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Crystalline Ropes of Single Wall Carbon Nanotubes: Structure, Electronic Transport and Intercalation

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X-ray diffraction and resistivity measurements on bulk single-wall carbon nanotube material are described. The tubes self-organize during growth into a triangular lattice. The temperature dependence of the resistivity is consistent with a metallic system at high temperatures.

Keywords: nanotubes, intercalation, resistivity

Single wall carbon nanotubes (SWNT) are obtained in high yield by metal-catalyzed double-laser ablation of graphite [1]. X-ray diffraction, electron microscopy and electron diffraction [2] indicate a remarkable uniformity of diameter and (10,10) wrapping, and self-organization into two-dimensional "rope" crystallites consisting of hundreds of 13.6 Å diameter close-packed tubes at the van der Waals separation 3.2 Å. In Figure 1 we have subtracted the background (top curve, +++++) and compare the result with a calculated profile (solid curve) which is the convolution of a 2-D triangular lattice with **a** = 16.95 Å, a size-limited linewidth and a form factor which approximates the tube as a 13.8 Å diameter cylinder (dashed curve). The observation of well-defined 2-D lattice reflections is *prima facie* evidence that the SWNT diameters are highly uniform.

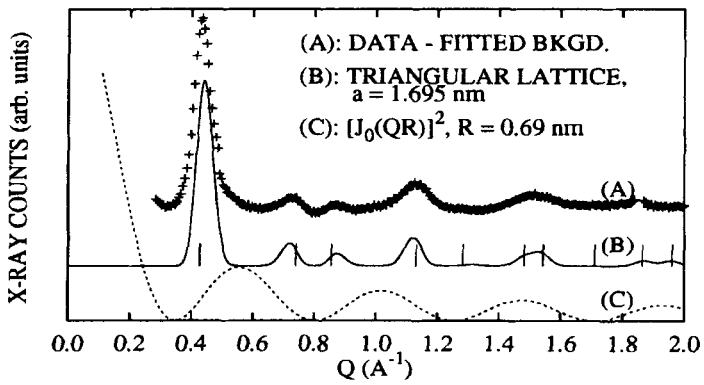

Figure 1. Background-corrected x-ray profile of bulk SWNT material (top) compared with a model calculation (solid curve) assuming uniform cylinders of charge (dashed curve = form factor). Vertical ticks are the predicted Bragg positions for an infinite crystal.

The most striking evidence that these are metallic (as predicted) is a positive ρ(T) slope, observed both from single ropes and from unoriented bulk samples above $\sim$ 30 K and 200 K respectively [3]. This high-T behavior is accounted for semi-quantitatively by electron backscattering from torsional shape fluctuations, a process which is not frozen out below Θ_D (as in Bloch-Gruneisen theory) due to the unusual 1-D Fermi surface [4]. At low T, dρ/dT becomes negative.

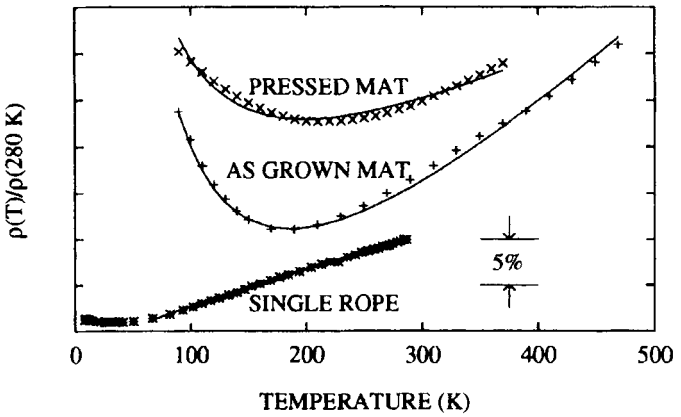

Figure 2. Relative resistivity vs. temperature for SWNT rope materials: as-grown and lightly pressed mat (4-point, unoriented) and oriented bundle of ropes (2-point, scaled to 4-point measurement at ambient T). Solid curves are polynomial fits.

The rope lattice provides an obvious new candidate for intercalation, perhaps with redox chemistry similar to that of graphite intercalation compounds or fullerides, but with quasi-1D guest-host structures more analogous to doped conjugated polymers. In common with graphite but in contrast to solid C_{60}, C_{70} etc., exposure of bulk SWNT samples to bromine vapor leads to a rapid decrease (minutes) in resistance by more than an order of magnitude [5]. The fast kinetics are consistent with the very porous, $(CH)_x$-like morphology of the as-deposited bulk material, while the resistance drop suggests that the cylindrical isomorph of 3-coordinated carbon may be amenable to oxidative intercalation, in contrast to the more spherical fullerenes. Vapor phase reactions with potassium produce a similar conductivity enhancement [5]. Figure 3 shows a series of ρ(T) measurements on one such sample intercalated at 200°C. Curve (A) is the pristine sample, and curve (B) was measured after transferring the doped sample from the reaction tube into the cryostat. The overall reduction in ρ is about a factor of 30 at 300 K, the high T behavior remains metallic, and T* is now below our 90 K measurement limit. Heating overnight to 580 K in the cryostat vacuum yielded curve (C), from which we find a smaller d$< \rho >$/dT slope with $< \rho >$ still 1/10 the pristine value.

For both dopants the R(T) slope is positive, suggesting metallic behavior of either n or p-type. The weight uptakes correspond approximately to $C_{25}Br$ and KC_8 respectively, yet these samples contain negligible amounts of graphite, nanocapsules or multi-wall tubes. Rationalizing these large weight uptakes within a model of uniform intercalate superlattice formation requires either multiple "rods" of intercalate per channel or a GIC-like tiling on the outer surface of each tube.

The conductivity enhancement with doping is consistent with Raman scattering data for the same dopants [5], indicating that electron or hole doping accompanies reductive or oxidative intercalation, as in graphite, with enhanced metallic behavior in either case due to increased carrier density. X-ray work is in progess to identify the structures of the doped systems. If the doping concentration can be appropriately fine-tuned (e.g. solid solution as opposed to line phase behavior as in GIC's and fullerides), then perhaps the intrinsically weak electron-phonon interaction can be overcome by a large $N(E_F)$ to obtain superconductivity.

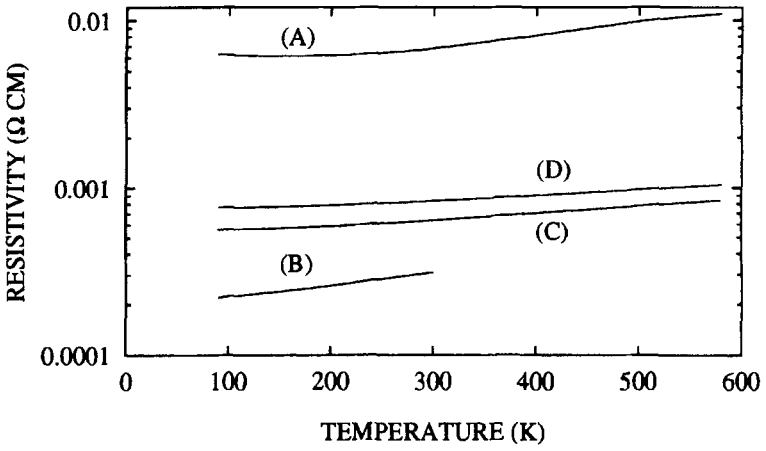

Figure 3. Resistivity vs. temperature for a bulk SWNT sample. (A) pristine; (B) after K doping at 473 K; (C) after 580 K overnight; (D) after 3 days at 580 K.

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