Lattice Dynamics and Electron-Phonon Interaction in (3,3) Carbon Nanotubes

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We present a detailed study of the lattice dynamics and electron-phonon coupling for a (3,3) carbon nanotube which belongs to the class of small diameter based nanotubes which have recently been claimed to be superconducting. We treat the electronic and phononic degrees of freedom completely by modern *ab initio* methods without involving approximations beyond the local density approximation. Using density functional perturbation theory we find a mean-field Peierls transition temperature of ≈ 240 K which is an order of magnitude larger than the calculated superconducting transition temperature. Thus in (3,3) tubes the Peierls transition might compete with superconductivity. The Peierls instability is related to the special $2k_F$ nesting feature of the Fermi surface. Because of the special topology of the (n, n) tubes we also find a phonon softening at the Γ point.

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During the past ten years carbon nanotubes have gained a lot of attention [1]. This is due to their potential for applications (e.g., for molecular electronics) as well as to the fact that they allow the study of electronic systems in one dimension. Thus, they offer the opportunity to investigate effects like Peierls transition, superconductivity, electron-phonon interaction, and the interplay between them in a low-dimensional system. Despite the great interest in these materials, progress has been hindered until recently due to the difficulty of producing carbon nanotubes with well-defined radii as well as due to the difficulty to determine in detail the structure of nanotubes present in a given sample. Recently, however, very promising progress in identifying the structure of nanotubes has been made by combining Raman and photoluminescence measurements [2]. Size selection has been also achieved in certain cases. For example, growing nanotubes in zeolite crystals has made it possible to produce tubes with a very narrow radii distribution [3] thus allowing for a detailed comparison with modern density functional theory (DFT) based calculations [4–6]. Recently, superconductivity has been reported for nanotubes with radii of 4 Å [7]. This immediately raises the question as to the origin of superconductivity, the importance of Peierls distortions, and of electron-electron correlations. Dealing with electron-lattice and strong electron-electron interaction in a materials specific way from *ab initio* methods has not been possible so far even for much simpler systems than nanotubes. Thus, in the past either one had to restrict oneself to model studies of the electron-electron aspect [8] or study the electron-lattice interaction with correlations taken into account only on the level of local density approximation (LDA) based functionals [9,10].

In the latter case, however, modern DFT-based methods allow for the parameter free microscopic calculation of phonon modes. So far, for nanotubes this scheme has been used nearly exclusively for the determination of Raman active modes. The results are generally in good agreement with available Raman data, thus emphasizing the reliability of this approach. Calculation of the full phonon dispersion for a given nanotube is a much more elaborate task. Based on supercell calculations the phonon dispersion for a small number of tubes could be determined recently [6,10]. This approach, however, has a certain disadvantage if one is interested in phonon anomalies and electron-phonon coupling. Anomalies show up in most cases at phonon wave vectors which are not commensurable with the underlying lattice, thus even for approximate treatments, huge supercells would be needed to study, for example, a Peierls transition by this method. Only in very favorable cases, these anomalies appear at high-symmetry points and can be dealt with accurately by the supercell approach (as, e. g., for graphite [10,11]). Also the calculation of superconducting properties in the framework of the Eliashberg theory requires a detailed knowledge of the phonon dispersion over the whole Brillouin zone (BZ). Especially systems which show phonon anomalies require usually a very dense mesh of phonon wave vectors which can not be obtained with supercell methods. The calculations get even more demanding if the phonon anomalies are related to special nesting features of the Fermi surface. Since in one-dimensional systems the Fermi surface consists only of isolated points, the most extreme case for nesting properties is reached here. This requires also a very dense k-point mesh for calculating the electronic band structure and wave functions. Already, for simple systems like graphene and graphite, this effect can be seen easily. It is reflected in the high sensitivity of certain phonon modes at the K point to sampling effects of the Fermi surface as reported recently [10,11].

An alternative method is offered by using density functional perturbation theory (DFPT) which allows for the

calculation of phonon modes at arbitrary wave vectors without relying on large supercells [12]. Using this approach we have studied in detail the complete lattice dynamics and electron-phonon interaction for a (3,3) nanotube. This belongs to the class of small-radii tubes which have been reported to be superconducting. Our Letter will try to answer the question whether or not electron-phonon coupling can explain superconductivity in this tube. A special complication arises from the Peierls instability which has to show up in all one-dimensional metallic systems. However, this has not received much attention in the past since general belief was that the mean-field Peierls transition temperature for nanotubes is always very low so that it is of no practical consequence. These arguments are based on information from graphite using the folding concept [1]. However, this approach breaks down for tubes with small diameter which is seen, e.g., in the prediction of the wrong ground state for small-radii nanotubes [4,13]. Recently an approximate treatment of the lattice dynamics for (5,0), (6,0), and (5,5) tubes has been presented which showed for (5,0) tube, indeed, that the estimated transition temperature is of the order of 160 K and thus not negligible [14]. However this approach was based on a nonselfconsistent tight-binding scheme and did use only an approximate treatment of the polarization eigenvectors; thus results might be questioned.

In contrast, our DFT-based method allows for a consistent calculation of electronic states, phonon modes and electron-phonon coupling without introducing approximations beyond the LDA level. In this Letter we present fully *ab initio* results for phonon dispersion and eigenvectors as well as for the electron-phonon coupling for the (3,3) nanotubes using a well-tested norm-conserving pseudopotential of Hamann-Schlüter-Chiang type [15]. We use DFPT in the mixed-basis pseudopotential formalism [16] which has been successfully applied to study electron-phonon-mediated superconductivity [17,18]. As basis functions localized $2s$ and $2p$ functions are used together with plane waves up to an energy cutoff of 20 Ry. For integration over the BZ, a Gaussian broadening scheme is employed. As test of the reliability of our phonon approach we have calculated the phonon dispersion for graphene. Comparison with results published recently show excellent agreement among the different calculations except for the highest mode at the K point which is very sensitive to k-point mesh and broadening as already mentioned [10,11]. With a very dense k-point mesh of 5184 points in the BZ we found still a fluctuation of 1.5 meV for the highest mode when going from a broadening of 0.05 to 0.2 eV. The authors of Ref. [10] tried to avoid the complications due to very dense k-point sampling by increasing the broadening; however, for studying instabilities due to Fermi surface nesting that is not a practical way since any instability will be broadened substantially. Thus, one of the complication for the calculations for the nanotube is the requirement of a very dense k-point mesh and a small broadening.

Our calculations for the (3,3) nanotubes were done in a supercell geometry so that all tubes are aligned on a hexagonal array with a closest distance between adjacent tubes of 10 Å. The tube-tube interactions are very small [4]. We used 129 k points in the irreducible part of the BZ and a broadening of 0.2 eV. The structure was fully relaxed and the optimal geometry agreed very well with those given in Refs. [4,5]. The phonon calculation was carried out with the DFPT method. For calculation of the electron-phonon matrix elements we even used up to 1025 k points. In Fig. 1 we have plotted the band structure close to the Fermi energy and for comparison also the band structure as obtained by using the folding method. Our results agree well with those obtained previously [4,5]. At $k = k_F = 0.284$ (in units of $2\pi/a$, where a is the lattice constant of the graphene honeycomb lattice) we see that two bands are crossing ϵ_F. This special feature which holds for all (n, n) tubes is important for phonon anomalies seen at the Γ point, as will be emphasized later. The dispersion differs most notably from those obtained by using the folding technique by a shift of the k_F value and a change in slope of the two bands crossing at ϵ_F. This has of course drastic consequences for the phonon modes.

Phonon results are shown in Fig. 2. Again we have plotted folding results together with the *ab initio* dispersion curves. These *ab initio* results were obtained by

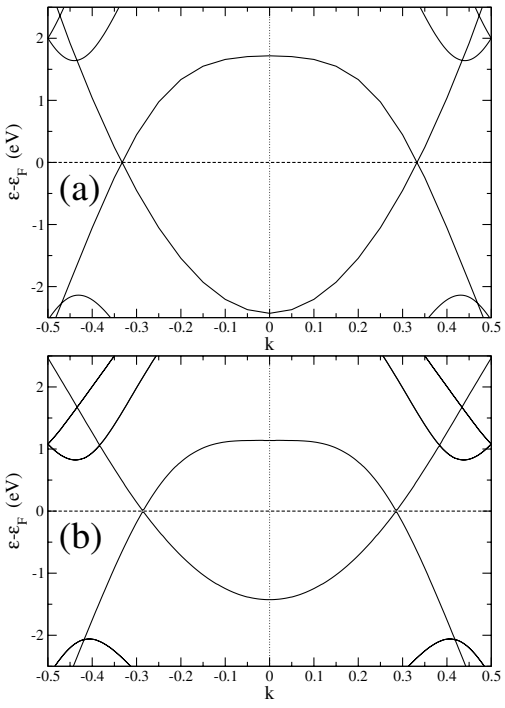

FIG. 1. Calculated band structure of the (3,3) nanotube. Compared are results obtained (a) from the calculated graphene band structure using the folding method, and (b) for the true nanotube geometry.

Fourier interpolation on a 16-point grid. The electronic wave functions were obtained from a calculation with a broadening width of 0.2 eV. In general, the *ab initio* phonon frequencies are softer than the folding results. Furthermore, near $q = 2k_F$ one sees phonon anomalies in certain phonon branches as well as a certain softening at the Γ point which is not present in the dispersion obtained by folding. The Γ-point softening has been seen and studied already for the G band in Refs. [9,10]. However, this effect is also present in another mode at ≈ 90 meV with the same symmetry. It is related to the fact that these Γ-point phonons couple the two electronic bands crossing right at k_F (Fig. 1), leading to a nesting vector $q = 0$. Therefore, this softening also indicates an underlying Peierls instability; however, the corresponding Peierls distortion does not change the lattice periodicity. Note that in our DFPT approach, the calculations of phonons include all screening effects due to lattice distortions in contrast to other treatments like, e.g., tight-binding methods (see Ref. [14]).

To study the anomalies near $q = 0$ and $q = 2k_F$ in more detail we have increased the number of k points and reduced the broadening from 0.2 to 0.025 eV. This can be interpreted as a variation of the electronic temperature from 1096 to 137 K. With finer sampling and reduced temperature one of the modes with the anomalous behavior at $q = 2k_F$ gets unstable. Results for $T_{el} = 137$ K are shown in Fig. 3. Here only those modes which are sensitive to the temperature variation are shown. The modes which show anomalous behavior at the Γ point stay stable for all temperatures studied but should eventually go soft at low enough temperatures. The Peierls transition temperature T_P is defined by $\omega_{2k_F}(T_P) = 0$. This leads immediately to a lower limit of 137 K for T_P which is of similar magnitude as the value given for a (5,0) tube in Ref. [14]. It is important to note that, contrary to early estimates of T_P for nanotubes of the order of 1 K [19], this temperature is of sizeable magnitude and, thus, the Peierls instability might compete with the superconducting transition.

To investigate the possibility of phonon-induced superconductivity, we have calculated the microscopic electron-phonon coupling parameters, which are central to the Eliashberg theory of strong-coupling superconductivity. The coupling constant for a phonon mode $q\lambda$ is given by

$$\lambda_{q\lambda} = \frac{2}{\hbar N(\epsilon_F)\omega_{q\lambda}} \sum_{k\nu\nu'} |g^{q\lambda}_{k+q\nu';k\nu}|^2 \delta(\epsilon_{k\nu})\delta(\epsilon_{k+q\nu'}), \quad (1)$$

where $N(\epsilon_F)$ is the density of states at the Fermi energy and all energies are measured with respect to ϵ_F. The electron-phonon coupling matrix element is given by a

$$g^{q\lambda}_{k+q\nu';k\nu} \propto \langle \phi_{k+q\nu'} | \delta V^{q\lambda}_{\text{eff}} \mid \phi_{k\nu} \rangle,$$

with $\delta V^{q\lambda}_{\text{eff}}$ being the change of the effective crystal potential due to a phonon $q\lambda$ and $\mid \phi_{k\nu}>$ being the electronic wave functions . Since this quantity is very sensitive to k-point sampling we have used a grid of 1025 points. Because of the self-consistent determination of δV, the matrix elements include all screening effects in contrast to tight-binding approaches. Because the Fermi surface consists only of the points $k = \pm k_F$, contributions to the total electron-phonon coupling constant

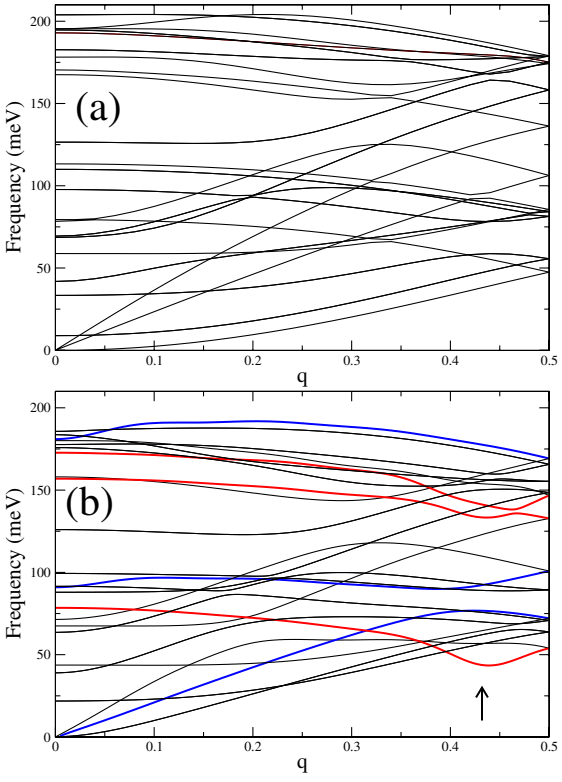

FIG. 2 (color online). Calculated phonon dispersion curves of the (3,3) nanotube as obtained (a) by the folding method from the graphene phonon dispersions and (b) for the true nanotube geometry. The latter corresponds to a high effective temperature of 1096 K. The arrow indicates $2k_F$ (folded back to the first Brillouin zone).

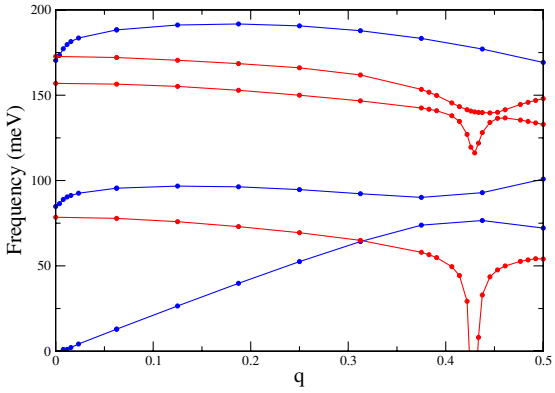

FIG. 3 (color online). Phonon dispersion curves for the two symmetry classes which are affected by electron-phonon coupling. Shown are results obtained on a fine q grid and for a small effective temperature of 137 K.

$\lambda = 1/N_q \sum_{q\lambda} \lambda_{q\lambda}$ are restricted to $q = 0$ and $q = 2k_F$. Roughly 20% comes from $q = 0$ while 80% is contributed from $2k_F$. An estimate for T_c can be obtained by using the Allen-Dynes formula [20]. Neglecting the effect of the electron-electron interaction on the pairing, it gives an upper limit of $T_c = 0.833\ \omega_{\ln} \exp\{-1.04(1 + 1/\lambda)\}$, where the effective phonon frequency is defined as

$$\omega_{\ln} = \exp\left\{\frac{1}{\lambda}\frac{1}{N_q}\sum_{q\lambda}\lambda_{q\lambda}\ln(\omega_{q\lambda})\right\}.$$

Using our results for $T_{el} = 1096$ K gives $\lambda \approx 0.25$ and $\omega_{\ln} \approx 60.4$ meV and as an upper limit $T_c = 3$ K. One has, however, to consider the possibility that the presence of the Peierls instability significantly alters this estimate. This is because in the expression (1) for the coupling constant $\lambda_{q\lambda}$ the renormalized phonon frequencies enter. The softening of the critical mode thus produces a strong temperature dependence of λ, which formally diverges at T_P. At the same time $\omega_{\ln}$ goes to zero. Simulation of this mode softening effect using the Allen-Dynes formula shows that T_c can be enhanced due to the softmode, but the obtained maximal value of ≈ 30 K is still significantly smaller that T_P. Taking into account a finite electron-electron interaction further reduces this value.

To get a more precise estimate of the Peierls transition temperature we have made connection with simple model studies which have been carried out in the past considering a Fröhlich Hamiltonian in random-phase approximation [21]. Extending this approach to the present 2-band case gives for the critical mode at $q = 2k_F$ a temperature dependence of the frequency as

$$\{\hbar\omega_{q=2k_F}(T)\}^2 = A\ln(T/T_P),$$

where

$$A = 2\hbar\omega^{bare}\sum_{\nu}(g_\nu)^2 N_\nu(\epsilon_F).$$

Here, $N_\nu(\epsilon_F)$ is the partial density of states per spin of band ν, ω^{bare} is the unrenormalized phonon frequency, and g_ν is the electron-phonon matrix element for scattering processes from k_F to $-k_F$ within the νth band induced by the critical phonon at $q = 2k_F$. Because of symmetry, only intraband scattering processes contribute. Estimates of the parameters from our *ab initio* calculations for different effective temperatures lead to $T_P \approx 240$ K and $A \approx (39\ \text{meV})^2$. Note that the expression for A does not depend on the phonon frequency but only on the phonon eigenvector due to the fact that $(g_\nu)^2 \sim 1/\omega^{bare}$. Our finding that T_P is an order of magnitude larger than T_c suggests that for the (3,3) nanotube the Peierls instability dominates over the superconducting one.

In summary we have presented here a fully *ab initio* calculation of the lattice dynamics and the electron-phonon coupling for the (3,3) carbon nanotube. Without relying on simplifying approximations the Peierls transition could be seen and a Peierls mean-field transition temperature $T_P \approx 240$ K was predicted. Calculating the electron-phonon coupling using the same scheme resulted in a superconducting transition temperature which was 1 order of magnitude smaller than T_P. This makes it not very likely that superconductivity based on the electron-phonon mechanism is present in (3,3) nanotubes. This does, however, not exclude the possibility that phonon-mediated superconductivity exists in the case of the (5,0) nanotube, which is another member of the class of 4 Å tubes for which superconductivity has been observed experimentally [7]. Effects which have been discussed here are not accessible with the folding method since they depend sensitively on the curvature of the nanotubes, the detailed band structure and nesting features. Since in our approach arbitrary q points are treated on the same footing we could easily see that the $q = 0$ anomaly is only a special case of strong electron-phonon coupling. In contrast to former studies we could show that this effect is not restricted to the G band but should be seen in another mode, too, belonging to the same symmetry class.

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