PHYSICAL REVIEW B VOLUME 61, NUMBER 8 15 FEBRUARY 2000-II

Electronic properties of amorphous carbon nanotubes

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(Received 5 October 1999)

A microscopic model describing the electronic structure of carbon nanotubes formed from two-dimensional disordered graphite sheets is presented. The strong electronic-lattice coupling of states near the Fermi energy is shown to result in the formation of an energy gap. The model predicts that the energy gap in these tubes is inversely proportional to the diameter with a larger magnitude than in crystalline tubes. Our results are shown to be in good agreement with experimental data for carbon nanotubes containing considerable structural defects.

I. INTRODUCTION

The substantial interest in carbon nanotubes has been due in large part to their unique electronic properties, predicted to be either metallic or semiconducting depending on the diameter and helicity of the tubes.[1] Recent advances in the synthesis of high-quality single-wall carbon nanotubes[2] (SWNT's) have enabled scanning tunneling microscopy (STM) and spectroscopy (STS) to be performed on individual crystalline SWNT's confirming the expected electronic behavior versus wrapping angle and diameter.[3–5]

On the other hand, the effect of defects and disorder on the electronic properties of carbon nanotubes has not been as well developed. Understanding the role of defects is important for fundamental investigations into nanotube electronic structure as well as transport properties[6] and, if modern semiconductor technology is any indication, may also be valuable for applications. In addition, the very recent successes in the large-scale fabrication of well-aligned[7,8] and highly periodic[9] carbon nanotube arrays suitable for device applications produced tubes with disorder due to the relatively low growth temperatures that are required for practical purposes. 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 a single sheet(s) of graphite onto the surface of a cylinder.[10]

In this work, we consider the opposite extreme; we examine the electronic properties of carbon nanotubes formed by folding two-dimensional *disordered* graphite sheets into cylinders. Using a microscopic model of electronic-lattice interactions in the resulting amorphous carbon nanotubes (aCNT's) we predict that these tubes are semiconducting with the remarkable result that the energy gap scales linearly with inverse diameter, as in crystalline carbon nanotubes (cCNT's) but with a considerably larger slope. We compare the predictions of our model with results of STM/STS measurements on individual carbon nanotubes known to contain considerable defects.

II. MODEL

We begin by considering the wall of a carbon nanotube: In aCNT's, because of the lack of long-range periodicity one cannot define primitive lattice vectors and consequently we cannot speak of a definite helicity in these tubes. In particular, the periodic boundary conditions along the circumference of the tube used to determine the electronic properties of cCNT's (Ref. 1) are absent in aCNT's. Therefore, *a priori*, it would seem difficult to predict whether aCNT's are metallic or semiconducting. Nevertheless, in the absence of long-range correlations in the plane of the tube the local characteristics of the π-electron states, which lie closest to the Fermi level (E_F), control the details of the electronic structure. In addition, unlike cCNT's, in aCNT's the lattice is ''softened,'' i.e., the elastic energy per carbon atom is less than in the crystalline case. This difference leads us to expect that in aCNT's electronic-lattice interactions are enhanced[11] and the electronic states at the Fermi energy could become unstable against perturbations which would open an energy gap at E_F and thereby lower the total system energy. Similar inferences have been drawn to study the effect of out-of-plane distortion[12] and nonadiabaticity[13] on the band structure of amorphous carbon. In the case of aCNT's, the displacement of carbon atoms perpendicular to the σ plane due to the curvature of the nanotube wall (Fig. 1) creates a distortion of chemical bonds, thereby changing the local symmetry of bonding to introduce sp^3-type features into the sp^2 hybridization. The key point is the possibility of a strong hybridization of electronic states of different symmetry at the top of a valence band.[14–16] The escape of an electron from one of these states leaves a hole. Incomplete screening (due to symmetry reasons[17]) of the hole results in the appearance of an effective electron-hole dipole. The interaction of this dipole with a transverse optical phonon can stabilize the associated lattice distortion resulting in the lowering of electron energies and the subsequent opening of an energy gap at E_F.

Since we are ultimately only interested in averaged system parameters, the above model can be quantified by a Hamiltonian similar to that used in the model of Frenkel small polarons [coherent potential approximation (CPA)] but with the electron-hole pair operators B_l^+, B_l (in the lattice site representation) replacing the electron operators:

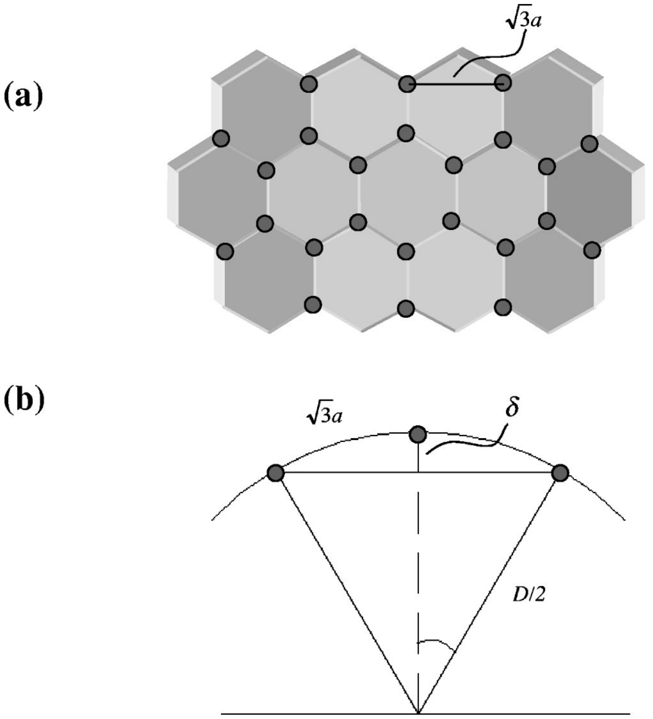

FIG. 1. Carbon nanotube wall schematic. (a) Front view. (b) Top view showing local atomic configuration and displacement, δ, of carbon atoms from basal σ plane.

$$H=\sum_l B_l^+B_lH_{l,l}+\sum_{l,l'}B_{l'}^+B_lW\begin{pmatrix} l & l' & l' & l\\ 1 & 2 & 1 & 2\end{pmatrix}$$
$$+\sum_{\alpha,q,l}\hbar\omega_q u_l(\alpha,q)B_l^+B_l[b_{\alpha,q}+b^+_{\alpha,-q}]$$
$$+\sum_{\alpha,q}\hbar\omega_q(b^+_{\alpha,q}b_{\alpha,q}+1/2). \qquad (1)$$

Here $H_{l,l}$ represents the pair one-site energy modified by taking the direct and exchange Coulomb interaction contributions into account[15] and the labels 1 and 2 refer to the π and σ states. The Coulomb interaction contribution

$$W\begin{pmatrix} l_1 & l_2 & l_3 & l_4\\ j_1 & j_2 & j_3 & j_4\end{pmatrix}$$

is given by[18]

$$\int\int dx\,dx'\,\phi^*_{j_1}(x-R^0_{l_1})\phi^*_{j_2}(x'-R^0_{l_2})$$
$$\times\frac{e^2}{\epsilon(x,x')|x-x'|}\phi_{j_3}(x'-R^0_{l_3})\phi_{j_4}(x-R^0_{l_4}),$$

with the electronic wave function $\phi_j(x-R_l^0)$ being the Wannier function centered at the l site of unperturbed lattice and $\epsilon(x,x')$ being the dielectric function. The phonon field is introduced by the creation and annihilation operators $b^+_{\alpha,q}$ and $b_{\alpha,q}$, with q and α denoting the wave vector and polarization direction, respectively. The strength of electron-hole coupling to phonons in Eq. (1) is measured by a coupling constant $\gamma_{\alpha,q}$ $[u_l\propto\gamma_{\alpha,q}\exp(iqR_l^0)]$ which is proportional to the scattering matrix element[15]

$$\int dx\,\phi_1^*(x-R_l)\phi_2^*(x-R_l)[e_{\alpha,q}\nabla H_{l,l}]$$
$$\times\phi_2(x-R_l^0)\phi_1(x-R_l^0),$$

where $e_{\alpha,q}$ is the polarization vector. When deriving Eq. (1) we omit the off-diagonal terms of the electron-phonon interaction matrix because of two reasons: first, the contribution of terms containing $B^+_{l'}B_l$ $(l'\neq l)$ is a factor

$$W\begin{pmatrix} l & l' & l' & l\\ 1 & 2 & 1 & 2\end{pmatrix}\bigg/ H_{l,l}\ll 1$$

smaller than that of the diagonal terms and, second, the contribution from excitonic states with charge transfer can be included into our consideration by choosing a modified set of electronic wave functions [see Eq. (4)].[16]

The CPA is known to combine two basic ideas: one is to calculate the average of a given quantity associated with a random medium by introducing a periodic effective medium; the second is to determine this effective medium by a self-consistency requirement, which is satisfied in our case by a proper choice of medium-related parameters such as $\bar{\omega}$, a, and V [see Eqs. (2) and (3), and discussion below]. The Lang-Firsov approach[19] was used to approximate the dependence of the lattice plane distortion (Fig. 1) on the electron-hole–phonon coupling in the above system as $[q=(q,\alpha)]$

$$\delta=2\left\langle\sum_q\frac{u_l(q)}{\sqrt{2M_iN\omega_q}}B_l^+B_l\right\rangle\simeq f_{exc}\left[\frac{2}{M_i\bar{\omega}^2}A\right]^{1/2}, \qquad (2)$$

where

$$A=\frac{1}{N}\sum_q|\gamma_q|^2\omega_q$$

is the eigenenergy shift due to the electron-hole–phonon coupling, M_i is the mass of carbon, N is the total number of atoms, $\bar{\omega}$ is the characteristic phonon frequency $(\hbar=1)$, and f_{exc} is the expectation value for the number operator of electron-hole excitations. It is possible to evaluate the eigenenergy shift as $A\sim M^2/\bar{\omega}$,[20] where M is the characteristic matrix element of the corresponding dipole-dipole interaction. In accordance with the Hamiltonian of Eq. (1), $M\simeq(u/a)V$, where u is the atom displacement, a is the C-C bond length and

$$V\sim\left|\tilde{\varepsilon}_1+\tilde{\varepsilon}_2-\sum_{l'\neq l}W\begin{pmatrix} l' & l & l & l'\\ 1 & 2 & 2 & 1\end{pmatrix}\right|, \qquad (3)$$

is the total self-consistent potential felt by an electron-hole pair $(V\sim E_g)$,[13] with $\tilde{\varepsilon}_1$ and $\tilde{\varepsilon}_2$ being the renormalized eigenvalues of electron energies in the modified set of wave functions[16]

$$\tilde{\phi}_j(x-R_l^0)=\phi_j(x-R_l^0)-\frac{1}{2}\sum_{i,l'\neq l}\phi_i(x-R^0_{l'})\Gamma^{ij}_{ll'}, \qquad (4)$$

with $\Gamma^{ij}_{ll'}$ being the overlap integral

$$\Gamma^{ij}_{ll'}=\int d^3x\, \phi_i^*(x-R^0_{l'})\,\phi_j(x-R^0_l).$$

At moderate temperatures ($T \ll T_D$, where T_D is the Debye temperature) the evaluation of the lattice deformation energy associated with the electron-hole–phonon coupling thus yields

$$A\sim \frac{V^2}{M_i\overline{\omega}^2a^2}. \tag{5}$$

The value of f_{exc} is estimated to be approximately 1 because the characteristic energy of the electrons which escaped the valence states leaving a hole $\varepsilon_c \sim E_g$ is as often more than V as it is less than V which fluctuates from site to site around E_g and, thus, $f_{exc}\sim\exp\{-(\varepsilon_c-V)/T\}\sim 1$.[13] Another way of looking at this problem is according to the carbon nanotube energy diagram (see, e.g., Ref. 21), where the lowest excited states are not those corresponding to electron escape from σ bonds, but rather from π bonds. If we consider the creation of high valence (sp^3-like) states in such a case, taking an extra charge from the π bond can be more favorable then taking it from σ bond, resulting in a π-hole creation. This situation somewhat resembles those in systems with a negative charge transfer gap where so-called ''self-doping'' takes place.[22] In this first-order approximation we finally get

$$\delta\simeq\sqrt{2}\frac{E_g}{M_i\overline{\omega}^2a}. \tag{6}$$

On the other hand, the displacement δ can also be derived from simple geometrical considerations (Fig. 1):

$$\delta=\frac{D}{2}\left[1-\sqrt{1-3\left(\frac{2a}{D}\right)^2}\right], \tag{7}$$

where D is the diameter of a nanotube. We calculated δ by assuming a local zigzag carbon atom configuration; there is no essential difference between this result and that for all other local orientations. For nanotube diameters $D \gg a$, Eqs. (6) and (7) result in the following estimate for the energy gap:

$$E_g\simeq\frac{3}{\sqrt{2}}M_i\overline{\omega}^2\frac{a^3}{D}. \tag{8}$$

Thus, apart from different numerical constants, our analysis predicts the energy gap in aCNT's still obeys the $1/D$ dependence characteristic of cCNT's.[1] The result of evaluating Eq. (8) using values inherent to carbon nanotubes[10] ($M_i\approx 2\times10^{-23}$ g, $\overline{\omega}\approx 1600\ \mathrm{cm}^{-1}$, and $a=1.41$ Å) is shown in Fig. 2 along with the theoretical results[1] for crystalline carbon nanotubes.

III. DISCUSSION

We see from the plots in Fig. 2 that the band gap in aCNT's increases more rapidly with inverse diameter relative to cCNT's and is therefore more sensitive to changes in nanotube diameter. This is consistent with the lack of translational symmetry in aCNT's which favors electronic state localization and increases the band gap.

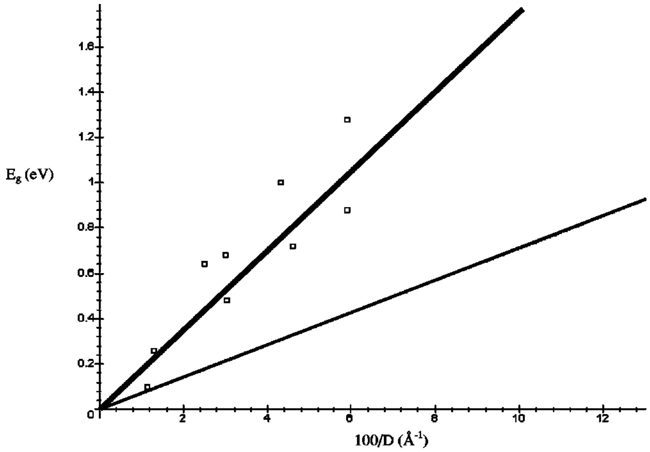

FIG. 2. The band-gap dependence on the inverse nanotube diameter. The thick line shows the result of the present work for disordered nanotubes, and the experimental results obtained by STM/STS study (□–Ref. 28) of carbon nanotubes known to contain defects are also plotted. The results of theoretical calculations for crystalline tubes within the tight-binding approximation (Ref. 1) (thin line) are shown for comparison.

The approach we chose to describe the electron-phonon interaction is somewhat different from the regularly used phonon modulated hopping that introduces specific electron-lattice coupling through an expansion of the electronic parameters of the tight-binding Hamiltonian in the local atomic displacements. The explicit inclusion of phonon modulated hopping in our model would result in a modification of the potential felt by the electron-hole pair, V. In our treatment we include such processes where an electron leaves the hole, thereby destroying the pair, implicitly by choosing a modified set of wave functions extended to comprise neighboring sites [Eq. (4)]. The system property which provides grounds for using our model is the existence of multiple choices of possible quasistable local atomic configurations, where there is an instability of chemical bonding or electronic hybridization type with respect to the local structure distortion. This is possible for sp^2-like carbon-based disordered systems (such as aCNT's) because of the possibility for carbon to adopt different bonding configurations sp^2 and sp^3, and the potential barriers between them being decreased due to a lattice softening characteristic for amorphous-like systems.

To test the validity and applicability of our model a good starting point might be measurements on multiwall carbon nanotubes (MWNT's). It has been shown using Raman spectroscopy,[23,24] conductivity measurements,[25,26] and electron spin resonance[27] that certain fabrication methods produce MWNT's that contain significant disorder and defects in their structure. Thus for the purposes of comparison with our theory we turn to the detailed combined STM/STS study performed by Olk and Heremans[28] on individual semiconducting MWNT's The technique used to produce the carbon nanotubes for this work has been shown to result in nanotubes with considerable disorder and defects.[27,24] These experimental results, shown in Fig. 2, are in good agreement with the predictions of Eq. (8). For further verification of our model, one possibility might be to damage metallic cCNT's via ion-(electron) beam exposure and then measure their electronic properties. After a certain exposure dosage a band gap should open up with the corresponding dependence on inverse diameter given by Eq. (8).

In summary, we have presented a microscopic model to describe the effect of disorder on the electronic properties of carbon nanotubes. We began by assuming an amorphous nanotube structure with a locally ''soft'' lattice and considered the resulting enhanced lattice-electronic interaction. The mixing of states of different symmetry near the Fermi level, namely, the π and σ orbitals due to nanotube curvature, creates an effective electronic dipole which couples strongly to the lattice distortion, thereby lowering electronic energies below the Fermi level and forming an energy gap. Our results predict that these amorphous nanotubes display a semiconductor band gap that scales inversely with the nanotube diameter, remarkably similar to crystalline nanotubes but with a more rapid increase with inverse diameter. Comparison with experimental data on carbon nanotubes known to contain substantial defects shows good agreement with our model. In addition to the fundamental contribution of this work in helping determine the effect of defects and disorder on experimental measurements of nanotube electronic properties, the prediction of our theory that carbon nanotubes with large amounts of defects still retain unique and controllable electronic properties is important for applications. For example, the large-scale, well-aligned carbon nanotube arrays being actively pursued for potential nanodevices are formed at relatively low temperatures resulting in tubes with significant defects. Rather than being viewed as detrimental, our model predicts that the defects can be beneficial since they can create appreciable nanotube band gaps (even for large diameter tubes) which can be sensitively tuned by adjusting the diameter.

ACKNOWLEDGMENT

One of the authors (A.R.) is grateful to D. Davydov and A. Shik for valuable discussions.

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