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Optimized 3D structures and energy bands of peanut-shaped C_{60} polymers

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Abstract. Optimized three-dimensional (3D) cell structures and energy bands of fused (peanut-shaped) C_{60} polymers (p55 and p66) have been investigated using the first-principles pseudopotential approach within the local density approximation of the density functional theory. We found that the resulting electronic structure is either metal or semiconductor depending on the shape of the polymer chains and the unit cell structure.

PACS. 71.20.Tx Fullerenes and related materials; intercalation compounds – 31.15.Ar Ab initio calculations – 61.48.+c Fullerenes and fullerene-related materials – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 81.05.Tp Fullerenes and related materials

1 Introduction

Recently, carbon nanomaterials such as fullerene polymers as well as carbon nanotubes have attracted considerable interests both experimentally and theoretically. Quite recently, one of the authors (J.O.) confirmed experimentally that fullerene polymers exhibiting semiconducting behavior can be created by exposing the C_{60} film under the UV-visible irradiation [1]. In addition, fullerene polymers exhibiting metallic behavior can be created by exposing the C_{60} film under the electron-beam (EB) irradiation [2]. These properties are considerably different from the original C_{60} crystal. Such irradiated samples would have more coalesced cross-linkage (peanut-shaped) than [2+2] cycloadditional bonds.

In a theoretical aspect, peanut-shaped C_{60} dimers were first proposed by Strout et al. [3]. Then, one of the authors (J.O.) and co-workers [4] investigated peanut-shaped C_{60} dimers by means of the tight-binding molecular dynamics and compared the resulting infrared modes with their experimental data [2,5]. Quite recently, using an ab initio self-consistent field crystal orbital (SCF-CO) approach, Wang et al. calculated the electronic structure of 1D fused C_{60} polymers (peanut-shaped carbon nanotubes) and obtained band structures indicating semiconductor or metal according to the crosslinking structure [6]. This is a very interesting finding, but, since they considered only an isolated 1D polymer chain of different kinds, the possibility that an additional 3D array structure would make the non-metallic 1D fused C_{60} polymers metallic is not yet scrutinized. In this sense, a first-principles study on the 3D array structure of peanut-shaped fullerene polymers is highly desired.

In the present study, we analyze the electronic structure of 3D structures of fused (peanut-shaped) C_{60} polymers crosslinked by either seven-membered rings or eight-membered rings. As discussed by Wang et al. [6], the present two structures, p55 and p66 (T5 and T6 in their notation), are energetically most stable among possible peanut-shaped polymers crosslinked by either (p55) seven-membered rings or (p66) eight-membered rings, and can be considered to be most easily created by the electron-beam irradiation.

2 Method and geometries

For the first-principles calculation, we use the plane-wave method (Vienna ab-initio simulation package, VASP) [7,8] with ultrasoft pseudopotentials on the basis of the local density approximation of the density functional theory. Cutoff energy for plane waves is set to be 286.6 eV. The number of **k**-points is $4 \times 4 \times 4$. For all the structures described below, we perform structural optimization including unit cell, and then calculate their energy bands.

We assume evenly spaced three-dimensional stack (i.e., periodic lattice) of two types of fused C_{60} polymer chains: One has a fused link composed of six-membered and seven-membered rings, which we call p55. The other has a fused

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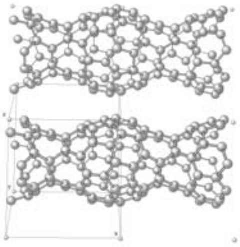

Fig. 1. Geometry of (A) monoclinic (hexagonal) unit cell with $a \sim b = c$, $\alpha = 60°$ and $\beta = \gamma = 90°$, in which p55 is put perpendicular to the rhombus (hexagonal) plane. The polymers form triangular lattice in the directions perpendicular to the polymer axis.

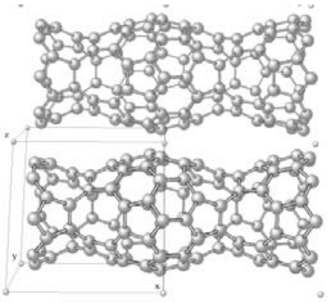

Fig. 2. Geometry of (A) monoclinic (hexagonal) unit cell with $a \sim b = c$, $\alpha = 60°$ and $\beta = \gamma = 90°$, in which p66 is put perpendicular to the rhombus (hexagonal) plane. The polymers form triangular lattice in the directions perpendicular to the polymer axis.

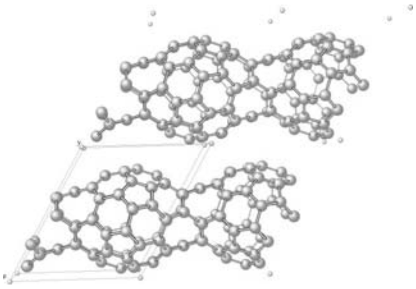

Fig. 3. Geometry of (B) monoclinic (hexagonal) unit cell with $a \sim b \sim c$, $\alpha = \beta = 90°$ and $\gamma = 60°$, in which p55 is put parallel to one of the hexagonal axes. The polymers form square lattice in the directions perpendicular to the polymer axis.

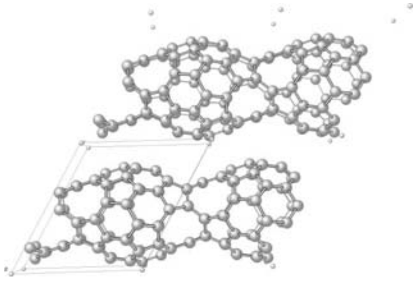

Fig. 4. Geometry of (B) monoclinic (hexagonal) unit cell with $a \sim b \sim c$, $\alpha = \beta = 90°$ and $\gamma = 60.5°$, in which p66 is put parallel to one of the hexagonal axes. The polymers form square lattice in the directions perpendicular to the polymer axis.

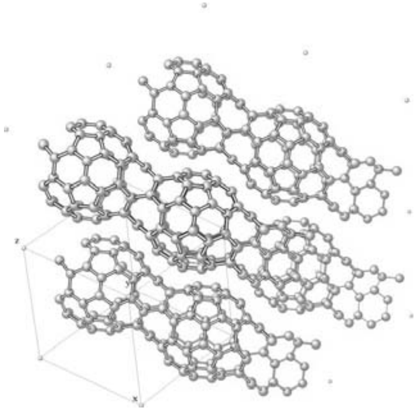

Fig. 5. Geometry of (C) triclinic unit cell with $a \sim b \sim c$, $\alpha \sim \gamma = 62°$ and $\beta = 90°$, in which p55 is put toward two of the adjacent unit cells. The polymers form triangular lattice in the directions perpendicular to the polymer axis.

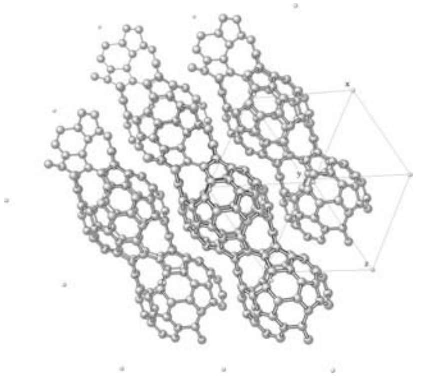

Fig. 6. Geometry of (C) triclinic unit cell with $a \sim b \sim c$, $\alpha = 80°$, $\gamma = 63°$ and $\beta = 116.6°$, in which p66 is put toward two of the adjacent unit cells. The polymers form triangular lattice in the directions perpendicular to the polymer axis.

link composed of five-membered and eight-membered rings, which we call p66. For the three-dimensional stacking geometry, we assume three types of unit cells: (A) monoclinic (hexagonal) unit cell with $a \sim b = c$, $\alpha = 60°$ and $\beta = \gamma = 90°$ in which one polymer chain is put perpendicular to the rhombus (hexagonal) plane (see Fig. 1 for p55 and Fig. 2 for p66), (B) monoclinic (hexagonal) unit cell with $a \sim b \sim c$, $\alpha = \beta = 90°$ and $\gamma = 60°$ in which one polymer chain is put parallel to one of the hexagonal axes (see Fig. 3 for p55 and Fig. 4 for p66), and (C) triclinic unit cell with $a \sim b \sim c$ ($\alpha \sim \gamma = 62°$, $\beta = 90°$ for p55 and $\alpha = 80°$, $\gamma = 63°$, $\beta = 116.6°$ for p66) in which one polymer chain is put toward two of the adjacent unit cells (see Fig. 5 for p55 and Fig. 6 for p66). In all these three cases, unit cell has just one C_{60} unit in a part of the fused polymer chains of either p55 or p66. In addition to these three cases, we assume (D) double-size nearly haxagonal unit cell with $a = b$, $c \sim 2a$, $\alpha = \beta = 90°$

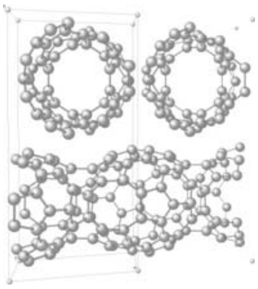

Fig. 7. Geometry of (D) double-size nearly haxagonal unit cell with $a = b$, $c \sim 2a$, $\alpha = \beta = 90°$ and $\gamma = 63.3°$, in which p66 is put parallel to the rhombic (hexagonal) axes alternately.

Table 1. Cartesian components (in units of Å) of the primitive lattice vectors ***a***, ***b*** and ***c*** of each polymer geometry. a_y and a_z are zero except for $a_y = -0.1$ of (B) p66 and $a_y = -0.2$ of (D) p66.

	a	***b***			***c***		
	a_x	b_x	b_y	b_z	c_x	c_y	c_z
(A) p55	8.6	0.0	9.0	0.0	0.0	4.5	7.8
(A) p66	8.7	0.0	9.0	0.0	0.0	4.5	7.8
(B) p55	8.5	4.9	8.7	0.0	0.0	0.0	8.8
(B) p66	8.6	4.9	8.5	0.0	0.0	0.0	8.9
(C) p55	8.5	4.3	7.4	4.6	0.0	0.0	9.1
(C) p66	8.6	4.4	7.5	4.2	−4.3	−0.2	8.5
(D) p66	8.7	4.2	7.7	0.0	0.0	0.0	16.2

and $\gamma = 63.3°$ in which p66 is put parallel to the rhombic (hexagonal) axes alternately (see Fig. 7).

The structure (A) has an interchain geometry such that all chains are triangularly close packed in the plane perpendicular to the chain axis. However, as seen in Figures 1 and 2, the thick equator of one chain adjoins the thick equator of the other chain, and the thin equator of one chain adjoins the thin equator of the other. The structure (B) has an interchain geometry such that the thick equator of one chain adjoins the thin equator of the other chain as seen in Figures 3 and 4, although it forms a square lattice in the plane perpendicular to the chain axis. The structure of (C) shown in Figures 5 and 6 can be realized if all C_{60} molecules in the original fcc C_{60} crystal are connected each other with changing the unit cell geometry. The structure (D) is an alternate stack of the p66 polymer chains. The optimized size of the unit cells are summarized in Table 1.

3 Results

The resulting band structure for (A) monoclinic (hexagonal) unit cell with a polymer chain perpendicular to the rhombus (hexagonal) plane is shown in Figure 8 for p55 and in Figure 9 for p66; (B) monoclinic (hexagonal) unit cell with a polymer chain parallel to one of the rhombus (hexagonal) axes is shown in Figure 10 for p55 and in Figure 11 for p66; (C) triclinic unit cell with a polymer chain toward two adjacent unit cells is shown in Figure 12 for p55 and in Figure 13 for p66; and (D) double-size

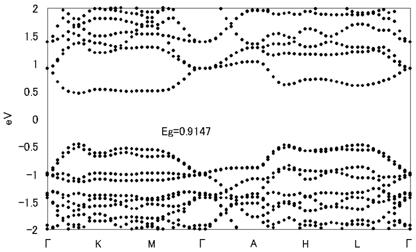

Fig. 8. Resulting energy bands of (A) hexagonal unit cell, in which p55 is put perpendicular to the hexagonal plane.

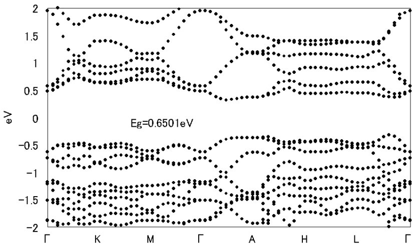

Fig. 9. Resulting energy bands of (A) hexagonal unit cell, in which p66 is put perpendicular to the hexagonal plane.

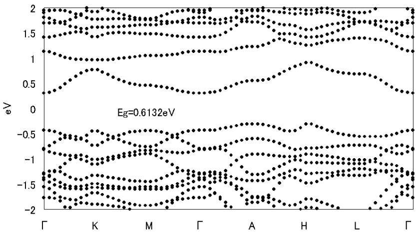

Fig. 10. Resulting energy bands of (B) hexagonal unit cell, in which p55 is put parallel to one of the hexagonal axes.

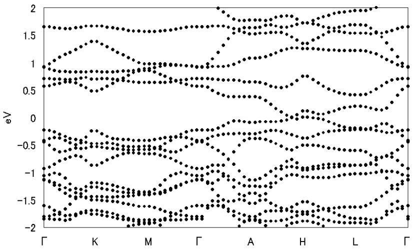

Fig. 11. Resulting energy bands of (B) hexagonal unit cell, in which p66 is put parallel to one of the hexagonal axes.

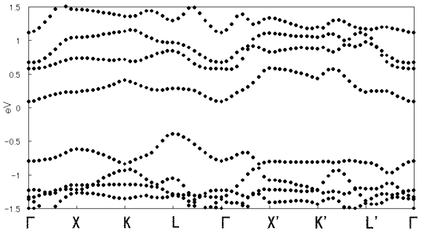

Fig. 12. Resulting energy bands of (C) triclinic unit cell, in which p55 is put toward two of the adjacent unit cells.

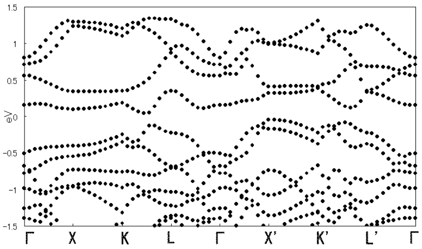

Fig. 13. Resulting energy bands of (C) triclinic unit cell, in which p66 is put toward two of the adjacent unit cells.

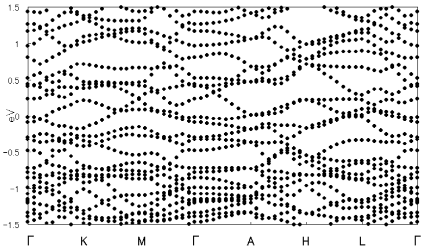

Fig. 14. Resulting energy bands of (D) double-size nearly haxagonal unit cell, in which p66 is put parallel to the rhombic (hexagonal) axes alternately.

Table 2. Energy gap and total energy of the calculated systems.

	energy gap	total energy/carbon atom
(A) p55	0.92 eV	−9.7620 eV
(A) p66	0.65 eV	−9.7157 eV
(B) p55	0.61 eV	−9.7731 eV
(B) p66	zero gap	−9.7327 eV
(C) p55	0.53 eV	−9.7787 eV
(C) p66	0.18 eV	−9.7348 eV
(D) p66	zero gap	−9.7066 eV

nearly haxagonal unit cell with two p66 polymers parallel to the rhombic (hexagonal) axes alternately is shown in Figure 14.

The result is either semiconductor with band gap or metal without band gap as summarized in Table 2. Comparing p55 and p66 in the same unit cell geometry, the energy gap of p55 is wider than p66. The metallic behavior is only observed for p66 for the unit geometries, (B) and (D).

For both p55 and p66, it is seen in Table 2 that the structure (C) has the lowest total energy. In this structure, the shortest distance between the adjacent polymer chains, which is in the direction of shorter diagonal of a rhombic unit cell boundary surface, becomes much shorter than the other interchain distance in the direction of longer diagonal of a rhombic unit cell boundary surface. Hence, in this structure, the polymer chains are not all mutually connected three-dimensionally but connected only two-dimensionally, and the energy gap is small but nonzero.

For the other structures (B) and (D), the connection between polymer chains is three-dimensional, and therefore the energy gap can be further small. In particular, for p66, the structure (C) is gapless and its total energy is only very slightly higher than the lowest energy structure of (B).

Although the structures assumed here are not identical to the structures realized experimentally, the present results may serve a hint to understand the experimental results of metallic current-voltage characteristics [2] and valence photoelectron spectra [5]. Experimentally, by the electron-beam irradiation, C_{60} molecules form fused connections in three-dimensional array. The structure may be energetically higher but the energy gap is zero due to the three-dimensional links among polymer chains.

4 Discussions

Although detailed comparison between the present theory and experiments is left for the future study, our results can explain the metallic behavior observed by the experiment [2]. In our recent work [5], in situ photoelectron spectra of a peanut-shaped C_{60} polymer showed that the density-of-states (DOS) of the polymer came across the Fermi edge and the DOS shape is quite similar to that of quasi-one-dimensional materials with a metallic phase [9]. Accordingly, the quasi-one-dimensional peanut-shaped C_{60} polymer with a cross-linkage consisting of eight-membered rings (p66), as shown in Figure 4, is a candidate to explain the metallic behaviors observed by the experiments [2,5]. A more detail discussion including the first-principles results of several other structures under zero pressure and the comparison with experiments will be given in our future publication [10].

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