

Isotope Effect on the Thermal Conductivity of Boron Nitride Nanotubes

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(Received 17 February 2006; published 24 August 2006)

We have measured the temperature-dependent thermal conductivity $\kappa(T)$ of individual multiwall boron nitride nanotubes using a microfabricated test fixture that allows direct transmission electron microscopy characterization of the tube being measured. $\kappa(T)$ is exceptionally sensitive to isotopic substitution, with a 50% enhancement in $\kappa(T)$ resulting for boron nitride nanotubes with 99.5% ^{11}B . For isotopically pure boron nitride nanotubes, κ rivals that of carbon nanotubes of similar diameter.

DOI: [10.1103/PhysRevLett.97.085901](https://doi.org/10.1103/PhysRevLett.97.085901)

PACS numbers: 65.80.+n, 61.46.Fg, 68.65.-k

The isotopic content of materials is relevant to a vast number of physics-related disciplines. In molecular chemistry, isotopic substitutions can affect reaction rates, dramatically so when the substituted isotopes participate directly in the chemical bonds that are broken or formed. In biology, unstable nuclei are often exploited as tracers in complex reaction pathways, and in nuclear physics special isotopes can be fused or fragmented to release large amounts of energy. Nuclei with suitable magnetic moments are indispensable in solid and liquid magnetic resonance studies. Isotope substitutions have played key roles in some of the most important problems of solid state physics. For example, the observation [1,2] that the superconducting transition temperature of metals is isotope dependent demonstrated a phonon-driven mechanism and helped motivate the phenomenally successful Bardeen-Cooper-Schrieffer theory of superconductivity [3]. In exotic superconductors such as high- T_c oxides and fullerenes, the isotope effect has again been used to explore possible electron pairing mechanisms [4–6].

Given that phonons contribute to the thermal conductivity of solids, it is expected that the temperature-dependent thermal conductivity [$\kappa(T)$] be somewhat sensitive to the isotopic content of the material. Indeed, room temperature κ enhancements of 10%–30% have been achieved in Si and Ge via isotopic enrichment [7,8], with enriched carbon (diamond) showing the largest effect at $\sim 35\%$ [9]. In low-dimensional nanostructured materials, phonon confinement can lead to phenomena unseen in bulk materials [10,11]. In particular, cylindrical nanotubes formed from carbon or boron nitride support phonons possibly free from boundary scattering which could impair the thermal conductivity, and recent experiments have shown that carbon nanotubes are in fact excellent thermal conductors [12–15]. It has been suggested that the thermal isotope effect in low-dimensional conductors could be anomalously large

[16], but this has received no experimental investigation. Theoretical studies demonstrating that the Young's modulus and the phonon dispersion relation of boron nitride nanotubes are similar to those of carbon nanotubes [17,18] suggest that the thermal conductivity (κ) of boron nitride nanotubes might be comparable to that of carbon nanotubes [19]. Furthermore, boron has larger natural isotopic disorder (19.9% ^{10}B and 80.1% ^{11}B) than does carbon (98.9% ^{12}C and 1.1% ^{13}C), further suggesting that an enhancement of κ due to isotope enrichment could be large in boron nitride nanotubes [20]. Although previous work on boron nitride nanotube mats has yielded estimates for κ [21,22], most desirable would be a direct measurement of κ for an isolated, individual boron nitride nanotube, with full knowledge of the geometric structure and isotopic content of that particular tube.

We here report measurements of the temperature-dependent thermal conductivity $\kappa(T)$ of isotopically enriched, individual, isolated multiwall boron nitride nanotubes using a microfabricated test fixture that allows high-resolution transmission electron microscopy imaging of the sample under study. A dramatic dependence of κ on isotopic disorder is found, with a room temperature enhancement in κ of 50%, the largest for any material. For comparison purposes κ of individual (natural abundance isotope) multiwall carbon nanotubes has also been measured. Isotopically enriched boron nitride nanotubes have κ values nearly identical to those of carbon nanotubes with similar geometry.

Multiwall boron nitride nanotubes were synthesized using an adaptation of a previously reported method [23], yielding samples with typical outer diameter 30–40 nm and length $\sim 10\ \mu\text{m}$. Isotopic percentages were controlled using commercially available boron isotopes (99.56% ^{11}B , Cambridge Isotope Laboratories, Inc.). Carbon nanotubes with diameters ranging from 10 to 33 nm were prepared

using conventional arc methods. Individual tubes were placed on a custom designed microscale thermal conductivity test fixture using a piezodriven manipulator operated inside a scanning electron microscope. Details of the test fixture fabrication process have been published elsewhere [24]. In brief, the fixture incorporates independently suspended heat source and heat sink pads, with integrated Pt film resistors serving symmetrically either as heaters or sensors (i.e., thermometers). Nanotubes were bonded to the source or sink pads using trimethyl cyclopentadienyl platinum ($C_9H_{16}Pt$) for mechanical strength and to reduce contact thermal resistance.

Most importantly, the fixture was made adaptable to transmission electron microscope imaging by wet etching a window through the exposed Si below the sample mount region. Figure 1(a) shows a scanning electron microscopy image of the central portion of the test fixture with a boron nitride nanotube (barely visible) spanning the heat source and sink pads, and the inset shows a (low resolution)

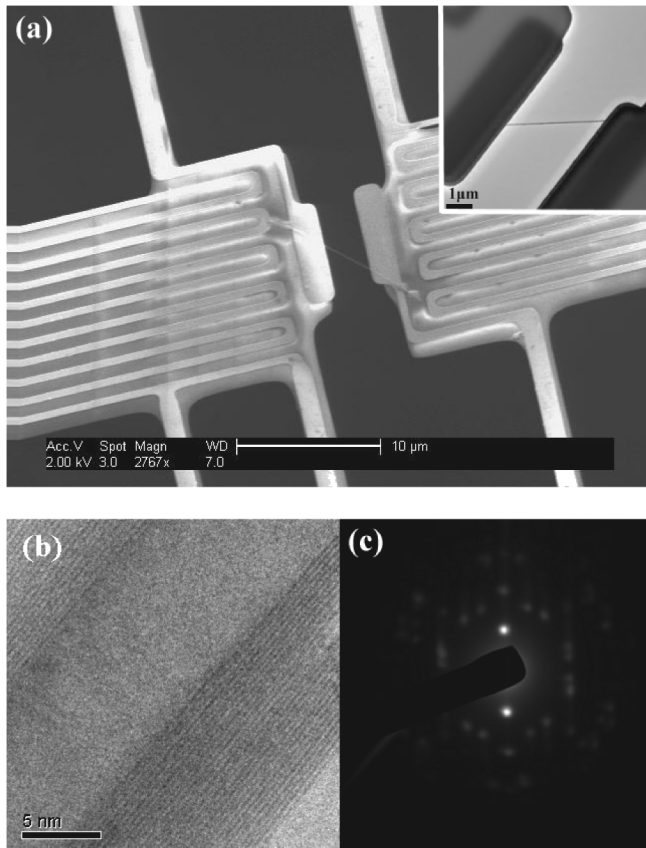


FIG. 1. (a) A scanning electron microscope image of the microfabricated test fixture with a boron nitride nanotube on it (scale bar = 10 μm). The inset shows the corresponding transmission electron microscope image of the same device (scale bar = 1 μm). (b) A high-resolution transmission electron microscope image of the boron nitride nanotube (scale bar = 5 nm). (c) The corresponding electron diffraction pattern of the boron nitride nanotube.

transmission electron microscope image corresponding to the same device. Figures 1(b) and 1(c) show, respectively, a high-resolution transmission electron microscope image of a mounted boron nitride nanotube and its corresponding electron diffraction pattern. The majority of the boron nitride nanotubes investigated exhibited nearly zigzag structure [as for Fig. 1(c)], with only a few showing mixed chirality [25].

For $\kappa(T)$ measurements, the sample base temperature was regulated and a known power (P) was supplied to the heater. Resistance changes of the heater and sensor were used to determine the resulting temperature changes of the heater and sensor pads, ΔT_h and ΔT_s . A blank device (with no nanotube present) was also used to determine the background heat leakage, subsequently used for data correction. Symmetrical measurements (switching the heater and sensor sides) were performed to estimate the error due to the asymmetry of the test fixture (generally <10%). The thermal conductance (K) of the nanotube was determined from ΔT_h and ΔT_s using the relation

$$K = \frac{P}{\Delta T_h - \Delta T_s} \left(\frac{\Delta T_s}{\Delta T_h + \Delta T_s} \right). \quad (1)$$

The thermal conductivity κ was then evaluated by incorporating the nanotube length and the annular area between inner and outer nanotube radius, as determined from transmission electron microscope imaging. The lack of transmission electron microscope characterization in earlier experiments has been known to cause significant error in determining κ of multiwall carbon nanotubes [12,15].

Figure 2 shows $\kappa(T)$ for an isotopically impure (natural abundance) boron nitride nanotube, an isotopically pure ^{11}B boron nitride nanotube, and a carbon nanotube, all with similar outer diameters. For all materials, κ increases

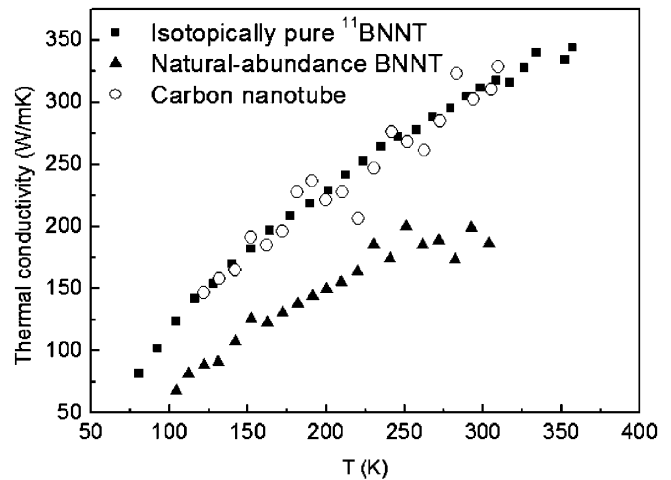


FIG. 2. The $\kappa(T)$ of a carbon nanotube (open circles), a boron nitride nanotube (BNNT, solid triangles), and an isotopically pure boron nitride nanotube (solid squares) with similar outer diameters.

with increasing temperature with no sign of saturation up to 300–350 K. Isotopic enrichment is seen to have a dramatic effect on the thermal conductivity of boron nitride nanotubes, with an enhancement of approximately 50% throughout the measured temperature range. Furthermore, the overlap of the data sets for the isotopically enriched boron nitride nanotubes and carbon nanotubes is striking; it reveals similarities of the intrinsic phonon dispersion relations and demonstrates that the thermal conductivity of an isotopically pure boron nitride nanotube is virtually identical to that of a carbon nanotube. These results are consistent with theoretical calculations that suggest similar phonon dispersion relations between hexagonal boron nitride and graphene [17,18].

Previous experiments on carbon nanotubes suggest that the thermal conductivity may depend strongly on nanotube outer diameter [13]. To verify this effect for carbon nanotubes and to investigate it for boron nitride nanotubes we have systematically measured $\kappa(290\text{ K})$ for boron nitride nanotubes and carbon nanotubes with different diameters. As shown in Fig. 3, for boron nitride nanotubes in the range 30–40 nm κ increases with decreasing outer diameter. A similar diameter dependence is also observed for carbon nanotubes, measured over the broader diameter range (10–33 nm). For large outer diameter ($d_{\text{out}} \sim 35\text{ nm}$) carbon nanotubes $\kappa \sim 300\text{ W/mK}$, while for small outer diameter ($d_{\text{out}} \sim 10\text{ nm}$) carbon nanotubes $\kappa \sim 1100\text{ W/mK}$. Our observed diameter dependence of κ is qualitatively similar to, though less pronounced, than reported in Ref. [13]. The origin of this diameter dependence is unclear. It has been suggested that, since in conventional thermal conductivity experiments heat is injected from the contacts into the nanotube via the outermost shell and the coupling is much weaker along the c axis than in the a - b plane of graphite or hexagonal boron nitride, it is possible that the

outermost shell dominates the thermal transport. However, when plotting the thermal *conductance* data with respect to $2\pi d_{\text{out}}$, we do not observe a clear correlation between them, making such a nonuniform heat flow explanation unlikely. Alternatively, theoretical studies have suggested that interlayer phonon scattering can significantly reduce the thermal conductivity of graphite [26], and similar inter-shell scattering mechanisms might be expected for multi-wall nanotubes. From transmission electron microscope imaging we find that nanotubes with $d_{\text{out}} \sim 10\text{ nm}$ generally have ~ 10 shells, while nanotubes with $d_{\text{out}} = 30\text{--}40\text{ nm}$ generally have 60–90 shells. Thus the increasing shell number with increasing d_{out} supports the inter-shell scattering picture.

The thermal conductivity can be used to estimate the phonon mean free path using the expression $\kappa(T) = \sum Cvl$, where C , v , and l are, respectively, the specific heat, group velocity, and phonon mean free path, and the sum is over all phonon states. Since currently there are no available data for heat capacity of boron nitride nanotubes, we assume the ratio of heat capacity of hexagonal boron nitride to graphite to be the same as that of boron nitride nanotubes to carbon nanotubes. Choosing $v = 10\text{ km/s}$ estimated by theory [27] and following the diameter dependence of κ in Fig. 3, we estimate that the room temperature phonon mean free path would reach 200 nm for isotopically pure boron nitride nanotubes with diameter 10 nm, comparable to $l = 500\text{ nm}$ determined from previous experiments on an isolated carbon nanotubes with a similar diameter [15].

The isotope enhancement factor of 50% for boron nitride nanotubes is dramatic. From simple models we infer that this enhancement has several contributing factors. First, as previously stated, natural abundance boron has a significant isotopic disorder (19.9%). Second, the one-dimensional structure of nanotubes should further increase the isotope enhancement factor by promoting phonon localization due to isotope scattering. Third, it has been suggested that the isotope effect can change the phonon scattering time (τ) by [9]

$$\frac{1}{\tau} = \frac{c_i a^3 \omega^4}{4\pi v^3} \left(\frac{\Delta M}{M} \right)^2, \quad (2)$$

where c_i is the fractional density summing over all scattering sites, ω is the frequency, v is the average sound velocity, and ΔM is the mass deficit associated with the lattice atoms of mass M and atomic spacing a . Equation (2) favors light elements such as boron.

It is interesting to note that the observed strong diameter dependence of κ may influence the isotope enhancement factor. For large-diameter nanotubes with many walls, for which intershell phonon scattering dominates the phonon transport, isotopic disorder effects play only a secondary role, and hence the isotope enhancement factor might be depressed. For small-diameter nanotubes with few walls,

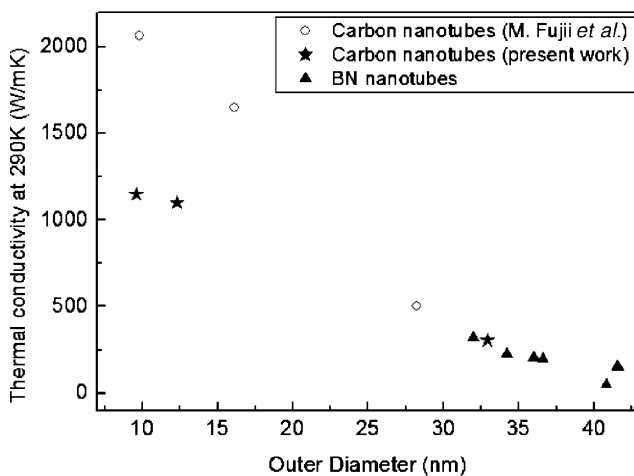


FIG. 3. The $\kappa(290\text{ K})$ vs outer diameter of various boron nitride nanotubes (solid triangles) and carbon nanotubes (solid stars). Data from Ref. [13] are also shown for comparison (open circles).

the phonon mean free path becomes more limited by isotope or impurity scattering along the nanotube axis. Thus, the isotope enhancement factor of 50% here observed for large-diameter boron nitride nanotubes may well represent a lower limit for boron nitride nanotubes in general [16,28].

In summary, a giant ($\sim 50\%$) thermal isotope effect has been observed for quasi-one-dimensional boron nitride nanotubes, supporting predictions that low-dimensional materials can have dramatic thermal isotope effects. Isotopically enriched boron nitride nanotubes have $\kappa(T)$ similar to carbon nanotubes. The high thermal conductance of individual tubes or tubes in arrays might be exploited for thermal management applications, an issue of great current concern in electronics and power industries. Specifically, boron nitride nanotubes could serve as electrically insulating yet highly thermally conducting wires, efficiently removing heat locally and piping it away via nanotube-based phonon waveguides.

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC03-7600098, and by the NSF under Grant No. EEC- 0425914.

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