

POLARONS IN LINEAR CHAINS OF FULLERENES

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Polaron states in linear chains of fullerenes are studied with the use of the generalized model of Su-Shrieffer-Heeger (SSH) for the intermolecular and intramolecular degrees of freedom. Electron charge distributions over the molecular surface and Jahn-Teller distortions of carbon atoms in C_{60} are calculated self-consistently for linear C_{60} polymer and C_{60}^- polyanion chains. A polaron band narrowing is examined. It is shown that the polymerization of C_{60} molecules under phase transitions may be caused by the cooperative Jahn-Teller effect.

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Recently, a number of structural and electron phase transitions have been found in fullerides. In particular, the existence of a phase consisting of linear polymer chains in A_1C_{60} compounds ($A = K, Rb, Cs, Na_2Cs, Na_2Rb$) came into focus [1-6]. The low temperature structure of A_1C_{60} is orthorhombic with an unusually short separation of 9.1 Å- 9.3 Å between the centers of C_{60} molecules along one of the crystallographic directions. It has been suggested that the anions in the orthorhombic phase of these compounds are linear chains of covalently bonded C_{60} molecules. Moreover, the amorphization of C_{60} under pressure has become a hot issue in high-pressure science and material science [7, 8]. Amorphous-carbon structures based on linear-polymerized C_{60} molecules have been found under a pressure of above 5 GPa [9]. Details of the reaction mechanism for the C_{60} and C_{60}^- chain formation are yet unclear [10-12].

It is well known that the Jahn-Teller effect leads to a dynamic instability of symmetrical configuration of molecules. In crystal structures this effect can possibly become static. The band structure of alkali-doped fullerides reflects primarily the molecular orbitals of high-symmetrical C_{60} . It is now well established that the three fold degenerate t_{1u} lowest unoccupied state of C_{60} is the conduction band of A_xC_{60} compounds.

In our previous work [9] we studied the band reconstruction of the K_xC_{60} ($x = 1, 2, 3, 4$) crystals caused by the cooperative Jahn-Teller effect. A simple model was proposed there to describe non-rigid-band effects in alkali-doped fullerides. The band structures of solid K_xC_{60} ($x = 1, 2, 3, 4$) and the cooperative Jahn-Teller distortions of C_{60} molecules were calculated self-consistently. The band calculations were performed in the framework of the SSH model. The model takes into account the π -electron hopping between carbon atoms, local electron-phonon interactions, and adiabatic approximation. The SSH model have been extended to the case of the doped fulleride crystals [9]: besides the intramolecular electron transfer, we introduced there the π -electron hopping between the nearest neighbor molecules in crystal lattice. Electron correlation effects and lattice oscillations were ignored.

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Here we consider two types of linear chains. The first is a C_{60}^- polyanion chain in the orthorhombic phase of A_1C_{60} [1-6], and the second is linear-polymerized C_{60} molecules in the amorphous-carbon structures [7-9]. We assume neutral and charged molecules to have the same position and orientation in the chain. The main purpose of the present work is to study how the band structure of C_{60} and C_{60}^- linear chains and Jahn-Teller distortions of carbon atoms in C_{60} depend on the ratio of the intermolecular overlap of the π -electron orbital to the intramolecular one.

The SSH Hamiltonian has the following form :

$$H = H_{el,el-ph} + H_{ph}, \quad (1)$$

$$H_{el,el-ph} = - \sum_m \sum_{\langle l,l' \rangle_s} (t - \alpha \rho_{ll'}^m) c_{l,s}^{m+} c_{l',s}^m - \sum_{\langle mn,m'n' \rangle_s} T_{nn'}^{mm'} c_{n,s}^{m+} c_{n',s}^{m'} + h.c., \quad (2)$$

$$H_{ph} = \frac{\kappa}{2} \sum_m \sum_{\langle l,l' \rangle} (\rho_{ll'}^m)^2. \quad (3)$$

Here $c_{l,s}^{m+}$ creates an electron of spin s on carbon site l of molecule with order number m . $T_{m,m'}^{n,n'}$ and t are the intermolecular and intramolecular hopping integrals, respectively. The intermolecular hopping matrix elements $T_{m,m'}^{n,n'}$ are determined by the π -electron overlaps between carbon atoms n and n' of the different molecules m and m' . There is only one type of elastic terms that enter the potential energy: the bond-stretching energy with spring constant k , $\rho_{l,l'}^m$ is the change of the bond length between sites l and l' at the molecule m . The term proportional to α is the coupling between the bond-stretching modes and the electronic structure. The notation $\langle l,l' \rangle$ and $\langle mn,m'n' \rangle$ refers, respectively, to the bonds between nearest-neighbor sites of the single molecule and to the carbon pairs of nearest-neighbor molecules in the one-dimensional structure.

The polymer bond is formed if the midpoints of two nearly parallel double bonds belonging to neighboring molecules fall into the intermolecular axis [1, 10, 7]. Two facial pairs of two carbon atoms in the adjacent C_{60} molecules form intermolecular bridges. Due to the translation invariance, on each molecule $\rho_{l,l'}^m = \rho_{l,l'}$ and $T_{m,m'}^{n,n'} = T$.

After substituting the sum (2) over m for the sum over the vector k of the inverse lattice and averaging the Hamiltonian (1) over

$$\psi_{l,s}(\mathbf{k}) = c_{l,s}^{\mathbf{k}+} | 0 \rangle$$

under condition :

$$\sum_{\langle i,j \rangle} \rho_{ij} = 0, \quad (4)$$

we obtain the system yielding the minimum of the energy $H(1) - (3)$:

$$\rho_{ij} = \frac{\alpha}{\kappa N} \sum_{n,\mathbf{k},s}^{occ} \psi_{i,s}^{n*}(\mathbf{k}) \psi_{j,s}^n(\mathbf{k}) - \frac{\alpha}{90\kappa N} \sum_{\langle i,j \rangle} \sum_{n,\mathbf{k},s}^{occ} \psi_{i,s}^{n*}(\mathbf{k}) \psi_{j,s}^n(\mathbf{k}) - \quad (5)$$

$$-\sum_{l'}(t - \alpha\rho_{ll'}) + T \sum_a \delta_{ln_a} \delta_{l'n'_a} e^{-ika} \psi_{l',s}^n(k) = E^n(k) \psi_{l,s}^n(k). \quad (6)$$

The condition (4) means that in contrast to [12], the changes of the σ bond lengths, including the dimerization, are determined only by the π -electron interaction with phonons. N is the number of the unit cells of the chain, and a is the fundamental translation vector of the one-dimensional lattice. The electron wave eigenfunctions $\psi_{l,s}^n(k)$ at the site l correspond to the eigenenergy $E^n(k)$. The energy levels are counted off the π -orbital energy of carbon atom. The summation in (5) is over all occupied states. The self-consistent system (5), (6) was solved numerically for the following parameters: $t = 2.1 \text{ eV}$, $\alpha = 6.0 \text{ eV/\AA}$, $\kappa = 52.5 \text{ eV/\AA}^2$ [10]. The T was varied from $0.1t$ to $1.5t$.

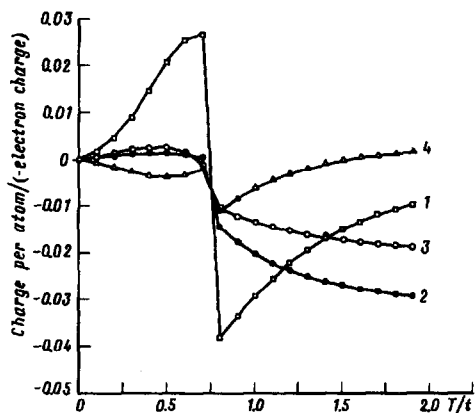


Fig.1. The linear chain without doping: 1 - bridge-head atoms; 2,3,4 - atoms situated near the bridge-head atoms. T and t are the intermolecular and intramolecular hopping integrals, respectively

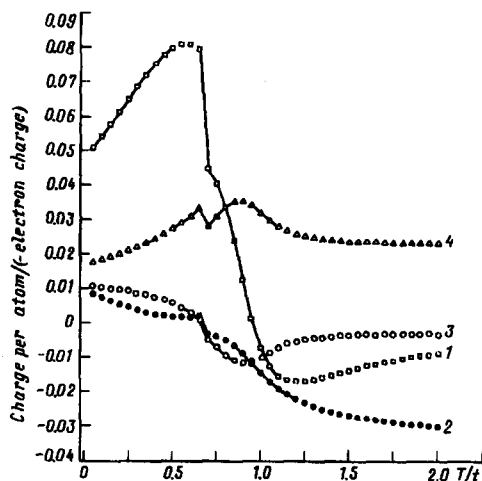


Fig.2. The linear chain with one doping electron on each molecule: 1 - bridge-head atoms; 2,3,4 - atoms situated near the bridge-head atoms

Calculations of charge distributions over the C_{60} surface and Jahn-Teller distortions of carbon atoms for the cases of neutral and charged molecules in the linear chain were performed. Due to the Jahn-Teller effect, the carbon atoms are displaced from their normal position in the isolated C_{60} . It should be noted that distortions of the C_{60} cage have been found experimentally by the Reitveld refinement [6]. The model predicts shortening of intraball bonds between the bridge-head carbon atoms with increasing T/t . It is found that charge distributions, the width of bands, the gap Δ between the highest valence band and the conduction band, and Fermi level positions of the π -electron subsystem depend nonmonotonically on the ratio of the intermolecular hopping integral T to the intramolecular hopping t . Δ decreases as T approaches the critical value T^* and increases again when $T > T^*$. The dependencies of the charge density per bridge-head atom and per atoms situated near the it vs T/t in C_{60} and C_{60}^- are shown in Fig.1 and Fig.2, respectively. The charges on the intermolecular bondings change their sign at $T/t \approx 0.68$ for the C_{60}^- (Fig. 1) and at $T/t \approx 0.74$ for the

C_{60} (Fig.2) chains. This transition is more smoothed in the C_{60}^- chain than in the C_{60} linear polymer. The widening of the half-filled band ($\sim 0.1 eV$) when $T \rightarrow T^*$ is followed by its polaronic narrowing when T becomes larger than T^* . With increasing T/t an extra electron spreads from the regions of intermolecular bonds to the equator of the C_{60}^- ball (polaron state) (Fig.3,4). Despite the rigid-band predictions, the conduction band is of very small width ($\sim 0.01 eV$) and has weak dispersion both in the charged and the neutral systems for $0.1 < T/t < 1.5$. One can suggest that small polarons may act as charged carriers in the chain when $T > T^*$.

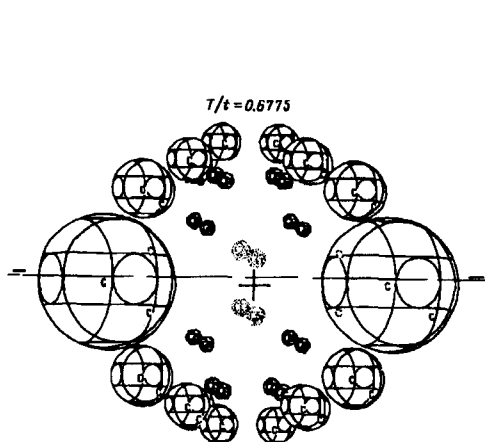


Fig.3. The charge density over the surface of C_{60} for $T/t = 0.68$. The radii of the spheres are proportional to the absolute value of the charge. Positive and negative charges are shown as light and dark spheres, respectively

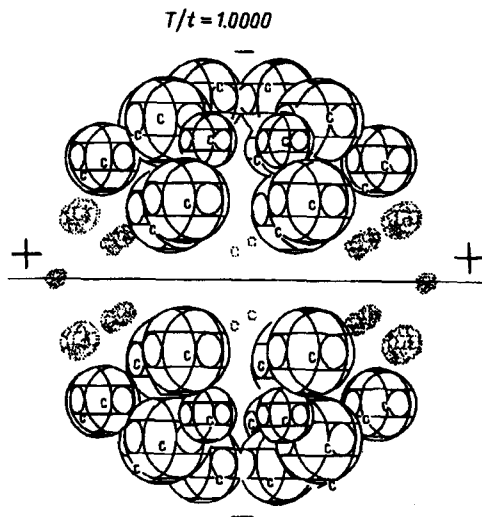


Fig.4. The charge density over the surface of C_{60}^- for $T/t = 1.00$. The radii of the spheres are proportional to the absolute value of the charge

When the lowering of the electronic energy of a carrier due to its being self-trapped exceeds the electronic bandwidth, this state collapses to a single molecule ($T > T^*$). In contrast with three-dimensional cases, here this effect is enhanced by the one-dimensionality. Usually, the extremely narrow band that characterizes small-polaron provides the hopping-type motion of carriers, although magnetic data indicate a metallic state in C_{60}^- chain [1, 7]. However, the coherent small-polaron motion may occur under special conditions, for example, at low temperatures and $\bar{T} > U$, where U is the effective energy of the screened Coulomb repulsion of electrons and \bar{T} is the polaronic bandwidth. If this motion really occurs, the free-carrier absorption in optical spectra due to the coherent motion in the conduction band of small-polaronic carriers should be limited to frequencies below the characteristic intramolecular frequencies. Also it is expected that the present approach for the neutral chain will give a deeper insight into the polymerization and the amorphization of pure fullerene crystals under pressure [7-9].

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