Electronic structure of polychiral carbon nanotubes

Ph. Lambin\textsuperscript{a}, V. Meunier\textsuperscript{b}, and A. Rubio\textsuperscript{c}
\textsuperscript{a} D\textsuperscript{é}partement de physique, FUNDP, 61 Rue de Bruxelles, B 5000 Namur, Belgium.
\textsuperscript{b} Department of Physics, North Carolina State University, Raleigh NC 27695, USA.
\textsuperscript{c} Departamento F\textsuperscript{í}sica Te\textsuperscript{ó}rica, Universidad de Valladolid, E 47011 Valladolid, Spain and Donostia International Physics Center, San Sebastian, Spain
(March 21, 2022)

Abstract

Most of the works devoted so far to the electronic band structure of multiwall nanotubes have been restricted to the case where the individual layers have the same helicity. By comparison, much less is known on the electronic properties of multiwall nanotubes that mix different helicities. These are interesting systems, however, since they can be composed of both metallic and semiconducting layers. For the present work, tight-binding calculations were undertaken for polychiral two-layer nanotubes such as (9,6)@(15,10), (6,6)@(18,2), and others. The recursion technique was used to investigate how the densities of states of the individual layers are affected by the intertube coupling. Constant-current STM images were also calculated for these systems. The result obtained is that the image of a two-wall nanotube is pretty much the same as the one of the isolated external layer. It is only in the case of monochiral, commensurate structures like (5,5)@(10,10) that interlayer effects can be seen on the STM topography.
**I. INTRODUCTION**

Multiwall nanotubes (MWNT) have not attracted as much attention from the theoreticians as the single-wall carbon tubes did, although they may be useful in many applications. Multiwall nanotubes are obviously more complex than the one-layer tubules, which explains why the former are much less documented. As far as the electronic structure is concerned, calculations have already been performed for the simplest MWNTs, those made of non-chiral layers. The systems that were investigated in these works were all made of either zig-zag or armchair nanotubes, without mixing. The reason was simply that mixing nanotubes with incommensurate periods along their axis leads to an non-periodic system, which therefore precludes the use of Bloch theorem and makes the calculations more difficult. However, there are many indications from electron diffraction and STM that the layers in a multiwall nanotube often have different helicities with nearly random distribution.

The aim of the present paper is to investigate the electronic properties of polychiral nanotubes, namely multiwall structures mixing layers with different helicities. The motivation of this work is twofold. First, to find out in which way electronic states can be induced in the band gap of a semiconducting layer by its coupling to a metallic tube of different chirality. The resulting interlayer coupling varies from site to site in a pseudo-random manner that could be responsible for localization of the electronic wave functions. No such effects were found in the present study. The second motivation was to see whether the electronic local density of states of the external layer of a MWNT can reflect the atomic structure of the underlying layers, leading to a pattern that could be observed with an STM. In some cases, MWNT analyzed with the STM appear like graphite, where only every other two atoms of the external layer are clearly imaged. In other cases, there is a spatial modulation of the image intensity, most obviously because a perfect lattice coherence cannot be realized between two cylindrical graphitic sheets when the layers have different helicities. Our calculations show that, indeed, a site asymmetry of the STM image of a MWNT similar to that of graphite may appear, but this requires a special monochiral geometry like (5,5)@(10,10). In polychiral nanotubes, by contrast, there is no site asymmetry and no Moiré pattern in the STM images computed for bilayer systems. This conclusion is in agreement with recent STM images with atomic resolution obtained on MWNTs, although Moiré patterns have frequently been observed in other experiments as recalled here above.

All these effects were explored within a tight-binding description of the $\pi$ electronic states, using the methodology presented in section 2. The results on the local DOS calculations for nanotubes mixing semiconducting and metallic layers are given in sections 3-4, and the STM image simulations are reported to section 5. All the calculations were restricted to bilayer nanotubes to keep the computing load reasonable.

**II. METHODOLOGY**

Several two-wall nanotubes were generated on the computer, with the requirement that the layer radii differ by approximately 0.34 nm which corresponds to the observed interlayer distance in MWNTs. In the $\pi$-electron tight-binding Hamiltonian used, the first-neighbor C pairs within a same shell received a hopping interaction $\gamma_0 = -2.75$ eV. This value was used for consistency with previous calculations of ours. That value slightly underestimates a recent
experimental estimation of $\gamma_0$ (-2.9 eV) which simply means that our energies should be scaled by a factor 1.05. This scaling does not alter any of the conclusions of the present work related to the interlayer interaction and STM imaging. The interlayer interactions were written as $W \cos \phi \exp \bigl[-(d - \delta)/L\bigr]$ with $d$ the distance between the coupled atoms, $\phi$ the angle between the $\pi$ orbitals on these two atoms, $\delta = 0.334$ nm, and $L = 0.045$ nm. Two values of $W$ were used to describe the graphite AA, BB or AB-like interactions: $W = 0.36$ eV for the first two and $W = 0.16$ eV for the latter. The range of the interlayer interactions was limited to a maximum distance $d = 0.39$ nm. This parameters reproduce well first-principles calculations for MWNTs.

Local densities of states in the multiwall nanotubes were computed by the recursion method. This technique does not rely on the Bloch theorem. It gives rise to a continued-fraction development of the Green’s function diagonal elements in the complex energy plane, $G_{ii}(z) = \langle i | (z - H)^{-1} | i \rangle$. For each atomic site $i$ of interest, $n = 500$ levels of continued fraction were computed. When the continued fraction is truncated after $n$ levels, the resulting density of states is composed of $n$ Dirac delta peaks. With $n - 1$ levels, another set of $n - 1$ peaks is obtained. These two, interlaced sets were mixed with equal weights, and each delta peak was represented by a Gaussian function with standard deviation 0.023 eV (the band width, $6|\gamma_0|$, divided by $\sqrt{2n}$). Due to this broadening, all the singularities of the densities of states, including the band edges, are slightly smoothed out. Due to its smallness, this broadening should not alter a main conclusion of the work, namely the absence of localized states in the gap of the semiconducting layer.

The change of density of states brought about by the interlayer coupling is expected to be small. The first-order perturbation expression of the Green function is indeed $G = G_0 + G_0 W G_0$. The unperturbed Green function $G_0$ is made of blocks corresponding to the individual layers that $W$ couples together. Due to that structure, all the diagonal elements of $G_0 W G_0$ are zero, which means that the density of states is not perturbed at first order in the interlayer interaction.

STM image simulations of multiwall nanotubes were performed for comparison with experiment. These calculations are based on a simple tight-binding theory of the STM current

$$ I = (2\pi)^2 \frac{e}{h} \int_{E_F - eV}^{E_F} dE \ n_t(E_F^t - E_F^s + eV + E) \sum_{i, i' \in s} v_{ti} v_{ti'}^* n_{ii'}^s(E) $$

where the $E_F$'s are the Fermi levels of the tip (t) and sample (s) and $V$ is the tip–sample bias potential. The tip is treated as a single atom with an s orbital and a Gaussian density of states $n_t(E)$. $v_{ti}$ is the tight-binding hopping interaction between the tip atom and $\pi$ orbital located on site $i$ of the nanotube sample, and $n_{ii'}^s(E) = (-1/\pi) \text{Im} G_{ii'}^s(E)$. The Green function elements $G_{ii'}$ of the nanotube were computed by recursion with 200 continued-fraction levels that give converged results for the present imaging studies. Similarly to the density of states calculations, a small imaginary part was added to the energy to force the convergence.
We first consider two-wall nanotubes having a metal at the inner shell and a semiconductor at the outer shell. Table I gives a few such metal-semiconductor nanotubes. The first system mixes an armchair and a zig-zag nanotube. Although these two nanotubes are non-chiral, their chiral angles differ by $30^\circ$, their translation periods differ by a factor of $\sqrt{3}$, and the combined system may be described as polychiral. The next three nanotubes of table I are real polychiral systems. By contrast, the fifth nanotube is monochiral since its layers have the same helicity. Hence, the two layers in the $(15,-6)@(15,10)$ nanotube have the same Bravais period but have opposite chiral angles. This last nanotube differs from the fourth one by the fact the inner layers $(15,-6)$ and $(9,6)$ are enantiomers.

Local density of states in the external layer were computed in a slice of 0.2 nm height, which contained between 32 and 40 atoms, depending on the nanotube. Although the coupling to the inner layer varies from site to site, all the atoms of the external layer were found to have pretty much the same density of states.

For all the polychiral nanotubes investigated, the density of states of the semiconducting layer was found to be weakly affected by its coupling to the inner metallic layer, at least in an interval between -1 and +1 eV (the zero of energy is always considered to be at the Fermi level). In that interval of energy, the metallic tube presents a constant density of states – hereafter called the metallic plateau – with no van Hove singularities. Fig. 1(a), which concerns with $(15,-6)@(15,10)$, is a typical example of this effect. As compared to the single-wall $(15,10)$ nanotube (dashed curve), there is a minute downshift of the bottom of the conduction band of the semiconducting layer (full curve), whereas the top of the valence band does not move. The shapes of the gap edges are not modified. If the hopping interactions between the layers introduce a tailing of the valence and conduction states inside the gap, the decay will take place in an energy range shorter than the peak broadening used (0.023 eV). The metallic layer induces a few states in the band gap of the semiconductor (the total number of states in the band gap is $0.42 \times 10^{-4}$ per atom of the semiconducting layer, see table I). The density of states in the gap region is approximately uniform and very small.

The interlayer coupling is much more efficient in the monochiral $(9,6)@(15,10)$ nanotube, as shown in fig. 1(b). The density of states in the band gap region is approximately five times larger than in fig. 1(a) and reaches 2.5% of that of the metallic layer. It must be stressed out that both nanotubes in fig. 1 exhibit exactly the same electronic structure when the interlayer coupling is switched off. In other words, all the differences between the full curves in figs. 1(a) and (b) come out from the different environments the $(15,10)$ layer feel in both systems. The monochiral tubes constitute a particular case in which the electronic properties are much affected by specific symmetries in MWNTs, both as pseudogaps in the local density of states or as a change in the intensity of every two atom of the STM image (see below). A change of the width of the metallic gap was also found in the case of commensurate three-wall armchair tubes.
IV. SEMICONDUCTOR-METAL NANOTUBES

We now consider two-wall nanotubes having the semiconducting layer at the interior and the metallic layer outside. A list of such nanotubes which mix different helicities is given in table II. Local density of states in the inner layer were computed in a slice of 0.3 nm height, which contained between 24 and 32 atoms depending on the nanotube. Here again, the fluctuations of densities of states in the semiconducting layer, although two times as large as in Sect. III, remained small (see table II). The local densities of states were then averaged as before.

The ratio between the band gap of the semiconductor and the width of the metallic plateau of the metal is now approximately 2:3, instead of 1:6 as for the previous configurations (Sect. III). For instance, the metallic plateau of the (10,10) nanotube is bounded by two Van Hove singularities at $E = \pm 0.9$ eV. These singularities can be seen in the density of states of the (6,4) layer in the (6,4)@(10,10) bilayer (fig. 2(a)). In the conduction band for instance, the singularity leads to a resonance followed by an anti-resonance. This kind of structure was frequently observed among the nanotubes of table II. In a systematic way, also, the band gap of the semiconductor is reduced by the coupling to the outer layer: the top of the valence band has moved upwards by approximately 0.03 eV.

As shown in fig. 2(a), the density of states in the band gap of the inner semiconducting tube is small, but still significantly higher than in fig. 1(a) for instance. The difference between these two situations is that the semiconducting layer is now at the interior rather than at the exterior, and the inner layer is more perturbed than the outer one. Indeed the average numbers of intersheet bonds per atom in layers 1 and 2 are inversely proportional to the number of atoms in these layers. Since there are approximately two times less atoms in the inner shell than in the outer (for those systems we are investigating), the interlayer coupling is two times more efficient on layer 1 than on layer 2. Since, in addition, the (6,4) semiconductor has a larger band gap than those of the semiconducting layers of table I (due to its smaller diameter), the number of states in the gap has increased. As revealed by table II, the number of states in the gap looks remarkably constant for all the nanotubes examined, around $2.3 \times 10^{-4}$ per atom.

As for the metallic layer, one can hardly see any change in its density of states around the Fermi level (fig. 2(b)). The site-to-site fluctuations of densities of states near the Fermi level are less than 1% of the (10,10) density of states at $E_F$. This kind of weak disorder, here due to the coupling with a chiral nanotube, is small but is perhaps sufficient to affect the transport properties of a MWNT in the weak localization regime.\[\text{\textsuperscript{5}}\] Clear effects of the coupling to the inner layer appear below -0.5 eV and above +0.5 eV, where the (6,4) nanotube has its band edges. It is clear from this example that the amplitudes of the Van Hove singularities at $E = \pm 0.9$ eV are reduced as compared with the single-wall nanotube. This is due to the breaking of the translational symmetry brought about by the coupling between layers of different chiralities.

V. SIMULATION OF THE STM IMAGE OF TWO-WALL NANOTUBES

Several constant-current STM images of multiwall nanotubes show intensity or contrast modulations.\[\text{\textsuperscript{12, 17}}\] Such modulations have been interpreted as being a Moiré pattern formed...
by the atomic structure of the last two layers. In graphite, Moiré pattern effects have clearly been identified with an STM in regions where the last layer was folded back on the surface with a misorientation of its crystallographic directions.

As pointed out in the previous sections, the local DOS show only little variations on going from one site to another in a multiwall nanotube. To quantify that property, the fluctuations (rms) of the local DOS were computed on a chain of 25 first-neighbor atoms located as close as possible to a generator of the external layer. These atoms were selected because they would be probed in a scan of the topmost part of the nanotube by a STM tip. The DOS fluctuations, averaged over the energy interval (-1,+1) eV, are listed in the last row of tables I and II. They are small, less than 1% of the mean density of states. According to these data, the spatial variations of the density of states in polychiral nanotubes cannot explain the modulations of the STM image intensity.

Fig. 3 is a simulation of the STM image of (6,6)@(19,0) computed with the methodology described in section II. The tip is at a potential of 0.5 V with respect to the sample. For that polarity, the most prominent features in the STM image of the semiconducting (19,0) layer are the CC bonds not parallel to the axis, which appear as bright stripes at 60° to the axis. All along the portion of nanotube displayed, the periodicity of the image is that \((\sqrt{3}a, a)\) with \(a\) the lattice parameter of graphene) of the external zig-zag layer. There is no visible sign of the underlying armchair nanotube with its shorter period \(a\). The topographic line cut shown at the bottom of fig. 3 clearly proves that statement. The sharp minima of the curve correspond to the centers of the hexagons. The apparent variations of their depth are due to the pixel discretization. The maxima correspond to the atoms, the secondary minima are at the center of the CC bonds parallel to the axis.

Nothing similar to a Moiré pattern appears in the computed STM image of fig. 3 nor in the simulations we carried out for other polychiral nanotubes. However, these patterns occur occasionally in the experimental images of multiwall nanotubes, as reported above. It is not impossible that a mechanical deformation of outer layer of the tube caused by the STM tip induces metallic islands (with a much larger density of states) at special places where the layers are in suitable registry. The pressure of the tip may also induce better electric contact with the substrate at some places, leading to a larger tunneling current.

The atoms in fig. 3 all look the same, unlike the case of multilayer graphite where the STM current at low bias (\(\sim 0.1\) V) shows a strong site asymmetry. This asymmetry is already present with two layers only since the coupling makes the atoms having a neighbor underneath different from those that have not (A and B atoms, respectively).

In a multiwall nanotube, it is impossible to realize the same stacking as in natural graphite all around the cross section. However, at least one multiwall nanotube exists where the topographic STM image is predicted to look like that of graphite. This case is \((5,5)@(10,10)\). This system is known to exhibit small pseudo-gaps near \(E_F\) as the consequence of avoided band crossings for relative tube orientations such that the mirror planes of \((5,5)\) do not coincide with those of \((10,10)\). Local DOS calculations then show that the atoms (of the external layer) are not equivalent, at least in a small interval around the Fermi level. Interestingly, first-neighbor atoms have a peak or a deep at \(E_F\), alternatively, very much like in graphite where the A and B atoms alternate. This effect is shown in fig. 4. The explanation of this bi-partition of the honeycomb lattice is presented in the Appendix. A consequence of it is that the STM image of the \((5,5)@(10,10)\) nanotube at low bias resembles
that of graphite, with maxima of protrusion on every other two atoms (those with the largest DOS at $E_F$), see fig. 3. However, for other relative orientations of the tubes, no bipartition effect is observed (in agreement with first-principle calculations). What is special about (5,5)@(10,10) is that this system has at least a five-fold common symmetry. In (6,6)@(11,11) for instance, there is no axial symmetry, which destroys the effects of the interlayer coupling on the DOS around the Fermi level, very much like in polychiral nanotubes. The resulting intertube interaction averaging reduces any symmetry related feature such as the opening of pseudo-gaps and the bipartition of the honeycomb lattice. The STM image of (6,6)@(11,11) is then similar to that of the isolated single-wall (11,11) nanotube (see fig. 5). With other metallic nanotubes such as (7,4)@(12,9) which we also have examined, some variations of the local DOS from one atom to the other were detected in the metallic plateau, but these were two small to lead to a clear site asymmetry in the STM image.

The property that (5,5)@(10,10) presents a site asymmetry that depends on the relative orientation of the layers can be illustrated by giving a uniform torsion to the (10,10) nanotube. At regular intervals along the axis, the planes that bisect the CC bonds perpendicular to the axis of (10,10) coincide with the mirror planes of (5,5) ($C_{5v}$ symmetry, no site asymmetry). Away from these positions, the local symmetry of the atomic structure is lower and the two-site asymmetry of the DOS should come out and reach a maximum in between.

The twist is equivalent to applying a shear of the honeycomb network, which affects the bond lengths and opens a small gap at the Fermi level. The calculations were performed for a twist of 1.5° (shear strain) corresponding to a torsion angle of 2.2°/nm, which leads to a band gap of 0.25 eV (the $\gamma_0$ parameter was scaled according to a $d^{-2}$ law, with $d$ the bond length). In the (5,5)@(10,10) distorted nanotube, the local DOS of the twisted (10,10) layer has a peak near the Fermi energy induced by the interactions with the inner (5,5) nanotube (fig. 6(b)). The shear also affects the Brillouin zone of the rolled-up graphene sheet, which moves the Fermi points of the twisted (10,10) nanotube away from those of the (5,5) layer. As a consequence, the minigaps of the bilayer are no longer located at the center of the metallic plateau (where the semiconducting gap of the twisted nanotube has opened) but are shifted 0.25 eV on both sides of the Fermi level. As can be seen in fig. 3(a), the DOS features in the mini-gaps at ±0.25 eV resemble the two-site asymmetry observed near $E_F$ in fig. 4 for the perfect (5,5)@(10,10), except that the magnitude of the asymmetry now varies along the tube. The DOS curves in fig. 3(a) correspond to 25 successive atoms along a longitudinal zig-zag chain on the external tube. The curves at the center look all the same, while the local symmetry of the (5,5)@(10,10) distorted nanotube is close to $C_{5v}$. By contrast, the curves at the bottom and at the top have peaks and deeps at $E = ±0.25$ eV that alternate from one site to the next. The local symmetry has been changed to $C_5$ in these regions. The modulation of the degree of unequivalence between the atoms is due to the continuous change of the local symmetry along the nanotube axis. Unfortunately, this modulation did not appear clearly in the STM images that we computed for bias potentials of −0.3 and +0.3 V. The reason is that the expression of the STM current (sect. II) is an integral of the Green’s function elements over the bias window, to which the site-dependent features in the density of states in fig. 3(a) contribute little. However, these features might be observed by current imaging tunneling spectroscopy.
VI. CONCLUSION

Two-wall nanotubes mixing metallic and semiconducting layers retain the basic properties of the uncoupled constituents, as shown previously for monochiral nanotubes. The intertube interactions induce a small continuous distribution of states in the band gap of the semiconducting layer. The electronic states near the Fermi level come from the metallic tube and they will dominate the transport properties in the weak localization regime. Constant-current STM images computed for polychiral nanotubes are pretty much the same as the ones obtained on the isolated external layer. It is only in the case of monochiral and commensurate structures like (5,5)@(10,10) that interlayer effects can be seen in the STM topography. The interlayer coupling gives rise to a site asymmetry in the STM image at low voltage (~0.1 V), similar to that obtained on multilayer graphite. This site bipartition is maximum when the symmetry of the two-wall nanotube is reduced to $C_5$, and it disappears when the symmetry is higher. The site asymmetry also disappears in relationally-incommensurate nanotubes like (6,6)@(11,11). In polychiral nanotubes, there is no site asymmetry and no Moiré patterns appear in the computed STM images. From the few cases we have investigated, it can be concluded that the superstructures often observed in the STM images of MWNTs cannot be ascribed to pure electronic effects.

ACKNOWLEDGMENTS

This work has been partly funded by the interuniversity research project on reduced dimensionality systems (PAI P4/10) of the Belgian Office for Scientific, Cultural and Technical affairs, the EU NAMITECH contract: ERBFMRX-CT96-0067 (DG12-MITH) and by a JCyL (Grant: VA28/99). The authors acknowledge Laszlo P. Biró for helpful discussions.

APPENDIX: MULTI-WALL ARMCHAIR NANOTUBES

In a single-wall armchair nanotube, the two bands that cross each-other at the Fermi level correspond to the irreducible representation $A_1$ and $A_2$ of the symmetry group $C_{5v}$ of the wave function for a general Bloch wave vector $k$. These wave functions are respectively symmetric and antisymmetric upon a reflection on the “vertical” mirror planes that bisect the CC bonds perpendicular to the nanotube axis. When all curvature effects are neglected in the Hamiltonian as here, the Fermi wave vector is independent on the tube diameter. This means that in a two-wall nanotube such as (5,5)@(10,10), the states at the Fermi points have a fourfold degeneracy when the interlayer coupling is ignored. In the presence of the coupling, the wave functions adapted to the perturbation $W$ are linear combinations of the four Fermi states $\psi_1^i$, $\psi_2^i$, $\psi_1^e$, and $\psi_2^e$ of the internal and external layers (upper indices $i$ and $e$) corresponding to $A_1$ and $A_2$ symmetries (lower indices 1 and 2). These combinations of states diagonalize the perturbation matrix

$$
\begin{pmatrix}
0 & 0 & w_{11}^{ie} & w_{12}^{ie} \\
0 & 0 & w_{21}^{ie} & w_{22}^{ie} \\
0 & 0 & w_{11}^{ei} & w_{12}^{ei} \\
0 & 0 & w_{21}^{ei} & w_{22}^{ei}
\end{pmatrix}
$$
where \( w_{12}^{ie} = \langle \psi_1^e | W | \psi_2^e \rangle \), etc. In any case, the perturbation is sufficient to split off the degeneracy of the Fermi states. In general, also, the eigenvector of the perturbation matrix will mix the four Fermi states. This means in particular that the perturbed wave functions at the Fermi level mix the \( \psi_1^e \) and \( \psi_2^e \) states of the external layer. By mixing these states, which are respectively even and odd with respect to the center of each CC bond, one forms a disymmetric combination. As a result, there are now two kinds of unequal atoms in each layer, as shown by the density of states in fig. 4, which explains the site asymmetry of the computed STM images.

An exception to this explanation arises when the four matrix elements of the kind \( w_{12}^{ie} \) along the ascending diagonal vanish for symmetry reason. This takes place when the symmetry of the two-wall nanotube preserves the mirror planes of the inner layer. Then, \( A_1 \) and \( A_2 \) remain valid irreducible representations of the symmetry group of the coupled system, band crossings remain allowed, and there is no pseudo-gap formation in the density of states. This also means that the site asymmetry of the STM image disappears. For the \((5,5)@(10,10)\) nanotube, this happens with \( C_{5v}, D_{5h} \) and \( D_{5d} \) configurations of the layers. The latter configuration corresponds to the minimum of the total energy of the nanotube.

In the case where the two nanotubes have no axial symmetry in common, such as for instance with \((6,6)@(11,11)\), all band crossings are avoided and two kinds of unequal atoms are formed in each layer, as above. However, due to a cancellation effect, all the elements in the perturbation matrix are found to be small except the ones derived from the totally-symmetric states, \( w_{11}^{ie} \) and \( w_{11}^{ei} \). In practice, then, all the atoms look equivalent. Also, the pseudo-gaps near the Fermi level are much weaker than for the \((5,5)@(10,10)\) case.
REFERENCES

1. R. Saito, G. Dresselhaus, and M.S. Dresselhaus, J. Appl. Phys. 73, 494 (1993).
2. J.C. Charlier and J.P. Michenaud, Phys. Rev. Lett. 70, 1858 (1993).
3. Ph. Lambin, L. Philippe, J.C. Charlier, and J.P. Michenaud, Comput. Mater. Sci. 2, 350 (1994).
4. Ph. Lambin, J.C. Charlier, and J.P. Michenaud, in Progress in fullerene research, edit. H. Kuzman, J. Fink, M. Mehring, and S. Roth (World Scientific, Singapore, 1994), 130-134.
5. D. Östling, D. Tománek, and A. Rosén, Phys. Rev. B 55, 13980 (1997).
6. Y.K. Kwon and D. Tománek, Phys. Rev. B 58, R16001 (1998).
7. A. Rubio, Appl. Phys. A 68, 275 (1999).
8. S. Iijima, Nature 354, 56 (1991).
9. X.F. Zhang, X.B. Zhang, G. Van Tendeloo, S. Amelinckx, M. Op de Beeck, and J. Van Landuyt, J. Crystal Growth 130, 368 (1993).
10. M. Liu and J.M. Cowley, Carbon 32, 393 (1994).
11. S. Iijima, MRS Bull. Nov 1994, 43-9.
12. M. Ge and K. Sattler, Science 260, 515 (1993).
13. A. Hassanien, M. Tokumoto, S. Ohshima, Y. Kuriki, F. Ikazaki, K. Uchida, and M. Yumara, Appl. Phys. Lett. 75, 2755 (1999).
14. P.W. Anderson Phys. Rev. 109, 1492 (1958).
15. P.A. Lee and T.V. Ramakrishnan, Rev. Mod. Phys. 57, 287 (1985) and references therein.
16. N. Lin, J. Ding, S. Yang, and N. Cue, Carbon 34, 1295 (1996).
17. L.P. Biró, J. Gyulai, Ph. Lambin, J. B.Nagy, S. Lazarescu, G.I. Márik, A. Fonseca, P.R. Surján, Zs. Szekeres, P.A. Thiry, and A.A. Lucas, Carbon 36, 689 (1998).
18. R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B 61, 2981 (2000).
19. V. Meunier and Ph. Lambin, Phys. Rev. Lett. 81, 5888 (1998).
20. Ph. Lambin, V. Meunier, and A. Rubio, in Science and Applications of Carbon Nanotubes, edit. D. Tománek and R.J. Enbody (Kluwer Academic Publisher, New York, 2000), 17-34.
21. L. Langer, V. Bayot, E. Grivei, J.P. Issi, J.P. Heremans, C.H. Olk, L. Stockman, C. Van Haesendonck, and Y. Bruynseraede, Phys. Rev. Lett. 76, 479 (1996).
22. Schönberger, A. Bachtold, C. Strunk, J.P. Salvetat, and L. Forró, Appl. Phys. A 69, 283 (1999).
23. H. Beyer, M. Müller, and Th. Schimmel, Appl. Phys. A 68, 163 (1999).
24. C.L. Kane and E.J. Mele, Phys. Rev. B 59, R12759 (1999).
25. D. Tománek and S.G. Louie, Phys. Rev. B 37, 8327 (1988).
26. A. Rochefort, Ph. Avouris, F. Lesage, D.R. Salahub, Phys. Rev. B 60, 13824 (1999).
27. L. Yang, M.P. Anantram, J. Han, and J.P. Lu, Phys. Rev. B 60, 13874 (1999).
TABLES

TABLE I. Two-wall nanotubes with a metallic inner shell and a semiconducting outer shell. The second row is the intersheet distance, the third is the number of states induced in the gap, and the fourth column is the standard deviation of the local density of states in the external layer (see sect. V).

| nanotube       | $R_2 - R_1$ (nm) | gap states/atom | rms (eV$^{-1}$/atom) |
|----------------|------------------|-----------------|----------------------|
| (6,6)@(19,0)   | 0.337            | $0.17 \times 10^{-4}$ | $3.7 \times 10^{-4}$ |
| (6,6)@(18,2)   | 0.340            | $0.28 \times 10^{-4}$ | $2.4 \times 10^{-4}$ |
| (10,-2)@(16,3) | 0.337            | $0.56 \times 10^{-4}$ | $2.7 \times 10^{-4}$ |
| (15,-6)@(15,10)| 0.341            | $0.42 \times 10^{-4}$ | $3.2 \times 10^{-4}$ |
| (9,6)@(15,10)  | 0.341            | $2.28 \times 10^{-4}$ | $2.8 \times 10^{-4}$ |

TABLE II. Same as table I for polychiral two-wall nanotubes having a semiconducting inner shell and a metallic outer shell.

| nanotube       | $R_2 - R_1$ (nm) | gap states/atom | rms (eV$^{-1}$/atom) |
|----------------|------------------|-----------------|----------------------|
| (6,4)@(10,10)  | 0.337            | $2.4 \times 10^{-4}$ | $7.6 \times 10^{-4}$ |
| (7,3)@(13,7)   | 0.340            | $2.2 \times 10^{-4}$ | $5.0 \times 10^{-4}$ |
| (7,6)@(13,10)  | 0.341            | $2.1 \times 10^{-4}$ | $5.5 \times 10^{-4}$ |
| (10,0)@(15,6)  | 0.342            | $2.6 \times 10^{-4}$ | $6.1 \times 10^{-4}$ |
FIGURES

FIG. 1. Average density of states (eV$^{-1}$/atom) in the external layer of (a) (15,-6)@(15,10) and (b) (9,6)@(15,10) nanotubes (full curves). The dashed curve is the density of states of the single-wall (15,10) nanotube. The differences between the DOS's of the two-layer and one-layer systems are shown by a dotted curve, displaced vertically for clarity (the horizontal bar indicates zero difference), and multiplied by a factor of 10.

FIG. 2. Average density of states in (a) the inner and (b) the outer layer of (6,4)@(10,10) (full curves). The dashed curves in (a) and (b) show the density of states of the isolated (6,4) and (10,10) nanotubes. The differences between the full and dashed curves are shown by the dotted curves after amplification by a factor of 10.

FIG. 3. Top: computed constant-current image of the topmost part of the (6,6)@(19,0) two-layer nanotube. The nanotube axis is parallel to the horizontal x direction. The tip potential is 0.5 V, the height of the tip above the atom at the origin of the x, y coordinates is 5 Å (all the coordinates are in Å). Bottom: topographic line cut across the image, along the y = 0 line.

FIG. 4. π-electron band structure of (5,5)@(10,10) and local density of states on the sites labeled 1-8 of the external layer. The configuration of the nanotube, with symmetry C$_{5h}$, is sketched in the top-left part, with a cross section (large and small dots correspond to the atoms located in the plane of the drawing and those outside the plane, respectively), and the planar development of a short azimuthal portion of the external layer (with the 8 labeled sites, the projections of the inner sites being indicated by black dots).

FIG. 5. Gray-scale representation of the radial distance ρ(x, y) at constant current of the STM tip apex above a short azimuthal portion of (5,5)@(10,10) (left) and (6,6)@(11,11) (right). The orientation of the two layers in (5,5)@(10,10) is the C$_{5h}$ configuration of fig. 4. The tube axes are along the horizontal direction and the tip potential is fixed at 0.1 V.

FIG. 6. Local DOS in the outer layer of (5,5)@(10,10) obtained by twisting the (10,10) nanotube with a uniform torsion equal to 2.2°/nm. (a) Variations of the local DOS along a chain of 25 atoms located as close as possible to a generator of the external tube. (b) The average of the 25 curves shown in (a) (full curve) is compared to the DOS of the isolated twisted (10,10) nanotube (dashed curve).
