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Electronic structure of metallic rhombohedral C_{60} polymers

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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.

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I. INTRODUCTION

Polymerized phases of C_{60}s 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[1–5] and drastically modulate electron states of the C_{60} unit.[6,7] 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,[1] alkaline-atom-induced,[2] and pressure-induced[3–5] 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.[8,9] Three different types of the polymerized phases have been experimentally synthesized under moderate hydrostatic pressure at elevated temperature.[3–5] 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.[6,7] Furthermore, the electronic structures of these phases are considerably different from that of a face-centered cubic phase of C_{60} fullerite[10] due to the presence of the sp^3-like carbon atoms which modulate network topologies of π-electron system.[11–13]

Recently, anisotropic metallic properties were reported on highly oriented rhombohedral C_{60} polymer.[14,15] Furthermore, possible ferromagnetic spin ordering was also reported on the rhombohedral C_{60} polymers.[16] These results are obviously inconsistent with the previous electronic structure calculations.[6,7] 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 clarifies 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).[17,18] 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.[19,20] Norm-conserving pseudopotentials generated by using the Troullier-Martins scheme are adopted to describe the electron-ion interaction.[21,22] 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.[21,23] We adopt the conjugate-gradient minimization scheme both for the electronic structure calculation and for

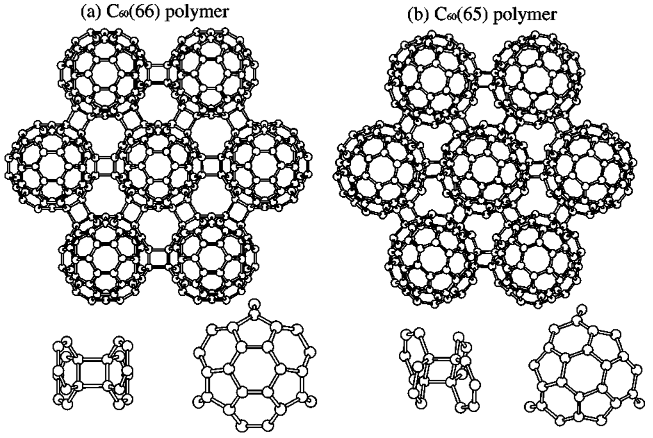


FIG. 1. Optimized geometries of each polymerized layer of (a) $C_{60}(66)$ polymer and (b) $C_{60}(65)$ polymer. Bottom of left in each figure shows the atomic structure at the interfullerene covalent bonds. Bottom right in each figure shows network geometries of sp^2-like (threefold coordinated) carbon atoms.

the geometry optimization.[24] 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 $C_{60}(66)$ polymer reported by Núñez-Regueiro [Fig. 1(a)], polymerization is attained via formation of the four-membered ring from two

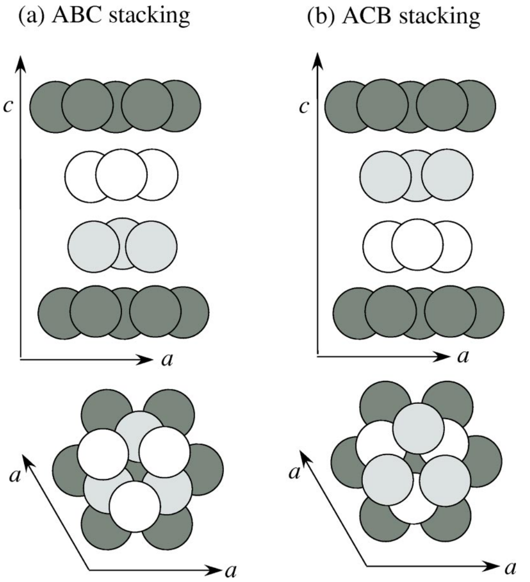
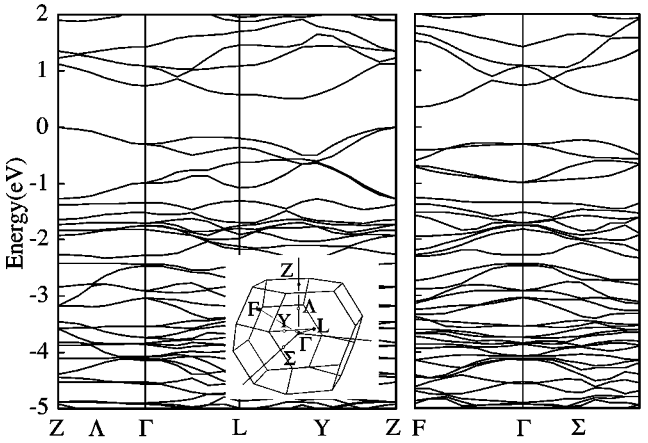


FIG. 2. Schematic side and top views of the rhombohedral polymers with (a) the *ABC*-stacking and (b) the *ACB*-stacking structures. Dark shaded, pale shaded, and white circles denote the C_{60} molecules belonging in *A*, *B*, and *C* polymerized layers, respectively.

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.

	Total energy (eV)
$C_{60}(66)$ *ABC* stacking	0.428
$C_{60}(66)$ *ACB* stacking	0.428
$C_{60}(65)$ *ABC* stacking	0.702
$C_{60}(65)$ *ACB* stacking	0.719
fcc	0.427

(a) $C_{60}(66)$ ABC stacking



(b) $C_{60}(66)$ ACB stacking

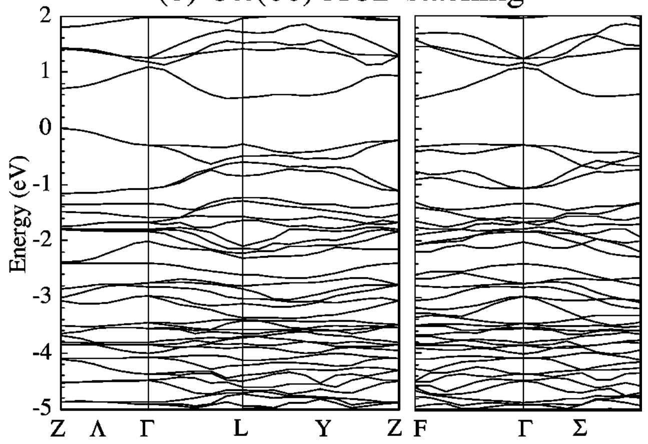


FIG. 3. Electronic energy bands of (a) the *ABC*-stacking[6] and (b) the *ACB*-stacking $C_{60}(66)$ polymers. Energies are measured from the top of the valence band at *Z* point. Symmetry points and lines in the first Brillouin zone of the rhombohedral lattice are shown in inset.

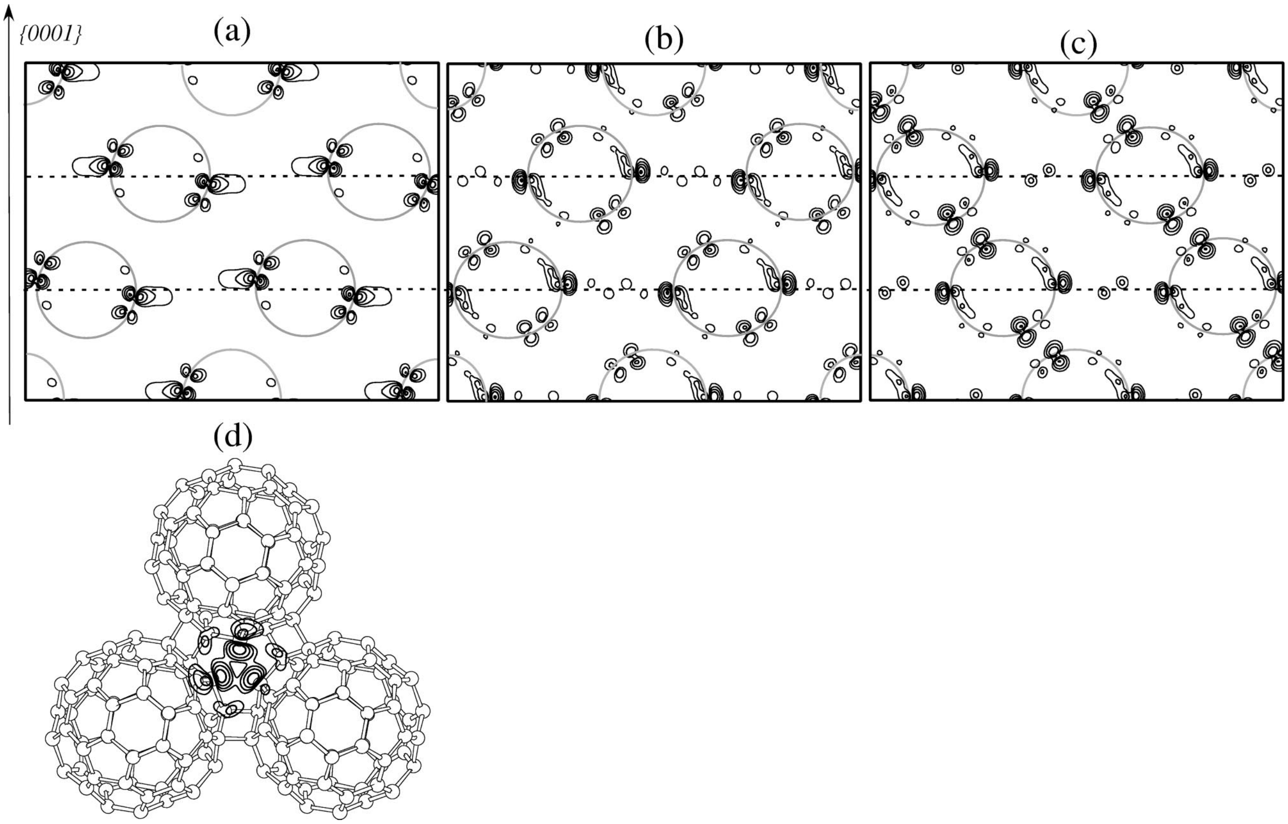


FIG. 4. (a) Contour plot on the $[2\bar{1}\bar{1}0]$ plane of the squared wave function of the lowest unoccupied state of the rhombohedral $C_{60}(66)$ polymer with the *ACB*-stacking at the Γ point. Contour plots on the $[2\bar{1}\bar{1}0]$ plane of the squared wave function around the E_F of the rhombohedral $C_{60}(65)$ polymers with (b) the *ABC*-stacking and (c) the *ACB*-stacking structures. The circles and dashed lines denote the C_{60} molecules and polymerized planes, respectively. (d) Contour plot on [0001] plane of the wave function around the E_F of the rhombohedral C_{60} polymers of the *ABC* stacking. Each contour represent twice (or half) the density of the adjacent contour lines. The lowest-density contour represents 0.03 $e/\text{a.u.}^3$.

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 C_{60} (65) polymers hereafter. The 65 bond is classified as the single bond on the C—C network in the C_{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.

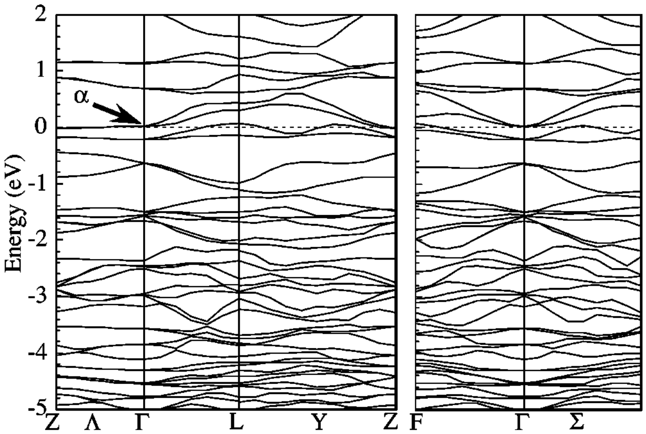
A. $C_{60}(66)$ polymer

We study the stability and the electronic structure of the $C_{60}(66)$ polymer with the *ABC*-stacking structure. Our previous local-density approximation (LDA) calculation has shown that the *ABC*-stacking $C_{60}(66)$ polymer is a semiconductor with narrow indirect energy gap and the polymerized structure is energetically as stable as the fcc C_{60}.[6,7] In this section, we clarify the electronic structure and the stability of the $C_{60}(66)$ polymer with the *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 *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 states of the *ABC*-stacking polymer at the Γ point. The wave function clearly possesses an antibonding character and is localized at the edge atomic sites of the π network [onefold coordinated *C* site on the network of 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 $C_{60}(66)$ polymer does not depend on the stacking difference.

B. $C_{60}(65)$ polymer

In this section we discuss the geometric and electronic structures of the rhombohedral $C_{60}(65)$ 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 $C_{60}(65)$ polymer with the *ABC*-stacking order in Fig. 1(b). Optimized bond length between adjacent C_{60} molecules is 1.56 Å which is

(a) $C_{60}(65)$ ABC stacking



(b) $C_{60}(65)$ ACB stacking

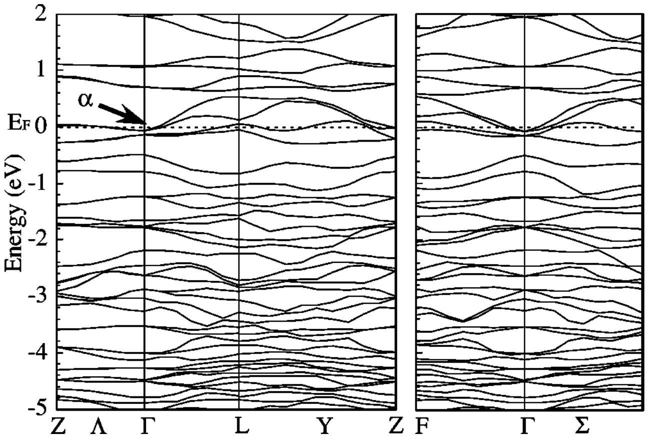


FIG. 5. Electronic energy bands of (a) the *ABC*-stacking and (b) the *ACB*-stacking $C_{60}(65)$ polymers. Energies are measured from the Fermi-level energy which is denoted by dashed lines.

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.*[14,15] 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.

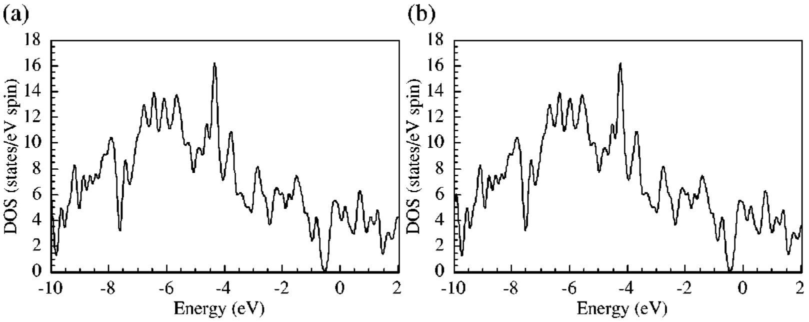


FIG. 6. Density of states for the rhombohedral C_{60} polymers with (a) the *ABC*-stacking and (b) the *ACB*-stacking structures. Energies are measured from the Fermi-level energy.

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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[1] A.M. Rao, P. Zhou, K. Wang, G.T. Hager, J.M. Holden, Y. Wang, W. Lee, X. Bi, P.C. Eklund, D.S. Cornett, M.A. Duncan, and I.J. Amster, Science **259**, 955 (1993).

[2] O. Chauvet, G. Oszlanyi, L. Forro, P.W. Stephens, M. Tegze, G. Faigel, and A. Janossy, Phys. Rev. Lett. **72**, 2721 (1994).

[3] Y. Iwasa, T. Arima, R.M. Fleming, T. Siegrist, O. Zhou, R.C. Haddon, L.J. Rothberg, K.B. Lyons, H.L. Carter, Jr., A.F. Hebard, R. Tycko, G. Debbagh, J.J. Krajewski, G.A. Thomas, and T. Yagi, Science **264**, 1570 (1995).

[4] M. Núñez-Regueiro, L. Marques, J-L. Hodeau, O. Béthoux, and M. Perroux, Phys. Rev. Lett. **74**, 278 (1995).

[5] G. Oszlanyi and L. Forro, Solid State Commun. **93**, 265 (1995).

[6] S. Okada and S. Saito, Phys. Rev. B **55**, 4039 (1997).

[7] S. Okada and S. Saito, Phys. Rev. B **59**, 1930 (1999).

[8] Y. Iwasa, Solid State Phys. (Kotai Buturi) **31**, 909 (1996) (AGNE, Tokyo).

[9] L. Marques, J-L. Hodeau, M. Núñez-Regueiro, and M. Perroux, Phys. Rev. B **54**, R12 633 (1996).

[10] S. Saito and A. Oshiyama, Phys. Rev. Lett. **66**, 2637 (1991).

[11] A.M. Rao, P.C. Eklund, J-L. Hodeau, L. Marques, and M. Núñez-Regueiro, Phys. Rev. B **55**, 4766 (1998).

[12] C. Goze, F. Rachidi, M. Núñez-Regueiro, L. Marques, J-L. Hodeau, and M. Mehring, Phys. Rev. B **54**, R3676 (1996).

[13] Y. Maniwa, M. Sato, K. Kume, M.E. Kozolv, and M. Tokumoto, Carbon **34**, 1287 (1996).

[14] T.L. Makarova, P. Scharff, B. Sundqvist, B. Narymbetov, H. Kobayashi, M. Tokumoto, V.A. Davydov, A.V. Rakhmanina, and L.S. Kashevarova, Synth. Met. **121**, 1099 (2001).

[15] M. Tokumoto, B. Narymbetov, H. Kobayashi, T.L. Makarova, V.A. Davydov, A.V. Rakhmanina, and L.S. Kashevarova, in *Electronic Properties of Novel Materials-Molecular Nanostructures*, edited by Hans Kuzmany, Jörg Fink, Michael Mehrang, and Siegmer Roth, AIP Conf. Proc. 544 (AIP, Melville, New York, 2000), pp. 73–76.

[16] T.L. Makarova, B. Sundqvist, R. Hohne, P. Esqulnazl, K. Kopelevich, P. Scharff, V.A. Davydov, L.A. Kahsevarova, and A.V. Rakhmanina, Nature (London) **413**, 716 (2001).

[17] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).

[18] W. Kohn and L.J. Sham, Phys. Rev. A **140**, 1133 (1965).

[19] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[20] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[21] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).

[22] L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[23] S. Okada, S. Saito, and A. Oshiyama, Phys. Rev. Lett. **86**, 3835 (2001).

[24] O. Sugino and A. Oshiyama, Phys. Rev. Lett. **68**, 1858 (1992).

[25] A.V. Okotrub, V.V. Belavin, L.G. Bulusheva, V.A. Davydov, T.L. Makarova, and D. Tománek, J. Chem. Phys. **114**, 5637 (2001).