## m38.o01

# Macroscopic assemblies of aligned nanotubes studied by X-ray diffraction and microdiffraction

Vincent Pichot, Pascale Launois

*Laboratoire de Physique des Solides (UMR CNRS 8502), bât. 510, Université Paris Sud, 91 405 Orsay CEDEX, France*

**Keywords: nanotubes, X-ray diffraction, microdiffraction**

Single-walled and multi-walled carbon nanotubes (SWNT, MWNT) have unique physical properties associated to their one-dimensional nanostructures. Obtaining assemblies of nanotubes with interesting macroscopic properties often requires aligned nanotubes materials [1]. We present here the structural analysis, using X-ray scattering, of two sorts of samples: nanotube fibers [2] and nanotube "carpets" [3]. For fibers, structural properties are shown to strongly influence mechanical properties. Structural studies performed on carpets allow a better understanding of their growth mechanism.

Fibers of nanotubes, where the nanotubes are oriented preferentially along the fiber axis, are intensively studied, in order to exploit the remarkable mechanical properties of individual SWNTs at the macroscopic scale. Record tensile strengths have for instance been reported [4, 5]. A stretching process was developed to improve nanotube alignment [6], which is studied quantitatively by X-ray scattering. Its improvement with stretching of the fibers is well understood within an affine model of induced orientation. It is shown that both Young's modulus and tensile strength of the fibers increase with nanotube alignment. The Young's modulus evolution is analyzed using continuum mechanics [7].

The synthesis of macroscopic nanotube carpets of several $cm^2$, composed of mm long MWNTs, partially filled with iron nanowires and aligned perpendicularly to the surface of a substrate is a challenge for many applications, from high density magnetic storage [8] to chemical separation [9]. Aerosol-assisted Catalytic Chemical Vapor Deposition synthesis is one of the routes to obtain large scale production [10]. Both base-growth and tip-growth mechanisms have been proposed to explain nanotube growth. Definitive evidence of base-growth mechanism was given recently [11]. The contribution of X-ray scattering experiments to solve this question will be discussed. Emphasis will be put on microdiffraction experiments, which allowed us to analyze locally the carpet structure from its basis to its top [12]. Other structural results concerning the nature of the particles that catalyze nanotube growth [13], the nanotube alignment and the structure and growth axis of metallic nanowires [3] inside nanotubes -of strong importance for high density magnetic storage- will also be discussed.

[1] P. Launois and P. Poulin, Encyclopedia of Nanoscience and Nanotechnology, vol. 4, 1 (2004).
[2] P. Launois, A. Marucci, B. Vigolo, P. Bernier, A. Derré and P. Poulin, J. Nanosc. Nanotech. 1, 125 (2001).
[3] V. Pichot, P. Launois, M. Pinault, M. Mayne-L'Hermite and C. Reynaud, Appl. Phys. Lett. 85, 473 (2004).
[4] A.B. Dalton, S. Collins, E. Mun[00f2]Cz, J.M. Razal, V.H. Ebron, J.P. Ferraris, J.N. Coleman, B.G. Kim and R.H. Baughman, Nature 423, 703 (2003).
[5] P. Miaudet, S. Badaire, M. Maugey, A. Derré, V. Pichot, P. Launois, P. Poulin and C. Zakri, Nanoletters 5, 2212 (2005).
[6] B. Vigolo, P. Poulin, M. Lucas, P. Launois and P. Bernier, Appl. Phys. Lett. 81, 1210 (2002).
[7] T. Liu and S. Kumar, Nanoletters 3, 647 (2003).
[8] N. Grobert, W.K. Hsu, Y.Q. Zhu, J. P. Hare, H.W. Kroto, D.R.M. Walton, M. Terrones, H. Terrones, P. Redlich, M. Rühle, R. Escudero and F. Morales, Appl. Phys. Lett. 75, 3363 (1999).
[9] B.J. Hinds, N. Chopra., T. Rantell, R. Andrews, V. Gavalas and L.G. Bachas., Science 303, 62 (2004).
[10] M. Mayne, N. Grobert, M. Terrones, R. Kamalakaran, M. Rühle, H. W. Kroto and D. R. M. Walton, Chem. Phys. Lett. 338, 101 (2001).
[11] M. Pinault, V. Pichot, H. Khodja, P. Launois, C. Reynaud and M. Mayne-L'Hermite, Nanoletters 12, 2394 (2005).
[12] V. Pichot, P. Launois, M. Pinault, M. Mayne-L'Hermite, C. Reynaud, M. Burghammer and C. Riekel, AIP conference proceedings 786, p.158 (2005).
[13] M. Pinault, M. Mayne-L'Hermite, C. Reynaud, V. Pichot, P. Launois and D. Ballutaud, Carbon 43, 2968 (2005).

## m38.o02

# Recognition-controlled molecular crystals of fullerenes with cubane

S. Pekker[a*], G. Oszlányi[a], G. Bortel[a], É. Kováts[a], I. Jalsovszky[b], G. Faigel[a]

*[a]Research Institute for Solid State Physics and Optics, Budapest, Hungary. [b]Department of Organic Chemistry, Eötvös Loránd University, Budapest, Hungary. E-mail: pekker@szfki.hu*

**Keywords: fullerenes, cubanes, molecular recognition**

Fullerenes form 1:1 stoichiometry molecular crystals with cubane. The new materials exhibit rich phase diagrams, unusual dynamics and topochemistry [1]. They can be originated from the fcc lattice of $C_{60}$: cubane molecules occupy the octahedral voids while the parent sublattice expands significantly. The major stabilizing factor is the molecular recognition of the convex fullerene and concave cubane surfaces, combined with high symmetry of the constituents. Cubane molecules are octahedrally coordinated by the fullerenes. The perfect mach of the complementary surfaces results in an efficient packing and aligns the $C_4$ axes of cubane parallel with the edges of the unit cell. The atomic arrangement of the fullerene surface is incommensurate with that of cubane, therefore, the rotation of fullerenes has no influence on the match. Thus, the six nearest neighbor cubanes behave as a molecular bearing for the freely rotating fullerene, giving rise to unusually low temperature of orientational ordering. The alternating array of static and rotating components distincts the new fullerene-cubane materials from both the orientationally ordered and plastic crystals.

The simple intermolecular interactions make possible an efficient crystal engineering of related materials. The lattice parameters depend on the sizes of fullerenes and cubane, and can be designed with high accuracy. Cubane forms similar rotor-stator structures with the fullerenes in the range of $C_{60}$-$C_{84}$, and host-guest crystals with the higher fullerenes. Anisometric fullerenes may modify the rocksalt structures: At ambient temperature the $C_{70}$ derivative has a tetragonal lattice with static and oriented cubanes, and uniaxially rotating and precessing fullerenes. This complex motion corresponds to a maximum efficiency of molecular recognition. The racemic mixture of $D_2$-$C_{76}$ molecules favours a nickel arsenide type of lattice, with the same fullerene-cubane distances as calculated. Substituted cubanes also form molecular crystals with fullerenes but the lower symmetry and the higher volume have significant influence on the structure. Rhombohedral distortion takes place in the 1,4-diethynyl cubane derivative of $C_{60}$. The $C_3$ axis of cubanes are aligned in parallel; the acetylene groups are locked at the trigonal points of the structure. This geometry reduces the influence of molecular recognition, allowing high amplitude uniaxial libration of the cubane units, which may give rise to their uniaxial rotation in higher fullerene derivatives. The thermal decomposition of cubane also takes place in the fullerene derivatives, resulting in the formation of alternating copolymers. The chemical reactions occur in the parent lattice of the monomers, without significant change of the volume. Single crystals retain their shiny flat faces also in the polymerized materials. The independent local reactions may result in the formation of interpenetrating polymer networks in the four primitive cubic sublattices of the parent monomer phases. This work has been supported by the grants OTKA T046700, T043237.

[1] Pekker, S., Kováts, É., Oszlányi, G., Bényei, Gy., Klupp, G., Bortel, G., Jalsovszky, I. Jakab, E., Borondics F., Kamarás, K., Bokor, M., Kriza, G., Tompa, K., Faigel, G., *Nature Materials*, 2005, 4, 764.