

# Linear chains of fullerenes under pressure

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Electron structure of 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. Band structures of linear  $C_{60}$  polymer and  $C_{60}^-$  polyanion chains and Jahn-Teller distortions of molecule are calculated self-consistently as a functions of applied pressures. The role of electron-phonon interaction in polymerization mechanism is discussed.

Three routes are known to prepare linear chains of fullerenes: polymerization by pressure, charge transfer and light [1]. In particular, amorphous-carbon structures based on linear-polymerized  $C_{60}$  molecules have been found at pressure above 5 GPa [2,3], the anions in the orthorhombic phase of  $A_1 C_{60}$  compounds ( $A = K, Rb, Cs, Na_2 Cs, Na_2 Rb$ ) are linear chains of covalently bonded  $C_{60}^-$  molecules [4,5]. The mechanism for the formation of covalent bond between molecules is as yet unclear. It is known neutral and charged molecules have the same position and orientation in the chain [1]. A polymer bond is formed if midpoints of two nearly parallel double bonds belonging to neighboring molecules fall on the intermolecular axis. Two facial pairs of two carbon atoms in the adjacent  $C_{60}$  molecules form intermolecular bridges.

It is well known that the band structures of solid  $C_{60}$  and alkali-doped fullerides reflect primarily the molecular orbitals of high-

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symmetry  $C_{60}$  and electron-phonon interactions have a large influence on the electronic spectrum of these compounds.

In our previous work a simple model was proposed to describe non-rigid-band effects in fullerenes. The SSH tight-binding model [6] applied for isolated  $C_{60}$  in Ref. [7] have been extended to the case of  $c_{60}$  crystals [8,9]. The model takes into account the  $\pi$ -electron hopping between carbon atoms, local electron-phonon interactions, and employs adiabatic approximation. Electron correlation effects and lattice oscillations were ignored.

We considered two types of linear chains [1]. The first type is linear-polymerized  $C_{60}$  molecules in the amorphous-carbon structures [2,3] and the second is a  $C_{60}^-$  polyanion chain in the orthorhombic phase of  $A_1 C_{60}$  [5,6]. The main purpose of the present work is to study how the band structure of linear chains and Jahn-Teller distortions of molecules depend on pressure.

The SSH Hamiltonian has the following form:

$$\hat{H} = \hat{H}_{el, el-ph} + \hat{H}_{ph} \quad 1$$

$$\hat{H} = - \sum_m \sum_{\langle l, l' \rangle_s} (t - \alpha \rho_{ll'}^m) c_{l,s}^{m+} c_{l',s}^m - T \sum_{\langle mn, m'n' \rangle_s} c_{n,s}^{m+} c_{n',s}^{m'} + h.c. \quad 2$$

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

Here  $c_{l,s}^{m+}$  creates an electron of spin  $s$  on carbon site  $l$  of molecule with order number  $m$ ,  $(t - \alpha \rho_{ll'}^m)$  and  $T$  are the intramolecular and intermolecular hopping integrals, respectively,  $\kappa$  is the spring constant of the bond-stretching energy,  $\rho_{ll'}^m$  is the change of the bond length between sites  $l$  and  $l'$  at the molecule  $m$ . The term proportional to  $\alpha$  is the coupling between the bond-

stretching modes and the electronic structure. The notation  $\langle l, l' \rangle$  and  $\langle m n, m' n' \rangle$  refers, respectively, to the bonds between nearest-neighbor sites of the single molecule and to the carbon pairs of nearest-neighbor molecules. Due to the translation invariance, on each molecule  $\rho_{ll'}^m = \rho_{ll'}$ . The hopping integral  $T$  was varied from  $0.05t$  to  $1.85t$ .

We calculated the band structure of linear chains and Jahn-Teller distortions of  $C_{60}$  cage for the cases of neutral and charged molecules.

Due to electron-phonon interaction, the carbon atoms are displaced from their normal position in the undeformed  $C_{60}$  ( $\alpha \neq 0$ ). This model predicts significant elongation of intraball bonds between the bridge-head carbon atoms (Fig.1) with increasing  $T$ . One can assume that the intermolecular overlap of the  $\pi$ -electron orbitals  $T$  is a strictly increasing function of applied pressure. The dependencies of width of conduction and valence bands and its positions of polymer chains vs  $T/t$  for two different  $\alpha = 0$  and  $\alpha \neq 0$  cases are shown in Fig.2 and Fig.3, respectively. In the absence of electron-phonon interaction  $\alpha = 0$ . It is found that when  $\alpha \neq 0$  the gap  $\Delta$  between the valence and the conduction band decreases as  $T$  approaches the critical value  $T^*$  and increases again when  $T > T^*$ .

The conduction band is of very small width ( $\approx 0.3$ ). Unlike the case  $\alpha = 0$  (Fig.2) the finite jump of the gap takes place at  $T = T^*$  when  $\alpha \neq 0$  (Fig.3). We obtain the similar results for  $C_{60}^-$  chains, but this transition near  $T^*$  is more smoothed than in the  $C_{60}$  linear polymer. This jump is caused by the electron-phonon interaction.

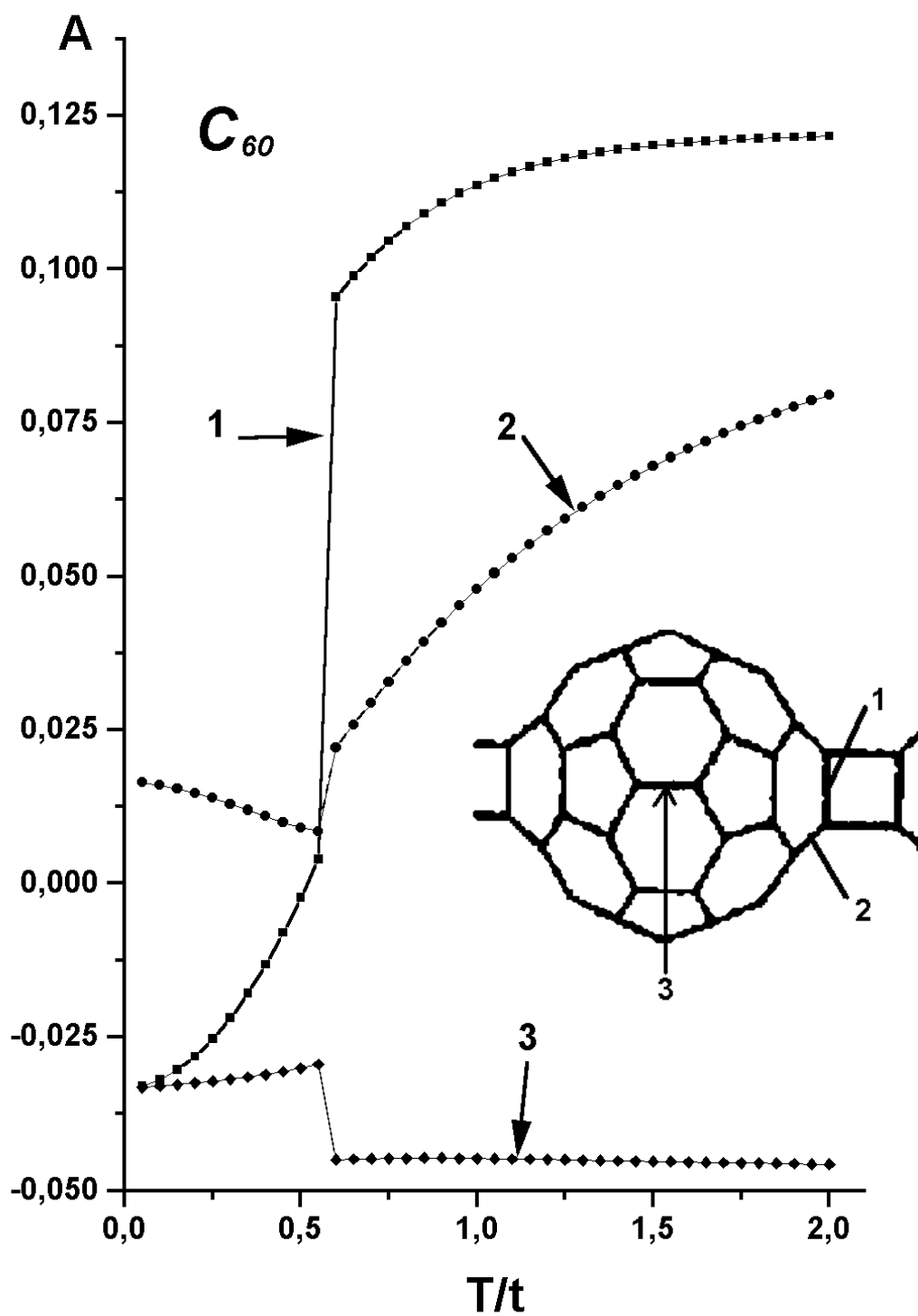
Effects described above may be followed by the one-dimensionality of linear chains in great numbers of degrees of freedom on the single site. All our results indicate the formation of

covalent inter- $C_{60}$  bonds and some breaking of intra- $C_{60}$  bonds in linear chains under pressure.

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**Fig. 1.** Changes of the 1, 2, 3 bond lengths vs  $T/t$

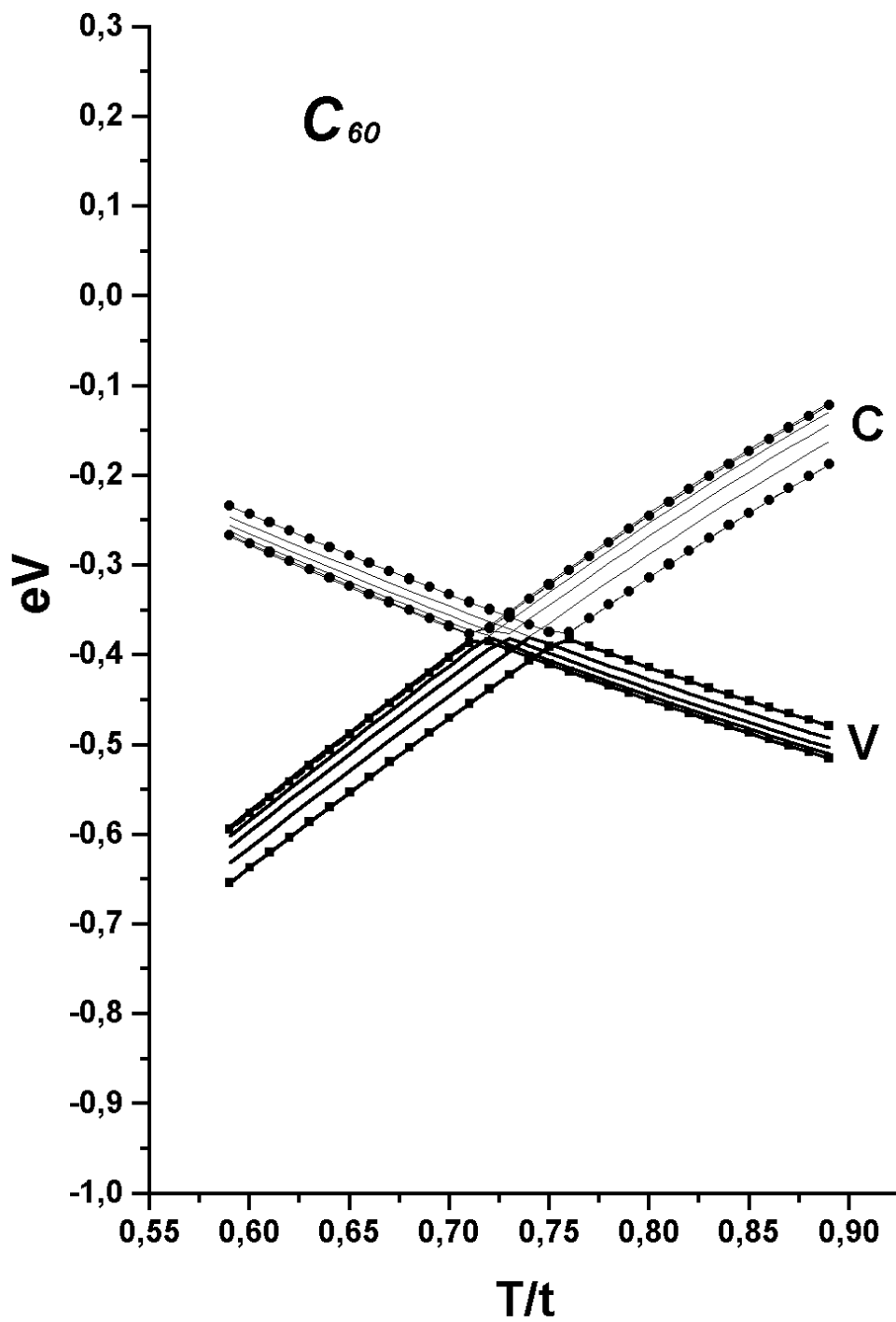
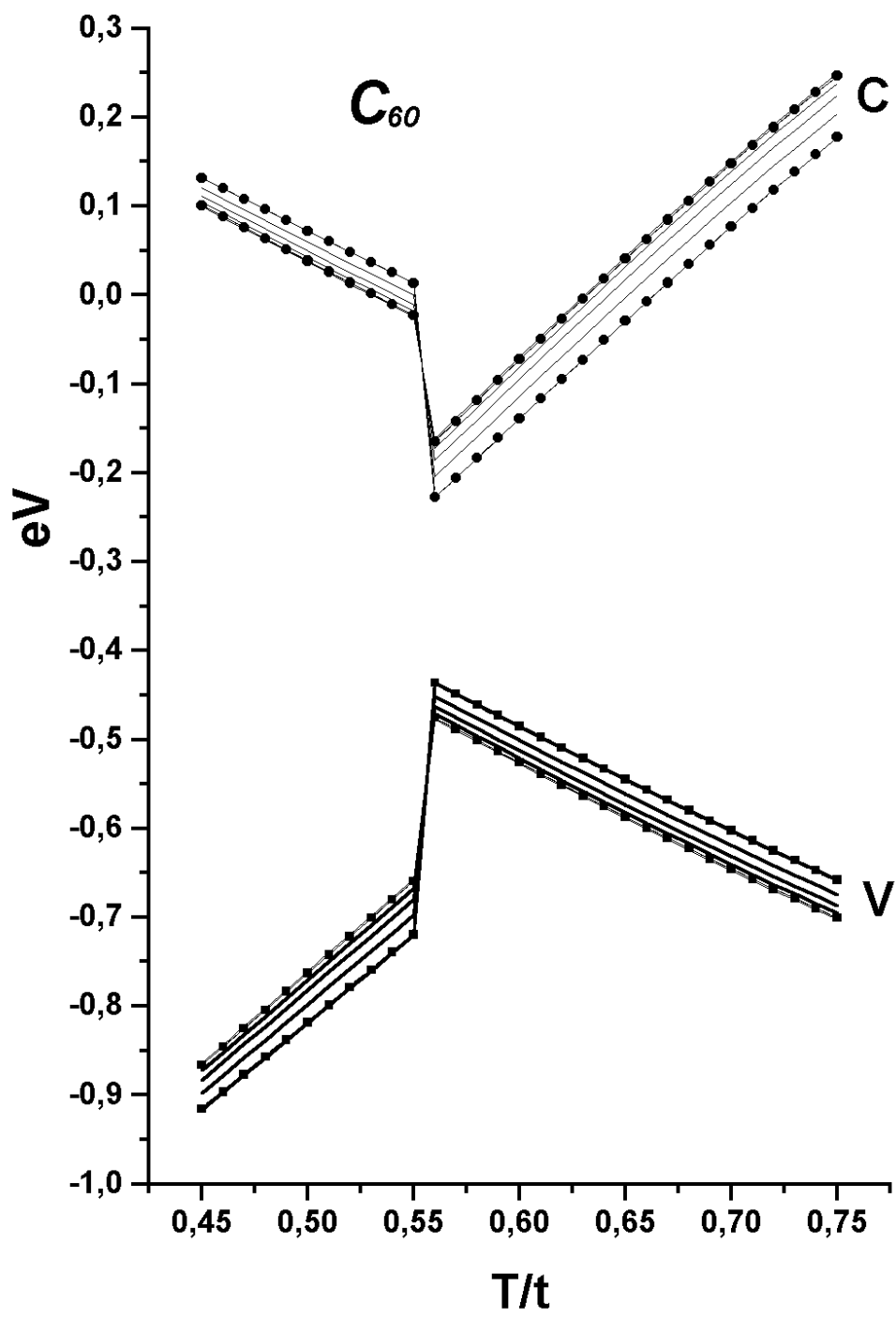


Fig. 2. V Valence and C conduction bands vs  $T/t$  in case of  $\alpha = 0$



**Fig. 3.** V Valence and C conduction bands vs  $T/t$  in case of  $\alpha \neq 0$