

Is the Intrinsic Thermoelectric Power of Carbon Nanotubes Positive?

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The thermoelectric power (TEP) of single-walled carbon nanotubes (SWNTs) is extremely sensitive to gas exposure history. Samples exposed to air or oxygen have an always positive TEP, suggestive of holelike carriers. However, at fixed temperature the TEP crosses zero and becomes progressively more negative as the SWNTs are stripped of oxygen. The time constant for oxygen adsorption/desorption is strongly temperature dependent and ranges from seconds to many days, leading to apparently “variable” TEP for a given sample at a given temperature. The saturated TEP can be accounted for within a model of strong oxygen doping of the semiconducting nanotubes.

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Thermoelectric power (TEP) is an extremely sensitive and incisive transport coefficient. Because it is related to the energy derivative of the electrical conductivity probed at the Fermi energy, it yields directly the sign of the charge carriers within a metallic conductor. For a semiconductor, the TEP probes the sign of the dominant carriers as well as the energy gap magnitude. Single-walled carbon nanotubes (SWNTs) [1] typically cluster in crystalline bundles or “ropes” [2], where each bundle comprises an apparently random collection of metallic and semiconducting nanotubes. Thus, one expects transport measurements of SWNT bundles to reflect this parallel metal/semiconductor combination. The TEP of SWNTs was measured previously by various groups [3–6] with apparently inconsistent results and with significantly different interpretations. Electron-hole symmetry breaking [3] and Kondo effects [4] are among the mechanisms that have been invoked to account for the experimental results.

Recently Collins *et al.* [7] reported that SWNT electronic properties, including local densities of electronic states, electrical resistance, and TEP, are extremely sensitive to the presence of oxygen. Kong *et al.* [8] have reported related room-temperature resistances changes upon exposing SWNTs to NO₂ and NH₃ gas. As pointed out by Collins *et al.*, the methods commonly used to prepare SWNTs for measurement generally result in oxygen-contaminated tubes, and it is not obvious that simply placing SWNTs in vacuum at room temperature (as is typically done as an initial step in TEP measurements) reverses this condition. It is thus possible that previous SWNT TEP measurements represent not intrinsic behavior but rather reflect various degrees of oxygen doping.

We here reexamine SWNT TEP with a view to identifying the true, intrinsic behavior. We find that SWNTs stripped of oxygen indeed have a very different TEP from that of “as prepared” SWNTs. Most importantly, at all temperatures the TEP of oxygen-depleted SWNT’s is negative, rather than positive. By using the TEP as a probe, we determine for SWNTs explicitly the time constant for oxygen adsorption/desorption. A strong tem-

perature dependence is found, and time constants ranging from seconds to days are observed. The temperature dependence of the “saturated” TEP is interpreted within a new model in which oxygen doping causes metallic behavior in a fraction of the semiconducting nanotubes.

SWNTs were synthesized by using conventional pulsed laser deposition or arc discharge methods as described elsewhere [1,9]. Collections of purified [10] SWNT ropes were mounted either as free-standing “mats” or more commonly dispersed from methanol onto quartz substrates, forming thick films. The TEP was measured using a quasi-dc method in a specialized ultrahigh vacuum (UHV) chamber containing a custom-made TEP probe formed entirely from UHV-compatible materials and fitted with a residual gas analyzer. In the case of film samples, each end of the coated substrate was mechanically clamped to a copper block. A slowly varying temperature difference was applied to the sample by silicon chip heaters mounted on each block. Throughout the experiment this temperature difference was kept at 1 K or 2% of the absolute temperature, whichever was smaller. Thin gold wires were glued to the edges of the SWNT sample using silver epoxy, and thin thermocouple wires were attached to the back side of the substrate opposite the electrical contacts. The pressure inside the sample chamber could be varied by using a specified environmental gas species from atmospheric pressure to less than 10⁻⁸ torr. The temperature of the sample could be varied from 4.2 K to over 550 K, but TEP measurements were performed only below 400 K.

Figure 1 demonstrates the extreme gas sensitivity and associated thermal time constant of the TEP of SWNTs. The plots show the measured TEP (S) as a function of time for two different sample temperatures T . At selected times during the run, the sample environment is switched between 1 atm O₂ and vacuum (<10⁻⁸ torr). For $T = 350$ K (filled circles), S switches from a value of $-12 \mu\text{V/K}$ in vacuum to $+20 \mu\text{V/K}$ in O₂. At this sample temperature the response time for the TEP is moderately fast, and the final steady-state oxygen-free and oxygen-dosed TEP values are achieved on a time scale

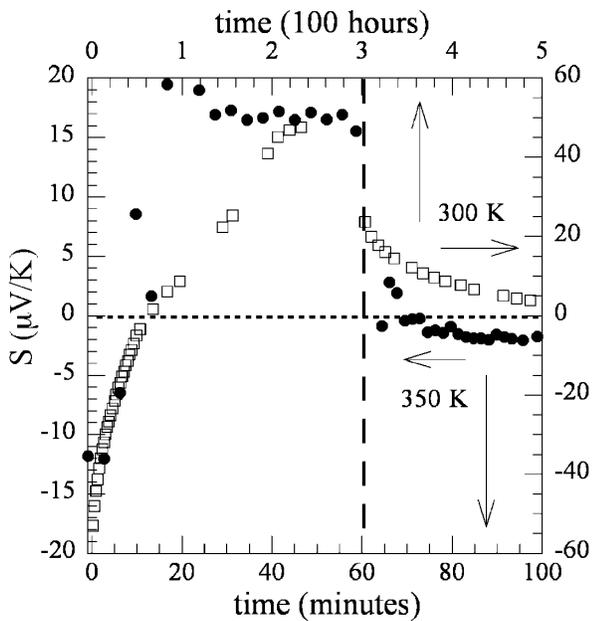


FIG. 1. Thermopower histories of two different samples. Filled circles are at 350 K; open squares are at 300 K. In each case the samples in their stable “vacuum” states were exposed to oxygen at $t = 0$. At the time marked by the dashed vertical line, the samples were reexposed to vacuum. Note the two different x-axis scales.

of minutes. Although not shown in Fig. 1, at slightly higher temperatures (380 K) the TEP response was even faster, limited by the TEP measurements themselves. Figure 1 also shows similar TEP data taken for a different sample at room temperature $T = 300$ K. Here the TEP again reversibly switches from positive to negative as the environment is switched from O_2 to vacuum, but the time scale for TEP response is much slower: it takes 200 h for S to recover its final positive value upon oxygen exposure and much longer to approach its final negative value upon oxygen depletion. At $T < 300$ K, even longer time constants are involved for oxygen depletion. The results of Fig. 1 suggest a complex O_2 -pressure/temperature/time phase diagram for the TEP of SWNTs, and illustrate the dangers of measuring S without proper control of environmental conditions and respect for the possibly very long time constants involved.

The variable TEP shown in Fig. 1 is suggestive of a gas diffusion process, and the natural assumption is that the TEP of SWNTs is exceedingly sensitive to adsorbed oxygen. As expected, the precise time constant for TEP response in SWNTs was found to be sample dependent. Thick films displayed significantly longer time constants than did dilute thin films. The temperature dependence of the time constant reflects the binding energy of the adsorbed oxygen, which we estimate to be 5000 ± 600 K. We found that the TEP of deoxygenated samples could always be restored to its original “in air” oxygenated value by introducing as little as 10^{-5} torr of pure O_2 . Higher pressures of O_2 decreased the relevant time constant, but

did not affect the steady-state saturated TEP value. We found it difficult to reliably “tune” the TEP to selected intermediate values (such as zero) by using selected fixed pressures below 10^{-5} torr [11].

Of interest is the temperature dependence of the steady-state, saturated TEP of SWNTs for different oxygen coverage conditions. We explore here the reliably achieved extremes: the TEP of SWNTs in the “fully oxygenated” condition, and the TEP of SWNTs largely depleted of oxygen. Figure 2 shows $S(T)$ for the same SWNT specimen for these two extremes. The upper curve shows $S(T)$ under fully oxygenated conditions [12]. The TEP is always positive and extrapolates to zero as $T \rightarrow 0$. Notably, we see here no convincing evidence for a lower temperature bump or peak in S , as might be expected from a Kondo impurity mechanism [4]. The lower curve in Fig. 2 represents S after the sample has been deoxygenated. In this case S is always negative, with a room temperature magnitude comparable to that measured under oxygenated conditions. Again, S smoothly approaches zero as $T \rightarrow 0$, and no anomalous low temperature bump or peak is observed. Interestingly, the functional forms of $S(T)$ for fully oxygenated and deoxygenated SWNTs appear to be rough “mirror images” of one another, reflected about the horizontal axis. We have observed this apparent symmetry, suggestive of a universal $|S(T)|$, in all of the SWNT samples that we have measured. This similarity suggests that a common mechanism may account for the TEP of both oxygenated and deoxygenated SWNTs.

Different SWNT TEP models have been proposed, which we briefly review and discount in light of the data presented above. We first note that the observed TEP of SWNTs is much larger in magnitude than that of graphite ($\sim 5 \mu\text{V/K}$) [13]. Graphite-intercalation-based effects [14] are not applicable to SWNTs stripped of intercalants

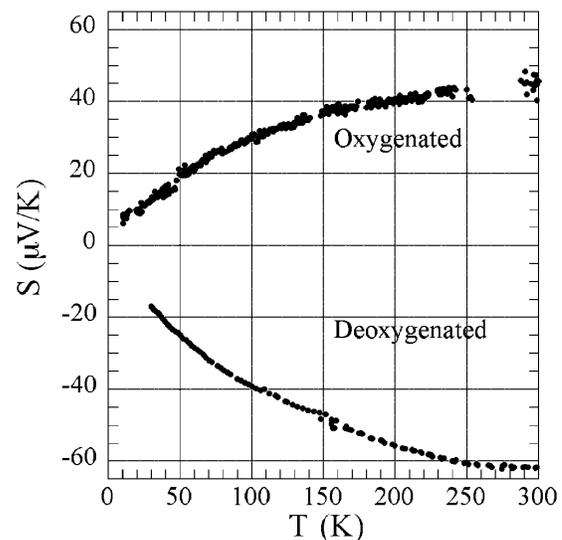


FIG. 2. The temperature dependence of thermopower for a single sample in its “oxygenated” and “deoxygenated” states.

by high temperature, high vacuum treatments. We do not observe Kondo peaks [4] in the TEP, and so rule out a Kondo-based mechanism. An obvious possibility previously considered is a simple two-band model in which the total TEP is a parallel combination of TEPs from semiconducting and metallic tubes [3,5]. The TEP curves of Fig. 2 can be fit reasonably well using such a model, but the fitting parameters are less than satisfactory in several respects. The extracted semiconducting tube energy gap values of 10–20 meV are significantly smaller than observed in single-tube transport [15,16] and scanning tunneling spectroscopy measurements [17,18]. This model consequently predicts conductances for the semiconducting tubes that are considerably larger than typical observations [19]. Similarly, the model predicts an unphysically large TEP magnitude (tens of mV/K at room temperature) for the metallic tubes. Within this model the measured magnitude of the (temperature dependent) TEP is due to a near cancellation of very large metallic and semiconducting TEPs of opposite sign, a situation we regard as unlikely.

Our new model calculations below, for the effect of oxygen on nanotubes, provide a consistent explanation for the thermopower of SWNTs. We expect that oxygen exposure will have little direct effect on metallic armchair nanotubes. In order to investigate the effect of oxygen doping on semiconducting nanotubes, we carried out pseudopotential first principles calculations on an oxygen-doped (8,0) semiconducting nanotube [20]. O_2 is found to bind to the nanotube with an adsorption energy of about 0.3 eV, in reasonable agreement with our measurement of 0.4 eV. Our band structure shows that O_2 molecular levels lie at the top of the valence band of the carbon nanotube and overlap slightly with carbon states. About 0.1 electron transfers from the nanotube to an oxygen molecule, supplying hole carriers to the nanotube.

Figure 3 shows the calculated density of states (DOS) of an oxygen-doped (8,0) tube. The intrinsic DOS, not shown in the figure, features a gap of 0.6 eV centered on the Fermi level at zero energy. As the oxygen molecule breaks the symmetry of the nanotube, the twofold degenerate valence bands split and give two peaks in the density of states. Near the Fermi level, the DOS of the doped semiconducting tube can be written as

$$D_s(\epsilon) \propto [\Delta^2 - (\epsilon - \epsilon_0)^2]^{-1/2}, \quad (1)$$

where Δ is the bandwidth [$\sim O(1)$ eV] and ϵ_0 is the center of the band energy.

The oxygen doping significantly enhances the conductivity of the semiconducting nanotubes [20]. As a crude estimation, we found that the conductivity of semiconducting tubes at moderate oxygen doping can be comparable to that of graphite [21]. The TEP of the mats can then be written as [22]

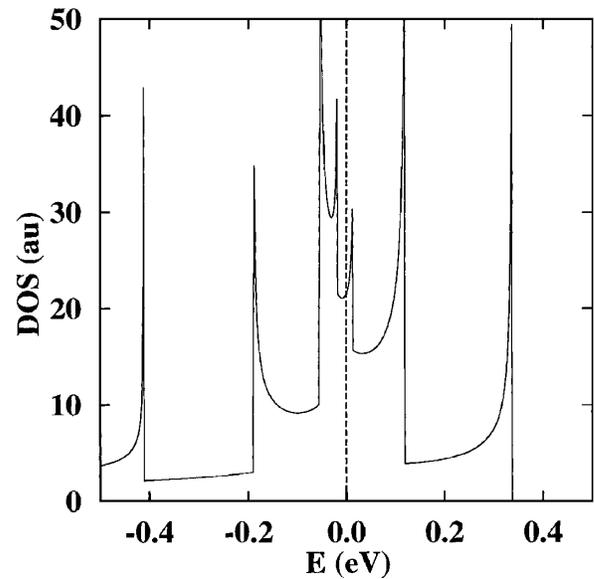


FIG. 3. Calculated density of states for an (8,0) nanotube doped by adsorbed oxygen molecules.

$$S = -\frac{\pi^2}{3} \frac{k}{e} kT \left(C + \alpha \frac{D'_s}{D_s} \right), \quad (2)$$

where the constant C accounts for the small thermopower of the normally metallic tubes, D_s is the DOS for the semiconducting tube, and D'_s is the derivative of D_s with respect to energy at the Fermi level. The α denotes the ratio of the conductivity of the semiconducting tubes to the total conductivity of tube mats. We have used a metallic TEP expression for the semiconducting nanotubes because the strong oxygen interaction produces states at the Fermi level.

By using Eq. (1) for the DOS of the semiconducting tubes, the second term in the TEP is

$$S_s = -\frac{\pi^2}{3} \frac{k}{e} kT \alpha \frac{\Delta - \delta}{2\Delta|\delta|} \text{sgn}(D'_s), \quad (3)$$

where $\delta = \Delta - (\mu - \epsilon_0)$. When the chemical potential μ is near the band edge, the magnitude of S_s can be very large. At room temperature, the second term in S is estimated to be about $60 \mu\text{V/K}$ with $\delta \sim 0.01$ eV and $\alpha \sim 0.2$ [23]. This magnitude agrees well with the data in Fig. 2, suggesting that the first term in S , which is due to the metallic armchair nanotubes, is relatively small. This is reasonable since they have smooth DOS and electron-hole symmetry. The value of α for a particular sample will depend on the fraction of semiconducting tubes. Our model therefore provides a natural explanation for the different magnitudes of S that are observed [3–5].

Because of the weak hybridization, the DOS of the carbon bands has a tail above the peak of the DOS. By changing the pressure of oxygen, we vary the doping level of the tubes, moving the Fermi level. Because the sign of S_s depends on that of D'_s , the sign of the measured TEP changes

when the Fermi level crosses from one side of the peak to the other. The sharpness of the peak accounts for our observation that the TEP cannot be easily stabilized at zero.

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