

DOPED SINGLE WALL CARBON NANOTUBES - PRESSURE EFFECTS

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Introduction

Purified single wall carbon nanotubes (SWNT) produced by double laser ablation of metal-doped graphite targets* show a diameter distribution peaked around 13.6 Å, close to that of a (10,10) nanotube. The tubes are packed in a two-dimensional triangular close-packed lattice, with inter-tube spacing 3.4 Å typical of van der Waals interactions. The interstitial channels in the bundles are ~2.5 Å in diameter, providing easy chemical access of dopant atoms and molecules to the interior of the bundle. It has been demonstrated that SWNT can be doped with either donors (alkali metals) or acceptors (Br₂, I₂) [1,2].

Recently we have shown that quasi-hydrostatic compression of purified, unoriented, highly crystalline single-wall carbon nanotube material reveals an exceptionally large and reversible volume reduction [3]. We suggested that it originates from the crushing and flattening of tangled ropes of nanotubes, changing the tube cross-section from circular to elliptical. The proposed distortions in tube shape and lattice symmetry would have profound implications for chemical doping/intercalation. At sufficient pressures, the trigonal channels initially present between the circular tubes may become too small for many guest species to enter the lattice. Similarly, a doped SWNT lattice should be considerably stiffer than the pristine material at modest pressures; at sufficiently high P one might expect phase separation into pure guest and pure SWNT according to le Chatelier's principle.

Here we present *in situ* measurements of four probe dc resistance vs. pressure of potassium and iodine doped SWNT mats, performed in a Bridgman-type anvil apparatus under quasihydrostatic pressures up to 90 kbar.

Experimental

Sample preparation. - Doping with potassium was carried out by standard (in case of graphite intercalation) two bulb vapor-phase technique in sealed pyrex tubes at 270°C for 20 hours. I₂ intercalation was performed by immersing

* The authors are grateful to A. Thess, A.G. Rinzler and R.E. Smalley of Rice University, Houston, USA for providing the laser-produced purified SWNT material.

SWNT mats in molten iodine in evacuated pyrex tubes at a temperature 160°C for 8 hours [2].

High pressure & transport properties. - Four-probe dc measurements of resistance R vs. pressure P up to 90 kbar were performed under quasi hydrostatic conditions in a Bridgman-type anvil apparatus and a double-acting hydraulic cylinder with 500-ton capacity. We used rectangular strips 2 mm wide and 6mm long (2 mm between the potential contacts). Potassium doped samples were transferred into teflon ampoule with leading-out contacts in an inert argon atmosphere. The ampoule was sealed by pressurization and placed into high pressure assembly. All I₂ sample handling was done in open air, as iodine-intercalated samples were reported to be stable under ambient conditions [2]. In case of I₂-SWNT we used a standard NaCl assembly (details of high pressure assemblies, contact arrangement and pressure experiment are given in [4]).

Results and discussion

Figure 1 presents temperature dependence of four-probe resistance R of pristine (Fig.1^a) and K-doped (Fig.1^b) mats. By 10 kbar pressure the resistance of doped samples drops by 40%, the similar abrupt resistance decrease (but higher by an order of magnitude) is typical for the initial low-density unpurified (~70% SWNT) material, and is associated with the compaction which improves number and density of contacts between ropes. From 10-50 kbar K-SWNT resistance decreases gradually with pressure contrary to that of pristine nanotubes (Fig. 1^a). The characteristic increase of resistance of pristine nanotubes above 10 kbar we associate with the formation of local deformations (from elastic elliptical flattening to the formation of graphite at higher pressures). On doping the substantial electron density added to the host carbon framework should favor one of the mechanisms responsible for transport properties - hopping or tunneling between tubes or ropes, and probably may inhibit the formation of some kind of defects in this pressure range. On the other hand, doping is known to reduce inter-tube correlations and this may affect the resistance much more significantly, masking the pressure effect of imposing

dilute concentration of small defects. At higher pressures - above ~50 kbar, the resistance slightly increases denoting the irreversible local deformations of some kind (leading to 20-30% increase of 1 atm. resistance after the first pressurization to 90 kbar).

After exposing of K doped SWNT sample to open air resistance vs. pressure dependence exactly restores $R(P)$ behavior of pristine nanotubes, proving the reversibility of potassium vapor-transport doping.

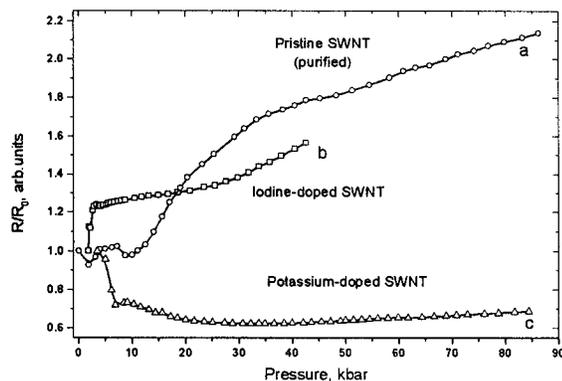


Figure 1 Pressure dependence of four-probe resistance R of pristine (a), iodine- (b) and potassium-doped (c) SWNT mats (normalized to their respective ~ambient P values).

The pressure dependence for resistance for iodine doped sample is presented on Figure 1^b. In the whole pressure range we observe the increase of mat resistance over the entire pressure range. The strongly positive pressure coefficient of I_2 -SWNT sample is surprising. Since we measure some average of $R_{||}$ (along the tube or rope axis) and R_{\perp} , we observe the net effect of two mechanisms - hopping or tunneling between tubes or ropes and quasi-metallic conduction along the tube or rope. Expecting $R_{||}$ to decrease with pressure (or at least not to depend on P), the increase of average resistance may be attributed to the impairing of hopping or tunneling mechanism with pressure. The precipitous drop in c -axis conductivity is well known for acceptor graphite intercalation compounds due to the decrease in p_x overlap and weak hybridization between intercalant and p_z orbitals. $R(P)$ behavior observed suggests that hopping or tunneling transport process becomes the dominant one under pressure.

We should consider another possibility for R increasing - partial deintercalation of iodine under pressure. Since intercalation leads to the significant expansion of the rope lattice, the high pressure, diminishing the trigonal channels between the circular tubes, shall lower the stability of the intercalated sample. Despite the fact that on heating under pressure we observe the irreversible increase of the resistance which we attribute to the partial

deintercalation of iodine, the doped sample appears to be rather stable as the intercalated iodine can be essentially removed only at $T \sim 300^\circ\text{C}$ at 20 kbar (250°C at ambient pressure [2]). Although after the first pressurization to 45 kbar we observe an increase in ambient P resistance by ~12%, also attributed to the partial deintercalation, on the subsequent pressure run, when the "excessive" iodine fraction is supposed to be removed by the first pressurization procedure, we still observe the strongly positive pressure coefficient ($(1/R)dR/dP \sim 0.006/\text{kbar}$ in 10-30 kbar pressure range).

Conclusion

In situ measurements of four probe dc resistance vs. pressure of potassium and iodine doped single wall carbon nanotubes show completely different behavior of donor and acceptor doped SWNT mats. $R(P)$ dependencies observed suggest that hopping or tunneling transport process becomes the dominant one under pressure. The substantial electron density added by potassium donor atoms to the host carbon framework leads to the resistance decrease in the whole pressure range, whereas iodine doped SWNT mats show strongly positive pressure coefficient up to 45 kbar pressure. The increasing resistance in the latter case is unlikely to be due to the iodine deintercalation under high pressure conditions.

References

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Acknowledgments

The Moscow part of this work was supported by grants from INTAS (96-0927) and RFBR (98-03-32573); the Moscow/Penn collaboration was supported by NATO Linkage Grant 921350 (Moscow-Penn) and the Department of Energy, DE-FC02-86ER45254.