STRUCTURAL CHANGES IN SINGLE-WALL CARBON NANOTUBE BUNDLES UNDER PRESSURE

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The physics of single-wall carbon nanotubes (SWNT) is of great interest because of their unique anisotropic structure and outstanding mechanical and electronic properties. SWNT usually self assemblate into a two-dimensional hexagonal close packed lattice (SWNT bundles or ropes) as schematically illustrated in the inset of Fig. 1, with the d(100) inter-tube spacing 3.2 Å typical of van der Waals interaction. A SWNT sample is a collection of such bundles. In a bundle, all the tube diameters range around the same average diameter and the average diameter can vary from a bundle to another (defining the diameter polydispersity). Even though it is usually assumed that SWNT's cross section is circular, several theoretical models have predicted a progressive elliptical deformation and/or six-fold symmetry faceting of the tubes' section when the van der Waals interaction between the tubes in the bundles is increased. This enhancement is effective when the diameter of the tubes is large or when an external strain is applied as it is the case when an external pressure is applied perpendicular to the tubes' surface (radial compression). The objective of the present study was to evidence the tube faceting under pressure. In this aim, the structural changes of SWNT ropes were investigated using neutron diffraction experiments in an extended pressure range (up to 50 kbars). For the SWNT samples used in this study, the mean diameter of the tubes is 1.32 nm with a dispersion of about 0.2 nm, and the (10) Bragg peak (the most intense peak) which is characteristic of the SWNT organization into bundle-like 2D hexagonal lattice of finite size is expected to occur around Q ≈ 0.45 $Å^{-1}$. The neutron diffraction measurements were performed on the G6-1 diffractometer, using the 4.734 Å incident wavelength and the investigated Q range: 0.1, 2.5 $Å^{-1}$, perfectly matches that of the 2D organization response for nanotube bundles. Samples were placed into the cylindrical hole of a gasketed saphir anvil cell. In order to test a possible anisotropy of the diffraction response of SWNT samples under pressure, two different orientations of the anvil cell with respect to the neutron beam were used : in the V configuration, the axis of the anvil cell is perpendicular to the diffraction plane ; in the H configuration, the axis of the anvil cell lies in the diffraction plane and along the direction of the Q(10) scattering vector.

Figure 1 shows the raw experimental diffraction patterns recorded at 0, 18, 28 and 47 kbars in the V and H configurations. The signal is normalized to the incoming neutron flux and the diffraction intensities measured in the two configurations are therefore comparable both qualitatively and quantitatively. The peak in Fig. 1 is the (10) Bragg peak. It is a direct probe of the bundle organization and it allows an indirect estimation of the tube shape. The position of the (10) Bragg peak is derived from a Lorentzian fit of the (10) peak profile in the background subtracted data. Then, the lattice parameter a(P) is derived from the modulus Q(10) using the expression : $a(P)=4\pi/Q(10)\ 3^{0.5}$. For each anvil cell configuration we observe an upshift of the (10) Bragg peak assigned to a contraction of the lattice under pressure. More striking, the intensity of that contraction is found to be higly configuration dependent. Qualitatively, at low and intermediate pressures, the (10) Bragg peak position is more upshifted, its width sharper and its intensity stronger in the H configuration than in the V configuration. In figure 2, the a(P) experimental data are compared with the pressure dependence of the lattice parameter due to the van der Waals compression of bundle of circular (model I, Fig. 2, dashed line) and hexagonal (model II, Fig. 2, dot-dashed line) tubes respectively. For **the V configuration** and in the [0, 20 kbars] range we observe a small dependence of the lattice parameter with pressure. Above 20 kbars, a significant softening of the lattice parameter occurs. At the highest pressure the lattice parameter takes the value calculated using model II. In **the H configuration**, the lattice parameter

exhibits an immediate and strong decrease as soon as the pressure is applied. At 30 kbars and above, its value is in good agreement with that expected from model II. All these results suggest that the tubes undergo a progressive faceting, from a cylindrical to a hexagonal tube section and this process is complete for high pressure around 50 kbars. The key to explain the significant anisotropy in the behavior of the lattice parameter under pressure, is to consider the presence of an uniaxial component along the axis of the anvil cell acting on the nanotube bundles. The effect of the uniaxial component is enhanced by the strong anisotropy of the nanotube bundles. The diffraction signal is due to bundles having their long axis in a plane perpendicular to the Q(10) scattering vector. In the V configuration, the strength of the uniaxial component which acts perpendicular to the bundles surface depends on the orientation of the axis of the bundle with respect to the axis of the anvil cell. Consequently, the profile of (10) Bragg peak results from the sum of signals due to bundles compressed in different ways (distribution of the applied pressure). In consequence the peak is expected to be broad. The experimental data are in agreement with this prediction (fig. 1). Above 20 kbars the significant decrease of the lattice parameter is assigned to an important deformation in the tubes section under pressure, from a circular to an hexagonal shape. By contrast to the V configuration, all the bundles involved in the diffraction process for the H configuration are bundles perpendicular to the axis of the anvil cell. Consequently, the uniaxial pressure component felt by the radial surface of the bundle is maximum and it is the same for all the bundles (no distribution of the applied pressure in this configuration). Consequently, a sharper peak is expected in the H configuration than in the V configuration in agreement with the experimental data (Fig. 1). On the other hand, the high pressure leads to an immediate and concomitant radial compression of the bundles and tubes deformation which explains the significant pressure dependence of the lattice parameter observed as soon as the pressure is applied (Fig. 2).

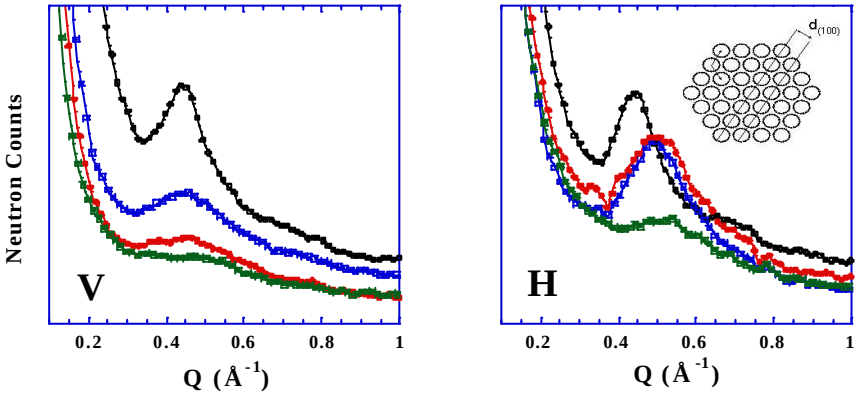
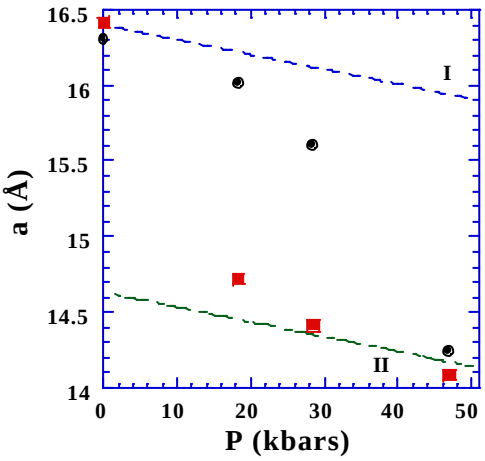


Figure 1. Raw experimental diagrams in the V and H configurations. black: 0 kbar, blue: 18 kbars , red: 28 kbars and green : 47 kbars. Inset: schematic view of a bundle



In conclusion, we have stated that under pressure the tubes section develops facets which optimise the van der Waals intertube bonding and a complete faceting is achieved at high pressure in agreement with the dependence of a(P) observed in both configurations. The results confirm theoretical predictions, and also allow one to interpret previous high pressure experiments by Raman scattering

Figure 2 Experimental pressure dependence of the lattice parameter a(P) measured in the V (circle) and H (square) configurations. Calculated pressure dependence of a(P) in model I (circular tubes, blue dashed line) and model II (hexagonal tubes, green dot-dashed line), see text .