Metallic and insulating states in two-dimensional C$_{60}$-polymers

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Abstract

Variations in the band structures of the two-dimensional C$_{60}$-polymers are studied, when $\pi$-conjugation conditions are changed. We investigate the rectangular and triangular polymers, in order to discuss metal-insulator transitions, using a semiempirical model with the Su-Schrieffer-Heeger type electron-phonon interactions. We find that electronic structures change among direct-gap insulators and the metal, depending on the degree of $\pi$-conjugations in the rectangular polymer. The triangular polymer changes from the indirect gap insulator to the metal as the $\pi$-conjugations increase. High pressure experiments could observe such pressure-induced metal-insulator transitions.

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1. Introduction

Recently, it has been found that the linear (one-dimensional) C$_{60}$-polymers are realized in alkali-metal doped C$_{60}$ crystals: A$_1$C$_{60}$ (A = K, Rb) [1-4], and their solid state properties are intensively investigated. One electron per one C$_{60}$ is doped in the polymer chain. It seems that Fermi surfaces exist in high temperatures, but the system shows antiferromagnetic correlations in low temperatures [1]. The C$_{60}$-polymer has lattice structures where C$_{60}$ molecules are arrayed in a linear chain. The bonds between C$_{60}$ are formed by the [2+2] cycloaddition mechanism. And, quite recently, the other new phases of C$_{60}$ systems which are synthesized at high pressures have been reported [5,6]. The two-dimensional polymer structures [6,7] have been proposed and a tight-binding calculation [8] has been already reported. It has been discussed [8] that their lattice structures can be explained by the calculation. The two kinds of lattice structures – rectangular and triangular structures – are present in the two-dimensional polymers. The structures are shown in Fig. 1. Figure 1(a) is for the rectangular polymer, and Fig. 1(b) displays the triangular polymer. There are four membered rings between neighboring C$_{60}$ molecules. These rings are the results of the [2+2] cycloaddition.

In this paper, we shall study variations in the band structures of the two-dimensional C$_{60}$-polymers when the $\pi$-conjugation conditions are changed. We assume that the bonding states between C$_{60}$ might be changed easily possibly by applying high pressures. As illustrated in Fig. 3 of the ref. [2], there are three candidates for the classical bonding structures around the four membered ring. The first case (A) is that there are only weak van der Waals interactions between C$_{60}$, and the classical double bonds remain as in the isolated C$_{60}$
molecule. The second case (B) is that all the bonds of the four membered
ring are the single bond, so they are $\sigma$-like in the quantum chemistry. All the
four-membered rings in Fig. 1 are formed by the $\sigma$-bonds in this case. Then,
the third case (C) is that the bonds which connect the neighboring molecules
are the double bonds, and the bonds derived from the isolated $C_{60}$ – the bonds,
$\langle 1, 2 \rangle$, $\langle 3, 4 \rangle$, $\langle 5, 6 \rangle$, $\langle 7, 8 \rangle$, of Fig. 1(a) – are destroyed completely. Here, $\langle i, j \rangle$
indicates the pair of the neighboring $i$ and $j$th atoms. In this case, the bonds
between $C_{60}$ – the bonds, $\langle 1, 5 \rangle$, $\langle 2, 6 \rangle$, $\langle 3, 8 \rangle$, $\langle 4, 7 \rangle$, of Fig. 1(a) – have the
$\sigma$- as well as $\pi$-characters. In other words, the degree of the $\pi$-conjugations
between the molecules becomes maximum. The main purpose of this paper is
to propose a model which can deal with changes of $\pi$-conjugation conditions
among the above three cases, and to look at electronic band structures of the
two types of $C_{60}$-polymers. We note that the operator at the lattice sites of the
four membered rings is one of the relevant linear combinations of the effective
$\sigma$-like components, assuming a possibility of local $\sigma$-conjugations at the four
membered rings. The similar assumption of the $\sigma$-conjugation has been used
in Si-based polymers, for example, in ref. [9]. We, however, use the term
“$\pi$-conjugation” for simplicity in this paper, because the local $\sigma$-conjugations
can be regarded as a part of the global $\pi$-conjugations which are extended over
the system.

We propose a semiempirical tight-binding model analogous to the Su-
Schrieffer-Heeger (SSH) model [10] of conjugated polymers. The electronic
structures may depend sensitively upon the $\pi$-conjugation conditions even
in the neutral polymer, because the several bonds connecting neighboring
molecules are largely distorted, and the mixing between $\sigma$- and $\pi$-orbitals
will change only by slight change of the bond structures [2]. We would like to study effects of the change of the \( \pi \)-conjugation conditions by introducing a phenomenological parameter in a tight-binding model. The model is an extension of the SSH-type model which has been applied to \( \text{C}_{60} \) [11,12] and \( \text{C}_{70} \) [12,13] molecules. The model is solved with the assumption of the adiabatic approximation, and band structures are reported in order to discuss metal-insulator changes by varying \( \pi \)-conjugations.

We will conclude that the electronic structures change among direct-gap (indirect-gap) insulators and the metal, depending on the degree of \( \pi \)-conjugations. In the rectangular polymer, the electronic structures change from the direct gap insulator with the gap at the \( \Gamma \) point, through the metal, to the insulator with the direct gap at the \( \text{K} \) point, as increasing the \( \pi \)-conjugation between \( \text{C}_{60} \) molecules. The high pressure experiments may be able to change \( \pi \)-conjugation conditions between \( \text{C}_{60} \) molecules, and the electronic structure changes could be observed. It may seem that the transition to metals in high pressure is a general fact which is common to various materials [14]. However, in the present theory, the rectangular polymer changes from an insulator through a metal, and finally changes into an insulator again. This reentrant behavior is specific to the present \( \text{C}_{60} \)-polymer systems, and is not a guess from the general knowledge about high pressure effects. In the triangular polymer, there is an indirect energy gap at the intermediate \( \pi \)-conjugations. And, the system changes into a metal at the maximum \( \pi \)-conjugation.

In the next section, our tight-binding model is introduced and an idea of changing \( \pi \)-conjugation conditions is discussed. The sections 3 is devoted to numerical results. The paper is closed with a summary in section 4.
2. Model

We would like to apply an SSH-type model to the two-dimensional \(C_{60}\)-polymers. In the previous works [11-13], we have proposed the extended SSH model to \(C_{60}\) and \(C_{70}\) molecules. In \(C_{60}\), all the carbon atoms are equivalent, so it is a good approximation to neglect the mixing between \(\pi\)- and \(\sigma\)-orbitals. The presence of the bond alternation and the energy level structures of the neutral \(C_{60}\) molecule can be quantitatively described by the calculations within the adiabatic approximation. In \(C_{70}\), the molecular structure becomes longer, meaning that the degrees of the mixing between \(\pi\)- and \(\sigma\)-characters are different depending on carbon sites. In this respect, the extended SSH model does not take account of the differences of the mixings. However, it has been found [12,13] that qualitative characters of the electronic level structures are reasonably calculated when the extended SSH model is applied to the \(C_{70}\). This is a valid approach because the \(\sigma\)-orbitals can be simulated by the classical harmonic springs in the first approximation.

In this paper, we assume the same idea that the lattice structures and the related molecular orbitals of each \(C_{60}\) molecule in the \(C_{60}\)-polymers can be described by the SSH-type model with the hopping interactions for the \(\pi\)-orbitals and the classical springs for the \(\sigma\)-orbitals. However, the mixings between the \(\pi\)- and \(\sigma\)-orbitals near the eight bonds, \(\langle i, j \rangle (i, j = 1-8)\), shown in Fig. 1(a) are largely different from those of regions far from the four bonds. We shall shed light on this special character of bondings between the neighboring \(C_{60}\). Electronic structures would be largely affected by changes of \(\pi\)-conjugation conditions (or local \(\sigma\)-conjugations as in Si-based polymers [9]) around the four bonds. We shall introduce a semiempirical parameter \(a\) as shown in the
following hamiltonian:

$$H_{pol} = a \sum_{l,\sigma} \sum_{\langle i, j \rangle}^{'} (-t + \alpha y_{l,\langle i, j \rangle}) (c_{l,i,\sigma}^\dagger c_{l+1,i,\sigma} + \text{h.c.})$$

$$+ \sum_{l,\sigma} \sum_{\langle i, j \rangle}^{''} (-t + \alpha y_{l,\langle i, j \rangle}) (c_{l,i,\sigma}^\dagger c_{l,j,\sigma} + \text{h.c.})$$

$$+ \frac{K}{2} \sum_{i} \sum_{\langle i, j \rangle} y_{l,\langle i, j \rangle}^2,$$

where $t$ is the hopping integral of the system without the bond alternations in the isolated C$_{60}$ molecule; $\alpha$ is the electron-phonon coupling constant which changes the hopping integral linearly with respect to the bond variable $y_{l,\langle i, j \rangle}$, where $l$ means the $l$th molecule and $\langle i, j \rangle$ indicates the pair of the neighboring $i$ and $j$th atoms; the atoms with $i = 1 - 8$ of the rectangular polymer are shown by numbers in Fig. 1(a), and the atoms with $i = 1 - 12$ of the triangular polymer are in Fig. 1(b); the other $i$ and $j$ in the third column of eq. (1) label the nonnumbered atoms in the same molecule; $c_{l,i,\sigma}$ is an annihilation operator of the $\pi$-electron at the $i$th site of the $l$th molecule with spin $\sigma$; the sum is taken over the pairs of neighboring atoms; and the last term with the spring constant $K$ is the harmonic energy of the classical spring simulating the $\sigma$-bond effects. Note that the sum with the prime is performed over $\langle i, j \rangle = \langle 1, 5 \rangle, \langle 2, 6 \rangle, \langle 3, 8 \rangle, \langle 4, 7 \rangle$ for the rectangular polymer, and it is performed over $\langle i, j \rangle = \langle 1, 8 \rangle, \langle 2, 7 \rangle, \langle 3, 10 \rangle, \langle 4, 9 \rangle, \langle 5, 12 \rangle, \langle 6, 11 \rangle$ for the triangular polymer. The sum with the double prime is performed over $\langle i, j \rangle = \langle 1, 2 \rangle, \langle 3, 4 \rangle, \langle 5, 6 \rangle, \langle 7, 8 \rangle$ for the rectangular polymer, and it is performed over $\langle i, j \rangle = \langle 1, 2 \rangle, \langle 3, 4 \rangle, \langle 5, 6 \rangle, \langle 7, 8 \rangle, \langle 9, 10 \rangle, \langle 11, 12 \rangle$ for the triangular polymer.

As stated before, the parameter $a$ controls the strength of $\pi$-conjugations
between neighboring molecules. When \( a = 1 \), the \( \sigma \)-bondings between atoms, 1 and 2, 3 and 4, 5 and 6, 7 and 8, in Fig. 1(a) are completely broken and the orbitals would become like \( \pi \)-orbitals. The bond between the atoms 1 and 5 and the equivalent other bonds become double bonds. This is the case (C). As \( a \) becomes smaller, the \( \pi \)-conjugation between the neighboring molecules decreases, and the \( C_{60} \) molecules become mutually independent. In other words, the interactions between molecules become smaller in the intermediate \( a \) region. In this case (B), the operator \( c_{l,i,\sigma} \) at the lattice sites of the four membered rings is one of the relevant linear combinations of the effective \( \sigma \)-like components. Here, we assume a possibility of local \( \sigma \)-conjugations at the four membered rings. The similar assumption of the \( \sigma \)-conjugation has been used in Si-based polymers, for example, in ref. [9]. When \( a = 0 \) [the case (A)], the \( C_{60} \) molecules are completely isolated each other. The band structures of the \( C_{60} \)-polymers will change largely depending on the \( \pi \)-conjugation conditions. We discuss this effects in the next section.

The present unit cell consists of one \( C_{60} \) molecule for the two polymers shown in Fig. 1. Using the lattice periodicity, we suppress the index \( l \) of the bond variable \( y_{l,(i,j)} \). In other words, all the molecules in the polymers are assumed to have the same lattice structures. The bond variables are determined by using the adiabatic approximation in the real space. The same numerical iteration method as in ref. [12] is used here. We will change the parameter, \( a \), within \( 0.5 \leq a \leq 1.0 \). We consider the neutral case so the electron number is 60 for one \( C_{60} \). The other parameters, \( t = 2.1 \text{eV}, \alpha = 6.0 \text{eV/Å}, \) and \( K = 52.5 \text{eV/Å}^2 \), give the energy gap 1.904\text{eV} and the difference between the short and bond lengths 0.04557\text{Å} for an isolated \( C_{60} \) molecule. We shall use
the same parameter set here.

3. Numerical results

We show band structures of the rectangular polymers for the \( \pi \)-conjugation conditions, \( a = 0.5, 0.7, 0.8, 0.9, \) and \( 1.0 \), as the representative cases in Fig. 2. In Figs. 2(a) and (b), the highest occupied states and the lowest unoccupied states are named as “HOMO” and “LUMO”. At \( a = 0.5 \), there is a direct energy gap at the \( \Gamma \) point. The system is an insulator. As discussed in ref. [8], the density of states of the system in the room pressures is large and the band widths are narrow. The parameter \( a = 0.5 \) seems to be large for the rectangular polymer in room temperatures and pressures [6]. However, we shall report the relatively large \( a \) cases, because our central interests are the behaviors of the system in the large conjugations which could be realized in high pressures. As the parameter \( a \) increases, the HOMO moves upward and the LUMO goes downward. The energy gap decreases as shown for \( a = 0.7 \) in Fig. 2(b). The deep and high energy bands do not move so apparently because they have large amplitudes of wavefunctions in the central parts of the \( C_{60} \) balls. In Fig. 2(c) (\( a = 0.8 \)), the crossing of the HOMO and LUMO of the smaller \( a \) cases occurs. There is Fermi surfaces at about \(-0.3\) eV, and the system is metallic. The crossing becomes more apparent for \( a = 0.9 \) as shown in Fig. 2(d). At the maximum conjugations with \( a = 1.0 \), the direct energy gap appears again at the K point, as shown in Fig. 2(e). The system changes into an insulator again.

Why do such the reentrant changes take place? In order to discuss the
reason, we show the magnitudes of wavefunctions at the Γ point for (a) \( a = 0.5 \) and (b) \( a = 1.0 \), in Fig. 3. The nonequivalent sites with respect to symmetries are labelled as A-I, as shown in Fig. 1(a). The wavefunctions can be taken as real, so we use this convention. The HOMO is shown by white bars, and the LUMO is displayed by the black bars. In Fig. 3(a), the HOMO has the negligible amplitude at the site E, and the LUMO is near zero at the site I. In contrast, as in Fig. 3(b), the LUMO is negligible at the site E and the HOMO is near zero at the site I. This fact indicates that the symmetries of the HOMO and LUMO are reversed in the two insulators with the small and large \( a \)'s. Therefore, the crossing of the HOMO and LUMO should occur at the intermediate \( a \) in the present model. This is the origin of the metallic band structures. Applying high pressures might decrease the distances between \( C_{60} \) molecules and thus increase \( a \). The insulating system changes into a metal and then an insulator again. This behavior is specific to the rectangular \( C_{60} \)-polymers, and it seems a quite interesting finding.

Next, we shall discuss band structures of the triangular \( C_{60} \)-polymer shown in Fig. 1(b). There are six nonequivalent sites, and they are named as A-F. As the qualitative features of the band structure changes are similar to those of the rectangular polymer, we show band structures only for (a) \( a = 0.5 \) and (b) \( a = 1.0 \), in Fig. 4. For \( a = 0.5 \), the HOMO has the maximum at the Γ point, and the LUMO has the minimum at the K point. The system is an indirect gap insulator. For \( a = 1.0 \), there are Fermi surfaces at about -0.1eV. Therefore, a metallic transition could be observed in the triangular polymer, too. In this system, a reentrant behavior is not found in the large \( a \) region. This might come from the geometry difference between the rectangular and
triangular polymers.

4. Summary

We have studied the variations of the band structures in rectangular and triangular phases of the two-dimensional C\textsubscript{60}-polymers. We have changed the conjugation conditions between molecules. A semiempirical model with SSH-type electron-phonon interactions has been proposed. The band structures have been shown, in order to discuss metal-insulator changes. A possibility of observing electronic structure changes in high pressure experiments, which may increase \pi-conjugations between C\textsubscript{60} molecules, has been pointed out. The reentrant behavior in the rectangular polymer, which is special to the C\textsubscript{60} systems, is a quite interesting finding. We have discussed that the metallic state is the result of the crossing of the bands, relating with the symmetry properties of wavefunctions.
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**Figure Captions**

Fig. 1. The crystal structures of the two-dimensional $C_{60}$-polymers. The rectangular polymer is shown in (a), and the triangular polymer is displayed in (b). The labels, A-I, indicate carbon atoms which are not equivalent due to the symmetries. These labels are used in Fig. 3. The carbon sites which constitute the four membered rings are named with numbers. In (a), the sites 2 (and 6) overlap with the sites 1 (and 5), respectively, and cannot be seen from the front. The parenthesis mean the overlapped sites.

Fig. 2. The band structures of the rectangular $C_{60}$-polymer of the cases (a) $a = 0.5$, (b) 0.7, (c) 0.8, (d) 0.9, and (e) 1.0. In (a), (b), and (e), the highest fully occupied band is named as “HOMO”, and the lowest empty band as “LUMO”.

Fig. 3. The magnitudes of the wavefunctions of the HOMO and the LUMO at the Γ point for (a) $a = 0.5$ and (b) 1.0, in the rectangular polymer. The nonequivalent sites are labelled as A-I, as shown in Fig. 1(a). The HOMO is shown by the white bars, and the LUMO is displayed by the black bars.

Fig. 4. The band structures of the triangular $C_{60}$-polymer of the cases (a) $a = 0.5$ and (b) 1.0. In (a), the highest occupied band is named as “HOMO”, and the lowest empty band as “LUMO”.