Thermoelectric Power of Single-Walled Carbon Nanotubes

J. Hone, I. Ellwood, M. Muno, Ari Mizel, Marvin L. Cohen, and A. Zettl
Department of Physics, University of California at Berkeley, Berkeley, California 94720, and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Andrew G. Rinzler and R. E. Smalley
Center for Nanoscale Science and Technology, Rice Quantum Institute, Houston, Texas 77721, and Departments of Chemistry and Physics, MS-100, Rice University, Houston, Texas 77721
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We have measured the temperature-dependent thermoelectric power (TEP) of crystalline ropes of single-walled carbon nanotubes. The TEP is large and holelike at high temperatures and approaches zero as $T \rightarrow 0$. The results argue against the opening of a gap at low temperature in these materials. When derived from a simple band structure picture, the TEP of a single metallic nanotube is significantly lower than the measured TEP, strongly suggesting that the predicted electron-hole symmetry of metallic nanotubes is broken when the tubes self-assemble into ropes. Different models for the symmetry breaking are considered. [S0031-9007(97)05214-9]

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Since their discovery in 1991 [1], carbon nanotubes have been the subject of intensive research, motivated both by intrinsic scientific richness and diverse applications potential. Because of geometrical complications it has been difficult to characterize the electronic properties of nanotubes. Until recently, most measurements were performed on multiwalled carbon nanotube (MWNT) samples [2–9] whose geometrical and electronic structures are especially complex. Such specimens consist of a collection of concentric tubes of different radii and chirality, parameters to which the electronic structure is especially sensitive [10–12].

Crystalline "ropes" of single-walled carbon nanotubes (SWNT's) [13] represent a significant step toward the ultimate goal of nanotube samples with a specified single diameter and chirality. The distribution of tube diameters in SWNT samples is narrowly peaked [13,14], and a large proportion of the tubes in the rope is predicted to have "armchair" chirality, with the $(10, 10)$ tube predominant.

Previous measurements [15,16] of the temperature-dependent dc and ac electrical resistivity ρ of macroscopic mats and single SWNT ropes show qualitatively similar behavior: at high temperature, they are metallic (positive $d\rho/dT$) and exhibit a crossover to nonmetallic behavior (negative $d\rho/dT$) at low temperature. The crossover temperature varies from sample to sample and is sensitive to mechanical handling. It has been suggested that the origin of the low-temperature nonmetallic behavior is 1D localization, but it is still unknown whether the transport behavior of these bulk samples is dominated by interrope contacts or on-rope or on-tube effects.

In this Letter, we report dc electrical resistivity and thermoelectric power (TEP) measurements of SWNT bundles from 300 to 4.2 K. We are motivated to examine the TEP of single-walled nanotubes in order to understand further their electrical transport properties, to answer some of the questions raised by the dc resistivity measurements, and to attempt to provide experimental confirmation of band structure calculations for single-walled nanotubes. Because it is sensitive to the curvature of the bands at the Fermi level, the sign of the TEP indicates the sign of the dominant current carrier. The temperature dependence of the TEP can give information about the type of conduction: the TEP of a simple metal is linear in T, while that of a true-gap semiconductor displays $(1/T)$ dependence. Thus we can examine whether the low-temperature upturn in the resistivity of the SWNT's is linked to the opening of a gap at the Fermi level. In addition, we examine the role of intertube and interrope contacts by sintering a SWNT mat under pressure to improve the contacts between ropes in a given sample.

SWNT samples used in this study were synthesized at Rice University using the laser vaporization method [13]. The samples were subsequently heated to 1000 °C in vacuum to remove impurities. Electrical leads were attached to small nanotube bundles (approximately 5 mm $\times$ 0.5 mm $\times$ 0.5 mm) so that successive measurements of TEP and resistivity could be performed on the same samples. Voltage and current leads were attached with conducting silver paint, and thermocouple leads were attached with high thermal conductivity epoxy. A portion of the batch of SWNT's was sintered in vacuum under mechanical pressure by passing a high current ($\geq$200 A/cm^2) through it as it was pressed between two electrodes. A small piece of the sintered mat was then sliced off and mounted in the same way as the unsintered bundles. dc electrical resistivity was measured by the usual four-probe technique. The TEP was measured at a number of fixed target temperatures by alternately heating each end of the sample to create a temperature difference of maximum $\pm$0.2 K, measuring the voltage induced in the sample by

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the temperature gradient, and then correcting the data for the thermopower of the gold leads.

Figure 1 shows the dc electrical resistivity of two SWNT samples, one pristine and one sintered, as a function of temperature from 300 to 4.2 K. The unsintered sample is metallic above 180 K, and shows an upturn in resistivity below that temperature similar to previous measurements. The sintered sample, on the other hand, displays negative $d\rho/dT$ over the entire temperature range. This gives evidence that the low-temperature resistivity upturn is caused not by poor contact between different ropes, but rather by on-rope effects such as tube-tube interactions or on-tube defect structure.

Figure 2 shows the experimentally determined TEP of three different SWNT samples, two pristine and one sintered, as a function of temperature from 300 to 4.2 K. All samples show similar behavior: at high temperatures the TEP is positive and of moderate magnitude (order 50 μV/K), while at low temperatures the TEP is linear in temperature and approaches zero as $T \to 0$. There is a notable change in the temperature dependence of the TEP near 100 K. The insensitivity of the magnitude and functional form of the TEP to sample preparation (i.e., sintering) indicates that the measured TEP, unlike the measured resistivity, is an intrinsic quantity.

The TEP can be used to elucidate the electronic structure of the sample. A simple interpretation of the rather large positive high-temperature TEP indicates holelike carriers. This result is surprising in that metallic tubes [such as $(10, 10)$ tubes] are predicted to have electron-hole symmetry [17] and thus a TEP close to zero. It is also noteworthy that the magnitude of the measured TEP is considerably larger than that of graphite [18], simple metals, or MWNT's [19]. The vanishing of the TEP at low temperatures argues against the opening of a semiconducting or localization-induced mobility gap at the Fermi level, which might be invoked to account for the observed increase in electrical resistivity at low temperature. The temperature dependence of the TEP is also unusual; it does not correspond to that of a simple metal or semiconductor, nor does it display a power-law dependence as might be expected for hopping-type conductivity [20].

We now examine various models which might account for the observed TEP behavior. Because our samples consist of ropes, with each rope comprising a parallel (crystalline) array of individual SWNT's largely of the $(10, 10)$ variety, we first compare the measured TEP to that of an individual metallic $(10, 10)$ tube. An (n, n) tube is predicted to have a 1D band structure formed by slicing the band structure of a single graphene sheet along the Γ-K line [17]. Two pairs of one-dimensional bands cross at the Fermi level, forming a conduction band and a valence band, with a Fermi surface consisting of two points. The bands are highly linear near the Fermi level ($\hbar v_F = 5.3$ eV Å [16]), and thus display electron-hole symmetry.

The TEP of a nanotube will, in general, include contributions from electronic effects (the "drift" TEP) and electron-phonon effects ("phonon drag"). We first calculate the drift thermopower using the standard Mott form for the thermopower of a metal. It reduces in one dimension to

$$S_d = -\frac{\pi^2 k_B^2 T}{3e}\left(\frac{v'}{v} + \frac{\tau'}{\tau}\right), \tag{1}$$

where v is the band velocity and τ is the electron relaxation (scattering) time. The derivatives are with respect to energy, and the expression is evaluated at the Fermi points. The first term in the brackets is strictly zero for linear bands. Because of the near-linear band structure and high band velocity of metallic nanotubes near the Fermi level, we estimate an upper limit of $\sim$0.5 μV/K on the room-temperature contribution from the first term. The energy-dependent relaxation time $\tau(E)$ is determined by electron-phonon scattering. Assuming that the phonon energies can be neglected, Fermi's golden rule gives

$$\frac{1}{\tau(E)} = \frac{2\pi}{\hbar}\,|V(E)|^2 N(E)\,, \tag{2}$$

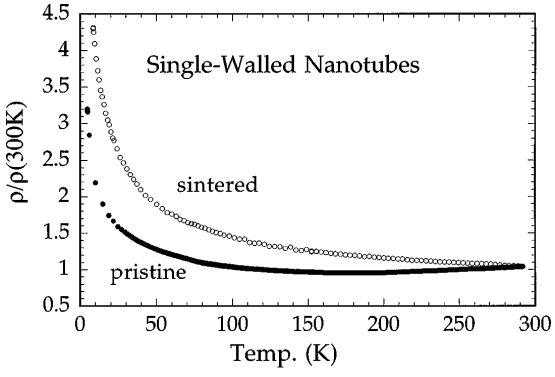

FIG. 1. Temperature-dependent resistivity of sintered and unsintered SWNT samples.

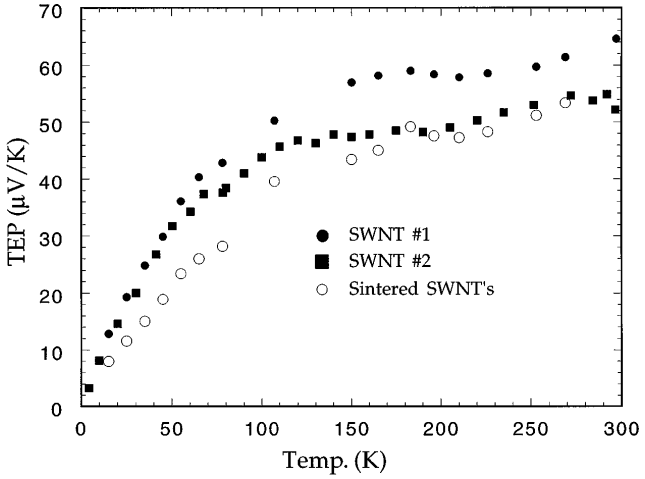

FIG. 2. Thermoelectric power of three SWNT samples. The sintered sample has been pressed and heated to improve the contacts between tubes.

where $V(E)$ is an electron-phonon scattering matrix element and $N(E)$ is the electron density of states. In 1D, with linear bands, $N(E)$ is constant. $V(E)$ should vary slowly near the Fermi level, and thus $\tau(E)$ will be nearly constant over this energy range as well, yielding a negligible contribution from the τ'/τ term in Eq. (1). Hence, the total drift contribution to the TEP of individual $(10, 10)$ tubes [Eq. (1)] is insufficient to account for the observed TEP.

In addition to the drift term, the TEP may contain a phonon-drag component. In a semiclassical model, phonon-drag thermopower can be expressed as [21]

$$S_{e-p} = \frac{-CR}{3ne}, \tag{3}$$

where C is the phonon specific heat, n is the carrier density, and $R = \tau_p/\tau_{ep}$ is the ratio of total phonon relaxation time to the electron-phonon relaxation time. The sign of the phonon-drag thermopower is determined by the charge carriers, and in a single metallic nanotube the electron and hole contributions should cancel exactly. A more rigorous treatment [22] of the phonon-drag thermopower again yields a zero result if energy-independent band velocity and scattering times are assumed as in the above drift TEP calculation.

Therefore, a single metallic nanotube with perfect electron-hole symmetry should have an identically zero thermopower. While the small deviations from linearity in the band structure of a nanotube might result in finite drift or phonon-drag thermopower contributions, it is unlikely that these can account for the relatively large magnitude of the observed TEP.

We thus speculate on some possible processes by which the electron-hole symmetry of metallic nanotubes could be broken, thereby yielding substantial TEP contributions. One possibility is that the assembly of individual $(10, 10)$ tubes into a rope is sufficient to break the single-tube electron-hole symmetry. An interaction which changes the dimensionality of the electronic structure might break the electron-hole symmetry by causing an energy dependence of the density of states and the area of the Fermi surface. Recent theoretical work [23] has predicted that tube-tube interactions in a rope of $(10, 10)$ tubes cause the opening of a "pseudogap" in the density of states of the rope at the Fermi level. Symmetry breaking such an interaction mechanism could cause a contribution to the thermopower from both drift and phonon-drag effects, although the magnitude of the effect has not been calculated.

Alternatively, the contribution of a minority of semiconducting tubes in a rope of predominantly metallic tubes could account for the observed TEP. To explore this possibility, we model SWNT ropes as comprising semiconducting and metallic tubes in parallel. In a simple two-band model, the total TEP is given by

$$S_{\text{tot}} = \frac{G_{\text{met}} S_{\text{met}}}{G_{\text{tot}}} + \frac{G_{\text{semi}} S_{\text{semi}}}{G_{\text{tot}}}, \tag{4}$$

where G is the electrical conductance of each channel. To develop a functional form for the total TEP, we first insert generic forms for the metallic and semiconducting TEP and conductivity. A simple metal will have a linear TEP, while a semiconductor will have a constant term and a term proportional to λ/T, where λ is the gap temperature. We assume an activated form for the semiconducting conductance, $G_{\text{semi}} \propto -\lambda/T$, and that the total conductance is dominated by the metallic channel. The conductivity of an ideal metallic nanotube is difficult to model in a compact way. A $1/T$ dependence is probably best near room temperature, but fails to take into account the low-temperature residual resistivity. Likewise, a temperature-independent conductivity is probably better at low temperature and less accurate at high temperature. We consider both extreme cases below. If a $1/T$ dependence for the metallic conductivity is assumed, we obtain

$$S_{\text{tot}} = AT + (B\lambda + CT)\exp\left(\frac{-\lambda}{T}\right), \tag{5}$$

while a constant metallic conductivity yields

$$S_{\text{tot}} = AT + \left(\frac{B\lambda}{T} + C\right)\exp\left(\frac{-\lambda}{T}\right). \tag{6}$$

In both cases the first term in the sum is the thermopower of the metallic channel and the second is the conductance-weighted thermopower of the semiconducting channel.

In attempting to fit the observed TEP using the above model, we will first use the predicted (near-zero) TEP of an isolated $(10, 10)$ tube [Eq. (1)] to provide the A parameter, and then attempt to fit the data by adjusting the values of B, C, and λ. Next, we will consider the TEP of a broken-symmetry metallic tube in parallel with a semiconducting tube by allowing the A parameter to vary.

The lines in Fig. 3 represent fits of Eqs. (5) and (6) to one of the data sets (SWNT #2) shown in Fig. 2. The solid line represents the first attempt to fit the data, using the TEP of an isolated metallic tube in parallel with a semiconducting tube with a gap temperature of 200 K. This model fails to fit the data for any reasonable choice of λ. This failure can be understood by examining Eq. (4). The low-temperature thermopower of a metal and a semiconductor in parallel will always be dominated by the metal, because the conductance of the semiconductor decreases exponentially, overwhelming its increasing thermopower. Therefore we conclude that the introduction of semiconducting tubes into a rope, without any interaction between tubes to break the symmetry of the metallic tubes, cannot explain the measured thermopower. This leads us to expand the model to consider a metallic tube with broken electron-hole symmetry in parallel with a semiconducting tube.

The dashed lines in Fig. 3 represent fits of Eqs. (5) and (6) to the same data set, where now the metallic thermopower and the gap temperature are left as fitting parameters. Both forms fit the measured data quite well;

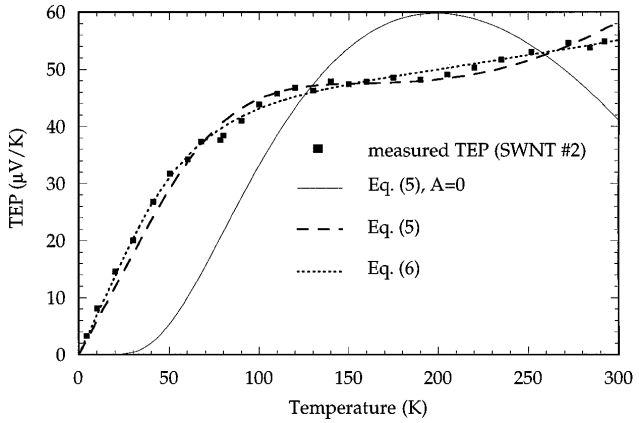

FIG. 3. Fits to measured TEP data using a two-band model to simulate semiconducting and metallic tubes in parallel. The solid curve represents a fit to the data using Eq. (5), with $A = 0$ to represent the TEP of an isolated metallic nanotube. The two dashed lines represent fits to the data using Eqs. (5) and (6); in these cases, A is allowed to vary in order to simulate a metallic nanotube with broken electron-hole symmetry. The fitting parameters extracted from the fit to Eq. (5) are $A = 0.70\ \mu\mathrm{V/K^2}$; $B = -0.46\ \mu\mathrm{V/K^2}$; $C = -0.65\ \mu\mathrm{V/K^2}$; $\lambda = 179$ K. The fitting parameters extracted from the fit to Eq. (6) are $A = 0.59\ \mu\mathrm{V/K^2}$; $B = -0.1\ \mu\mathrm{V/K}$; $C = -343\ \mu\mathrm{V/K}$; $\lambda = 302$ K.

the exact form of the metallic conductivity is not critically important, and in both cases the total conductivity is dominated by that of the metallic tube, in agreement with the observed metallic conductivity in this system. The fitting parameters obtained in both cases are given in the caption of Fig. 3. The temperature coefficient of the metallic thermopower is given by the A parameter; its value implies a positive TEP, with a room-temperature magnitude of $\sim 200\ \mu\mathrm{V/K}$ in both cases. λ is of order 200–300 K, indicating that small-gap semiconductors are necessary to produce the observed TEP. Significantly, the B and C parameters are negative in both cases, indicating that the semiconducting contribution is electronlike. The success of this model in fitting the measured data suggests a physical mechanism for symmetry breaking in nanotube ropes, in which a "self-doping" process, by which electrons are transferred from metallic to semiconducting tubes, results in holelike metallic tubes and electronlike semiconducting tubes. The contributions from both species acting in parallel could reproduce the measured thermopower.

In conclusion, the thermopower of ropes of single-walled nanotubes is positive and moderately large, approaches zero as $T \to 0$, and exhibits an unusual temperature dependence. The similar TEP of sintered and un-sintered samples confirms that the TEP is intrinsic, and the metallic low-T behavior of the TEP gives evidence that the low-temperature upturn in resistivity of SWNT ropes is not the result of the opening of a gap. The magnitude and temperature behavior of the TEP cannot be explained using a naive single metallic tube band structure approach, giving strong evidence that the electron-hole symmetry in metallic nanotubes is broken when the tubes are assembled into ropes. A parallel-conduction model is successful in fitting the measured data, leading to the speculation that charge transfer occurs between different species of SWNT's in a rope.

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