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Linear specific heat of carbon nanotubes

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The specific heat and thermal conductivity of millimeter-long aligned carbon multiwall nanotubes (MWNT's) have been measured. As a rolled-up version of graphene sheets, a MWNT of a few tens nm diameter is found to demonstrate a strikingly linear temperature-dependent specific heat over the entire temperature range measured (10–300 K). The results indicate that interwall coupling in MWNT's is rather weak compared with its parent form, graphite, so that one can treat a MWNT as a few decoupled two-dimensional single wall tubules. The thermal conductivity is found to be low, indicating the existence of substantial amounts of defects in the MWNT's prepared by a chemical-vapor-deposition method.
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While the electronic properties of carbon nanotubes have been intensively studied and shown to be peculiar, such as the sensitive dependence of the electronic structure on the diameter and chirality of the tubule, the thermal properties of the material are not well characterized experimentally, though they are as important as the former both from the viewpoint of basic research and for possible application. Benedict *et al.*[1] predicted that the temperature dependence of specific heat would depend on the diameter of the tubule, and might even show a sign of dimensional crossover as the temperature is varied. However, an experimental test of the thermal properties of the material is frustrated because the samples usually available are in a matlike form, in which each individual tubule, or rope of tubes, is rather short and only loosely connected to each other, which prevents a reliable and equilibrium thermal measurement. The recent success in synthesis of millimeter-long highly aligned array of MWNT's (Ref. 2) enables us to perform specific heat and thermal conductivity measurements on well defined samples.

The MWNT's were synthesized through chemical vapor deposition (CVD).[2] High magnification scanning electron microscopy (SEM) analysis shows that the tubules grow out perpendicularly from the substrate and are evenly spaced at an averaged intertubule distance of ~ 100 nm, forming a highly aligned array. A high-resolution transmission electron microscopy (HRTEM) study shows that most of the tubules are within a diameter range of 20–40 nm. The mean external diameter is ~ 30 nm. A tubule may contain 10–30 walls, depending on its external diameter. The continuity of the tubules, which is of crucial importance for the interpretation of the thermal-conductivity data, is indicated by SEM studies, and by Young's modulus measurement where several tenths of TPa, a value higher than that of steel, was reached.[3] The final samples used in our measurements were 1–2 mm long bundles of MWNT's stripped off from the bulk array. The apparent cross section of the samples spreads from 10^{-10} to 10^{-8} m^2. The filling factor of MWNT's in the bundles is $\sim 1.5\%$, estimated from SEM observation. This estimation may bring some uncertainty in determining the absolute values of the thermal conductivity and specific heat of the MWNT's. However, their temperature dependence is not affected by this uncertainty.

Measurements of thermal conductivity and specific heat on such tiny but well defined samples were made possible by using a self-heating 3ω method. The basic idea of the method can be traced back to 1910,[4] and was carefully tested later on. If both voltage contacts of the sample are ideally heat sunk to the substrate, but keeping the in-between part suspended (illustrated in Fig. 1), an ac current of the form $I_0 \sin \omega t$ passing through the sample will create a temperature fluctuation at 2ω, which will further cause 3ω voltage harmonics, $V_{3\omega}$, across the voltage contacts. $V_{3\omega}$ can be solved explicitly to an accuracy of $\sim 1/81$:[5]

$$V_{3\omega} = \frac{2I_0^3 LR(dR/dT)}{\pi^4 \kappa S \sqrt{1+(2\omega\gamma)^2}} \sin(3\omega t - \phi_0), \tag{1}$$

$$\tan \phi_0 = 2\omega\gamma, \tag{2}$$

where $\gamma = L^2/\pi^2 a^2, a^2 = \kappa/C_p \rho_m$ is the diffusivity coefficient, κ, the thermal conductivity, C_p, the specific heat, ρ_m, the density, R, the resistance, L, the length (between voltage contacts), and S, the cross section of the sample. By measuring the frequency dependencies of the amplitude and the phase shift ϕ_0 of $V_{3\omega}$ in proper ω and I_0 ranges (typical results are shown in Fig. 1), both κ, a^2, and hence C_p of the sample can be determined. This method was verified to be reliable on pure Pt-wire samples. The measured C_p of Pt agrees with the standard data within an accuracy of 5% from 10 K to 300 K.

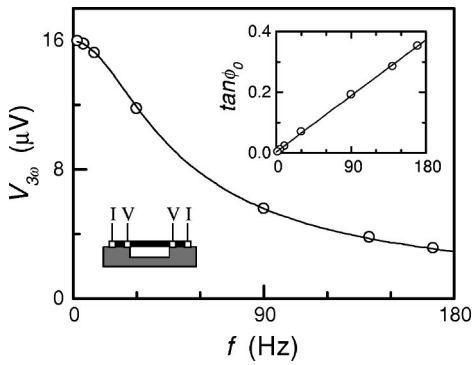

FIG. 1. The frequency dependence of the amplitude (main frame) and the phase shift ϕ_0 (upper right inset) of the 3ω voltage measured on one of the samples at $T=50$ K. Solid lines are the predictions of Eqs. (1) and (2). Lower left inset: schematic diagram of sample mounting. The samples were glued to sapphire substrate with silver paint in such a way that the inner part between two voltage contacts was suspended. The silver paint contacts serve both as electrodes and heat sinkers of the sample. The 3ω voltage was measured by using a lock-in amplifier (SR850). The whole setup was heat shielded to the substrate temperature and was maintained in a high vacuum, to preclude heat leakage through air. The total heating power at each measured temperature was adjusted to be small comparing to the value of the sample's thermal conductance. The heat leakage through radiation is estimated to be less than 5%.

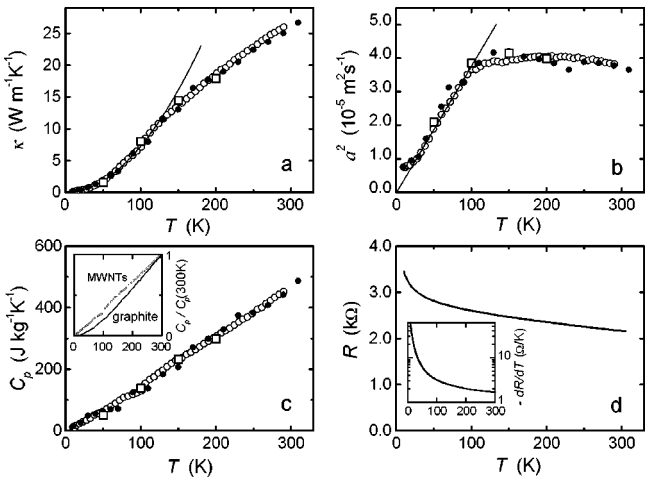

FIG. 2. (a) Temperature dependence of the thermal conductivity of three MWNT samples. It is roughly linear above ~120 K, but becomes quadratic at temperatures below: $\kappa \propto T^{1.98\pm0.03}$ (the solid line). (b) The thermal diffusivity coefficient of the samples. (c) The specific heat of the samples, calculated using the data in figures (a) and (b), showing a linear temperature dependence, which differs significantly from that of graphite (Ref. 12) (see the inset). For graphite, $C_p(300\text{ K}) \simeq 720\text{ Wm}^{-1}\text{K}^{-1}$. We note that the absolute values of the thermal conductivity, and hence the specific heat, suffer an uncertainty because of the difficulty in accurately determining the filling factor of MWNT's in the arraylike samples. However, their temperature dependencies as well as the absolute values of the diffusivity are intrinsic. (d) Typical resistance R (main frame) and dR/dT (inset) of the samples, which are used by Eq. (1) to calculate the κ and a^2.

Shown in Fig. 2 are the main results. First we notice that, while both κ and a^2 are significantly nonlinear, C_p calculated from them follows a pretty linear T dependence over the entire temperature range measured. We note that a T-linear phonon specific heat was predicted for some special systems, but seldom observed experimentally over such a wide temperature range. This behavior is dominated by the phonon contribution, since the electron contribution is negligible in the temperature range of this experiment, as expected from the fact that the electron density of states is either very low or gapped at the Fermi surface of carbon nanotubes.[6–8]

The phonon contribution can generally be written as

$$C_p = \int_0^{\omega_{\max}} k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\hbar\omega/k_B T}\rho(\omega)\,d\omega}{(e^{\hbar\omega/k_B T}-1)^2}, \tag{3}$$

where $\rho(\omega)$ is the phonon spectrum determined by the phonon energy dispersion $\omega(k)$ of different modes, and by the occupational dimensionality of phonon excitations in k space. Detailed explanation of the T dependence of C_p requires the information on the $\rho(\omega)$ of the MWNT's. While the $\rho(\omega)$ and $\omega(k)$ for single wall tubules of ~1 nm diameter have been calculated numerically and shown to have a linear phonon dispersion and one-dimensional (1D) behavior,[9–11] such calculation is virtually impossible to be performed on tubules of a few tens nm diameters, containing over hundreds of hexagonal cells along the circumference. Nevertheless, one can still find immediately from Eq. (3) that a constant $\rho(\omega)$ would result in a linear T dependence of C_p when $T \ll \Theta_D = \hbar\omega_{\max}/k_B$, the Debye temperature. This condition is believed to hold in our case, referring to the fact that the C-C bond configuration within the wall is pretty much the same as in graphite, hence its Θ_D should not be far from ~2400 K[12]. Therefore, we conclude that the linear T-dependence of C_p represents a constant $\rho(\omega)$ of the MWNT's for the phonon states excitable in the temperature range of this experiment.[13] Strictly speaking, due to the rolled-up nature of the material, there should exist some spikelike structures over the flat background of an MWNT's $\rho(\omega)$. Such structure is most significantly seen in tubules with the smallest diameter.[10] Nevertheless, thermal properties like C_p are integrated quantities over a wide frequency range and hence would be rather insensitive to the local spiky structures.

A constant $\rho(\omega)$ usually originates from linearly dispersed branches in a 1D system, or from one or more quadratically dispersed branches in a 2D system. The dimensionality of our MWNT's can be determined through the following criteria.[1] Because of the rolled up structure, the allowable phonon states are quantized in k space, forming some discrete lines parallel to the tubule axis. A tubule is strictly 1D-like if only those states on the central line are thermally excitable; otherwise, if many lines are occupied with phonons then the tubule should be 2D-like. A simple estimation shows that even at the lowest temperature of this experiment (~10 K), and even for the innermost wall of our MWNT's (which has the largest interline distance), the thermally excitable phonon states would cover several to several tens of lines, depending on whether a linear or a quadratic dispersion is assumed. Therefore, our MWNT at higher tem-

peratures (i.e., $\geqslant 10$ K) can approximately be regarded as a 2D system with a constant $\rho(\omega)$.[14]

Such a phonon structure is similar to, but still different from, that of graphite, whose $\rho(\omega)$ is only roughly flat in a moderate frequency range.[15] The similarity is easy to understand, for graphite is the parent material of MWNT's. The central issue now is how to understand the difference in $\rho(\omega)$ induced by the rolling up of graphene sheets. For flat sheet, as in graphite, its hexagonal symmetry leads to a quadratically dispersed acoustic-phonon branch, corresponding to the out-of-plane vibration mode of the sheet. This branch contributes to a constant term in $\rho(\omega)$.[15–17] However, there are at least two reasons that prevent graphite from strictly demonstrating a constant $\rho(\omega)$ and a linear C_p. First, interlayer coupling could not be neglected at low frequencies, which gives $\rho(\omega) \sim \omega$ and $C_p \sim T^2$ (in the temperature range of interest here we do not consider the case of very low frequencies). Second, the other two linearly dispersed in-plane branches, which gives $\rho(\omega) \sim \omega$ and $C_p \sim T^2$, also contribute to the total specific heat.[16] Therefore, no strictly T-linear C_p as well as strictly flat $\rho(\omega)$ exist.[12]

From the above discussion, the fact that an MWNT's linear $C_p(T)$ extrapolates to the (0, 0) point seems to indicate that the out-of-plane acoustic mode (as in a graphene sheet) dominates the thermal properties of this 2D-like material, and that the two in-plane acoustic modes, presumably linearly dispersed, give a negligible contribution. Here an assumption has spontaneously been made: for a MWNT of a few tens nm diameter, its acoustic phonon modes can still be classified as one LA and two TA's, as in graphite. This assumption should be true, for at most temperatures of this experiment the wavelengths of the majority of phonons are much shorter than the tubules' diameter, i.e., many lines in k space are occupied with phonons. The striking linearity of C_p further indicates that the coupling between the walls in MWNT's is much weaker than that in graphite, so that one can treat a MWNT as a few decoupled single wall tubules, as far as their vibrational properties are concerned.

Two facts may be responsible for the weak interwall coupling: the larger interwall distance in MWNT's than the interlayer distance in graphite, and the turbostratic stacking of adjacent walls which is unavoidable in the rolled-up structures. Although there are a number of experiments indicating that the interwall distance in MWNT's is larger than that in graphite,[18,19] a recent HRTEM study[20] shows that the interwall distance decreases as a tubule's diameter increases. At diameters $\geqslant 10$ nm it saturates to ~ 0.344 nm, a characteristic interlayer distance in turbostratic stacking. Therefore, we believe that the weak interwall coupling in MWNT's is rather caused by the turbostratic stacking of adjacent walls.

The thermal conductivity of our MWNT's is rather low compared to what is generally expected.[21] Since the apparent Wiedemann-Franz ratio $R(\kappa S/L)/T$ is about two orders of magnitude larger than the free-electron Lorenz number, the measured κ essentially reflects the phonons' contribution, similar to the cases of graphite and carbon fibers. Whereas κ of graphite shows a marked maximum around 100 K, κ of our MWNT's monotonously decreases with lowering temperature. If roughly expressing κ as $\kappa \sim T^n$, then n is a little

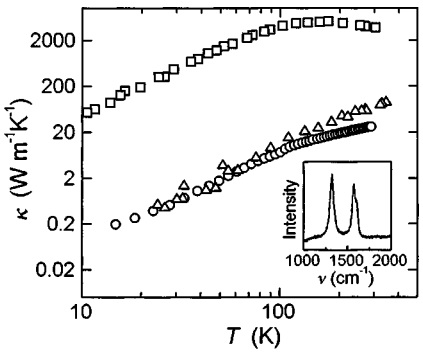

FIG. 3. A log-log plot of the thermal conductivity of our samples (O) compared with that of vapor-grown carbon fibers (Ref. 25) (△: as-grown, □: heat treated at 3000 °C). Inset: First-order Raman spectrum of our MWNT's.

less than unity above ~ 120 K, resulting in a faint hump of diffusivity a^2 between 120–300 K. Below ~ 120 K, κ follows almost a quadratic T dependence, i.e., $n \simeq 1.98$, leading to a nearly linear decrease of a^2, and hence, a nearly linear decrease of the apparent phonons mean-free path with temperature. This behavior indicates that a drastic change in the phonon scattering mechanism occurs at ~ 120 K. Compared with graphite, although the κ of the latter also roughly takes a quadratic temperature dependence at low temperatures, the mean-free path of phonons in graphite is rather confined by boundary scattering, because the C_p of graphite is quadratically temperature dependent at low temperatures [i.e., below 70 K (Ref. 22)]. An energy-dependent mean-free path in MWNT's contradicts the usual boundary scattering mechanism seen in graphite and other solids at low temperatures. One difference between nanotubes relative to graphite sheets is the existence of the radial breathing mode in the former.[23] Perhaps the thermal excitation of such phonons is responsible for the change in scattering mechanism around 120 K. Further investigation is needed to clarify the issue.

The MWNT's grown by the CVD method at temperatures as low as ~ 600 K are far from perfect, as indicated by the fact that their thermal conductivity and electrical conductivity are about two orders of magnitude lower than those of perfect crystalline graphite at room temperature.[24] Figure 3 shows that the T-dependent behavior of MWNT's resembles those of not well-graphitized materials such as the as-grown carbon fibers and glassy carbons,[25] whose in-plane domain size of the hexagonal ordering is only a few nm. It has been shown in those materials that the mean-free path of the phonons deduced from the κ data is well correlated with the domain size [25,26]. We therefore speculate that the domain size of our CVD-derived MWNT's is the same as the phonon mean-free-path l, which is a few nm if estimated using the classical relation $\kappa \sim C_p v l$ and assuming a characteristic sound velocity $v \sim 10^4$ m/s. This picture is further supported by micro-Raman investigation wherein the 1360 cm^{-1} band, which is prohibited in perfect graphite, becomes substantially high in our MWNT's, resembling the case of as-grown CVD carbon fibers.[25] Nevertheless, the gross phonon spectrum is unlikely to be significantly altered upon the reduction of the domain size to a few nm.[25] Therefore, our previous discussions on the C_p and the phonon structure of the MWNT's should still be valid.[27]

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