Phonon Softening in Metallic Nanotubes by a Peierls-like Mechanism

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The radial dependency of the vibrational frequencies of single-wall carbon nanotubes in the G band $(1500-1600 \text{ cm}^{-1})$ is studied by density functional theory. In metallic nanotubes, a mode with A_1 symmetry is found to be significantly softer than the corresponding mode in insulating tubes or graphite. The mechanism that leads to the mode softening is explored. It is reminiscent of the driving force inducing Peierls distortions. At ambient temperature, the energy gained by opening the gap is, however, not sufficient for a static lattice distortion. Instead the corresponding vibrational frequency is lowered.

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The discovery that a graphite layer can be rolled up to form nanoscaled tubes [1] has attracted great interest in the experimental and theoretical materials science community. On one side, such nanotubes (NT's) might aid to build nanoscaled mechanical or electronic devices (e.g., [2-4]). On the other hand, one-dimensional metallic wires exhibit new—previously unstudied—physical properties, such as superconductivity in low dimension [5], uncommon magnetic properties [6,7], strong tendency towards symmetry reduction at zero temperature [8-10], or peculiar phonon-electron coupling mechanisms [10,11]. Our study concentrates on the latter point, i.e., the coupling of the continuum states around the Fermi level to a particular phonon mode. The mechanism studied here is found to be similar to the well-known Peierls mechanism [12], but differs insofar as no increase in the translational period is involved (compare also Ref. [10]). In addition, the electron-phonon coupling is not sufficiently strong to allow the gap to open at ambient temperatures. Instead, the gap widens and closes periodically, when the atoms of the tube oscillate back and forth according to this particular phonon mode, and as a result the mode is found to be significantly softer than the corresponding mode in graphite. Since the mode does not cause an increase of the translational period, it corresponds to a Γ centered phonon, which is directly observable in Raman spectroscopy. Therefore, the comparison of the Raman spectra of insulating tubes (without mode softening) with those of metallic tubes offers a direct experimental view of this coupling mechanism and allows one to validate the theoretical picture.

This work was initiated by a remarkable experimental observation. In Raman spectroscopy, one particular mode exhibits a Breit-Wigner-Fano (BWF) line shape, which is usually an indication of a coupling to continuum states. The position of the BWF line exhibits a significant radius dependency, with frequencies varying between 1547 cm⁻¹, for NT's with an average diameter of d =15 Å, and 1530 cm⁻¹, for d = 8.5 Å [13]. Recent experimental studies suggest that the mode might correspond to an optic phonon with A_1 symmetry (i.e., totally symmetric in the circumferential direction), but the experimental evidence is only circumstantial [13]. The precise mechanism driving this softening is as yet unknown and will be determined in this paper. Additionally, the radial dependency of other phonon modes in the G band will be discussed.

To investigate the vibrational properties of NT's we performed an *ab initio* density functional study in the local density approximation employing a plane wave basis set. The Kohn-Sham equations were solved using the Vienna ab initio simulation package [14], and the electron-ion interaction was described by the projector augmented-wave (PAW) method [15]. The study was performed with a relatively soft carbon PAW potential at an energy cutoff of 250 eV. Calculations for selected cases using a very accurate potential yielded identical results. The correct sampling of the electronic states in the vicinity of the Fermi energy, ϵ_F , requires particular attention, since these states couple to the aforementioned mode. For zigzag tubes, 33 k points with the coordinates $2\pi n/(64a)$, $n = 0, \dots, 32$ were applied, and, for armchair tubes, 57 points were used, resulting in roughly similar k-point densities (a is the translational period of the NT). Additionally, the eigenstates were broadened (smeared) by 0.1 eV to make the density of states smooth and continuous around the Fermi level [16]. The calculations exhibited a fairly large dependency on the applied width and k-point sampling, and the present setup was chosen, since it yields a reasonable compromise between computational demands and accuracy ($\pm 5 \text{ cm}^{-1}$).

The phonon frequencies were evaluated by displacing a single atom in the primitive unit cell of the NT and diagonalizing the resulting matrix of the symmetrized force constants [17,18]. This approach yields exact frequencies at the Γ point only; results for the dispersion relations will be presented elsewhere [18]. In the following, we will refer to these results as the "*ab initio*" results. Additionally, the full phonon dispersion relation of a single layer of graphite was calculated [18]. An important finding of this calculation is that the theoretical frequency for the longitudinal optic mode at Γ is roughly 1% larger than in the experiment, an error that has to be taken into account, when the theoretical results are compared to experiment. The resulting phonon dispersion relation of graphite was used in a simple zone-folding calculation to estimate the

vibrational frequencies of NT's ("zone folding" in the following) [19,20]. A comparison of these zone-folding results with the *ab initio* results allows us to access systematically the effects of curvature on the phonon frequencies.

Our main results are presented in Fig. 1, where the zone-folding predictions and the *ab initio* calculations and experiments are shown by lines and symbols, respectively [21,22]. Deviations between the symbols and lines are a consequence of the modification of the interatomic force constants by wrapping (e.g., curvature). Zone folding predicts a single A_1 mode, since the longitudinal optic and shear horizontal modes are identical at the Γ point in graphite. Additionally, zone folding shows a small splitting between the longitudinal and transversal E_1 modes, and a larger splitting between the two E_2 modes [20]. Since our force constants lead to a rather strong increase of the longitudinal optic frequency from Γ to M in graphite (overbending), the average frequency is higher than for graphite.

The full *ab initio* calculations show a similar behavior, but some details are clearly different. Generally, the exact results are lower then the zone-folding values. The softening is explained by the fact that curvature weakens the π contribution to the bonds in the circumferential direction, which also explains why the $A_1(T)$ mode is affected most strongly by curvature, whereas the $A_1(L)$ mode is essentially radius independent in insulating tubes. For di-



FIG. 1. Phonon frequencies of (n, 0) zigzag, (n, n) armchair tubes and the (12, 6) chiral tube in the *G* band calculated by *ab initio* density functional theory (symbols) and zone folding (lines). Phonons are characterized by their symmetry and the direction of vibration *L* (longitudinal)—parallel to the tube axis, *T* (transversal)—perpendicular to the tube axis. The lower axis and upper axis show the diameter and the index for zigzag tubes (n, 0), respectively. Experimental results for the frequency of the BWF line from Refs. [21,22] are shown by open and filled diamonds. Zigzag (n, 0) tubes with $n \neq 3m$ are insulating; all other tubes are metallic.

mately 1613 cm⁻¹ and 1570 cm⁻¹) are symmetrically split by 22 cm⁻¹ with respect to the central graphite frequency $\omega_g = 1595$ cm⁻¹ (theory). Since curvature shifts the $E_1(T)$ mode to lower values, the frequencies of the $E_1(T)$ and $A_1(L)$ mode (open triangles and asterisks) almost coincide for insulating tubes and are located at about 1597 cm^{-1} , a little bit higher than the theoretical central G mode of graphite. The $E_1(L)$ and $A_1(T)$ modes (filled triangles and open circles) also have rather similar frequencies and are found at roughly 1580 cm^{-1} , i.e., 20 cm⁻¹ lower than the $E_1(T)$ and $A_1(L)$ modes. Experimentally, it is generally agreed that there are at least two characteristic sets of frequencies in the G band, and that both sets contain E_1 and A_1 modes [20,22–24]. In a recent polarized Raman study of Jorio *et al.*, one E_1 and one A_1 mode were observed at about 1590 cm⁻¹, and another set of E_1 and A_1 modes was measured at 1567 cm⁻¹, in good agreement with our data [23]. The agreement with recent micro-Raman data of Jorio et al. is also reasonable for insulating tubes, although theory predicts no A_1 mode at 1590 cm⁻¹ for metallic tubes [22]. For the experimental position of the E_2 modes, controversy exists. Jorio et al. observed a symmetric splitting of the E_2 modes by 29 cm⁻¹ with respect to the central G mode of graphite, whereas experiments using parallel, crossed, and circular polarized light find the E_2 modes overlapping in frequency with the A_1 modes [24]. Our calculations seem to favor the first conjecture, but the separation between the E_2 and other modes is so small at large radii, that the definite answer is still open.

ameters at about 14 Å, the E_2 modes (squares at approxi-

The most relevant outcome of the calculation is the significant drop of the frequency of the $A_1(L)$ mode in metallic tubes compared to insulating ones (asterisks at low frequencies in Fig. 1). The corresponding displacement patterns of the A_1 modes in zigzag and armchair tubes are indicated in Figs. 2a and 2b. The frequency shift is certainly not a simple result of curvature, since it occurs abruptly for the transition from insulating to metallic tubes. Although it is roughly the same for zigzag and armchair tubes with similar radii, the $A_1(L)$ mode is Raman active only in tubes with a chirality close to zigzag tubes, since it has A_{1g} symmetry in zigzag and A_{1u} symmetry in armchair tubes [25]. Compared to graphite, the frequency shift is roughly proportional to α/d with $\alpha = 600 \text{ cm}^{-1}\text{ Å}$, where d is the diameter of the tube. This is in reasonable agreement with the experimental value of 440 $\text{cm}^{-1}\text{ Å}$ [13]. But contrary to Refs. [13,22], we assign the softened mode to $A_1(L)$ instead of $A_1(T)$ symmetry.

The reason for the large down-shift is revealed by further density functional calculations. If a displacement commensurate to the $A_1(L)$ modes is superimposed on the NT's, a band gap opens independently of the sign of the displacement, as indicated in Fig. 3. The gap size increases linearly with the amplitude of the displacement δd and is roughly equal to 26 eV/Å × $|\delta d|$. It is generally accepted



FIG. 2. Displacement patterns of the longitudinal (transverse) A_1 mode in (a) zigzag (armchair) and (b) armchair (zigzag) tubes. (c) Conventions used in the tight binding Hamiltonian

that the formation of such a band gap lowers the band structure energy of the system, since filled states are moved to lower energies. At intermediate (electronic) temperatures, the energy gain is roughly proportional to the square of the gap [8,12]. In addition, the conventional restoring forces, stemming from the other parts of the electronic spectrum and from the direct interaction between the ionic cores, are operative. These contributions are similar for insulating and metallic tubes. The formation of the band gap therefore reduces the energy required to distort metallic NT. Since the density of states around ϵ_F is additionally inverse proportional to the radius of the tube, the $A_1(L)$ mode is softer for smaller tubes with a larger density of states at ϵ_F [13].

To corroborate this model, calculations on a metallic (12,0) tube were performed at a very high electronic temperature, which was simulated by a large smearing parameter $\sigma = 0.8$ eV. It is expected that such a large electronic temperature suppresses contributions from the electronic states at the Fermi level. Indeed, the vibrational frequencies of this artificially electronically heated metallic NT are found to be similar to that of an insulating tube with similar radius, in particular, the $A_1(L)$ mode is raised to 1580 cm^{-1} . Further details are revealed by the energy versus displacement curve calculated for the small and large smearing parameters for the $A_1(L)$ mode in the (12,0) NT (Fig. 3d). The energy difference between these two calculations (dotted curve) is proportional to the lowering of the total energy by the gap formation. One important point is that zigzag tubes have a small curvature induced band gap at their equilibrium position (Fig. 3a), which we find



FIG. 3. Band structure obtained by *ab initio* calculations in the vicinity of k_F for the (12,0) zigzag nanotube in (a) the equilibrium positions, (b) for a distortion compatible with the $A_1(T)$ mode, and (c) for a distortion compatible with an $A_1(L)$ mode ($\delta d = 0.02$ Å). (d) Total energy (eV) versus distortion (Å) diagram for a small (solid line) and large (dashed line) electronic temperature, and the difference between both (dotted curve).

to close for a displacement $\delta d_{gap=0}$ commensurate with the $A_1(L)$ mode. The maximum of the dotted curve is also moved towards this point. The frequency reduction is, however, proportional to the second derivative of the dotted curve and not related to the exact position of its maximum.

To rationalize the band gap opening, we turn to the electronic band structure of graphite. It is well established that the bands around the Fermi level of graphite are dominated by *p*-type orbitals aligned normal to the tubule surface (π bonding). Their behavior can be modeled by a tight binding Hamiltonian with zero on-site energy [8], in which the eigenstates and eigenenergies are obtained by the diagonalization of a 2 \times 2 matrix:

$$\begin{pmatrix} 0 & \text{complex conjugate} \\ V_0 + V_1 e^{i2\pi k_1} + V_2 e^{i2\pi k_2} & 0 \end{pmatrix},$$
(1)

where V_0 , V_1 , and V_2 are the tight binding hopping elements between nearest neighbors (compare Fig. 2c), and k_1 and k_2 are parametrizing the \vec{k} point ($\vec{k} = k_1\vec{b}_1 - k_2\vec{b}_2$, \vec{b}_i being the reciprocal lattice vectors of the graphite plane). This Hamiltonian describes two bands that intersect at one particular point in the Brillouin zone. Additionally, for half filled π bands, as in the case of undoped graphite, the Fermi level is located exactly at the position where the two bands intersect. One can determine this point by the requirement that the off-diagonal elements of the matrix should become zero:

$$|V_0 + V_1 e^{i2\pi k_1} + V_2 e^{i2\pi k_2}| = 0.$$

Then the Hamiltonian has only one double degenerated eigenvalue $\epsilon = 0$. For a perfect graphite layer (corresponding to $V_0 = V_1 = V_2$) this condition is satisfied for $k_1 = -k_2 = \pm 1/3$, which corresponds to the *K* point in graphite $\pm 1/3(\vec{b}_1 + \vec{b}_2)$ [8,9]. It can be shown that the crossing point moves to $\pm (1/3 - \delta)(\vec{b}_1 + \vec{b}_2)$ for the displacement pattern shown in Fig. 2a, and $\pm (1/3 + \delta)\vec{b}_1 \pm (1/3 - \delta)\vec{b}_2$ for the pattern shown in Fig. 2b [18].

The shift of the band crossing point has important consequences for the band structure of NT's. To show this, we first turn to a three-dimensional representation of the band structure of graphite in the vicinity of K indicated in Fig. 4a. The two intersecting bands $\epsilon(k)$ are forming two cones around K, with one negative branch at energies lower than ϵ_F (filled states) and one positive branch at higher energies (empty states). The resulting modificated in Figs. 4b and 4c. The electronic band structure of NT's is obtained by simple zone-folding arguments, i.e., by the intersection of the two-dimensional band structure of graphene (cones) with those planes that are allowed by the conditions imposed by the wrapping procedure [26]. For armchair tubes, the resulting band structure at about



FIG. 4. (a) Electronic band-structure of graphene in the vicinity of the K point. Panel (b) and (c) indicate the changes in the band-structure for two phonon modes. For the $A_1(T)$ mode in armchair tubes [and $A_1(L)$ mode in zigzag tubes], the crossing point shifts away from K towards Γ . For the $A_1(L)$ mode in armchair tubes [and $A_1(T)$ mode in zigzag tubes], the crossing point moves perpendicular to the line ΓK . The thick lines indicate the band structure of an armchair tube obtained by intersecting the gray plane with the two cones.

 ϵ_F is indicated in Fig. 4 by the thick lines. The longitudinal mode opens a gap in the armchair tube, since the tip of the cones has moved perpendicular to the allowed lines, whereas the transverse mode leads only to a shift of k_F to a different k point (cf. Fig. 3). For the zigzag tubes, the arguments are similar, but the allowed lines are perpendicular to those for armchair tubes, and hence it is again the longitudinal mode that opens the gap. In general, the displacement pattern that moves the cone perpendicular to the lines allowed by the periodicity imposed by the wrapping procedure creates the largest gap. This is, irrespective of chirality, the $A_1(L)$ mode. As a result of the induced band gap the frequency of the $A_1(L)$ mode is lowered by an amount that depends essentially only on the radius of the tube.

In summary, we have discussed and rationalized the grouping of the vibrational modes in the *G* band of nanotubes. The most relevant outcome of our study is a peculiar electron-phonon coupling mechanism that opens a band gap when NT's swing back and forth in a manner compatible to the totally symmetric longitudinal A_1 mode. The oscillating band gap lowers the frequency of this mode compared to graphite and insulating tubes. The underlying mechanism resembles that of a usual Peierls distortion, but at ambient conditions a regime well above the critical temperature T_c is explored. Three points should be highlighted here. First, armchair tubes possess a small nonvanishing gap at zero temperature, because the $A_1(L)$ mode freezes at $T < T_c$ (compare also Ref. [10]). The estimated transition temperature T_c is, however, only a few degrees Kelvin [18]. Second, the strong radial dependency of the $A_1(L)$ mode makes it an ideal candidate for measuring the radius of metallic tubes, supplementing the current methods that rely on the radial breathing mode [27]. Third, it is still unclear how the discussed electron-phonon coupling affects the conductivity at low temperature or the electronic behavior in general, offering a field for further studies.

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