

Boosting Electronic Transport in Carbon Nanotubes by Isotopic Disorder

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The current-voltage curve of metallic carbon nanotubes (CNTs) displays at high bias a sudden increase of the resistivity due to the scattering of electrons with phonons having an anomalously high population (hot phonons). Here, we show that it is possible to improve the electrical performances of metallic CNTs by ^{13}C isotope enrichment. In fact, isotopic disorder creates additional channels for the hot-phonon deexcitation, reduces their population and, thus, the nanotube high-bias differential resistance. This is an extraordinary case where disorder improves the electronic transport.

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Introduction.—Metallic single-wall carbon nanotubes (CNTs) are quasi one-dimensional wires which can carry the highest current density (10^9 A/cm^{-2}) [1] of any material. This makes them the best candidates as interconnects in future high-power electronic devices. The measured current-voltage (IV) curve of metallic single-wall CNTs with Ohmic contacts [1–3] displays at high bias (voltages higher than ~ 0.2 Volts) a sudden increase of the resistivity, due to the scattering of conducting electrons with optical atomic vibrations (phonons) [1]. The largest part of this resistivity is due to the presence of an anomalously high optical-phonon occupation (hot phonons) [4,5]. Indeed, the rate at which optical phonons are excited (by the scattering with conducting electrons) is faster than the rate at which they are deexcited. The large hot-phonon population determines an important part of the electrical resistivity, limiting the performances of CNTs. So far, the most direct experimental observations of the phenomenon are given by Refs. [6,7], where an important increase of the optical-phonon population during electron transport is measured by Raman spectroscopy. Also, in Ref. [8] a negative differential resistance in tubes suspended between the two electrodes is interpreted as due to hot phonons.

In this Letter, we show that it is possible, in practice, to improve the electrical performances of metallic nanotubes by ^{13}C isotope enrichment. Isotopic substitution changes the nuclear masses but not the nuclear charges and thus introduces elastic scattering mechanisms for phonons but not for electrons (i.e., it does not degrade the electronic transport properties) [9]. In fact, the introduction of isotopic disorder creates additional deexcitation channel for the hot phonons. This results in a reduction of the hot-phonon population and in an important decrease of the nanotube high-bias differential resistance. The phenomenon is quantified by means of a coupled Boltzmann transport equation (BTE) for both phononic and electronic populations, in which all the relevant scattering parameters are obtained from *ab initio* calculations based on density functional theory (DFT).

Interplay between electron-phonon scattering and thermalization.—The scattering processes involved in the degradation of the electronic transport are represented in Fig. 1. In metallic CNTs, conducting electrons can scatter mainly with two optical phonons, corresponding in graphene to the longitudinal E_{2g} phonon near Γ ($\Gamma E_{2g}\text{LO}$) and to the A'_1 near K ($\text{K}A'_1$) [10]. Their momentum is localized in a small region of the Brillouin zone (BZ) [5,10] and their energy is $\sim 0.2 \text{ eV}$. For voltages higher than 0.2 Volts , conducting electrons have sufficient energy to excite the two phonons. As a consequence, the electron scattering and, thus, the resistance increase. For tubes with a diameter of 2 nm (typically found in experiments) the $\Gamma E_{2g}\text{LO}$ and $\text{K}A'_1$ phonons are excited with a characteristic electron-phonon scattering time $\tau_{ep}^\Gamma \sim 0.5$ and $\tau_{ep}^{\text{K}} \sim 0.2 \text{ ps}$, respectively [11]. In a defect-free tube, the two phonons are deexcited (or thermalized) with characteristic times $\tau_{pp}^\Gamma \sim 3$ and $\tau_{pp}^{\text{K}} \sim 5 \text{ ps}$ which are due to anharmonic phonon-phonon scattering [11]. In fact, anharmonicity couples the

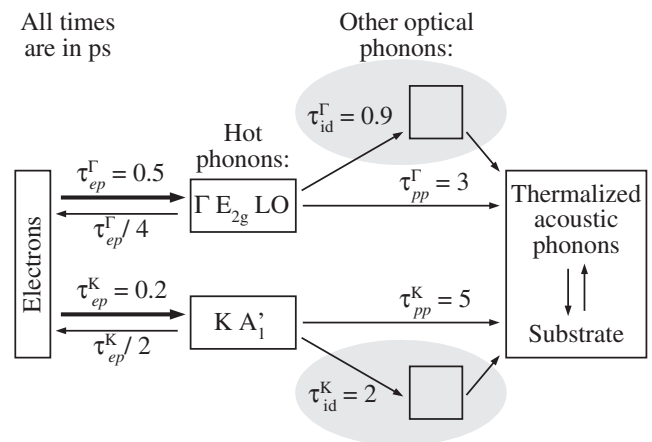


FIG. 1. Schematic view of the hot-phonon generation (see the text). In a defect-free tube, the hot phonons are generated and thermalized with characteristic times τ_{ep} and τ_{pp} , respectively. Isotopic disorder introduces additional thermalization channels (shaded area) with characteristic times τ_{id} .

two phonons with acoustic phonons which can be considered thermalized in the typical experimental conditions (when the tubes are lying on a substrate) [16]. In practice, the excitation of the two optical phonons is faster than their thermalization ($\tau_{ep} \ll \tau_{pp}$). Because of this, the two optical phonons cannot be thermalized with the rest of the tube and their occupation is expected to increase during high-bias electronic transport (hot phonons). This, in turn, will result in a larger electron-phonon scattering and a larger electronic resistance.

A quantitative description of the process can be obtained by means of a coupled BTE for both phononic and electronic populations, as in Ref. [5] (see note [17]). The resulting IV curve reproduces very well experiments (compare the red curve with measurements in Fig. 2, upper panel). The red curve of Fig. 2 is obtained by letting the phonon population evolve according to BTE and is associated to an important increase of the optical-phonons population. To show the relevance of this, in Fig. 2 we also show the IV curve obtained by imposing the phonon population to be zero (blue curve). As already remarked in Ref. [5], in this case the high-bias current is much higher, that is an important part of the measured high-bias resistance is due to the presence of hot phonons. We stress that in the calculations of Fig. 2 all the relevant parameters are

obtained from DFT and no parameters are present which can be tuned in order to recover agreement with measurements [17].

The bottleneck for hot-phonon generation is the large phonon thermalization time. Thus, the set up of a mechanism to decrease it will diminish the hot-phonon population improving the electron conduction. This goal could be reached by changing the isotopic composition of the nanotubes, since isotopic disorder provides a new phonon-phonon scattering mechanism. On the other hand, the possibility of synthesizing isotopically enriched nanotubes has been actually demonstrated [18–20].

In a defect-free crystal, a phonon is characterized by a momentum \mathbf{q} and a branch index ν . When isotopic disorder can be considered as a perturbation, the dynamic of the system can be described by the evolution of the unperturbed $\mathbf{q}\nu$ states. Isotopic-disorder results in the creation of additional scattering channels between the phonons, characterized by a time τ_{id} (Fig. 1). In particular, an initial hot-phonon $\mathbf{q}\nu$ can now scatter with numerous other phonons $\mathbf{q}'\nu'$ at the same energy $\hbar\omega_{\mathbf{q}'\nu'} \sim 0.2$ eV (the scattering is elastic). Since such phonons are distributed in a large zone of the BZ, they are not directly coupled with conducting electrons and are, thus, mostly not “hot” (their occupation is thermalized and very small). In practice, isotopic disorder allows the scattering of a hot phonon with other cold phonons adding a deexcitation channel and, thus, increasing the thermalization rate from τ_{pp}^{-1} to $\tau_{pp}^{-1} + \tau_{id}^{-1}$.

Computation of the isotopic-disorder scattering-times.—Let us consider an isotopically enriched tube, with disorder parameter x . m ($m + \Delta m$) is the mass of the ^{12}C (^{13}C) isotope. The atomic mass m_i is $m + \Delta m$ with probability x , being in average $\bar{m} = m + x\Delta m$. In perturbation theory with respect to $\Delta m/m$, the lifetime $\tau_{id}^{\mathbf{q}\nu}$ due to isotopic disorder of a phonon $\mathbf{q}\nu$ with pulsation $\omega_{\mathbf{q}\nu}$ is given by the Fermi golden rule [21,22]

$$(\tau_{id}^{\mathbf{q}\nu})^{-1} = g_2(x) \frac{\pi}{2N_q} \omega_{\mathbf{q}\nu}^2 \sum_{\mathbf{q}', \nu'} \delta_\eta(\omega_{\mathbf{q}\nu} - \omega_{\mathbf{q}', \nu'}) \times \sum_s |\mathbf{e}_{\mathbf{q}, \nu}(s) \cdot \mathbf{e}_{\mathbf{q}', \nu'}(s)|^2, \quad (1)$$

where the sum is performed on N_q \mathbf{q} -points, s is an atomic index, $\mathbf{e}_{\mathbf{q}\nu}(s)$ is the phonon polarization normalized as $\sum_s |\mathbf{e}_{\mathbf{q}\nu}(s)|^2 = 1$ in the unit-cell and δ_η is a Lorentzian with full-width at half maximum η , which is determined self-consistently from $\eta = [\tau_{id}^{\mathbf{q}\nu}(\eta)]^{-1}$. $g_2(x)$ describes the mass disorder and is

$$g_2(x) = \frac{\langle (m_i - \bar{m})^2 \rangle}{\bar{m}^2} = x(1-x) \left(\frac{\Delta m}{\bar{m}} \right)^2. \quad (2)$$

$\omega_{\mathbf{q}, \nu}$ and $\mathbf{e}_{\mathbf{q}, \nu}$ are computed from DFT [12,23].

To verify the validity of Eq. (1), $\tau_{id}^{\mathbf{q}\nu}$ are also determined exactly, following Ref. [24]. Let us consider a supercell containing N atoms and let us call $\mathbf{D} = \mathbf{M}^{-1/2} \mathbf{K} \mathbf{M}^{-1/2}$, where \mathbf{M} is the diagonal $3N \times 3N$ matrix describing the

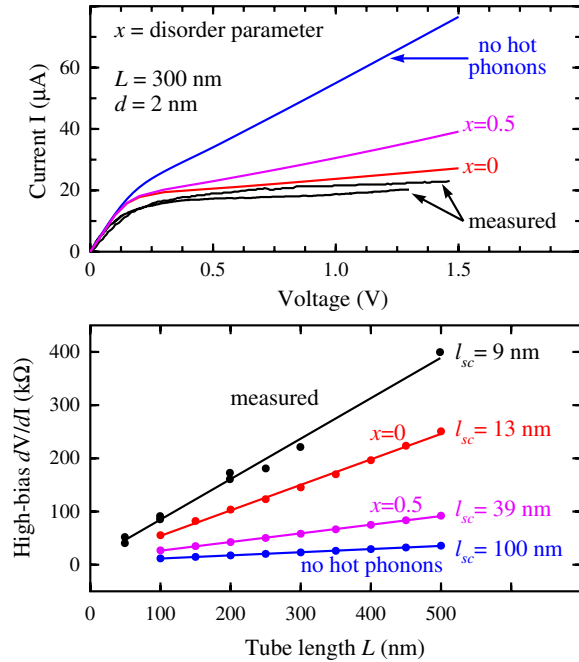


FIG. 2 (color online). Upper panel: IV curve of a (14,14) nanotube with length L and diameter d . Black lines are measurements from Refs. [2,3]. Red and violet lines are calculations for an isotopically pure ($x = 0$) and enriched tube ($x = 0.5$). The blue line is obtained by imposing the phonon populations to be zero. Lower panel: high-bias differential resistance for (14,14) tubes with different lengths (same color code as in the upper panel). Lines are linear fit to the points and l_{sc} is the resulting scattering length [Eq. (4)].

random distribution of the masses ($M_{ij} = m_i \delta_{ij}$) and \mathbf{K} are the interatomic harmonic force constants. The phonon spectral function is given by

$$A(\mathbf{q}\nu, \omega) = -\frac{1}{\pi} \text{Im} \langle V_{\mathbf{q}\nu} | \frac{2\omega}{(\omega + i\xi)^2 - \mathbf{D}} | V_{\mathbf{q}\nu} \rangle, \quad (3)$$

where $V_{\mathbf{q}\nu}$ are the atom displacements of the unperturbed $\mathbf{q}\nu$ phonon (normalized to 1 in the supercell) and ξ is a small positive number. Using the DFT force-constants [12,23] and computing $A(\mathbf{q}\nu, \omega)$ with a Lanczos method [24], $\tau_{\text{id}}^{\mathbf{q}\nu}$ are obtained as the inverse of the full-width at half maximum of $A(\mathbf{q}\nu, \omega)$ [25].

τ_{id} are computed for several tubes with different diameters d with both Eqs. (1) and (3). Figure 3 shows the results for the two-phonon branches relevant in electronic transport for a $d = 2$ nm tube. The results from the two methods are very similar. Thus, the perturbative approach [Eq. (1)] is a good approximation to the exact one [Eq. (3)]. Moreover, the results obtained for a $d = 2$ nm nanotube are very similar to those for two-dimensional graphene. Thus, the results for tubes with $d > 2$ nm are not strongly dependent on the diameter.

It is now important to remark that the τ_{id} for the two hot phonons ($\tau_{\text{id}}^{\Gamma}$ and $\tau_{\text{id}}^{\mathbf{K}}$ in Fig. 1) are smaller than the corresponding τ_{pp} . Thus, the new thermalization channels (due to isotopic disorder) are more efficient than those present in a defect-free tube (due to anharmonicity) and are expected to influence the IV curve.

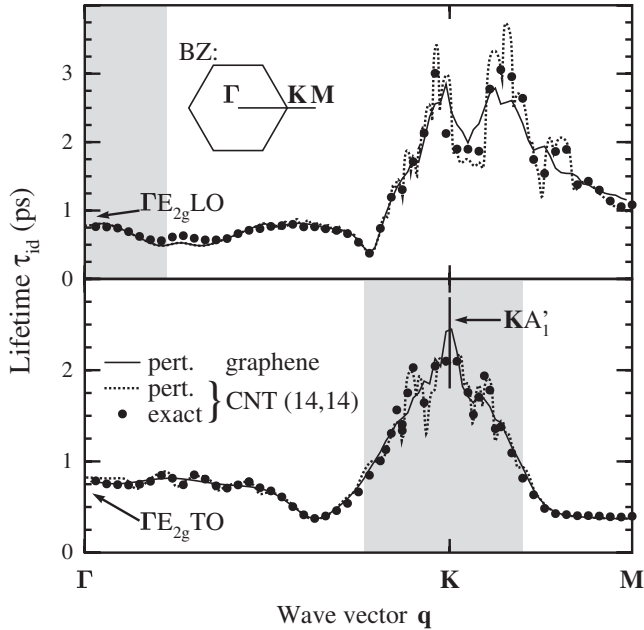


FIG. 3. Phonon lifetimes due to isotopic disorder ($x = 0.5$) in a (14,14) CNT and in graphene computed with the perturbative (pert.) and exact approach of Eqs. (1) and (3), respectively. The phonons in the two panels correspond to the highest optical branches of graphene including the ΓE_{2g} LO and $\mathbf{K}A'_1$ modes. The gray areas correspond to phonons with high occupation (hot phonons) at 1 V.

Computation of the IV curve.—To quantify the impact of isotopic disorder (id) on the high-bias electrical resistivity, we use the BTE as in Ref. [5]. The id scattering rate of an initial $\mathbf{q}\nu$ phonon can be decomposed as a sum of scattering rates into the other $\mathbf{q}'\nu'$ phonons, by rewriting Eq. (1) as $(\tau_{\text{id}}^{\mathbf{q}\nu})^{-1} = \sum_{\mathbf{q}'\nu'} \tau_{\mathbf{q}\nu \rightarrow \mathbf{q}'\nu'}^{-1}$. The thermalization process due to id is then taken into account by adding to the collision term for the phonons [Eq. (4) of Ref. [5]] $[\partial_t n^\nu(\mathbf{q})]_{\text{iso}} = \sum_{\mathbf{q}'\nu'} \tau_{\mathbf{q}\nu \rightarrow \mathbf{q}'\nu'}^{-1} (n^{\nu'}(\mathbf{q}') - n^\nu(\mathbf{q}))$, where $n^\nu(\mathbf{q})$ is the occupation of the $\mathbf{q}\nu$ phonon.

First, Fig. 4 reports as example the id transition rates for a particular hot-phonon $\mathbf{q}\nu$. The majority of the $\mathbf{q}'\nu'$ states are not hot (we checked that more than the 90% of the scattering rate is due to phonons which are not hot). Second, for each of the $\mathbf{q}'\nu'$ phonons, $\tau_{\mathbf{q}\nu \rightarrow \mathbf{q}'\nu'}$ is much larger than their anharmonic scattering rate (as obtained in Ref. [14]). A consequence of these two facts is that the population of the phonons which are not directly coupled to conducting electrons, $n^{\nu'}(\mathbf{q}')$, is negligible and one can rewrite $[\partial_t n^\nu(\mathbf{q})]_{\text{iso}} \sim -(\sum_{\mathbf{q}'\nu'} \tau_{\mathbf{q}\nu \rightarrow \mathbf{q}'\nu'}^{-1}) n^\nu(\mathbf{q})$. That is, one can directly use Eqs. (1)–(4) of Ref. [5], replace the thermalization time τ_{th}^{-1} by $(\tau_{pp}^{\mathbf{q}\nu})^{-1} + (\tau_{\text{id}}^{\mathbf{q}\nu})^{-1}$ corresponding to the two hot-phonons and consider the \mathbf{q} dependence of τ_{id} [26].

In Fig. 2 we report the IV curve for the isotopically enriched ($x = 0.5$) carbon nanotube. Indeed, the conduction properties are ameliorated with respect to the isotopically pure case ($x = 0$). To be quantitative, we notice that at high-bias the differential resistance dV/dI is almost independent from the voltage and is linear with respect to the tube length (lower panel of Fig. 2). This allows to define a resistivity ρ and an effective scattering length l_{sc} , by

$$\rho = \frac{1}{L} \frac{dV}{dI} = \frac{1}{l_{\text{sc}}} \frac{h}{4e^2}, \quad (4)$$

where $h/(2e^2) = 12.9$ k Ω is the quantum of resistance. From Fig. 2, the introduction of isotopic disorder enhances the scattering length (and thus reduces the high-bias differential resistance) by a factor of 3.

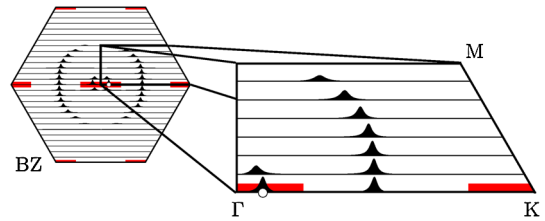


FIG. 4 (color online). Transition rates $\tau_{\mathbf{q}\nu \rightarrow \mathbf{q}'\nu'}^{-1}$ from an initial $\mathbf{q}\nu$ phonon (white dot) into $\mathbf{q}'\nu'$ phonons (see the text) due to isotopic disorder ($x = 0.5$). Horizontal lines are the wave vector in graphene Brillouin zone (BZ) compatible with the (14,14) CNT. Filled curves are proportional to $\tau_{\mathbf{q}\nu \rightarrow \mathbf{q}'\nu'}^{-1}$. The red zones correspond to phonons with high occupation (hot phonons) at 1 V.

Conclusions.—The introduction of isotopic disorder in metallic carbon nanotubes creates an effective channel for the thermalization of the hot phonons without introducing an additional scattering process for the conducting electrons. This is expected to reduce the actual electronic differential resistance. In particular, according to a Boltzmann transport treatment (in which all the relevant parameters are obtained from *ab initio* and no semiempirical parameters are present which could be tuned to reproduce the experimental results), isotopic disorder reduces the high-bias electronic differential resistance by a factor of 3 in tubes with a diameter of 2 nm. This amelioration of the transport properties is expected to have important technological consequences in view of the use of metallic carbon nanotubes as interconnects in tomorrow electronics. Further improvement could be reached by adding other sources of phonon scattering which are transparent to electrons as, e.g., by cycloaddition functionalization [27].

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Note added.—After submission of the present work, another paper appeared proposing isotopic enrichment to reduce hot-phonon population in GaN transistors [28].

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- [1] Z. Yao, C. L. Kane, and C. Dekker, *Phys. Rev. Lett.* **84**, 2941 (2000).
- [2] A. Javey *et al.*, *Phys. Rev. Lett.* **92**, 106804 (2004).
- [3] J.-Y. Park *et al.*, *Nano Lett.* **4**, 517 (2004).
- [4] M. Lazzeri *et al.*, *Phys. Rev. Lett.* **95**, 236802 (2005).
- [5] M. Lazzeri and F. Mauri, *Phys. Rev. B* **73**, 165419 (2006).
- [6] M. Oron-Carl and R. Krupke, *Phys. Rev. Lett.* **100**, 127401 (2008).
- [7] A. W. Bushmaker, V. V. Deshpande, M. W. Bockrath, and S. B. Cronin, *Nano Lett.* **7**, 3618 (2007).
- [8] E. Pop *et al.*, *Phys. Rev. Lett.* **95**, 155505 (2005).
- [9] Within the Born-Oppenheimer approximation, the electronic Hamiltonian depends on the nuclear charges and positions but not explicitly on the nuclear masses. If the nuclear motion is harmonic, the average nuclear-positions do not depend on the nuclear masses. Thus, isotopic substitution scatters electrons only by mechanisms (which in general are negligible) beyond the Born-Oppenheimer approximation and/or beyond the harmonic approximation for interatomic force-constants and for electron-phonon couplings. These mechanisms have been studied in literature [see, e.g., Sect. 4.2 of A. P. Zhernov and A. V. Inyushkin, *Phys. Usp.* **45**, 527 (2002)] with predicted electron scattering-lengths of the order of the millimeter. These scattering lengths are undetectable with respect to those due to other sources of electron scattering found in bulk metals and in carbon nanotubes, where the relevant lengths range from 10 (electron-phonon scattering) to 1600 nm (elastic scattering) [3].
- [10] In metallic CNTs, the electronic bands cross the Fermi energy at two equivalent points of the reciprocal space corresponding to the symmetry points \mathbf{K} and \mathbf{K}' of the graphene BZ [4]. Because of momentum conservation, the conducting electrons of the tube can scatter only with phonons with momentum near to the zone-center Γ or to \mathbf{K} . The phonons mostly involved in this process correspond to the E_{2g} at Γ (the component longitudinal to the tube axis, LO) and to the A'_1 at \mathbf{K} of graphene, since these are the phonons with the strongest electron-phonon coupling [4]. Their momentum, \mathbf{q} and $\mathbf{K} + \mathbf{q}$, is localized in the BZ region defined by $|\mathbf{q}| < 2Ve/(\hbar v_F)$, where V is the applied voltage and v_F is the Fermi velocity.
- [11] τ_{ep} is the average time a conducting electron can travel before emitting an optical phonon by backscattering due to electron-phonon coupling. It is determined by DFT calculations [4,12] and agrees very well with Raman measurements of the phonon G -linewidth in graphite, graphene, and metallic CNTs [13,14]. τ_{pp} is determined by the anharmonic phonon-phonon interaction via DFT in graphene [14] and agrees very well with measurements of the phonon decay time from ultrafast spectroscopy measurements [15].
- [12] S. Baroni, S. de Gironcoli, and A. Dal Corso, *Rev. Mod. Phys.* **73**, 515 (2001).
- [13] M. Lazzeri *et al.*, *Phys. Rev. B* **73**, 155426 (2006).
- [14] N. Bonini, M. Lazzeri, N. Marzari, and F. Mauri, *Phys. Rev. Lett.* **99**, 176802 (2007).
- [15] T. Kampfrath *et al.*, *Phys. Rev. Lett.* **95**, 187403 (2005).
- [16] For isolated nanotubes suspended in vacuum (as in Ref. [8]) the acoustic phonons cannot be considered thermalized with the environment and experimentally a negative differential resistance can be observed (see discussion in Ref. [5]). This situation is not treated here.
- [17] Ref. [5] describes the coupled BTE for the populations of both conducting electrons and optical phonons. It does not rely on any further approximation than those inherent to the Boltzmann one. The optical-phonon evolution is determined by the electron-phonon scattering times (τ_{ep}) and the thermalization-time. Contrary to Ref. [5], here we consider as thermalization times the anharmonic scattering times (τ_{pp}) obtained from DFT calculations (see the text and note [11]).
- [18] C. W. Chang *et al.*, *Phys. Rev. Lett.* **97**, 085901 (2006).
- [19] V. Zolyomi *et al.*, *Phys. Rev. B* **75**, 195419 (2007).
- [20] F. Simon *et al.*, *Phys. Rev. Lett.* **95**, 017401 (2005).
- [21] F. Widulle, J. Serrano, and M. Cardona, *Phys. Rev. B* **65**, 075206 (2002).
- [22] S. I. Tamura, *Phys. Rev. B* **27**, 858 (1983).
- [23] Force constants are computed in a 9×9 graphene supercell with the same computational details as in [14] and then refolded to obtain those of the nanotube.
- [24] N. Vast and S. Baroni, *Phys. Rev. B* **61**, 9387 (2000).
- [25] The disordered system is simulated with supercells containing over 10 000 atoms. Spectral functions are averaged over five different mass distributions and then fitted with a Lorentzian distribution to obtain the lifetime.
- [26] The isotope substitution slightly modifies also ω , τ_{ep} , and τ_{pp} , which scale as $\bar{m}^{-1/2}$, $\bar{m}^{1/2}$, and \bar{m} , respectively. We checked that such modifications do not affect the IV curves of Fig. 2 in a detectable way.
- [27] Y. S. Lee and N. Marzari, *Phys. Rev. Lett.* **97**, 116801 (2006).
- [28] J. B. Khurgin, D. Jena, and Y. J. Ding, *Appl. Phys. Lett.* **93**, 032110 (2008).