Thermoelectric Power and Thermal Conductivity of Single-Walled Carbon Nanotubes

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We have measured the temperature-dependent thermopower (TEP) and thermal conductivity (κ) of bulk samples of single-walled nanotube (SWNT) bundles. The TEP of SWNT's approaches zero as $T \rightarrow 0$, indicating a metallic density of states at the Fermi level in spite of their non-metallic resistivity behavior. At moderate temperatures, the TEP is large and positive, while a single metallic tube should have electron-hole symmetry and thus a zero thermopower. The measured data can be fit using a model comprising hole-like metallic tubes and electron-like semiconducting tubes in parallel. The thermal conductivity of SWNT's is found to be large, and dominated by phonons at all temperatures. At low temperature, $\kappa(T)$ is linear. The data can be fit by a single-scattering-time model; the model confirms that the low-temperature linear behavior is due to the thermal conductivity of a single one-dimensional phonon subband, and that the phonon mean free path is of order 100 nm.

Introduction

Most investigations into the properties of carbon nanotubes have focused on either their electrical properties or their mechanical properties. However, their thermoelectric and thermal properties are equally interesting. Thermopower is a sensitive probe of the bandstructure of materials, and in particular can discriminate between different possible mechanisms for the low-temperature resistivity upturn seen in bulk single-walled nanotube (SWNT) samples. The thermal concuctivity of nanotubes has been predicted to be quite large--similar to that of diamond or graphite; such a large thermal conductivity could represent a significant advantage for nanotubes in electronic device applications. In addition, nanotubes are an ideal system in which to study low-dimensional thermal conduction effects.

The samples used in this study are 'mats' of SWNT bundles. The bundles contain tens to hundreds of nanotubes in a triangular lattice, and can be microns in length. They were synthesized by an arc-vaporization method[1]; samples synthesized by the laser-vaporization method[2] were used to check the results. A portion of the tubes were 'sintered' by resistively heating them under pressure in an attempt to improve the contacts between tubes. It was found that the electrical conductivity of these sintered tubes is in fact lower than that of the as-grown samples, and that the conductivity shows nonmetallic temperature dependence at all temperatures.

Thermoelectric Power

Figure 1 shows the measured thermoelectric power (represented as the solid squares) of a representative SWNT mat, taken at a number of fixed temperature points from 300 K to 4 K. The TEP of other samples, including the sintered sample, shows similar behavior. Thus we believe that the measured TEP represents the intrinsic properties of the SWNT bundles composing the mat. The measured thermopower is large

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and positive, indicating hole-like conduction, and approaches zero as T approaches zero. Because a system with a gap at the Fermi level should display a (1/T)-dependent thermopower, we conclude that the opening of a gap is not the cause of the nonmetallic resistivity observed in SWNT mats at low temperature.

We first examine the predicted one-dimensional bandstructure of a metallic armchair nanotube to examine whether it is consistent with the observed TEP. The Mott formula for the thermopower of a metal reduces in one dimension to

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

where v is the band velocity, τ is the electron relaxation time, the derivatives are with respect to energy, and the expression is evaluated at the Fermi points. An armchair nanotube is expected to have two one-dimensional bands which cross at the Fermi points[3]. These bands are highly linear, and thus should exhibit electron-hole symmetry and a thermopower close to zero; we calculate a maximum contribution of 0.5 μV/K for the room temperature contribution from Eq. (1). This is two orders of magnitude smaller than the observed TEP. Likewise, the electron-hole symmetry of this tube should produce a small phonon drag contribution to the TEP. Therefore we conclude that the expected contribution from an armchair tube is insufficient to account for the measured thermopower.

Since nanotube bundles likely contain tubes with a range of chiralities, we consider the possibility that semiconducting tubes, in parallel with metallic tubes, could be producing the measured TEP. We do this by employing a two-band model. By assuming simple functional forms for the thermopower and conductivity of the metallic and semiconducting contributions, we obtain

$$S = AT + (B\lambda + CT)\exp\left(\frac{-\lambda}{T}\right). \qquad (2)$$

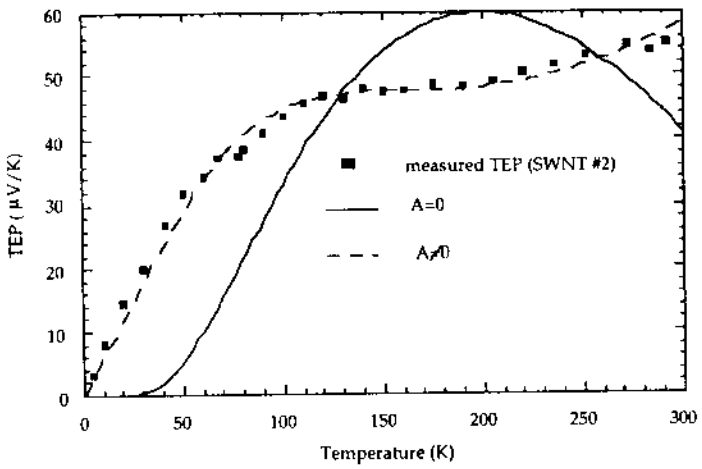

Figure 1. Thermopower of SWNT's. The solid line is a fit to the measured TEP data to Eq. (2) with A=0, representing metallic tubes with electron-hole symmetry; the dashed line represents a fit with an arbitrary contribution from the metallic tubes.

In this formula, the first (linear) term represents the contribution of the metallic channel, while the second represents the contribution of the semiconducting channel. We first assume that the metallic tube retains its electron-hole symmetry, and thus A=0. The solid line in Fig. (1) represents an attempt to fit the measured data to Eq. 2 using A=0. This clearly does not produce a good fit--

the observed low-temperature behavior cannot come from semiconducting tubes, because their contribution freezes out at low temperature. Therefore we conclude that there must be at least some metallic tubes with broken electron-hole symmetry. We model this by allowing the A parameter to vary arbitrarily. The dashed line in Fig. (1) represents this fit to the measured data. The high quality of this fit leads us to the conclusion that a model comprising hole-like metallic tubes and electron-like semiconducting tubes is a viable explanation for the magnitude and temperature dependence of the measured thermopower.

Thermal Conductivity

Figure (2) represents the thermal conductivity $\kappa(T)$ of a representative SWNT sample as a function of temperature from 350 K to 8 K. The same temperature dependence was observed in as-grown samples and the sintered sample; and therefore we conclude that it reflects the intrinsic $\kappa(T)$ of SWNT's. The thermal conductivity is near-linear at all temperatures, in contrast to that of graphite and carbon fibers, which display a T^2-like $\kappa(T)$. The inset to figure (2) represents the low-temperature behavior of κ. It is strictly linear in T, and extrapolates to zero as $T \rightarrow 0$. This linear behavior is usually associated with electron thermal conductivity; however, we will demonstrate below that it is in fact the signature of one-dimensional phonon thermal conductivity.

We first attempt to deduce the magnitude of the thermal conductivity of SWNT's from the measured data. Using just the dimensions and measured thermal conductance of the sample, we obtain a room-temperature thermal conductivity of 0.7 W/m-K. Because the filling fraction of the tubes in a mat is only about 2%, we correct for this factor to obtain a value of 36 W/m-K for the thermal conductivity of a dense-packed SWNT mat. However, even a dense-packed mat will have a disordered structure: the longitudinal thermal conductiviy of a single tube or rope will likely be significantly larger. To deduce this value, we note that the longitudinal electrical conductivity of a single rope has been measured to be 50-150 times that of the bulk mat[4]. If the same holds true for the thermal conductivity, then the longitudinal thermal conductivity of a single rope is 1800-6000 W/m-K (comparable to or greater than that of graphite or diamond) at room temperature.

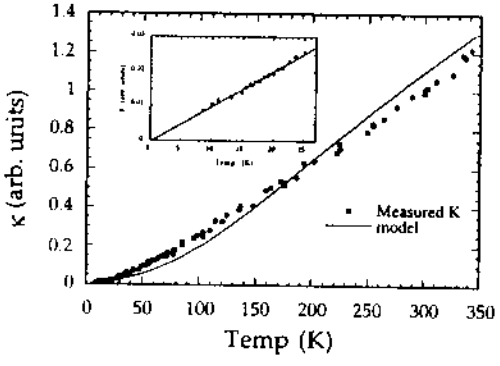

Figure 2. Thermal conductivity of SWNT's. The inset highlights the low-temperature behavior.

We now address the observed temperature dependence of the thermal conductivity. We first seek to determine whether κ is due to electrons or phonons. To do this, we measure the thermal and electrical conductivity of each sample using identical contact geometries to determine the Lorentz ratio $\kappa/\sigma T$. All samples displayed a Lorentz ratio which ranged from $2\text{-}6 \times 10^{-6}$ W-Ω/K^2 over the measured temperature range; this value is

two orders of magnitude larger than what would be expected for electrons. The thermal conductivity of SWNT's is dominated by phonons at all temperatures.

We next attempt to model κ(T) by calculating the phonon thermal conductivity of a single tube. The diagonal term of the thermal conductivity tensor is given by

$$\kappa_{zz} = \sum C v_z^2 \tau, \qquad (3)$$

where C is the heat capacity and v is the sound velocity of a given phonon state; the sum is over all phonon states. We consider only the four acoustic modes of a tube (one longitudinal, one twist, and two transverse) as contributing significantly κ, and use estimates of 2, 1, and 0.8×10^6 cm/s for their sound velocities. In addition, we carefully consider the circumferential quantization of the phonon wavevector: this has the effect of splitting up the phonon modes into multiple 'subbands,' with $\Delta k_\chi = 1/R_{tube}$[5]. Figure 3 shows the results of Eq. (3), evaluated separately for all of the subbands of the 'twist' mode, for a 1.4 nm diameter tube. The zero-order subband passes through the center of the Brillouin zone; as a true one-dimensional acoustic mode, it provides a linear κ(T) at low temperature. Higher subbands do not contribute to κ at low temperature; the first subband begins to contribute significantly near 30 K, just the point where the measured κ(T) diverges from linearity.

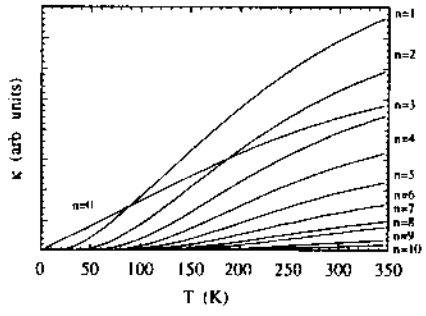

Figure 3. Calculated contribution (Eq. (3)) to the thermal conductivity from each subband of the 'twist' acoustic mode

The solid line in Fig. (2) shows the total expected contribution to κ(T) from all four phonon branches, scaled to best fit the measured data. This line represents a fit with only one free parameter, the scattering time τ. It clearly matches the overall behavior of the measured κ(T), and confirms that the low-temperature linear behavior is in fact due to the thermal conductivity of a single one-dimensional phonon subband--the first observation of one-dimensional phonon thermal conductivity. From the measured magnitude of κ(T), we can extract an estimate of τ; its value of $\approx 10^{-11}$s implies a scattering length of ≈100 nm, smaller than the length of a single tube, but consistent with the distance between inter-tube contacts; these contacts could in fact be acting to scatter phonons.

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[1]C. Journet, et al., Nature **388**, 756 (1997).

[2] A. Thess, et al., Science **273**, 483 (1996).

[3] N. Hamada, S.-I. Sawada and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).

[4]J. E. Fischer, et al., Phys. Rev. B **55**, R4921 (1997).

[5]L.X. Benedict, S.G. Louie, and M.L. Cohen, Solid State Comm. **100**, 177 (1996)