

Cooperative Jahn-Teller effect and the band structures of K_xC_{60} crystals

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Abstract

Band reconstructions upon doping are studied with the use of a generalized version of the Su-Schrieffer-Heeger model for the intermolecular and intramolecular degrees of freedom. A simple model describing the covalent bond formation in C_{60} compounds is proposed. 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. It is shown that the polymerization of equally oriented C_{60} molecules under phase transitions may be caused by the cooperative Jahn-Teller effect.

Keywords: electron density, structural phase transitions, fullerenes

Introduction

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_xC_{60} compounds ($A = K, Rb, Cs, Na_2Cs, Na_2Rb$) came into focus [1-6]. The low temperature structure of A_xC_{60} is orthorhombic with an unusually short separation of 9.1Å - 9.3Å 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]. Amorphous-carbon structures based on linear-polymerized C_{60} molecules have been found under a pressure of above 5 GPa [8]. Details of the reaction mechanism for the C_{60} and C_{60}^- chain formation are yet unclear [9, 10].

In our previous work [11] we studied the band reconstructions 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. According to these calculations, K_xC_{60} and $K_xC_{60}^-$ appear to be semiconducting with a small Jahn-Teller gap at the Fermi level. The shifts of the Fermi level depend nonmonotonically on x , and the conduction band width changes strongly upon doping.

Here we study, self-consistently, the band structure of C_{60} and C_{60}^- linear chains and Jahn-Teller distortions

of carbon atoms in C_{60} . It is well known that 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. 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.

Model

Our band calculations are performed in the framework of the Su-Schrieffer-Heeger (SSH) model. The model takes into account the π -electron hopping between carbon atoms, local electron-phonon interactions, and adiabatic approximation. Previously [11], we have extended the SSH model to the case of the doped fulleride crystals. Besides the intramolecular electron transfer, we introduced there the π -electron hopping between the nearest neighbor molecules in crystal lattice. In the case of translational symmetry, SSH Hamiltonian for fullerides has the following form:

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

$$H_{el,el-ph} = - \sum_m \sum_{\langle l,l' \rangle} (t - \alpha \varphi_{ll'}^m) c_{l,s}^{m+} c_{l',s}^m - \quad (2)$$

$$- \sum_{\langle nn',m'm' \rangle} T_{mm'}^{nn'} c_{n,s}^{m+} c_{n',s}^{m'} + \hbar \cdot c$$

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

Electron correlation effects and lattice oscillations are ignored. We consider two types of linear chains. The first is a C_{60}^- polyanion chain in the orthorhombic phase of A_7C_{60} [1-6], and the second is linear-polymerized C_{60} molecules in the amorphous-carbon structures [7, 8]. Here $c_{i,s}^m$ creates an electron of spin s on carbon site i of molecule with order number m .

There is one type of elastic terms that enter the potential energy: the bond-stretching energy with spring constant k , $\rho_{ll'}^m$ is the change of the bond length between sites l and l' at the molecule m . Due to the translation invariance $\rho_{ll'}^m$ is the same on each molecule $\rho_{ll'}^m = \rho_{ll'}$. The term proportional to α is the coupling between the bond-stretching modes and the electronic structure. The intermolecular hopping matrix elements $T_{mm'}$ are determined by the π -electron overlaps between carbon atoms n and n' of the different molecules m and m' . We take $T_{mm'} = T$. The C-C bond distances between the unit cells and between the bridge-head atoms depend on the intermolecular hopping integral T . Moreover, a polymer bond is formed if the midpoints of two nearly parallel C=C double bonds belonging to neighboring molecules fall into the intermolecular axis [1], [9], [10]. Two facial pairs of two carbon atoms in the adjacent C_{60} molecules form intermolecular bridges. t is the intramolecular hopping integral. The notation $\langle ll' \rangle$ 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.

After the averaging of Hamiltonian (1) over $\Psi_{i,s}(k) = c_{i,s}^m |0\rangle$ 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):

$$\rho_{ij} = \frac{\alpha}{kN} \sum_{n,k,s} \Psi_{i,s}^{n*}(k) \Psi_{j,s}^n(k) - \frac{\alpha}{90kN} \sum_{\langle j, j' \rangle} \sum_{n,k,s} \Psi_{i,s}^{n*}(k) \Psi_{j,s}^n(k), \quad (5)$$

$$\sum_{i'} (t - \alpha \rho_{i'i} + T \sum_{\nu} \delta_{i\nu} \delta_{i'\nu} e^{-ik\nu}) \Psi_{i',s}^n(k) = E^n(k) \Psi_{i,s}^n(k), \quad (6)$$

where k is the vector of the inverse lattice, N is the number of the unit cells of the chain, and ν is the fundamental translation vector of the one-dimensional lattice. The electron wave eigenfunctions $\Psi_i^n(k)$ at the site i correspond to the eigen energy $E^n(k)$. The energy levels are counted off the π -orbital energy of carbon atom. The summation in (5) is over all occupied states. The number of occupied states in our consideration was varied from $60N$ to $61N$. The self-consistent system (5) was solved numerically upon weak electron-phonon coupling constant for the following parameters:

$t=2.1\text{eV}$, $\alpha=6.0\text{eV/\AA}$, $k=52.5\text{eV/\AA}^2$. The ratio T/t was varied from 0.1 to 1.0. We assumed neutral and charged molecules to have the same position and orientation in the chain.

Results and Conclusion

The band structures of fulleride crystals and the cooperative Jahn-Teller distortions of C_{60} molecules upon doping are calculated. The conduction bandwidth and the shifts of the Fermi level change strongly with x in K_4C_{60} crystals. Furthermore, numerical self-consistent calculations of charge distribution over the C_{60} surface and Jahn-Teller distortions of carbon atoms for the cases of neutral and charged molecules in the linear chain have been 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 the distortion of the C_{60} cage has been found experimentally by the Reitveld refinement [6]. Such a deformed molecule belongs to D_{2h} symmetry [9]. Nonmonotonic dependence is found of charge distributions, the width of bands and Fermi level position of the π -electron subsystem on the ratio of the intramolecular hopping integral T to the intermolecular hopping t . The charges on the intermolecular bondings change their sign at $T/t=0.75$ for the C_{60}^- and the C_{60} chains. This transition is more smooth in the C_{60}^- chain than in the C_{60} linear polymer. The population analyses have shown that the bridge-head atoms become charged positive when $T/t > 0.75$ and negative when $T/t < 0.75$. The width of the lowest unoccupied band is very small. This band has weak dispersion in both cases. The Fermi level is located in a weakly dispersive band in KC_{60} crystals. In this way a covalent bond can be created if the size of the unit cell of linear C_{60} chain becomes less than the critical one. The present approach is expected to give a deeper insight into the polymerization mechanism under phase transitions.

Acknowledgments

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References

- [1] S.Pekker et al., Science **265** (1994) 1077
- [2] P.W.Stephens et al., Nature **370** (1994) 636
- [3] A.M.Rao et al., Science **259** (1993) 955
- [4] C.Michael et al., Phys.Rev.B **51** (1995) 3210
- [5] H.Hirai et al., Phys.Rev.B. **51** (1995) 15555
- [6] Q.Zhu, Phys.Rev.B **52** (1995) R723
- [7] O.Chauvet et al., Phys.Rev.Lett. **72** (1994) 2721
- [8] V.D.Blank et al., Phys.Lett.A **204** (1995) 151
- [9] K.Tanaka et al., Sol.State Commun. **93** (1995) 163
- [10] T.Pusztai et al., Europhys.Lett. **32** (1995) 721
- [11] A.Remova et al., Phys.Rev.B **52** (1995) 13715