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Abstract

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Thermoelectric power of p-doped single-wall carbon nanotubes and the role of phonon drag

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We measured thermoelectric power S of bulk single-wall carbon nanotube (SWNT) materials p-doped with acids. In contrast to oxygen-exposed or degassed samples, S is very small at the lowest temperatures, increases super-linearly above a characteristic and sample-dependent T, and then levels off. We attribute this unusual behavior to 1-D phonon drag, in which the depression of the Fermi energy cuts off electron-phonon scattering at temperatures below a characteristic T_0. This idea is supported by a model calculation in which the low temperature behavior of phonon drag is specifically related to the one-dimensional character of the electronic spectrum.

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The unusually high thermopower S of single wall carbon nanotubes (SWNT) has attracted a lot of attention. It was shown that the typically observed large and positive values are a consequence of oxygen doping, to which S is extremely sensitive [1–3]. Adsorbed oxygen provides acceptor states in the SWNT electronic spectrum, such that ~ 0.1 electron is transferred from the nanotube to an oxygen molecule [2]. High values of S can then be explained by changes in the density of states at the Fermi energy $D(E_F)$ and/or pinning E_F at the top of the valence band of semiconducting tubes. To the best of our knowledge there is no microscopic model which explains the large thermopower and its temperature dependence.

Removing oxygen by degassing does not result in zero thermopower as would be expected from particle-hole symmetry of both metallic and semiconducting tubes present in bulk samples. Instead, extended annealing in clean vacuum produces negative values of similar magnitude to the oxygen-doped state [1–3]. This suggests the presence of very stable donor levels, possibly due to defects.

Here we present a combined experimental and theoretical study of thermopower in p-type acid-doped samples. At low temperature the measured $S(T)$ exhibits distinctly different behaviour compared to what is typically observed from oxygen-doped samples. A model is presented which explains this new behavior as due to one-dimensional (1-D) phonon drag, or electron-phonon scattering in a 1-D electronic system. At higher temperature S shows dominantly metallic behaviour, $S \sim T$. We previously proposed phonon drag to explain differences between $S(T)$ of peapods and unfilled SWNT [4]. Recently Romero *et al.* [5] attributed a broad feature at ~ 100 K in the negative $S(T)$ of fully-degassed SWNT to phonon drag.

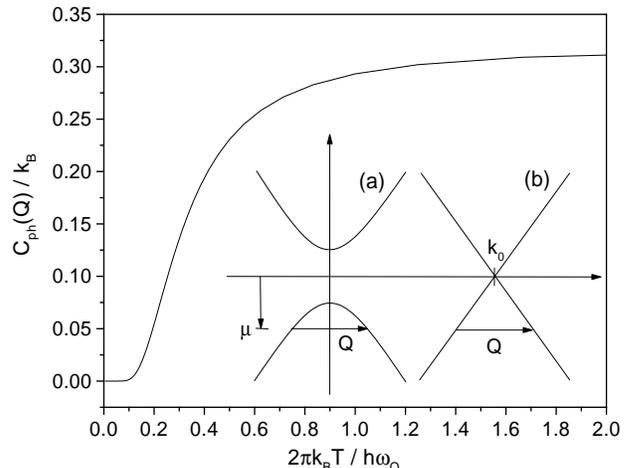For SWNT p-doped with acids, we expect E_F to shift

Fig.1: Calculated temperature dependence of $C_{ph}(Q)/k_B$. This function has an upturn at $k_B T_0 \approx 0.1\,\hbar\omega_Q$ and is constant for $k_B T > \hbar\omega_Q$. The inset shows the process in which an electron in a p-doped semiconducting (a) and metallic (b) SWNT scatters from the right- to left-moving branch by absorbing a phonon with wavevector Q. The Fermi level for acid-doped tubes is in the valence band, so the originally semiconducting tube now behaves like a 1-D metal.

down from the neutrality condition into the valence band of semiconducting tubes, causing them to behave like 1-D metals (see inset to Figure 1). This expectation is borne out by resistivity measurements; ρ of a sulfuric acid doped fiber is lower than that of the de-doped fiber by a factor ~ 10 at 300 K and ~ 40 at 10 K, similar to the reductions observed from alkali metal doping [6]. In contrast, oxygen doping pins E_F at the top of the valence band of semiconducting tubes and $\rho(300\text{K})$ is reduced by

only 25% with respect to the degassed state [1].

The Fermi surface consists of two points separated in k by momentum $|Q|$. Phonon drag, arising from electron-phonon scattering, involves only acoustic phonons with wave vector Q which are absorbed or emitted as electrons scatter from left-moving to right-moving branch and vice versa. Consequently the magnitude of the phonon drag contribution S_g to thermopower depends on the thermal population of these phonons, more specifically on their heat capacity as shown in Eq. (9) below, resulting in exponentially small ($\sim [k_B T^2 \exp(\hbar\omega_Q/k_B T)]^{-1}$) phonon drag thermopower below a characteristic upturn temperature $T_0 \approx 0.1\hbar\omega_Q/k_B$. This behaviour differs from the 2-D and 3-D cases for which the Fermi surface is continuous and electrons can be scattered by all long-wavelength phonons leading to $S_g \sim T^2$ and T^3 respectively. Because the Fermi surface of a 1-D electron gas consists of discrete points, we cannot simply extrapolate from higher dimensions and expect $S_g \sim T$. Assuming a T-independent phonon scattering length at low T, the temperature dependence of S_g is determined by the temperature dependence of the heat capacity contribution from phonons with energy $\hbar\omega_Q$, shown schematically in Figure 1. Combining this with the linear temperature dependence of the diffusion thermopower, we can expect that the slope of $S(T)$ will increase at $T_0 \approx 0.1\hbar\omega_Q/k_B$ and then decrease at higher temperatures, producing a peak in dS/dT at $T \approx 0.23\hbar\omega_Q/k_B$. This is different from the behaviour observed for oxygen doped samples where the slope decreases continuously with increasing T.

We measured two samples prepared from HiPco material [7], one in the form of filter-deposited buckypaper and the other a fiber extruded through a 125 μm syringe needle from a 6 wt% sulfuric acid suspension of purified HiPco [8]. The buckypaper was p-doped by immersion in concentrated nitric acid for 4 hours and then air-dried at 400 K. The fiber became p-doped by HSO_4^- ions present in the sulfuric acid-based suspension. After measurement, the fiber was vacuum-annealed at 1420 K for 2 hours to recover the neutral state. Thermopower was measured from 10 to 300 K; no attempt was made to avoid exposure to air. The results are shown in Figures 2 and 3 for fiber and buckypaper respectively. In the acid-free state (undoped buckypaper or de-doped fiber), both exhibit large positive S which increases monotonically with T (empty squares). This is typical of oxygen-saturated but otherwise pristine SWNT materials [1,4]. Acid doping (filled circles) reduces the magnitude of S at all T for both doped samples. More importantly, we now observe slopes dS/dT which increase with T at the lowest temperatures up to an inflection point, above which $S(T)$ is qualitatively similar to the acid-free state. We calculated $\Delta S/\Delta T$ after smoothing the data, as shown in the insets. The most prominent features are peaks at about 50 K and 30 K for the acid-doped fiber and buckypaper respectively. Conversely, the derivative curves for the acid-free samples decrease monotonically with
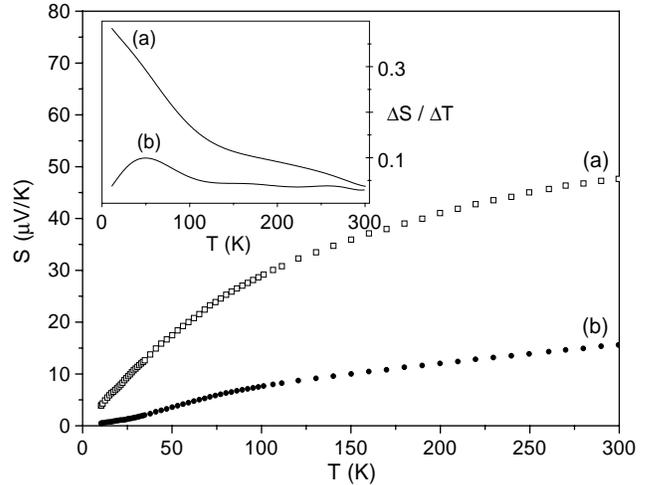

Fig. 2: Thermopower of SWNT fibers extruded from sulfuric acid before [(b), acid-doped] and after [(a), acid-free] vacuum annealing at 1423 K. For the doped fiber, S starts to increase more rapidly at about 25 K, corresponding to a relevant phonon energy ~ 0.02 eV. This effect is absent in the dedoped fiber. The inset shows dS/dT which behaves monotonically for the dedoped fiber but shows a peak at ~ 50 K for the doped one, as expected from Eq. (9).
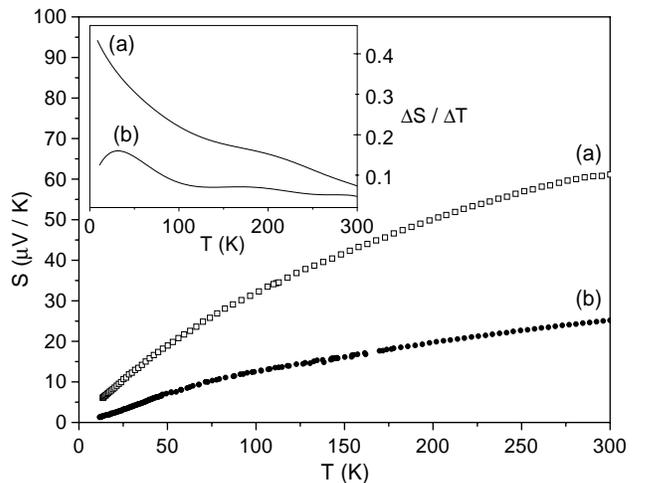

Fig. 3: Thermopower of pristine (a) and nitric acid doped (b) buckypaper. The effect of phonon drag is less visible than for the sulfuric acid doped fibre, which we attribute to smaller charge transfer. The relevant phonon energy is reduced to ~ 0.01 eV; the peak in dS/dT is now at ~ 25 K, see inset.

increasing T. We demonstrate below that the unique low T behavior of the acid-doped samples is a signature of 1-D phonon drag. We further show that phonon drag is unimportant at very low $T < 0.1\hbar\omega_Q/k_B$ in the acid-doped state because the downshift of E_F freezes out electron-phonon scattering as suggested in Figure 1. Be-

havior similar to that reported here was also observed with iodine doping [9].

We attempt to explain the novel low-T behavior of acid-doped SWNT, in particular the super-linear $S(T)$ at low T. For simplicity we calculate the phonon-drag thermopower S_g of an armchair SWNT in the Boltzmann transport approximation. However the model and results apply to any 1-D metal, in particular to degenerately doped semiconducting SWNTs. We do not consider the effect of rope-rope contacts on S since it was shown experimentally [5] that, unlike the resistivity, the thermopower does not depend on applied pressure. We include only the long-wavelength twistons, i. e. the acoustic torsional modes which can be emitted or absorbed by electrons in interband scattering processes [10]. We do not consider modification of the phonon dispersion by tube-tube coupling in ropes because we assume that the Fermi energy is depressed sufficiently that the energy of the relevant phonons is high compared to the tube librational frequency, 4-6 meV [11].

The band structure of armchair tubes is metallic with two nondegenerate bands crossing at the points $k = \pm k_0$, k_0 being $2\pi/3a$, of the 1-D Brillouin zone. Since we are only interested in electrons with k not very far from $\pm k_0$ we use the linearized dispersion relation

$$\varepsilon(p,k) = p(|k| - k_0)\hbar v_F \quad (1)$$

where p takes values ± 1, $v_F = \sqrt{3} J_0 a/2$, $J_0 = 2.7$eV is the first-neighbor C-C tight binding overlap energy [12] and a is the graphene lattice constant.

To calculate S_g of a 1-D electron gas interacting with 1-D phonons, we adapt a model developed for a quasi-2D electron gas coupled to 3-D phonons [13]. It is based on coupled Boltzmann equations for electrons and phonons and can be readily formulated in our 1-D case. Then we have

$$S_g = \frac{|e|}{\pi \sigma k_B T^2} \sum_{p=\pm 1} \sum_k \sum_q \hbar \omega_q \Gamma(-p, k+q, p, k)$$

$$\times L_{ph}(q)\Theta(q)[\tau_{p,k}v_{p,k} - \tau_{-p,k+q}v_{-p,k+q}] , \quad (2)$$

where σ is the electrical conductivity, q and $L_{ph}(q)$ are a twiston wave vector and scattering length, $\tau_{p,k}$ is an electron relaxation time, $v_{p,k}$ is an electron group velocity, $\Theta(q)$ determines the sign of q

$$\Theta(q) = \begin{cases} -1 & \text{if } q < 0 \\ +1 & \text{otherwise} \end{cases} , \quad (3)$$

and $\Gamma(-p, k+q, p, k)$ is a function given by

$$\Gamma(-p, k+q, p, k) = f_0(\varepsilon(p,k))(1 - f_0(\varepsilon(-p, k+q)))$$

$$\times P_0(p, k, -p, k+q) . \quad (4)$$

$P_0(p, k, -p, k+q)$ is the equilibrium transition rate at which an electron in state (p, k) is promoted to a state

$(-p, k+q)$ by absorbing one twiston with wave vector q, and $f_0(\varepsilon)$ is the Fermi-Dirac function. Using the Fermi Golden Rule we have

$$P_0(p, k, -p, k+q) = \frac{2\pi}{\hbar} N_0(q)|A(k,q)|^2$$

$$\times \delta(\varepsilon(-p, k+q) - \varepsilon(p, k) - \hbar \omega_q) , \quad (5)$$

where $\delta(\varepsilon(-p, k+q) - \varepsilon(p, k) - \hbar \omega_q)$ is the Dirac delta function expressing energy conservation, $N_0(q)$ is the Bose-Einstein phonon distribution and $A(k, q)$ is the electron-twiston interaction matrix element.

To proceed further, we assume that the electron relaxation time $\tau_{p,k}$ is a function of energy only and that $|A(k, q)|^2 N_0(q)L_{ph}(q))\tau(p, k)$ is slowly varying with $\varepsilon(p, k)$. These allow us to use the following approximation [14]:

$$f_0(\varepsilon(p,k))(1 - f_0(\varepsilon(p,k) + \hbar \omega_q)) =$$

$$\frac{\hbar \omega_q}{1 - \exp(-\hbar \omega_q/k_B T)} \delta(\varepsilon(p,k) - \mu) , \quad (6)$$

where $\mu = E_F$ is the chemical potential. The integration in Eq. (2) is now trivial. Employing the fact that electrons interact with long-wavelength twistons ($\Theta(k+q) = \Theta(k)$, see inset to Figure 1), we can write

$$S_g = \frac{-1}{4\pi|e|} \sum_{p=\pm 1} \sum_{s=\pm 1} \hbar \omega_{Q_{p,s}} \frac{dN_0(Q_{p,s})}{dT} \frac{|A(K_{p,s}, Q_{p,s})|^2}{(\hbar v_F)^2}$$

$$\times L_{ph}(Q_{p,s})\Theta(|K_{p,s}| - k_0) \frac{pv_F}{v_F - v_{ph}\Theta(|K_{p,s}| - k_0)p} , \quad (7)$$

where

$$K_{p,s} = s\left(k_0 + \frac{p\mu}{\hbar v_F}\right) , \quad (8)$$

and $Q_{p,s}$ is the wave vector of a twiston which can be absorbed by an electron specified by $K_{p,s}$. If we neglect the phonon velocity v_{ph} compared to v_F, then $Q_{p,s} \approx -2ps\mu/\hbar v_F = psQ$ and Eq. (7) can be written in the form

$$S_g = -\Theta(\mu)\frac{|A(K,Q)|^2}{(\hbar v_F)^2}\frac{C_{ph}(Q)L_{ph}(Q)}{|e|} , \quad (9)$$

where $K = K_{1,1}$. $C_{ph}(Q)$ is related to the heat capacity of the twiston mode with energy $\hbar \omega_Q$ and is equal to

$$C_{ph}(Q) = \hbar \omega_Q \frac{dN_0(Q)}{dT}\frac{1}{\pi} . \quad (10)$$

The temperature dependence of $C_{ph}(Q)$ is shown in Figure 1. $C_{ph}(Q)$ shows a sharp upturn which extrapolates back to zero at the temperature $k_B T_0 \approx 0.1 \hbar \omega_Q$. It then

rolls over and becomes constant for $k_B T > \hbar\omega_Q$, with the maximum slope occurring at $k_B T \approx 0.23\hbar\omega_Q$. Thus the characteristic features of the phonon-drag contribution S_g are the upturn at T_0 and a peak in dS_g/dT at $2.3\,T_0$. If the phonon scattering length L_{ph} decreases with increasing T, S_g itself will show a peak at $k_B T \approx \hbar\omega_Q$. Note that this result differs dramatically from what would be predicted by extrapolating to 1-D from higher dimensions.
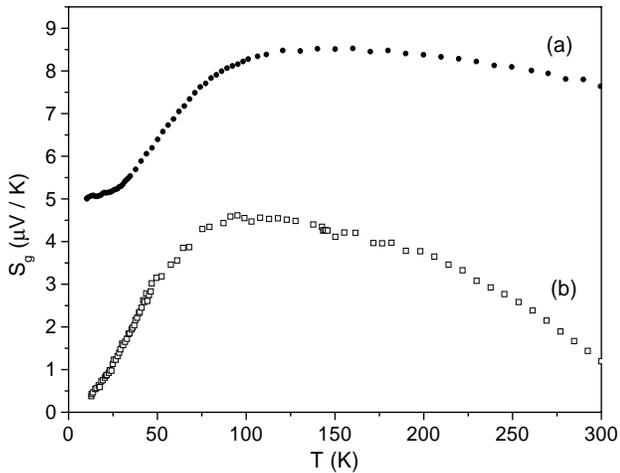

Fig. 4: Temperature dependence of the phonon drag thermopower S_g of sulfuric acid doped fiber (a) and nitric acid doped buckypaper (b). Data were obtained from the measured thermopower by subtracting a linear term bT which represents diffusion thermopower. The upper curve is offset for clarity.

We used Eq. (9) to estimate the relevant phonon energy $\hbar\omega_Q$ and the phonon scattering length. We model the data by a sum of phonon drag thermopower $S_g(T)$ shown in Figure 4 and a linear term bT which represents diffusion thermopower. To calculate $S_g(T)$ numerically we used the electron-twiston interaction matrix element $A(k,q)$ for (5,5) SWNT [10]. Then for the acid-doped fiber we get the phonon energy $\hbar\omega_Q = 0.02$ eV, diffusion thermopower coefficient $b = 0.04\ \mu V/K^2$, and twiston scattering length $L_{ph}(Q)$ to be 0.3 μm and 0.2 μm at 10 K and 300 K respectively. Using the same approach for the acid-doped buckypaper we get $\hbar\omega_Q = 0.01$ eV, $b = 0.08\ \mu V/K^2$, and $L_{ph}(Q) = 0.5$-0.1 μm. The $L_{ph}(Q)$'s are only approximate because we did not account for different matrix elements and different Q's for a given μ in metallic and semiconducting tubes.

Our model for thermopower of SWNTs fits very well with the data for acid-doped SWNT samples, although the origin of the very large diffusion thermopower coefficient b remains unclear. Romero $et\ al.$ proposed [5] that impurities and dopants can cause broad resonances in the density of states near the Fermi level, which can provide large nonzero values for the diffusion thermopower. This

proposal needs to be studied in detail.

We can explain the thermopower of acid-doped samples as a combination of phonon drag and diffusion thermopower in metallic SWNT, but our model does not explain the high thermopower of oxygen-doped samples. We expect that in our doped samples the majority of the tubes are metallic (*i. e.* most of the originally semiconducting tubes are now degenerately doped, with the Fermi level in the valence band), while in oxygen-doped samples the majority are semiconducting with E_F pinned near or at the top of the valence band. The present model does not apply in this case; a calculation of the effect of phonon drag in semiconducting tubes is in progress.

We showed that the phonon drag contribution to SWNT thermopower is important at low temperature if E_F is depressed by acceptor doping even deeper into the valence band than upon exposure to oxygen. Presumably the same will occur in n-doped SWNT where the donor concentration is sufficient to overcompensate the oxygen acceptors. We emphasize that this contribution and its low-T behavior are direct results of the 1-D character of the electron gas in SWNT, which cannot be appreciated simply by extrapolating from higher dimensions.

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