

## Dimensional Dependence of Electronic Structure of Fullerene Polymers

Sho Ueda,<sup>†</sup> Kaoru Ohno,<sup>\*,†</sup> Yoshifumi Noguchi,<sup>†</sup> Soh Ishii,<sup>†</sup> and Jun Onoe<sup>\*,§</sup>

Department of Physics, Yokohama National University, 79-5 Tokiwadai, Yokohama 240-8501, Japan,  
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1 Ookayama,  
Tokyo 152-8550, Japan, and Japan Science and Technology Agency (JST), 4-1-8 Honmachi,  
Kawaguchi, Saitama 332-0012, Japan

Received: June 4, 2006; In Final Form: August 18, 2006

Fullerene polymers made of C<sub>60</sub> are systematically investigated by means of a first-principles pseudopotential approach within the local density approximation of the density functional theory. We assume 10 different structures of fullerene polymers. The first three are C<sub>60</sub> polymer networks cross-linked by [2+2] cycloaddition four-membered rings, and the other seven are composed of peanut-shaped fused C<sub>60</sub> polymer chains cross-linked by either seven-membered rings or eight-membered rings. Owing to the overlap of wave functions as well as the hybrid networks of sp<sup>2</sup>-like (3-fold coordinated) and sp<sup>3</sup>-like (4-fold coordinated) carbon atoms, the electronic structure is considerably different from each other. We find that the resulting electronic structure is either semiconductor or semimetal depending on the spatial dimensionality of materials.

## 1. Introduction

Recently, carbon nanomaterials such as fullerene polymers as well as carbon nanotubes have attracted considerable interest both experimentally and theoretically. The most abundant C<sub>60</sub> or other fullerene molecules consist of sp<sup>2</sup> bonds between carbon atoms, and have a zero-dimensional (0D) carbon network, which is quite different from two-dimensional (2D) graphite or three-dimensional (3D) diamond structures. If assembled fullerenes have a one-dimensional (1D) or higher dimensional network architecture, their electronic structure becomes further different from that of an isolated fullerene molecule.

Historically, the possibility of polymerization of C<sub>60</sub> has been investigated in several kinds of C<sub>60</sub> samples. For example, in alkali-metal-doped C<sub>60</sub> such as A C<sub>60</sub> with A = K, Rb, Cs, the existence of a linear polymer network of C<sub>60</sub> was reported by Stephens et al.<sup>1</sup> Here, it was expected that every two facing double bonds form an intermolecular four-membered ring called the [2+2] cycloaddition. Also, by applying visible or ultraviolet (UV) light,<sup>2</sup> electron beam from the STM tip,<sup>3</sup> or mechanical pressure,<sup>4,5</sup> the possibility of polymerization of C<sub>60</sub> was reported.

The experimental and theoretical aspects of the electronic structures of polymerized fullerene structures under pressure were reported in detail by Núñez-Regueiro et al.<sup>6</sup>

Quite recently, one of the authors (J.O.) confirmed experimentally that fullerene polymers exhibiting semiconducting behavior can be created by exposing the C<sub>60</sub> film under UV–visible irradiation.<sup>7</sup> In addition to this, fullerene polymers exhibiting metallic behavior can be created by exposing the C<sub>60</sub> film under electron-beam (EB) irradiation.<sup>8</sup> These properties are considerably different from those of the original C<sub>60</sub> crystal. Such irradiated samples would have many fused fullerene networks as well as [2+2] cycloaddition bonds.

In the theoretical aspect, Okada et al.<sup>9</sup> investigated the electronic structure of quasi-2D [2+2] cycloaddition C<sub>60</sub>

polymers in rhombohedral and tetragonal unit cells from first principles within the local density approximation (LDA) of the density functional theory. Their result showed a semiconducting behavior with an energy gap (0.35 eV for a rhombohedral structure and 0.72 eV for a tetragonal structure) smaller than that of the original face-centered cubic (fcc) or simple cubic (sc) C<sub>60</sub> crystals (~1.1 eV).<sup>9,10</sup> Since these energy gaps are calculated within the LDA as in the present study, they are certainly underestimations of real systems. Slightly later, Cabrera-Trujillo and Robles<sup>13</sup> investigated planar fullerene clusters of up to 7 C<sub>60</sub> molecules cross-linked by [2+2] cycloaddition bonds in semiempirical AM1 and PM3 approaches and suggested that the energy gap decreases as the cluster size increases. On the other hand, peanut-shaped C<sub>60</sub> dimers were first proposed by Strout et al.<sup>11</sup> Then, one of the authors (J.O.) and co-workers<sup>12</sup> investigated peanut-shaped C<sub>60</sub> dimers by means of the tight-binding molecular dynamics and compared the resulting infrared modes with their experimental data. More recently, using a semiempirical electronic Hamiltonian, Berber et al.<sup>14</sup> investigated several rigid crystalline phases of polymerized fullerenes and obtained both metallic and nonmetallic behaviors according to the structures. Quite recently, using an ab initio self-consistent field crystal orbital (F-CO) approach, Wang et al. calculated the electronic structure of 1D fused C<sub>60</sub> polymers (peanut-shaped carbon nanotubes) and obtained band structures indicating semiconductor or metal according to the cross-linking structure.<sup>15</sup> 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 nonmetallic 1D fused C<sub>60</sub> polymers metallic has not yet been scrutinized. In this sense, a systematic first-principles study on the spatial dimensionality of fullerene polymer arrays is highly desired.

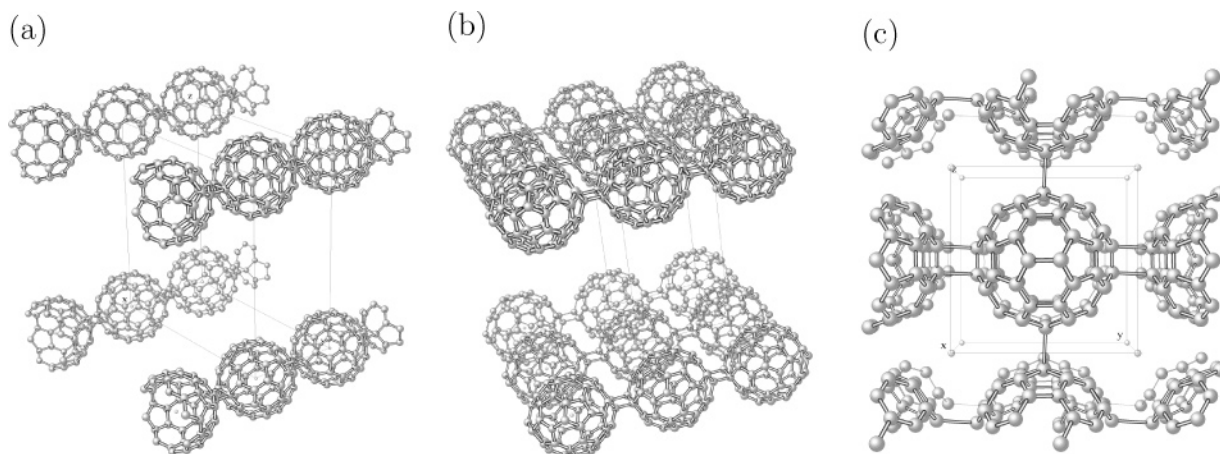
In the present study, we analyze the electronic structure of different types of C<sub>60</sub> polymers by means of a first-principles pseudopotential approach. Here we consider fullerene polymers with three kinds of cross-links. One is the cross-link via [2+2] cycloaddition four-membered rings between nonfused C<sub>60</sub>

\* Address correspondence to this author.

<sup>†</sup> Yokohama National University.

<sup>‡</sup> Tokyo Institute of Technology.

<sup>§</sup> Japan Science and Technology Agency.



**Figure 1.** Assumed structure of the (a) 1D, (b) 2D, and (c) 3D polymers cross-linked by [2+2] cycloadditional four-membered rings.

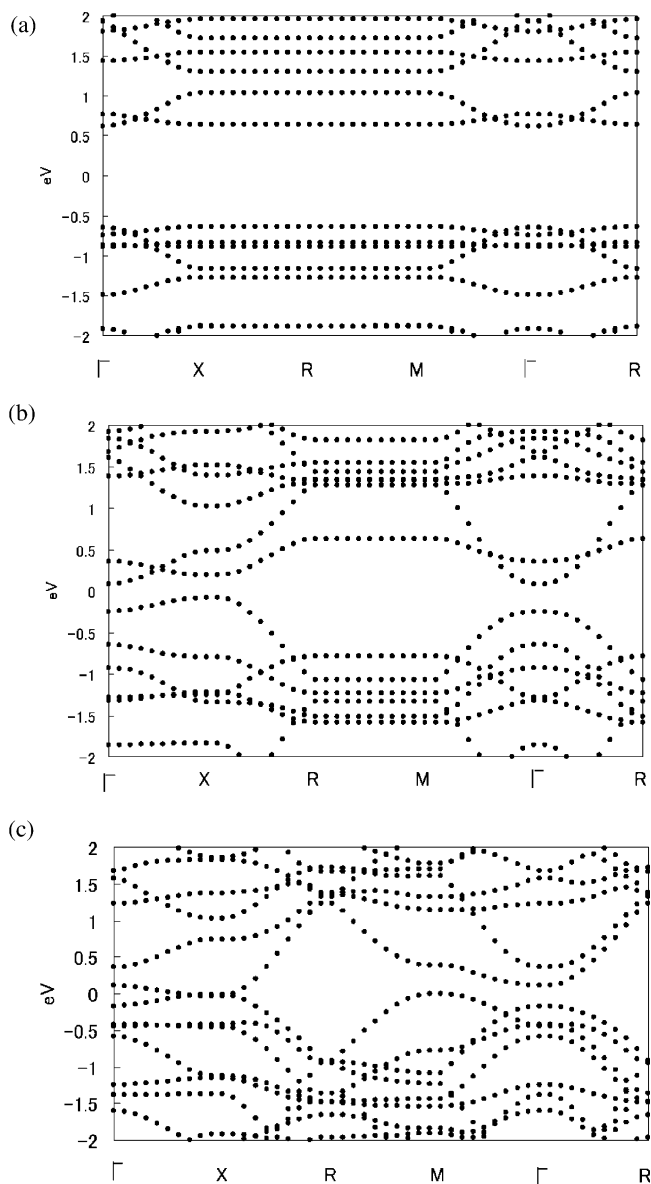
molecules. The other two are the fused (peanut-shaped) cross-links via either seven-membered rings or eight-membered rings. As discussed by Wang et al.,<sup>15</sup> the present two structures (T5 and T6 in their notation) are energetically most stable among possible peanut-shaped polymers cross-linked by either seven-membered rings or eight-membered rings and can be considered to be most easily created by the electron-beam irradiation.

For these three different types of cross-links, we first consider 1D polymer network structures in a large wide tetragonal periodic supercell. Then to realize 2D and 3D structures, we compress this periodic supercell under pressure in one or two directions perpendicular to the chain axis, making the unit cell small long tetragonal and small simple cubic (sc), respectively, for the 2D and 3D structures. In the case of [2+2] cycloadditional links, 2D and 3D network structures are realized in this way, while in cases of the other fused (peanut-shaped) links, 1D polymer chains are densely packed in two or three dimensions; they partly have a multidimensional network. In this way, we consider altogether nine different structures of fullerene polymers. The compressed structures realized in this way can provide information on the clear dimensional dependence. In addition to them, just for a 3D structure of peanut-shaped polymers cross-linked by eight-membered rings, we perform a first-principles structural optimization involving also the unit cell structure (in this case, the external pressure becomes rigorously zero), and calculate its electronic structure to demonstrate the irrelevance of the external compression in our result. The present analysis is relevant to the experimental situations of the electron-beam irradiation to the fcc C<sub>60</sub> crystal, because 2D and 3D structures are at least partly realized in the samples. The main purpose of this paper is to investigate how their electronic structure depends on the spatial dimensionality of the C<sub>60</sub> polymer array structures.

The rest of this paper is organized as follows: In section 2, we briefly describe the method we used in this study and then present our results for the three kinds of cross-links separately. In each subsection, we show the geometries and the resulting energy bands of the 1D, 2D, and 3D structures for one type of cross-link. The discussion including a comparison with previous calculations and our result of a structural optimization including the unit cell is given in section 3. The last section (section 4) is devoted to concluding this paper.

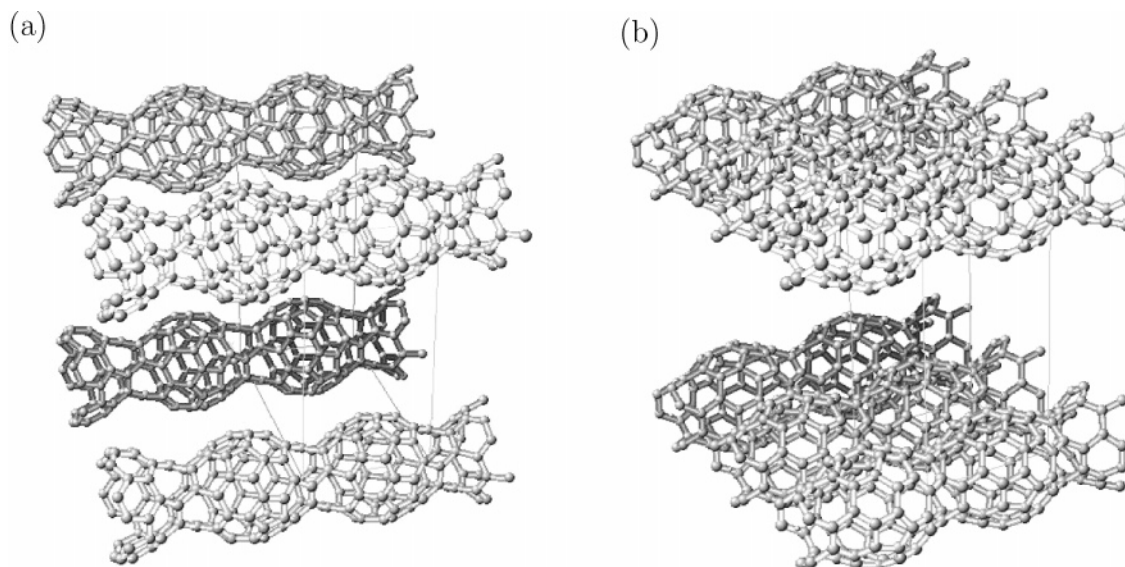
## 2. Calculations and Results

Throughout this paper, we use the plane-wave method (Vienna ab initio simulation package, VASP)<sup>16–19</sup> with Vander-

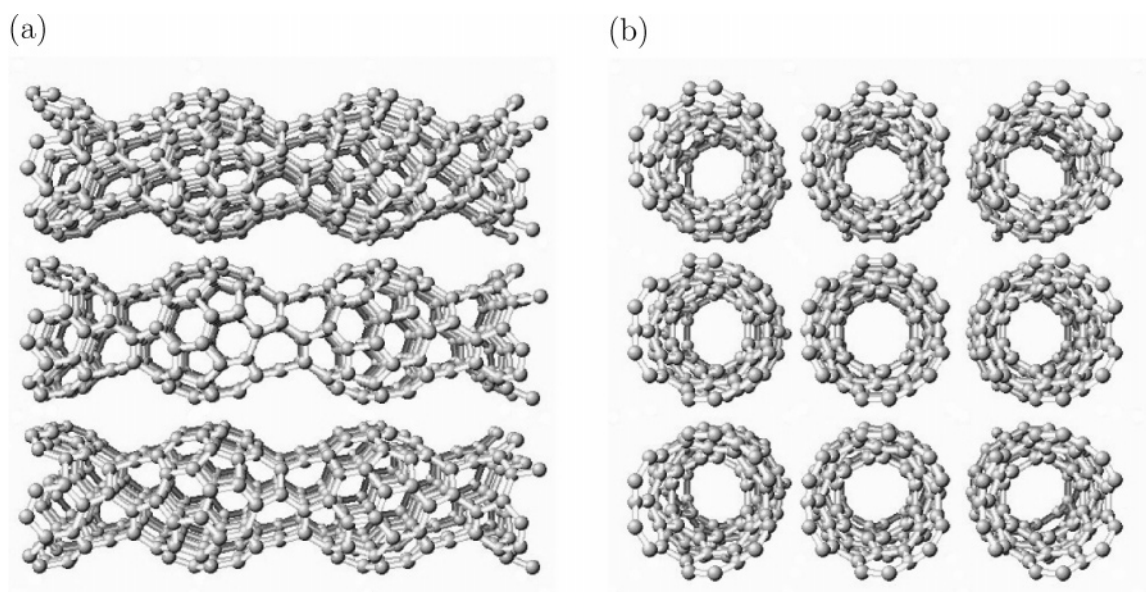


**Figure 2.** Calculated energy band of (a) 1D, (b) 2D, and (c) 3D polymers cross-linked by [2+2] cycloadditional four-membered rings shown in Figure 1.

bilt ultrasoft pseudopotentials<sup>20</sup> on the basis of the LDA. The Ceperley-Alder<sup>21</sup> form fitted by Perdew and Zunger<sup>22</sup> is used for the exchange correlation potential. Cutoff energy for plane



**Figure 3.** Assumed structure of (a) 1D and (b) 2D structures of peanut-shaped polymers cross-linked by seven-membered rings.



**Figure 4.** Assumed structure of 3D structures of peanut-shaped polymers cross-linked by seven-membered rings: (a) a side view and (b) a view of the cross section of this structure.

waves is set to be 286.6 eV. The number of  $k$ -points is  $4 \times 4 \times 4$ . For all the structures assumed, we perform structural optimization and then calculate their energy band structure.

**2.1. Fullerene Polymers Cross-Linked by [2+2] Cycloadditional Four-Membered Rings.** The three structures considered here are as follows: First is the dumbbell-shaped 1D structure shown in Figure 1a, which has the cross-links involving [2+2] cycloadditional four-membered rings and connecting the double bonds of  $C_{60}$  molecules. The unit cell is tetragonal, and its size is  $9.068 \times 19.628 \times 19.628 \text{ \AA}^3$ . The C–C distance between adjacent polymer chains is about 13 Å. Second is the 2D structure shown in Figure 1b. It is realized by reducing the length of one supercell edge perpendicular to the 1D polymer axis. The unit cell is also tetragonal, but its size is smaller and  $9.068 \times 9.068 \times 19.628 \text{ \AA}^3$ . The C–C distance between two adjacent polymer sheets in this 2D structure is also about 13 Å. Third is the 3D structure shown in Figure 1c. This structure is repeated by a sc unit cell with the lattice constant of 9.068 Å. A complete 3D network is realized in this structure.

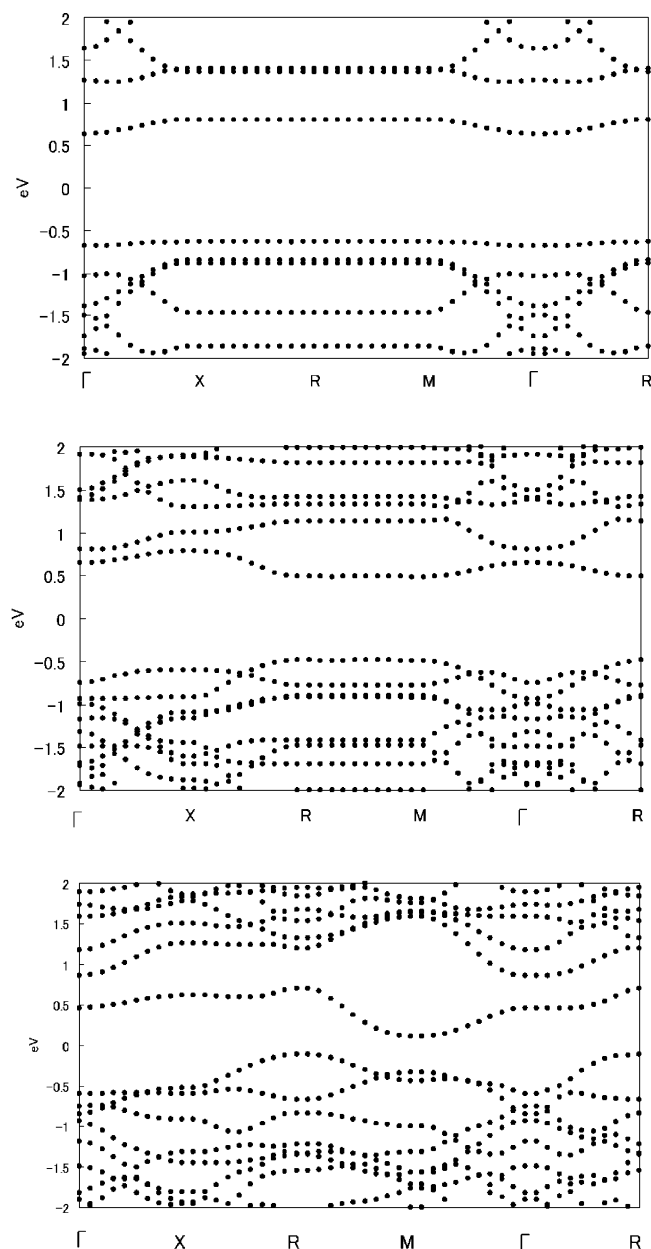
The calculated energy bands of these fullerene polymers are shown in Figure 2, where the energy zero is located at the Fermi level.

In the case of the isolated 1D polymer (Figure 1a), the band structure is shown in Figure 2a. Both the valence and conduction bands are found to be flat near the X, R, and M points. Obviously, the vacuum space in the two (mutually orthogonal) interchain directions causes this flat band structure. The energy gap is about 1.25 eV.

In the case of the isolated 2D polymer (Figure 1b), the band structure is shown in Figure 2b. The valence band top and the conduction band bottom approach each other near the X and  $\Gamma$  points. An indirect gap between the top of the valence band (X point) and the bottom of the conduction band ( $\Gamma$  point) is about 0.16 eV, showing a semiconductor.

In the case of the 3D polymer (Figure 1c), we find from Figure 2c that the valence and conduction bands overlap near the X points, and that this 3D polymer can be identified to be a semimetal. The band structure is quite different from that of





**Figure 5.** Calculated energy band of (a) 1D, (b) 2D, and (c) 3D structures of peanut-shaped polymers cross-linked by seven-membered rings shown in Figures 3 and 4.

the sc  $C_{60}$  crystal;<sup>10</sup> band dispersions are much larger in the present case. In particular, a large band dispersion is observed in both valence and conduction bands near the R point. It is interesting to say that this polymer behaves as a semimetal despite its loosely packed simple cubic lattice structure.

**2.2. Fullerene Polymers Cross-Linked by Seven-Membered Rings.** The three structures we consider next are the peanut-shaped polymers cross-linked by seven-membered rings together with six-membered rings. The 1D structure is shown in Figure 3a. The size of the unit cell is  $8.619 \times 17.238 \times 17.238 \text{ \AA}^3$  in this 1D case. The C–C distance between adjacent polymers is about 11 Å. The 2D structure is shown in Figure 3b. It is realized by reducing the length of a unit cell edge in a direction perpendicular to the polymer axis. In this 2D structure, the fused links with seven-membered rings exist only in one direction. The unit cell is tetragonal and its size is  $8.619 \times 8.619 \times 17.238 \text{ \AA}^3$ . The distance between adjacent polymerized planes in this 2D structure is 17.238 Å. The 3D structure is shown in Figure 4. In this 3D structure also, the links exist only in one

direction. They are repeated by the sc unit cell of  $8.619 \times 8.619 \times 8.619 \text{ \AA}^3$ . Figure 4b represents a cross section of the 3D structure.

The calculated energy bands of these structures are shown in Figure 5, where the energy zero is located at the Fermi level.

In the case of the isolated 1D peanut-shaped polymer (Figure 3a), it is seen from Figure 5a that the valence and conduction bands are flat near the X, R, and M points. Obviously, the structure with no link in the interchain directions causes this flat band. The energy gap is 1.23 eV. This energy gap is very close to that of the 1D polymer with [2+2] cycloaddition bonds.

In the case of the isolated 2D structure (Figure 3b), the band structure is shown in Figure 5b. The energy gap is 0.97 eV. This energy gap is a little smaller than that of the 1D polymer with the same cross-links, but considerably larger than that of the 2D polymer with [2+2] cycloaddition bonds.

In the case of the 3D structure (Figure 4), it is seen from Figure 5c that the top of the valence band is located at the R point and the bottom of the conduction bands is at the M point. An indirect gap between the top of the valence band (R point) and the bottom of the conduction band (M point) is 0.22 eV. So we identify this 3D structure as a semiconductor. Note that this value of the band gap is considerably smaller than that of the 2D structure having the same kind of cross-linkage.

**2.3. Fullerene Polymers Cross-Linked by Eight-Membered Rings.** The last three structures are also peanut-shaped but have the cross-links involving eight-membered rings together with five-membered rings. The 1D structure is shown in Figure 6a. The size of the unit cell is  $8.717 \times 17.433 \times 17.433 \text{ \AA}^3$  in this case. The C–C distance between adjacent chains is again about 11 Å. Next, the 2D structure is shown in Figure 6b. It is realized by reducing the length of a unit cell edge. In this 2D structure, the fused links involving eight-membered rings exist only in one direction. The unit cell is tetragonal, and its size is given by  $8.717 \times 8.717 \times 17.433 \text{ \AA}^3$ . The distance between adjacent polymerized planes in this 2D structure is 17.433 Å. Last, the 3D structure is shown in Figure 7. Here also the links exist only in one direction. The 1D polymers are repeated by the sc unit cell. The size of the unit cell is  $8.717 \times 8.717 \times 8.717 \text{ \AA}^3$ . Figure 7b represents a cross section of this 3D structure.

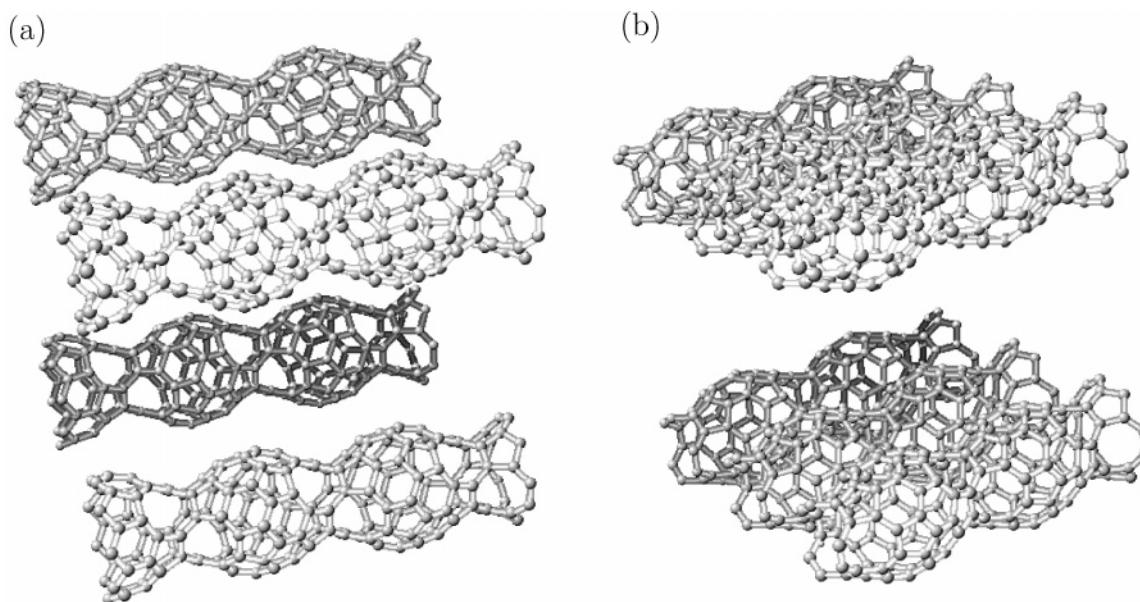
The calculated energy bands of these structures are shown in Figure 8, where the energy zero is located at the Fermi level.

In the case of this isolated 1D peanut-shaped polymer (Figure 6a), we see from Figure 8a that the valence band and the conduction band are flat except near the  $\Gamma$  point. Again, the structure with no link in the interchain directions causes this flat band structure. The energy gap is 1.00 eV. This energy gap is slightly smaller than that of the other two isolated 1D dumbbell-shaped and peanut-shaped fullerene polymers.

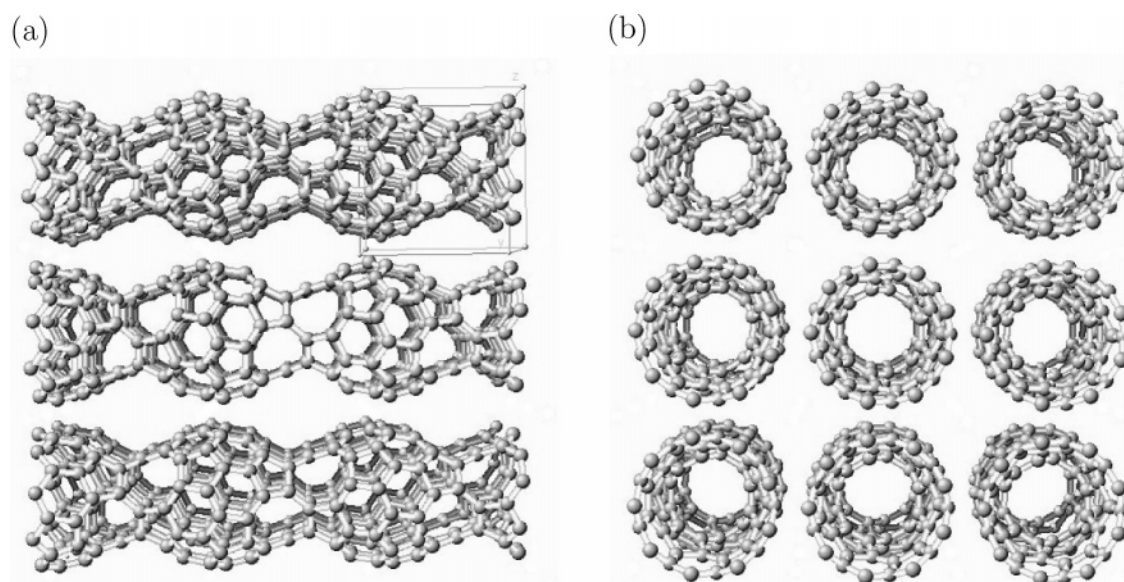
In the case of the 2D structure (Figure 6b), the band structure is shown in Figure 8b. The energy gap is 0.54 eV. This energy gap is smaller than the 2D structure cross-linked by seven-membered rings, and larger than the 2D polymer with [2+2] cycloaddition bonds.

In the case of the 3D structure (Figure 7), we see from Figure 8c that the top of the valence band is near the R point and the bottom of the conduction bands is between the R point and the M point. A fundamental gap between the top of the valence band (R point) and the bottom of the conduction band (between R and M points) is found to be negative, i.e., there is a slight overlap near the Fermi level. So we identify this 3D structure as a semimetal.

The values of the energy gap of these three peanut-shaped polymers cross-linked by eight-membered rings are relatively



**Figure 6.** Assumed structure of (a) 1D and (b) 2D structures of peanut-shaped polymers cross-linked by eight-membered rings.



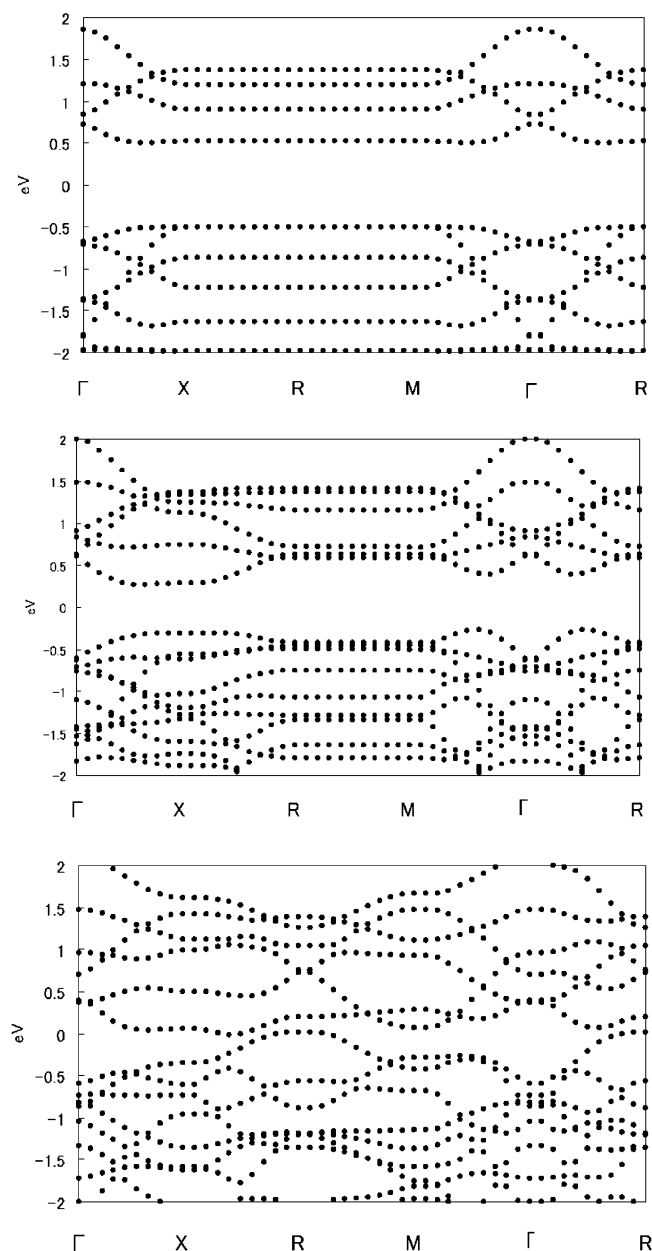
**Figure 7.** Assumed structure of the 3D structure of peanut-shaped polymers cross-linked by eight-membered rings: (a) a side view and (b) a view of the cross section of this structure.

smaller than those of the previous three peanut-shaped polymers cross-linked by seven-membered rings.

### 3. Discussions

The resulting band gap,  $E_g$ , total energy,  $E_{\text{tot}}$ , per 60 carbon atoms relative to an isolated  $\text{C}_{60}$  molecule, and external pressure,  $P$ , are summarized in Tables 1–3. To determine the total energy of an isolated  $\text{C}_{60}$  molecule, we used a simple cubic unit cell of  $19.628 \times 19.628 \times 19.628 \text{ \AA}^3$ , 286.6 eV cutoff energy for the plane waves, and  $4 \times 4 \times 4$   $k$ -points similar to the calculations done for the other structures. Since the LDA usually underestimates the amount of the band gap of semiconductors and insulators at most only about  $2/3$  of the experimental value,<sup>23</sup> the true band gap would become larger than the present results. The resulting values of the band gap  $E_g$  should be compared with that of the fcc or sc  $\text{C}_{60}$  crystals ( $\sim 1.1 \text{ eV}$ ).<sup>9,10</sup> Except for the 1D structures, the resulting band gap energies are all smaller than this value. We find from our result that the band gap energy systematically decreases as the spatial dimensionality increases.

For the 3D structures, both polymers cross-linked by [2+2] cycloadditional four-membered rings and by (peanut-shaped) eight-membered rings exhibit zero gap indicating that they are semimetal. Since the presently assumed 2D and 3D crystalline structures of the  $\text{C}_{60}$  polymers have relatively loose networks among all possible structures within the same spatial dimensionality, one may expect that more densely packed 3D structures would behave more possibly like a metal. Looking at the total energy and the pressure, we find that the presently calculated structures are not energetically most stable, but correspond to either compressed or expanded systems. However, as the estimated external pressure is not very large, these structures may exist in the experimental samples irradiated by electron beams. Indeed, if we perform the first-principles structural optimization including unit cell,<sup>24</sup> we find that, under zero pressure also, the resulting 3D structure cross-linked by eight-membered rings exhibits zero gap for a monoclinic unit cell ( $a = 8.64 \text{ \AA}$ ,  $b = 9.814 \text{ \AA}$ ,  $c = 8.92 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$  and  $\gamma = 60.5^\circ$ ). The resulting optimized geometry is shown in Figure



**Figure 8.** Calculated energy band of (a) 1D, (b) 2D, and (c) 3D structures of peanut-shaped polymers cross-linked by eight-membered rings shown in Figures 6 and 7.

**TABLE 1: The Values of the Obtained Energy Gap,  $\Delta E$ , Total Energy,  $E_{\text{tot}}$ , per 60 Carbon Atoms Relative to an Isolated  $C_{60}$  Molecule, and External Pressure,  $P$ , for the  $C_{60}$  Polymers Cross-Linked by [2+2] Cycloadditional Four-Membered Rings**

	1D	2D	3D
$E_g$ (eV)	1.25	0.16	zero gap
$E_{\text{tot}}$ (eV)	-3.514	-2.867	-2.263
$P$ (GPa)	-0.56	-0.50	0.56

9, while the resulting band structure is shown in Figure 10, in which we find that the top of the valence band and the bottom of the conduction band overlaps near the H point. The total energy per 60 carbon atoms relative to an isolated  $C_{60}$  molecule amounts to  $-2.932$  eV, which is the deepest among all the structures made of the peanut-shaped  $C_{60}$  polymers cross-linked by eight-membered rings (compare this value with those in Table 2). Thus, we conclude that the 3D structures of these peanut-shaped polymers may behave as a semimetal or perhaps a semiconductor with a quite small energy gap.

**TABLE 2: The Values of the Obtained Energy Gap,  $\Delta E$ , Total Energy,  $E_{\text{tot}}$ , per 60 Carbon Atoms Relative to an Isolated  $C_{60}$  Molecule, and External Pressure,  $P$ , for the Peanut-Shaped  $C_{60}$  Polymers Cross-Linked by Seven-Membered Rings**

	1D	2D	3D
$E_g$ (eV)	1.23	0.97	0.22
$E_{\text{tot}}$ (eV)	-5.662	-4.866	-3.696
$P$ (GPa)	-0.94	-0.88	2.86

**TABLE 3: The Values of the Obtained Energy Gap,  $\Delta E$ , Total Energy,  $E_{\text{tot}}$ , per 60 Carbon Atoms Relative to an Isolated  $C_{60}$  Molecule, and External Pressure,  $P$ , for the Peanut-Shaped  $C_{60}$  Polymers Cross-Linked by Eight-Membered Rings**

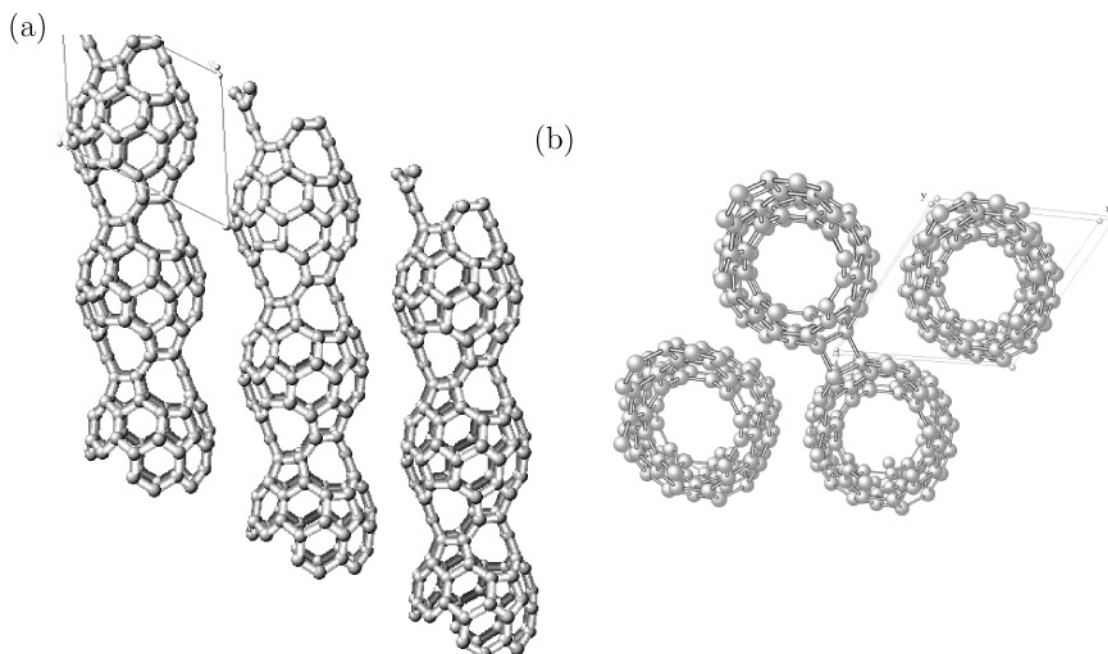
	1D	2D	3D
$E_g$ (eV)	1.00	0.54	zero gap
$E_{\text{tot}}$ (eV)	-2.722	-2.315	-1.949
$P$ (GPa)	-0.88	-1.02	1.19

Let us compare our result with other previous theoretical works in more detail. For the 2D  $C_{60}$  polymer cross-linked by [2+2] cycloadditional bonds, our result can be compared with the previous result for a tetrahedral structure of Okada and Saito.<sup>9</sup> In both calculations, the same LDA exchange-correlation functional is used and the lattice constants are similar (9.068 and 9.09 Å). Both results show finite energy gaps (0.16 and 0.72 eV). Their result for a rhombohedral structure shows a 0.35 eV energy gap. Although there is a slight difference in the values of the energy gap, all the results for the 2D structures show semiconducting behaviors. For the 3D  $C_{60}$  polymers cross-linked by [2+2] cycloadditional bonds, Berber et al.<sup>14</sup> used a semiempirical electronic Hamiltonian and obtained a result such that a body-centered orthorhombic (bco) structure is a metal and a sc structure with the lattice constant of 8.98 Å is a semiconductor with  $E_g = 1.41$  eV (see the first and eighth rows in their Table 1). Although their sc result is different from ours, their bco result is rather comparable to ours. In our calculation, clearly, the 3D network structure causes the strong overlap of the wave function as shown in the partial charge density distributions of the topmost valence band (Figure 11a) and of the lowermost conduction band (Figure 11b), resulting in the strong dispersion of the bands and the zero energy gap.

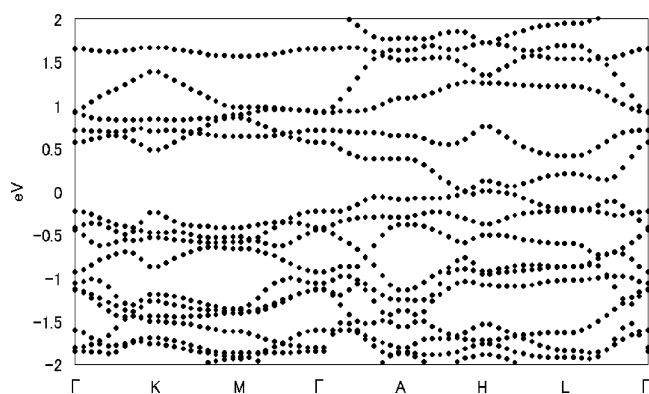
On the other hand, the presently assumed two peanut-shaped  $C_{60}$  polymers (one cross-linked by seven-membered rings and the other cross-linked by eight-membered rings) are identical to T5 and T6 of Wang et al.,<sup>15</sup> although they treated isolated 1D structures only. They calculated the 1D dispersion curves using the SCF-CO method. Both our result for the 1D structure and the result by Wang et al. show finite energy gaps (their results are  $E_g = 2.28$  and 2.04 eV respectively for the polymers cross-linked by seven-membered rings (T5) and eight-membered rings (T6)). The 2D and 3D structures considered in the present work are quite distinct from those considered in these previous works. The resulting very small or zero energy gap is due to the overlap of the wave functions belonging to adjacent  $C_{60}$  polymers in the 3D architectures as well as the hybrid networks of  $sp^2$ -like (3-fold coordinated) and  $sp^3$ -like (4-fold coordinated) carbon atoms.

The 2D and 3D peanut-shaped polymers considered here interact with each other not by van der Waals forces but by weak covalent bonds because the edge length of the unit cell is 8.717 Å and the smallest C–C distance between adjacent polymers is about 1.7 Å. There, a weak cycloadditional four-membered ring is formed between adjacent polymers. In fact,





**Figure 9.** Optimized 3D structure of peanut-shaped polymers cross-linked by eight-membered rings in a monoclinic unit cell: (a) a side view and (b) a view of the cross section of this structure.

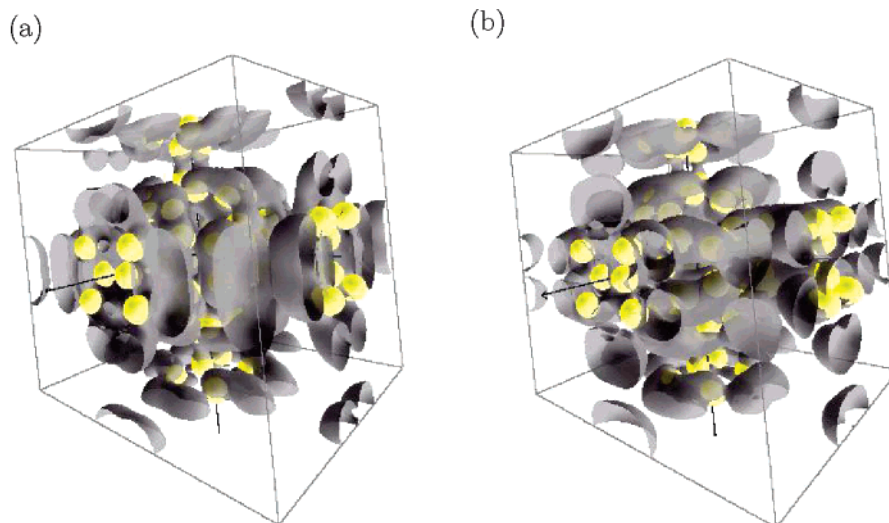


**Figure 10.** Calculated energy band of the optimized 3D structure in a monoclinic unit cell of peanut-shaped polymers cross-linked by eight-membered rings shown in Figure 9.

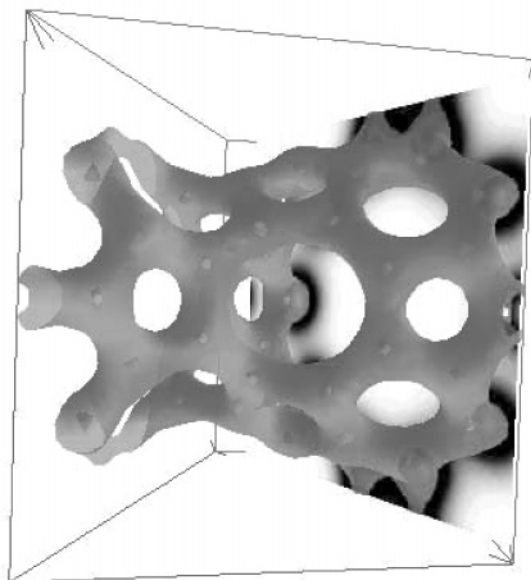
in the cross-section view in Figure 9b, one can clearly see the bonds between adjacent peanut-shaped polymers. (In this

structure, the smallest C—C distance between adjacent polymers is about 1.5 Å.) Figure 12 shows the valence charge density of the optimized 3D structure shown in Figure 9. As seen in this figure, one peanut-shaped polymer is clearly connected by a cycloaddition bond to the other peanut-shaped polymer in the adjacent unit cell. In this sense, the interchain bonds between peanut-shaped polymers are quite similar to those of the [2+2] cycloaddition four-membered rings of the structures considered in section 2.1.

Recently, Reich et al.<sup>25</sup> predicted by LDA calculations that metallic behavior may be observed also in the bundles of carbon nanotubes. The adjacent nanotubes assumed in their 3D structure have, however, a 3.1 Å wall-to-wall distance and are bonded by van der Waals forces. This distance is clearly much larger than the C—C distance (about 1.7 Å) between the peanut-shaped polymers assumed in the present paper. Therefore, the reason of their result showing metallic behavior is fundamentally different from the reason for our result showing metallic



**Figure 11.** The partial charge density distributions of (a) the topmost valence band and (b) the lowermost conduction band of the 3D  $C_{60}$  polymer cross-linked by [2+2] cycloaddition bonds shown in Figure 1c. Small bright spheres indicate the positions of carbon atoms.



**Figure 12.** Calculated electron density inside the monoclinic unit cell of peanut-shaped polymers cross-linked by eight-membered rings shown in Figure 9.

behavior. Ours is clearly due to the cycloadditional bonds between adjacent peanut-shaped polymers.

Although detailed comparison between the present theory and experiments is left for future study, our results can explain the metallic behavior observed by the experiment.<sup>8</sup> In our recent work,<sup>26</sup> 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.<sup>27</sup> Accordingly, the quasi-one-dimensional peanut-shaped  $C_{60}$  polymer with a cross-linkage consisting of eight-membered rings, as shown in Figure 7, is a candidate to explain the metallic behaviors observed by the experiments.<sup>8,26</sup> A more detailed discussion including the first-principles results of several other structures under zero pressure and the comparison with experiments will be given in a future publication.<sup>24</sup>

#### 4. Concluding Remarks

In this paper, we have analyzed the electronic structure of fullerene polymers by using the first-principles pseudopotential approach on the basis of the density functional theory. In the present calculation, we assumed 10 different fullerene polymer assemblies that have three different dimensionalities (1D, 2D, and 3D). The 2D and 3D structures were made respectively from the 1D and 2D structures by shrinking the lattice constant of the tetrahedral supercell. We have considered three different kinds of cross-links ([2+2] cycloadditional link and fused links with either seven- or eight-membered rings). We found that the resulting band structure of these fullerene polymers is strongly dependent on the spatial dimensionality of the polymer array structure. The result also gives a clear distinction between different cross-linkage structures. The common feature of our results can be summarized as follows: The 1D fullerene

polymers behaving as a semiconductor are still semiconductor in 2D array, but may be either semiconductor or semimetal in 3D array. Comparing the peanut-shaped polymers, the energy gap of the polymers cross-linked by eight-membered rings is smaller than that of the polymers cross-linked by seven-membered rings. The former energy gap is comparable to that of the polymers cross-linked by [2+2] cycloadditional four-membered rings. The present study may shed a light on the classification of various experimentally realized fullerene polymers.

**Acknowledgment.** This work has been partly supported by the Grant-in-Aid for scientific research B (Grant No. 17310067) from the Japan Society for the Promotion of Science (JSPS).

#### References and Notes

- (1) Stephens, P. W.; Bortel, G.; Faigel, G.; Tegze, M.; Jánossy, A.; Pekker, S.; Oszlany, G.; Forró, L. *Nature* **1994**, *370*, 636–639.
- (2) Rao, A. M.; Zhou, P.; Wang, K.-A.; Hager, G. T.; Holden, J. M.; Wang, Y.; Lee, W.-T.; Bi, X.-X.; Eklund, P. C.; Cornett, D. S.; Duncan, M. A.; Amster, I. J. *Science* **1993**, *259*, 955–957.
- (3) Zhao, Y. B.; Poirier, D. M.; Pechman, R. J.; Weaver, J. H. *Appl. Phys. Lett.* **1994**, *64*, 577–579.
- (4) Iwasa, Y.; Arima, T.; Fleming, R. M.; Siegrist, T.; Zhou, O.; Haddon, R. C.; Rothberg, L. J.; Lyons, K. B.; Carter, H. L., Jr.; Hebard, A. F.; Tycko, R.; Dabbagh, G.; Krajewski, J. J.; Thomas, G. A.; Yagi, T. *Science* **1994**, *264*, 1570–1572.
- (5) Núñez-Regueiro, M.; Marques, L.; Hodeau, J.-L.; Béthoux, O.; Perroux, M. *Phys. Rev. Lett.* **1995**, *74*, 278–281.
- (6) Núñez-Regueiro, M.; Marques, L.; Hodeau, J.-L.; Xu, C. H.; Scuseria, G. E. *Polymerized Fullerite Structures, Experiments and Theory. In Fullerene Polymers and Polymer Composites*; Springer Series in Materials Science; Eklund, P. C., Rao, A. M., Ed.; Springer: Berlin, Germany, 2000; Vol. 38, pp 241–264.
- (7) Onoe, J.; Nakayama, T.; Aono, M.; Hara, T. *J. Appl. Phys.* **2004**, *96*, 443–445.
- (8) Onoe, J.; Nakayama, T.; Aono, M.; Hara, T. *Appl. Phys. Lett.* **2003**, *82*, 595–597.
- (9) Okada, S.; Saito, S. *Phys. Rev. B* **1999**, *59*, 1930–1936.
- (10) Ohno, K.; Maruyama, Y.; Takahashi, M.; Yu, J.-Z.; Gu, B.-L.; Kawazoe, Y. *Surf. Rev. Lett.* **1996**, *3*, 735–740.
- (11) Strout, D. L.; Murry, R. L.; Xu, C.; Eckhoff, W. C.; Odom, G. K.; Scuseria, G. E. *Chem. Phys. Lett.* **1993**, *214*, 576–582.
- (12) Onoe, J.; Hashi, Y.; Esfarjani, K.; Hara, T.; Kawazoe, Y.; Takeuchi, K. *Chem. Phys. Lett.* **1999**, *315*, 19–24.
- (13) Cabrera-Trujillo, J. M.; Robles, J. *Phys. Rev. B* **2001**, *64*, 165408; 1–6.
- (14) Berber, S.; Osawa, E.; Tománek, D. *Phys. Rev. B* **2004**, *70*, 085417; 1–6.
- (15) Wang, G.; Li, Y.; Huang, Y. *J. Phys. Chem. B* **2005**, *109*, 10957–10961.
- (16) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558–561.
- (17) Kresse, G.; Hafner, J. *Phys. Rev. B* **1994**, *49*, 14251–14269.
- (18) Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15–50.
- (19) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186.
- (20) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892–7895.
- (21) Ceperley, D. M.; Alder, B. J. *Phys. Rev. Lett.* **1980**, *45*, 566–569.
- (22) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048–5051.
- (23) Ohno, K.; Esfarjani, K.; Kawazoe, Y. *Computational Materials Science*; Springer Series in Solid State Sciences; Springer-Verlag: Berlin, Germany, 1999; Vol. 129.
- (24) Onoe, J.; Itoh, T.; Kimura, S.; Ueda, S.; Noguchi, Y.; Ohno, K. Submitted to *Phys. Rev. B*.
- (25) Reich, R.; Thomsen, C.; Ordejón, P. *Phys. Rev. B* **2002**, *65*, 155411; 1–11.
- (26) Onoe, J.; Nakao, A.; Hida, A. *Appl. Phys. Lett.* **2004**, *85*, 2741–2743.
- (27) Dardel, B.; Malterre, D.; Grioni, M.; Wiebel, P.; Baer, Y.; Levy, F. *Phys. Rev. Lett.* **1991**, *67*, 3144–3147.