電子構造の研究：六方形のC60ポリマーの金属性

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Electronic structure of metallic rhombohedral C_{60} polymers

Susumu Okada and Atsushi Oshiyama
Institute of Physics, University of Tsukuba, Tennodai, Tsukuba 305-8571, Japan
and Center for Computational Physics, University of Tsukuba, Tennodai, Tsukuba 305-8577, Japan
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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}; in another, the two C atoms shared by a hexagon and a pentagon in a C_{60} are bonded to the adjacent C_{60}. 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 are adopted to describe the electron-ion interaction. The valence wave functions are expanded by the plane-wave 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, 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 C$_{60}$ molecule possesses 12 $sp^3$-like carbon atoms which form covalent bond between adjacent C$_{60}$ molecules. As stated above, we consider two different polymerized structures. In a C$_{60}$ polymer reported by Núñez-Regueiro [Fig. 1(a)], polymerization is attained via formation of the four-membered ring from two

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FIG. 1. Optimized geometries of each polymerized layer of (a) C$_{60}$(66) polymer and (b) C$_{60}$(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 C$_{60}$ molecules belonging in A, B, and C polymerized layers, respectively.

FIG. 3. Electronic energy bands of (a) the ABC-stacking and (b) the ACB-stacking C$_{60}$(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.

TABLE I. Total energies per atom of rhombohedral C$_{60}$(66) polymers and the C$_{60}$(65) polymers for different stacking orders. Energies are measured from the total energy of graphite. Total energy per atom of fcc C$_{60}$ is also shown. In the rhombohedral and the fcc phase, geometries are fully optimized under the measured lattice constants.
66 bond (double bond) each of which is shared by the two hexagons. On the other hand, Okotrub recently proposed a different polymerized structure.\textsuperscript{25} As shown in Fig. 1,\textsuperscript{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 C\textsubscript{60} (66) polymers hereafter. The 65 bond is classified as the single bond on the C\textsubscript{u}C network in the C\textsubscript{60}. Furthermore, there are two different stacking sequences, i.e., ABCABC\ldots [ABC stacking: Fig. 2(a)] and ACBACB\ldots [ACB stacking: Fig. 2(b)], along the c-axis direction.

A. C\textsubscript{60}(66) polymer

We study the stability and the electronic structure of the C\textsubscript{60}(66) polymer with the ABC-stacking structure. Our previous local-density approximation (LDA) calculation has shown that the ABC-stacking C\textsubscript{60}(66) polymer is a semiconductor with narrow indirect energy gap and the polymerized structure is energetically as stable as the fcc C\textsubscript{60}.\textsuperscript{6,7} In this section, we clarify the electronic structure and the stability of the C\textsubscript{60}(66) polymer with the ABC-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 ABC-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 C\textsubscript{60}(66) polymer at the $\Gamma$ point. The wave function clearly possesses an antibonding character and is localized at the edge atomic sites of the sp\textsuperscript{2}-like carbon atoms [Fig. 1].

B. C\textsubscript{60}(65) polymer

In this section we discuss the geometric and electronic structures of the rhombohedral C\textsubscript{60}(65) polymers. We perform the structural optimization under the experimentally observed lattice parameters ($a=9.19$ Å and $c=24.5$ Å). We show optimized atomic geometry of the C\textsubscript{60}(65) polymer with the ABC-stacking order in Fig. 1(b). Optimized bond length between adjacent C\textsubscript{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 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} 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 66 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 the both electronic structures and energetics. In sharp contrast to the C$_{60}(66)$ polymers, the C$_{60}(65)$ polymers are a 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.

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