

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 in phase transitions may be caused by the cooperative Jahn–Teller effect. © 1996 American Institute of Physics. [S0021-3640(96)00220-4]

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Recently a number of structural and electronic phase transitions have been found in fullerides. In particular, the existence of a phase consisting of linear polymer chains in A_1C_{60} compounds ($A=K, Rb, Cs, Na_2Cs, Na_2Rb$) has come into focus.^{1–6} The low temperature structure of A_1C_{60} is orthorhombic with an unusually short separation of 9.1–9.3 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 materials science.^{7,8} Amorphous-carbon structures based on linear-polymerized C_{60} molecules have been found at pressures above 5 GPa.⁹ The details of the reaction mechanism for the C_{60} and C_{60}^- chain formation are as yet unclear.^{10–12}

It is well known that the Jahn–Teller effect leads to a dynamic instability of symmetrical configurations 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-symmetry C_{60} . It is now well established that the threefold degenerate t_{1u} lowest unoccupied state of C_{60} is the conduction band of A_xC_{60} compounds.

In our previous work⁹ we studied the band reconstruction of 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 and local electron–phonon interactions and employs the adiabatic approximation. The SSH model has been extended to the case of 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.

Here we consider two types of linear chains. The first is a C_{60}^- polyanion chain in the orthorhombic phase A_1C_{60} (Refs. 1–6), and the second consists of linear-polymerized C_{60} molecules in the amorphous-carbon structures.^{7–9} We assume that the neutral and charged molecules 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 the 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:

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

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

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

Here $c_{l,s}^{m+}$ creates an electron of spin s on carbon site l of molecule 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 term that enters 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.

A polymer bond is formed if the midpoints of two nearly parallel double bonds belonging to neighboring molecules fall on the intermolecular axis.^{1,7,10} 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 \mathbf{k} of the reciprocal lattice and averaging the Hamiltonian (1) over

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

under the condition

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

we obtain the system yielding the minimum of the energy H defined by Eqs. (1)–(3):

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

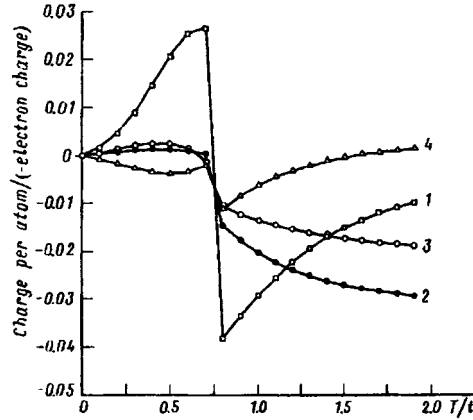


FIG. 1. The linear chain without doping: 1—bridge-head atoms; 2,3,4—atoms situated near the bridge-head atoms. T and t are the intermolecular and intramolecular hopping integrals, respectively.

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

The condition (4) means that in contrast to Ref. 12, the changes of the σ bond lengths, including the dimerization, are determined solely by the π -electron interaction with phonons. N is the number of unit cells of the chain, and \mathbf{a} is the fundamental translation vector of the one-dimensional lattice. The electron wave eigenfunctions $\psi_{l,s}^n(\mathbf{k})$ at the site l correspond to the eigenenergy $E^n(\mathbf{k})$. The energy levels are counted from 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: $t=2.1$ eV, $\alpha=6.0$ eV/Å, $\kappa=52.5$ eV/Å² (Ref. 10). The hopping integral T was varied from $0.1t$ to $1.5t$.

We calculated the charge distributions over the C_{60} surface and the Jahn–Teller distortions of carbon atoms for the cases of neutral and charged molecules in the linear chain. 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 the charge distributions, the widths of the 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 integral t . The gap Δ decreases as T approaches the critical value T^* and increases again when $T > T^*$. The charge densities per bridge-head atom and per atom situated near it are plotted as functions of T/t for C_{60} and C_{60}^- in Figs. 1 and 2, respectively. The charges on the intermolecular bonds change sign at $T/t \approx 0.68$ for the C_{60} chain (Fig. 1) and at $T/t \approx 0.74$ for the C_{60}^- chain (Fig. 2). This transition is smoother in the C_{60}^- chain than in the C_{60} linear polymer. The widening of the half-filled band

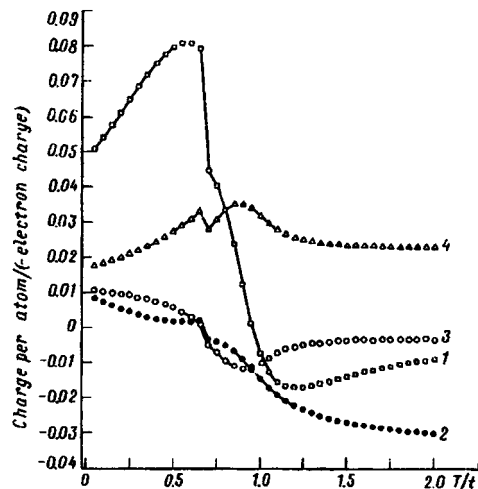


FIG. 2. The linear chain with one doping electron on each molecule: 1—bridge-head atoms; 2,3,4—atoms situated near the bridge-head atoms.

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

When the lowering of the electronic energy of a carrier due to its being self-trapped exceeds the width of the electronic band, this state collapses to a single molecule ($T > T^*$). In contrast with three-dimensional cases, here this effect is enhanced by the

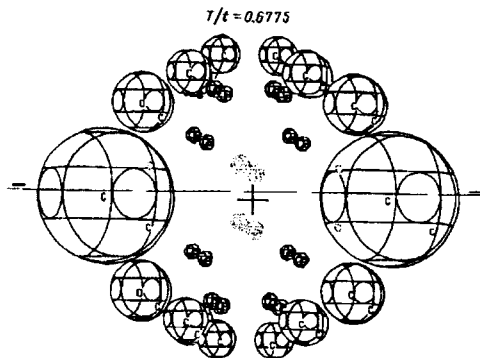


FIG. 3. The charge density over the surface of C_{60} for $T/t=0.68$. The radii of the spheres are proportional to the absolute value of the charge. Positive and negative charges are shown as light and dark spheres, respectively.

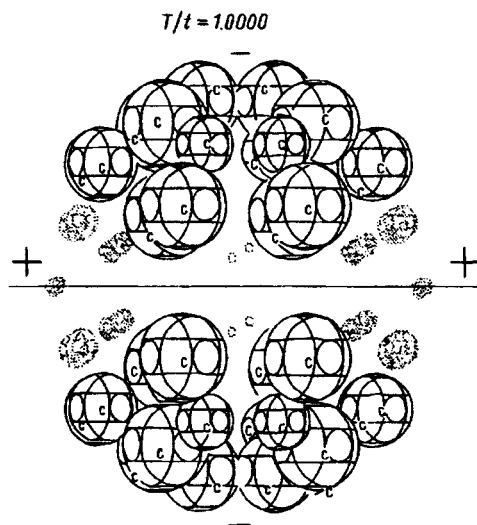


FIG. 4. The charge density over the surface of C_{60}^- for $T/t=1.00$. The radii of the spheres are proportional to the absolute value of the charge.

one-dimensionality. Usually the extremely narrow band that is characteristic of a small polaron provides a hopping-type motion of carriers, although magnetic data indicate a metallic state in the C_{60} chain.^{1,7} However, coherent small-polaron motion can occur under special conditions, for example, at low temperatures and $\tilde{T} > U$, where U is the effective energy of the screened Coulomb repulsion of electrons and \tilde{T} is the width of the polaronic band. If this motion really does occur, the free-carrier optical absorption due to the coherent motion in the conduction band of small-polaronic carriers should be limited to frequencies below the characteristic intramolecular frequencies. 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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