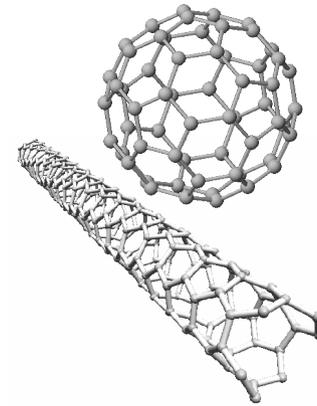
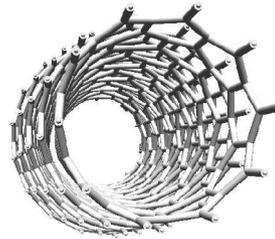
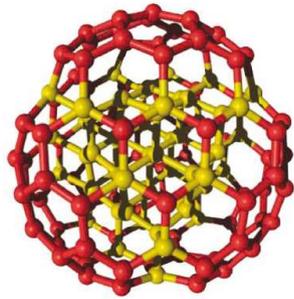
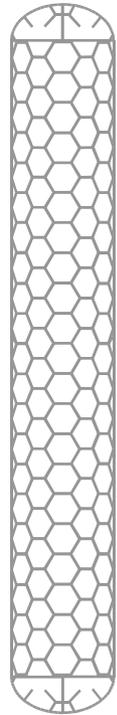


Nanomécanique des Nano-objets individuels



II. Nanotubes, nanofils et fullerenes

Nanotube



Length:
typical few μm

High aspect ratio:

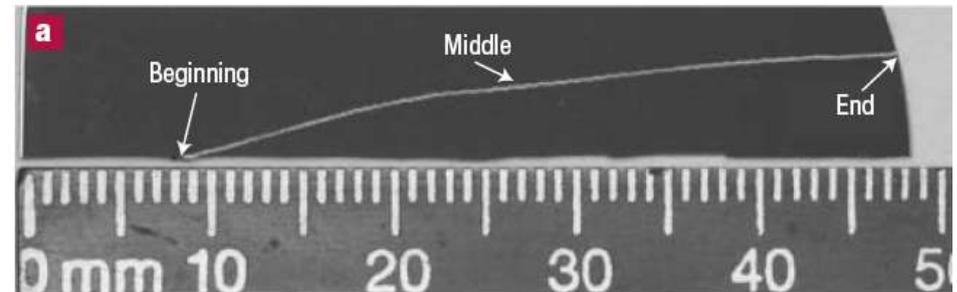
$$\frac{\text{length}}{\text{diameter}} > 1000$$

→ quasi 1D solid



Diameter:

as low as 1 nm



SWCNT – 1.9 nm

Zheng *et al.* Nature Materials **3**
(2004) 673.

Du graphite au nanotube de carbone

Le Graphite :

Très anisotrope

Module de Young dans le plan : 1.06 TPa

Limite élastique à la traction : 130 GPa (théorique)

.....

Tout ça laisse à penser que les propriétés mécaniques des nanotubes de carbone pourraient être remarquables

Nanotubes

Carbon nanotubes are the strongest ever known material.

- **Young Modulus (stiffness):**

Carbon nanotubes	~ 1000 GPa
Carbon fibers	425 GPa (max.)
High strength steel	200 GPa

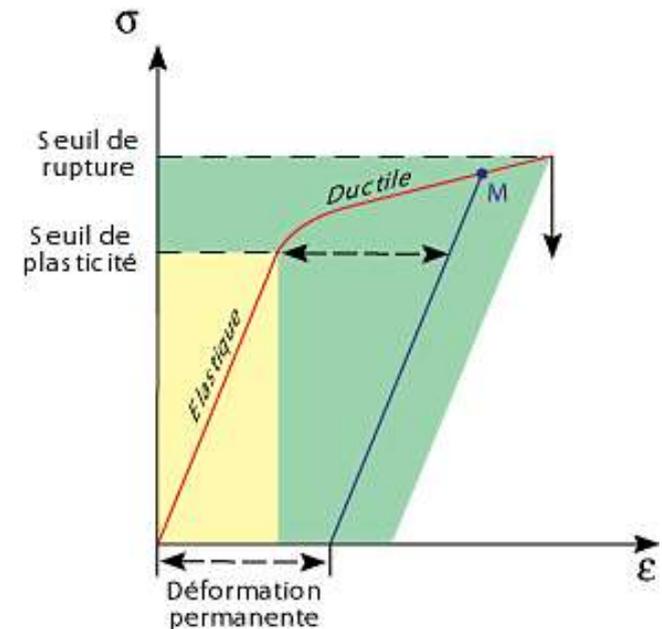
- **Tensile strength (breaking strength)**

Carbon nanotubes	11- 63 GPa
Carbon fibers	3.5 - 6 GPa
High strength steel	~ 2 GPa

- **Elongation to failure : ~ 20-30 %**

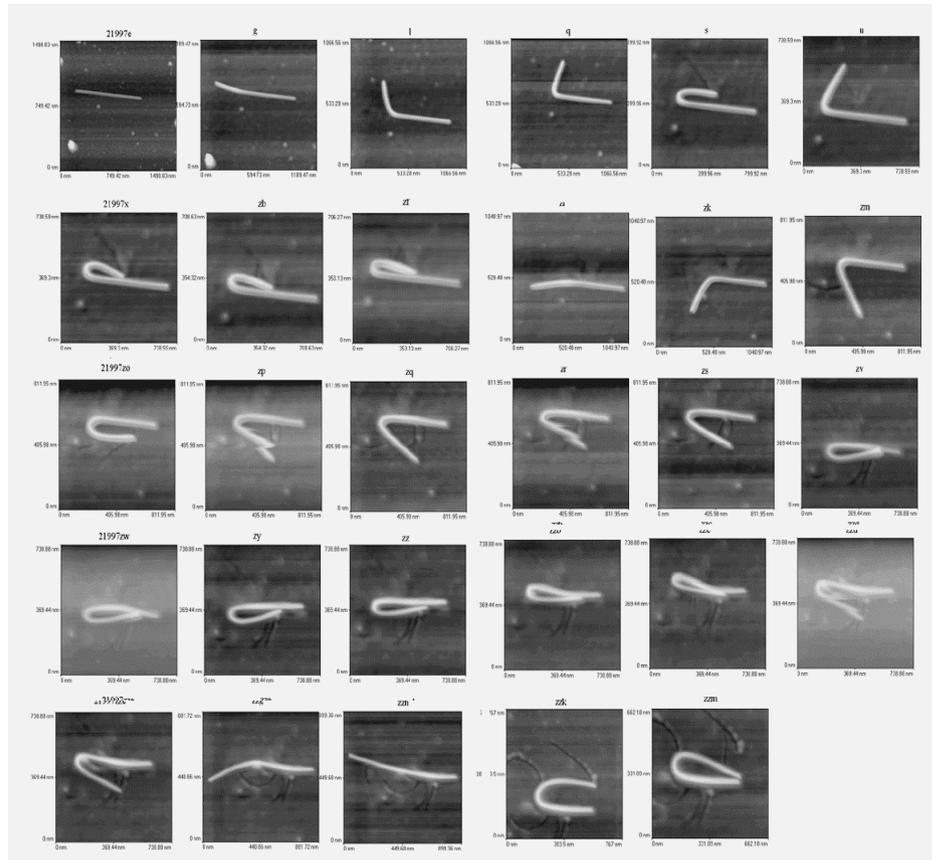
- **Density:**

Carbon nanotube (SW)	1.33 – 1.40 gram / cm ³
Aluminium	2.7 gram / cm ³



Flexibility

- Carbon nanotubes are very flexible

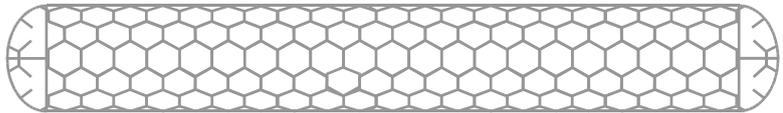


*Nanoscience Research Group
University of North Carolina (USA)
<http://www.physics.unc.edu/~rsuper/research/>*

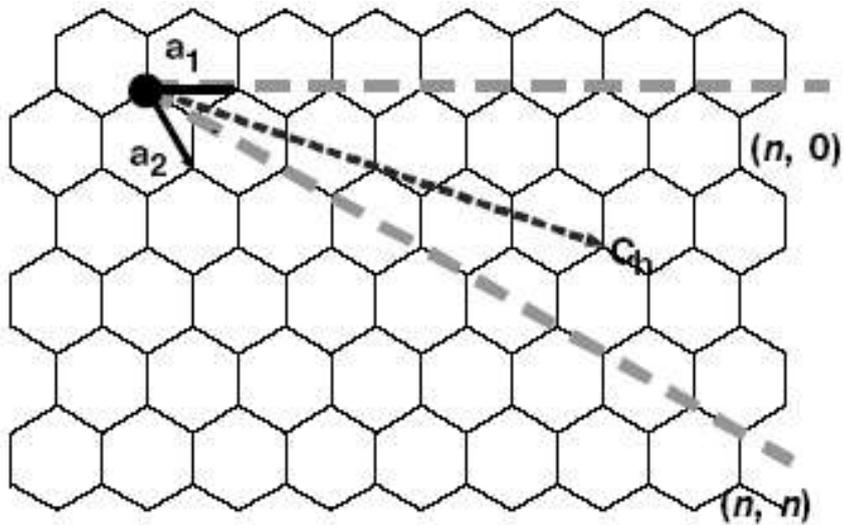
- Can sustain almost reversibly high pressures up to more than 40 GPa.

Nanotube

- Discovered 1991, Iijima

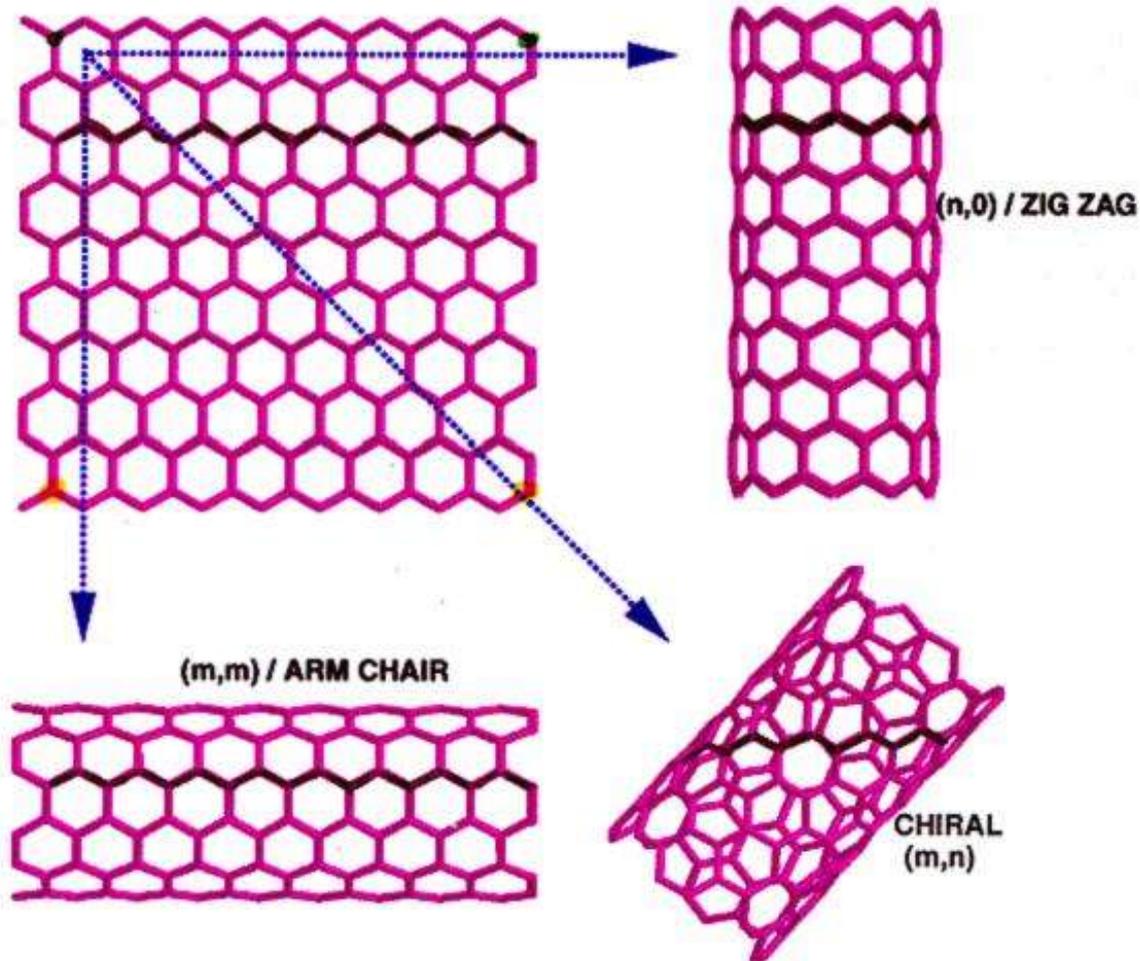


• STRIP OF A GRAPHENE SHEET ROLLED INTO A TUBE



Roll-up vector:

$$C_h = n \vec{a}_1 + m \vec{a}_2$$

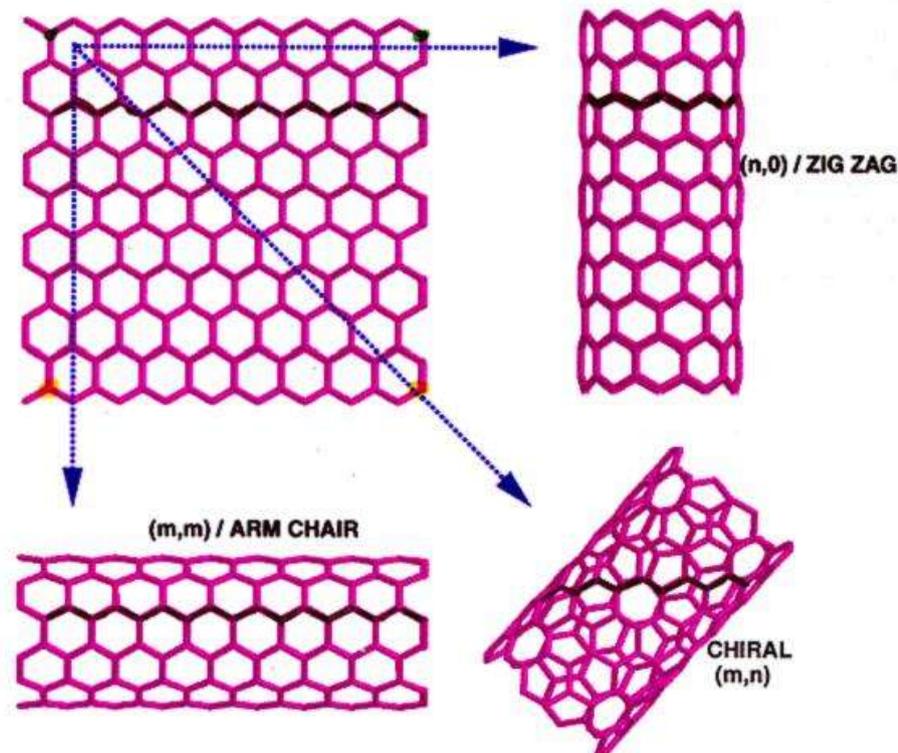


Nanotube

Electrical conductance depending on helicity

$$C_h = n \vec{a}_1 + m \vec{a}_2 \quad \text{If } \frac{2n+m}{3} = i, \text{ then metallic} \\ \text{else semiconductor}$$

• STRIP OF A GRAPHENE SHEET ROLLED INTO A TUBE



Nanotube

Electrical conductance depending on helicity

$$C_h = n \vec{a}_1 + m \vec{a}_2 \quad \text{If } \frac{2n+m}{3} = i, \text{ then metallic} \\ \text{else semiconductor}$$

- Current capacity

Carbon nanotube 1 GAmps / cm²

Copper wire 1 MAmps / cm²

- Heat transmission

Comparable to pure diamond (3320 W / m·K)

- Temperature stability

Carbon nanotube 750 °C (in air)

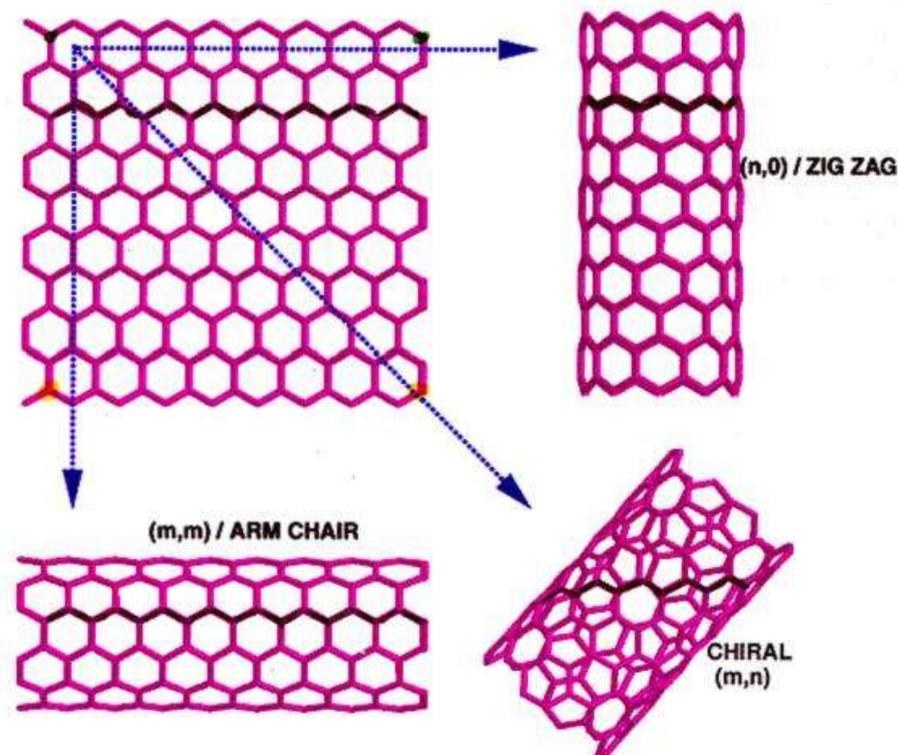
Metal wires in microchips 600 – 1000 °C

- Caging

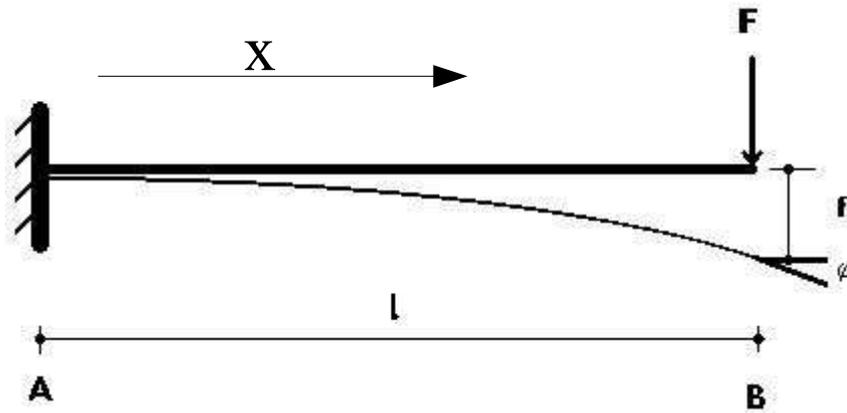
May change electrical properties

→ sensor

• STRIP OF A GRAPHENE SHEET ROLLED INTO A TUBE



Elasticité d'une poutre



Pour une poutre homogène et élastique, une déformation transverse est donnée par l'équation de Bernoulli-Euler :

$$\frac{d^2 u_z}{d x^2} = -\frac{M(x)}{Y I} \quad (1)$$

$M(x)$: Moment de flexion dans la position x (solicitation)

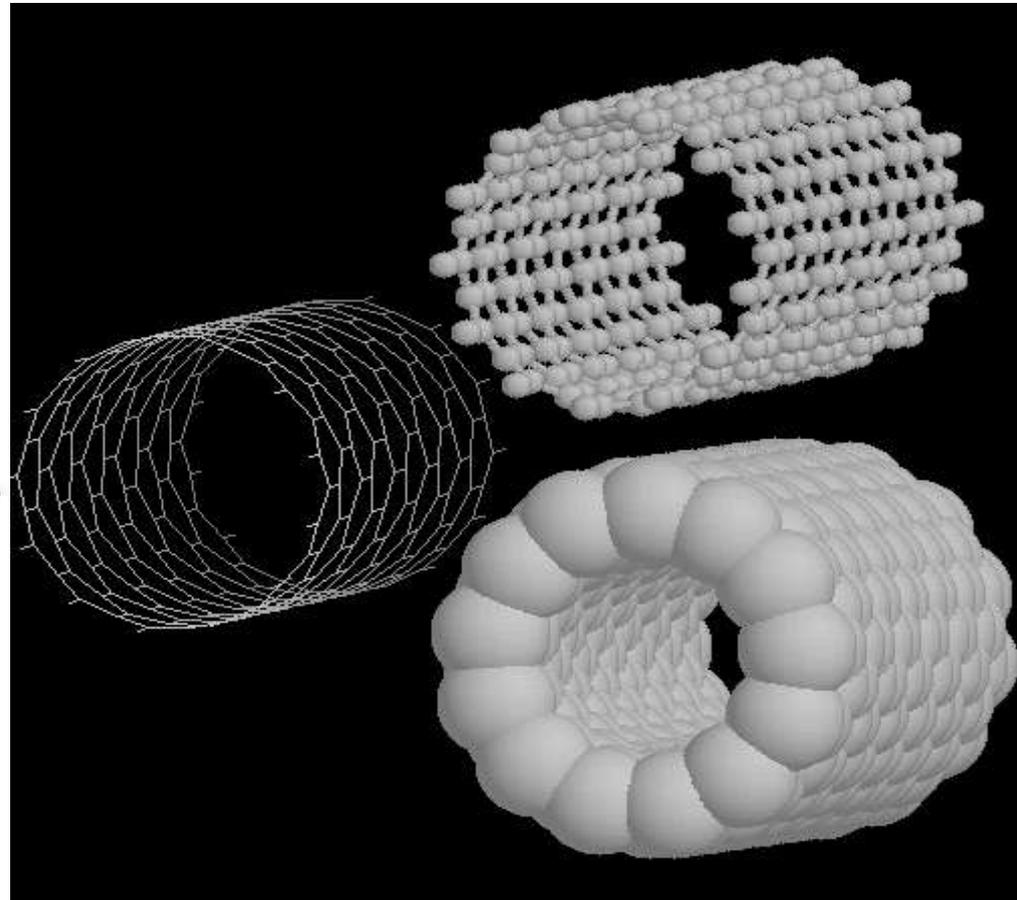
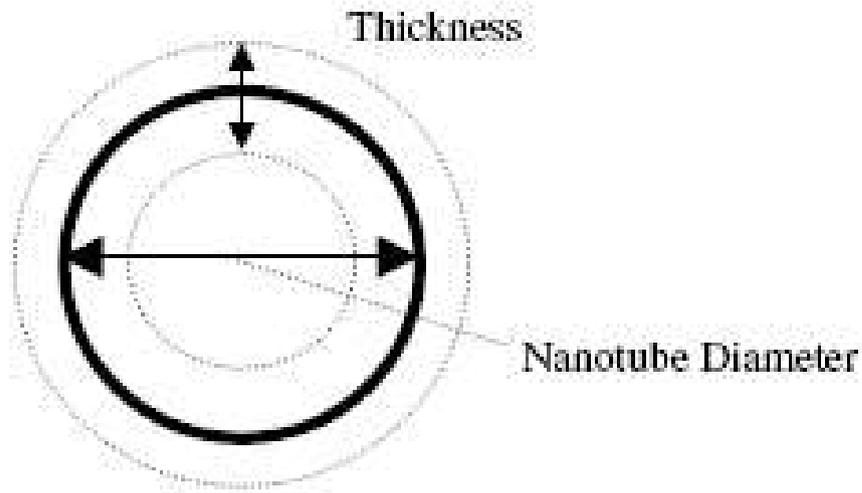
I : Moment d'inertie surfacique : $I = \iint_S z^2 dy dz$

De (1) on obtient la déflexion d'une poutre encastree de longueur L

soumise à une force F à l'extrémité opposée : $\delta = \frac{F L^3}{3 Y I}$

Pour un tube : $I = (\pi/64)(D_e^4 - D_i^4)$

Mais peut-on considérer un nanotube comme un milieu continu avec une épaisseur donnée ?



Ce n'est pas de tout évident. On retrouve deux valeurs dans la littérature:

- **0.07 nm** (valeur adopté dans un plan de graphite combinant calculs/expériences)
- **0.34 nm** (demi-distance des plans de graphene dans le graphite)

C'est donc le couple (t, Y) qu'a une valeur. Pour les SWNT on retrouve typiquement :

(1 TPa, 0.34 nm)

(5 TPa, 0.07 nm)

C'est à dire : $t Y \approx 0.35 \text{ nm TPa}$

MWNT : Y depend du nombre de tubes, N

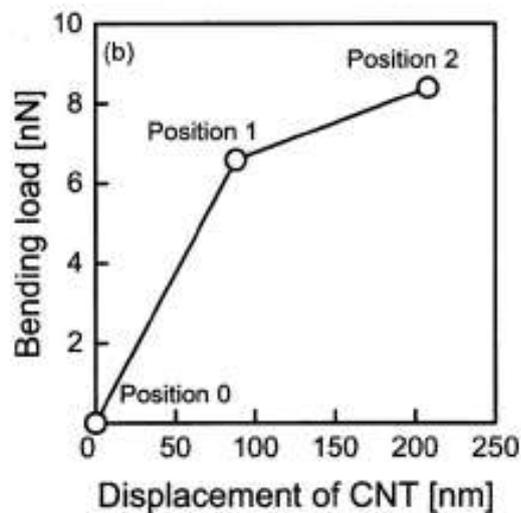
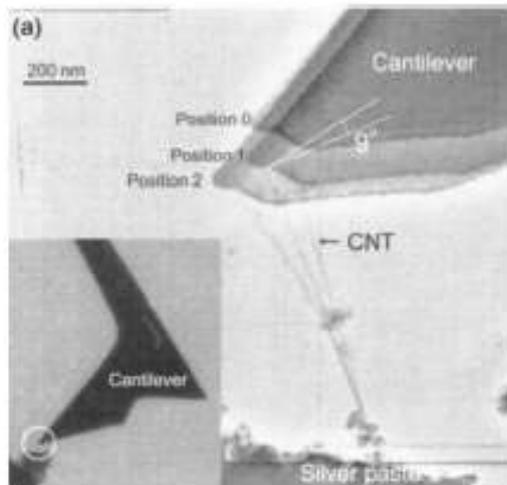
$$Y_N = \frac{N}{N-1 + (t/d_i)d_i} \frac{Et}{d_i}$$

avec $d_i \approx 0.34 \text{ nm}$ la distance entre tubes

N	1	2	3	4	5	8	10	20	100
Y_m	4.70	1.70	1.41	1.29	1.23	1.15	1.13	1.08	1.05

Mesure de Y dans des MWNT-individuels par MET + déplacement mécanique avec un nano-manipulateur

K. Enomoto, App. Phys. Lett. 88 153115 (2006)



Le déplacement, d , de l'extrémité d'une poutre sur laquelle on exerce une force F est :

$$d = \frac{F L^3}{3 Y I}$$

Y dans MWNT-individuels et défauts

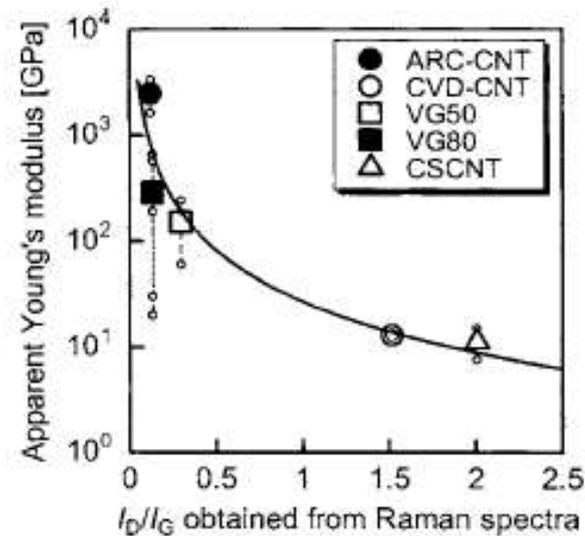
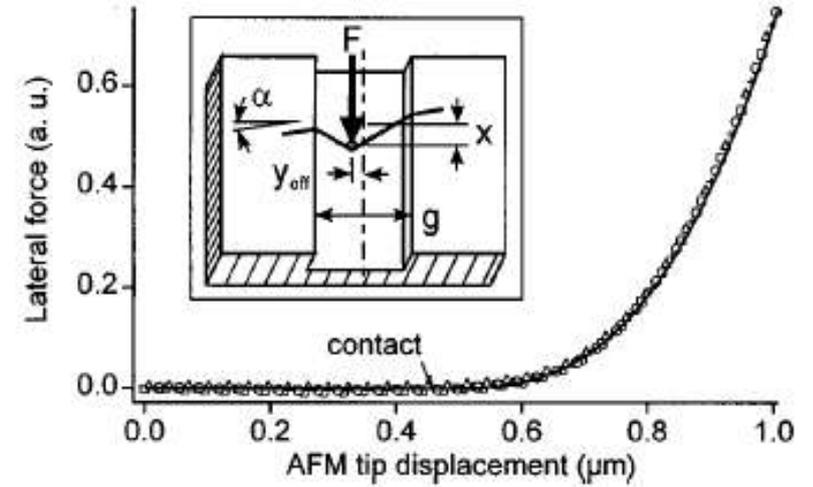
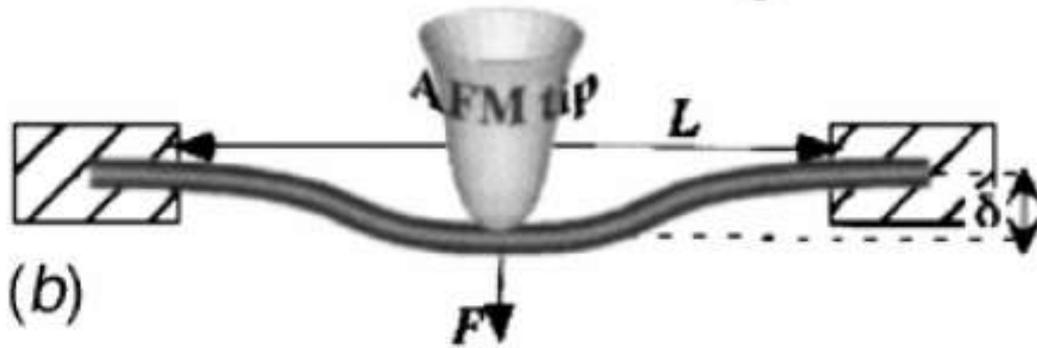
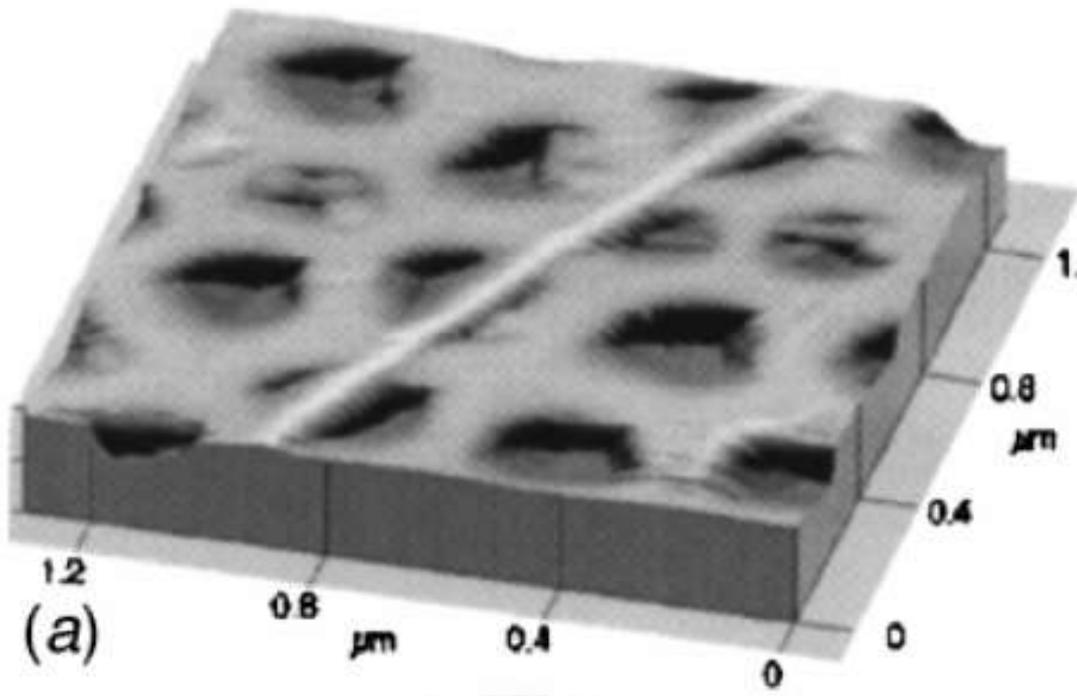


FIG. 4. Relationship between apparent Young's modulus obtained from each measurement and I_D/I_G obtained from Raman spectra. The small open circles indicate experimental values. The average apparent Young's moduli obtained from each series of experimental values are shown as large plots in this figure.

Déformation avec une pointe AFM



Vibrations d'une poutre

Pour des petites deformations, l'équation du mouvement d'une poutre de section A , masse volumique ρ module de Young E et moment d'inertie I est

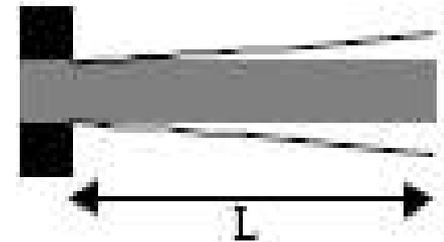
$$\rho A \frac{\partial^2 u}{\partial t^2} + E I \frac{\partial^4 u}{\partial x^4} = q(x)$$

où $q(x)$ est une charge distribuée

La solution de cette équation permet d'obtenir les fréquences propres de vibration de la poutre :

$$\omega_i = \frac{\beta_i^2}{L^2} \sqrt{\frac{E I}{\rho A}}$$

avec β_i les racines d'un équation qui dépend des conditions limites.

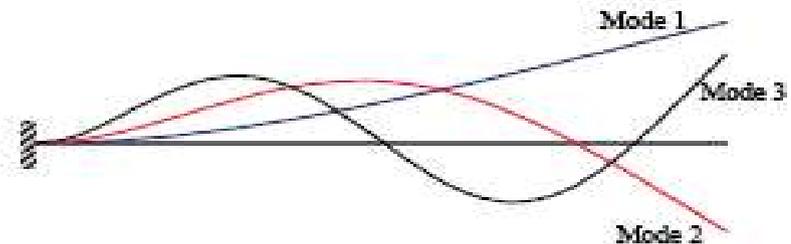


Dans le cas d'une poutre fixé à une extrémité :

$$\cos \beta_i \cosh \beta_i + 1 = 0$$

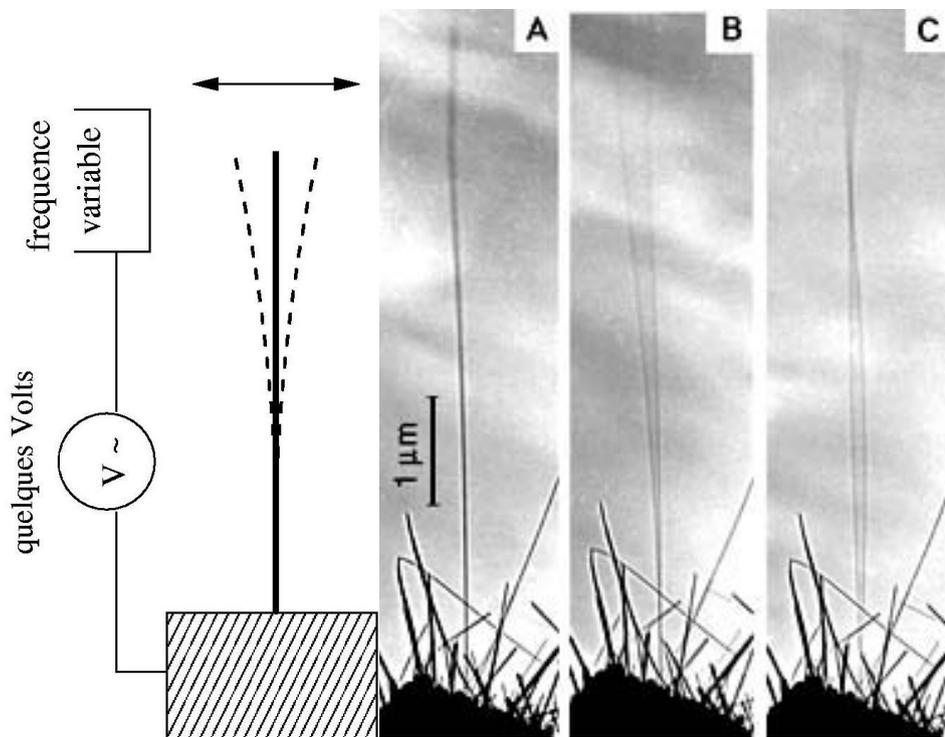
On obtient pour les trois premiers modes :

$$\beta_1 \approx 1.875 \quad \beta_2 \approx 4.691 \quad \beta_3 \approx 7.855$$



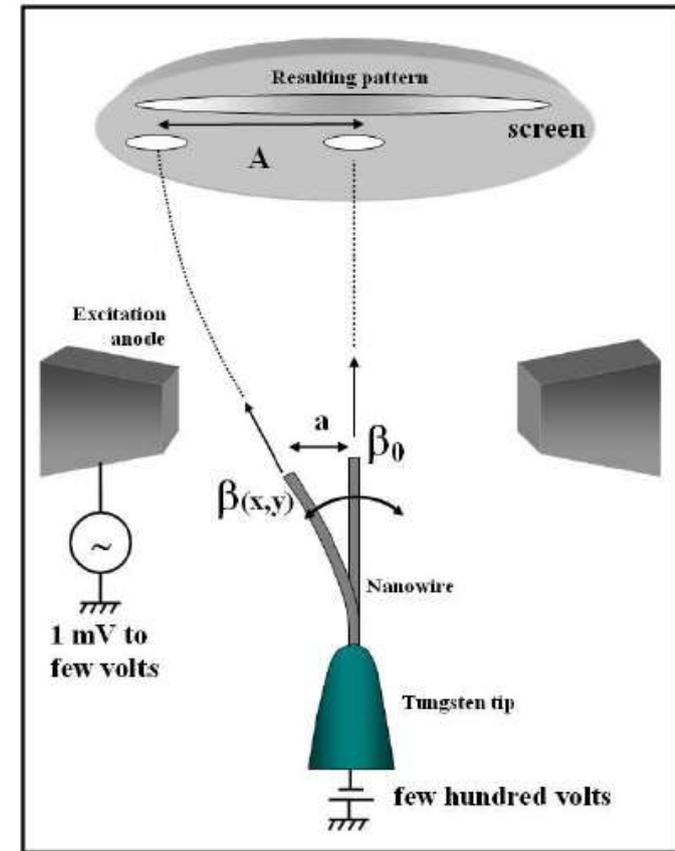
Excitation des vibrations avec un champ électrique variable

Observation avec un microscope électronique



Poncharal et al., Science (283) 1999

Observation par emission de champ



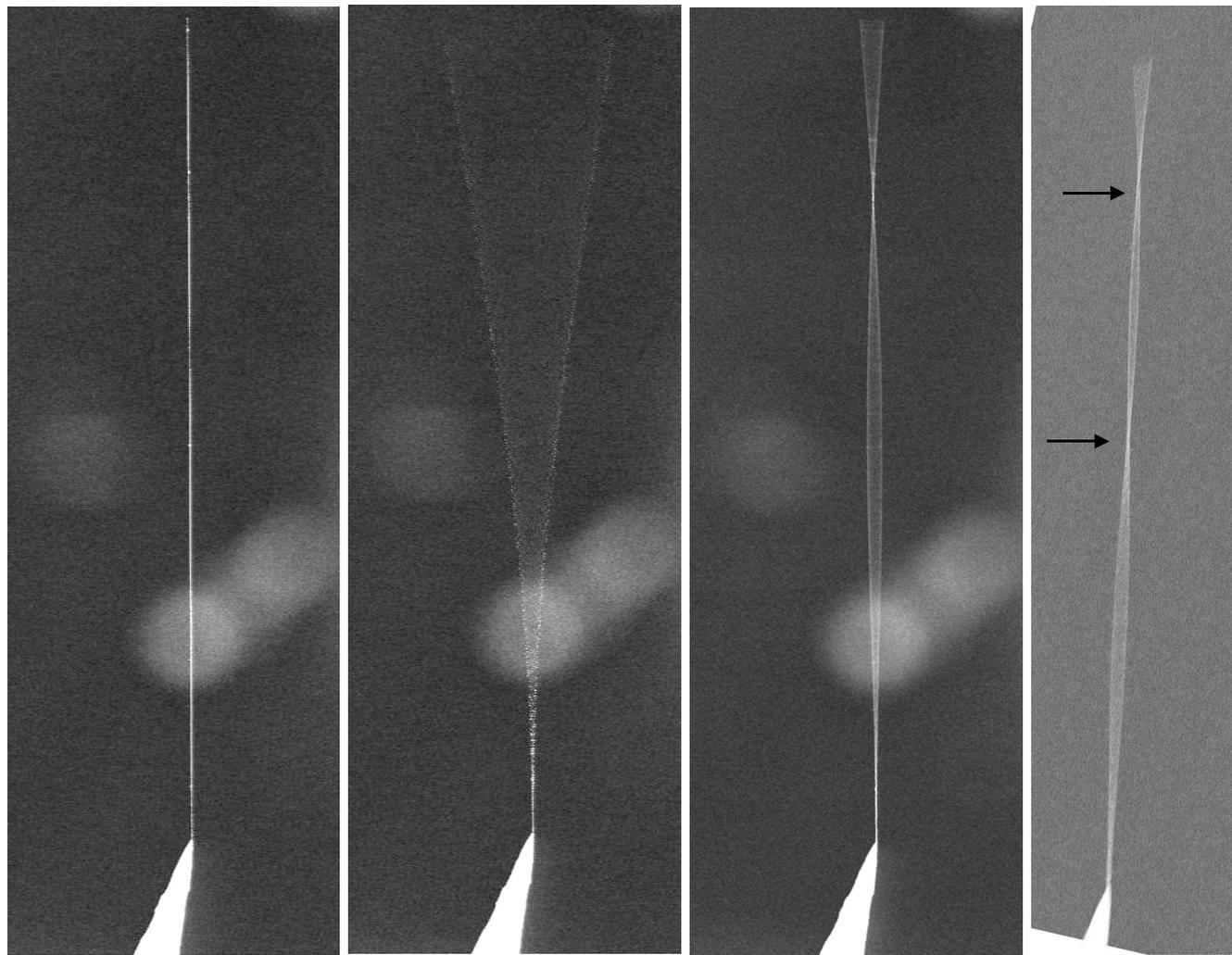
S.T. Purcell, et al., Phys. Rev. Lett., 89, 276103 (2002).

Fagots de SWNT : Toujours Y dans l'ordre du TPa

Vibrations in a SEM

- Measure the frequencies by direct imaging or line mode
- Resonance frequencies for $V = 0$

Visualization of 1st, 2nd and third order modes



$$\omega_{\text{exc}} = 2\omega_i/n$$

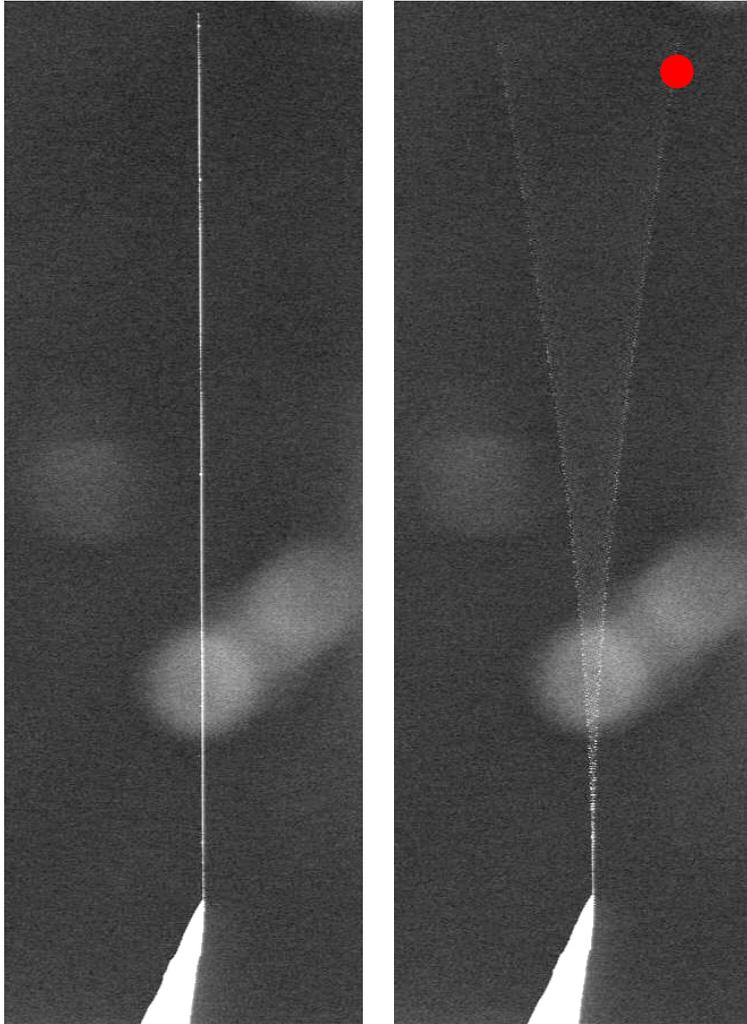
ω_i - harmonics

$$n = 1, 2, 3, 4, \dots$$

Young's modulus?

Vibrations in SEM for an SiC nanowire

Fundamental



15280 Hz

7751 Hz



3900 Hz

2588 Hz

1940 Hz

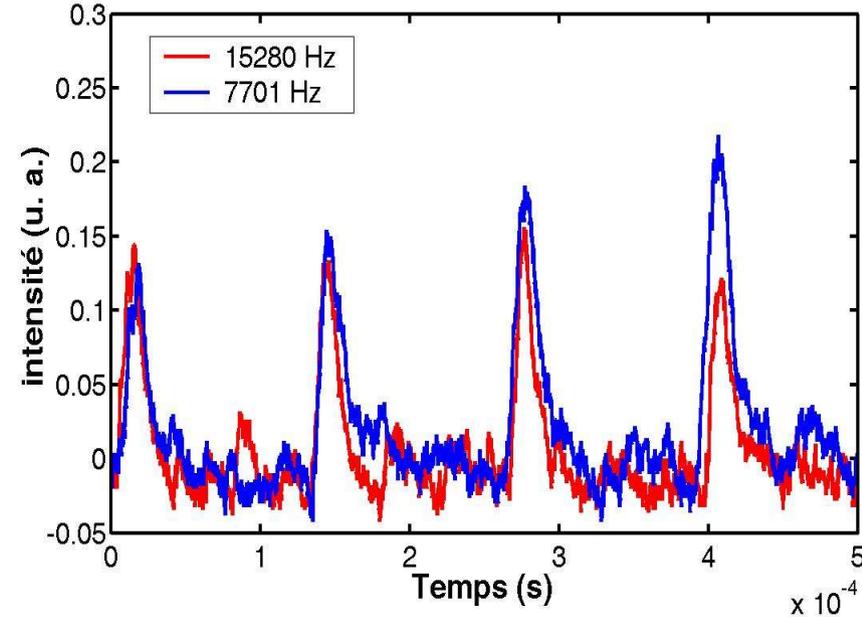
1552 Hz

1293 Hz

1192 Hz

1108 Hz

969 Hz



- Elastic glue must be taken into account

- Young's modulus:

$$E = 530 \text{ GPa}$$

equal to bulk SiC

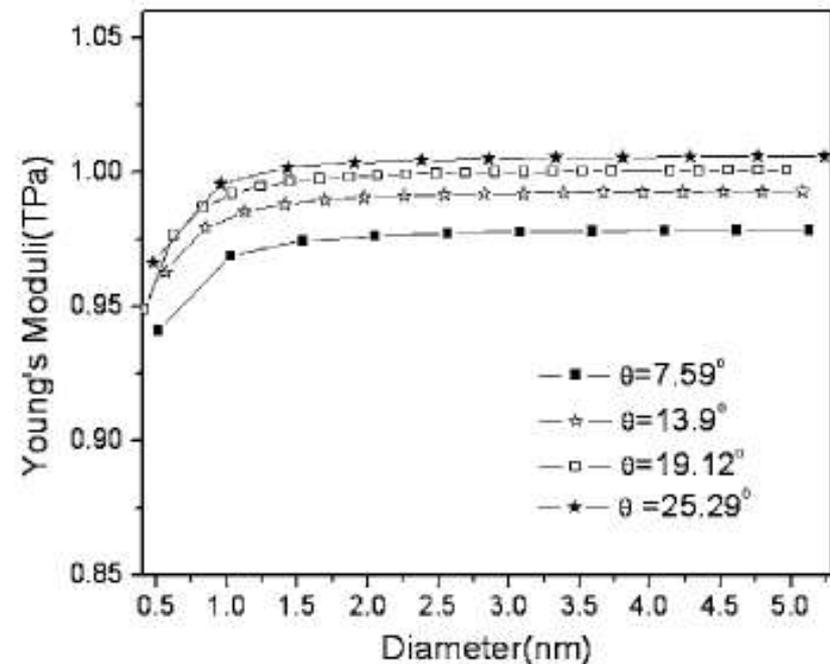
$$\omega_1 = \left(\frac{1.875}{L}\right)^2 \sqrt{\frac{EI}{\rho S}}, \quad \omega_2 = \left(\frac{4.694}{L}\right)^2 \sqrt{\frac{EI}{\rho S}}, \quad \omega_3 = \left(\frac{7.855}{L}\right)^2 \sqrt{\frac{EI}{\rho S}}$$

Dependence du Y des SWNT avec le diamètre et la chiralité

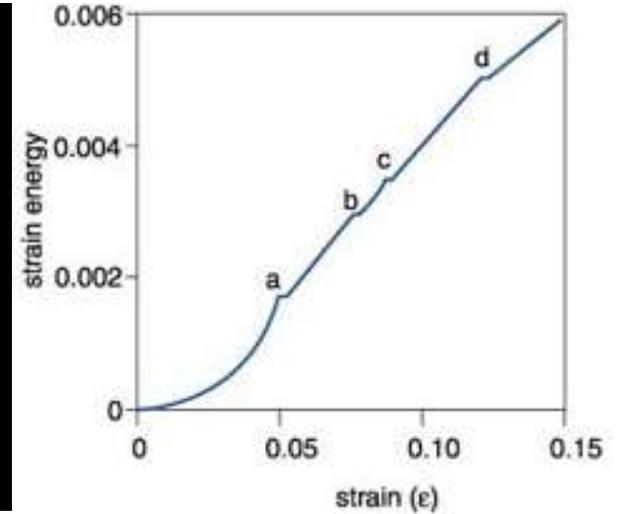
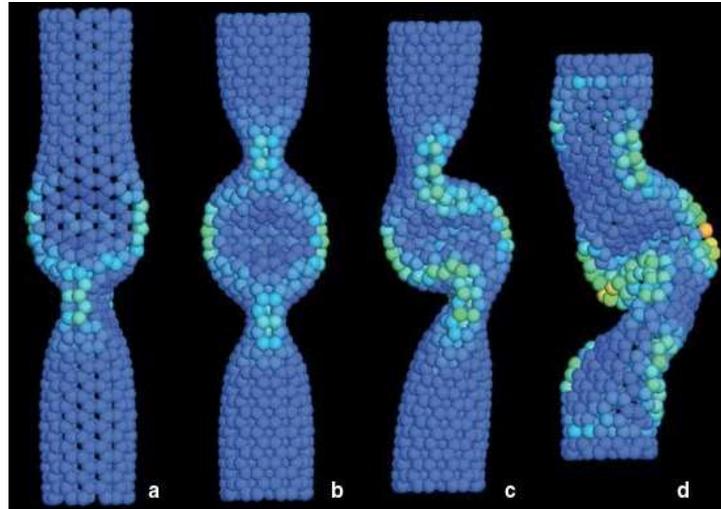
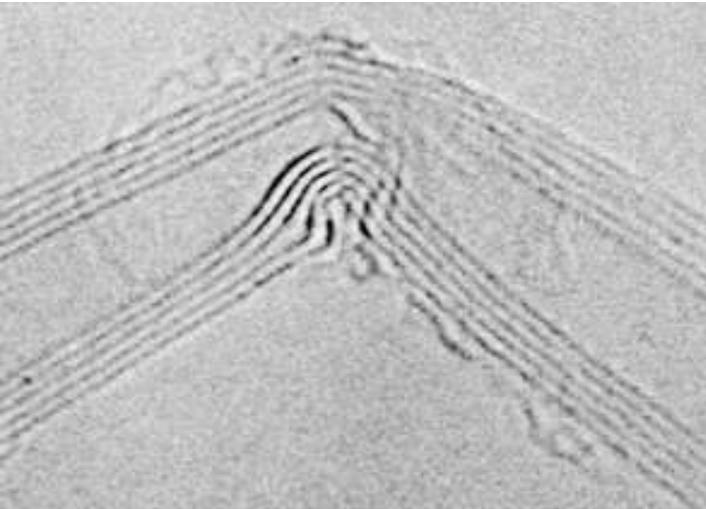
- Pas de mesure decisive
- Sujet encore de controverses.

Basic approach : to curve a bond weakens it, then for smaller diameters Y gets lower and some dependence should appear on chirality.

The opinion of specialists :
the above mentioned effects are small and the dominant effect in an experiment will be the presence of defects.



Deformation et « buckling »

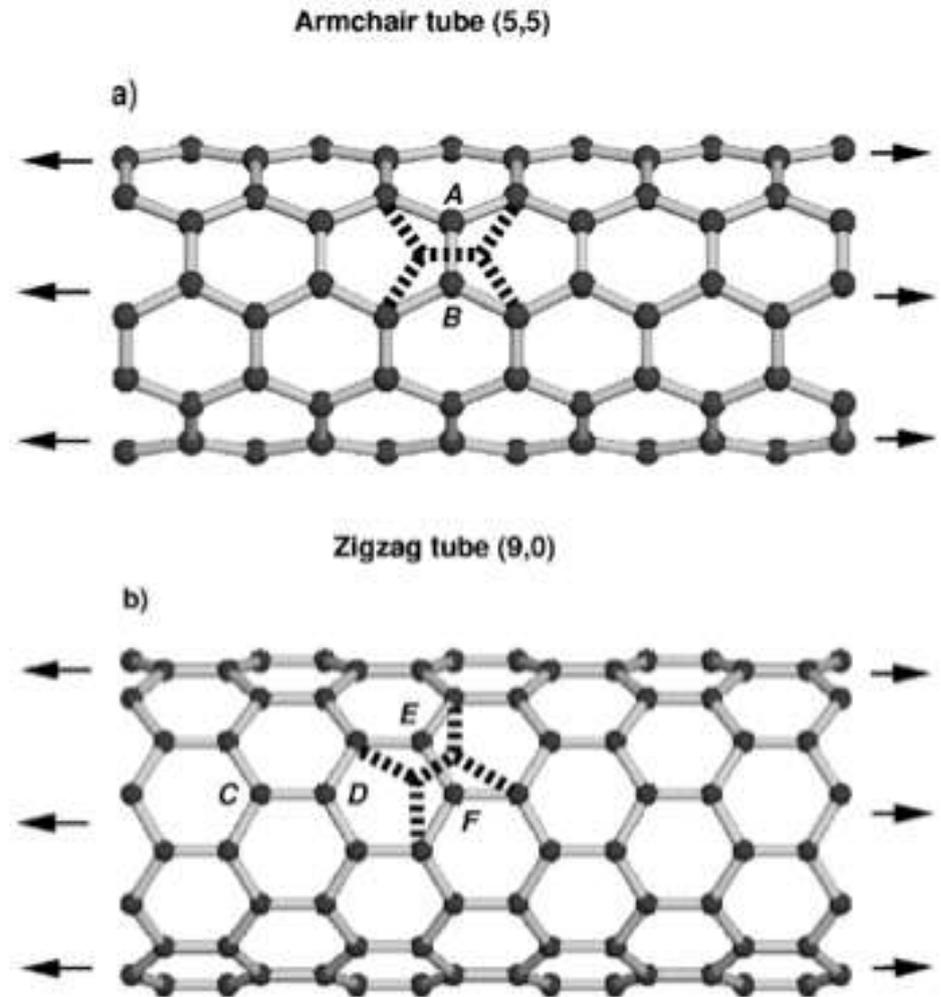


- Tubes undergo abrupt shape shift under stress, emitting phonons, or crunching. These correspond to singularities in the stress/strain curves
- Tubes bounce back from stress to reform original shape



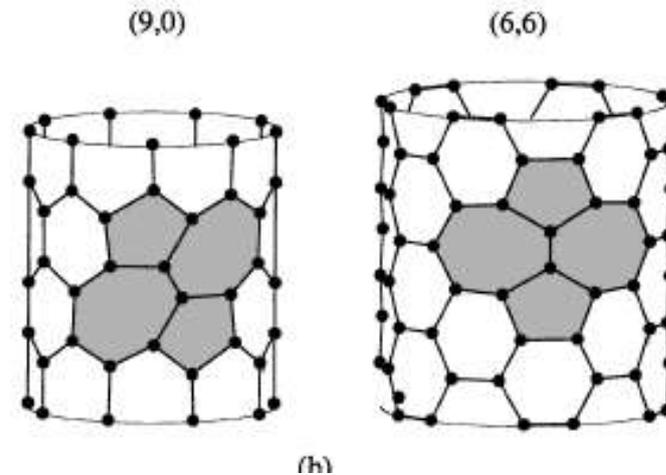
Strain

- a) “Transverse” strain finds a natural release in a bond rotation of 90° for the armchair tube, thereby elongating the tube and releasing excess strain energy. Defect is formed, which leads to non-elastic behavior
- b) “Longitudinal” strain induces a 60° rotation in the zig-zag tube. Less tube elongation therefore more resistant to defect formation



Defects in nanotubes

Stone-Wales defects (5+7)



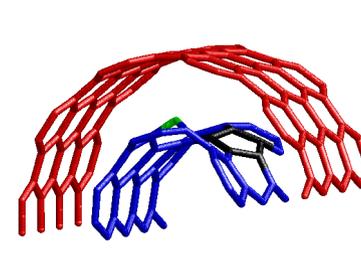
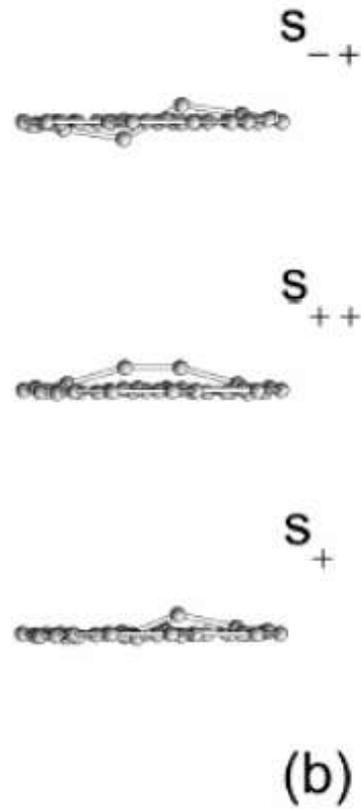
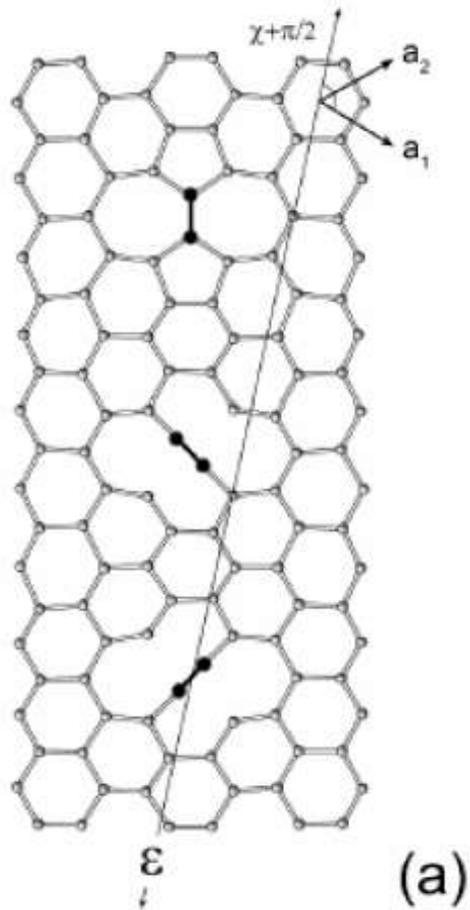
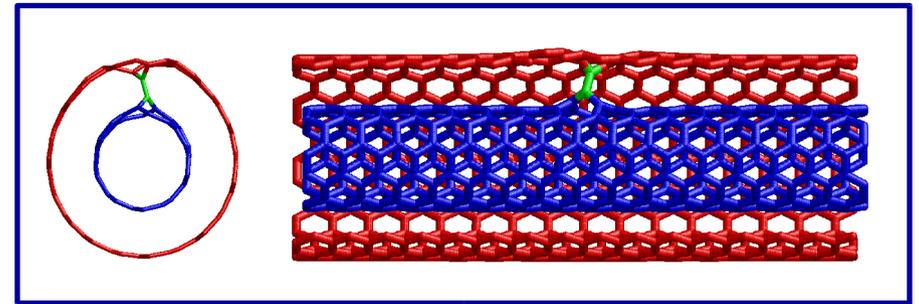
L'énergie de formation défauts de S-W depend de l'angle de chiralité :

$$E_{SW} = A - B\epsilon - C \sin\left(2\chi + \frac{\pi}{6}\right)\epsilon$$

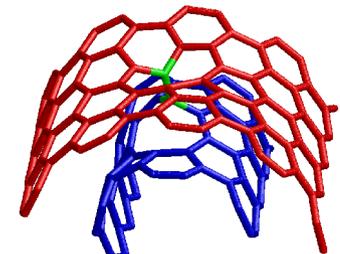
avec ϵ la tension appliquée

Other type of defects

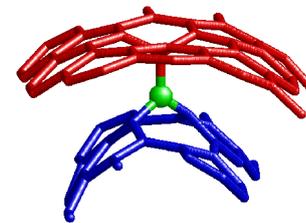
In MWNT



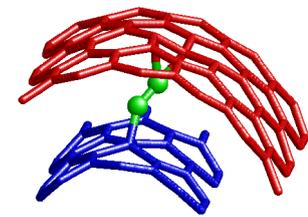
One vacancy
(not covalent)



Two
vacancies



Interlayer
interstitial



Interlayer
dimer

Glissement et « fracture » des défauts de S-W

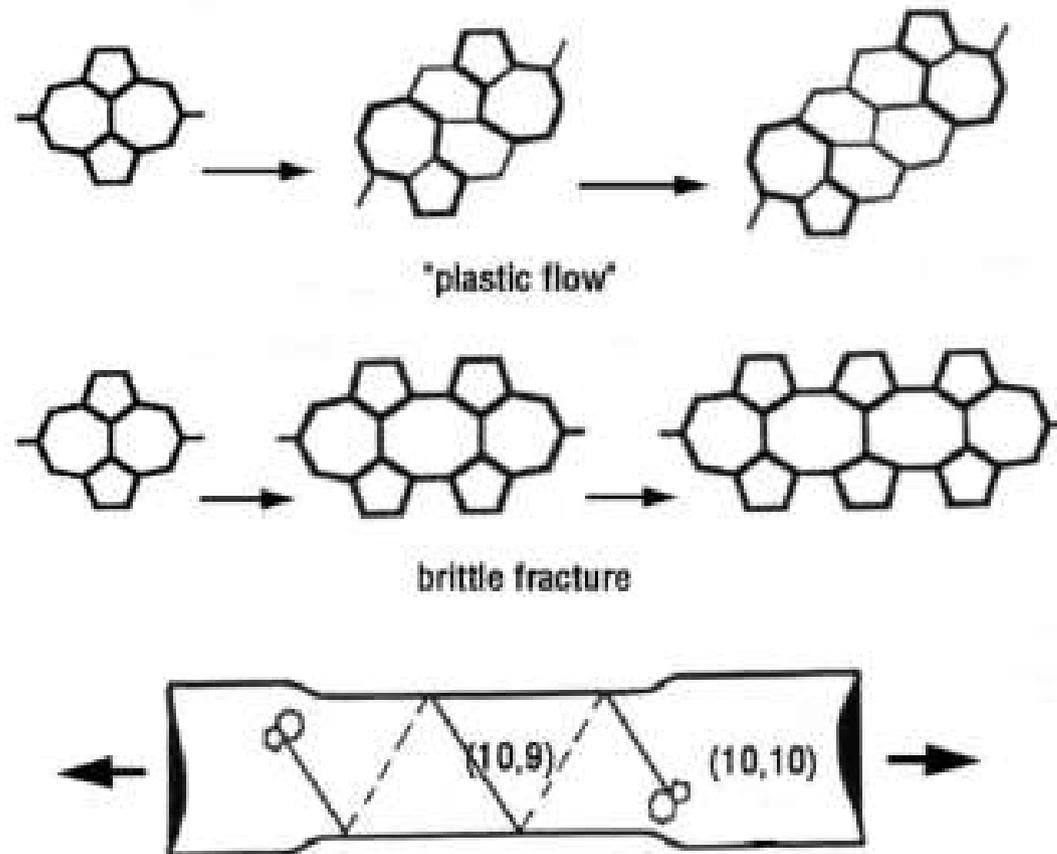
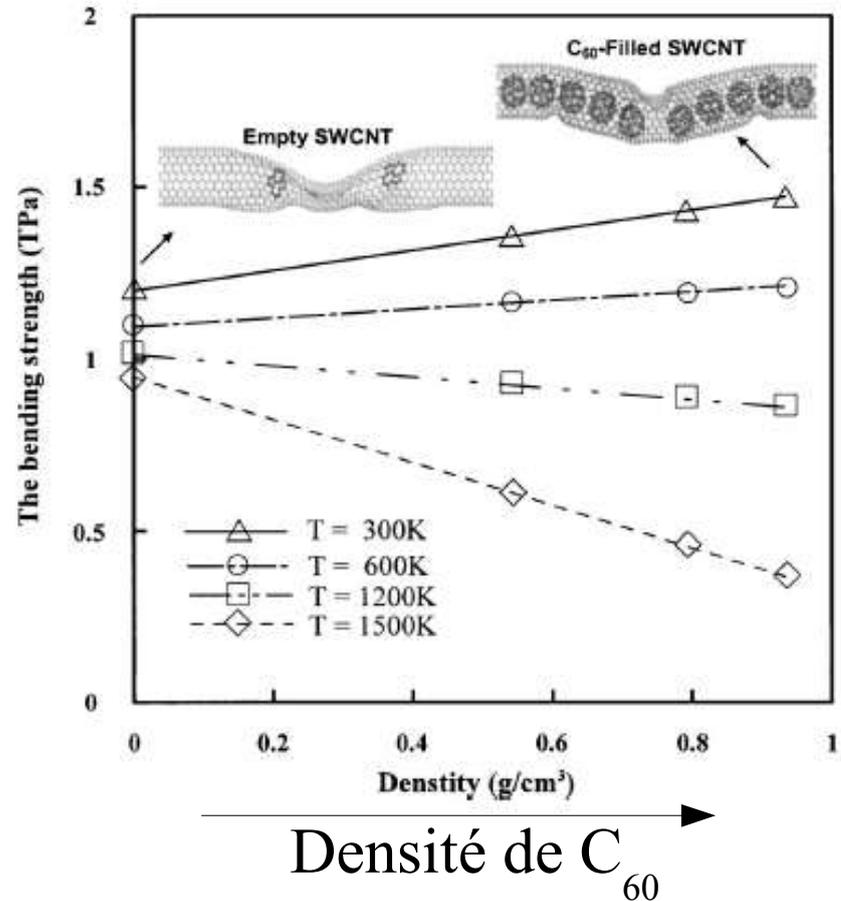
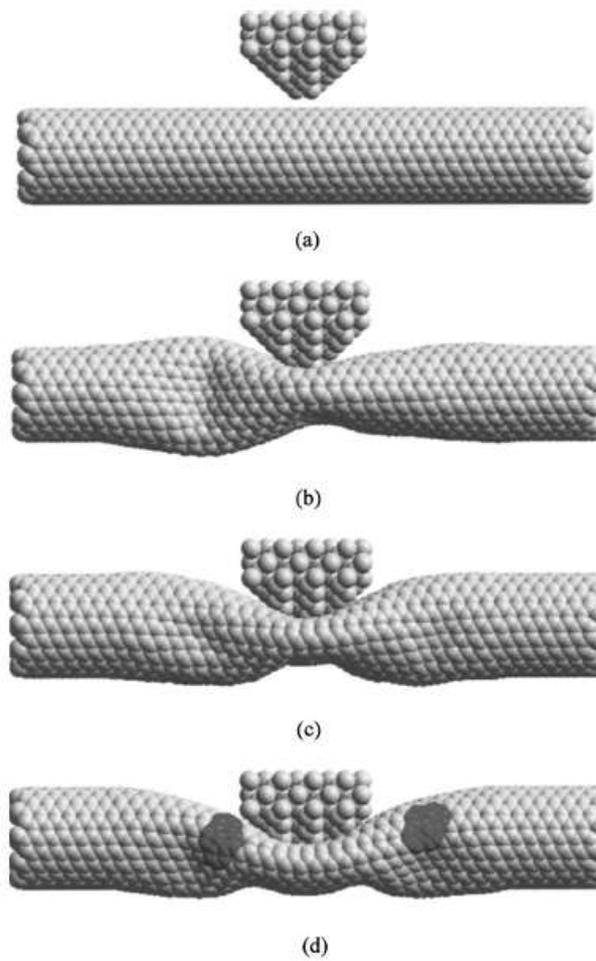


Fig. 15 The "5-7-7-5" dislocation evolves as either a crack (brittle cleavage), or as a couple of dislocations gliding away along the spiral *slip plane* (plastic yield). In the latter case, the change of the nanotube chirality is reflected by a stepwise change of diameter and by corresponding variations of electrical properties (Reprinted from [99] with permission from Elsevier Science).



- A densité 0 : la limite de déformation de nanotube diminue avec T
- Le remplissage de nanotubes permet de moduler ce comportement mais sa sensibilité à la température augmente.

Module de Young et rupture des C-MWNT

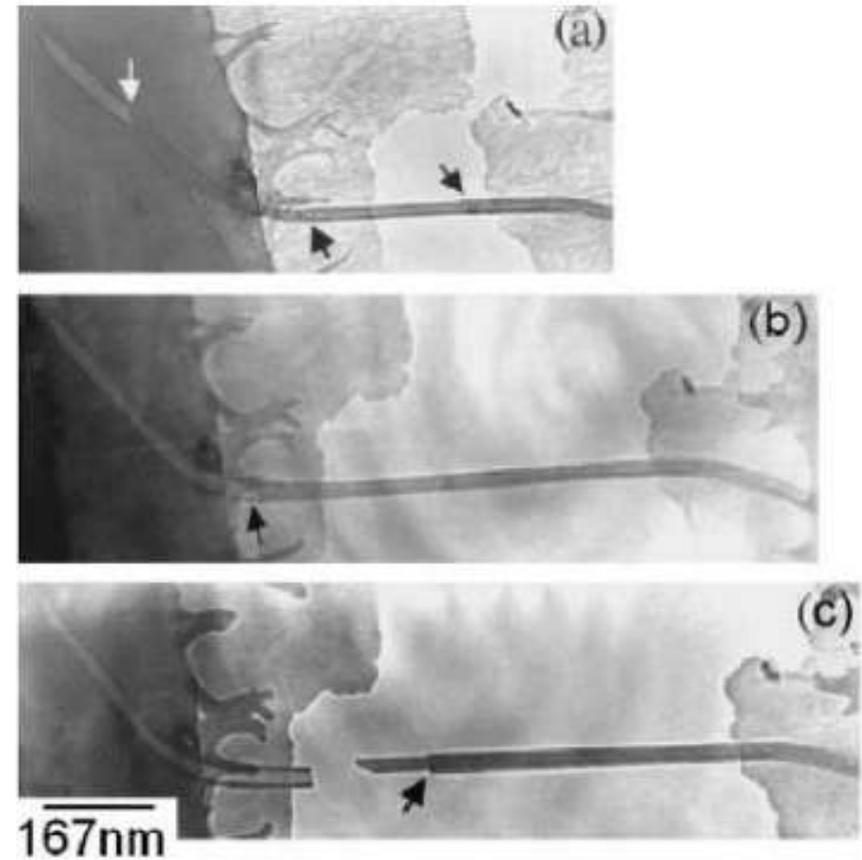
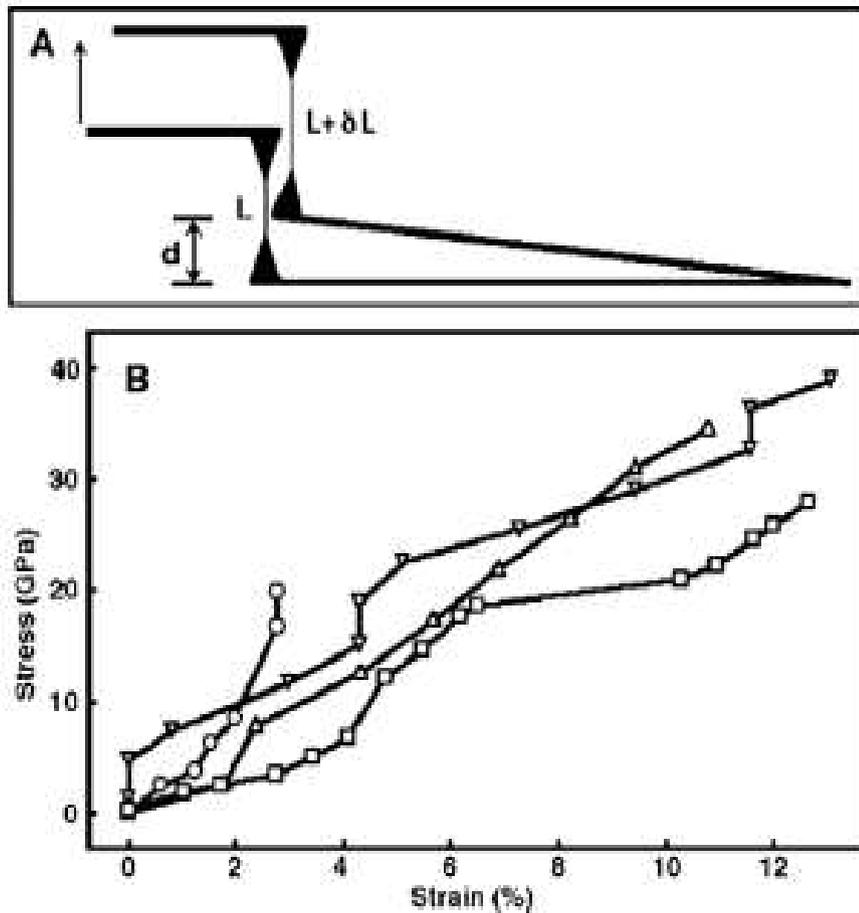
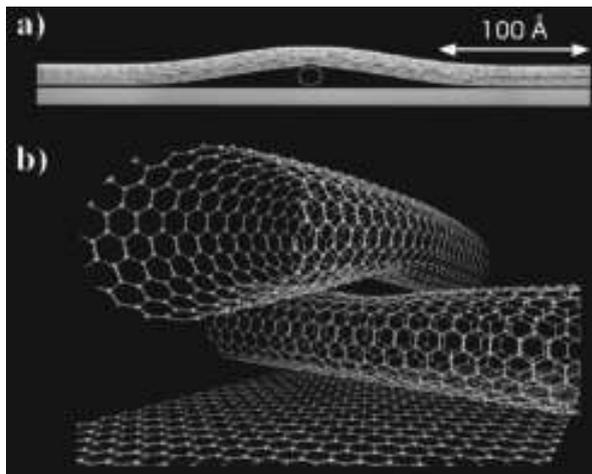
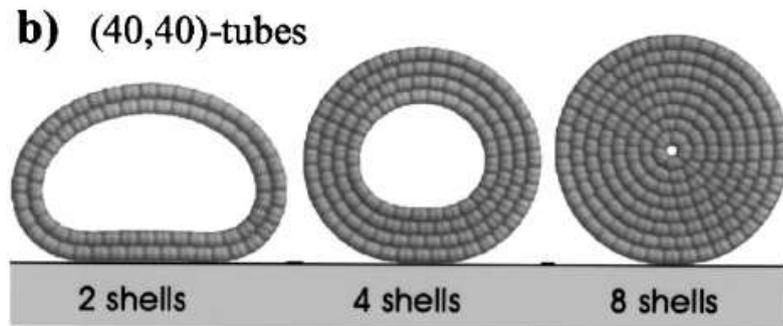
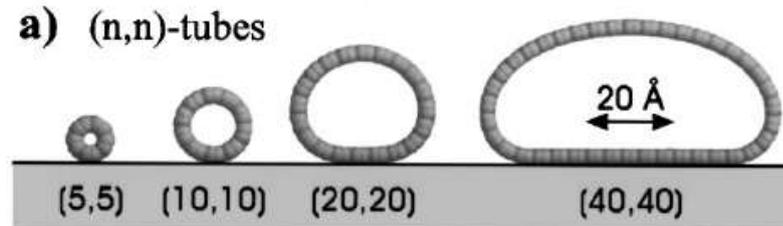
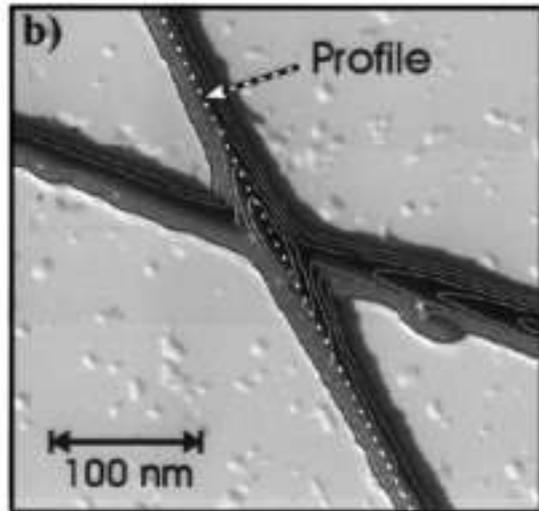


Fig. 17. TEM images showing failure of a MWNT bridging a gap in a composite film as can be seen in (c) the nanotube fails by the sword and sheath mechanism. Reproduced from [135].

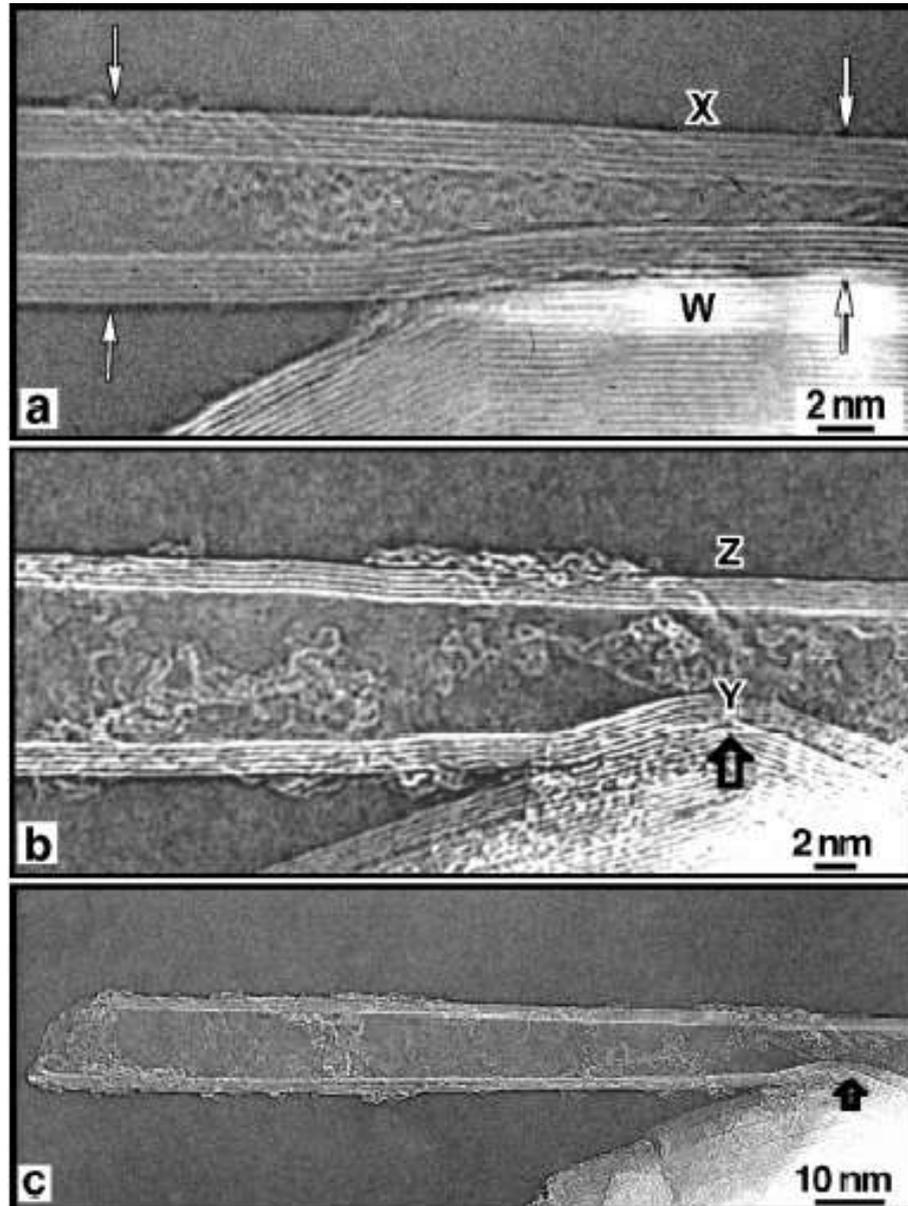
Déformation radiale des tubes

Pour des grands diamètres les interactions de van der Waals suffisent pour déformer radialement un tube

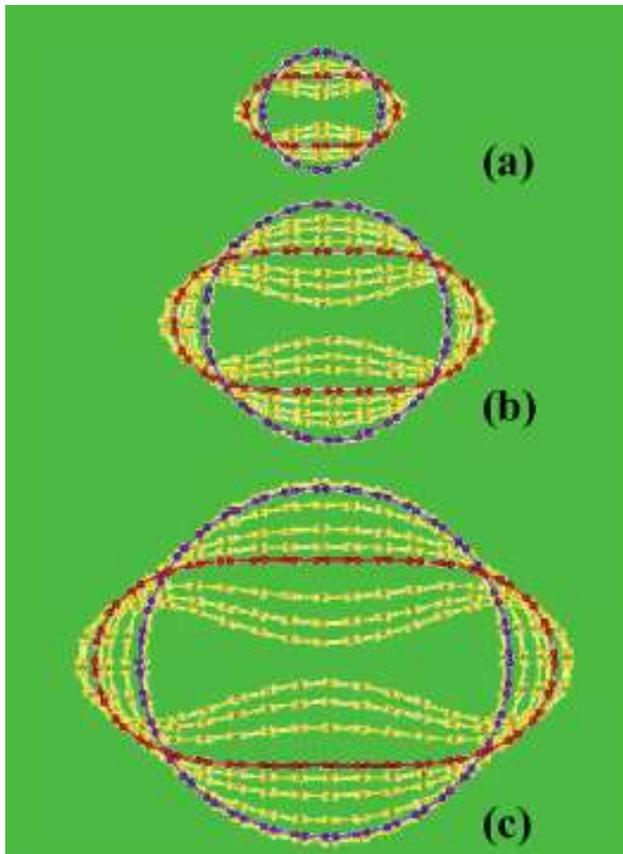


Simulations de nanotubes sur silicium

Nanotube sur nanotube



Résistance à la
compression radiale de
nanotubes : V. Lordi and
N. Yao, J. Chem. Phys.
109, 2509 (1998).

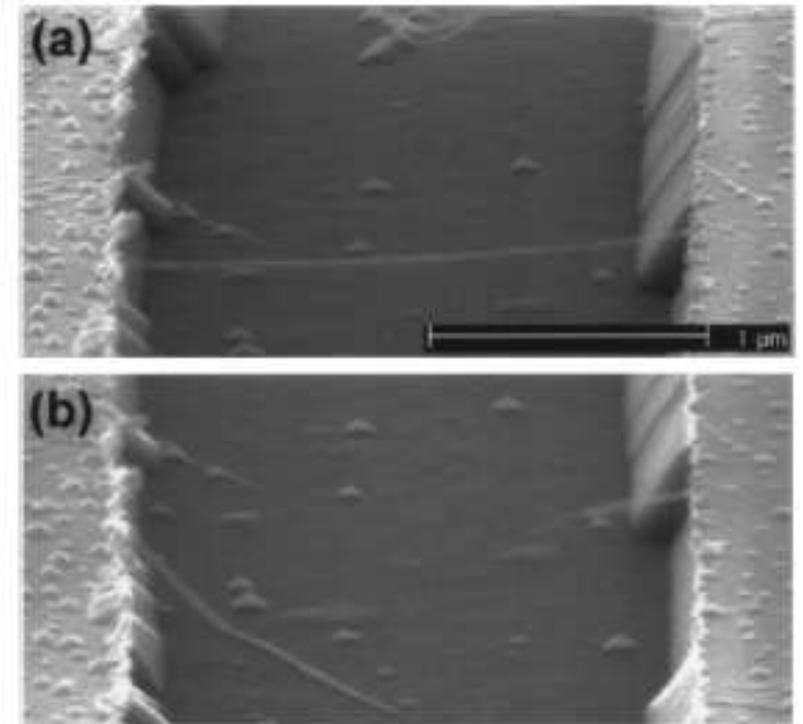
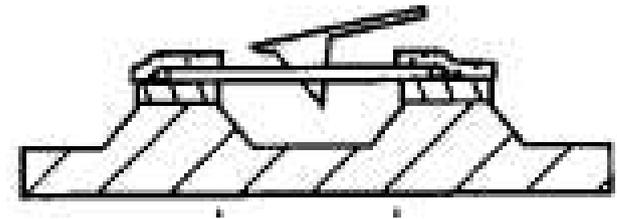
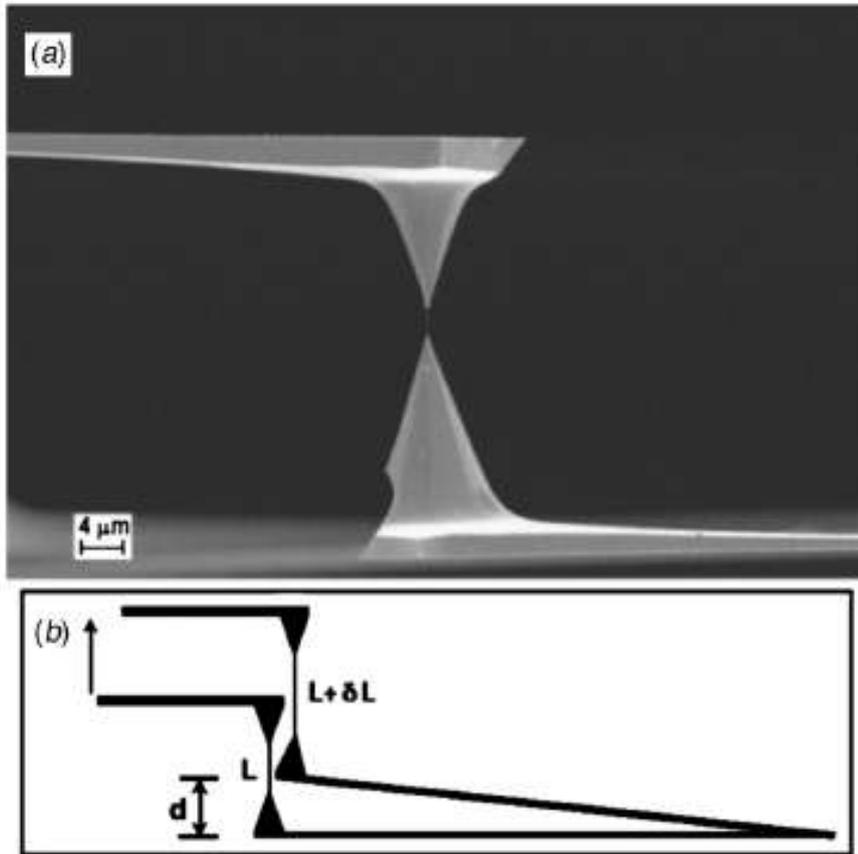


Pression de déformation d'un tube (passage

$$P_t = 3D/R^3$$

Avec D la rigidité à la flexion et R le diamètre

Limite d'élasticité de fagots de SWNT



Détermination de la limite d'élasticité : $> 45\ \text{GPa}$

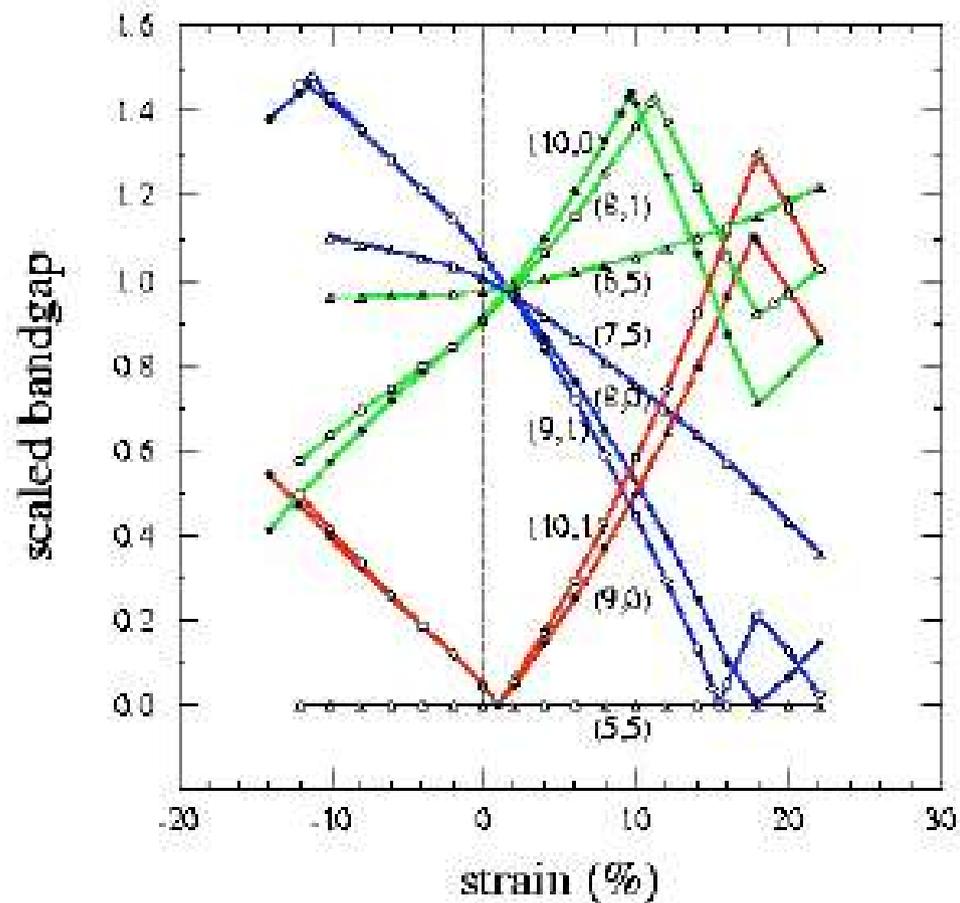


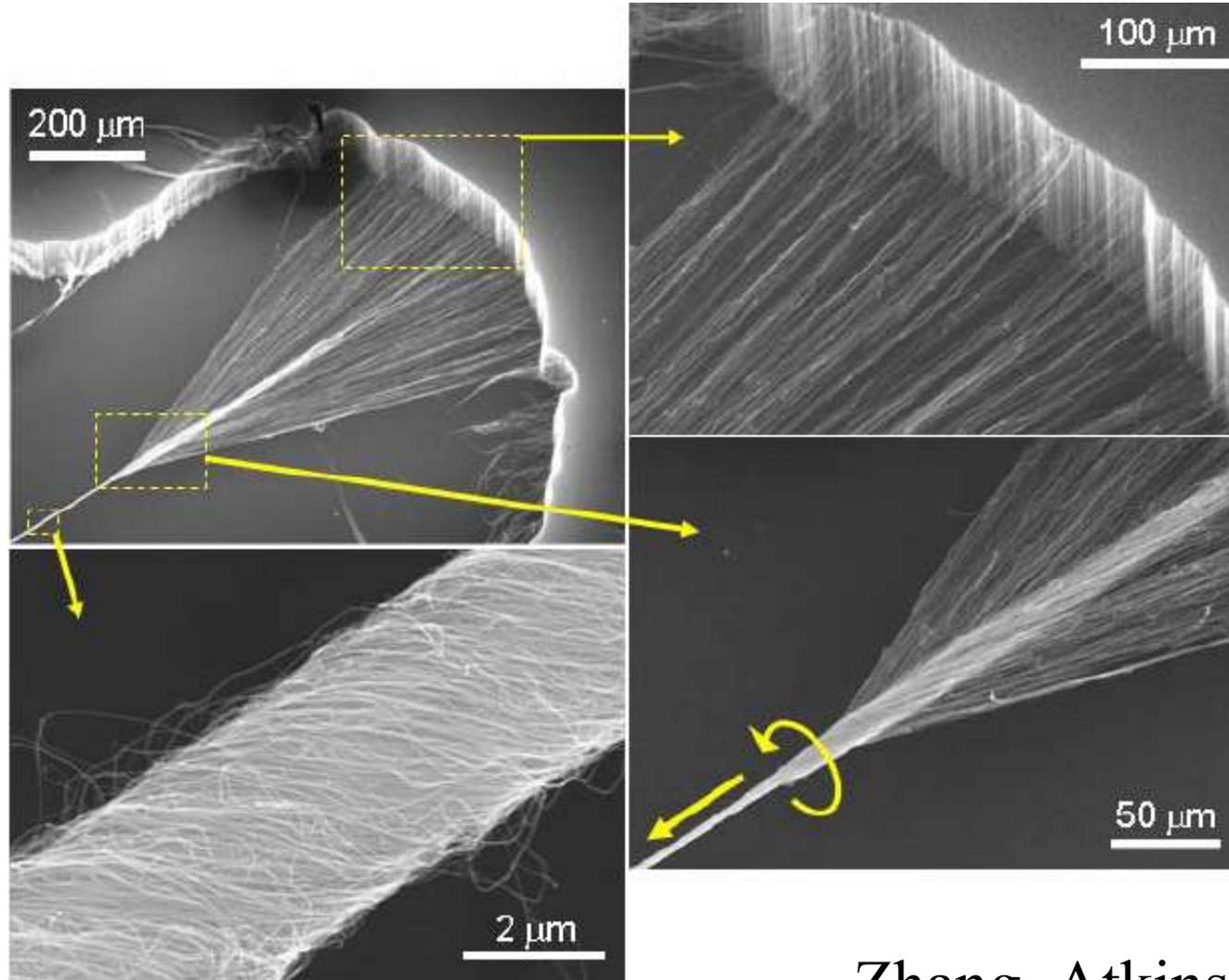
Fig. 15. Effect of strain on bandgap.

Legend: $n - m = 3q + 1$,

$n - 3 = 3q$, $n - 3 = 3q - 1$,

where n , m and q are integers.

Fibres de nanotubes

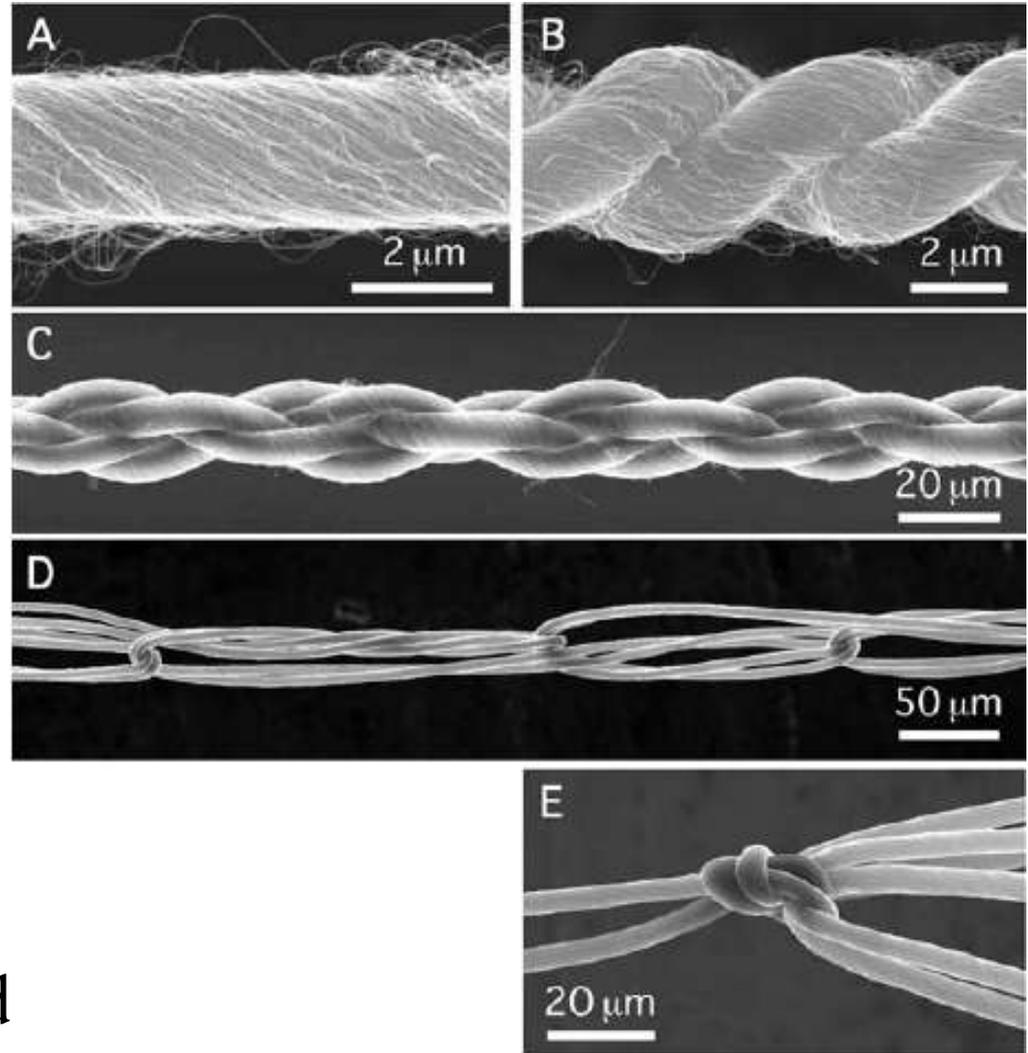


Zhang, Atkinson and
Baughman, *Science* **306**
(2004) 1358.

Fibres de nanotubes

MWCNT

- Operational $-196^{\circ}\text{C} < T < 450^{\circ}\text{C}$
- Electrical conducting
- Toughness comparable to Kevlar
- No rupture in knot



Zhang, Atkinson and
Baughman, *Science* **306**
(2004) 1358.

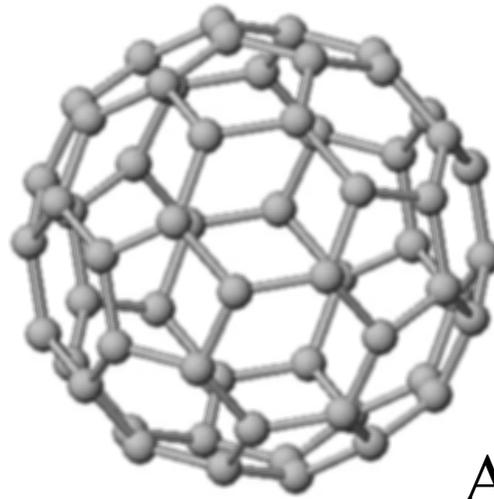
Fullerene

”The most symmetrical large molecule”

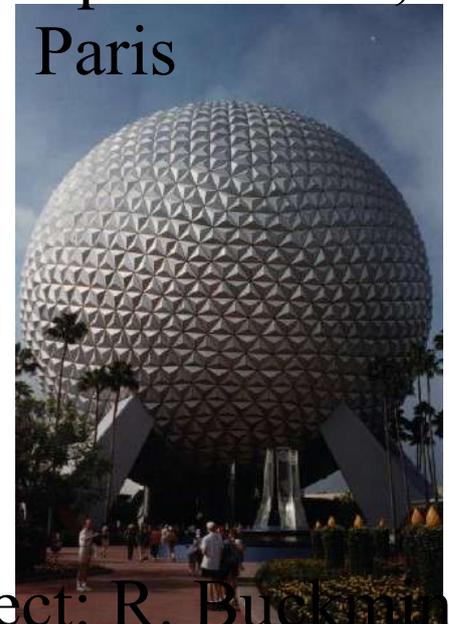
- Discovered in 1985
 - Nobel prize Chemistry 1996, Curl, Kroto, and Smalley
- C₆₀, also 70, 76 and 84.
 - 32 facets (12 pentagons and 20 hexagons)
 - prototype



~1 nm



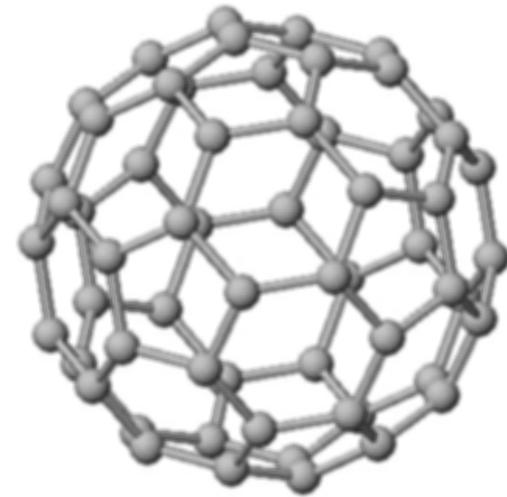
Epcot center,
Paris



Architect: R. Buckminster
Fuller

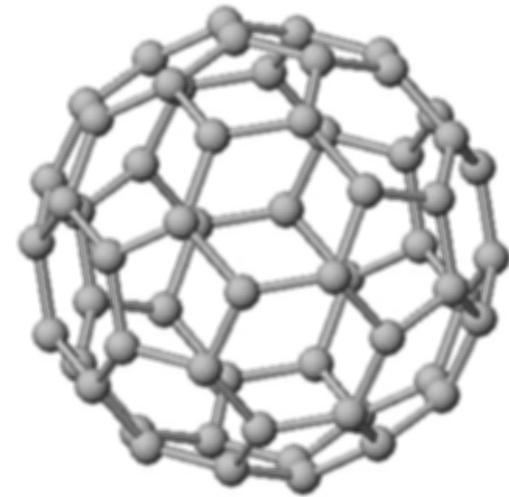
Fullerene

- Symmetric shape
→ lubricant
- Large surface area
→ catalyst



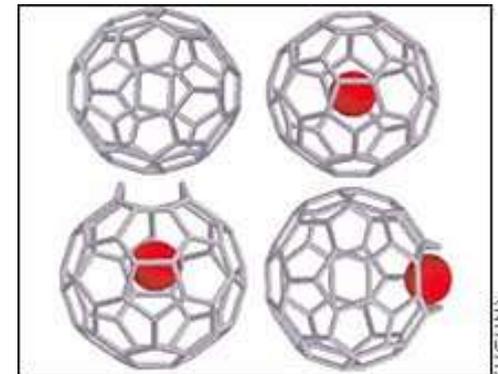
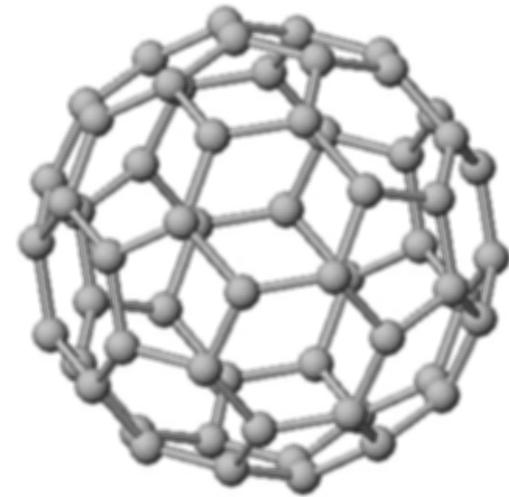
Fullerene

- Symmetric shape
→ lubricant
- Large surface area
→ catalyst
- High temperature ($\sim 500^{\circ}\text{C}$)
- High pressure



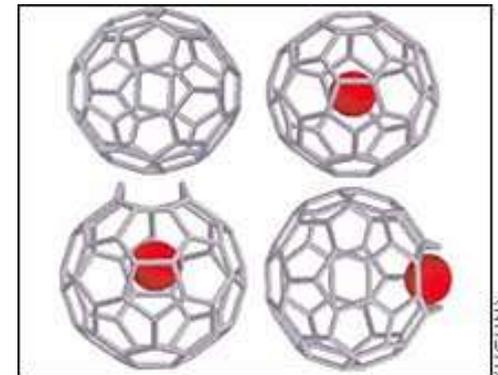
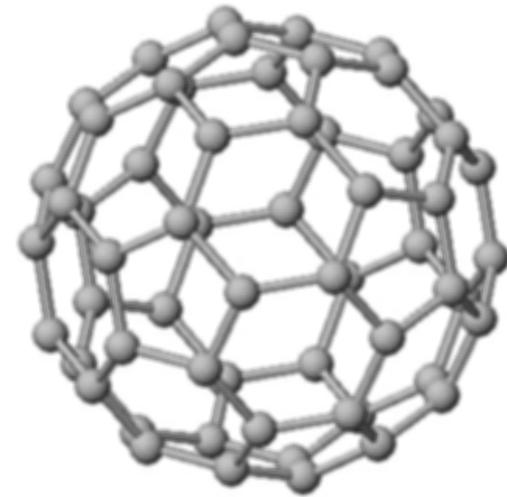
Fullerene

- Symmetric shape
→ lubricant
- Large surface area
→ catalyst
- High temperature ($\sim 500^{\circ}\text{C}$)
- High pressure
- Hollow
→ caging particles



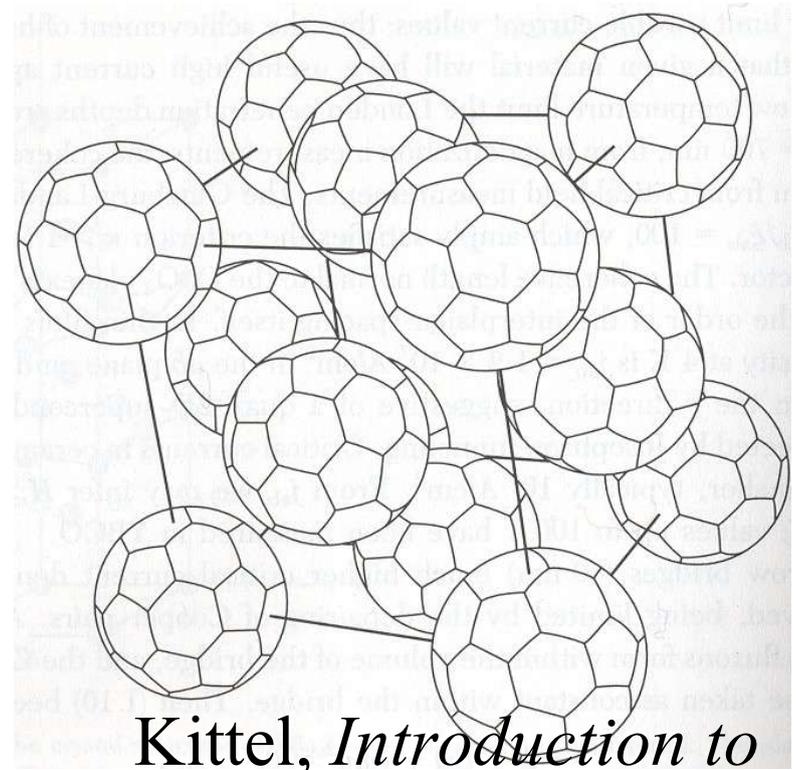
Fullerene

- Symmetric shape
 - lubricant
- Large surface area
 - catalyst
- High temperature ($\sim 500^{\circ}\text{C}$)
- High pressure
- Hollow
 - caging particles
- Ferromagnet?
 - polymerized C_{60}
 - up to 220°C



Fullerene

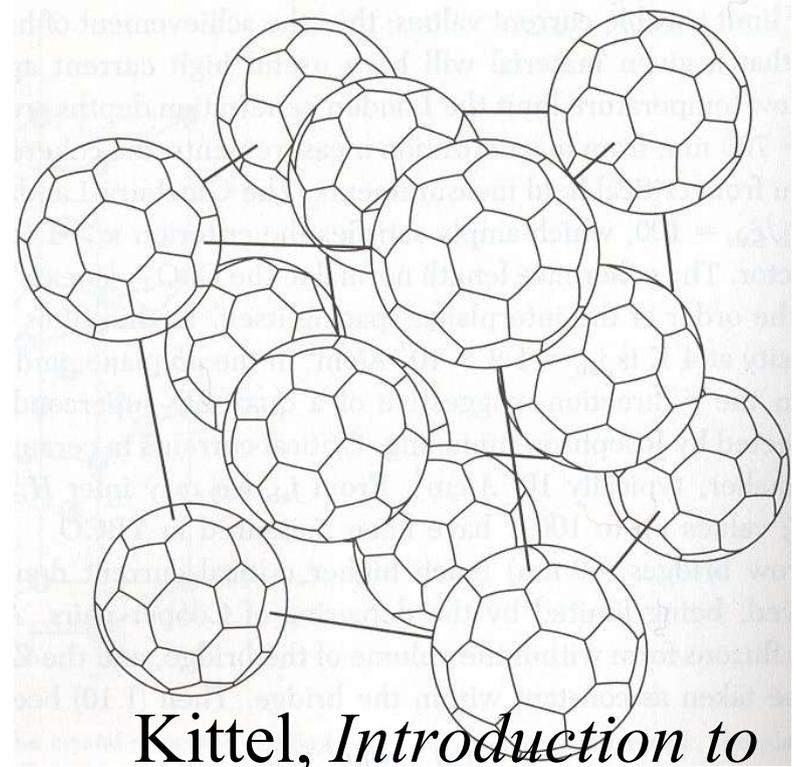
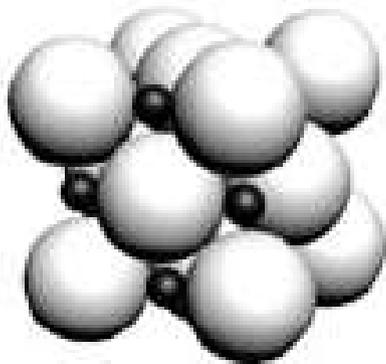
- Chemically stable as graphite
 - most reactive at pentagons
- Crystal by weak van der Waals force



Kittel, *Introduction to Solid State Physics*, 7th ed. 1996.

Fullerene

- Chemically stable as graphite
 - most reactive at pentagons
- Crystal by weak van der Waals force
- Superconductivity
 - K_3C_{60} : 19.2 K
 - $RbCs_2C_{60}$: 33 K



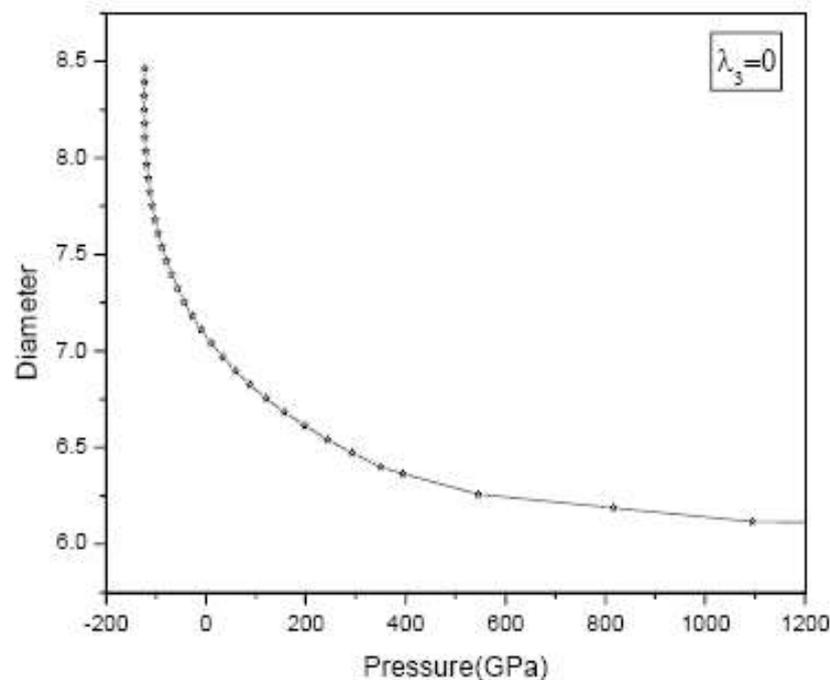
Kittel, *Introduction to Solid State Physics*, 7th ed. 1996.

Fullerenes

Bulk modulus of a sole C_{60} molecule has been only calculated.

It is found to lie between 650 and 850 GPa.

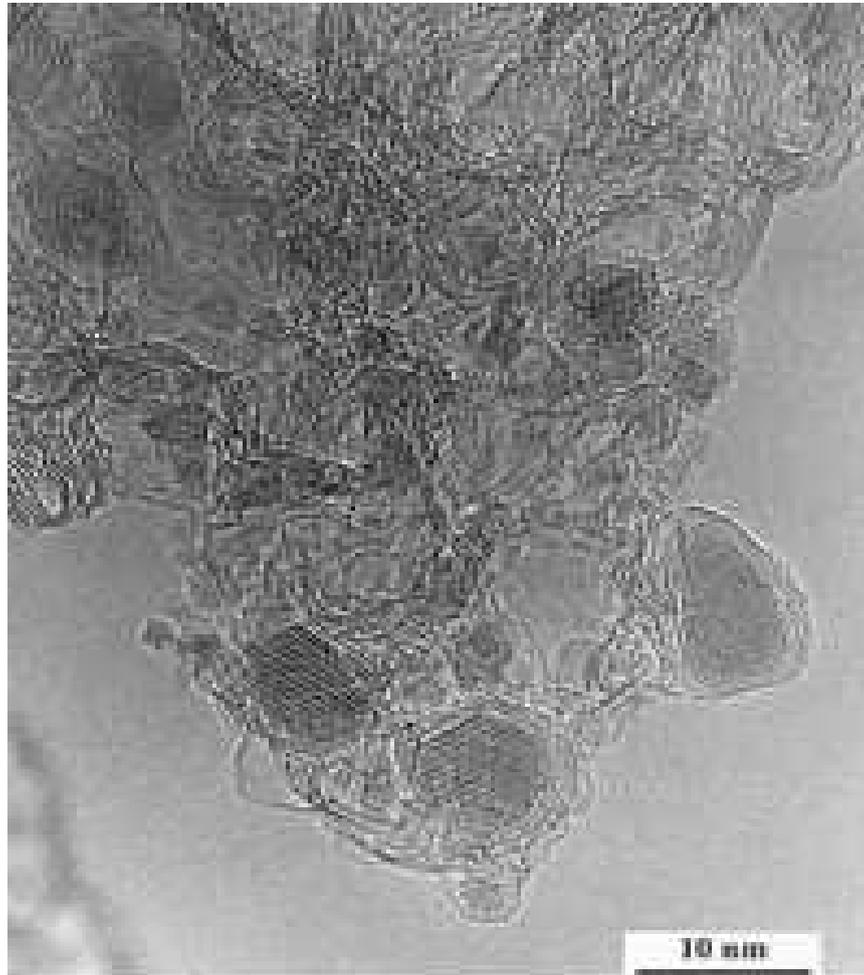
There is no material exhibiting such high bulk modulus !.



Pressure needed to attain different diameters of the molecule

Fullerenes in meteorites

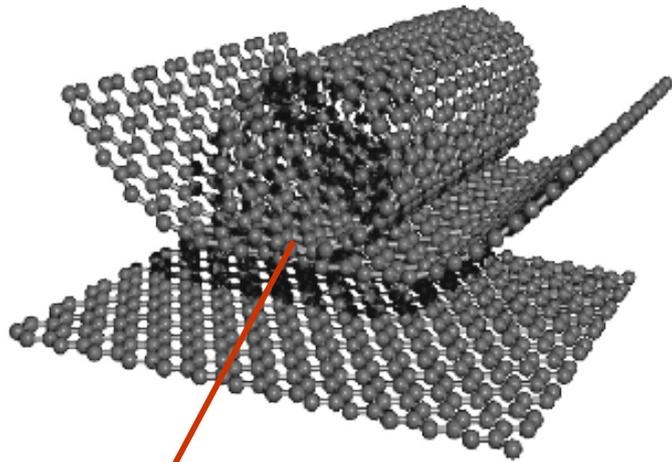
And ... fullerenes have been found in the Allende meteorite which fell on Mexico in 1969, reinforcing the idea that the molecule is associated with the origin of life...



Exemple de recherche réalisé dans le groupe
« Nanomatériaux sous conditions extrêmes »

Peapods C₇₀@SWNT
sous pression

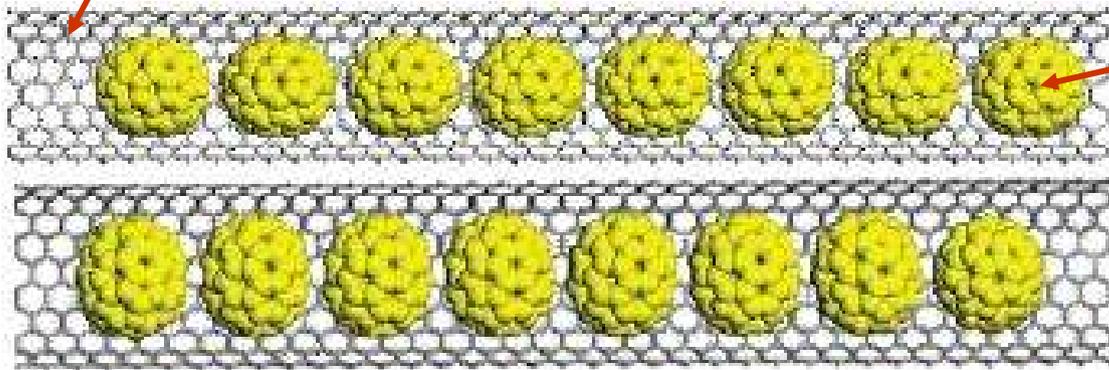
Qu'est-ce qu'un peapod $C_{70}@SWNT$?



Nanotube monofeuillet (SWNT)

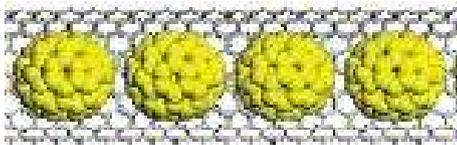
+

Fullerènes C_{70}

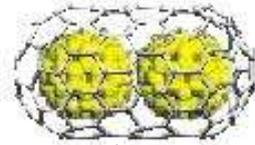


Motivations

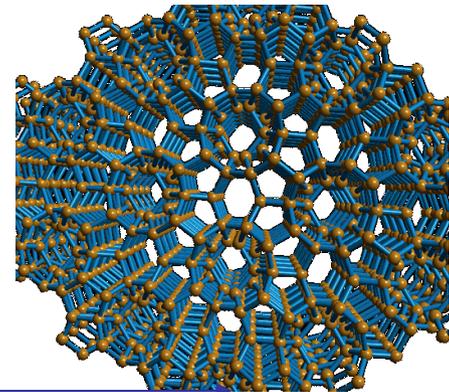
- Etude des Peapods sous pression :
 - Comparaison avec les SWNT vides
 - Nature des transitions des SWNT
 - Interaction SWNT/fullerènes
 - Effet sur les C70
 - Protection des fullerènes
 - Polymérisation avec contrainte directionnelle
 - Nouvelles structures carbonées
 - Transformation 0D, 1D, 3D ?



?

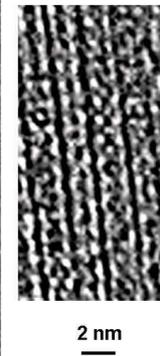
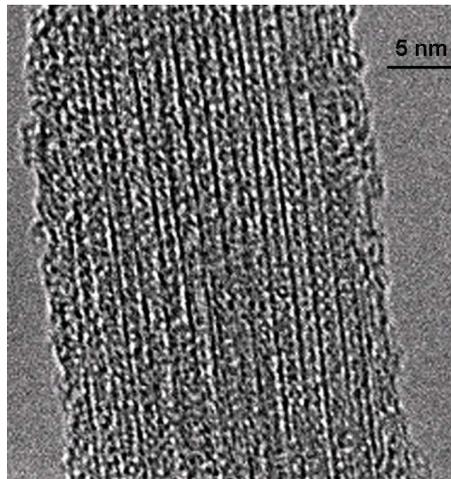
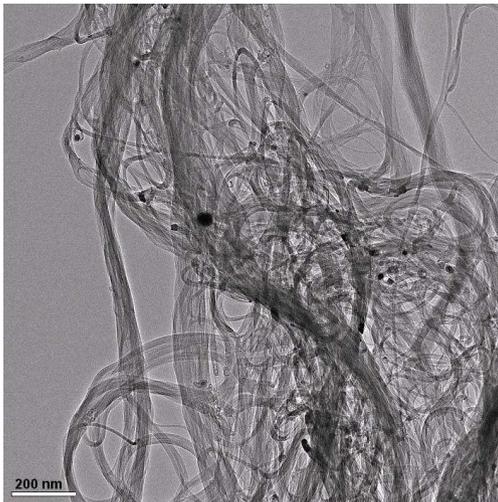
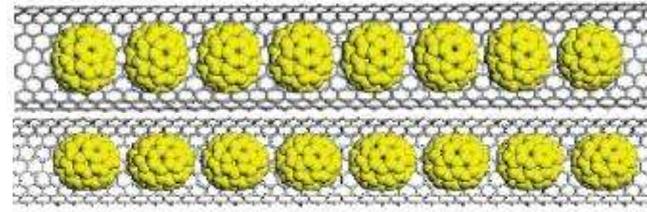


?



Description de l'échantillon

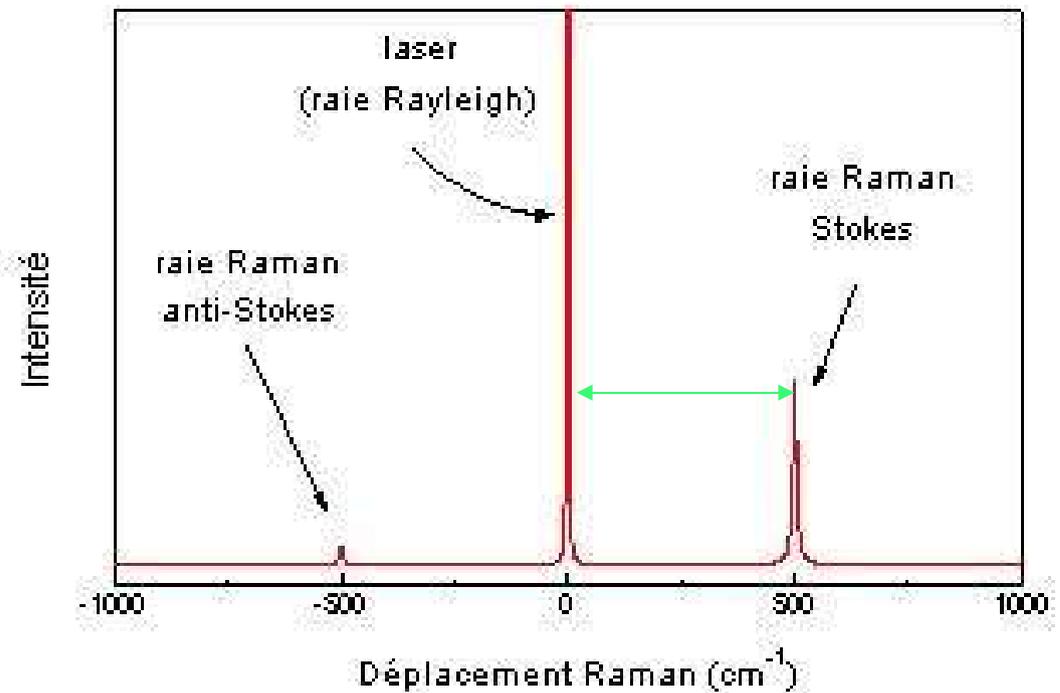
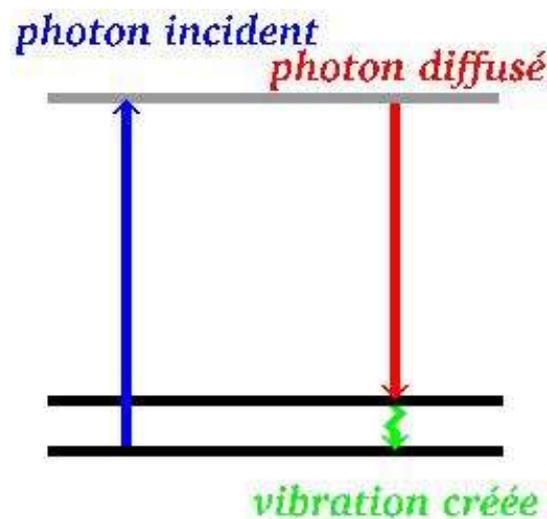
- Production et premières analyses : L. Kavan
- Diamètres des tubes : 1,25 à 1,47 nm
- Taux de remplissage > 72%
- Deux distances inter-fullerènes
 - 1,00 nm : position **debout**
 - 1,10 nm : position **couchée**



Images MET : Raul Arenal
Argonne National Laboratory,
EMC group

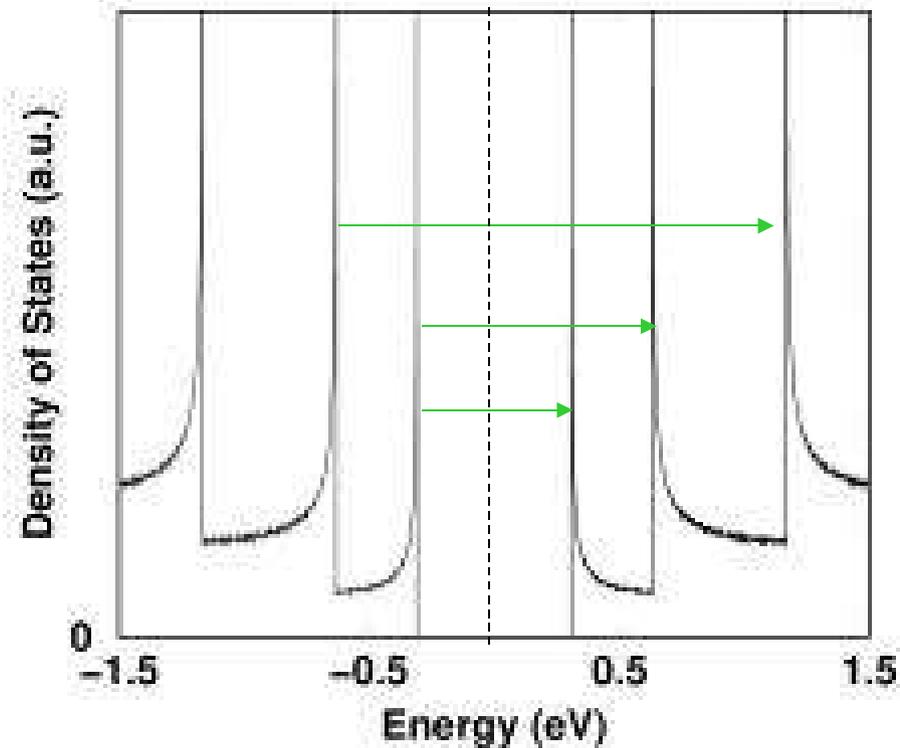
Spectroscopie Raman

- Principe physique :



Spectroscopie Raman

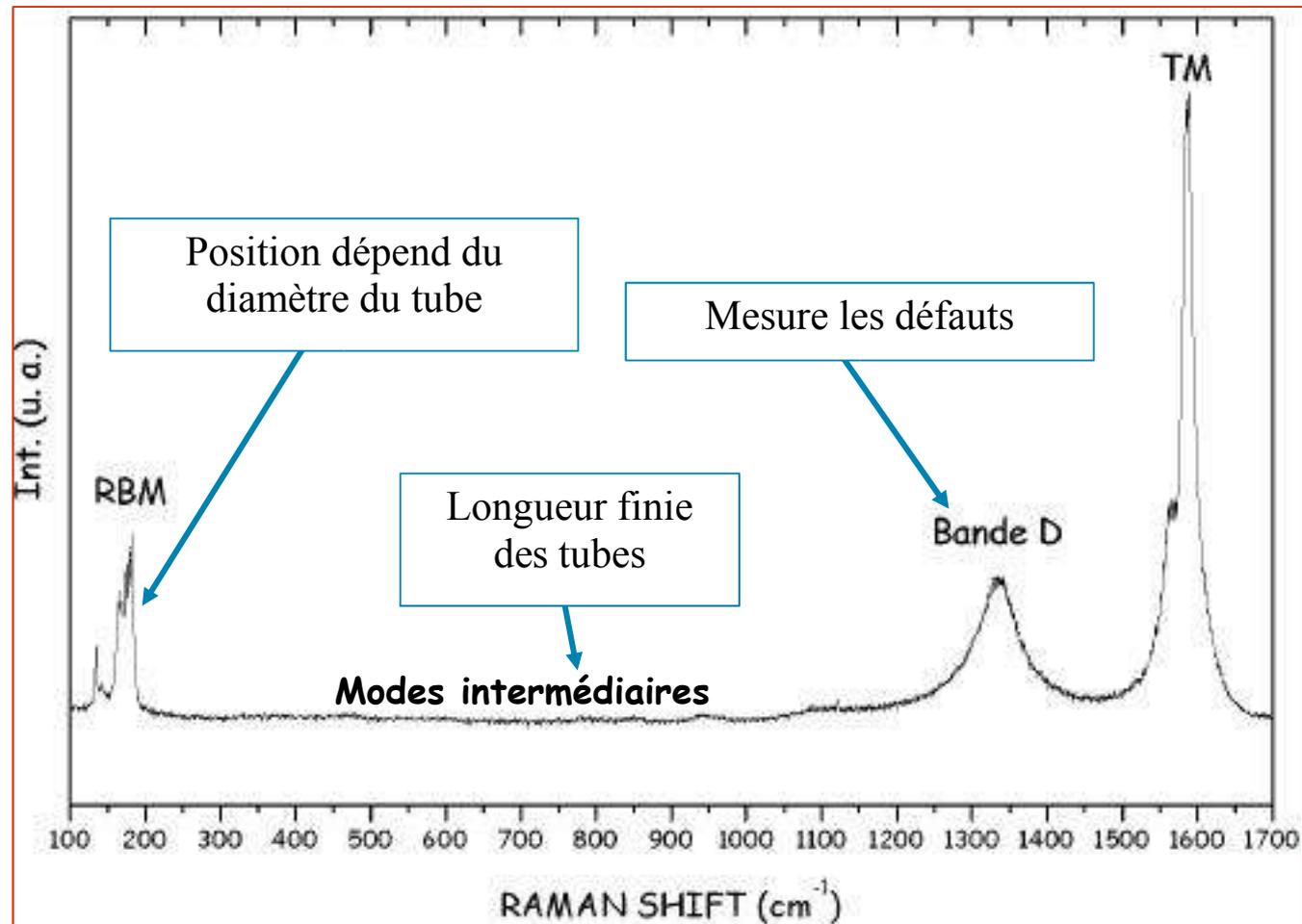
- Résonance des nanotubes



Singularités de Van Hove

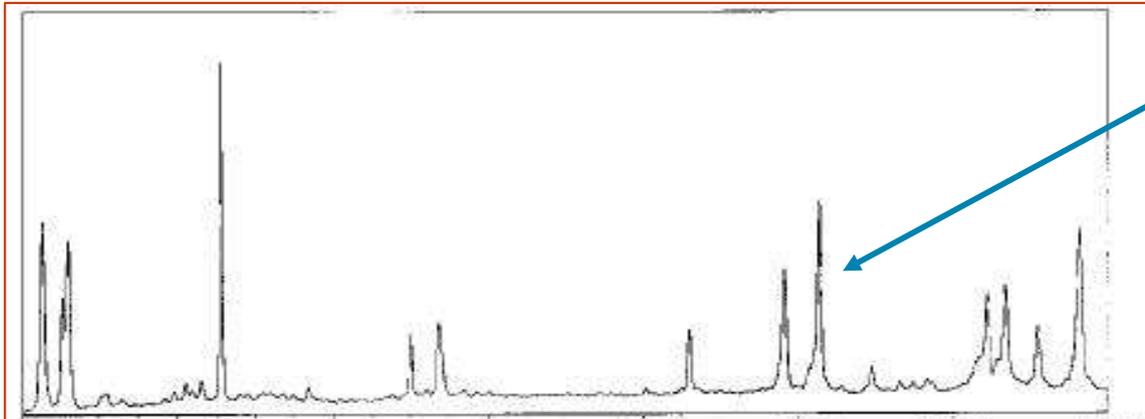
Spectroscopie Raman

- Spectre Raman des nanotubes (résonnant)

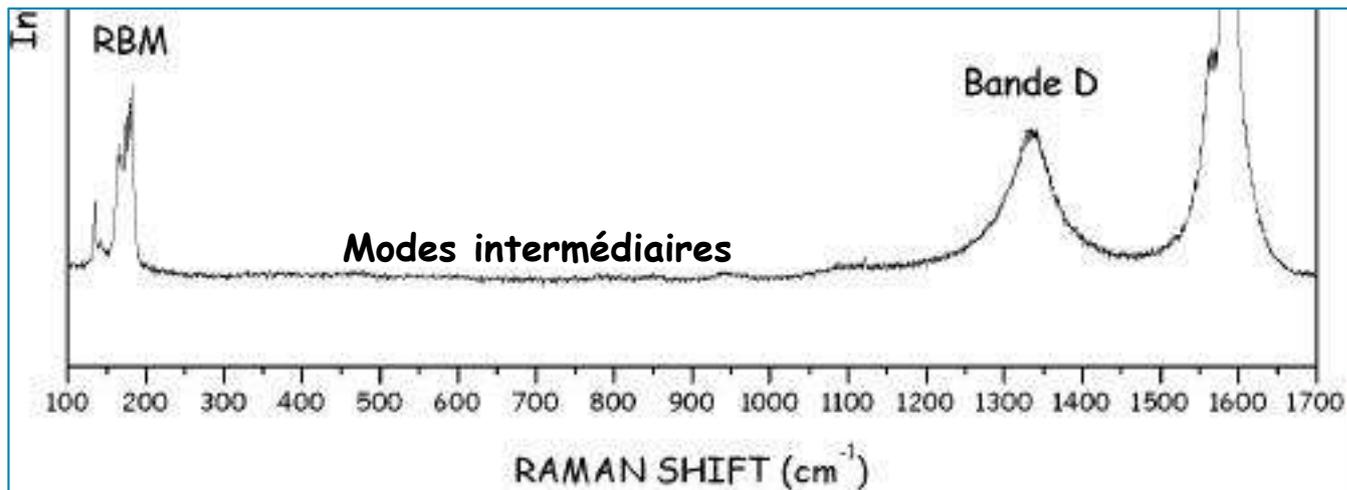


Spectroscopie Raman

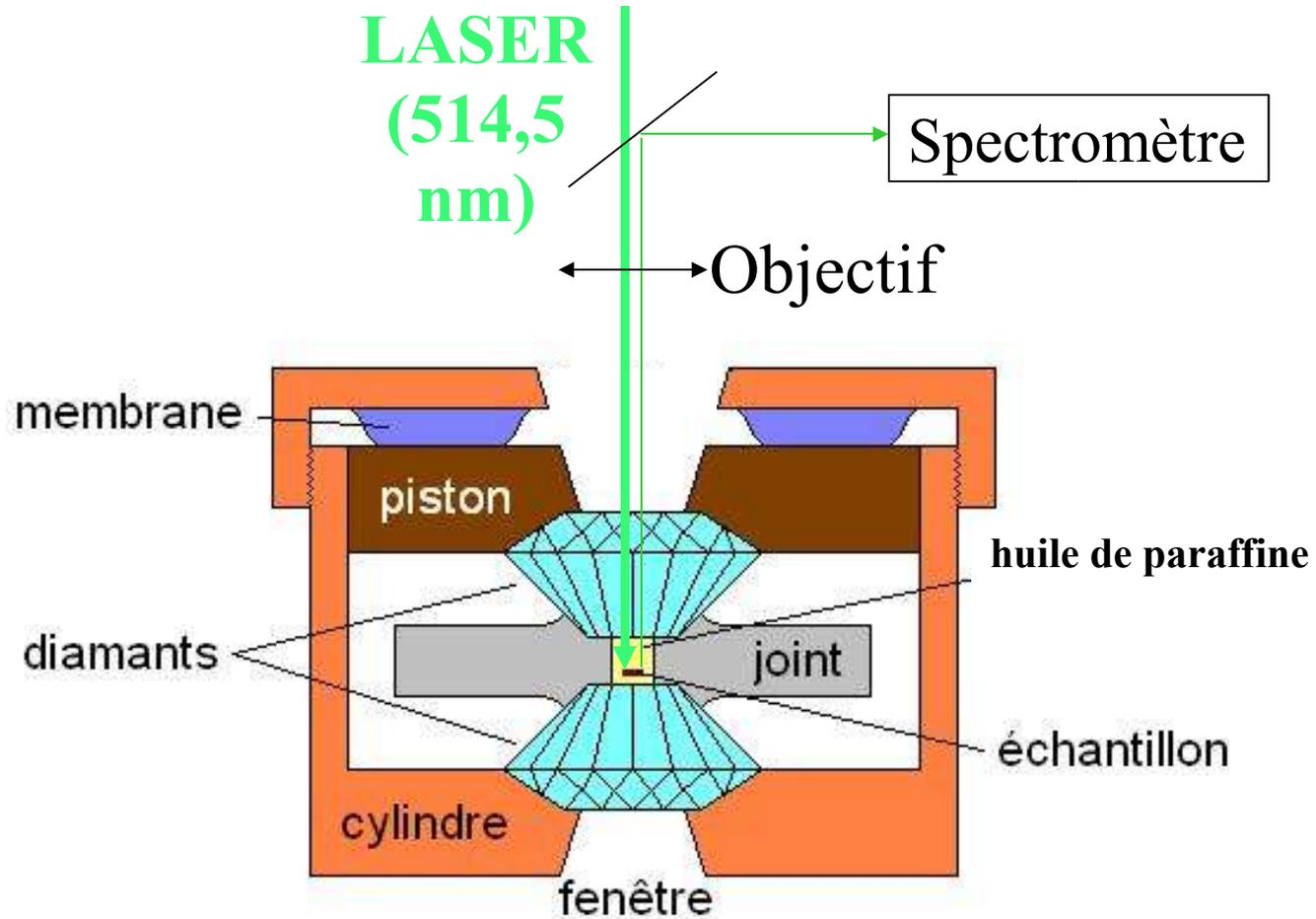
- Spectre Raman des C_{70}



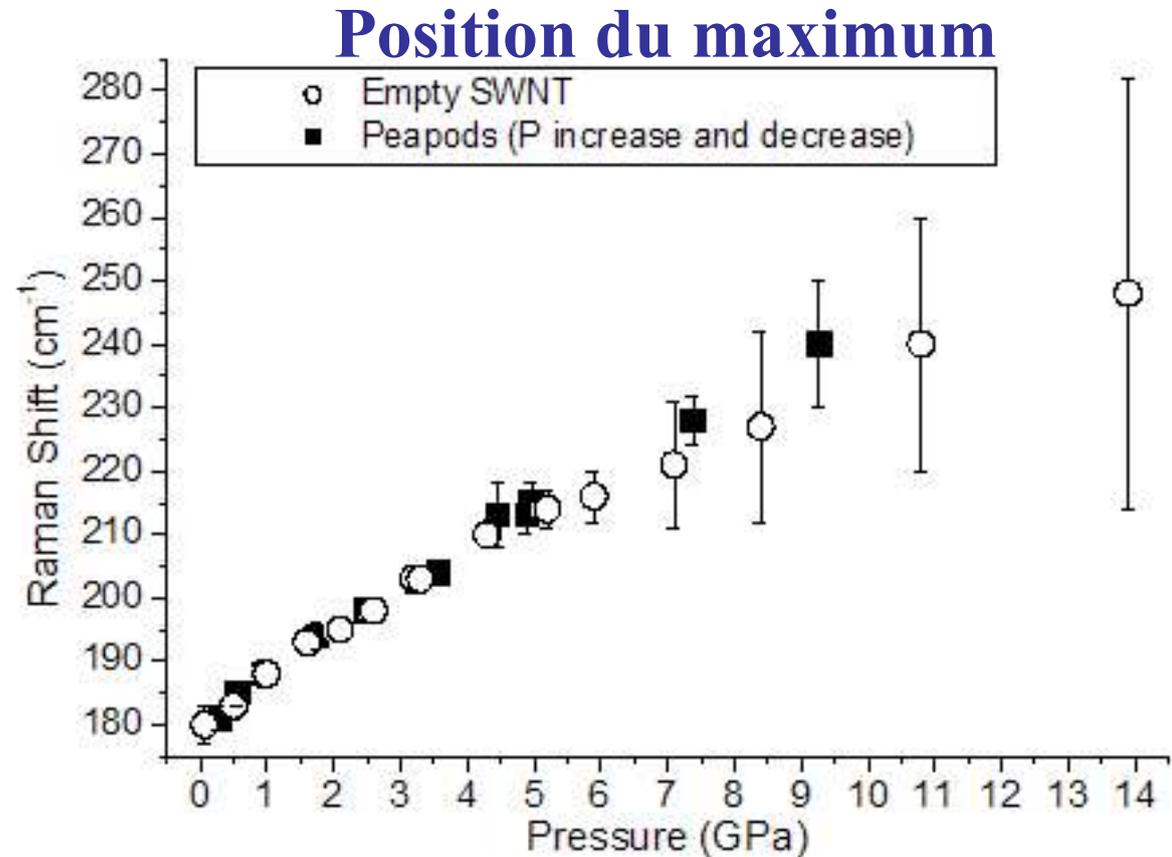
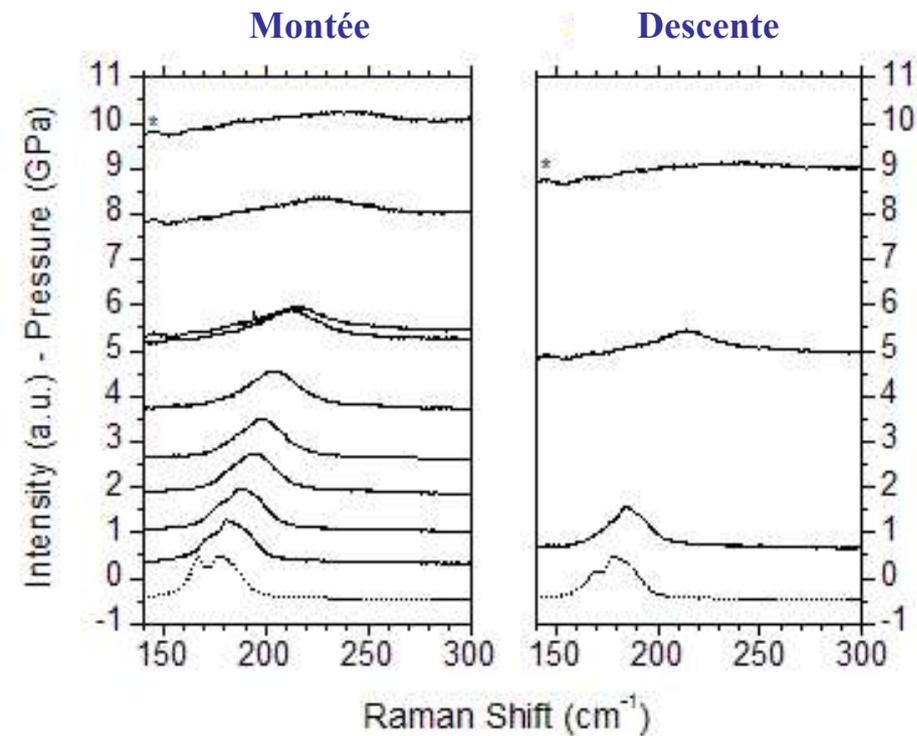
Pics fins et de faible intensité



Montage expérimental

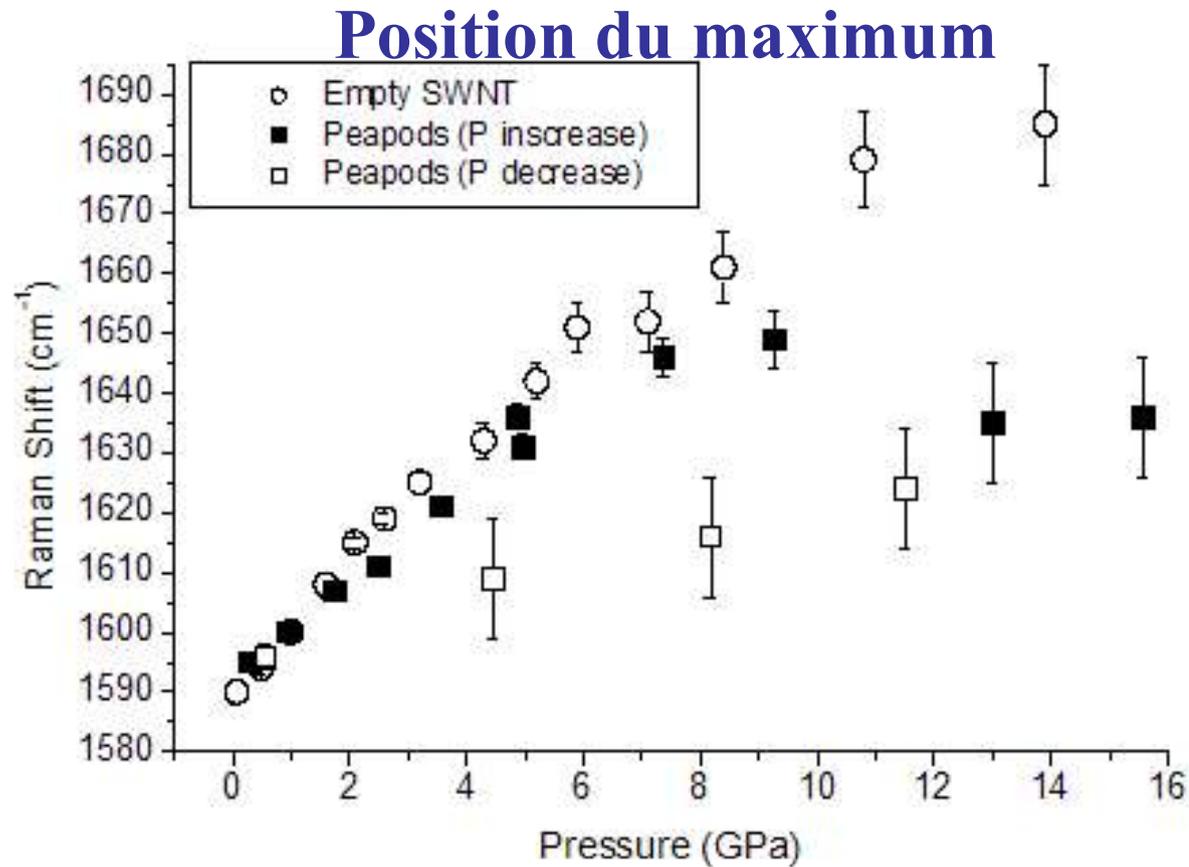
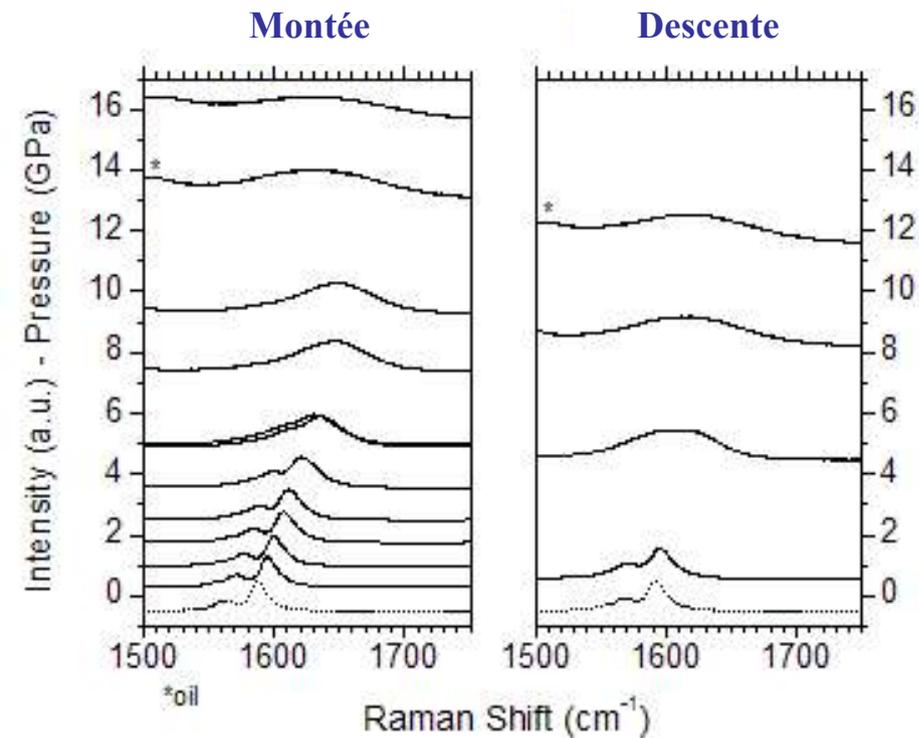


RBM



- ✓ Même évolution que SWNT vides
- ✓ Monotone et réversible
- ✓ Disparition vers 9,5 GPa

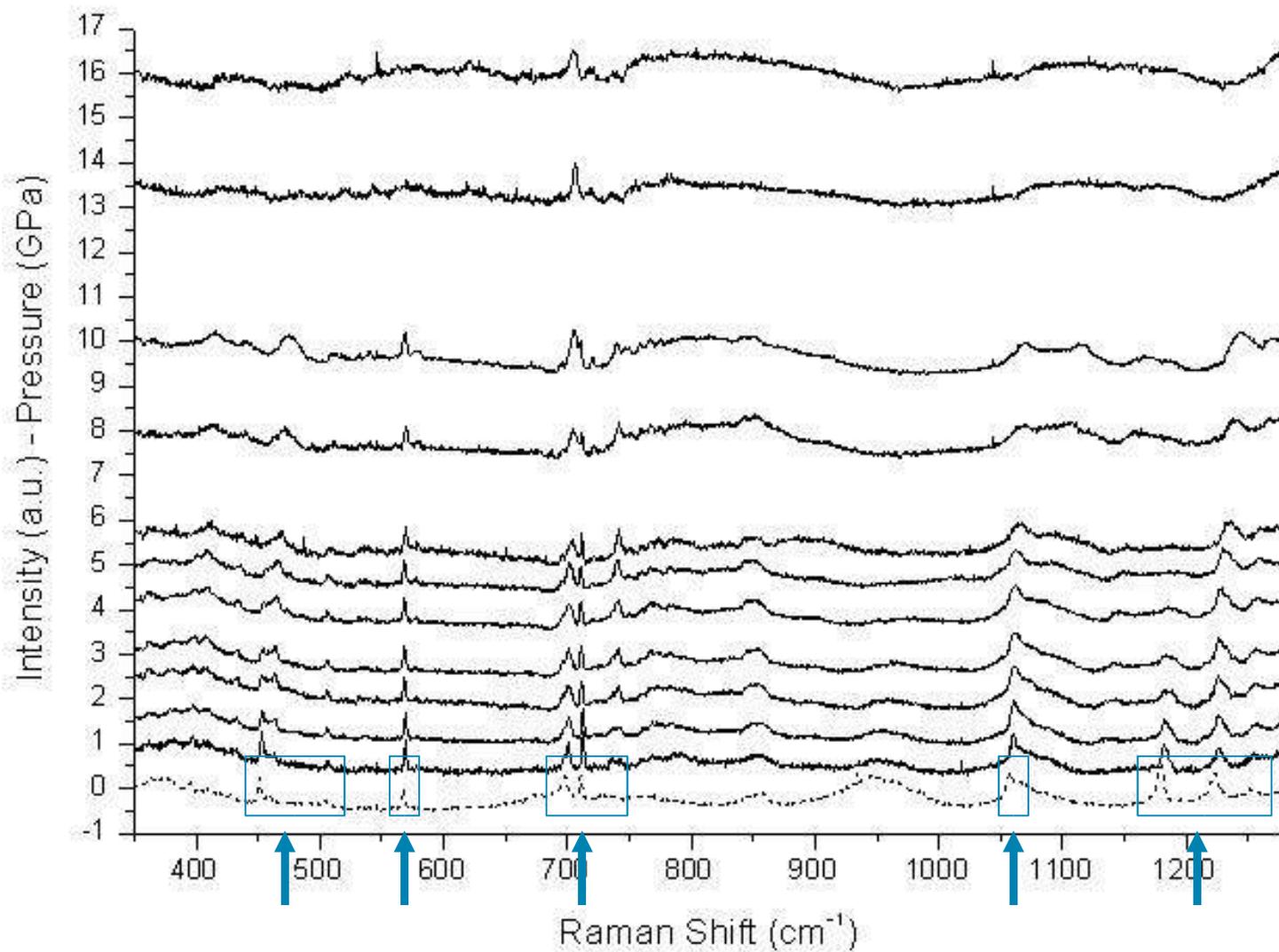
TM



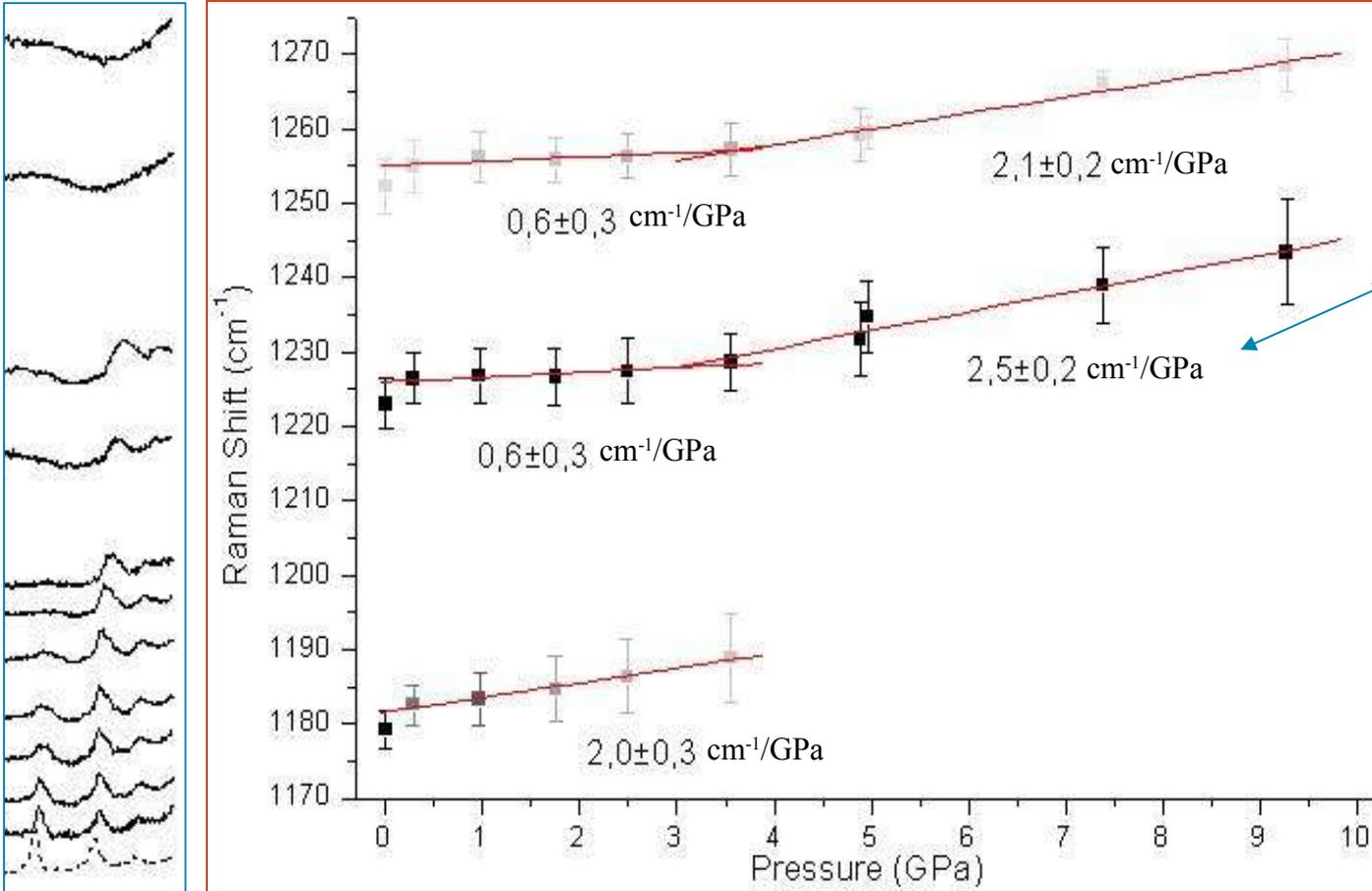
- ✓ Palier à partir de 8 ± 1 GPa
- ✓ Hystérésis de 6 GPa
- ✓ Peapods plus fragiles que SWNT vides

Zone des fullerènes C₇₀

Pression

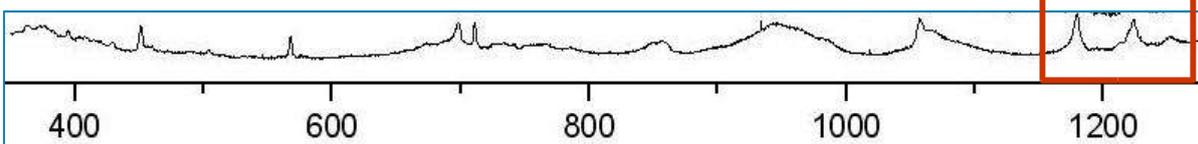


Fullerènes



Observé dans C70 pur:
à 1224cm⁻¹: 3.2cm⁻¹/GPa

- ✓ disparition d'un mode à partir de 2 GPa
- ✓ rupture de pente vers 3,5 GPa
- ✓ disparition des autres modes vers 9,5 GPa



Principaux faits marquants (C_{70})

- 2 GPa
 - Apparition d'un pic / Disparition de deux pics
- 3,5 GPa
 - Rupture de pente des modes C_{70}
 - Avant 3,5 GPa : pentes très faibles
 - Après 3,5 GPa : pentes \approx pentes C_{70} purs
- 9,5 GPa
 - Disparition de tous les modes, sauf un
- Retour après 15 GPa
 - Très bonne réversibilité

