Properties of 4 Å carbon nanotubes from first-principles calculations

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Local-density-functional method is used to study the electronic properties of single-wall carbon nanotubes with very small diameters of about 4 Å, which have recently been synthesized inside zeolite channels. Our calculated results indicate that both the (5,0) and (3,3) tubes are metallic, while the (4,2) tube is semiconducting with a small indirect band gap. The metallicity of (5,0) is due to strong σ^* and π^* mixing induced by the large curvature of the tube. The calculated dielectric functions and breathing mode frequencies agree with experimentally measured absorption spectrum and Raman spectrum, respectively, giving strong support that these small radius tubes are indeed present inside the zeolite crystals.

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I. INTRODUCTION

Since its discovery in 1991,¹ carbon nanotubes have attracted a lot of attention from the science community because of their interesting quasi-one-dimensional character. These tubes are also believed to have great application potentials in nanotechnology. The novelty of these tubes is mainly due to their small diameter, and therefore there is great motivation to achieve the smallest possible diameter within this family. Recently, ultrasmall radius single-wall carbon nanotubes (SWNT) have been successfully fabricated inside inert $\text{AlPO}_4\text{—}5$ zeolite channels.² The final products are perfectly aligned mono-sized SWNT with very small diameters (about 4 Å) confined inside the zeolite channels with inner diameters of about 7.3 Å. The ultrasmall diameter of these tubes gives them many unusual properties such as superconductivity.³ Understanding these tubes is more challenging than tubes with larger diameters, which can essentially be understood using the band-folding picture.⁴ Due to the embedded geometry, the characterization of these tubes experimentally is also a challenge. Nevertheless, their existence has now been supported by techniques including Raman, x-ray, and direct TEM imaging.² Raman scattering showed the existence of peaks with frequencies expected from the breathing modes of small radius nanotubes, as well as high-frequency graphitic modes. Both x-ray and TEM found that the diameter is slightly larger than 4 Å.

In this paper, we use density-functional calculations to study the structural, electronic, vibrational, and optical properties of these ultrasmall radius single-wall carbon nanotubes. The calculations are important for these systems for at least two reasons. First, the extremely small radius of these tubes means that the simple band-folding picture can no longer predict the electronic structure reliably. For example, we are going to see that tube (5,0), which should be a semiconductor according to zone folding, becomes a metal as a consequence of large curvature effect.⁵ This in turn will play an important role in determining their electronic structure. Second, the characterization of these tubes is difficult, and both x-ray and TEM are probably operating near the margin of their sensitivity. If the calculated structural, vibrational, and optical properties of these tubes do compare favorably

with those measured experimentally, the agreement between theory and experiment can be taken as an indirect, yet convincing evidence that these tubes are indeed there. In addition, there are three kinds of tubes that have ≈ 4 Å diameter, and there is no compelling reason that one type of tube should dominate in population. We shall see that the comparison between calculated and measured optical data showed that all three types of tubes are inside the zeolite crystal.

II. METHOD OF CALCULATIONS

Our calculations have been performed using a plane-wave pseudopotential formulation⁶ within the framework of local-density approximation (LDA), with generalized gradient correction in the form of Perdew-Wang-91.⁷ We use ultrasoft pseudopotentials for the carbon atoms and a plane-wave cut-off of 26.34 Ry. The $\mathbf{k}$ points are sampled on a uniform grid along the tube axis. Optimal atomic positions are determined until the magnitude of the forces acting on all atoms became less than 0.1 eV/Å, which also converge the total energy within 1 meV. We adopt a supercell geometry so that the tubes are aligned in a hexagonal array with the closest distance between adjacent tubes being 10 Å. At such a separation, the tube-tube interactions are very small so that they can be treated as independent entities. We note that a similar supercell configuration (using a somewhat smaller tube-tube distance) has been used to calculate the band structure of the (6,0) tube.⁵ As a test, we have also done calculations for the (6,0) and our results agree very well with those of Blase *et al.*⁵ For optical calculations, we use the projector-augmented-wave method.⁸ Its reliability in calculating dielectric functions has been checked previously against all-electron approaches, and the general agreement is excellent.⁹ We use a cutoff energy of 29.40 Ry for the plane-wave expansion, and the tetrahedron method is used for the Brillouin-zone integration. Our results are carefully tested with respect to the number of conduction bands and $\mathbf{k}$ points in the irreducible part of Brillouin zone.

III. RESULTS AND DISCUSSIONS

As mentioned before, the diameters of the tubes confined inside the zeolite channels are about 4 Å. There are three

FIG. 1. Ball-and-stick model of finite sections of 4 Å single-wall carbon nanotubes (SWNT): (a) zigzag (5,0); (b) armchair (3,3); and (c) chiral (4,2). The unit cell of each nanotube contains 20, 12, and 56 carbon atoms, respectively. The arrows in the figure indicate those kinds of bonds that are aligned “along” the tube axis, other bonds are considered as that aligned “around” the tube circumference.

possible SWNT with such diameters and they are the zigzag (5,0), the armchair (3,3), and the chiral (4,2) tubes. Figure 1 is a schematic ball-and-stick picture of these nanotubes, showing the atomic arrangement. The unit cell of each tube contains 20, 12, and 56 carbon atoms, respectively. Calculated structural parameters for these three nanotubes are summarized in Table I. Both the atomic positions and the tube length are allowed to relax during the geometry optimization. The radius of the tube as listed in the Table is the average distance of all the atoms from the axis. The point-group symmetries of the tubes (when isolated) are also given for reference. In the fully relaxed structure, the radius of each tube is slightly larger than that resulting from an ideal rolling of a graphene sheet, while the length of translational vector along the tube axis is nearly the same as that of a rolled-up graphene. This is due to the curvature effect that weakens the carbon bonds that are wrapping around the circumference of the tube. We also calculated the bond lengths of these tubes, and find that the average length of carbon-carbon bonds “along” the tube axis (indicated in Fig. 1 by small arrows) is shorter than those strained bonds that are wrapping “around”

TABLE I. Calculated structural parameters for (5,0), (3,3) and (4,2) tubes. R is the average radius of the nanotube, T is the length of translational vector along the tube axis, E is the cohesive energy (relative to graphite) per carbon atom. $D1$ is the average bond length “along” the tube axis, and $D2$ is that “around” the circumference of the tube. The point group is that of a free-standing tube.

Tube	Group	R (Å)	T (Å)	$D1$ (Å)	$D2$ (Å)	E (eV)
(5,0)	D_{5d}	2.04	4.25	1.40	1.45	0.51
(3,3)	D_{3d}	2.10	2.46	1.43	1.44	0.49
(4,2)	C_{28}	2.14	11.27	1.42	1.44	0.46

the tube circumference. This is reasonable, since the curvature effect is more pronounced for the later case. In particular, this bond alternation is more significant for the (5,0) tube, since (5,0) has the smallest chiral angle among these three types of tubes. The behavior of bond angles is similar to bond lengths. There are two inequivalent bond angles in general, both are smaller than the ideal 120° . The difference between these two angles is biggest for (5,0), and smallest for (3,3). We note that the cohesive energies per carbon atom (relative to graphite) of these nanotubes are very similar to each other, with only a slight difference in the order $E_{(4,2)} < E_{(3,3)} < E_{(5,0)}$, while the radii of these tubes are in the reverse order. This agrees with the fact that the tube with a smaller radius has a larger strain and the strain energy per carbon atom is expected to be inversely proportional to the square of the nanotube radius.¹⁰

In Fig. 2, we show the band structure as well as the density of states (DOS) for these three tubes. The band structure is plotted with 50 uniform $\mathbf{k}$ points along tube axis; for the DOS, we use a very fine $\mathbf{k}$ mesh and a Gaussian smearing of 0.01 eV. On the basis of the band-folding scheme, tube (5,0) should be a semiconductor with an energy gap inversely proportional to the diameter. However, in Fig. 2(a), we find that the large curvature effect causes the σ^* band to mix with π^* band and pushes the band labeled as α down to cross the Fermi level, making (5,0) a metal. The physics is the same for the case of (6,0), as first explained by Blase *et al.*⁵ There are fairly large densities of states at the Fermi energy (0.35 states/eV per atom), indicating that the (5,0) tube may be a potential candidate exhibiting one-dimensional superconducting fluctuation. Figure 2(b) shows that the armchair (3,3) is metallic, as required by symmetry and suggested by the band-folding theory. The density of states at the Fermi level is found to be 0.06 states/eV per atom. It is interesting to note that the two bands crossing the Fermi level have very little dispersion near the zone center. There is a very sharp Van Hove singularity of the density of states at about 1.1 eV above the Fermi level. It has previously been shown that it is possible to intercalate 5 Å diameter tubes with Li.¹¹ If one can dope the 4 Å tubes, in particular, the (3,3) tube with alkali-metal atoms, we may be able to move the Fermi level to this energy to obtain a very high density of states. This implies good conductance or even superconductivity with higher mean field T_c . This is especially interesting in view of the fact that superconducting fluctuations have been observed³ for 4 Å tubes below 15 K. Unlike the tubes (5,0) and (3,3), we find in Fig. 2(c) that the tube (4,2) is semiconducting with a small indirect band gap of about 0.2 eV. The valence-band maximum appears about $1/5\Gamma$ X away from Γ point, while the conduction-band minimum appears at the X point. It is known that the DOS of nanotubes calculated from simple zone-folding or simple tight-binding model are typically symmetrical about the Fermi level. However, we note from Fig. 2 that the densities of states are by no means symmetrical about the Fermi level, a consequence of the small radius and large curvature.

The calculated band structures had been used to interpret experimentally observed optical absorption spectrum of these 4 Å nanotubes.¹² However, the previously published

FIG. 2. Band structure and density of states for (a) (5,0), (b) (3,3), and (c) (4,2) tubes. The Fermi level is at 0 eV.

results only showed that the measured peaks in the absorption spectrum can be identified with certain dipole-allowed transitions by considering the symmetry of the bands. To investigate absorption more explicitly, we are now calculating the interband contribution to the imaginary part of the dielectric function (ϵ_2), which includes the joint-density-of-states and matrix-element effects. We note that the zeolite crystal containing nanotubes is optically anisotropic, and the system is nearly transparent if the electric-field vector of light is polarized perpendicular to the tubes. Strong absorption occurs when the $\mathbf{E}$ field is aligned with the tube axis (z axis). We therefore focus on reporting the zz component of the dielectric tensor, and we consider energies up to 4 eV, which is the spectral range covered by the experiment. Although many properties of the tubes are governed by the radius, the optical absorption is strongly influenced by the symmetries and the details of the band structure, and thus we

FIG. 3. Imaginary part (ϵ_2) of the dielectric function (parallel to the tube axis) for the tubes (5,0), (3,3), and (4,2). Inset is the experimentally measured absorption spectrum for light polarized parallel to the tube axis.

expect large differences between different chiralities for small radius tubes.

In Fig. 3, we show the calculated imaginary part of the dielectric function (ϵ_2) of the three SWNT for the case of light polarized parallel to the nanotube axis. There is a strong peak at 1.2 eV and a weaker one near 2.3 eV for tube (5,0), and one sharp peak at 2.8 eV for tube (3,3). As for the (4,2) tube, we find a sharp peak at about 1.9 eV, with a long tail and some small peaks at 2.9 and 3.6 eV. The inset shows the measured absorption of zeolite crystals containing the 4 Å nanotubes. Comparing the calculated dielectric function with the measured absorption, we can clearly identify the feature A in the experiment with the peak of ϵ_2 at 1.2 eV for (5,0), and the feature C can be identified with the peak at 2.8 eV for (3,3). The broad shoulder marked as B in the absorption spectrum is probably due to the convolution of the sharp peak in (4,2) and the second peak in (5,0). It is also known¹³ that in some samples, the magnitude of the shoulder B can change rather significantly relative to the magnitude of the peak A. It is thus rather unlikely that the second peak of (5,0) can solely account for the shoulder B in the measured spectrum, and thus we conclude that (4,2) is also present. The energy of the peak of (4,2) also matches better with the position of B. We note that the LDA calculated eigenvalues do not correspond directly to optical spectrum, but previous GW calculations on graphite indicate that the LDA band structures are reasonably close to the quasiparticle dispersions, and the self-energy corrections causes a stretching of the bands by about 14%.¹⁴ Such corrections will make better agreement between calculation and experiment, but the current LDA calculations are good enough for identifying the chirality of the tubes. It is worth mentioning that the tubes confined in zeolite channels are initially thought to be (6,0) which is about 5 Å in diameter,² but was later determined to be closer to 4 Å by diffuse x-ray scattering and direct TEM imaging.² We have also calculated the dielectric function of (6,0), and found a sharp peak at 1.7 eV, and a small peak at 2.6 eV. There are no significant absorption peaks near these energies in the measured spectra. It is thus unlikely that the (6,0) tube can be present in appreciable quantities. The overall agreement between calculation and experiment can be

FIG. 4. Plotting $\omega = \sqrt{2\Delta E/m\Delta r^2}$ in units cm^{-1} as a function of Δr (in Å) for the (5,0) tube (circle), (4,2) tube (square), and (3,3) tube (triangle), respectively. The breathing mode frequencies are taken at $\Delta r = 0$.

taken as another evidence that the majority of the tubes inside the zeolite channels are indeed 4 Å rather than 5 Å in diameter. We note that the optical absorption of these tubes has recently been calculated using a parametrized local-density-matrix formalism,¹⁵ and the results are somewhat different from the current results. The differences are probably due to the fact that the parameters in the PM3 model give electronic structures that are different from those of LDA.

In the following, we discuss the vibrational modes of these three carbon nanotubes. We focus on the radial breathing mode (RBM), which has all the carbon atoms moving in phase perpendicular to the tube axis, resulting in a global change of tube radius r . The RBM is specific to the cylindrical geometry of a nanotube, and there are no such modes in planar graphitic fragments. The frequencies are determined by the frozen phonon method. We calculate the energy of each tube as a function of the tube radius around the equilibrium. Up to four configurations are calculated on either side of the equilibrium with a maximum change of 10% of the radius, and the RBM frequencies are found by plotting $\omega = \sqrt{2\Delta E/m\Delta r^2}$ as a function of Δr , and interpolated at $\Delta r = 0$ (see Fig. 4). For fully relaxed (5,0), (4,2), and (3,3) tubes, the calculated RBM frequencies are 525, 529, and 538 cm^{-1} , respectively. Thus, the (5,0) and (4,2) have rather close breathing mode frequencies, while the (3,3) frequency

is somewhat higher. These calculated RBM frequencies are in reasonably good agreement with the experimentally observed A_{1g} breathing mode in the measured Raman spectra,¹³ in which two peaks are found, one at 511 cm^{-1} , the other at 541 cm^{-1} . It is interesting to see that the (3,3) radius is in fact slightly larger than that of (5,0) and yet it has a higher frequency, and thus the usual notion that larger radius tubes have lower frequencies does not necessarily apply when the tubes are nearly of the same radius but of the different chirality. Our calculated frequencies are a bit lower than those obtained from parameters fitted to the breathing mode frequencies calculated for SWNT of larger radius.¹⁶ We also note that previous calculation¹⁶ also found that $(n,0)$ tubes have lower frequencies than (n,n) tubes of the same radius. The experimentally measured frequencies, of course, pertain to those of the tubes confined inside the zeolite channels, and the calculated frequencies correspond to freestanding tubes. The reasonably good agreement between the calculated values with the experiment is an indirect evidence that the tube-zeolite interaction is small, which is perhaps not too surprising since a 4 Å tube can fit very comfortably into the zeolite channels.

IV. SUMMARY

We have studied the physical properties of ultrasmall radius carbon nanotubes (5,0), (4,2), and (3,3) using first-principles calculations. The calculated dielectric function (ϵ_2) and radial breathing mode frequencies for these 4 Å tubes are in good agreement with experimental absorption and Raman spectra, and thus giving further support to the existence of these tubes inside the zeolite channels. The results also indicate that all three chiralities are present.

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