Electron-phonon coupling and superconductivity in double-walled carbon nanotubes

Jesse Noffsinger and Marvin L. Cohen

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Study of electron-phonon coupling and superconductivity in double-walled carbon nanotubes

Jesse Noffsinger and Marvin L. Cohen
Department of Physics, University of California at Berkeley, Berkeley, California 94720, and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720
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Using first principles techniques we study the electronic structure, deformation potentials and electron-phonon coupling in both single-walled and double-walled carbon nanotubes (CNTs). The calculations were done for metallic single-walled carbon nanotubes in the armchair configurations (5,5) and (10,10). Additionally, we study the effect of concentric multi-walled systems by peforming calculations on the double-walled tube (5,5)@(10,10). By comparing the properties of the (5,5) and (10,10) tubes both in isolated and concentric form arrangements, we are able to investigate the effect on electron-phonon coupling of the double-walled and consequently multi-walled carbon nanotube arrangement. No significant increase in total electron-phonon coupling is found in the double-walled tube as compared to the single-walled carbon nanotubes within the calculations of the isolated tubes under consideration.

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Following the discovery of the fullerene C60[1], extensive fundamental research attention has been devoted to fabricating, measuring and predicting the properties of novel carbon-based structures. From the fabrication of graphene[2] to applications such as measured superconductivity in fullerene-based materials[3–5], ARPES studies of graphene[6], predictions and measurements of graphene nanoribbons[7], and transport in carbon nanotubes[8] fullerene-related materials research and analysis has grown at a rapid pace.

Pioneering studies of carbon nanotubes[9] prompted the measurement and theoretical investigations of a wide range of properties in these novel systems[10,11]. Specifically relevant to this work, the phonons, thermal properties and electron-phonon coupling of nanotubes have been measured and calculated in single-walled systems[12–14]. These properties are relevant to the observation of such phenomena as the Kohn effect, possible Peirels distortion, ballstic transport and superconductivity.

Predictions of substantial electron-phonon coupling in doped ultra-small radius carbon nanobutes leading to possible superconductivity have been published[15]. Subsequent measurements of nanotubes embedded in a zeolite matrix show indications of superconductivity at 15 K[16,17]. While significant effort has been devoted to the study of individual nanotubes, fewer first-principles studies of the electron-phonon coupling and superconductivity in multi-walled systems exist.

In this work, we describe calculations of the electronic structure, deformation potentials and electron-phonon coupling parameters for the single-walled carbon nanotubes (5,5) and (10,10) as well as for the double-walled carbon nanotube (5,5)@(10,10). The armchair arrangement was decided upon because of the symmetry-imposed metallicity arising from the bandstructure of graphene which is present in all (n,n) tubes[10]. The calculated intertube spacing between the pair of concentric tubes in a (n,n)@(n+5,n+5) DWCNT is 3.4 Å. This result is very nearly that of the spacing between the van der Waals-bonded sheets in bulk graphite. Finally, these particular tubes were selected for the calculations of this work because the double-walled system composed of these tubes is invariant to a rotation of 72°, as in the (5,5) tube.

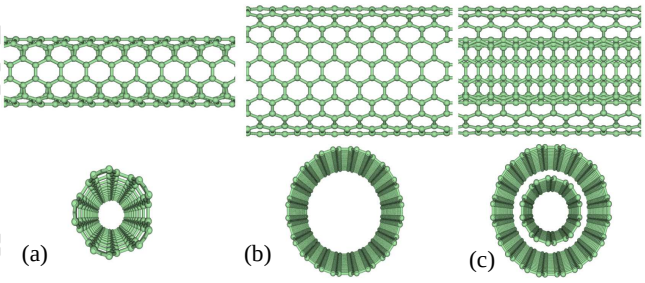

FIG. 1: (Color online) Carbon nanotube structures studied in the calculations of this paper. (a) The (5,5) carbon nanotube (b) (10,10) carbon nanotube and (c) (5,5)@(10,10) carbon nanotubes. The diameter D of the (5,5) tube is 6.75 Å, while the (10,10) and (5,5)@(10,10) tubes possess an outer diameter of $D = 13.56$ Å.

These first-principles calculations were performed within the local density approximation to density functional theory (DFT)[18,19]. The self-consistent Kohn-Sham eigenfunctions and charge density were computed using a plane-wave basis[20] with a kinetic energy cutoff of 60 Ry and charge density cutoff of 240 Ry, while total energies were computed on a Brillouin zone grid of $1 \times 1 \times 32$ electronic k-points. The core-valence interaction was taken into account through the use of a norm-conserving pseudopotential[21]. The lattice dynamics of the (5,5) CNT were described through density-functional

perturbation theory[22], while the total electron-phonon coupling of this tube was determined through isotropic Migdal-Eliashberg theory[23]. The total electron-phonon coupling of the (10,10) and DWCNT was determined through a scaling estimation argument based on the results of the (5,5) CNT. The carbon nanotubes were constructed in a supercell arrangement, each metallic tube separated by 10 Å from its neighbors to eliminate spurious interactions[24].

The nanotubes, as depicted in Figure 1, were initially constructed with a nominal C-C bond distance of 1.41 Å. A fully self-consistent structural relaxation was performed on each system such that the interatomic forces were less than 0.02 eV/Å. The unit cell of an (n, n) nanotube contains $4n$ carbon atoms, therefore the calculations on the single- and double-walled nanotubes of this work were performed using 20, 40 and 60 atoms, respectively.

In each of the three carbon nanotube systems considered, maximally localized Wannier functions (MLWFs) were constructed which allow for the precise sampling of the electronic structure[25,26]. The ground state charge density was computed using a grid of $1 \times 1 \times 24$ k-points, while the MLWFs were constructed on a line of $1 \times 1 \times 8$ points, creating a real-space separation of 9.7 Å between identical Wannier functions. In each CNT, Wannier functions were utilized such that five functions described each two atom graphene-like unit cell. This resulted in calculations composd of 50, 100 and 150 Wannier functions for the separate systems. The nature of these Wannier functions was such that one out-of-plane π orbital was localized around each C, and one localized on the $sp2$ bond between neighboring atoms. The spread, Ω, of these Wannier functions was 0.91 Å and 0.62 Å, respectively[26].

The Wannier-interpolated electronic bandstructure and density of states are shown in Figures 2, 3 and 4. The densities of states in both single-walled tubes is almost the same, a result which is explained by the zone-folding of the graphene bandstructure. In a single-walled armchair carbon nanotube, a graphene K-point is folded into each zone, leading to the presence of a pair of linear bands crossing the Fermi level. In this work, we will refer to the Fermi point where the graphene K-point has been folded into the one-dimensional zone as the K-point of the one-dimensional Brillouin zone (BZ). In the relaxed (5,5) carbon nanotube, K lies at a point between the zone center Γ and the zone edge X such that $K = 0.64\overline{\Gamma X}$. In the (10,10) tube, $K = (0, 0, 0.335)$, while the bandstructure of the DWCNT is very nearly the superposition of the (5,5) and (10,10). In this case $K_5 = (0, 0, 0.317)$ and $K_{10} = (0, 0, 0.334)$.

The bandstructures of these nanotubes leads to a density of states at the Fermi level per unit cell in the double-walled tube which differs from the sum of the single-walled densities of states by less than 1%.

The phonon dispersions of the (5,5) CNT have been calculated and are in agreement with previous first-principles lattice dynamical results[27,28]. However, the lattice dynamics of the (10,10) and (5,5)@(10,10) CNTs were not explicitly calculated via density functional perturbation theory because of the significant computational cost associated with these large systems.

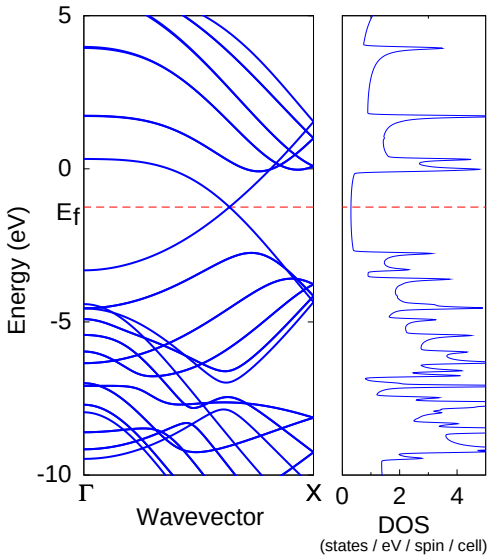

FIG. 2: (Color Online) Electronic bandstructure and density of states for the (5,5) carbon nanotube. The DOS at E_f is 0.607 states/ eV / spin / cell.

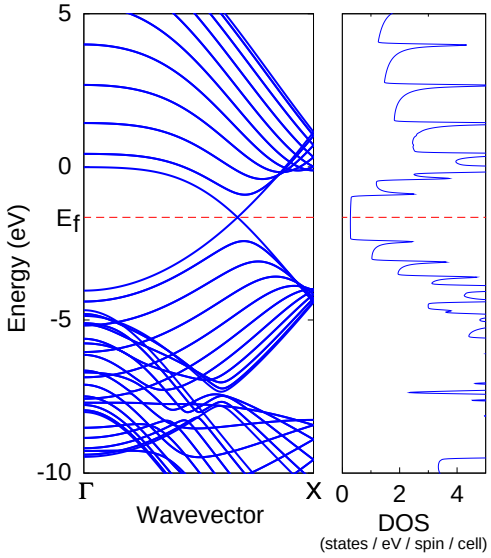

FIG. 3: (Color Online) Electronic bandstructure and density of states in the (10,10) carbon nanotube. The DOS at E_f is 0.570 states/ eV / spin / cell.

We have calculated the total electron-phonon coupling from first principles for the (5,5) CNT. The coupling to a single mode of a phonon wavevector is given by Eq. 1.

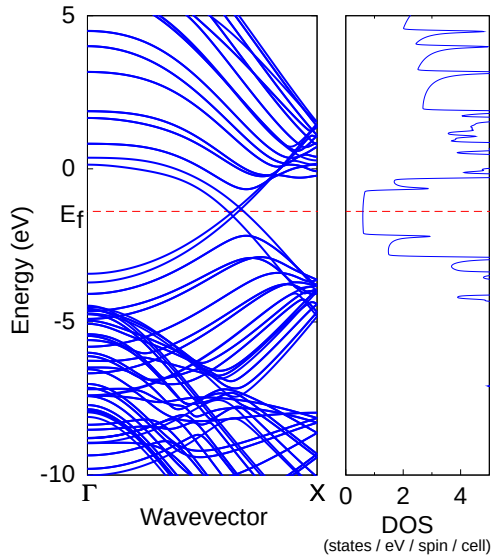

FIG. 4: (Color Online) Electronic bandstructure and density of states in the (5,5)@(10,10) double-walled carbon nanotube. The DOS at E_f is 1.190 states/ eV / spin / cell.

$$\lambda_{q\nu} = \frac{2}{N_k}\frac{1}{N_F\omega_{q\nu}}\sum_{mnk}|g^{\nu}_{mn}(k,q)|^2\delta(\epsilon_{k,m})\delta(\epsilon_{k+q,n}) \quad (1)$$

Here the electronic band indices are given by m and n, the phonon frequency at wavevector q and mode ν is denoted by $\omega_{q\nu}$, and N_k is the number of electronic k-points sampled in the BZ. To understand the electron-phonon coupling in these nanotubes, Eq 1 can be broken into contributions from its constituent elements. We see that the total coupling to a single mode depends on the electron-phonon matrix elements $|g^{\nu}_{mn}(k,q)|^2$, the phonon frequency $\omega_{q\nu}$, the density of states at the Fermi level N_F and finally on the particulary geometry of the Fermi surface through the nesting function $\chi(q)$ (Eq 2). The nesting function is a geometrical property of the Fermi surface in a material wherein peaks indicate particular wavevectors which connect large numbers of states on the Fermi surface. In the case of a one-dimensional BZ, the nesting function peaks at wavevectors which connect large numbers of the Fermi points.

$$\chi(q) = \frac{1}{N_k N_F^2}\sum_{mnk}\delta(\epsilon_{k,m})\delta(\epsilon_{k+q,n}) \quad (2)$$

Strictly speaking, the nesting function cannot be seen as a multiplicative factor of the total coupling because of the inclusion of the electron-phonon matrix elements in the sum over electron band indicies. However, under the assumption that these matrix elements do not vary significantly throughout the zone, $\chi(q)$ provides a solid physical foundation for understanding the appearance of particular values of coupling. Since the calculated optical phonon modes which couple electrons do not have a strong dispersion throughout the zone, we can reformulate the experession for the total coupling into Eq 3. In this way, the total coupling becomes the product of the sum of the average matrix elements of the phonon frequencies for a given mode with the nesting function and includes a Fermi level density of states prefactor.

$$\lambda \approx 2N_F\left(\sum_{\nu}\frac{|\overline{g_\nu}|^2}{\omega_\nu}\right)\left(\frac{1}{N_q}\sum_{q}\chi(q)\right) \quad (3)$$

In carbon nanotubes where the Brillouin zone consists of a line in reciprocal space, the nesting function is straightforward to calculate and intepret. Because of the simple electronic structure at the Fermi level, the nesting function consists only of two distinct and equal peaks; one peak is centered at Γ and represents the contribution from normal scattering processses of states near K. A second identical peak is centered at $2(\overline{\Gamma X} - K) \sim K$, and gives the total coupling which arises from Umklapp processes of $\mathbf{q}$-vectors equal to $2k_F$. An integration of χ throughout the zone includes half of the zone-center peak and the entire Umklapp peak. The intergral shows that two thirds of the weight of the nesting function arises from Umklapp processes while the remaining third results from zone-center phonons scattering electrons among states near the K-point.

In our (5,5) nanotube calculations, we have obtained the first-principles phonon linewidths and electron-phonon coupling for the phonon modes at the zone center as well as the nested wavevector K. At each wavevector, four optical modes contribute to the total coupling. The coupling at $q = (0,0,0)$ is found to be $\lambda_\Gamma = \sum_\nu \lambda_{\Gamma\nu} = 0.20$, while the coupling at $q = (0,0,0.32)$ is $\lambda_K = 0.32$.

We can therefore estimate the total electron-phonon coupling in a (5,5) tube by appropriately weighting the contributions from the phonons at the two relevant wavevectors. The broadening used to determine the peak height of the nesting function at each resonance is approximately the average frequency of the coupling phonons, 120 meV. The total coupling arising from the peaks near the relevant wavevectors is found by scaling the nesting function such that the values at Γ and K are equal to the first-principles calculations. In this way we utilize first-principles calculated values with an efficient sampling method to arrive at a good estimate of the total electron-phonon coupling in the (5,5) tube. Using this method, we find that the total electron phonon coupling in (5,5) isolated metallic carbon nanotubes is $\lambda = 0.08$. This value is of very similar size to that found in prior works[29,30].

To obtain an estimate the electron-phonon coupling in the larger SWCNT and in the DWCNT, we have calculated the deformation potential for a perturbation in the nanotubes along the radial direction. In addition to calculating the deformation potential for motions of all C

Nanotube	N_F (states/eV/spin/cell)	$\frac{\Delta E}{\Delta q}$ (eV/Å)	λ
(5,5)	0.607	5.31 eV/Å	0.08
(10,10)	0.570	4.87 eV/Å	0.07
(5,5) in DWCNT	0.607	5.86 eV/Å	0.09
(10,10) in DWCNT	0.570	5.15 eV/Å	0.08
(5,5)@(10,10) total	1.190	5.13 eV/Å	0.10

TABLE I: Calculated electronic density of states at the Fermi level, deformation potential and estimated electron-phonon coupling parameter for (5,5), (10,10), and (5,5)@(10,10) carbon nanotubes.

atoms in the DWCNT we attempt to estimate the effect of intertube coupling. To this end, we have calculated this potential for a deformation which perturbs only the (5,5) and (10,10) tubes in the double-walled configuration. Results for the change in total energy per C atom in the case of single-walled tubes compare favorably with previous calculations[31–34]. Table I gives the results of the deformation potential for each case under consideration.

It is found that the deformation potential in the (5,5) tube is 5.31 eV/Å for the bands which cross the Fermi level, while in the (10,10) case this potential is 4.87 eVÅ.

Using the deformation potential as an approximation for the electron-phonon matrix elements, we use a simple scaling argument to estimate the total electron-phonon coupling in double-walled carbon nanotubes. This method scales the total electron-phonon coupling in the (5,5) tube by the ratios of the densities of states, deformation potentials and the **q**-sums of the nesting functions in the remaining tubes. In the double-walled tube, the coupling can be interpreted as arising from 1) the coupling in the (5,5) tube, 2) the coupling in the (10,10) tube and 3) the coupling from electrons scattered from the (5,5) to the (10,10). As can be seen in Table I, the deformation potential of the bands crossing the Fermi level in the individual tubes while arranged in a double-walled structure is increased by $\sim 10\%$. The total deformation potential when the entire structure is perturbed, however leads to an average value of the deformation potential which is only slightly increased over that in the isolated tubes. Therefore we conclude that the construction of a multi-walled carbon nanotube system has a small affect on the total electron-phonon coupling as compared to separate tubes. Finally, the superconducting transition temperature estimated using the McMillan equation[35] arising from the calculated electron-phonon parameters in these tubes is much less than 1 K.

Strong Van Hove singularities are present in the densities of states of the one-dimensional CNTs of this work at points away from the undoped Fermi level. Because the calculations of this work have been performed within pristine, undoped nanotubes, these Van Hove singularities do not factor into the results of this work. In the case of doped nanotubes, the Fermi points and density of states at the Fermi level may be strongly affected, resulting in possible increased electron-phonon coupling and superconducting transition temperature. Additionally, the effects which may occur in the case of metallic single-walled or multi-walled CNTs in close proximity but not arraged concentrically are not addressed. Future studies to consider ropes of carbon nanotubes[36] are needed to fully consider the effects on total electron-phonon coupling of systems where a description of isolated single-walled does not accurately represent reality.

In conclusion, we have calculated from first principles the electronic structure of three carbon nanotube systems: the (5,5), (10,10) and (5,5)@(10,10) nanotubes. Additionally, first principles calculations of the lattice dynamics and electron-phonon coupling have been performed on the (5,5) tube. Using the above results, we have estimated the total electron-phonon coupling in an isolated, double-walled carbon nanotube. No appreciable increase in the total coupling from the separate tubes was found to result from a deformation potential estimate.

Calculations were performed using the `Quantum-ESPRESSO`[37] package and `wannier90`[38]. This work was supported by National Science Foundation Grant No. DMR10-1006184 and by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, U.S. Department of Energy under Contract No. DE- AC02-05CH11231. Computational resources have been provided DOE at Lawrence Berkeley National Laboratory's NERSC facility.

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