

Electronic structure of linear chains of fullerenes

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The band structure of linear chains of fullerene molecules is calculated as a function of the intermolecular π -electron overlap integral T , which increases under increasing external pressure. Chains consisting of neutral (C_{60}) and charged (C_{60}^-) molecules are studied. It is shown that there is a sharp transition from a metal (or narrow-gap semiconductor) to an insulator (with band gap ~ 1 eV) with increasing T . The proposed model makes it possible to describe the formation of solid-carbon structures, containing chains of covalently bound fullerene molecules, with different pressure-dependent semiconductor properties. © 1997 American Institute of Physics. [S0021-3640(97)01608-3]

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Linear chains of fullerenes were recently discovered in A_1C_{60} compounds ($A = K, Rb, Cs, Na_2Cs, Na_2Rb$).^{1–6} Phase transitions with a change of lattice symmetry are observed in these structures. In the orthorhombic phase the distance between the centers of the molecules in the direction of the crystallographic vector \mathbf{a} equals only 9.1–9.3 Å. It is conjectured that the fullerene molecules form in this direction a polyanion chain with covalently bound C_{60}^- molecules. It is believed that the polymer bond in polyanion A_1C_{60} chains forms if the midpoint of the two closest parallel double bonds belonging to neighboring molecules falls on the intermolecular axis; the π electron orbitals of the two closest pairs of carbon atoms form an intermolecular overlap. The observation of identically oriented linearly polymerized neutral C_{60} molecules in the solid phase was recently reported. Such chains are formed in amorphous fullerite structures at high pressures and temperatures.^{7–10} The details of the mechanism of formation of the polymer chains have not been adequately studied.

It is well known that the rigid-band model describes poorly the electronic structure of compounds of the type A_xC_{60} ($x = 1, 2, 3, 4$), where A is an alkali-metal atom. One reason for this could be the electron–phonon interaction. The band structure of fullerides reflects primarily the molecular structure of the highly symmetric C_{60} . Since the three-fold degenerate t_{1u} level forms the conduction band of A_xC_{60} compounds, the Jahn–Teller effect should play a fundamental role here.¹¹

The calculations were performed in a model proposed by Su, Schrieffer, and Heeger (SSH),¹² in which hops of the π electrons between neighboring carbon atoms are studied and the local electron–phonon interaction is treated in an adiabatic approximation. This approach was used in Ref. 13 to calculate the spectrum of an isolated fullerene molecule, and it was also shown that the formation of “long” and “short” bonds between the

carbon atoms on the surface of the C_{60} molecule could be due to the electron–phonon interaction. It is conjectured that the σ electrons do not directly affect the optical and chemical properties, but they do provide a bond between the carbon atoms on the surface of C_{60} , determining the energy of elastic deformation of the bonds.

In a previous work we extended this model to the case of fulleride crystals.¹¹ Besides intramolecular electronic transitions, intermolecular transitions between the nearest atoms to the neighboring molecules were also introduced. The main objective of present work was to study the behavior of the valence (h_u) and conduction (t_{1u}) bands as a function of the intermolecular overlap integral for neutral linearly polymerized C_{60} molecules in the amorphous phase and for polyanionic chains A_1C_{60} in the orthorhombic phase.

The interaction between the chains is assumed to be weak, and charge transfer from the alkali-metal atoms to the molecules is assumed to be complete. Furthermore, we neglect the electron–electron correlations. The interaction of the electrons with the intermolecular vibrations is weak compared with the intramolecular interactions, since the mass of the molecule is much greater than the mass of the carbon atom. The SSH Hamiltonian is given in the form^{11–13}

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

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

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

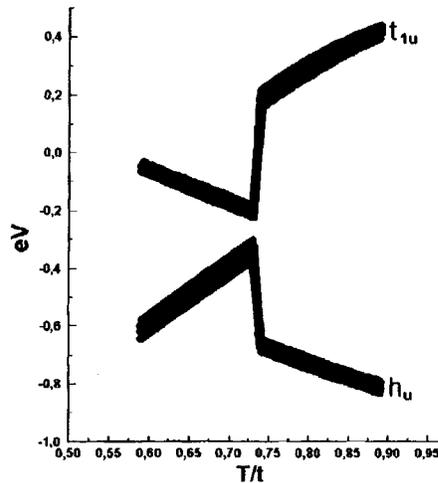


FIG. 1. Energy characteristics as a function of T for C_{60} . T and t — inter- and intramolecular overlap integrals of π electrons. The t_{1u} band in eV — conduction band, h_u — valence band.

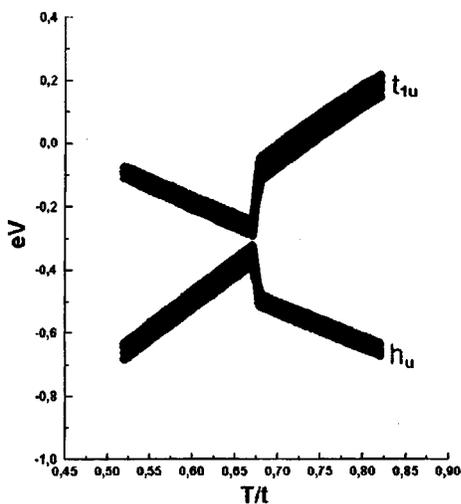


FIG. 2. Same as Fig. 1, for charged C_{60}^- molecules.

Here the operator $c_{l,s}^{m+}$ creates an electron with spin s at the l th carbon atom belonging to the m th molecule, and T and t are intermolecular and intramolecular ‘‘hopping’’ integrals, determined by the overlap of the π -electron clouds of the nearest carbon atoms. The term proportional to α reflects the dependence of the intramolecular overlap on the change in bond length $\rho_{ll'}^m$, between the nearest carbon atoms l and l' in the m th molecule. As a result of translational invariance, $\rho_{l,l'}^m = \rho_{l',l}^m$. The calculations were performed for the following values of the parameters: $t = 2.1$ eV, $\alpha = 6.0$ eV/Å, $\kappa = 52.5$ eV/Å² (Ref. 14); T was varied from $0.5t$ to $0.9t$.

The computational results for the Jahn–Teller distortions and the electron density distribution on the surface of molecules in a chain as a function of the intermolecular overlap integral T were presented in Ref. 14. It was shown that there exists a critical value T^* for which a redistribution of the electron density on the C_{60} surface occurs: $T^*/t \cong 0.74$ for neutral chains and $T^*/t \cong 0.68$ for charged chains.

The energy characteristics of the valence and conduction bands as a function of T for neutral and polyanionic chains are displayed in Fig. 1 and 2, respectively. For both the neutral and polyanionic chains the position of the valence and conduction bands is a nonmonotonic function of T , and their widths, remaining small ($\cong 0.5$ for both C_{60} and C_{60}^-), change very little. The bands closest to those under study do not overlap with them and are separated from them by an energy interval of the order of 1 eV near T^* . The threefold degeneracy of the t_{1u} level is completely lifted. In the limit $T \rightarrow T^*$ the band gap $\Delta \cong 0.5$ eV for C_{60} . For C_{60}^- the valence h_u and conduction t_{1u} bands merge. As the molecules come closer to one another (T increases), the band gap changes abruptly at the point T^* ($\Delta \cong 0.80$ eV for neutral chains and $\Delta \cong 0.35$ eV for charged chains). If T continues to increase in the above-indicated range, then the band gap will also increase. The decrease in Δ as $T \rightarrow T^*$ is a consequence of the one-dimensional character of the investigated periodic structures, when many degrees of freedom are present at one site of

a one-dimensional lattice, while the abrupt change in the band gap at $T=T^*$ is due to the Jahn–Teller effect. Having attributed the increase in the parameter T to the increase in pressure, it is natural to conclude that a transition of from a narrow-gap semiconductor to an insulator occurs in solid C_{60} at some pressure. The rapid increase in the band gap at pressures above some critical value indicates the possibility that strong covalent bonds are formed between the C_{60} molecules in a chain. Therefore the model makes it possible to describe the high-pressure formation of solid-hydrogen structures containing chains of covalently bound fullerene molecules and exhibiting different semiconductor properties. These properties can be varied by changing the pressure.

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