

ELASTIC PROPERTIES OF MULTIWALL CARBON NANOTUBES

D.E.Sklovsky*, H.Gaucher**, S.Bonnamy**, F.Beguin**, V.A.Nalimova*

* Department of Chemistry and Physics of High Pressures, Moscow State University, Moscow, 119899, Russia

** CRMD, CNRS - Universite d'Orleans, 1B rue de la Ferrollerie, 45071, Orleans Cedex 02, France

Introduction

Interesting physical and mechanical properties - high stiffness and axial strength were predicted for the carbon nanotubes [1-5] as a result of their cylindrical graphitic structure. Exceptionally high Young modulus was estimated for isolated nanotubes by measuring the amplitude of their intrinsic thermal vibrations in transmission electron microscope [6]. It was reasonable to expect the high Young modulus for carbon nanotubes close to in-plane modulus of single crystal graphite (an order of 1×10^{12} Pa). The actual experimental values vary in the range from 0.40 to 4.15×10^{12} Pa depending on the sizes of nanotubes, yielding the average value of 1.8×10^{12} Pa [6]. This high Young modulus imply very low compressibility along the nanotube axis. For graphite the compressibility along the *a* axis (in-plane) was reported to be even negative $K_a = -1.65 \times 10^{-12} \text{ Pa}^{-1}$ [7]. C-axis compressibility of graphite K_c (different authors report the values laying in the range $2.7-3.3 \times 10^{-11} \text{ Pa}^{-1}$ [7-10]) is determined by Van-der-Waals interactions between aromatic carbon nets.

We studied volume compressibility of multiwall carbon nanotubes under pressure upto 2.7 GPa at room temperature.

Experimental

Multiwall carbon nanotubes were produced by catalytic decomposition of acetylene with cobalt as catalyst at 900°C. After synthesis the nanotubes were heat treated to imperfect their structure. We studied the compression and compressibility of nanotubes "as synthesised" as well as heat treated at 2000 and 2800°C.

The measurements were carried out in a piezometer with tungsten carbide cylindrical pressure vessel, forced into the steel supporting rings and tungsten carbide pistons polished to fit the pressure vessel with the clearance not exceed 0.01 mm. The internal diameter of the cylinder was 8 mm. The pressure was loaded by 20 ton hydraulic press. The pressure was calibrated on the basis of wellknown phase transitions in bismuth, ammonium fluoride, cerium and cesium. Pressure determination accuracy varies from 0.014 to 0.047 GPa depending on pressure range. Piston displacement

was measured by the micrometer rigidly connected to the ram of piezometer. Estimating the volume of the sample under pressure we took into account the own elastic properties of the device, the increase of the cylinder bore under pressure, compression of steel sealing rings and steel self-sealing ampoule. Volume determination accuracy is 0.12-0.19%.

Results and Discussion

The volume vs pressure measurements were performed under pressure upto 2.7 GPa. For each sample 6-9 loading - unloading cycles (*l* vs *P*) were performed (Fig.1).

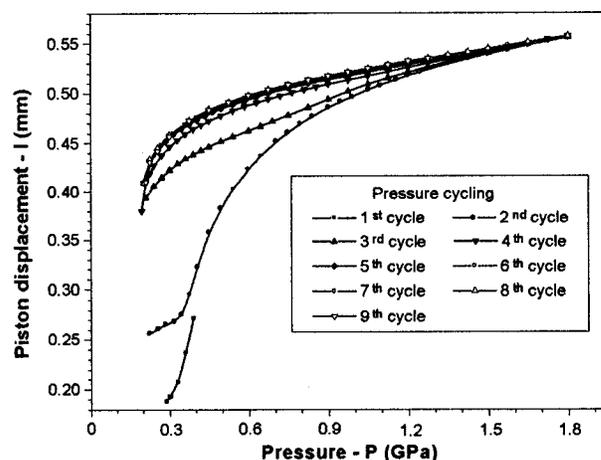


Figure 1. Piston displacement versus pressure for multiwall nanotubes sample

The first-second cycles in Fig.1 show irreversible decrease of the sample volume due to the porosity of the powdered nanotubes sample. For the following cycles $V(P)$ ($l(P)$) dependence becomes reproducible and completely reversible under pressure, retrieving the real elastic properties of the nanotubes.

Volume compressibility (K_v) of carbon nanotubes was estimated as a $V(P)$ dependence derivative. To simulate experimental data we used polynomial dependence, polynomial order being 2-6 depending on pressure range.

To estimate the compressibility of the sample we used the cycles which are reproducible at successive pressure scanning. The reproducibility is $\sim 2\text{-}3 \mu\text{m}$ ($\sim 0.05\text{-}0.1\%$). K_T versus pressure for three different samples is presented in Fig.2.

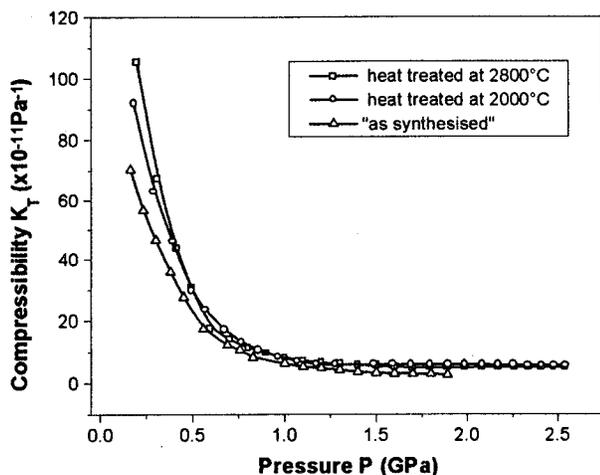


Figure 2. Pressure dependence of compressibility for the multiwall nanotubes: "as synthesised", heat treated at 2000°C, heat treated at 2800°C.

Carbon nanotubes show surprisingly high compressibility at low pressures (below 0.5 kbar): more than $20 \times 10^{-11} \text{ Pa}^{-1}$ which cannot be explained neither by the compression along the tubes nor by Van-der-Waals interactions. It cannot also be explained by the porosity of the sample as the change of the volume is reversible and reproducible and should be probably due to the elastic bending, kinking, folding of nanotubes under quasi-hydrostatic conditions. The most surprising is the perfect reproducibility of these results (high compressibility) on the cycling of the sample under pressure.

At higher pressures compressibility rapidly decreases and under pressure above 1.2 GPa becomes $(4\text{-}6) \times 10^{-11} \text{ Pa}^{-1}$. This value is quite reasonable considering graphite c -axis compressibility at this pressure $K_c \sim 2.1 \times 10^{-11} \text{ Pa}^{-1}$ [8] and volume compressibility of graphite $K_v \sim K_c$. For fullerene $K_a = 2.3$ (same units), $K_v = 3 \times K_a = 6.9 \times 10^{-11} \text{ Pa}^{-1}$. For carbon nanotubes under ideal hydrostatic conditions volume compressibility should be $K_v = K_c \times 2 = (4.2\text{-}5.5) \times 10^{-11} \text{ Pa}^{-1}$ close to the values observed.

Density versus pressure dependence (Fig.3) shows that at these pressures nanotubes reach their actual density ($2.1\text{-}2.2 \text{ g/cm}^3$) and their compressibility becomes close to that expected from their structure.

The behaviour of the nanotubes "as synthesised" and heat treated at different temperatures under pressure is similar but as a rule less perfect nanotubes have lower compressibility (Fig.2).

TEM and XRD investigations of the nanotubes after the high pressure application have shown that the structure of the nanotubes is preserved under these conditions and corresponds well to that of the initial material.

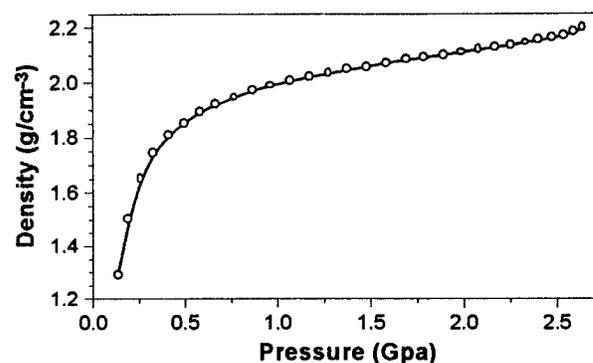


Figure 3. Pressure dependence of density for the carbon nanotubes heat treated at 2800°C.

Conclusions

Volume compressibility of multiwall carbon nanotubes estimated as a $P(V)$ dependence derivative appears to be very high at pressures below 0.5 GPa. Compressibility depends on pressure strongly and is $\sim (4\text{-}6) \times 10^{-11} \text{ Pa}^{-1}$ under pressure above 1.2 GPa, the nanotubes density at this pressure is about $2.1\text{-}2.2 \text{ g/cm}^3$. All changes under pressure are completely reversible and reproducible.

References

1. Ebbesen, T.W.A., *Rev. Mater. Sci.*, 1994, **24**, 235.
2. Robertson D.H., Brenner, D.W., Mintmire J.W., *Phys. Rev. B*, 1992, **45**, 12592.
3. Calvert, P., *Nature*, 1992, **367**, 365.
4. Ruoff R.S., Lorents D.C., *Carbon*, 1995, **33**, 925.
5. Dresselhaus, M.S., Dresselhaus, G., Sugihara, K., Spain, I.L., Goldberg, H.A., in *Graphite Fibers and Filaments*, ed. M. Cardona et al., Springer-Verlag, New-York, 1988, 188.
6. Treacy, M.M.J., Ebbesen, T.W., and Gibson, J.M., *Nature*, 1996, **381**, 678.
7. Losty, H.H.W., in *Modern Aspects of Graphite technology*, ed. L.C.F. Blackman. London, Academ. Press, 1970, p. 204.
8. Kabalkina, S.S., Vereschagin, A.F., *Dokl. AN SSSR*, 1960, **131**, N2, 300.
9. Nicklow, R.M., Wakabayashi, N., Smith, H.G., *Phys. Rev. B*, 1972, **5**, 4951.
10. Wada, N., Clarke, R., Solin, S.A., *Synth. Met.*, 1980, **2**, 27-34.