{C}_{66}(66) \) polymers and the \( \text{C}_{65}(65) \) polymers for different stacking orders. Energies are measured from the total energy of graphite. Total energy per atom of fcc \( \text{C}_{60} \) is also shown. In the rhombohedral and the fcc phase, geometries are fully optimized under the measured lattice constants.

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<th>Stacking Order</th>
<th>Total Energy (eV)</th>
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<tr>
<td>( \text{C}_{66}(66) ) ABC</td>
<td>0.428</td>
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<tr>
<td>( \text{C}_{66}(66) ) ACB</td>
<td>0.428</td>
</tr>
<tr>
<td>( \text{C}_{65}(65) ) ABC</td>
<td>0.702</td>
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<td>( \text{C}_{65}(65) ) ACB</td>
<td>0.719</td>
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<tr>
<td>fcc</td>
<td>0.427</td>
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FIG. 3. Electronic energy bands of (a) the \( ABC \)-stacking \( \text{C}_{66}(66) \) polymers. Energies are measured from the top of the valence band at \( Z \) point. Symmetry points and lines in the first Brillouin zone of the rhombohedral lattice are shown in inset.
66 bond (double bond) each of which is shared by the two hexagons. On the other hand, Okotrub recently proposed a different polymerized structure.25 As shown in Fig. 1(b), polymerization is attained by the formation of the four-membered ring from two 65 bonds each of which is shared by the hexagon and the pentagon. This structure is called \( \text{C}_{60} \) polymers hereafter. The 65 bond is classified as the single bond on the \( \text{C}_{60} \) network in the \( \text{C}_{60} \). Furthermore, there are two different stacking sequences, i.e., \( \text{ABCABC} \ldots \) [\( \text{ABC} \) stacking: Fig. 2(a)] and \( \text{ACBACB} \ldots \) [\( \text{ACB} \) stacking: Fig. 2(b)], along the \( c \)-axis direction.

### A. \( \text{C}_{60} \) (66) polymer

We study the stability and the electronic structure of the \( \text{C}_{60} \) (66) polymer with the \( \text{ABC} \)-stacking structure. Our previous local-density approximation (LDA) calculation has shown that the \( \text{ABC} \)-stacking \( \text{C}_{60} \) (66) polymer is a semiconductor with narrow indirect energy gap and the polymerized structure is energetically as stable as the \( \text{fcc} \) \( \text{C}_{60} \).\(^{67} \) In this section, we clarify the electronic structure and the stability of the \( \text{C}_{60} \) (66) polymer with the \( \text{ACB} \)-stacking structure. As shown in Table I, we do not find any significant difference in total energies between the two stacking structures in the accuracy of the present calculation. Furthermore, both stacking structures possess similar electronic band structures around the energy gap [Figs. 3(a) and 3(b)]. Thus, the \( \text{ACB} \)-stacking structure is also a semiconductor with indirect fundamental gap of about 0.5 eV. This insensitivity for the stacking difference is clarified by the wave function analysis for the electron states around the energy gap. Figure 4(a) shows the squared wave function of the lowest unoccupied state of the rhombohedral \( \text{C}_{60} \) (65) polymers at the \( \Gamma \) point. The wave function clearly possesses an antibonding character and is localized at the edge atomic sites of the \( \text{sp}^2 \)-like carbon atoms (Fig. 1). Furthermore, it is found that the wave function in each polymerized layer hardly overlaps due to the localized character. Therefore, the electronic structures and energetics of the \( \text{C}_{60} \) (66) polymer does not depend on the stacking difference.

### B. \( \text{C}_{60} \) (65) polymer

In this section we discuss the geometric and electronic structures of the rhombohedral \( \text{C}_{60} \) (65) polymers. We perform the structural optimization under the experimentally observed lattice parameters \( (a = 9.19 \, \text{Å} \) and \( c = 24.5 \, \text{Å}) \). We show optimized atomic geometry of the \( \text{C}_{60} \) (65) polymer with the \( \text{ABC} \)-stacking order in Fig. 1(b). Optimized bond length between adjacent \( \text{C}_{60} \) molecules is 1.56 Å which is...
close to that obtained in the C_{60}(66) polymers (1.64 Å) and that of the diamond. It is found that calculated total energies of the C_{60}(65) polymers are higher than those of the other C_{60} related materials. The total energy of the C_{60}(65) polymer is higher than that of the C_{60}(66) polymer by about 0.3 eV/atom (Table I). Thus, the C_{60}(65) polymer is considered to be a minor phase of the rhombohedral C_{60} polymer when equilibrium condition is attained. Among two different stacking orders of the C_{60}(65) polymers, we find that the ABC-stacking structure is more stable by 17 meV than the ACB-stacking structure. It should be noted that the layer-layer interactions in the graphite and the C_{60} polymers are considered to have the character of van der Waals interaction. Sufficiently accurate description of such interaction is unavailable at present: Our calculation with LDA is successful to provide reasonable binding energy of the graphite. Hence the calculated energy difference between two stacking structures is of qualitative nature to some extent and the quantitative value is to be studied in future.

Electronic energy bands of the ABC-stacking and the ACB-stacking structures of the C_{60}(65) polymers are shown in Figs. 5(a) and 5(b), respectively. Since we find the relatively flat dispersion bands near the Fermi level along the Λ line in both structures, spin polarization is expected to take place. However, we only find nonmagnetic and metallic electron states for both the ABC-stacking and the ACB-stacking structures of the C_{60}(65) polymers. The results indicate that the rhombohedral C_{60}(65) polymers are not candidates for the ferromagnetic C_{60} polymers. It is expected that the small dispersion band around the $E_F$ may cause large density of states at the $E_F$. As shown in Fig. 6, calculated $N(E_F)$ are 5.32 states/(eV spin) and 4.16 states/(eV spin) for the ABC-stacking and the ACB-stacking structures, respectively. The values are similar to the typical values of the alkali-metal doped fullerides.

To clarify mechanism of the metallization of the polymers, we analyze the wave function of the electron states at the $E_F$. Figures 4(b) and 4(c) show distribution of squared wave function C_{60}(65) polymers for the electron states at Γ labeled as α. The states are mainly localized at the edge of the π networks [Fig. 4(d)]. Furthermore, the distribution of the states around the edges of the $sp^2$-like carbon network is more localized on the polymerized plane than that in the case of the C_{60}(66) polymer. Consequently, this distribution causes large overlap of the wave function in the space among three adjacent C_{60}s so that the C_{60}(65) polymers exhibit metallic electronic structures [Fig. 4(d)]. Furthermore, distribution of the wave function indicates that the overlap between adjacent polymerized layer is considerably small in the ABC-stacking structure. Thus, the band dispersion along the Λ line is narrower than that along the in-plane direction and the system may exhibit the strong anisotropic conductance which have been experimentally reported by Makarova et al. On the other hand, in the ACB stacking, we find the significant wave function overlap between adjacent layers. Owing to the large wave function overlap, the system has larger band dispersions along the Λ-line than the ABC-stacking polymer.

FIG. 5. Electronic energy bands of (a) the ABC-stacking and (b) the ACB-stacking C_{60}(65) polymers. Energies are measured from the Fermi-level energy which is denoted by dashed lines.

FIG. 6. Density of states for the rhombohedral C_{60} polymers with (a) the ABC-stacking and (b) the ACB-stacking structures. Energies are measured from the Fermi-level energy.
IV. CONCLUSION

In the present paper, we studied the electronic structures and energetics of the rhombohedral C_{60} polymers by using the local spin-density approximation in the density-functional theory. We study two different polymerized structures of the rhombohedral C_{60} polymers: In the C_{60}(66) polymer, the polymerization is attained at the 65 bonds which are shared with the two adjacent hexagons, while, in the C_{60}(65) polymer, the polymerization is attained at the 65 bonds which are shared with the hexagon and pentagon. Electronic structures of the C_{60}(66) polymers are found to be semiconducting with small indirect energy gap between Z and F points. We also find that stacking effects of polymerized layers are not important for both electronic structures and energetics. In sharp contrast to the C_{60}(66) polymers, the C_{60}(65) polymers are metallic with relatively large Fermi level density of states. The calculated values of N(E_F) are 5.32 states/(eV spin) and 4.16 states/(eV spin) for the ABC stacking and the ACB stacking, respectively. Although the C_{60}(65) polymers possess substantial density of states at Fermi level, we only find nonmagnetic and metallic solutions in this calculation. Therefore, the C_{60}(65) polymers are unlikely to be a candidate for the ferromagnetic C_{60} polymer. We find significant differences of the energetics and electronic structures between ABC stacking and ACB stacking of the polymerized planes. The differences are mainly caused by the characteristic distribution of wave function at the Fermi energy. Furthermore, the distribution may also result in the anisotropic metallic property of the rhombohedral C_{60} polymers as reported in the recent experiment.

ACKNOWLEDGMENTS

We benefited from fruitful conversations with M. Tokumoto. This work was partly supported by ACT-JST (Japan Science and Technology Corporation), Special Research Project on Nanoscience in University of Tsukuba, NEDO under the Nanotechnology Materials Program, and Grant-in-Aid for Scientific Research from Ministry of Education, Science, and Culture of Japan. Computations were done at Institute for Solid State Physics, University of Tokyo, at Science Information Processing Center, University of Tsukuba, and at Research Center of the Computational Science, Okazaki National Institute.