Electronic Structure of Carbon Nanocones

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(Received 3 November 2000)

Topology related changes in the local density of states near the apex of carbon nanocones are investigated using both tight-binding and *ab initio* calculations. Sharp resonant states are found to dominate the electronic structure in the region close to the Fermi energy. The strength and the position of these states with respect to the Fermi level depend sensitively on the number and the relative positions of the pentagons constituting the conical tip. Carbon nanocones are thus proposed as good candidates for nanoprobes in scanning probe microscopy.

DOI: 10.1103/PhysRevLett.86.5970 PACS numbers: 73.20.At, 73.63.–b

Carbon nanocones have received less attention than fullerenes and nanotubes [1], although these conical topologies have been observed just after the nanotube discovery in 1991 [2] as caps on the ends of the nanotubes [3,4] or also as free-standing structures [5]. The occurrence of nanocones has been used to investigate the nucleation and growth of curved carbon structures [6], strongly suggesting that the presence of pentagons should play a key role in the atomic construction. When a pentagon is introduced into a graphite sheet, a 60° disclination defect is formed (Fig. 1a), leading to the formation of a cone structure (Fig. 1b). The presence of pentagons at the tip apex of the nanocone is analog to their occurrence in the nanotube tip topology. Such nanotube ends have recently attracted considerable attention [7,8], since peculiar electronic states, related to these topological defects in the graphitic network, were theoretically predicted [9]. Such resonant peaks in the density of states were subsequently observed experimentally in multiwall [7] and single-wall [8] nanotubes.

Carbon nanocones with cone angles (θ) of 19°, 39°, 60° (see Fig. 1c), 85°, and 113° have been observed in a carbon sample generated by pyrolysis of hydrocarbons [6]. The total disclinations of all these conical graphitic microstructures are multiples of $+60°$, corresponding to the presence of a given number ($P \geq 0$) of pentagons at the apices of the cones. By considering the symmetry of a graphite sheet and Euler's theorem, only five types of cones can be created from a continuous sheet of graphite, corresponding to values of P between one and five. The cone angle θ is given by $\sin(\theta/2) = 1 - (P/6)$, leading to the values mentioned above for the nanocone angle. Disks ($P = 0$) and one-open-end nanotube ($P = 6$) have also been observed in the same sample [6]. There can be a number of configurations for a given angle of nanocone, depending on the way pentagons are arranged in the conical tips. The 113° nanocone has only one pentagon in the center of the tip, and therefore only one configuration. The other structures have, however, two or more isomers as the pentagons can be organized in numerous ways. These topologies which contain more than one pentagon could lead to energetically stable conic structures. According to the isolated pentagon rule (IPR) derived from the study of fullerenes [10], isolated pentagons lead to more stable isomers than fused pentagons. Beyond this IPR, some simple rules have been derived from accurate *ab initio* quantum chemistry calculations [11] to evaluate energetically stable carbon nanocones with isolated and separated pentagons. The arrangements of two pentagons in a hexagonal network can be specified by hexagonal coordinate (a, b) with one pentagon at (a, b), and the other at $(0, 0)$, as suggested in Ref. [1]. In this notation, the nearest neighboring pentagons are only $(1, 1)$ coordinated in C_{60} (all pentagons are connected by a C-C bond), and are $(1, 1)$ and $(2, 0)$ coordinated in C_{70} (the latter corresponds to two pentagons separated by a hexagon). According to density functional theory calculations [11], $(1, 1)$ pentagons lead to more stable carbon nanoconic tip structures than $(2, 0)$ pentagons. This is attributed to less in-plane and out-of-plane strain induced by each $(1, 1)$ pair than by each $(2, 0)$ pair. In the present study, we investigate the electronic properties of nanocones containing from one to five pentagons at their apices, all pentagon pairs being connected by one C-C bond or separated by one hexagon. We show

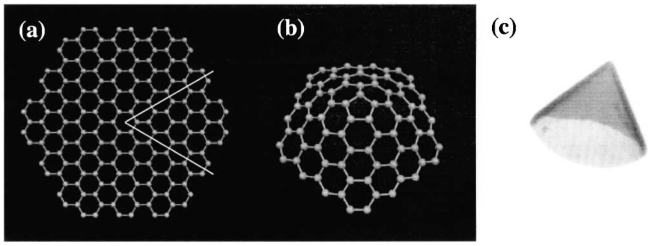

FIG. 1. (a) Extraction of a 60° section from a graphene sheet in order to form a cone structure (b) by incorporation of a single pentagon defect. (c) High-resolution transmission electron microscopy image of a nanocone which contains three pentagons at its tip apex (Ref. [6]).

that the local density of states (LDOS) at the apices of the nanocones is strongly dependent on the pentagon concentration and topology. By coupling tight-binding and *ab initio* calculations performed on several nanocone morphologies, we correlate sharp resonant features in the LDOS with the incorporation of pentagons in the hexagonal graphitic network. A peculiar nanocone, with three pentagons at the apex (as illustrated in Fig. 1c), is proposed as a good candidate for nanoprobes in scanning probe microscopy.

The electronic densities of states of different apices of nanocones (Fig. 2) are obtained by the recursion technique [12] applied to a tight-binding Hamiltonian that incorporates $2s$ and $2p$ electron orbitals. The nanocone clusters contain about 2000–2500 atoms, in order to avoid the effects of dangling bonds, present at the root, on the electronic properties. These atomic structures were optimized using tight-binding molecular dynamics simulations [13]. In this approach, we used an energy functional and parametrization which proved to be successful in the modeling of the different allotropic forms of carbon and various carbon-based systems [14], and which allows the treatment of huge systems since the computational effort is significantly reduced compared to *ab initio* calculations. In Fig. 2, only the topology of the apices of the cones are illustrated. Figure 2*a* shows the LDOS of an infinite graphene plane which behaves as a zero gap for a single sheet. Figure 2*b* illustrates the LDOS of a nanocone with a single pentagon at the apex. In the valence region, a sharp peak appears close-below the Fermi energy. The LDOS of two isomers for a nanocone containing two pentagons at the apex are represented in Figs. 2*c* and 2*d*. Figures 2*e*–2*h* show the LDOS of nanocones containing three, four (two iomers), and five pentagons, respectively. Note the prominent peak which appears just above the Fermi level (E_F) for the nanocone with three symmetrical pentagons (Fig. 2*e*). Taken as a whole, these calculations indicate that sharp resonant peaks found in the LDOS at the tip apex of nanocones mainly originate from the topological disorder introduced into the hexagonal bonding network by the presence of pentagons. As clear from Fig. 2, the strength and energy position of the computed resonant states depend sensitively on the relative position and degree of confinement of pentagonal rings at the tip apex of the cones. Similar conclusions have already been drawn for terminating caps of nanotubes [7,8], allowing the possibility to discriminate between different capping topologies. Densities of states have also been calculated for nanohorns [15], which can be considered as cone-shaped graphitic carbon structures with five pentagons at the apex, and significant differences in the DOS have been observed for various morphologies.

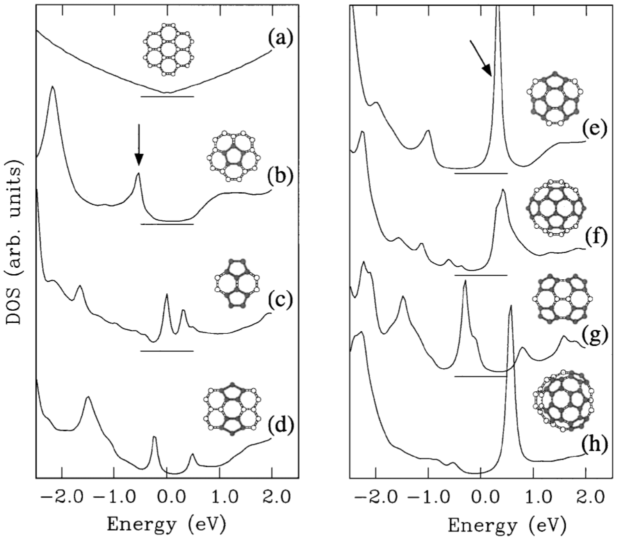

FIG. 2. Computed tight-binding LDOS for a single graphene sheet (*a*), and nanocones with one (*b*), two (*c*) and (*d*), three (*e*), four (*f*) and (*g*), and five (*h*) pentagons, respectively. The tip apex topology is illustrated close-above each corresponding curve. The Fermi level (E_F) is at zero energy. A value of 2.9 eV has been chosen for the hopping integral $V_{pp\pi}$ [25]. In all the LDOS related to nanocones, localized states are always present. Their locations clearly depend on the number and the relative positions of the pentagons.

A simple argument can help to elucidate the interplay of pentagonal rings immersed in a hexagonal graphitic network and the LDOS of the structure. The energy multiplet structure of the π electron states of an isolated pentagonal ring includes the most stable totally symmetric state and two occupied orthogonal bonding states having one nodal surface only [16]. Hence, this structure therefore has an "affinity" for a sixth electron in a bonding state. When the pentagonal ring is immersed in a metallic π-bonded hexagonal network, such a state will be occupied and screened by the other π electrons, becoming a resonant bonding state in the graphitic π band. This argument allows us to interpret the peak in the LDOS of Fig. 2*b* as an acceptor state. It is also clear, from the results exposed in Fig. 2, that whenever pentagons are located close to each other in a confined region of the structure, the LDOS is the result of some further interaction between individual pentagonal topological defects. This is consistent with the interpretation of the acceptor states as resonances in the π-bonded structure, and suggests that each of these states extends well outside the pentagonal rings which determine its main structure. The overall electronic structure for the nanocones, illustrated in Fig. 2, is thus the result of interacting topological defects. The relation between the position of the pentagons and the main structures in the LDOS shows that localized states are always present. This suggests an interesting experimental tool to correlate the LDOS of the nanocones, which could be measured experimentally using scanning tunneling spectroscopy techniques [7,8], to the topology of the nanocone tip apex.

The tight-binding recursion method does not provide information on the localization of individual states. To obtain direct insight into the structure of localized electron states, we perform *ab initio* computations [17] of two nanocones containing one (Fig. 3a) and three pentagons (Fig. 3b), respectively. *Ab initio* LDOS, averaged over the tip apex of the nanocones, exhibits strong and sharp peaks. The position of these resonant states are 0.6 eV below the Fermi energy for the nanocone with one pentagon, and at 0.3 eV above the Fermi energy for the nanocone with three pentagons. These *ab initio* results are in perfect agreement with the previous tight-binding calculations, especially for the locations of these resonant states as shown by arrows in Figs. 2*b* and 2*e* [18].

Figure 3a illustrates the calculated local electronic density for the two degenerated electronic states leading to the sharp resonant peak located 0.6 eV below the Fermi energy (as indicated by an arrow in Fig. 2*b*) for a nanocone with a single pentagon [19]. The local electronic density of charge is mainly localized on the unique pentagon. We notice that the single particle densities illustrated in Fig. 3a do reflect the fivefold symmetry of the nanocone tip apex.

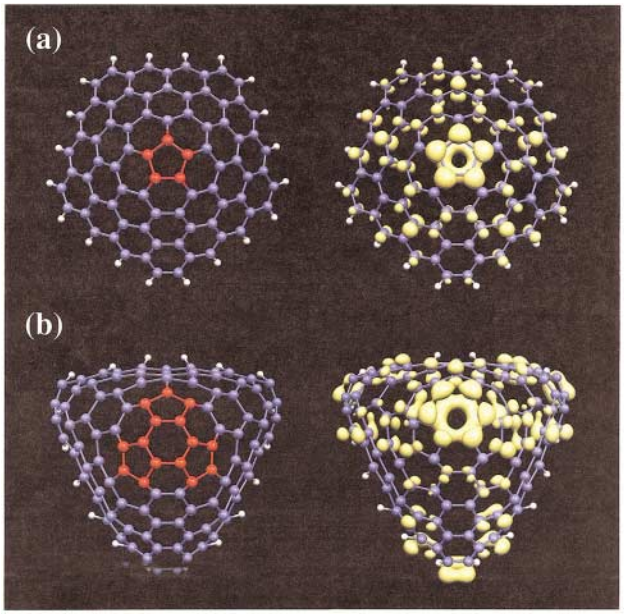

FIG. 3 (color). *Ab initio* electronic densities of charge on the tip apex of nanocones containing (a) one and (b) three pentagons for the electron states corresponding to the resonant peaks indicated by arrows in Fig. 2. These electron states are located, respectively, at -0.6 eV (a) and $+0.3$ eV (b), relative to the Fermi energy. The two conical atomic structures are presented on the left side of the figure; highlighting in red the number of pentagons at the tip apex. The clusters contain (a) 80 carbon atoms and (b) 100 carbon atoms, respectively (red and blue spheres). Edge carbon atoms are terminated with hydrogen atoms (20 small white spheres in both cases). On the right side, the isovalue surfaces of *ab initio* electronic densities of charge illustrate high electronic density. The density lobes, which have a clear π bonding character, are located either on the unique pentagon (a) or on neighboring atoms that are part of five-membered rings, pointing radially into the vacuum region. Where such states are found, the pentagons of the nanocone tip are expected to act as emitting centers when the cone is used as a field-emission electron source.

By analogy, Fig. 3b presents the local electronic density for the two degenerated electronic states corresponding to the sharp resonant peak located 0.3 eV close-above the Fermi energy (indicated by an arrow in Fig. 2*e*) for a nanocone with three pentagons. Again, most of the local density of charge is positioned on pairs of neighboring atoms that are part of the three pentagons, leading to a main charge density on the top of the nanocone. These single particle densities (Fig. 3b) do reflect the threefold symmetry of the nanocone.

These density lobes, as revealed in Fig. 3, point radially into the vacuum region, and therefore can act as emitting centers when the nanocone is used as a field-emission electron source. If resonant states located on pentagonal rings and containing π bonding lobes are present close to the Fermi energy in the LDOS of nanocone tips, these states should be revealed by field emission (FEM) experiments. In these experiments [20], the patterns collected by a charge-coupled device (CCD) camera are, to first approximation [21], a direct image of the emitting electronic states, and could thus offer a second possibility for its topological characterization with atomic resolution.

From classical electrostatics, the high field region of a nanocone immersed in a static electric potential is that of highest curvature, i.e., the tip apex region, where most pentagons are located. To be a good candidate for emitting tunneling electrons in a FEM experiment, an electronic state should be localized in the high field regions of the structure, and should be either close under or just over in energy to the Fermi level. Even if other electronic levels also contribute to the field emission, the greatest part of the emitted current is likely to come from states yielding a large LDOS at the tip close to the Fermi level.

The nanocones with three pentagons at the tip have the highest probability of nucleation [6] and are frequently observed (see Fig. 1c). Such cones possess a prominent sharp peak appearing just above the Fermi energy (Fig. 2*e*), and are thus excellent candidates for field emission. The huge increase of the density of states near E_F towards the apex would imply a corresponding enhancement of the field-emission current. By analogy with carbon nanotubes [22], the low-threshold voltage for field emitted electrons from a periodic array of such nanocones should be considered for flat panel displays [23] or any nanocone-based field-emission device. In addition, such nanocones might constitute well-defined tips with perfect atomic structure similar to nanotubes [24] for scanning probe microscopy. Because of their conical structures, nanocones will be less flexible than nanotubes, although they could also survive after "tip crash" with the surface of the sample. However, attached to the cantilever of a conventional scanning microscope, these nanocones would not vibrate similar to nanotube-based nanoprobes at ambient temperature, suppressing the noise often observed in the latter case and allowing the imaging of sharp recesses in surface topography.

In summary, we have investigated the tight-binding local density of states and the *ab initio* electronic density of charge of carbon nanocones. The correlation between the electronic structure and the conical atomic structure has been studied. The existence and the location of prominent sharp peaks in the LDOS have been attributed to the presence and the relative topology of the pentagons at the apex of the cone. For some peculiar nanocones, these resonant states are very close to the Fermi energy, corresponding to an enhancement of the field-emission properties and yielding to interesting potential applications in nanotechnology. We also hope that the present study will stimulate experimental works (such as scanning tunneling spectroscopy and FEM) on nanocones in order to provide experimental evidences of these resonant states and to characterize these nanostructures at the atomic level.

J. C. C. and G. M. R. acknowledge the National Fund for Scientific Research [FNRS] of Belgium for financial support. This paper presents research results of the Belgian Program on Interuniversity Attraction Poles initiated by the Belgian State-Prime Minister's Office-Science Policy Programming and FRFC Project No. N2.4556.99 "Simulations numriques et traitement des donnes." This work is carried out within the framework of the EU Human Potential-Research Training Network project under Contract No. HPRN-CT-2000-00128 and within the framework of the specific research and technological development EU programme "Competitive and Sustainable Growth" under Contract No. G5RD-CT-1999-00173.

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[17] The electronic properties of nanocones containing one and three pentagons, respectively, were obtained by performing first-principles calculations based on the density functional theory in the local density approximation. The interaction between valence electrons and ionic cores was described using norm-conserving pseudopotentials for carbon and hydrogen [N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991)]. Dangling bonds on the carbon atoms in the bottom ring of the cone were saturated with hydrogen atoms. Periodic boundary conditions were adopted, keeping a minimum 0.5 nm distance between repeated images. The two nanocone structures were initially relaxed to their ground-state equilibrium geometry by calculating the Hellmann-Feynman forces acting on the atoms. The electronic wave functions at the Γ point of the supercell Brillouin zone and the electron density were expanded into plane waves with kinetic energy cutoffs of 40 and 120 Ry, respectively.

[18] These *ab initio* results thus validate the use of the tight-binding technique, less accurate than *ab initio* but which takes into account the essential physicochemical considerations of covalent C-C bonds, satisfactorily describing hybridization states between sp^2 and sp^3.

[19] Note that, in our calculations, the two electronic states of Figs. 3a and 3b, corresponding to the sharp resonant states of Fig. 2, are nearly degenerate in energy. A perfect degeneracy is expected for a fully symmetric isolated cone. The small energy splittings observed ($\sim$10 meV) are due to the interaction of repeated images introduced into the calculation by the use of periodic boundary conditions.

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