RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 59, NUMBER 4 15 JANUARY 1999-II

Thermal conductivity of single-walled carbon nanotubes

J. Hone, M. Whitney, C. Piskoti, 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

(Received 15 October 1998)

We have measured the temperature-dependent thermal conductivity $\kappa(T)$ of crystalline ropes of single-walled carbon nanotubes from 350 K to 8 K. $\kappa(T)$ decreases smoothly with decreasing temperature, and displays linear temperature dependence below 30 K. Comparison with electrical conductivity experiments indicates that the room-temperature thermal conductivity of a single nanotube may be comparable to that of diamond or in-plane graphite, while the ratio of thermal to electrical conductance for a given sample indicates that the thermal conductivity is dominated by phonons at all temperatures. Below 30 K, the linear temperature dependence and estimated magnitude of $\kappa(T)$ imply an energy-independent phonon mean free path of $\sim$0.5–1.5 μm. [S0163-1829(99)50404-9]

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 (Ref. 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. Past measurement of the thermal conductivity of nanotubes has been limited by the low quality of available samples. Recent advances[4,5] in nanotube synthesis have made possible the growth of high-purity crystalline bundles of nearly monodisperse single-walled carbon nanotubes (SWNT's). Such materials are well suited to transport studies, including measurements of electrical and thermal conductivity.

In this work we report measurements of the thermal conductivity of single-walled carbon nanotubes from 350 K to 8 K. We are motivated to measure the thermal conductivity of SWNT's to test the speculation that nanotubes have an exceptionally high thermal conductivity, as well as to probe the phonon structure in these unique materials.

SWNT samples were synthesized by an arc-discharge method,[5] using graphite rods filled with a combination of nickel and yttrium. This method yields high-purity ''mats'' of tangled nanotube bundles. These bundles are composed of tens to hundreds of tubes, and can be microns in length; the individual tubes have a diameter distribution strongly peaked near 1.4 nm. Samples prepared by the laser vaporization method[4] were also used, and produced identical results. Samples were initially characterized by transmission electron microscopy and scanning electron microscopy to confirm their purity and composition. A portion of the tubes was also ''sintered'' by heating under moderate pressure, in order to increase the density of the sample and possibly improve the contacts between nanotube bundles. The density of a typical as-grown mat was approximately 2% of the theoretical density of a close-packed bundle of 1.4 nm tubes; the sintering process raised the filling fraction to 70%.

Thermal conductivity was measured using a comparative method. Small (approximately 5 mm × 2 mm × 2 mm) samples were mounted in series with a constantan rod whose temperature-dependent thermal conductance had been previously measured. Differential thermocouples were attached directly to the sample and the constantan rod to measure the temperature drops across each. A heater at one end of the constantan rod provided a heat current through the rod and sample to the cold temperature stage; the thermal conductivity could then be calculated by comparing the temperature drops across the sample and the constantan rod. In calibration runs, the apparatus accurately reproduced the known temperature-dependent thermal conductivity of a number of different standards. Nanotube samples of varying geometry and thermal conductance were measured, and produced identical results for the temperature-dependent thermal conductivity, further confirming that heat leaks or other spurious effects did not significantly influence the measurements. After the thermal conductivity of each mat was measured, its four-probe resistance was measured using the same contact points as were used for the thermal conductivity measurement, in order to compare the measured thermal and electrical conductances without regard for the geometry of the sample. Consistent with earlier reports,[6] the resistivity of the SWNT mats studied showed metallic temperature dependence at room temperature, and nonmetallic temperature dependence below $\sim$150 K.

Figure 1 represents the measured thermal conductivity κ of a representative SWNT sample as a function of temperature from 350 K to 8 K. From 350 K to 40 K, κ decreases smoothly with decreasing temperature with very little curvature. The inset to Fig. 1 shows the low-temperature behavior. Near 30 K, $\kappa(T)$ changes slope; below this temperature, $\kappa(T)$ is strictly linear in temperature and extrapolates to zero at $T=0$. κ displayed identical temperature dependence in all mat samples, as well as the sintered sample. Thus we conclude that the measured thermal conductivity reflects the intrinsic thermal conductivity of nanotube bundles rather than sample-dependent effects such as the junctions between bundles.

The observed thermal conductivity displays a temperature dependence that is markedly different from that of graphite,[1,7] even though both materials are composed of graphitic sheets. In high-quality graphite, the *ab*-plane thermal conductivity, which is dominated by acoustic phonons, var-

©1999 The American Physical Society

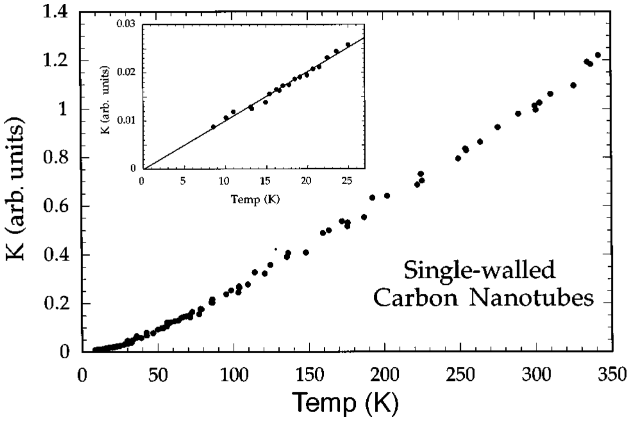

FIG. 1. Temperature-dependent thermal conductivity of single-walled nanotubes. The thermal conductivity decreases smoothly from 350 K to 8 K, and displays a change of slope near 30 K. The inset shows the low-temperature behavior in greater detail. The solid line is a linear fit to the data below 25 K, and extrapolates to zero at zero temperature.

ies as T^{2-3} up to ~150 K, at which point phonon-phonon umklapp scattering causes κ to decrease rapidly with increasing T. Highly pure graphite samples can have a thermal conductivity near 6000 W/m-K at the peak and 2000 W/m-K at room temperature.

Because of the irregular geometry of the nanotube samples, it is nontrivial to derive a value for the absolute magnitude of the thermal conductivity from the measured thermal conductance of a sample. As a first step, we calculate the thermal conductivity $\kappa(m)$ of a dense-packed mat of nanotube ropes using the sample's dimensions and then correcting for the volume filling fraction of the sample. Doing this, we obtain a value of 35 W/m-K for the corrected room-temperature thermal conductivity $\kappa(m)$ of an as-grown mat sample, and, surprisingly, only 2.3 W/m-K for the sintered sample.

The value of the thermal conductivity of a SWNT mat derived above is already large, but not comparable to that of pure metals or high-quality graphite at room temperature. However, the derived value does not take into account the highly tangled nature of the ropes in a mat. It has been shown previously[6] that the longitudinal electrical conductivity of a single SWNT rope $[\sigma_{\|}(r)]$ is 50 to 150 times greater than the corrected conductivity $[\sigma(m)]$ of a mat sample. It is likely, then, that the intrinsic longitudinal thermal conductivity $\kappa_{\|}(r)$ of a rope is also a good deal higher than the mat value. A naive approach is to assume that the intrinsic and bulk thermal conductivities are related in the same way as the intrinsic and bulk electrical conductivities, i.e., that

$$\frac{\kappa_{\|}(r)}{\kappa(m)} \approx \frac{\sigma_{\|}(r)}{\sigma(m)}. \tag{1}$$

If Eq. (1) is valid, we obtain a room-temperature value for $\kappa_{\|}(r)$ of 1750–5800 W/m-K, near to or larger than that of type-IIa diamond or in-plane graphite, and exceeding both at higher temperatures. More sophisticated models might be employed to accurately determine $\kappa_{\|}(r)/\kappa(m)$, but clearly even a modest value yields a large $\kappa_{\|}(r)$.

We now examine the temperature dependence of the measured thermal conductivity of SWNT bundles, and attempt to understand how it could be so different from that of graphite. In particular, we are interested in the low-T linear $\kappa(T)$, which, in a normal metal, is usually due to electrons. Therefore, as a first step, we attempt to discern whether the measured $\kappa(T)$ is due to electrons or phonons, by comparing the measured electrical and thermal conductivities of a given sample. An electron system with elastic scattering generally obeys the Wiedemann-Franz law[8]

$$\frac{\kappa}{\sigma T} \approx L_0, \tag{2}$$

where $L_0 = 2.45 \times 10^{-8} (V/K)^2$. If the geometrical factors involved in measuring κ and σ are identical, the measured Lorenz number $\kappa/\sigma T$ of a sample, compared to L_0, gives a good indication of what fraction of the heat is carried by electrons. The experimentally derived Lorenz number of the SWNT samples is large, ranging from $2-7 \times 10^{-6} (V/K)^2$ over the measured temperature range, at least two orders of magnitude higher than L_0. Therefore we conclude that, despite the linear temperature dependence of the thermal conductivity below 30 K, κ is dominated at all temperatures by phonons rather than electrons. This holds true for all of the measured samples, including the sintered sample. The sintering process appears to be introducing defects or disorder that reduce the electrical conductivity and the thermal conductivity equally.

We next seek to understand how phonons could produce the observed thermal conductivity behavior. In a simple model,[9] the diagonal term of the phonon thermal conductivity tensor is given by

$$\kappa_{zz} = \sum C v_z{}^2 \tau, \tag{3}$$

where C, v, and τ are the specific heat, group velocity, and relaxation time of a given phonon state, and the sum is over all phonon states; the dominant contribution is usually from acoustic phonons. Based on Eq. (3), there are a number of reasons why the observed $\kappa(T)$ of tubes could be different from that of graphite, in spite of the similarity[10] between the acoustic phonons in a graphene sheet and a nanotube. First, graphite has additional phonon modes, corresponding to interplanar vibrations, which are lacking in an isolated nanotube. Second, the scattering processes may be different in graphite and tubes, which could yield different scattering times for similar ones. Third, the ''rolling up'' of a graphene sheet to make a nanotube has significant effects on the phonon spectrum:[11] the transverse component of the phonon wave vector $(k_{\perp})$ is quantized due to the periodic boundary conditions imposed by the cylindrical geometry. All of these differences should have significant effects on the temperature dependence of the thermal conductivity, both at low temperature (where scattering is presumably off fixed sample boundaries or defects) and at higher temperature (where phonon-phonon scattering should dominate).

We now focus on the low-temperature behavior of $\kappa(T)$, where the small diameter of the nanotubes should most affect their phonon properties.[11] In a 1.4-nm diameter tube, all phonon states with $k_{\perp} \neq 0$ should be ''frozen out'' below 30 K, so that all of the remaining phonons are confined to a single one-dimensional band with $k_\perp = 0$. This is precisely the temperature below which we observe a linear $\kappa(T)$. At these temperatures, the specific heat per unit volume of a single acoustic phonon polarization with velocity v is[11]

$$C_v = \frac{k_B{}^2 T}{\pi\hbar v A} 3.292, \tag{4}$$

where A is the cross-sectional area of a tube in a bundle, about 2.5 nm^2 for the nanotubes studied. If the phonon relaxation time (and therefore the mean free path) is energy independent, the three-dimensional thermal conductivity of a single phonon polarization below 30 K will then be

$$\kappa = \frac{3.292 k_B{}^2 l T}{\pi\hbar A}, \tag{5}$$

where l is the phonon mean free path. Thus we can reproduce the observed linear temperature dependence below 30 K by using previously derived expressions for the nanotube specific heat and assuming an energy-independent mean free path.[12–14]

An energy-independent mean free path, as implied by the temperature dependence of the measured thermal conductivity, is usually the result of scattering off of the boundaries of the sample. Therefore, it is interesting to estimate the phonon mean free path in a nanotube rope, and examine whether it is consistent with boundary scattering. We can use Eq. (5) to evaluate the mean free path using the estimated magnitude of the thermal conductivity. There are four acoustic phonon branches in a nanotube (one longitudinal, two transverse, and one ‘‘twist’’ mode),[10] so that the phonon mean free path below 30 K is given by

$$l = \frac{\pi\hbar A}{4(3.292) k_B{}^2} \frac{\kappa(T)}{T}, \tag{6}$$

A room-temperature thermal conductivity of 1750–5800 W/m-K (the range derived above for the longitudinal thermal conductivity of a single rope) implies that κ(30 K)$\sim$60–180 W/m-K, and that $l \sim 0.5-1.5$ μm. The ropes in the sample are generally a few microns long, although individual nanotubes are generally observed to be $\sim$1 μm; both values are of the same order of magnitude as the range of mean free paths derived above. Thus boundary scattering is not inconsistent with the estimated magnitude of the mean free path, although other scattering processes might also produce an energy-independent phonon mean free path. A more direct measurement of the magnitude of $\kappa_\parallel(r)$, as well as modeling of possible phonon scattering processes, could help clarify this issue.

We thank W. Holmes and A. Mizel for useful discussions, and U. Varadarajan for help in the preparation and characterization of samples. We also thank R.E. Smalley for providing the laser-vaporization-prepared nanotube samples used in this study. This work was supported in part by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. J.H. acknowledges support from the U.S. Department of Education.

---

[1] G. W. C. Kaye and T. H. Laby, *Tables of Physical and Chemical Constants*, 16th ed. (Longman, London, 1995).

[2] S. Iijima, Nature (London) **354**, 56 (1991).

[3] Rodney S. Ruoff and Donald C. Lorents, Carbon **33**, 925 (1995).

[4] T. Thess *et al.*, Science **273**, 483 (1996).

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

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

[7] B. T. Kelly, *Physics of Graphite* (Applied Science Publishers, London, 1981).

[8] Charles Kittel, *Introduction to Solid State Physics*, 6th ed. (Wiley, New York, 1986).

[9] J. E. Parrott and Audrey D. Stukes, *Thermal Conductivity of Solids* (Pion, London, 1975).

[10] Jin Yu, Rajiv K. Kalia, and Priya Vashishta, J. Chem. Phys. **103**, 6697 (1995).

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

[12] R. Nicklow, N. Wakabayashi, and H. G. Smith, Phys. Rev. B **5**, 4951 (1972).

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

[14] J. W. Mintmire, D. H. Robertson, and C. T. White, J. Phys. Chem. Solids **54**, 1835 (1993).