Metal-Insulator Transition in C₆₀-Polymers

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(Received )

Abstract

Variations in the band structures of C₆₀-polymers are studied, when π-conjugation conditions are changed. We look at band structures in order to discuss a metal-insulator transition, using a semi-empirical 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 π-conjugations. High pressure experiments could observe such pressure-induced metal-insulator transitions.

PACS numbers: 71.30.+h, 71.38.+i, 71.25.Tn

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Recently, it has been found that the linear C\textsubscript{60}-polymer is realized in alkali-metal doped C\textsubscript{60} crystals: \(A_1C_{60}\) \((A = K, Rb)\) [1-4], and much attention has been focused on their solid state properties. One electron per one C\textsubscript{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 structure of the C\textsubscript{60}-polymer is displayed in Fig. 1. The C\textsubscript{60} molecules are arrayed in a linear chain. The bonds between C\textsubscript{60} are formed by the [2+2] cycloaddition mechanism.

Several calculations of the electronic structures have been performed. For example, a tight-binding calculation of a linear chain [5] has been reported, and the relation to the antiferromagnetic ground state has been discussed. A semi-empirical tight-binding model [6] analogous to the Su-Schrieffer-Heeger (SSH) model [7] of conjugated polymers has been proposed, and the possibility of the charge density wave state has been pointed out. The band calculation by the first principle method has also been done [8]. The electronic structures can become three dimensional when distances between C\textsubscript{60}-polymer chains are short, while they remain one dimensional when the distances are longer.

The above works have been focused upon electronic structures of the C\textsubscript{60}-polymer doped with one electron per one C\textsubscript{60}. 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 $C_{60}$ [9,10] and $C_{70}$ [10,11] molecules. We look at band structures, in order to discuss a metal-insulator transition in neutral systems.

In the previous works [9-11], we have proposed the extended SSH model to $C_{60}$ and $C_{70}$. In $C_{60}$, all the carbon atoms are equivalent, so it is a good approximation to neglect the mixings between $\pi$- and $\sigma$-orbitals. The presence of the dimerization 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 degree of the mixings between $\pi$- and $\sigma$-characters are different depending on carbon sites. In this respect, the extended SSH model does not take account of the difference of the mixings. However, it has been found [10,11] 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 energy positions of the $\sigma$-orbitals are deep enough to neglect them in the first approximation.

In this letter, we assume the same idea that the lattice structures and the related molecular orbitals of each $C_{60}$ molecule in the $C_{60}$-polymer can be described by the SSH-type model with the $\pi$-orbitals only. However, the mixings between the $\pi$- and $\sigma$-orbitals near the four bonds, $(i, j)$ $(i, j = 1 - 4)$, shown in Fig. 1 are largely different from those of regions far from the four bonds. We shall shed light on this special character of bondings between neighboring $C_{60}$. Electronic structures would be largely affected by changes of $\pi$-conjugation conditions around the four bonds. We shall introduce a semi-
empirical parameter $a$ as shown in the following hamiltonian:

$$H_{\text{pol}} = a \sum_{l, \sigma} \sum_{\langle i,j \rangle = (1,3),(2,4)} (-t + \alpha y_{l,\langle i,j \rangle}) (c_{l,i,\sigma}^\dagger c_{l+1,j,\sigma} + \text{h.c.})$$

$$+ (1 - a) \sum_{l, \sigma} \sum_{\langle i,j \rangle = (1,2),(3,4)} (-t + \alpha y_{l,\langle i,j \rangle}) (c_{l,i,\sigma}^\dagger c_{l,j,\sigma} + \text{h.c.})$$

$$+ \sum_{l, \sigma} \sum_{\langle i,j \rangle = \text{others}} (-t + \alpha y_{l,\langle i,j \rangle}) (c_{l,i,\sigma}^\dagger c_{l,j,\sigma} + \text{h.c.})$$

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

where $t$ is the hopping integral of the system without the dimerization 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 $i = 1 - 4$ are shown by numbers in Fig. 1 and the other $i$ within $5 \leq i \leq 60$ labels the remaining 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.

As stated before, the parameter $a$ controls the strength of $\pi$-conjugations in the chain direction. When $a = 1$, the $\sigma$-bonding between atoms 1 and 2 (and also 3 and 4) is completely broken and the orbitals would become like $\pi$-orbitals. The bond between the atoms 1 and 3 (and that between the atoms 2 and 4) becomes $\sigma$-like. As $a$ becomes smaller, the $\pi$-conjugation between the neighboring molecule decreases and the $C_{60}$ molecule becomes mutually independent. In other words, the interactions between molecules become smaller. When $a = 0$, the $C_{60}$ molecules are completely isolated each other. The band structures of the $C_{60}$-polymer will change largely depending
on the π-conjugation conditions. This problem is the central issue of this letter.

In the literature [6], the possibility of charge density wave states has been taken into account by regarding two molecule pair as a unit cell. In contrast, our interests are focused on the one-dimensional band structure in the spatially homogeneous system, so we do not consider the doubled unit cell. The present unit cell consists of one C$_{60}$ molecule. Using the lattice periodicity, we skip the index $l$ of the bond variable $y_{l,(i,j)}$. In other words, all the molecules in the polymer are assumed to have the same lattice structure. The bond variables are determined by using the adiabatic approximation in the real space. The same numerical iteration method as in [10] is used here. We will change the parameter, $a$, within $0 \leq a \leq 1.0$. 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 one C$_{60}$ molecule. We shall use this parameter set here. The labels A-I in Fig. 1 indicate carbon atoms which are not equivalent with respect to the symmetry. The model is solved by keeping this symmetry of the polymer chain.

Now, we discuss band structures of π-electrons. Figures 2(a), (b), and (c) display the band structures for the π-conjugation parameters, $a = 0.5$, 0.8, and 1.0, respectively. In each figure, the unit cell is taken as unity, so the first Brillouine zone extends from $-\pi$ to $\pi$. Due to the inversion symmetry, only the wavenumber region, $0 \leq k \leq \pi$, is shown in the figures. In Fig. 2(a), the highest fully occupied band is named as “HOMO”, and the lowest empty band as “LUMO”. There is an energy gap about 0.8 eV at the zone center. The
system is a direct gap insulator. As increasing the parameter $a$, the overlap of the HOMO and LUMO appears. This is shown for $a = 0.8$ in Fig. 2(b). There are Fermi surfaces, so the system changes into a metal. If $a$ increases further, the positions of the HOMO and LUMO of the smaller $a$ case are reversed as shown for $a = 1.0$ in Fig. 2(c). The system becomes a direct gap insulator again. The energy gap is at $k = \pi$.

The above variations of the energy gap are summarized in Fig. 3. The white (black) squares indicate that the system is a direct gap insulator where there is a energy gap at $k = 0$ ($\pi$). The crosses indicate the metallic cases. The energy gap decreases almost linearly for smaller $a$. The system changes into a metal as $a$ increases, and finally an energy gap appears again. As has been discussed in [2], the \( \pi \)-conjugations between the bonds, \( \langle 1, 2 \rangle \) and \( \langle 3, 4 \rangle \), might be weak. So, we can assume that the larger parameter $a$ is reasonable for the real C\(_{60}\)-polymer. There would be a good possibility that the realistic $a$ is in the region where we can expect metallic and insulating behaviors. Therefore, it would be interesting to do experiments which give a high pressure to neutral systems in order to change \( \pi \)-conjugation conditions.

In summary, we have studied the variations of the band structures of the C\(_{60}\)-polymer. We have changed \( \pi \)-conjugation conditions by a phenomenological parameter. A semi-empirical model with SSH-type electron-phonon interactions has been proposed. Band structures have been shown extensively, in order to discuss a metal-insulator transition. We have found that electronic structures change among direct-gap insulators and the metal, depending on the degree of \( \pi \)-conjugations. The high pressure experiments may be able to change \( \pi \)-conjugation conditions in the chain direction, and the electronic
structure changes could be observed.
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FIGURE CAPTIONS

Fig. 1. The crystal structure of the C\textsubscript{60} polymer. The labels, A-I, indicate carbon atoms which are not equivalent with respect to the symmetry. The \(\pi\)-conjugations along four bonds, which connect carbon atoms with labels, 1-4, are controled by the phenomenological parameter \(a\) in Eq. (1).

Fig. 2. Band structures of the C\textsubscript{60}-polymer of the cases (a) \(a = 0.5\), (b) 0.8, and (c) 1.0, respectively. In (a) and (c), the highest fully occupied band is named as “HOMO”, and the lowest empty band as “LUMO”. The lattice constant of the unit cell is taken as unity.

Fig. 3. The variations of the energy gap plotted against \(a\). The white (black) squares indicate that the system is a direct gap insulator where there is a energy gap at \(k = 0\) (\(\pi\)). The crosses are for metallic cases.