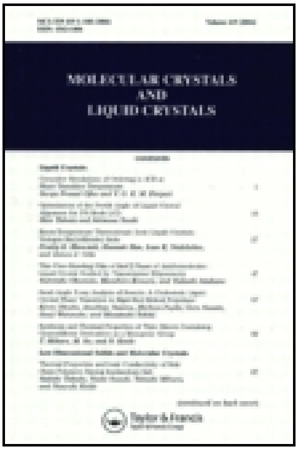

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Metallic and Insulating States in One- and Two-Dimensional C_{60}-Polymers

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METALLIC AND INSULATING STATES IN ONE- AND TWO-DIMENSIONAL C_{60}-POLYMERS

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Abstract Variations in the band structures of the one- and two-dimensional C_{60}-polymers are studied, changing conjugation conditions. We investigate the linear, rectangular, and triangular polymers, using a tight binding model with electron-phonon interactions. We find that electronic structures change among direct-gap insulators and the metal, depending on the degree of conjugations in the linear and rectangular polymers. The triangular polymer changes from the indirect gap insulator to the metal as the conjugations increase. High pressure experiments could observe such pressure-induced metal-insulator transitions.

INTRODUCTION

The linear (one-dimensional) C_{60}-polymers[1-4] realized in alkali-metal doped C_{60} crystals A_1C_{60} (A =K, Rb, Cs), and the two-dimensional C_{60}-polymers[5-7] synthesized in high pressure experiments, have been reported recently. The two structures – rectangular and triangular structures – are present in the two-dimensional polymers. The lattice structures are shown in Fig. 1. Between the neighboring C_{60} molecules, there are four membered rings which are formed by the [2+2] cycloaddition.

In this paper, we study the band structures of the C_{60}-polymers, changing conjugation conditions. We propose a model which simulates conjugation changes between neighboring molecules, and look at electronic band structures of the three types of C_{60}-polymers. The operator at the lattice sites of the four membered rings is one of the relevant linear combinations of the effective sp^3-orbitals, assuming possible local conjugations at the four membered rings. We use a tight-binding model analogous to the Su-Schrieffer-Heeger (SSH) model[8] of conjugated polymers. The model is solved with the adiabatic approximation, and band structures are reported.

MODEL

In the previous works,[9-11] we have proposed the extended SSH model to C_{60} and C_{70} molecules. The presence of the bond alternation and the energy level structures of the neutral C_{60} and C_{70} molecules can be quantitatively described by the calculations within the adiabatic 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 electrons and the classical springs for the σ-orbitals. However, the hopping interactions near the four membered rings are largely different. We take account of this special character of bondings between the neighboring C_{60}. Electronic structures would be largely affected by changes of conjugation conditions. We use the following hamiltonian:

$$\begin{aligned} H_{\rm pol} &= a \sum_{l,\sigma} {\sum_{(i,j)}}' (-t + \alpha y_{l,(i,j)})(c^\dagger_{l,i,\sigma} c_{l+1,j,\sigma} + {\rm h.c.}) \\ &+ (1-a) \sum_{l,\sigma} {\sum_{(i,j)}}'' (-t + \alpha y_{l,(i,j)})(c^\dagger_{l,i,\sigma} c_{l,j,\sigma} + {\rm h.c.}) \\ &+ \sum_{l,\sigma} \sum_{(i,j)={\rm others}} (-t + \alpha y_{l,(i,j)})(c^\dagger_{l,i,\sigma} c_{l,j,\sigma} + {\rm h.c.}) \\ &+ \frac{K}{2} \sum_{i} \sum_{(i,j)} y^2_{l,(i,j)}, \end{aligned} \tag{1}$$

where t is the hopping integral of the system without the bond alternations in the isolated C_{60} molecule; α is the electron-phonon coupling constant which changes the hopping integral linearly with respect to the bond variable $y_{l,(i,j)}$, where l means the lth molecule and $\langle i,j \rangle$ indicates the pair of the neighboring i and jth atoms; the numbered atoms in Fig. 1 are at the lattice sites of the four membered rings; 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 electron at the ith site of the lth molecule with spin σ; 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 σ-bond effects. Note that the sum with the prime is performed over the bonds $\langle i,j \rangle$ which connect the neighboring molecules, and the sum with the double prime is performed over the bonds $\langle i,j \rangle$ which are perpendicular to the bonds connecting molecules.

In the model, the parameter a controls the strength of conjugations between neighboring molecules. When $a = 1$, the bonds in the sum with the prime in Eq. (1) are completely broken, and the bonds connecting molecules become like double bonds. As a becomes smaller, the conjugations between the neighboring molecules decrease, and the C_{60} molecules become mutually independent. Here, the operator $c_{l,i,\sigma}$ at the lattice sites of the four membered rings is one of the relevant linear combinations of the sp^3-components. When $a = 0$, the C_{60} molecules are completely isolated each other. The band structures of the C_{60}-polymers will change largely depending on the conjugation conditions. We discuss the effects in the following sections.

The present unit cell consists of one C_{60} molecule for the three polymers shown in Fig. 1. Using the lattice periodicity, we suppress the index l of the bond variable $y_{l,(i,j)}$. The bond variables are determined by the adiabatic approximation in the

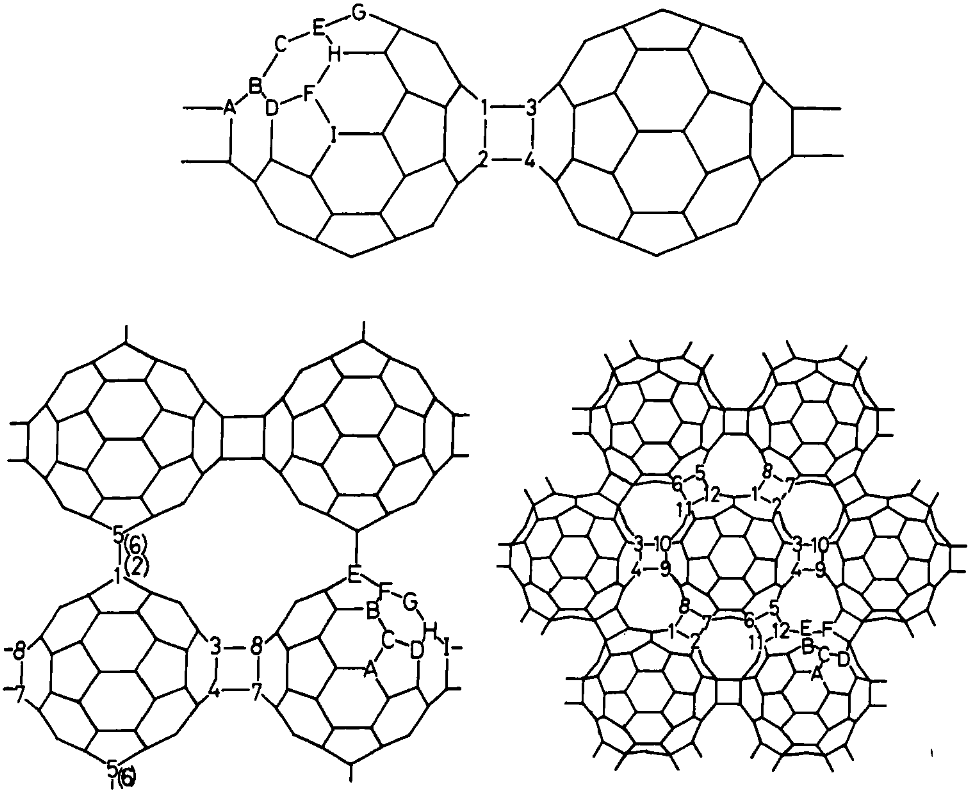

FIGURE 1 The crystal structures of the linear, rectangular, and triangular C_{60}-polymers. The labels, A-I, indicate carbon atoms which are not equivalent due to the symmetries. The carbon sites which constitute the four membered rings are named with numbers.

real space, using the numerical iteration method.[10] 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, $t = 2.1$eV, $\alpha = 6.0$eV/Å, and $K = 52.5$eV/Å^2, give the energy gap 1.904eV and the difference between the short and long bond lengths 0.04557Å for an isolated C_{60} molecule. We shall use the same parameter set here.

ELECTRONIC STATES IN ONE-DIMENSIONAL C_{60}-POLYMER

Figures 2(a), (b), and (c) display the band structures for the conjugation parameters, $a = 0.5$, 0.8, and 1.0, respectively. In Fig. 2(a), 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 bands appears. This is shown for $a = 0.8$ in Fig. 2(b). There are Fermi surfaces, so the system changes into a

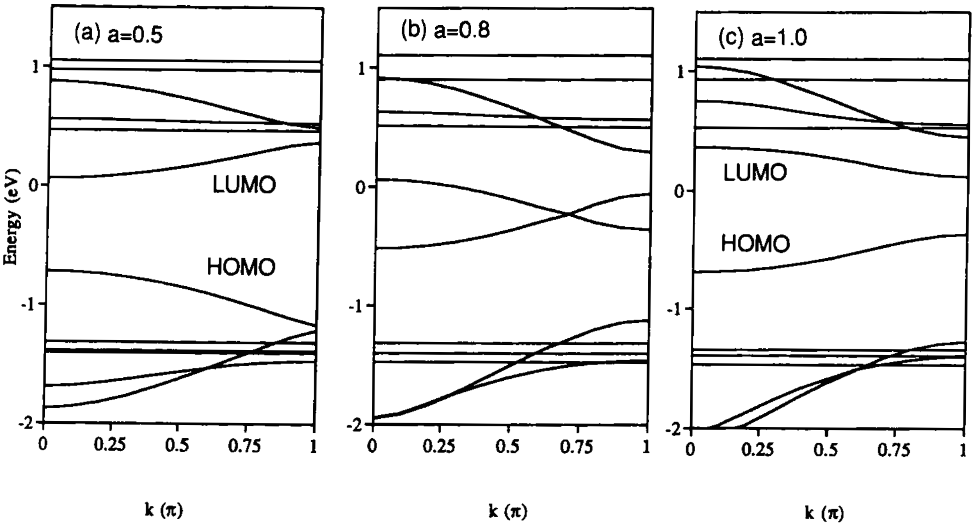

FIGURE 2 Band structures of the linear C_{60}-polymer of the cases (a) a = 0.5, (b) 0.8, and (c) 1.0. In (a) and (c), the highest fully occupied band is named as "HOMO", and the lowest empty band as "LUMO". The lattice constant of the unit cell is taken as unity.

metal. If a increases further, the positions of the HOMO and LUMO bands 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 $k = \pi$.

In order to discuss the reason that the changes among insulators and a metal are reentrant, we consider the amplitudes of wavefunctions at the wave number $k = 0$ for $a = 0.5$ and 1.0. The nonequivalent sites with respect to symmetries are labelled as A-I, as shown in Fig. 1. We find that the LUMO band has the negligible amplitude at the site G, and the HOMO band is near zero at the site I. In contrast, the HOMO band is negligible at the site G and the LUMO band is near zero at the site I. This fact indicates that the symmetries of the HOMO and LUMO bands are reversed in the two insulators with the small and large a's. Therefore, the crossing of the HOMO band and LUMO band 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 reentrant behavior is specific to the C_{60}-polymer, and it seems to be a quite interesting finding.

ELECTRONIC STATES IN TWO-DIMENSIONAL C_{60}-POLYMERS

We show band structures of the rectangular polymers for the conjugation conditions, $a = 0.5$, 0.8, and 1.0, in Fig. 3. At $a = 0.5$, there is a direct energy gap at the Γ point. The system is an insulator. As the parameter a increases, the HOMO band

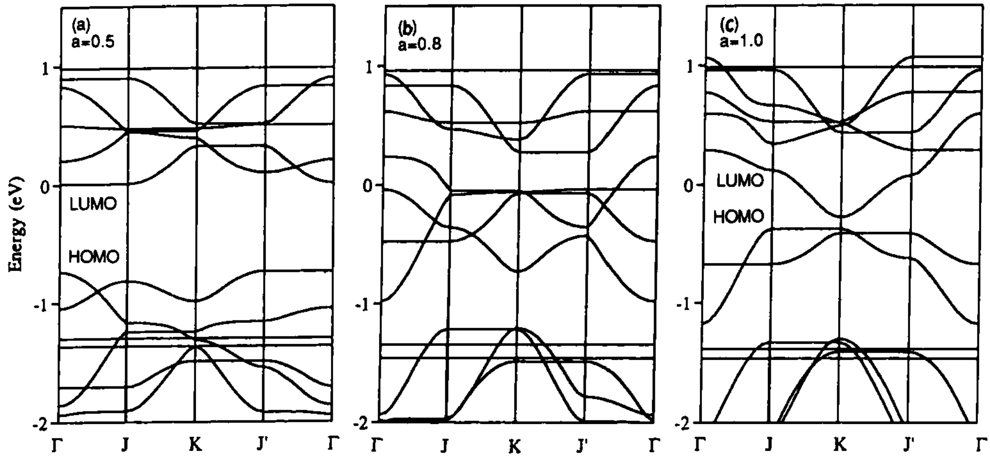

FIGURE 3 The band structures of the rectangular C_{60}-polymer of the cases (a) $a = 0.5$, (b) 0.8, and (c) 1.0. In (a) and (c), the highest fully occupied band is named as "HOMO", and the lowest empty band as "LUMO".

moves upward and the LUMO band goes downward. The energy gap decreases. In Fig. 3(b) ($a = 0.8$), the crossing of the HOMO and LUMO bands of the smaller a cases occurs. There is Fermi surfaces at about −0.3eV, and the system is metallic. At the maximum conjugations with $a = 1.0$, the direct energy gap appears again at the K point, as shown in Fig. 3(c). The system changes into an insulator again.

Next, we shall discuss band structures of the triangular C_{60}-polymer. The figures will be presented elsewhere[12] due to the space limitation. We only discuss the main results. We find that the HOMO band has the maximum at the Γ point and the LUMO band has the minimum at the K point for $a = 0.5$. The system is an indirect gap insulator. For $a = 1.0$, there are Fermi surfaces at about −0.1eV. A metallic transition could be observed in the triangular polymer, too. In this polymer, a reentrant behavior is not found in the large a region, coming from the geometry difference between the rectangular and triangular polymers.

SUMMARY

We have studied the variations of the band structures in the linear, rectangular, and triangular phases of the one- and two-dimensional C_{60}-polymers. We have changed the conjugation conditions between molecules. A tight binding model with electron-phonon interactions has been proposed. We have discussed metal-insulator changes. A possibility of observing electronic structure changes in high pressure experiments, which may increase conjugations between C_{60} molecules, has been pointed out. The reentrant behaviors in the linear and rectangular polymers, which are special to the C_{60} systems, are quite interesting findings. 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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