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 materials p doped with acids. In contrast to oxygen-exposed or degassed samples, S is very small at the lowest temperatures, increases superlinearly above a characteristic and sample-dependent T, and then levels off. We attribute this unusual behavior to 1D 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 large and positive thermopower S of single-wall carbon nanotubes (SWNT) is a consequence of exposure to oxygen [1–3], although the extent to which this represents p doping of semiconducting tubes has recently been called into question [4]. Electrical resistivity ρ differs little between oxygen-saturated and high-temperature degassed states [1], and the Fermi energy is not driven into the valence band of semiconducting tubes since the lowest energy intervalence band transition remains strong [5–7]. To the best of our knowledge there is no microscopic or semiempirical model which explains the unusual effects of oxygen on $S(T)$ of SWNT materials [8].

Here we present a combined experimental and theoretical study of a much simpler system, the results of which are consistent internally as well as with other data on the same materials. In p-type samples doped with acids, $S(T)$ at low temperature exhibits distinctly different behavior from oxygen-saturated and degassed SWNT. A model is presented which explains this new behavior as being due to one-dimensional (1D) phonon drag, or electron-phonon scattering in a 1D electronic system. At higher temperature S shows metallic behavior, $S \sim T$. Resistivity measurements show that p doping with acids decreases $\rho(300\text{ K})$ by factors of 10 or more, similar to alkali metals [9], the consequence of degenerate doping of the majority of semiconducting tubes.

The basic idea is as follows. The Fermi surface of a 1D metal consists of two points separated in k by wave vector of amplitude $|Q|$. Phonon drag, arising from electron-phonon scattering, involves only acoustic phonons with wave vector Q which are absorbed or emitted as electrons scatter from the 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. (7) below. This results in exponentially small ($\sim [k_B T^2 \exp(\hbar\omega_Q/k_B T)]^{-1}$) phonon-drag thermopower below a characteristic upturn temperature $T_0 \approx 0.1\hbar\omega_Q/k_B$ where ω_Q is controlled by E_F which in turn is depressed by p-type doping. This behavior differs from the 2D and 3D 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 1D 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 Fig. 1. Combining this with the linear temperature dependence of the diffusion thermopower, the slope of $S(T)$ should 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 behavior observed for air-exposed but otherwise undoped samples where the slope decreases continuously with increasing T.

We measured two samples prepared from HiPco material [10], 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 [11]. The buckypaper was p doped by immersion in concentrated nitric acid for 4 h 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 h to recover the acid-free state. Thermopower was measured from 10 to 300 K; no attempt was made to avoid exposure to air. The results are shown in Figs. 2 and 3 and for fiber and buckypaper, respectively. In the acid-free state (pristine buckypaper or annealed fiber), both exhibit large positive S which increases monotonically with T

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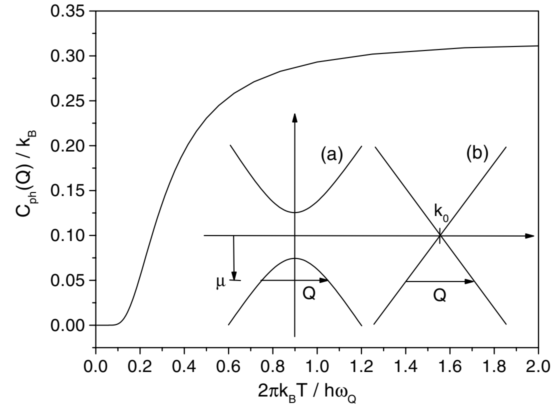

FIG. 1. Calculated temperature dependence of $C_{\mathrm{ph}}(Q)/k_B$. This function has an upturn at $k_B T_0 \approx 0.1\,\hbar\omega_Q$. The inset shows the process in which an electron in a *p* doped semiconducting (*a*) and metallic (*b*) SWNT scatters from the right- to left-moving branch by absorbing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

(empty squares). This is typical of air-exposed but otherwise pristine SWNT materials [1,12]. 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 and 30 K for the acid-doped fiber and buckypaper, respectively. Conversely, the derivative curves for the acid-free samples decrease monotonically with increasing T. We demonstrate below that the unique low T behavior of the acid-doped samples is a signature of 1D 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 Fig. 1. Behavior similar to that reported here was also observed with iodine doping [13].

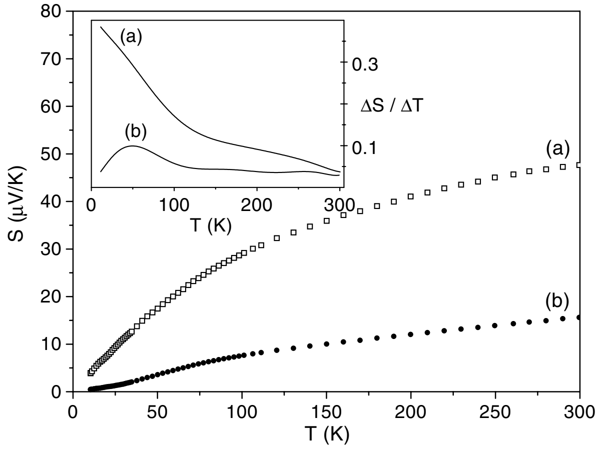

FIG. 2. Thermopower of SWNT fibers extruded from sulfuric acid before (*b*), acid-doped and after (*a*), acid-free vacuum annealing at 1423 K. For the acid-doped fiber, S starts to increase more rapidly at about 25 K, corresponding to a relevant phonon energy ~0.02 eV. This effect is absent in the annealed fiber. The inset shows dS/dT which behaves monotonically for the annealed fiber but shows a peak at ~50 K for the acid-doped one, as expected from Eq. (7).

For simplicity we calculate the phonon-drag thermopower S_g of an armchair SWNT in the Boltzmann transport approximation. We do not consider the effect of rope-rope contacts on S since it was shown experimentally [14] 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 [15]. We do not consider modification of the phonon dispersion by tube-tube coupling in ropes because we assume that E_F is depressed sufficiently that the energy of the relevant phonons is high compared to the tube librational frequency of 1.2 meV [16,17].

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 1D Brillouin zone. Since we are only interested in electrons with k not very far from $\pm k_0$ we use the linearized dispersion relation

$$\varepsilon(p, k) = p(|k| - k_0)\hbar v_F, \tag{1}$$

where p takes values ± 1, $\hbar v_F = \sqrt{3}J_0 a/2$, $J_0 = 2.7$ eV is the first-neighbor C-C tight binding overlap energy [18] and a is the graphene lattice constant.

To calculate S_g of a 1D electron gas interacting with 1D phonons, we adapt a model developed for a quasi-2D electron gas coupled to 3D phonons [19]. It is based on coupled Boltzmann equations for electrons and phonons and can be readily formulated in our 1D case. Then we have

$$\begin{aligned} S_g = \frac{|e|}{\pi\sigma k_B T^2} &\sum_{p=\pm 1}\sum_k \sum_q \hbar\omega_q \Gamma(-p, k+q, p, k) \\ &\times L_{ph}(q)\Theta(q)[\tau_{p,k}v_{p,k} - \tau_{-p,k+q}v_{-p,k+q}], \end{aligned} \tag{2}$$

where σ is the electrical conductivity, q and $L_{\mathrm{ph}}(q)$ 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, and $\Gamma(-p, k+q, p, k)$ is a function given by

$$\begin{aligned} \Gamma(-p, k+q, p, k) = f_0[\varepsilon(p, k)]\{1 - f_0[\varepsilon(-p, k+q)]\} \\ \times P_0(p, k, -p, k+q), \end{aligned} \tag{3}$$

$P_0(p, k, -p, k+q)$ 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

$$P_0(p,k,-p,k+q) = \frac{2\pi}{\hbar} N_0(q)|A(k,q)|^2 \times \delta[\varepsilon(-p,k+q) - \varepsilon(p,k) - \hbar\omega_q], \tag{4}$$

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 $|A(k,q)|^2 N_0(q) L_{\rm ph}(q)\tau(p,k)$ is slowly varying with $\varepsilon(p,k)$. These allow us to use the following approximation [20]:

$$f_0[\varepsilon(p,k)]\{1 - f_0[\varepsilon(p,k) + \hbar\omega_q]\} = \frac{\hbar\omega_q}{1 - \exp(-\hbar\omega_q/k_BT)} \delta[\varepsilon(p,k) - \mu], \tag{5}$$

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 Fig. 1], we can write

$$S_g = \frac{-1}{4\pi|e|} \sum_{p=\pm1} \sum_{s=\pm1} \hbar\omega_{Q_{p,s}} \frac{dN_0(Q_{p,s})}{dT} \frac{|A(K_{p,s}, Q_{p,s})|^2}{(\hbar v_F)^2} \times L_{ph}(Q_{p,s})\Theta(|K_{p,s}| - k_0) \frac{p v_F}{v_F - v_{\rm ph}\Theta(|K_{p,s}| - k_0)p}, \tag{6}$$

where $K_{p,s} = s(k_0 + p\mu/\hbar v_F)$ 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 $v_{\rm ph}$ compared to v_F, then $Q_{p,s} \approx -2ps\mu/\hbar v_F = psQ$ and Eq. (6) can be written in the form

$$S_g = -\Theta(\mu)\frac{|A(K,Q)|^2}{(\hbar v_F)^2}\frac{C_{\rm ph}(Q)L_{\rm ph}(Q)}{|e|}, \tag{7}$$

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

$$C_{\rm ph}(Q) = \hbar\omega_Q \frac{dN_0(Q)}{dT}\frac{1}{\pi}. \tag{8}$$

The temperature dependence of $C_{\rm ph}(Q)$ is shown in Fig. 1. $C_{\rm ph}(Q)$ shows a sharp upturn which extrapolates to zero at the temperature $k_BT_0 \approx 0.1\hbar\omega_Q$. It then rolls over and becomes constant for $k_BT > \hbar\omega_Q$, with the maximum slope occurring at $k_BT \approx 0.23\hbar\omega_Q$. 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 $2.3T_0$. If the phonon scattering length $L_{\rm ph}$ decreases with increasing T, S_g itself will show a peak at $k_BT \approx \hbar\omega_Q$.

We used Eq. (7) 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 Fig. 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 (10,10) SWNT [15]. Then for the acid-doped fiber we get the phonon energy $\hbar\omega_Q = 0.02$ eV, diffusion thermopower coefficient $b = 0.04$ μV/K^2, and twiston scattering length $L_{\rm ph}(Q)$ to be 0.6 μm and 0.4 μm at 10 and 300 K, respectively. Using the same approach for the acid-doped buckypaper we get $\hbar\omega_Q = 0.01$ eV, $b = 0.08$ μV/K^2, and $L_{\rm ph}(Q) = 1.0$–0.2 μm. The $L_{\rm ph}(Q)$'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.

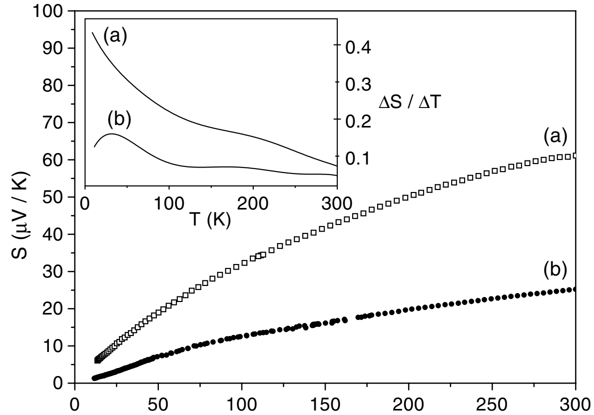

FIG. 3. Thermopower of pristine (*a*) and nitric acid doped (*b*) buckypaper. The effect of phonon drag is less visible than for the sulfuric acid doped fibre, which we attribute to smaller charge transfer. The relevant phonon energy is reduced to ~0.01 eV; the peak in dS/dT is now at ~25 K; see inset.

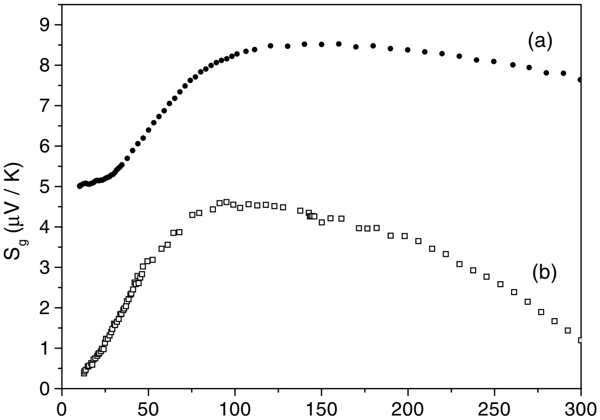

FIG. 4. Temperature dependence of the phonon drag thermopower S_g of sulfuric acid doped fiber (*a*) and nitric acid doped buckypaper (*b*). Data were obtained from the measured thermopower by subtracting a linear term bT which represents diffusion thermopower. The upper curve is offset for clarity.

The nearly linear dispersion of metallic bands implies a small diffusion contribution b, inconsistent with observations, so the semiconducting tubes must be accounted for. Optical absorption in undoped SWNTs shows a sharp band at 0.68 eV and a broader one at 1.2 eV [5–7], corresponding to 1D van Hove singularities of semiconducting tubes. Values of E_F extracted from the low T behavior of S_g are -0.3 and -0.6 eV, suggesting that E_F in acid-doped samples is near the top of or well into the semiconductor valence bands. Optical reflectivity measurements on a nitric acid-doped buckypaper show the disappearance of the first van Hove transition [21]. Applying a simple two-band model [22] and including dispersion in tube diameters and bandgaps, we find linear or nearly linear T dependence of S_d from 0 to 300 K in agreement with our data.

We can explain the thermopower of acid-doped samples as a combination of phonon drag in metallic SWNTs and diffusion thermopower in semiconducting SWNTs, but our model does not explain the high thermopower of air-exposed but otherwise pristine samples. We believe that in our acid-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 air-exposed but otherwise pristine samples the majority are semiconducting with E_F above the valence band. The present model does not apply in this case; for energies lower than 0.1 eV one has to consider the tube-tube interaction in ropes and the effects of finite curvature of tubes on the electronic band structure [23] together with the effect of adsorbed gases on electronic properties of tubes and ropes [14].

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 1D character of the electron gas in SWNT, which cannot be appreciated simply by extrapolating from higher dimensions.

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