Low-dimensional phonon specific heat of titanium dioxide nanotubes

C. Dames
Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467

G. Chen
Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 28 January 2005; accepted 26 May 2005; published online 11 July 2005)

The specific heat of multiwalled titanium dioxide (anatase phase) nanotubes has been measured between 1.5 and 95 K. Bulk anatase and rutile were also measured. The nanotube specific heat approaches that of bulk anatase at high temperatures. Below about 50 K the nanotube specific heat begins to show large enhancements compared to bulk. Using an anisotropic elastic continuum model, this can be understood qualitatively as a transition to low-dimensional behavior. Below about 3 K there is a second transition and the nanotube specific heat becomes nearly constant, exceeding bulk anatase by an order of magnitude or more at 1.5 K. © 2005 American Institute of Physics.

[DOI: 10.1063/1.1990269]

The lattice specific heat \( C \) contains important information about the modified phonon spectrum in low-dimensional systems such as nanotubes (NTs). For acoustic phonons with linear dispersion in systems of dimensionality \( D \) of 1 or higher, standard Debye theory predicts a density of states proportional to \( \omega^{D-1} \), where \( \omega \) is the frequency. At low temperatures \( T \) this corresponds to a specific heat proportional to \( T^D \), enhanced compared to bulk. Nanotubes may exhibit varying dimensionality at different temperatures as the thermal average wavelength evolves compared to the different length scales (wall thickness, diameter, and nanotube length). Nanotube phonons have been studied extensively in carbon nanotubes (CNTs).\(^1\) The specific heat of single-walled CNTs shows a large increase over that of graphite, in good agreement with theory down to 2 K,\(^2\) with evidence for an additional, but less-well-understood, contribution below about 0.6 K.\(^3\) Different multiwalled CNT samples have shown both large\(^4\) and small\(^5\) enhancements compared to graphite. Here, we extend the study of nanotube phonons by investigating the enhanced specific heat of multiwalled titanium dioxide (anatase phase) nanotubes.

These anatase nanotubes have potential applications for solar cells, electrolysis, and photocatalysis. Compared to the strongly anisotropic layering of graphite, anatase is more nearly isotropic, making this material system distinct from CNT. The optimized synthesis, described elsewhere,\(^6\) yields large quantities of crystalline nanotubes [Fig. 1(a)]. Typical dimensions are 500–1000 nm in length, 9 nm in outside diameter, and 2.5 nm in wall thickness. The nanotubes are believed to form by the rolling up of flat sheets,\(^7\) and the spacing of adjacent wall layers is about 0.70 to 0.75 nm. We also tested nanotubes with poor crystallinity and various levels of sodium contamination [estimated by energy dispersive x-ray analysis (EDX) to range from about 10 at. \% to less than 0.5 at. \%, the detection limit], obtained from suboptimal synthesis conditions.\(^6\) Table I summarizes the properties of the nanotube samples as well as anatase and rutile powder samples, which represent the specific heat of the bulk materials because the powder size is several microns.

For each specific-heat measurement, the as-prepared nanotubes, or as-received powders, were cold-pressed and cleaved into a pellet weighing about 10 mg. Although the cold-press pressure was varied from 80 to 800 MPa, no systematic influence on specific heat was observed. The measurements were performed in a commercial calorimeter (Oxford Instruments) using a standard relaxation method. The measurement uncertainties are dominated by the scatter in the total heat capacity data, and are estimated as ±4% (±1 standard deviation) for the nanotube specific heat. Because the bulk powder samples require a relatively larger addenda correction, their uncertainty is magnified to about ±10% at low temperatures.

![Fig. 1. (a) Transmission electron micrograph of high-quality anatase nanotubes. (b) Unrolling a nanotube into a rectangular parallelepiped for an elastic continuum model.](image)
The measurements were repeatable without hysteresis, even after He was introduced into the sample space and then pumped off at elevated temperatures (~70 K). Most of the sodium impurities are thought to be distributed and taken up in sodium titanate\(^6\) (Na\(_x\)H\(_{1-x}\)Ti\(_2\)O\(_7\), \(x = 0.75\)) with unknown specific heat, but if clusters of metallic Na are assumed then the contribution to the specific heat would be less than 10% for the most-contaminated samples. However, we cannot rule out the possibility of adsorbed gases influencing the low-temperature NT data because the samples typically were degassed only briefly (~30 min) under vacuum at 300 K prior to cooling.\(^5,3\) A later annealing study at 573 K in vacuum for 24 h suggests that the NT samples may have been contaminated by up to ~7.3% (NT1) or ~11% (NT2) by mass by an unknown adsorbate. EDX analysis leads us to suspect the contaminant was water. The bulk powder samples showed no evidence of similar contamination. Although it is difficult to account for the contribution of monolayers of water, we have used the mass-averaged properties of bulk anatase (our measurements) and bulk ice (Ref. 8) to estimate the impact of possible ice contamination.

Figure 2 shows the measured specific heat for bulk anatase, bulk rutile, and anatase nanotubes. The bulk rutile data are in good agreement with literature values above 20 K.\(^9\)\(^\text{--}\)\(^11\) Below 5 K, both the current and literature data for rutile follow a \(T^3\) trend down to 2.5 K where they transition to a \(T^{2.2}\) trend. However, below 9 K the current values are over twice as large as the only literature source,\(^11\) an unexplained discrepancy which far exceeds our experimental uncertainty.

The bulk anatase data are in good agreement with literature values above 50 K.\(^11\) As shown in Fig. 3(a), these data can be fit to within 10% using a combined Debye and Einstein model (\(T_D = 260 \text{ K}, T_E = 475 \text{ K}\)), implying an average sound velocity of 3560 m/s.

The anatase nanotube specific heat always exceeds that of bulk anatase, with the highest quality nanotube sample (NT1) showing the least enhancement. From 95 K down to about 60 K, the excess is about 20%–30%. From 50 K down to about 5 K, all of the nanotube curves shift to a \(T^{2.6}\) dependence, diverging from the bulk anatase. Below about 3 K the nanotube data show a second transition to a nearly constant value, exceeding the bulk anatase values by factors of 25 to 50 at 1.5 K. To estimate the impact of possible contamination of NT1 by ice, we assume that the bulk specific heat is due to 92.7% anatase and 7.3% ice. The adjusted bulk \(C(T)\) is shown in Fig. 3(b), best described with a sound velocity of 2970 m/s. In this scenario the behavior of the NT \(C(T)\) is qualitatively unchanged. The upper transition is delayed until below about 10 K, while the lower transition is unaffected.

The upper transition in \(C(T)\) can be understood qualitatively with a simple model that sums over all of the normal modes of an isolated elastic parallelepiped, assumed isotropic and incompressible for simplicity.\(^13\) [Fig. 1(b)]. Free boundary conditions are used for the length and wall thickness directions, while periodic boundary conditions are used for the circumferential direction. This is essentially a zone-folding scheme similar to those that have been applied to carbon nanotubes.\(^1,14\) Although our model does not explicitly distinguish between longitudinal, transverse, and twist acoustic modes, the method for counting modes should ensure the correct density of states at low energies as long as curvature effects can be neglected. This is expected to be a good approximation for these NT because of their relatively large diameters.\(^1\) This model requires the average sound velocity and Einstein temperature of bulk, which were taken from our fits to the bulk anatase measurements. Because of the uncertain coupling strength between layers of the wall, we have performed the calculation for assumed wall thickness of both 0.725 nm (model A: weak coupling) and 2.5 nm (model B: strong coupling). As shown in Fig. 3, these two calculations approximately bound the measurements of NT1.

Using this model the upper transition in the nanotube specific heat is interpreted as a shift from three-dimensional (3D) to two-dimensional (2D) behavior. A transition is expected because the average thermal wavelength \(\lambda\) is comparable to the nanotube wall thickness. Well below the Debye
temperature \( \lambda \) for anatase is conveniently estimated using \( \lambda T \approx 35 \) \( \text{nm K} \), analogous to Wein’s displacement law for photons.\textsuperscript{15} Above about 15 K model A (weak coupling/thin wall) is a good fit to the unadjusted data [Fig. 3(a)]. However, below 15 K the nanotube specific heat decreases more quickly than the models, and below about 6 K model B (strong coupling/thick wall) is a better fit to the data. After adjustment for possible ice contamination \( C(T) \) is well described by the thick-wall limit down to about 3 K [Fig. 3(b)].

Around 3 K the average phonon wavelength becomes comparable to the nanotube circumference, and the model predicts another transition from 2D to one-dimensional behavior. However, instead of the expected \( T^1 \) trend at the lowest temperatures, the data become essentially constant. Zero-dimensional (0D) behavior can be ruled out because \( \lambda \) is still much shorter than the nanotube length, and furthermore, 0D specific heat is known to fall off exponentially at low temperatures. The trend of flattening \( C(T) \) at low \( T \) is present in all of the samples, suggesting that the underlying mechanism is not dependent on Na contamination or on large amorphous fractions. One tentative explanation, which is not accounted for in our isolated-nanotube model, is low-energy vibrations of nanotubes against their neighbors. The flattening in \( C(T) \) is also reminiscent of that reported below about 0.6 K for single-walled CNT ropes,\textsuperscript{3} which was attributed to localized two-level systems of atomic rearrangement. The fact that the anatase nanotubes with more amorphous character show greater enhancement at low \( T \) would be consistent with this interpretation.

In summary, we have measured the specific heat of anatase nanotubes from 1.5 to 95 K and observed large enhancements of the specific heat compared to bulk anatase. Transitions are observed at approximately 10–50 K and at 3 K. Using an elastic continuum model, the higher-temperature transition can be understood qualitatively as a shift from 3D to 2D behavior as the average phonon wavelength becomes comparable to the wall thickness.

The authors thank Prof. M. S. Dresselhaus for critical comments. This work was funded by DOE (FG02-02ER45977), the US Army Research Development and Engineering Command Natick Soldier Center (DAAD16-03-0052), NASA, and NSF (NIRT-0210533).

\textsuperscript{6}B. Poudel, W. Wang, C. Dames, J. Huang, S. Kunwar, D. Wang, D. Banerjee, G. Chen, and Z. Ren, Nanotechnology (to be published).
\textsuperscript{15}Calculations show that the full range of transition is from about 12 nm K to about 200 nm K.