Curso de Nanomecánica

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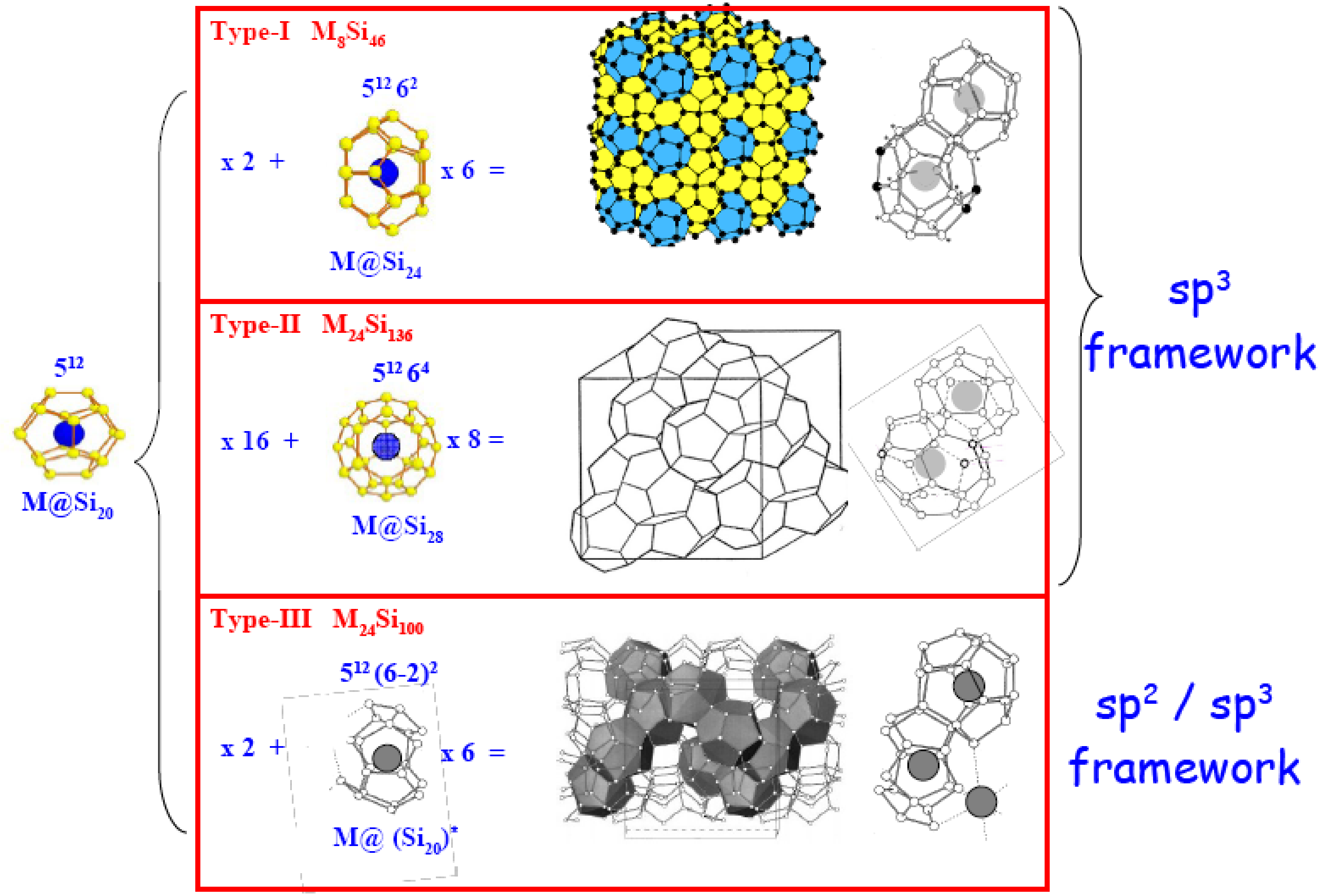
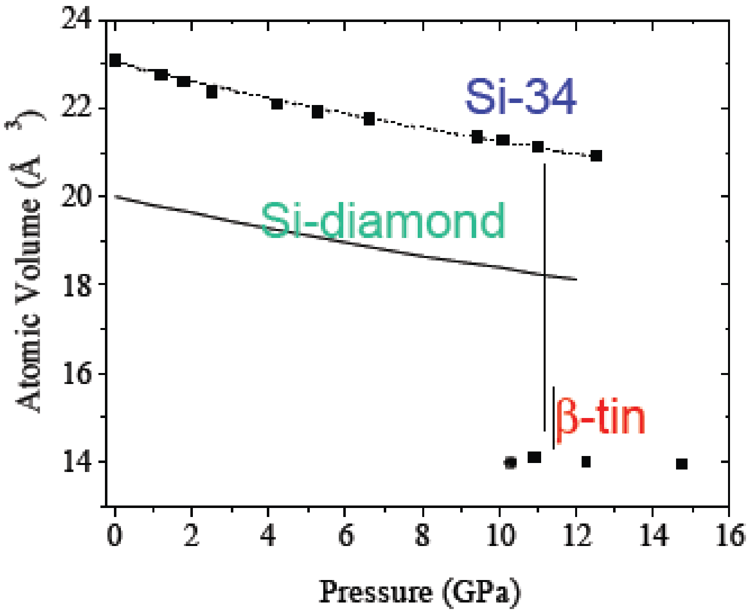
Clatratos de Si

- Son “estructuras-cajas”
- Sus propiedades físicas son gobernadas por los enlaces tetraédricos sp^3 y por las interacciones guest-host.
- La intercalación endoédrica da lugar a comportamientos únicos como su extrema estabilidad a altas presiones, así como a transformaciones de fase isoestructurales.
- Existen 3 tipos de clatratos de Si correspondiendo a diferentes etequiometrías:

Main clathrate structures



Stability @ HP of empty clathrates



- Nanocages network stable → 11 GPa !
- P_t (Si_{136}) ≈ P_t(Si-diamond)

- 1st order transition
- ΔV/V=0.33 !
- for P > P_t Si-diamond phase diagram

- $B_0(Si_{136})$ ≤ B_0(Si-diamant)
  = 90 GPa = 98 GPa

Clathrates = low compressible & very stable !

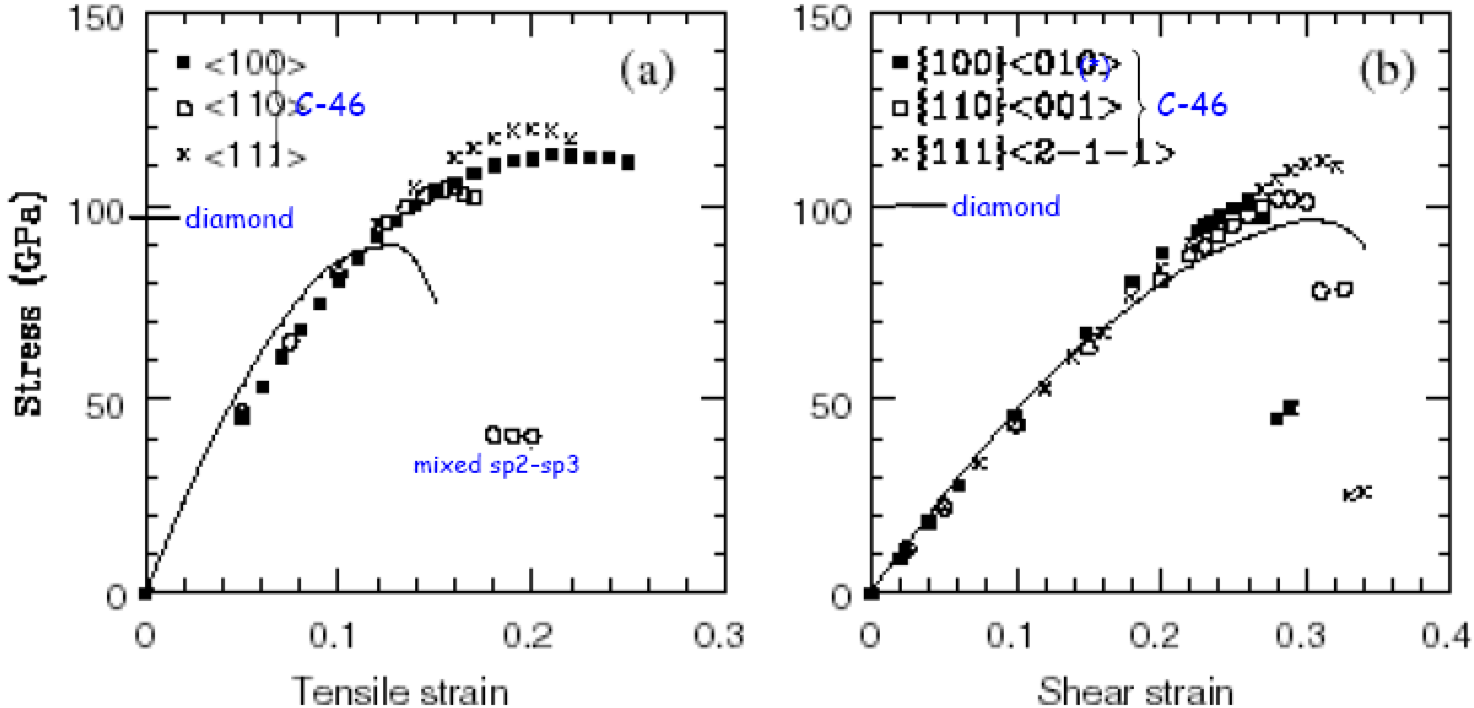
A. San Miguel et al.,
PRL 83 (1999), PRB 65 (2002).

And the compressibility of a carbon clathrate ?

Bo (GPa)	Measured	Calculated
Si-2 Si-34	97 90	96.7 87.7
C-2 C-34	446 -	462 398

Carbon clathrates : harder than diamond ?

Ideal strength : *maximum stress that a single crystal can sustain before yielding to a plastic deformation*

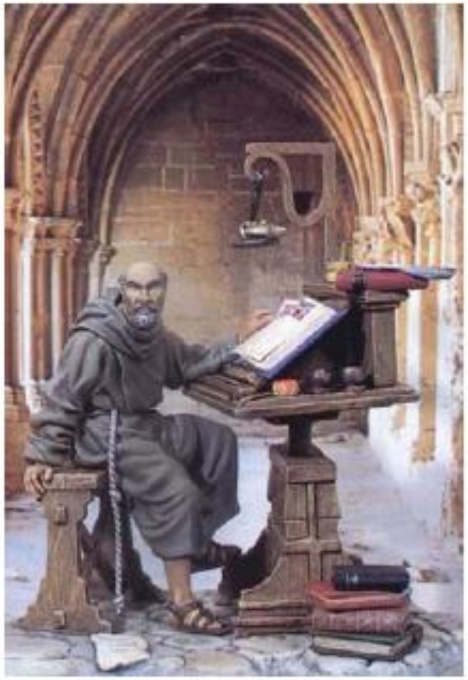


ab initio LDA-DFT Siesta

(*) Shearing the {100} slip plane along the <010> direction

X. Blase, Ph. Gillet, A. San Miguel and P. Mélinon, Phys. Rev. Lett. **92** (2004) but…

are carbon clathrates possible ?



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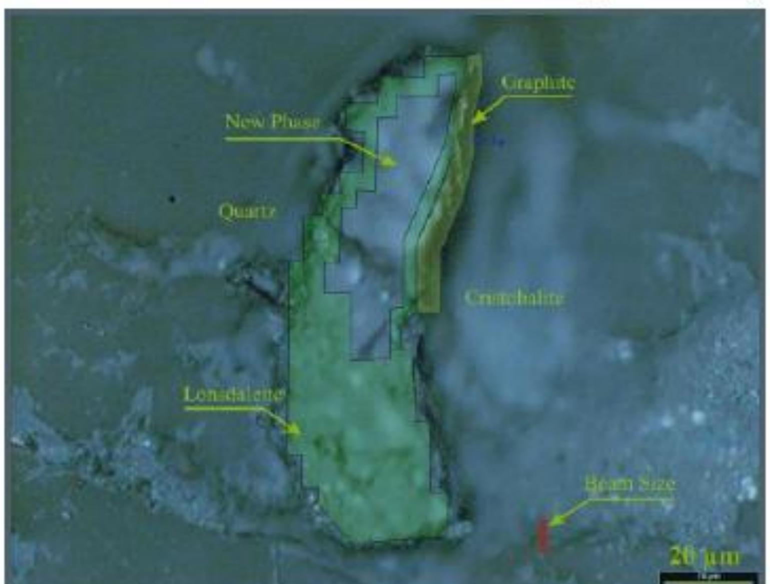
C. R. Geoscience 335 (2003) 889–898

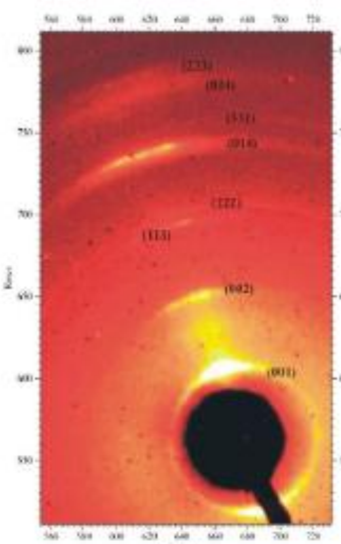
COMPTES RENDUS GEOSCIENCE

Geomaterials (Mineralogy)

A new natural, super-hard, transparent polymorph of carbon from the Popigai impact crater, Russia

Ahmed El Goresy [a,*], Leonid S. Dubrovinsky [b], Philippe Gillet [c], Smail Mostefaoui [a], Günther Graup [a], Michael Drakopoulos [d], Alexandre S. Simionovici [d], Varghese Swamy [e], Victor L. Masaitis [f]





- a = 14,697 A
- Pm3m
- Only sp^3 carbon

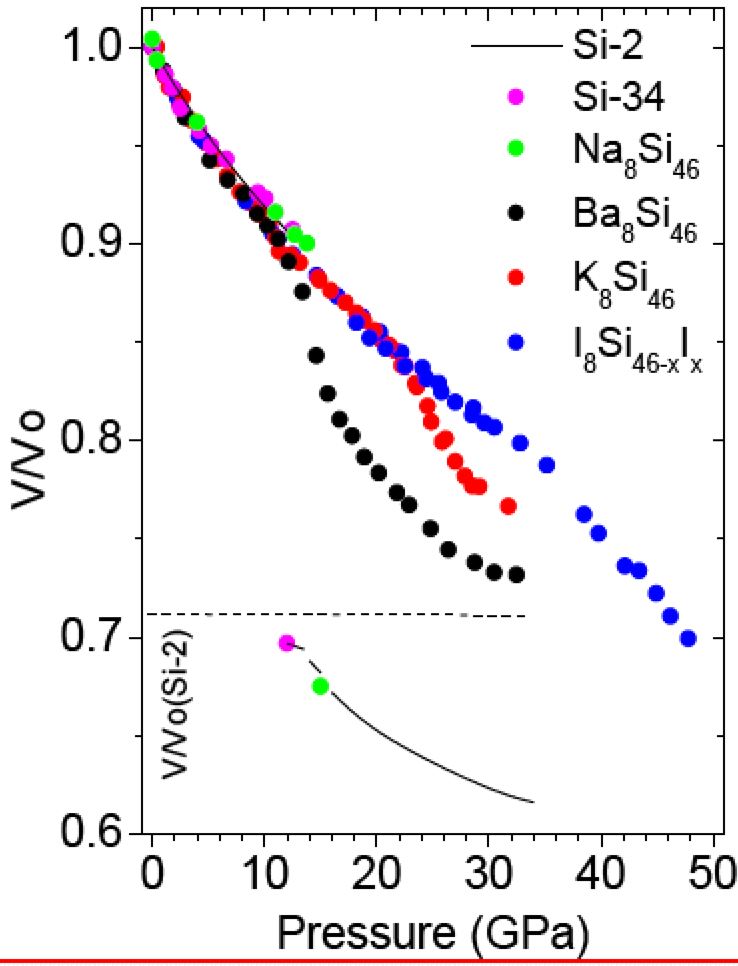
Cohesion of Si intercalated clathrates

	B_o exp. (GPa)	B_o calc. (GPa)	$B_o$calc - B_o(Si-2) (%)
Xe_8Si-46	N.S.	85	12
Si-46	N.S.	87	10
Si-34	90±5	87.5	9.5
Ba_8Si-46	93 ±5	-	-
I_8Si-46	95±5	91	6
Te_8Si-46	N.S.	95	2
Sn_8Si-46	N.S.	96	1
Si-2 diamond)	97.88	97	0

✓Intercalation can improve cohesivity

A. San Miguel, P. Mélinon, X. Blase et al., Phys. Rev. B. **65** (2002)

Stability of intercalated clathrates under high pressure



- Higher stability of the structure (up to x4) !
- Contrarely to intercalated fullerene crystals, the compression takes place without deformation of the nanocages

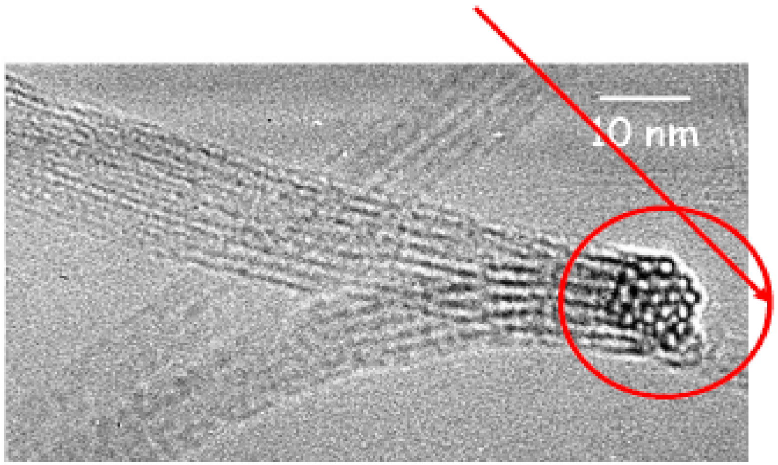
The Graal

Carbon Intercalated Clathrates

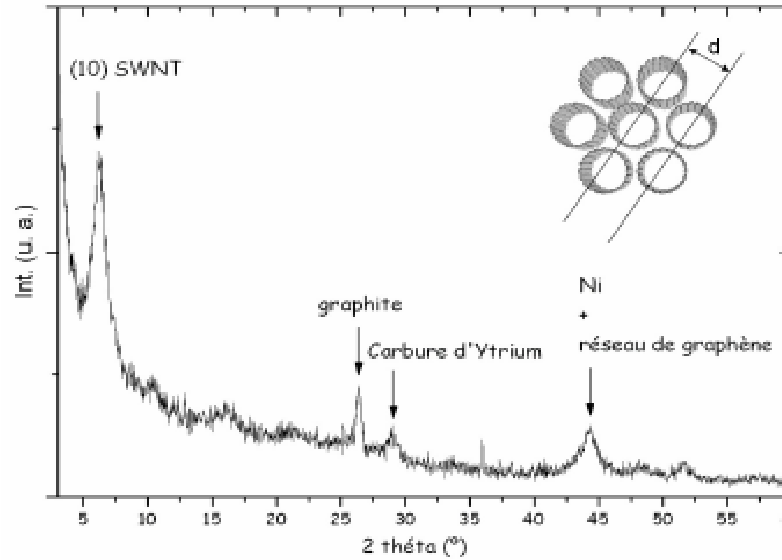
Ensambles de Nanotubos

Nanotubos de Carbón monopared
Estructura y Propiedades

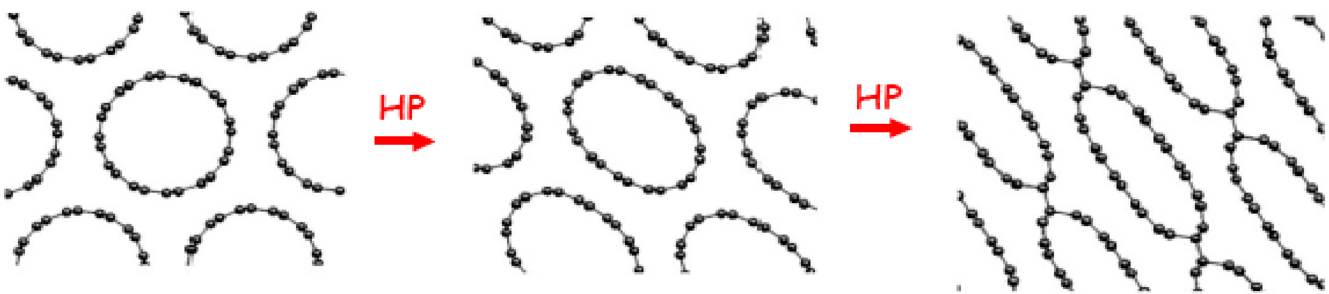
Organisation en fagots



C. Journet et al., Nature (1997)

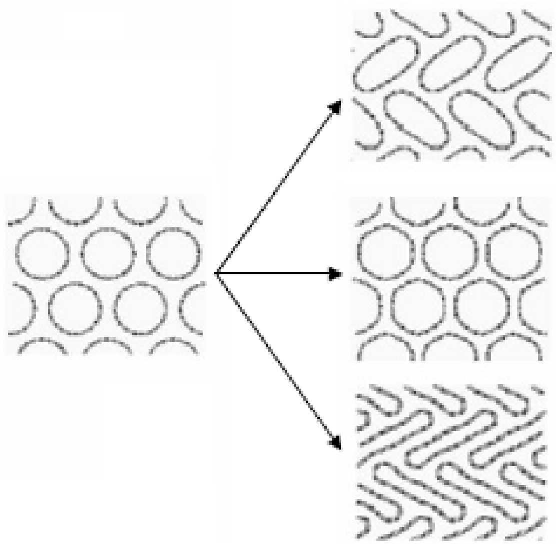


Diffraction de rayons X des fagots
des nanotubes de carbone



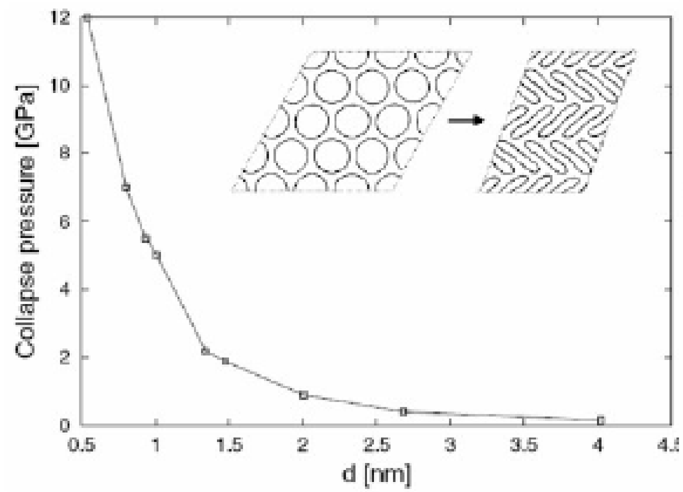
Reich et al.,
phys. Stat. Sol.
(b) (2003)

Changement de section



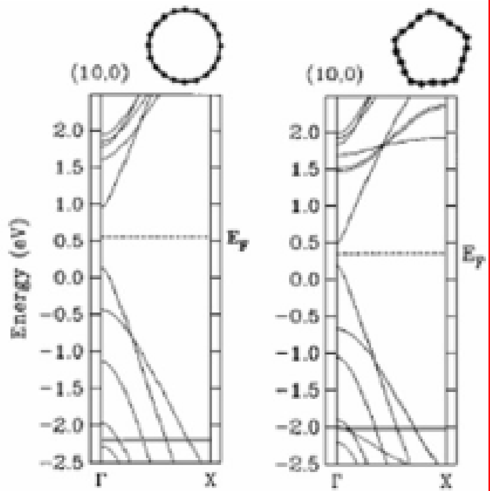
S.P. Chan et al. (2003)

Pression de transition



Elliot et al. (2004)

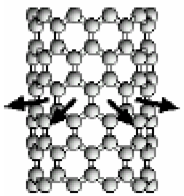
Évolution des propriétés électroniques



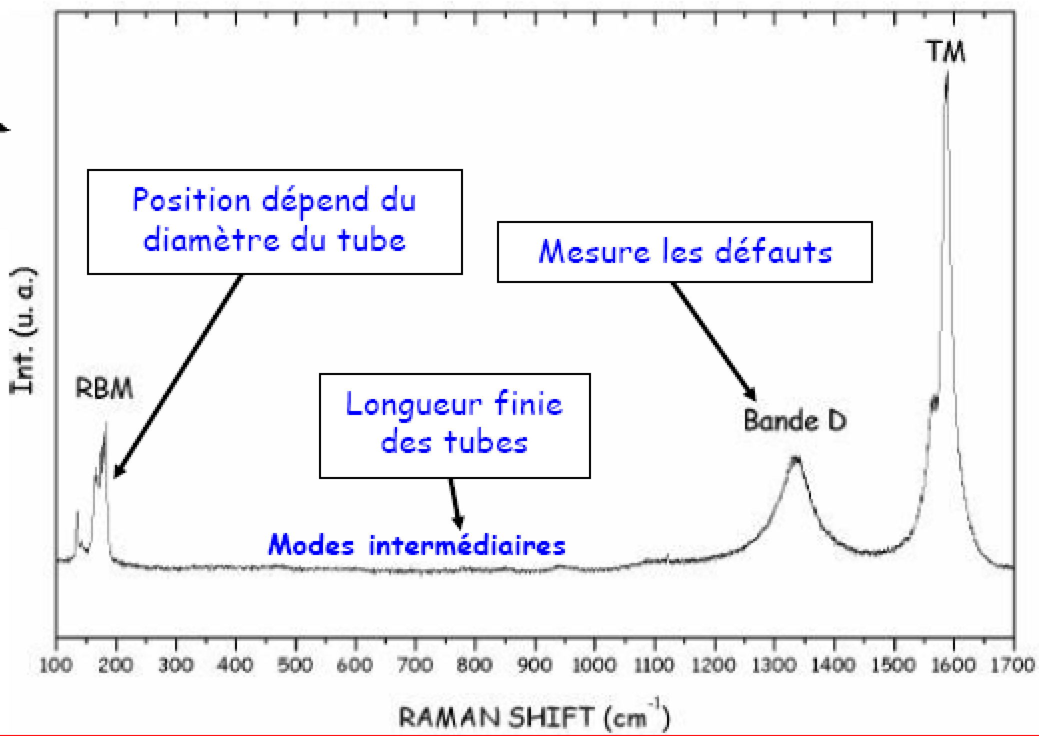
Charlier et al. (1996)

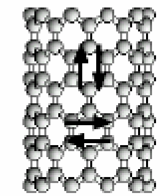
Spectroscopie Raman

- Spectre Raman des nanotubes (résonant)



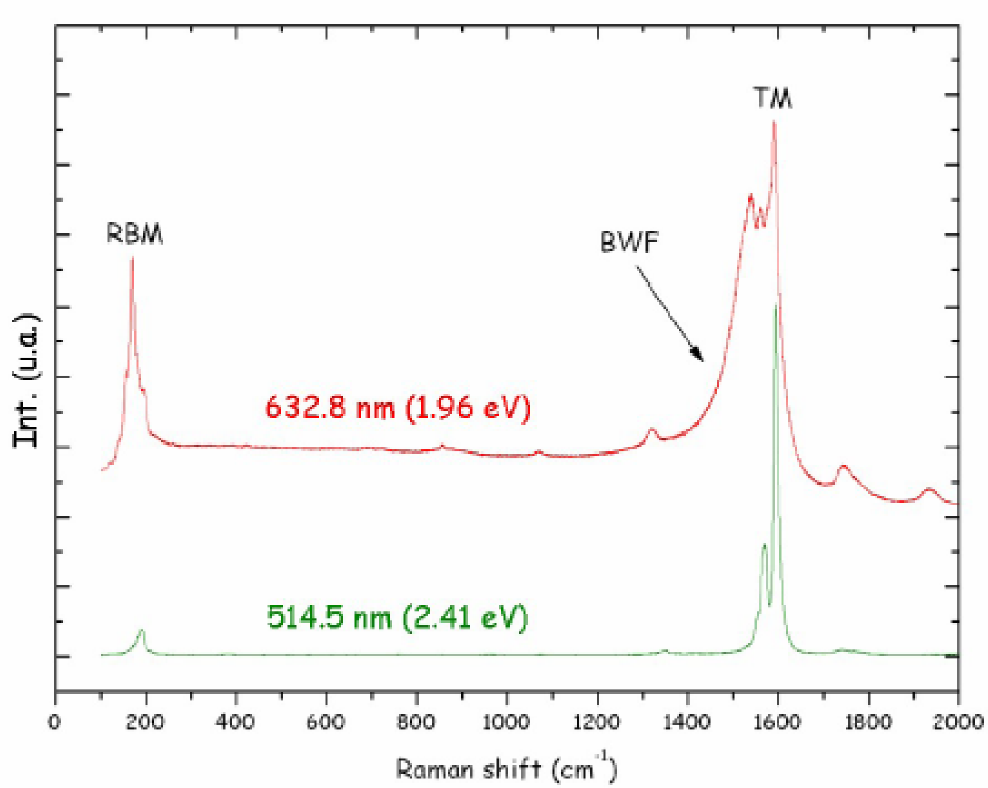
Radial Breathing Modes (RBM)

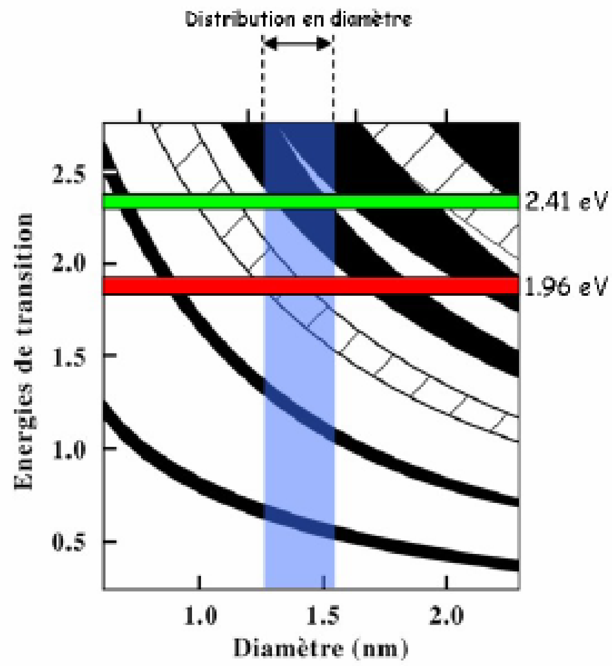


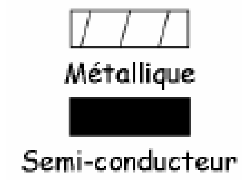


Tangencial Modes (TM or G)

Spectroscopie Raman résonnante





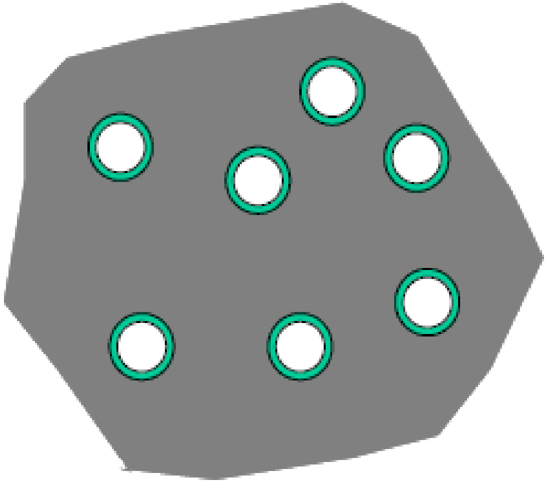


- Modes basses fréquences: modes de respiration

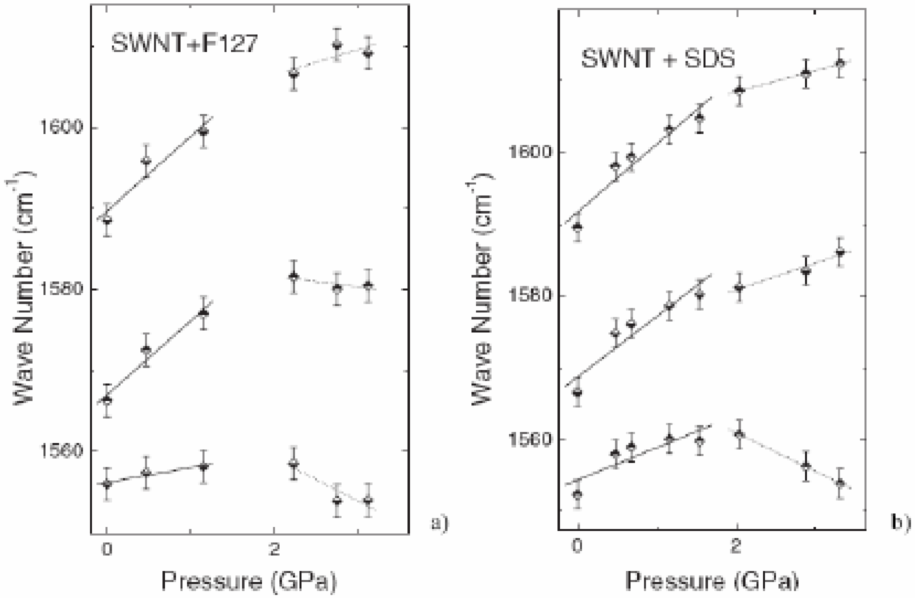
$$\nu_{RBM}(\text{cm}^{-1}) = 224(\text{nm cm}^{-1})/d(\text{nm}) + 14\ \text{cm}^{-1}$$

- Modes hautes fréquences: modes tangentiaux

Spectroscopie Raman résonnante: individualized SWNT

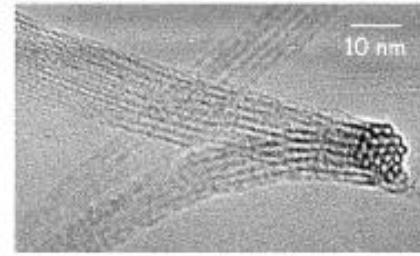


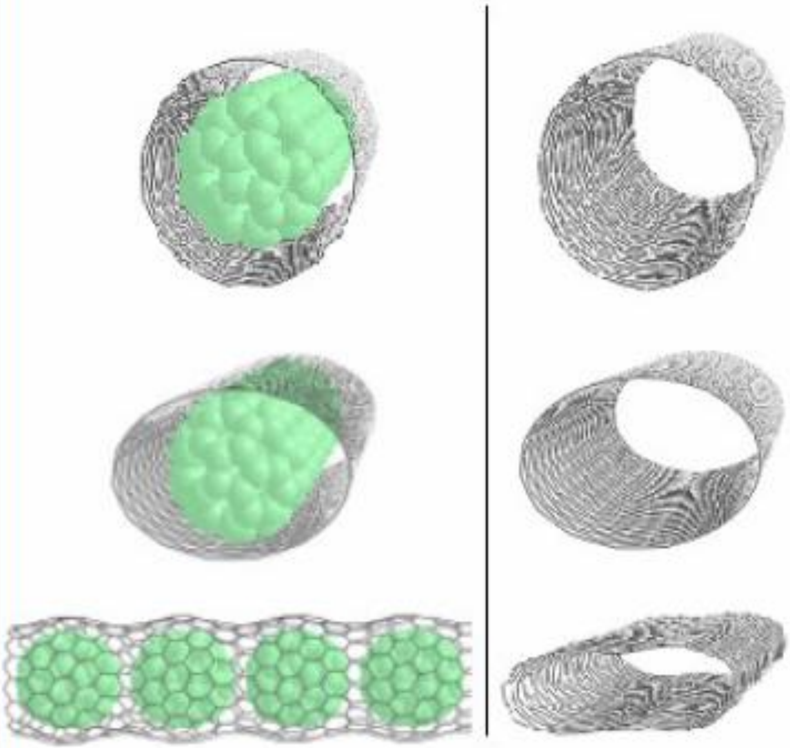
Evolution of the TM components with two different surfactants



Phase transition observed at ~2 Gpa

Phase transformation on SWNT bundles
(looking to nanotubes from inside)





Ambient conditions

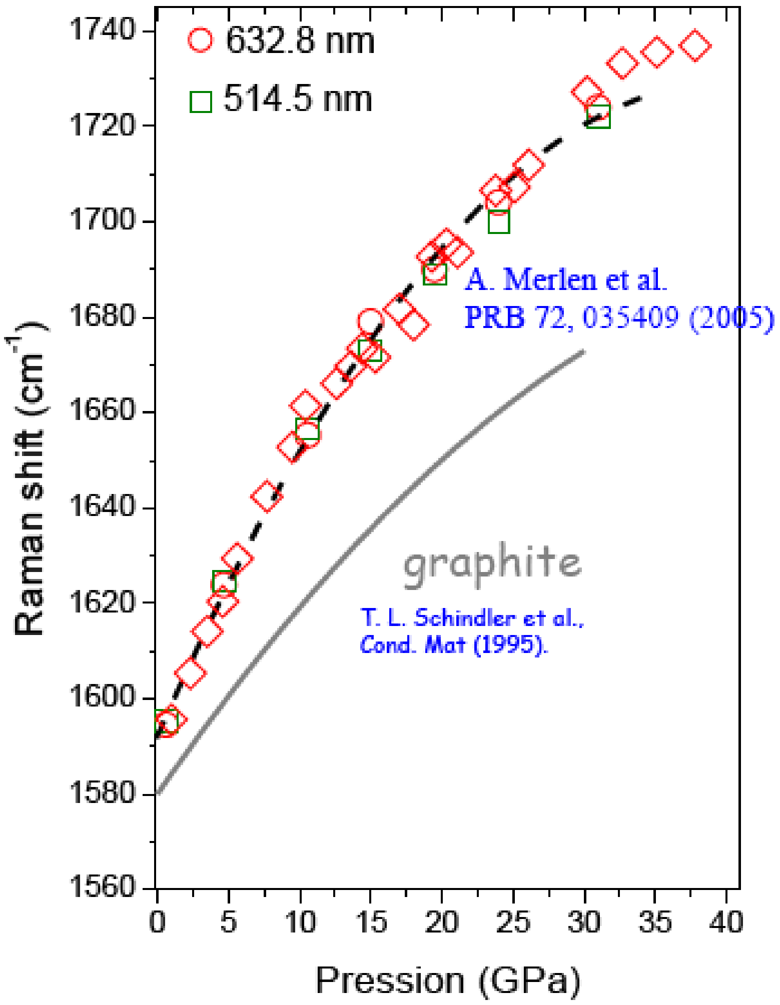
1^{st} phase transition at 2 Gpa
(OVALIZATION)

2^{nd} phase transition at 10-35 GPa
(COLLAPSE)

Avoiding the phase transitions: filling the nanotubes

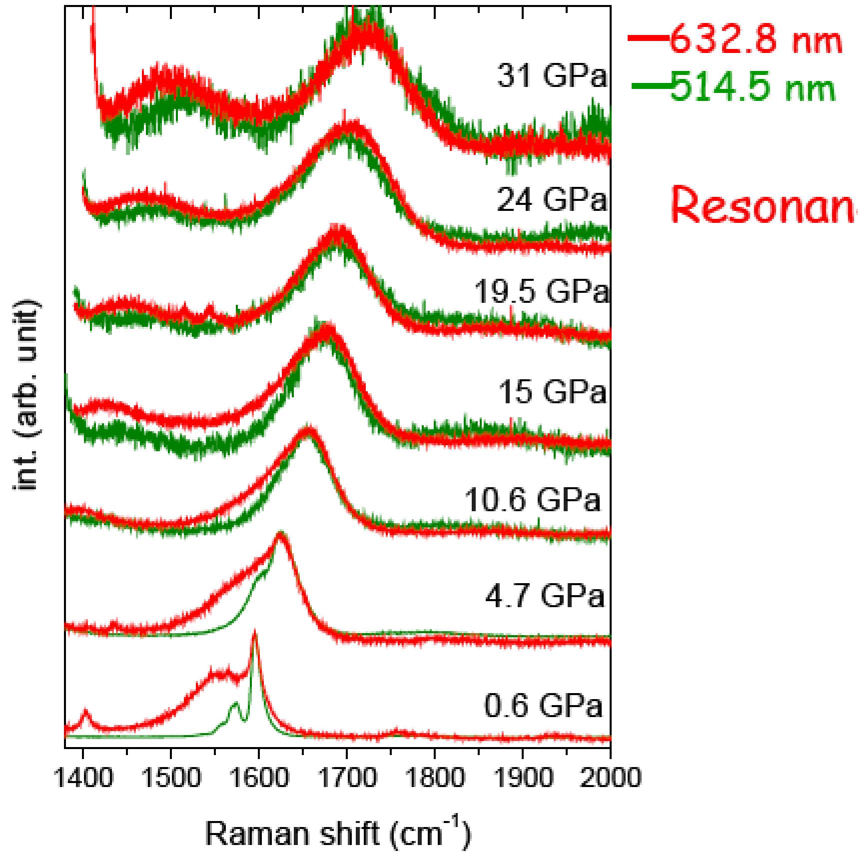
Ar@SWNT : NO Phase transformation

TM modes

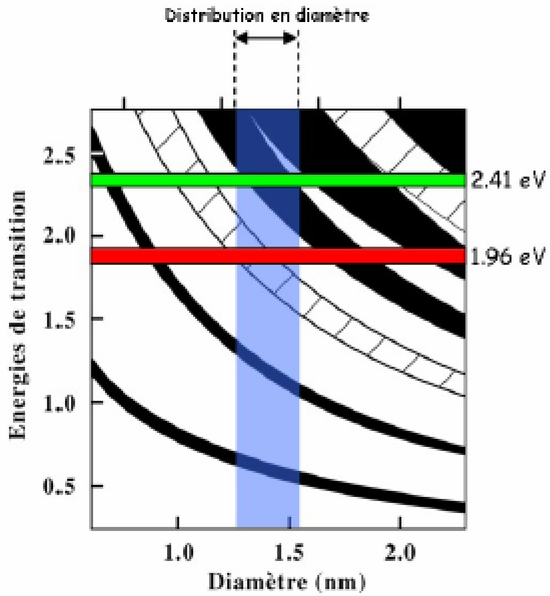


Changing the resonance conditions with pressure

Ar@SWNT: Transversal Modes under pressure



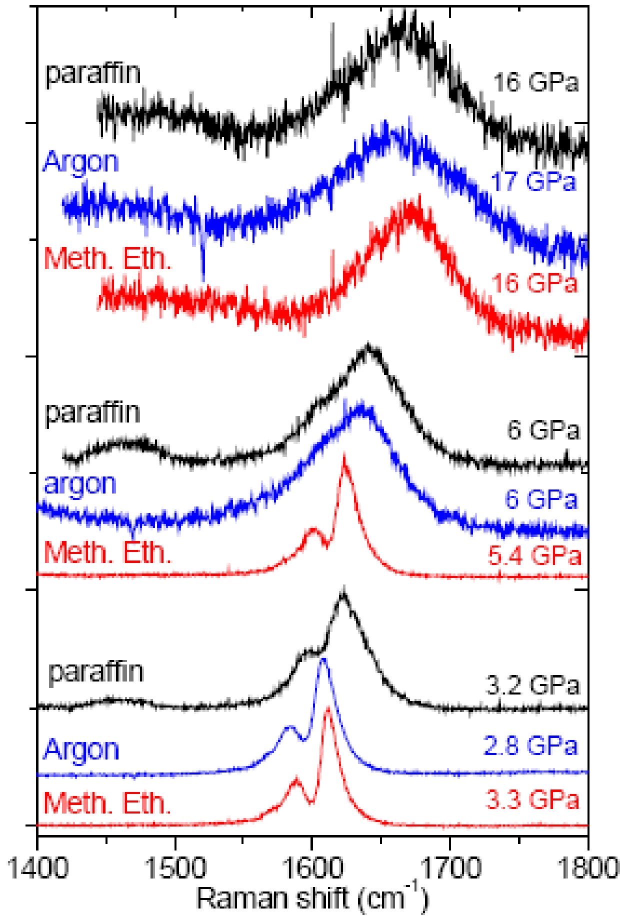
Resonance changes with pressure



A. Merlen et al., Phys. Rev B 72, 035409 (2005)

SWNT and interaction with pressure transmitting media

- ✓ Opened and closed nanotubes behave differently
- ✓ Raman is different with different pressure transmitting media.



A. Merlen et al., Physica Status Solidi b 243, 690 (2006)

Materiales de Nanotubos de Carbono

Industrial elaboration of C-NT Sheets

-Transparent sheets **5 cm wide and 1 m long and about 15 microns thickness.**

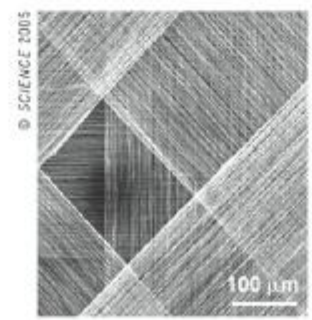
-Sheets made from CVD grown oriented MWNT

- Production rate : 7 meters per minute!

- Electronically conduting with a density of 0.0015 g/cm3

- Sheets can be densified (through surface-tension effects by inmersion in methanol) up to 0.5 g/cm3.

- An array of 8 sheets had a strength comparable to milar or capton.

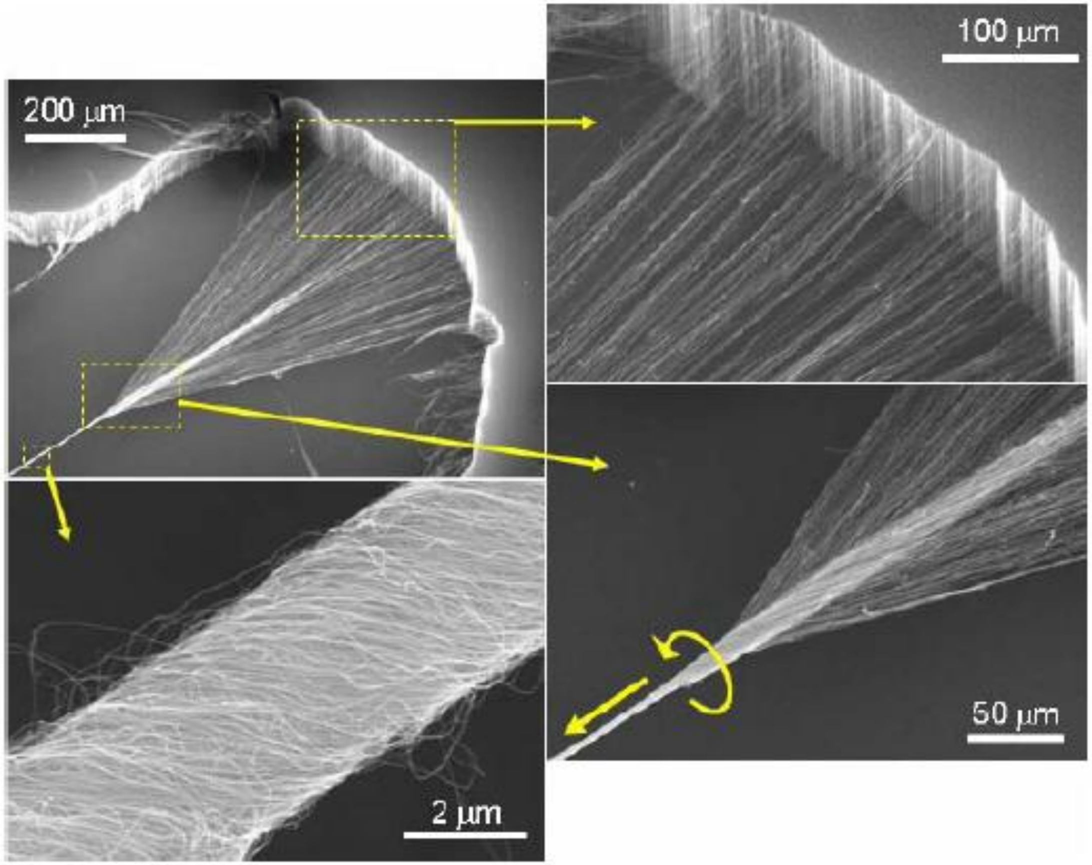


Four sheets cross-oriented to provide the same strength in all directions

M. Zhang et al. Science (2005) 309, 1215

Carbon Nanotube Fibers

Nanotube fibers

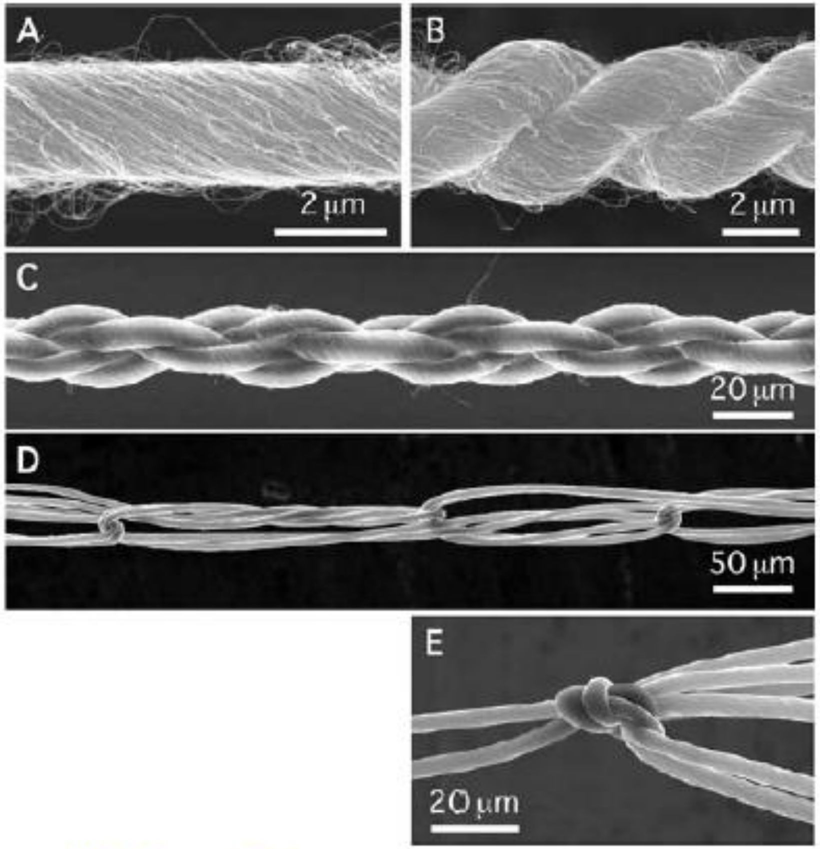


Zhang, Atkinson and Baughman, Science **306** (2004) 1358.

Nanotube fibers

MWCNT

- Operational -196°C < T < 450°C
- Electrical conducting
- Toughness comparable to Kevlar
- No rupture in knot



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

Gracias ☺