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Abstract

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Electrical and thermal properties of C_{60}-filled single-wall carbon nanotubes

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We report measurements of electrical resistivity, thermopower and thermal conductivity of highly filled C_{60}@SWNT (single-walled carbon nanotube) and unfilled controls, from 1.5 to 300 K. The data suggest that the C_{60} chains provide additional conductive paths for charge carriers, increase the rate of phonon scattering, and block interior sites from sorbing other gas molecules.

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Single-wall carbon nanotubes (SWNT) filled with C_{60} were discovered by Smith *et al.* [1]. These "peapods" generally occur as highly-ordered long chains with the same ~ 10 Å intermolecular spacing as in the fcc solid. Short clusters of 2-20 fullerenes are sometimes found. C_{60} - C_{60} and C_{60} - SWNT interactions are expected to influence structure, dynamics and electronic properties [2,3]. Elucidation of the growth mechanism [4] provided the basis for rational synthesis of highly filled samples [5]. This in turn enables the study of their physical properties, about which little is known. C_{60} is a strong electrophile, so one might expect the surrounding tubes to become hole-doped. However, theory predicts only weak occupancy of a quasi-1D band derived from a chain of C_{60} LUMO orbitals [3]. In the only experiment published to date, Hirahara *et al.* found that the electrical resistance diverged more steeply with decreasing T than for unfilled SWNT [6]. This was attributed to carrier scattering by the local electrostatic potential from (presumably charged) fullerenes. No absolute values were given.

Here we report temperature dependence of electrical resistivity ρ, thermal conductivity κ and thermoelectric power or Seebeck coefficient S, measured on buckypapers of highly filled and control samples [5], the only difference being the absence of C_{60} in the reaction tube during the filling step. The average tube diameter is around 1.3 nm. Transmission electron micrographs of the filled sample show a preponderance of well-ordered nanotube ropes filled with C_{60} molecules. Weight uptake measurements reveal a filling fraction of 90% [5].

Measurements of ρ(T) were carried out from 1.5 to 300 K in helium vapor. Filled and control samples for all measurements were cut from the same buckypaper. These were vacuum-degassed at 800°C for 1 hour in dynamic vacuum (5×10^{-6} Torr) and then exposed to air for about an hour during transfer to the cryostat. Adsorbed oxygen acts as a p-type dopant in nanotubes [7–9]. The effect on ρ at saturation is only about 25% [7] but much more dramatic on S (see below). The results are shown in Figure 1. The overall T dependence is non-metallic for both, while the low T upturn in ρ is strongly reduced in the filled sample. The ratio ρ(empty)/ρ(filled) decreases from $\sim$7 at 1.5 K to about 1.5 at 300 K. Both the small reduction in ρ at high T and the overall T dependence

suggest that charge transfer from C_{60} to SWNT is minimal, since alkali-doped buckypaper exhibits metallic ρ(T) from 7 to 300 K and a reduction in ρ(300 K) of a factor 40 [10]. Our results are qualitatively the opposite of what was reported in Ref. [6]. Electron diffraction of our samples confirms the existence of highly-ordered 1-D chains of C_{60} with period 9.9 Å [5], the consequence of dense filling and attractive intermolecular interaction. Long chains of C_{60} molecules can form new energy bands derived from the C_{60} LUMO. These will reduce ρ if they cross the Fermi level, which happens in theory for (10,10) SWNT with C_{60} lattice parameter 9.824Å [3]. However the new bands are only weakly occupied. It is not known if they also exist in zigzag or chiral tubes of similar diameter, so the quantitative effect on bulk resistivity is impossible to estimate while the qualitative effect is consistent with our data. The inset to Figure 1 suggests another mechanism whereby new conductive paths formed by C_{60} chains can effectively bridge defects on the tube walls and thereby reduce the effects of charge carrier localization at low temperature.
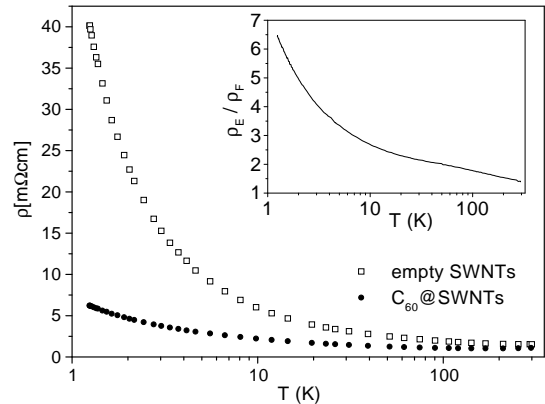

FIG. 1. Four-point resistivity vs. T for C_{60}@SWNT (filled circles) and empty control sample (open squares); the ratio of empty to filled is shown in the inset.

We measured κ(T) from 10 to 285 K on filled and control samples in vacuum. These were exposed to air for two weeks after the vacuum degassing prior to measure-

ment. The effect of air exposure on κ has not been studied to date. We used a comparative steady state method with two constantan standards attached to the ends of the sample [11]. These allow us to correct approximately for radiative heat losses by taking the average of upper and lower bounds on κ. Differential type-E thermocouples measured temperature drops across the sample and standards. The data are shown in Figure 2. The temperature dependence is essentially the same as has been reported for aligned buckypapers made from purified laser ablation SWNT [12] and is very closely the same for filled and control samples. The magnitude of κ(filled) appears to be ~20% higher than κ(control) at all T, although this difference is close to the experimental accuracy. A previous measurement of a sample comparable to the control gave ~ 30 W/m-K at 300 K [12] after correction for empty volume. This factor is generally ~ 0.5 so our result for the filled sample indeed indicates little or no contribution by the C_{60} chains to κ of the filled tubes.
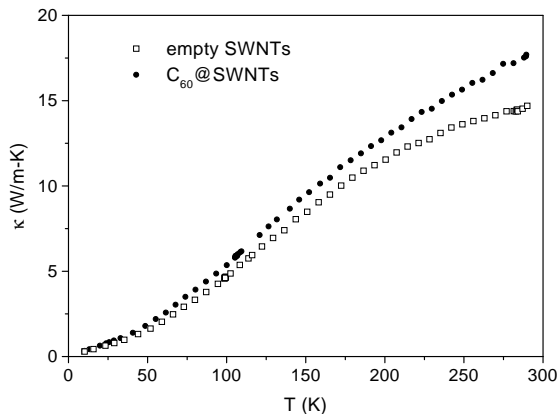

FIG. 2. Thermal conductivity vs. T for C_{60}@SWNT (filled circles) and empty control sample (open squares).

In general the presence of a C_{60} chain inside a SWNT introduces more phonons and κ should increase. However, most of the new modes are intramolecular, and will propagate very slowly along the chain. The only possibly relevant new phonon is the 1-D LA mode describing the center-of-mass molecular lattice vibrations. Assuming this mode is decoupled from the tube modes, and approximating the C_{60} as smooth spheres [13,14], the usual harmonic dispersion $\omega(q)$ gives a sound velocity 3817 m/s and Debye temperature 85.1 K. This is negligible compared to the LA-derived sound velocity of the tube, so unless the mode coupling between chain and tube is unusually large, we don't expect a significant enhancement in κ by filling the tubes.

A second mechanism which would enhance κ is the stiffening of the SWNT by forces acting between the C_{60} chain and the tube. We estimated these for several tube diameters using a continuum Lennard-Jones model [13]. Both the radial and longitudinal components decrease rapidly with increasing tube radius, and are very small

compared to the C-C interaction in graphene. As a worst case scenario, the largest force acting on a carbon atom for a tightly-fitting C_{60} filled 12.7 Å diameter tube was ~ 250 meV/Å. This translates to a radial displacement of only ~ 0.04 Å, too weak to stiffen the tubes significantly by displacing C atoms from their equilibrium positions. This conclusion is borne out by Raman scattering, which shows no significant upshift of the radial breathing modes [15,16].

A compensating effect might be the following. C_{60} molecules inside SWNT could lead to stronger phonon scattering and thus to a *reduction* in κ if small clusters dominated over long ordered chains. In this case the mean free path of LA tube modes would be limited by cluster size and/or density. This is probably not the case for the present samples. The electron diffraction results noted above show resolution-limited Bragg sheets from the 1-D C_{60} chains at 80 K [5], implying not only long-range order but also the same 1-D lattice constant for chains in tubes with different chiralities and diameters hence different axial periodicities. Thus the peapod is best described as a floating solid in which the two periodicities are completely decoupled.

Phonon scattering could also reduce κ by large-amplitude random thermal C_{60} displacements about their equilibrium positions, a more local effect than those considered above. With sufficient momentum transfer to the tube resulting from these stochastic events, the propagating tube modes may scatter from fluctuating atomic positions on the tube, decreasing the phonon mean free path. More accurate data and/or single tube experiments are necessary to assess the relative importance of the various mechanisms.
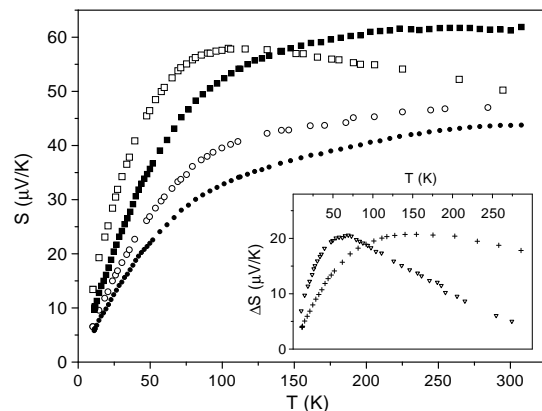

FIG. 3. Figure 3. Seebeck coefficient S vs. T for C_{60}@SWNT (circles) and empty control (squares). Open and full symbols refer to partial and full oxygen doping regimes (see text). The inset shows the difference between TEP of control and filled samples for partial ($\triangledown$) and full oxygen doping (+).

Thermopower is known to be extremely sensitive to air exposure [7–9]. All measurements of bulk material show strongly p-type behavior, which inverts to n-type

upon *in situ* degassing [7]. In an attempt to minimize this effect, both filled and control samples were additionally baked at 200° C for 24 hours in dynamic 2×10^{-7} Torr vacuum. Air exposure for about half an hour during mounting was unavoidable; we refer to this state as "partial doping". Measurements were repeated after one week additional air exposure for comparison. Assuming this suffices for saturation, we refer to this state as "full doping". Data for both exposure conditions are shown in Figure 3; the difference S(filled)−S(control) is plotted in the inset. For partial doping, S(T) of the filled sample increases monotonically (open circles) while the control (open squares) shows a broad maximum near 100 K and an overall larger value than the filled sample. The 60 μV/K value of S(max) for the control is typical for air-exposed mats and buckypapers [7–9]. We propose that the different S(T) behaviors for partial doping are due to the different effects of phonon drag in C_{60}-filled and control samples. The phonon drag contribution to S is inversely proportional to the charge carrier density and linearly proportional to the phonon relaxation time. As discussed above, phonons are more likely to scatter in filled than in empty tubes. The result is a larger phonon relaxation time and larger phonon drag contribution in empty tubes than in filled ones. Since phonon scattering increases with increasing T, the phonon drag contribution to S should vanish at high T; the difference plot (inverted triangles) bears this out, with S(filled) - S(empty) peaking near 50 K.

Full air doping gives substantially different results. Surprisingly, S(T) of the filled sample decreased at all T despite the additional exposure to air (filled circles). For the empty control, the low-T slope decreased and the peak vanished (filled squares), the net effect of the additional air exposure being smaller S below $\sim$ 130 K and larger above it. The difference between filled and empty is shown in the inset to Figure 3 (+++).

This behaviour can again be explained by the combined effect of C_{60} filling and gas sorption on phonon drag. We expect that brief exposure leads mainly to oxygen adsorption on exterior surfaces of tubes and ropes. For longer air exposure, the control sample is likely to take up more oxygen inside the tubes by diffusion, since the interiors are accessible and empty. Additional oxygen increases both the phonon scattering rate and the charge density, so the phonon drag contribution to S(control) is smaller than for partial doping. This explains the smaller slope of S(T) at low T and the absence of the peak in S(T). At high T the oxygen doping effect domimates, so S(control) is higher for full doping.

Conversely, for the filled sample we expect the presence of interior C_{60} to effectively block the in-diffusion of gas molecules during extended exposure to air. Further oxygen doping might occur via additional surface adsorption, but the dominant effect seems to be increased probability of phonon scattering from adsorbed molecules.

These observations suggest two important things: the phonon drag contribution to the Seebeck coefficient of SWNTs is substantial for a large temperature range (10-300 K), and interior sites for oxygen are more effective for charge transfer than surface sites. However, to explore the sensitivity of C_{60}@SWNT to oxygen doping *in situ* measurements are required. The energetics of an oxygen molecule inside a nanotube will have to be studied as well.

In summary, we measured electrical resistivity, thermal conductivity and thermopower for C_{60} filled and empty SWNT. Our observations suggest that long chains of C_{60} molecules inside SWNT form additional conductive paths, increase the phonon scattering and effectively prevent other molecules from entering a carbon nanotube.

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