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ELECTRONIC PROPERTIES OF CARBON NANOTUBES WITH A PENTAGON-HEPTAGON PAIR DEFECT*

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The features of energetics and electronic properties of carbon nanotubes, containing a pentagon-heptagon pair (5/7) topological defect in the hexagonal network of the zigzag configuration, are investigated using the extended Su-Schriffer-Heeger model based on the tight binding approximation in real space. Our calculations show that this pentagon-heptagon pair defect in the nanotube structures is not only responsible for a change in nanotube diameter, but also governs the electronic behaviour around Fermi level. Furthermore, we have calculated the densities of states of the (9,0)-(8,0) and (8,0)-(7,0) systems. For the (9,0)-(8,0) system, a narrow gap exists in the vicinity of the Fermi energy. In contrast, for the (8,0)-(7,0) system, a little peak of the density of states occurs at the Fermi energy. These can be attributed to the addition of a pair of pentagon-heptagon defects in the interface between two isolated carbon nanotubes.

Keywords: carbon nanotubes, pentagon-heptagon pair defect, electronic properties, densities of states
PACC: 7125, 7360

I. INTRODUCTION

Since the discovery in 1991 by Iijima,[1] carbon nanotubes have attracted much attention.[2,3] One of the most fascinating aspects of these systems is that their electronic properties are directly and sensitively related to their geometry. This has been the subject of intensive experiments and theoretical efforts.[4−6] Recently, much work has been done towards an understanding of the structural and electronic properties of carbon nanotubes.[7,8] It has been predicted that the electronic structure of a perfect nanotube is either metallic or semiconducting, depending on their diameter and chirality,[9,10] which can uniquely be determined by the chiral vector (n, m), where n and m are integers.[11] Both of these factors determine the symmetry operations that describe the structure of carbon nanotubes, and consequently determine their electronic and lattice properties.[12,13]

On the other hand, the effect of defects on the electronic properties of carbon nanotubes has not been as well developed. Experimental observations have shown that carbon nanotubes are rarely as perfect as they were once thought to be.[14,15] By introducing a pentagon-heptagon pair defect into the hexagonal carbon lattice, two tube segments with different atomic and electronic structures can be seamlessly fused together to create intramolecular metal-metal, metal-semiconductor, or semiconductor-semiconductor junctions.[16−18] In fact, a carbon nanotube which presents a near-rectifying behaviour has been experimentally found.[19] Most recently, transport measurements performed for roped single-wall nanotubes show evidence of resonant tunnelling through quantized energy levels.[17] Thus, understanding the role of topological defects in carbon nanotubes is important for fundamental investigations of nanotube electronic structure, as well as transport properties[20] and, if modern semiconductor technology shows any indication, it may also be valuable for applications. In contrast, most theoretical predictions assume pure and perfectly cylindrical defect-free carbon nanotubes, which are viewed as a conformal mapping of the two-dimensional honeycomb lattice of single sheet(s) of graphite onto the surface of the cylinder.[21]

In this paper, we address the effect of a pentagon-

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heptagon pair defect on the electronic properties of single-walled carbon nanotubes (SWNTs). A pair of pentagon and heptagon is the smallest possible defect structure in the cylindrical hexagonal network of the carbon nanotube that changes its chirality without drastically altering the local curvature.[22,23] In the absence of other cycles than hexagon rings, Euler's theorem imposes the inclusion of 12 pentagons in the hexagonal network to close the structure. However, the addition of one heptagon in the cylindrical surface of the nanotube will require the presence of 13 pentagons to close the structure as the heptagon and the pentagon induce opposite 60° disclinations in the surface. When the pentagon is attached to the heptagon as in the aniline structure, it only creates topological changes (but no net disclination) which can be treated as a single local defect. Such a pair will create only a small local deformation in the width of the nanotube, it may also generate a small change in the helicity, depending on its orientation in the hexagonal network.[24,25] So their presence is hard to detect experimentally, but observations of the diameter of the carbon nanotubes, which becomes gradually thicker and thicker, imply the existence of a very large number of these pentagon-heptagon (5/7) pair defects which are accidentally aligned.[14] In fact, it is possible to join two perfect nanotubes by introducing pentagon-heptagon pair(s) in the interface between them.[26] The resulting carbon nanotube heterojunction might have a different electronic structure on each side of the interface.[27] The heterostructures formed by joining nanotubes of different chirality may show unique quasi-one-dimensional transport properties. Here, we explore the electronic properties of zigzag nanotubes (n, 0), containing one pentagon-heptagon (5/7) pair defect, by using the Su-Schriffer-Heeger (SSH) model. We determine the density of states (DOS) of the system by tight binding approximation with one π orbital per atom. And the influence of the 5/7 pair defect on properties and topology of nanotube are discussed.

Ⅱ. THEORETICAL MODEL AND COMPUTATIONAL METHOD

We can write the SSH Hamiltonian as follows:[28]

$$H = -\sum_{<ij>,s} t_{i,j}(C^+_{i,s}C_{j,s} + \text{H.c.}) + \frac{K}{2}(u_i - u_j)^2, \quad (1)$$

where i denotes the ith lattice site, j the nearest-neighbour lattice site around the ith site, and $< ij >$ means two nearest-neighbour sites, s indicates the direction of spin, $C^+_{i,s}$ and $C_{i,s}$ are the creation and annihilation operators for a π-electron with spin s on the ith site, $t_{i,j}$ is the nearest-neighbour hopping, u_i the ith lattice displacement from the equilibrium position. K is the effective spring constant between the adjacent units. The on-site energy is set equal to zero. Within this theory, graphite sheets and defect-free nanotubes have complete electron-hole symmetry with their Fermi levels at zero.

In order to find the π-electron ground state, we expand $t_{i,j}$ to first order in ionic displacement u_i , for instance,

$$t_{i,j}C^+_{i,s}C_{j,s} \to \left[t^0_{i,j} + \frac{\partial t_{i,j}}{\partial u_i}(u_j - u_i)\right]C^+_{i,s}C_{j,s}. \quad (2)$$

For simplicity, we take

$$t^0_{i,j} = t_0, \quad \frac{\partial t_{i,j}}{\partial u_i} = \alpha, \quad (3)$$

where t_0 is the transfer or overlap integral when $u_j - u_i = 0$ for all $< ij >$, α is the rate of change of the overlap integral with distance between nearest neighbours.

In order to minimize the total energy in our self-consistent calculation, it is convenient to cast all quantities into dimensionless forms as,

$$h = \frac{H}{t_0}, \quad \lambda = \frac{2\alpha^2}{\pi t_0 K}, \quad y_{ij} = \frac{\alpha}{t_0}(u_j - u_i). \quad (4)$$

Then the Hamiltonian becomes

$$h = -\sum_{<ij>,s}(1 + y_{ij}(C^+_{i,s}C_{j,s} + \text{H.c.}) = \frac{1}{\lambda\pi}\sum_{<ij>} y^2_{ij}. \quad (5)$$

Using a self-consistent iterative method,[29] we can numerically solve the Schrödinger equation of the system as

$$h\,\Psi_\mu = \varepsilon_\mu\,\Psi_\mu, \quad (6)$$

$$-\sum_j [1 + y_{ij}]Z^s_{\mu,j} = \varepsilon^s_\mu Z^s_{\mu,i}, \quad (7)$$

$$y_{ij} = 2\pi\lambda\left[\sum_{\substack{\mu,s\\(\text{occ})}} Z^s_{\mu,i}Z^s_{\mu,j} - \frac{1}{N}\sum_{<ij>}\sum_{\substack{\mu,s\\(\text{occ})}} Z^s_{\mu,i}Z^s_{\mu,j}\right], \quad (8)$$

where ε_μ and Ψ_μ are the μth eigenvalue and eigenvector of Eq.(6), respectively, $Z^s_{\mu j}$ is the expansion coefficient, and N is the number of sites in the system. Here, periodic boundary conditions are used, and (occ) means those states occupied by electrons. New values of the displacement order parameter y_{ij} are calculated by minimizing the total energy $E(y_{ij})$

of the system with respect to y_{ij}.

$$E(y_{ij}) = -\sum_{<ij>}\left\{[1+y_{ij}]\sum_{\substack{\mu\\(\mathrm{occ})}}[Z^{s^*}_{\mu,j}Z^{s}_{\mu,i} + Z^{s^*}_{\mu,i}Z^{s}_{\mu,j}]\right\} + \frac{1}{\lambda\pi}\sum_{<ij>} y_{ij}^2. \quad (9)$$

Given the initial value of the lattice configuration, we can obtain the electron energy level ε^s_μ and the expansion coefficient $Z^s_{\mu j}$ from Eqs.(7) and (8).

The starting geometry in the iterative optimization process is usually the one with zero displacement. The stability of the optimized geometry is always tested by using another starting configuration and performing the optimization again. For all parameters included in this study, the same optimal ground state was reached, independent of the starting configuration. The criterion for terminating the optimization is that between two successive iterations, the difference is less than 10^{-6} for the displacement order parameter.

Ⅲ. RESULTS AND DISCUSSION

As a model system, we have chosen (9,0), (8,0) and (7,0) tubes. The (9,0) tube is a metallic tube, whereas the (8,0) and (7,0) tubes are semiconducting. We examine two junctions, namely, the metal-semiconductor (9,0)-(8,0) and the semiconductor-semiconductor (8,0)-(7,0) junctions, by introducing a pentagon-heptagon (5/7) pair defect at the interface between them, respectively. The former is composed of 375 atoms while the latter contains 331 atoms. The numbers chosen are large enough to avoid the effects of the dangling π bonds at the edges of the junctions. In the zigzag configuration the tubes have C–C bonds parallel to their axis. Each atom of these systems contains a π electron. In order to study the ground state, we always fill the π electrons in the lowest possible levels in every iterative step. In the following numerical calculations, we take parameter λ=0.24.[30] Figure 1 shows the schematic view of a (9,0) (or an (8,0)) tube joined to an (8,0) (or (7,0)) tube by introducing a pair of pentagon-heptagon defects. For simplicity, each aniline defect is made aligned along the tubule axis. The shaded atoms comprise the defect.

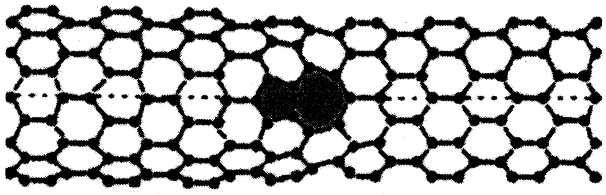


Fig.1. Schematic view of the atomic structure of the (9,0)/(8,0) or (8,0)/(7,0) carbon nanotube connection with its pentagon-heptagon pair defect. The shaded atoms comprise the defect.

Firstly, we discuss the atomic structural changes and the energy structure of the (9,0)-(8,0) and (8,0)-(7,0) systems. From the calculated results, we find that in each structure, the average bond length in the pentagon is slightly longer than one of the hexagons and the average bond in the heptagon is shorter than or nearly equivalent to one of the hexagons. For the pentagonal case, this could be explained by analogy with the fullerenes. In addition, the calculated results show that the pentagon is essentially planar with a very small distortion, although the heptagon is in a boat shape in order to reduce its bond angles to within the range 124°–126°, and to suitably accommodate the local negative curvature of the carbon network. The purely cylindrical shape of the nanotube is also perturbed by the presence of this 5/7 pair defect. The belt of hexagons containing the pentagon is found to be elliptical, with the long axis passing through the perturbing ring; while for the belt containing the heptagon, the section of the nanotube is elongated in the perpendicular direction. The ratios between the axes of the two ellipses of the joint are, respectively, about 0.8 (5) and 0.9 (7) for a single 5/7 defect. This process can be viewed as stretching by the pentagon, and reciprocally, flattening by the heptagon of the circular section of the tube. Moving away from the interface, the perfect-tube configuration is gradually recovered. That is, a few belts of hexagons moving away from the 5/7 defect, the cylindrical shape of the nanotube reappears.

The structural changes should affect the electronic structure, although only locally. The electronic properties of the (9,0)-(8,0) and (8,0)-(7,0) systems are explored by applying the recursion method[31] within a tight-binding description of the carbon bands. Only nearest-neighbour C–C interactions are considered. For simplicity, all nearest-neighbour hopping integrals are assumed to be equal, independent of the length, location and orientation of the bonds and the matched tubes. The recursion technique allows the

calculation of the DOS, directly related to the topology of the carbon network (i.e. how carbon atoms are connected). In addition, this scheme does not recur to Bloch's theorem, and consequently, the calculation is performed on the junctions without any periodical boundary condition along the direction parallel to the axis of the nanotube.

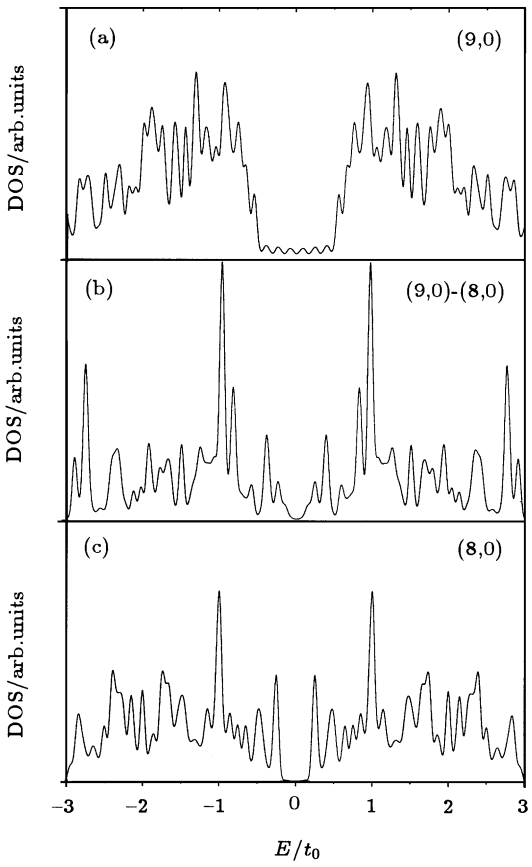


Fig.2. Density of π electronic states for (b) (9,0)-(8,0) zigzag tube system with a pair of pentagon-heptagon defects, as a function of E/t_0. For comparison, (a) and (c) illustrate densities of states in the isolated (9,0)-metallic and (8,0)-semiconducting nanotubes, respectively.

The electronic DOS of the metal-semiconductor (9,0)-(8,0) and semiconductor-semiconductor (8,0)-(7,0) tube systems containing a pair of pentagon-heptagon defects are illustrated in Figs.2 and 3, in units per energy t_0, as a function of E/t_0. The energies of all eigenstates are within $E/t_0 \leq 3$, which is consistent with those of three carbon bonds associated with each carbon atom. The (a) and (c) in Fig.2 show the densities of states of the isolated (9,0), (8,0), respectively. The (a) and (c) in Fig.3 show the densities of states of the isolated (8,0), (7,0) nanotubes, respectively. The Fermi energy is taken to be zero. The (9,0) tube is metallic, with a DOS at the Fermi energy, around 0.02 state (arb.units.), as shown in Fig.2(a). The (8,0) and (7,0) tubes are semiconducting with energy gaps E/t_0=0.4 and 0.6, respectively. The three isolated nanotube densities of states not only exhibit the two-dimensional van Hove singularities (VHS) of graphite at $E/t_0 = \pm 1.0$, but also show many sharp peaks coming from the inverse square-root divergence ($E^{-1/2}$) of the spectra of the one-dimensional bands. These singularities are due to the quantization of the one-dimensional energy bands in the circumferential direction.

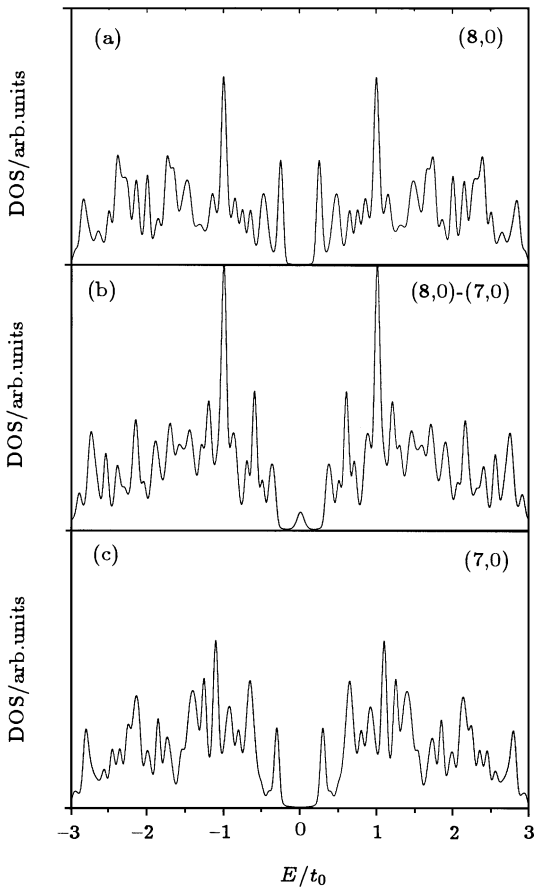


Fig.3. Density of π electronic states for(b) (8,0)-(7,0) zigzag tube system with a pair of pentagon-heptagon defects, as a function of E/t_0. For comparison, (a) and (c) illustrate densities of states in the isolated (8,0)-semiconducting and (7,0)-semiconducting nanotubes, respectively.

In Figs.2 (b) and Fig.3 (b), we can also see the VHS of graphite at $E/t_0 = \pm 1.0$, as well as many one-dimensional ($E^{-1/2}$) singularities. The DOS of the two-tube system can be understood as the sum of the densities of states of the two nanotubes. In the case of metal-semicondutor (9,0)-(8,0) zigzag nanotubes, we note that a pair of new VHS occurs near the Fermi energy. We believe that the translational symmetry is broken at the interface between (9,0) and

(8,0) because of the introduction of a pair of pentagon and heptagon in an otherwise perfect hexagonal network. This makes electron-hole symmetry of the DOS destroyed at the two defects, as they are odd-member rings.[32] As a consequence, the corresponding local DOS does not integrate exactly to 1 at the Fermi energy. There is a slight excess of electrons on the pentagonal ring and a small electron deficit on the heptagonal. Our results are in accordance with the general fact that, in a planar hexagonal network, even-member rings are neutral, five-member rings are attractive, and seven-member rings are repulsive of electrons.

Of special interest is the emergence of a gap in the vicinity of Fermi energy, which is similar to that of a nanotube with a vacancy.[32] It may be the cause of the absence of a finite DOS for (8,0) tube near the Fermi energy. From the detailed study, we believe that the origin should be attributed to the pentagon-heptagon defect in the interface between (9,0) and (8,0) nanotubes.

For the semiconductor-semiconductor (8,0)-(7,0) nanotube system, the DOS near the Fermi energy is larger than that of the (9,0)-(8,0) system. It is worth noting that a little peak occurs at the Fermi energy, which is different from the situation of the (9,0)-(8,0) system. It is shown that the geometric distortions due to the pentagon-heptagon pair in the matching region create states in the gap. As we have not changed the bond distances at the matching region, we attribute the appearance of these states to the changes in the lattice connectivity, that is, to the alternation of the network topology. These interface states may pin the Fermi level of the system.

In summary, we have made use of the extended SSH model in real space to study the electronic properties of carbon nanotubes with a pentagon-heptagon pair topological defect in the hexagonal network of the (9,0)-(8,0) and (8,0)-(7,0) two-tube zigzag configurations. We have calculated the densities of states of these two systems. For the metal-semiconductor (9,0)-(8,0) system, a narrow gap of the DOS exists near the Fermi energy. In contrast, in the semiconductor-semiconductor (8,0)-(7,0) system, a little peak of DOS occurs near the Fermi energy. These can be attributed to the addition of a pair of pentagon-heptagon defects in the interface between two isolated carbon nanotubes. As the calculations show here, the addition of a 5/7 pair defect to the nanotube allows the interesting connection between tubes having different properties. Chirality-changing pentagon-heptagon defects provide a wide range of device possibilities for doped and undoped carbon nanotubes. By arranging these defects along the length of a carbon nanotube, one could modulate the electronic structure and generate a variety of carbon-based quasi-one-dimensional quantum wells and superlattices with band offsets of $\sim$0.1 eV. Assuming that a suitable third terminal could be introduced adjacent to a semiconducting barrier within a metallic nanotube, one can easily envision a gated conductive channel. The Fermi level of a metallic pure carbon nanotube lies within the gap of a similar semiconducting tube. As such, either n-type or p-type doping of the semiconducting side of a metal/semiconductor interface should yield a device similar to a Schottky barrier. Therefore, studying local changes of the electronic structure induced by topological defect is very important in trying to understand the characteristics of the closed cylindrical graphite surfaces.

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