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Thermal conductivity of single-walled carbon nanotubes

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Abstract

We have measured the thermal conductivity (κ) of bulk samples of single-walled nanotube (SWNT) bundles. The thermal conductivity of SWNT's is found to be large, and dominated by phonons at all temperatures. κ(T) of SWNT's is linear in temperature from 7 K to 25 K, increases slope between 25 K and 40 K, and rises monotonically with temperature to above room temperature. 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.

Keywords: Heat conduction; Fullerenes and derivatives

1. Introduction

Carbon-based materials (diamond and in-plane graphite) display the highest measured thermal conductivity of any known material at moderate temperatures[1]. The discovery of carbon nanotubes in 1991[2] has led to speculation[3] that this new class of one-dimensional carbon could have a thermal conductivity equal to or greater than that of diamond and graphite. It is well known that the small diameter of carbon nanotubes enforces a low dimensionality on the electronic structure. In fact, the small size of the tubes also significantly reduces the dimensionality of the phonon structure; thermal conductivity can be used to probe these effects.

We report measurements of the thermal conductivity of bulk samples of single-walled carbon nanotubes from 350 K to 8 K. The single-walled nanotube (SWNT) samples used in this study are composed of bundles of SWNT's (of approx. 1.4 nm diameter) in a loosely-packed, tangled 'mat.' They were synthesized by arc-vaporization of a graphite anode containing Ni and Y catalysts.

2. Temperature-Dependent Thermal Conductivity of SWNT's

Figure (1) represents the thermal conductivity κ(T) of a representative SWNT sample as a function of temperature from 350 K to 8 K. The same temperature dependence was observed in all samples, regardless of mehcanical or thermal treatment; therefore we conclude that it reflects the intrinsic κ(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 κ(T). The inset to figure (1) represents the low-temperature behavior of κ. It is strictly linear in T, and extrapolates to zero as T→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.

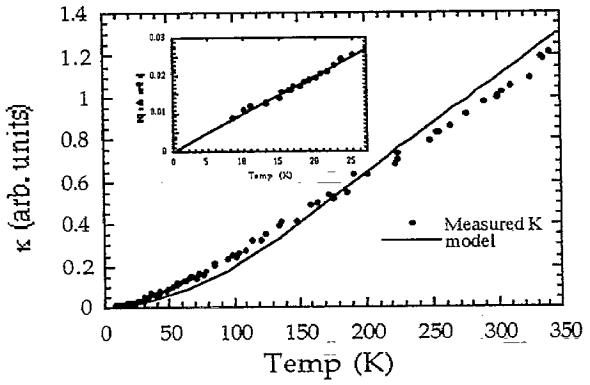

Fig. 1 Thermal conductivity of SWNT's. The inset highlights the low-temperature behavior.

The magnitude of the thermal conductivity of SWNT's can be deduced from the measured data. The bulk sample has a room-temperature thermal conductivity of 0.7 W/m-K. Correcting for the low density of the mat, we 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 is 50-150 times that of the bulk mat. 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.

Measurement of the Lorenz ratio κ/σT for a single sample can provide information on the relative contributions of electrons and phonons to the thermal conductivity. All samples displayed a

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Lorenz ratio which ranged from 2-6 × 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. Therefore, we conclude that the thermal conductivity of SWNT's is dominated by phonons at all temperatures.

3. Model for κ(T) of Nanotubes

We 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

$$\kappa_{zz} = \sum C v_z^2 \tau, \qquad (1)$$

where C is the heat capacity, v is the sound velocity of a given phonon state, and τ is its relaxation time; 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 $\Delta k_X = 1/R_{tube}$[4]. Figure 2 shows the results of Eq. (1), 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.

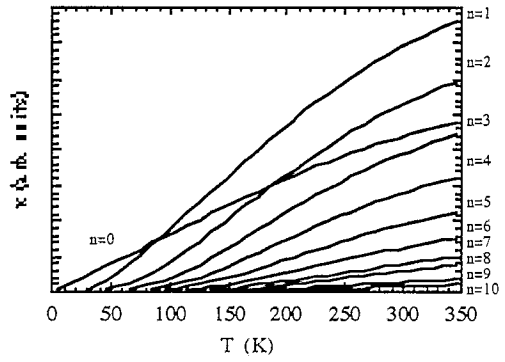

Figure 2. Calculated contribution (Eq. (1)) to the thermal conductivity from each subband of the 'twist' acoustic mode

The solid line in Fig. (1) 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. From the measured magnitude of κ(T), we can extract an estimate of τ; its value of ≈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.

Finally, we note that the high-temperature behavior of κ(T) of SWNT's is significantly different from that of graphite and related materials. Specifically, these materials show a decrease in κ(T) (which occurs near 150 K in highly crystalline samples and at higher temperatures in less well-ordered materials) with increasing temperature, due to the onset of phonon-phonon Umklapp processes. A truly 1-D system should have significantly reduced Umklapp scattering because it is impossible to conserve both energy and momentum if there is any nonlinearity in the phonon dispersion relation. While SWNT's are not strictly 1-D at high temperature, their reduced dimensionality could still have the effect of suppressing Umklapp processes.

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