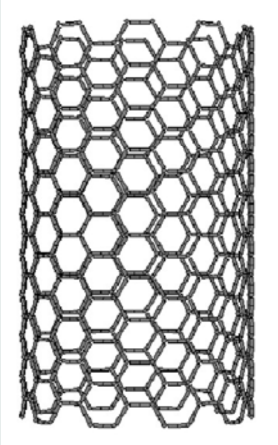
# Carbon Nanotubes - CNTs

R. NESPER ETH ZÜRICH & COLLEGIUM HELVETICUM



# SWCNTs – Single Wall Carbon Nanotubes

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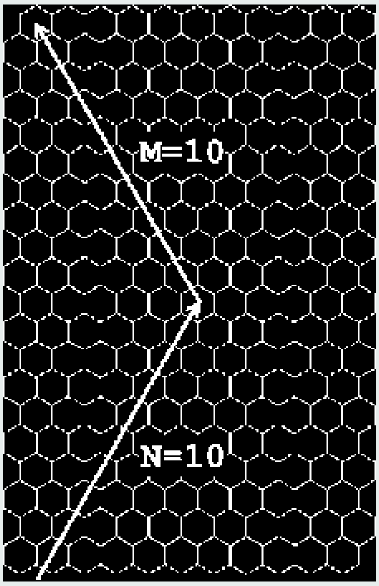
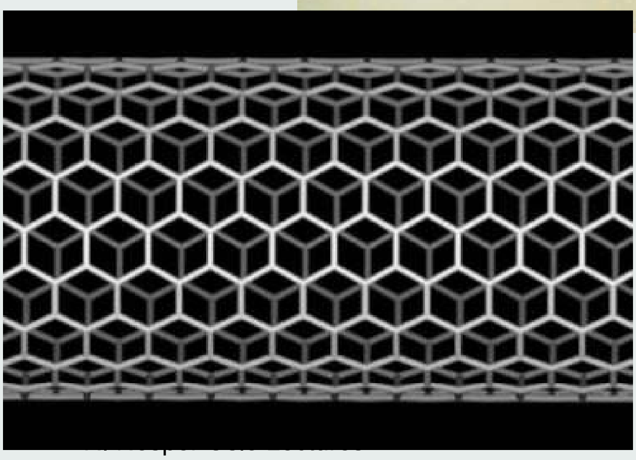
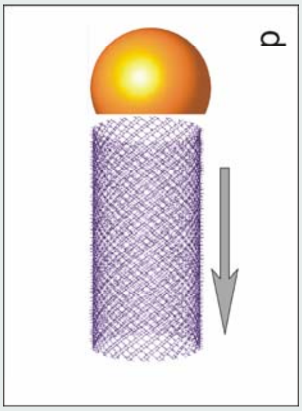
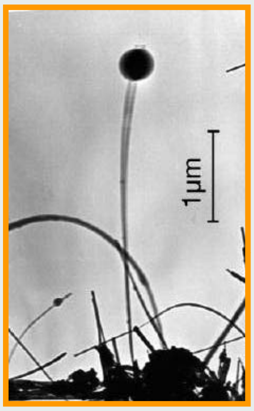


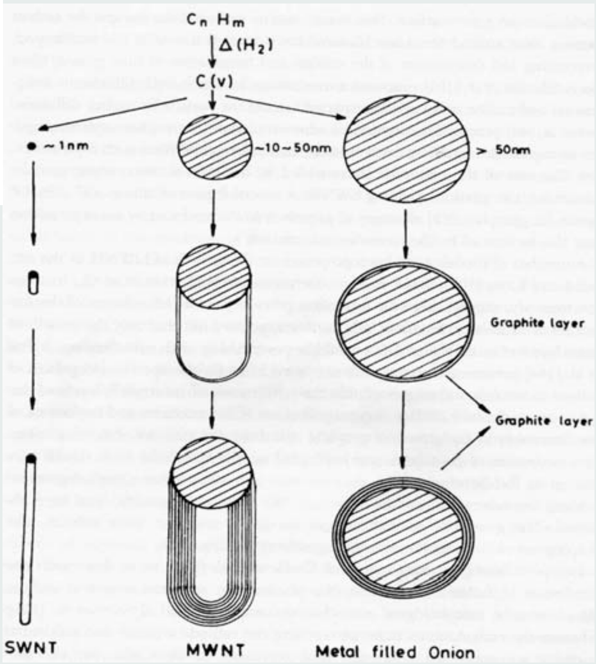



# Carbon Nanotubes - Growth

good physical and chemical properties.[1–3] Various methods for the synthesis of CNTs have been reported: arc-discharge,[3,4] laser ablation,[5] chemical vapor deposition,[6–10] flame synthesis,[11] and Smalley's recent invention of the high-pressure carbon monoxide (HIPCO) process.[12] However, none of these methods can be used at low temperature, so the synthesis of CNTs with low-melting point materials, such as organic polymers, has been severely limited. Furthermore, expensive vacuum equipment is necessary to lower the temperature of the synthesis.[13–16] Therefore, the strategy frequently used has been



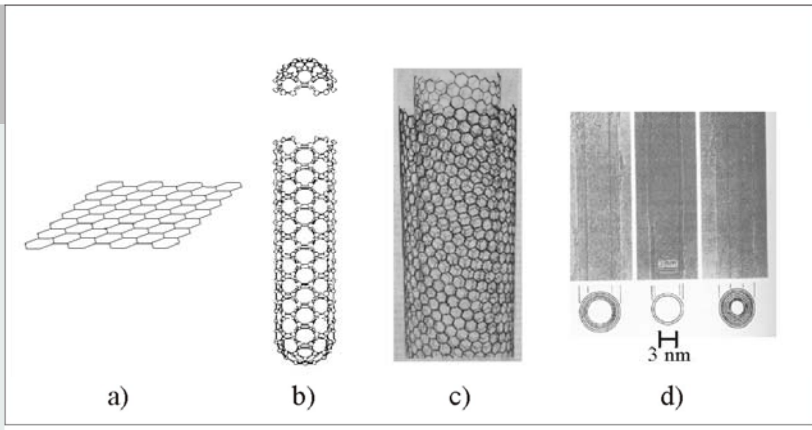



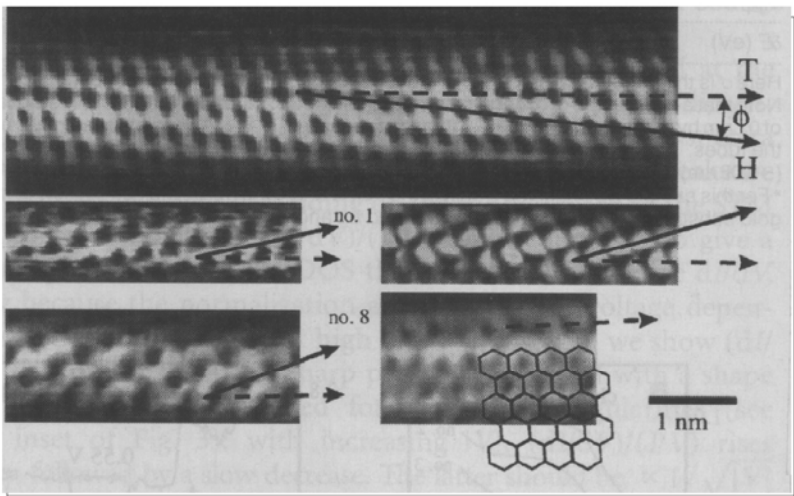







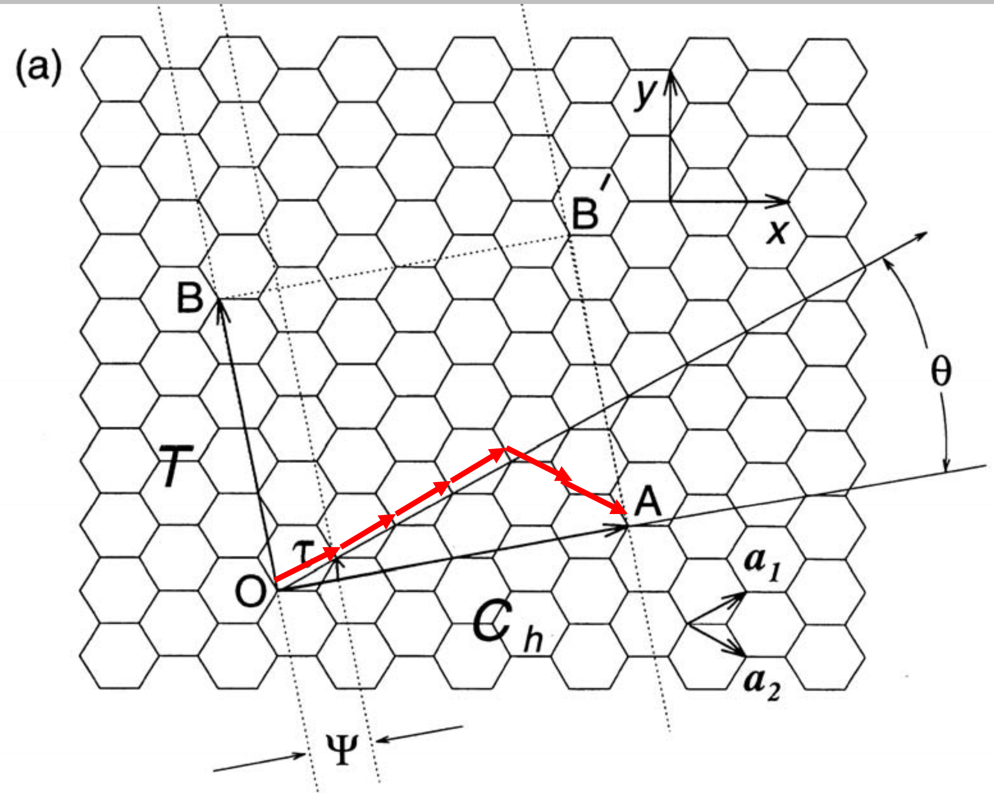

# Carbon Nanotubes - Building Principles



# Carbon Nanotubes – Building Principle








# Carbon Nanotubes – Building Principle

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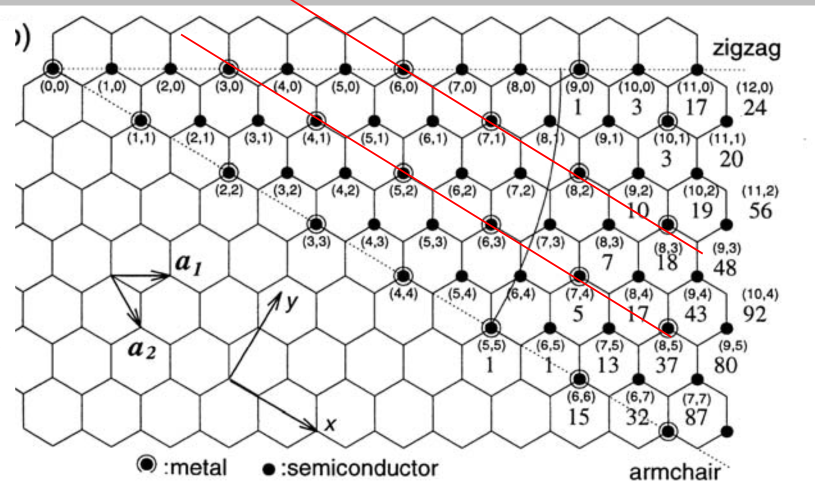


. 19.2. (a) The chiral vector $\overrightarrow{OA}$ or $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$ is defined on the honeycomb of carbon atoms by unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ and the chiral angle $\theta$ with respect to gzag axis. Along the zigzag axis, $\theta = 0°$. Also shown are the lattice vector $\overrightarrow{OB} = \mathbf{T}$ of D tubule unit cell and the rotation angle $\psi$ and the translation $\tau$ which constitute the symmetry operation $R = (\psi|\tau)$ for the carbon nanotube. The diagram is constructed for ) = (4, 2). (b) Possible vectors specified by the pairs of integers $(n, m)$ for general carbon s, including zigzag, armchair, and chiral tubules. Below each pair of integers $(n, m)$ is the number of distinct caps that can be joined continuously to the carbon tubule denoted $m)$ [19.4], as discussed in §19.2.3. The encircled dots denote metallic tubules while the dots are for semiconducting tubules.

# Carbon Nanotubes – Building Principle



Diameter of nanotube, $d_t = |\mathbf{C_h}| / \pi$

$$\therefore d_t = \frac{a\sqrt{n^2 + m^2 + nm}}{\pi}$$

Let $\mathbf{T} = t_1\mathbf{a_1} + t_2\mathbf{a_2}$ where $t_1$ and $t_2$ are integers

Since $\mathbf{T}$ is perpendicular to $\mathbf{C_h}$,

$t_1 = (2m + n) / d_R$ and $t_2 = -(2n + m) / d_R$

$d_R$ is the Greatest Common Divisor (GCD) of $(2m + n)$ and $(2n + m)$,

$d_R = d$ if $(n – m)$ is not a multiple of 3d

$d_R = 3d$ if $(n – m)$ is a multiple of 3d

d is the GCD of n and m

Let $\mathbf{T} = t_1\mathbf{a_1} + t_2\mathbf{a_2}$ where $t_1$ and $t_2$ are integers

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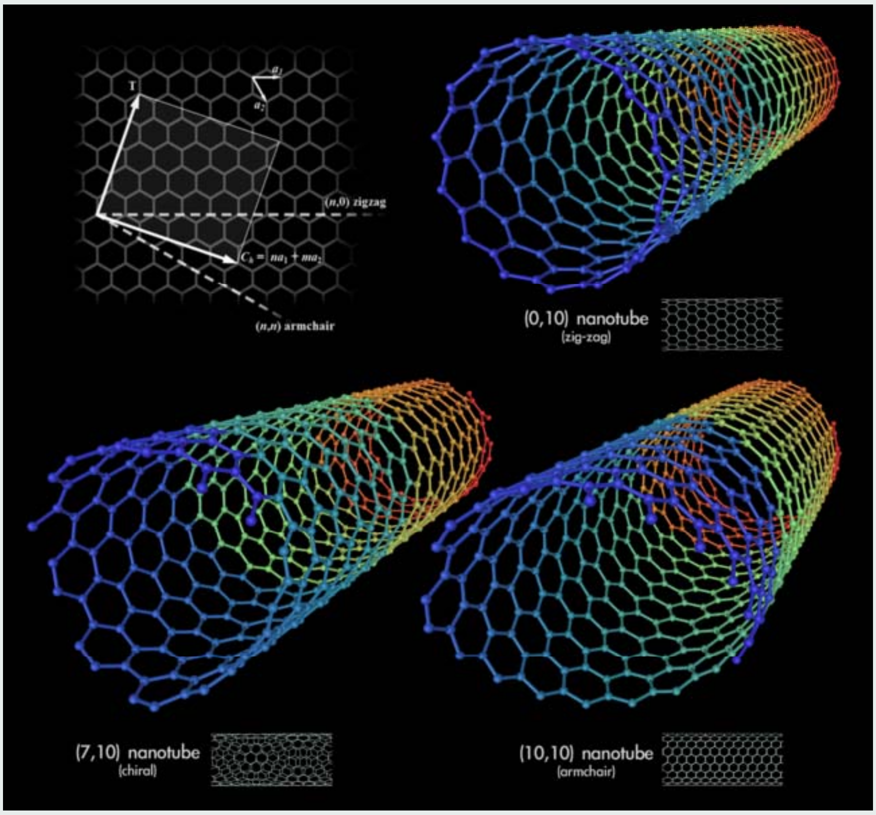
# Carbon Nanotubes – Building Principle





# Carbon Nanotubes – Building Principles

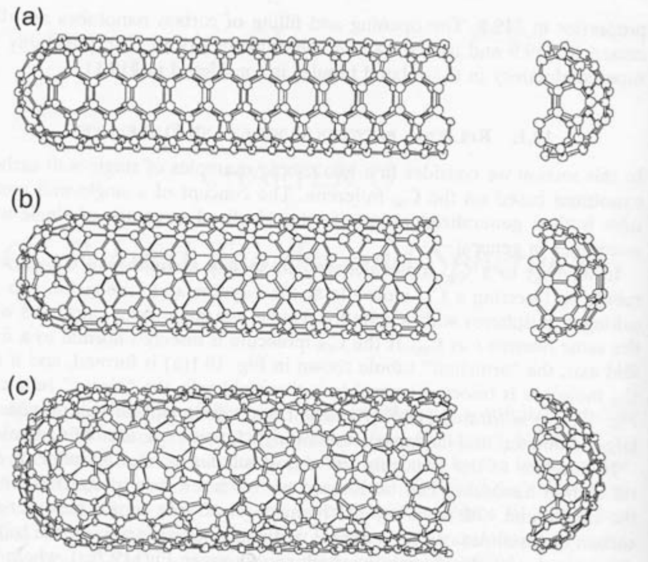



**Fig. 19.1.** By rolling a graphene sheet (a single layer from a 3D graphite crystal) into a cylinder and capping each end of the cylinder with half of a fullerene molecule, a "fullerene-derived tubule," one atomic layer in thickness, is formed. Shown here is a schematic theoretical model for a single-wall carbon tubule with the tubule axis normal to: (a) the $\theta = 30°$ direction (an "armchair" tubule), (b) the $\theta = 0°$ direction (a "zigzag" tubule), and (c) a general direction $0 < \theta < 30°$ (see Fig. 19.2) (a "chiral" tubule). The actual tubules shown in the figure correspond to $(n, m)$ values of: (a) (5, 5), (b) (9, 0), and (c) (10, 5) [19.5].

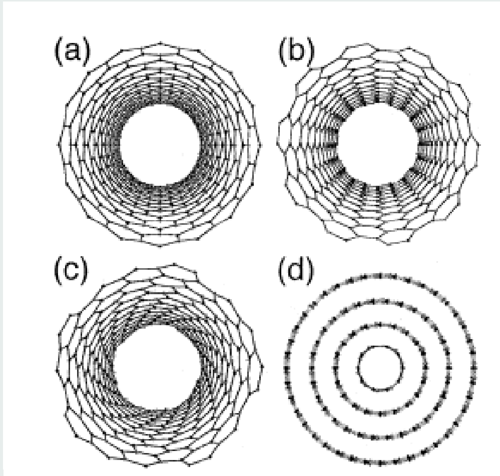
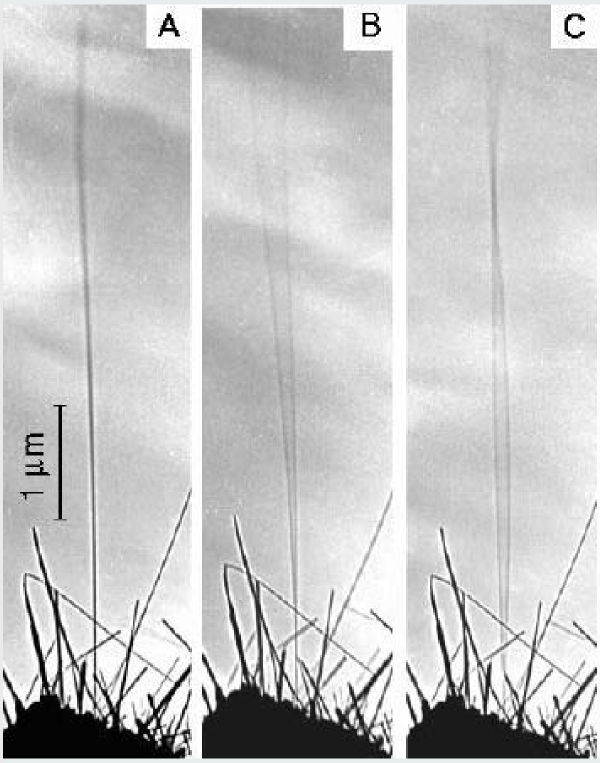


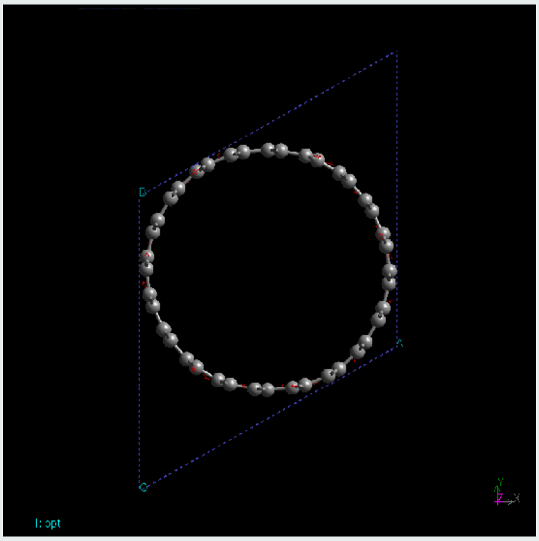

Fig. 1. Models of different nanotube structures. (a)–(c) are SWNTs of 1.25 nm diameter of (a) zig-zag, (b) armchair, and (c) chiral type. (d) represents a MWNT formed by four armchair tubes of increasing diameter with an interlayer separation of 0.34 nm. The image has been reduced by a factor of 2 with respect to images (a)–(c). The images have been generated with the software Mathematica 4.0 using a notebook by Brandbyge [197] that allows one to draw the structure as well as to compute the energy bands of SWNTs.



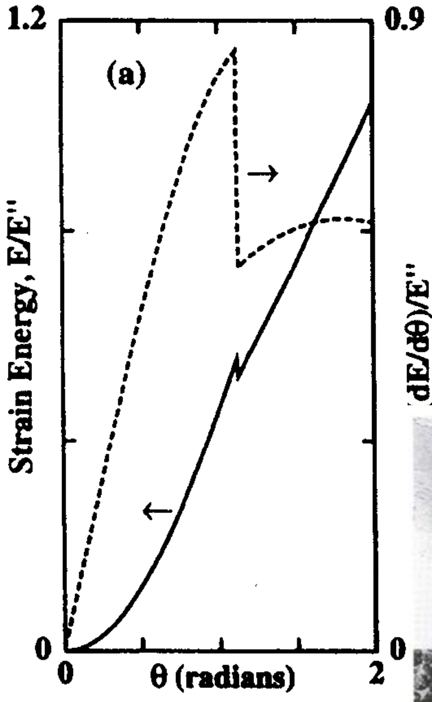
# Dynamics of C-NTs

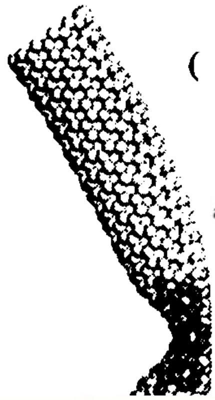


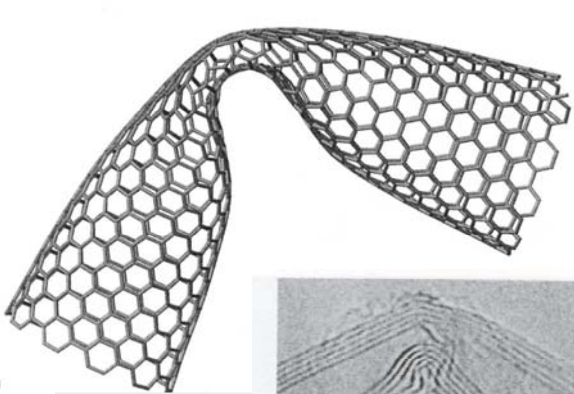


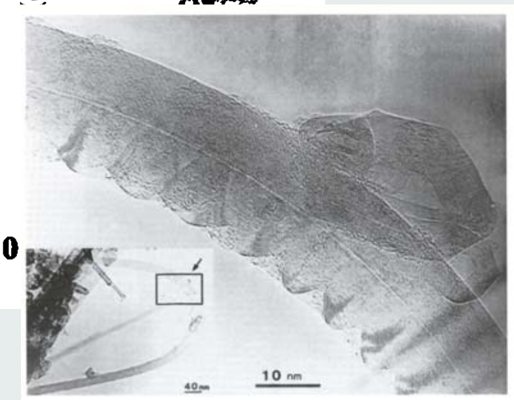



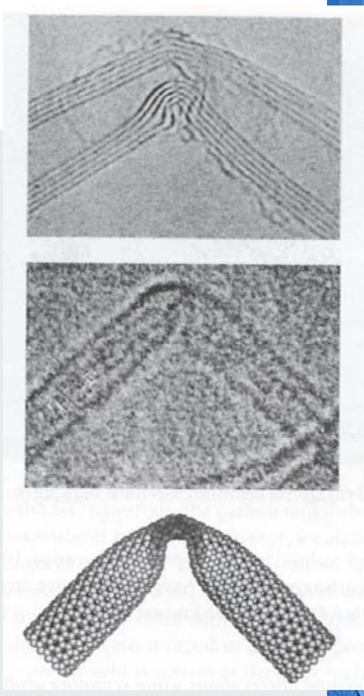
# Strength of CNTs



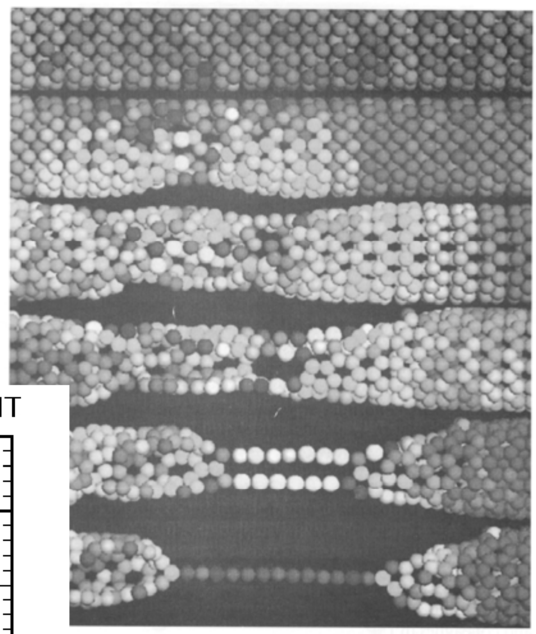


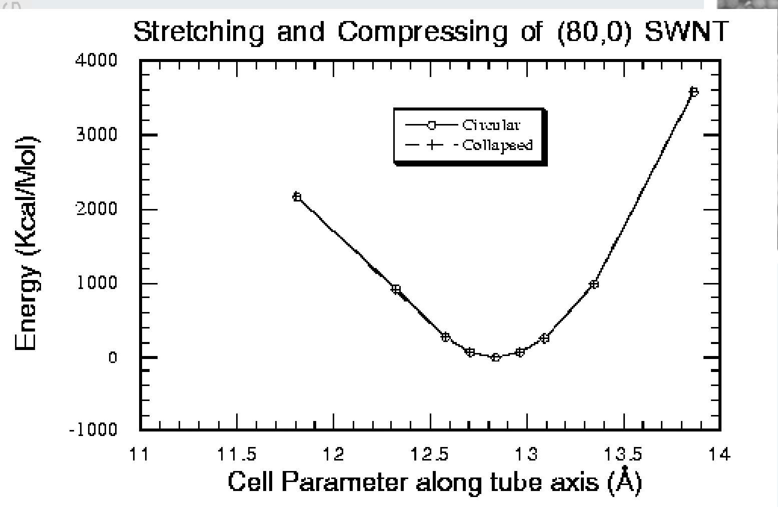




# Strength of CNTs





# SWCNT – Plastic Deformation



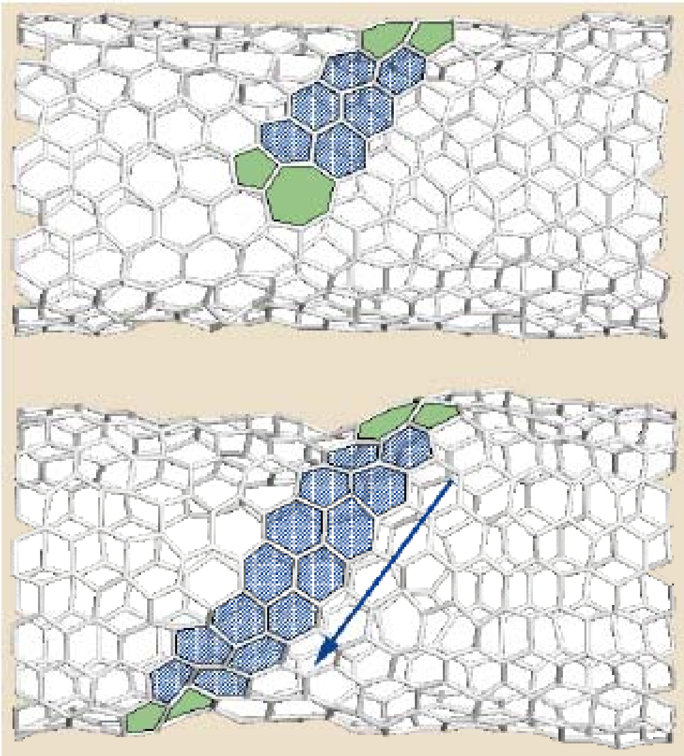


Figure 1 Plastic deformation of a carbon nanotube. Molecular dynamics simulations of a (10,10) nanotube under axial tension (J. Bernholc, M. Buongiorno Nardelli and B. Yakobson). Plastic flow behaviour is shown after 2.5 ns at $T = 3{,}000$ K and 3% strain. The blue area indicates the migration path (in the direction of the arrow) of the edge dislocation (green). This sort of behaviour might help make composite materials that are really tough (as measured by their ability to absorb energy).



# Carbon Nanotubes

http://www.pa.msu. edu/cmp/csc/nanotube.hmtl



**Characterization of each individual set of nanoparticles necessary**

| | |
|---|---|
| Density: | 1.35 g/cm$^3$ |
| Resistivity | $10^{-4}$ wcm |
| Maximum Current Density | $10^9$ A/cm$^2$ |
| Thermal Conductivity | ~2000 W/mK |
| Relaxation Time | ~$10^{-11}$ s |
| Elastic Behavior | |
| Young's Modulus (SWNT) | ~1 TPa |
| Young's Modulus (MWNT) | 1.28 TPa |
| Maximum Tensile Strength | ~100 GPa |

# Next Generation Aerospace Material ??



**Carbon Nanotube**

↓

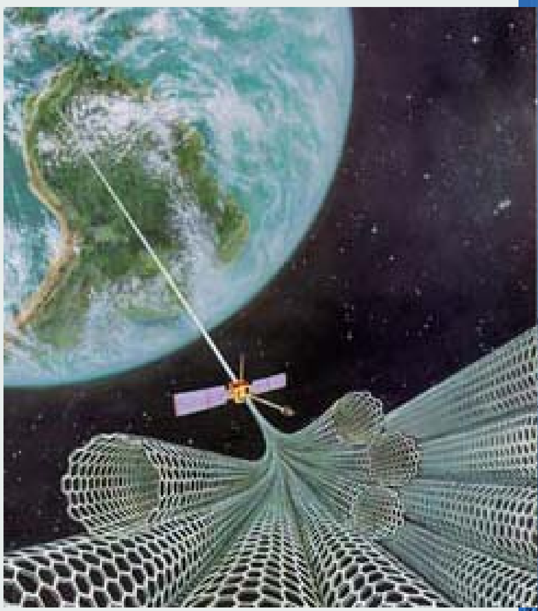
**Nanotube Fiber**

↓

**Nanotube/ Polymer**

↓

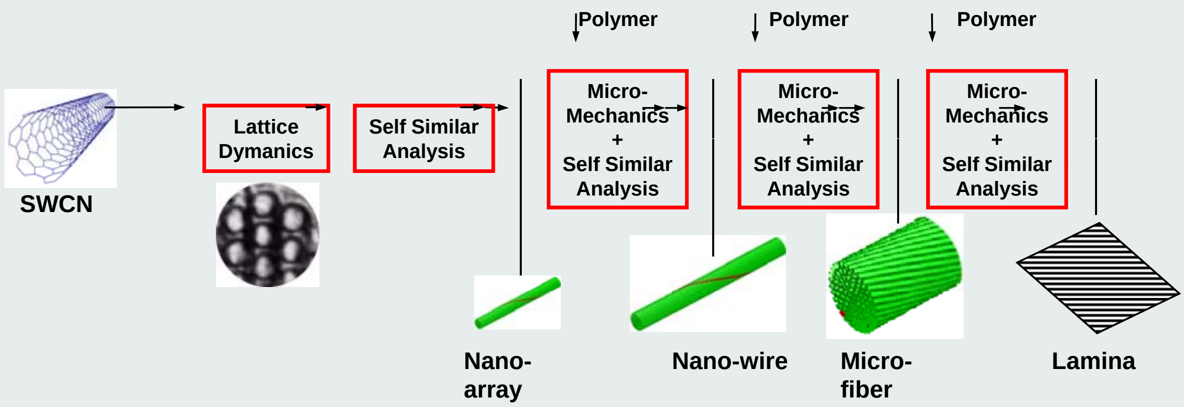
**Ultra Nanostructured Composite**





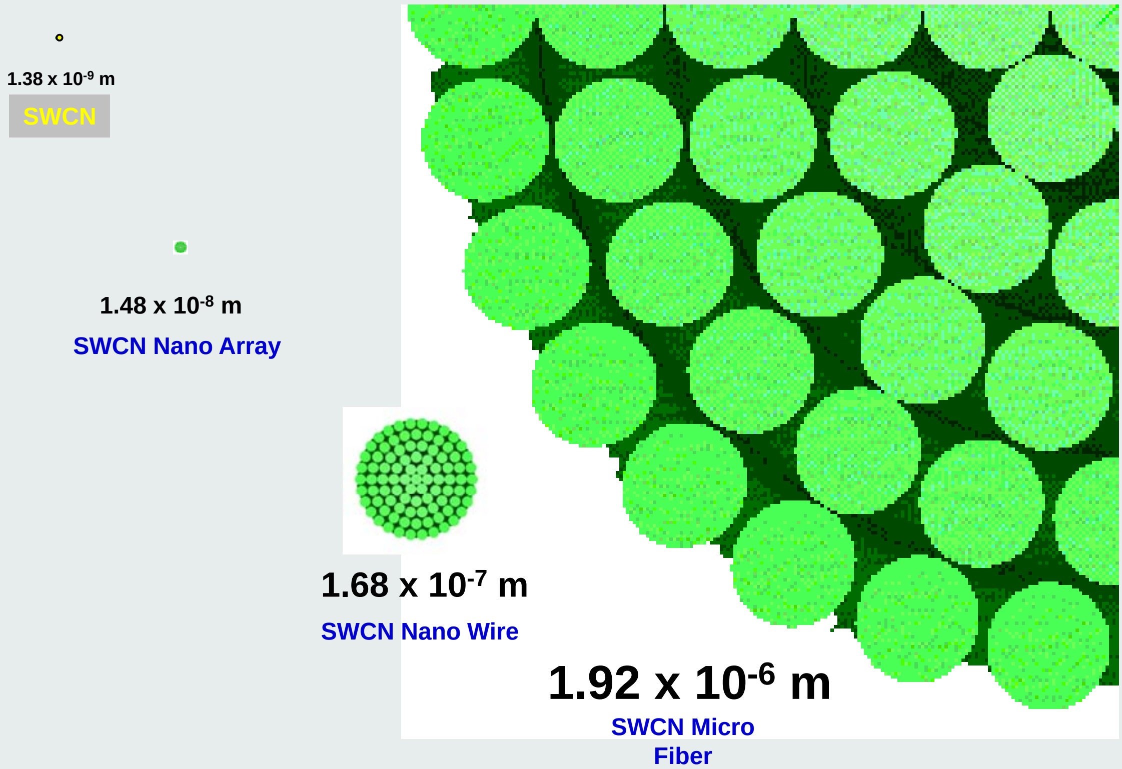
# Self Similar Helical Modeling





# Self-Similar Scales








# Self-Similar Scales

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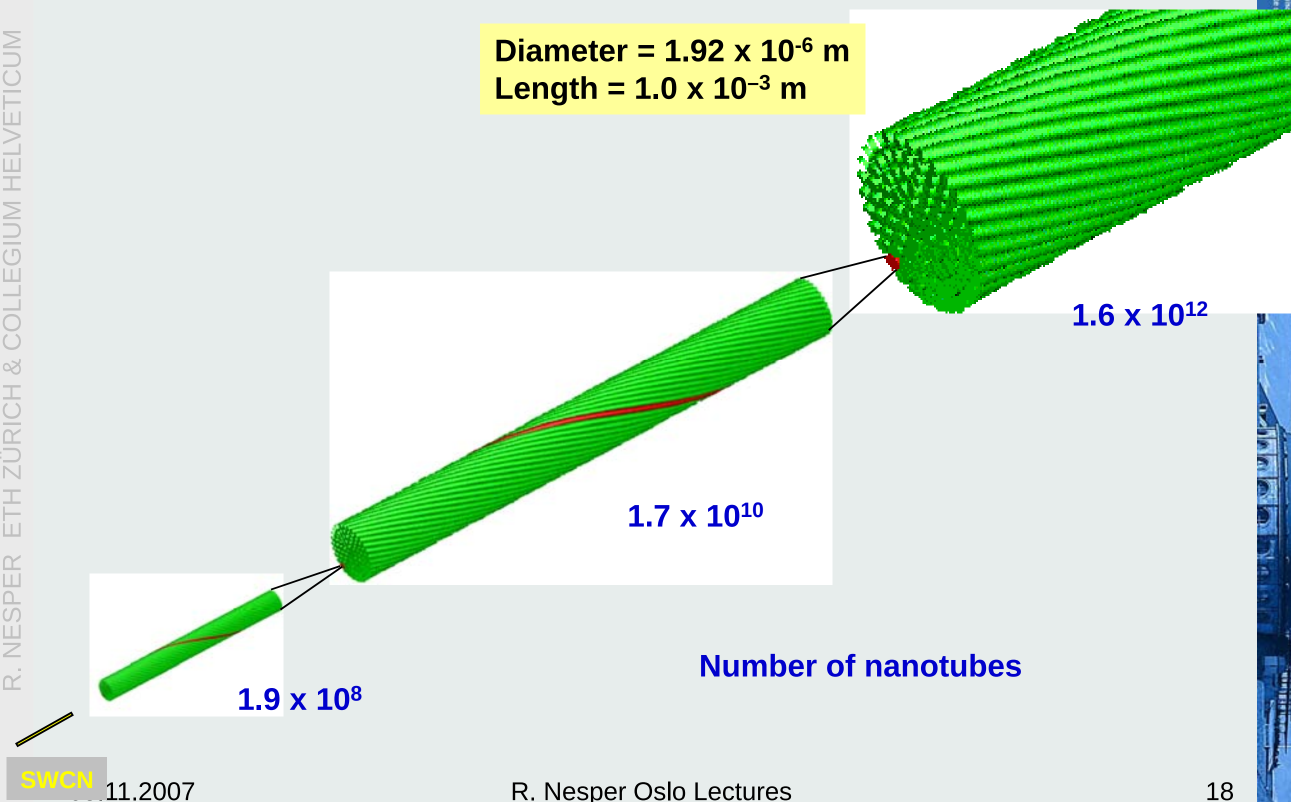
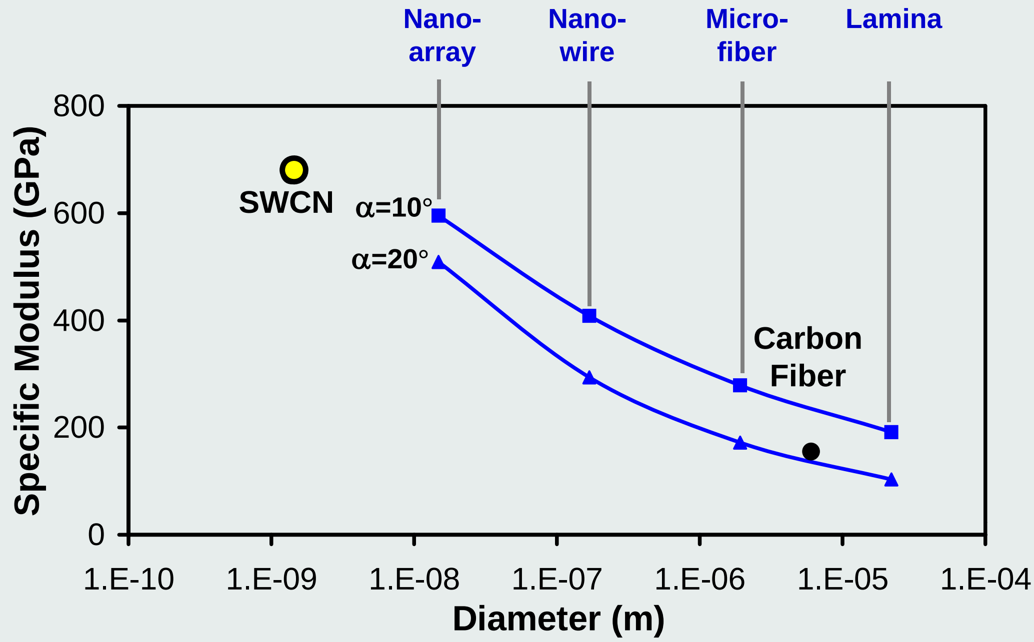


# Self-Similar Properties

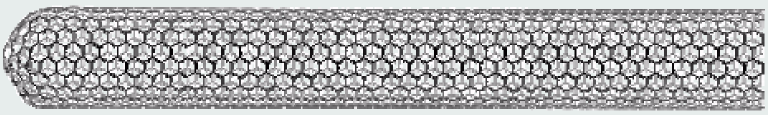


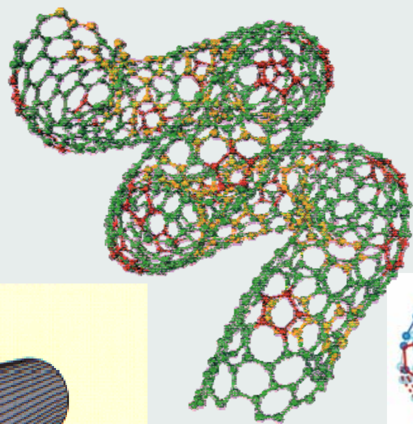


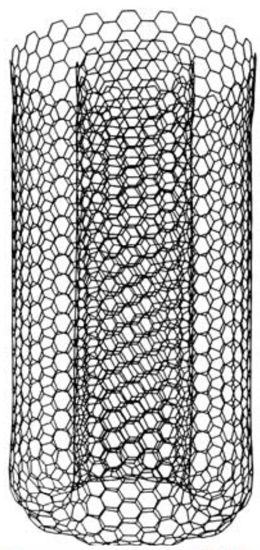


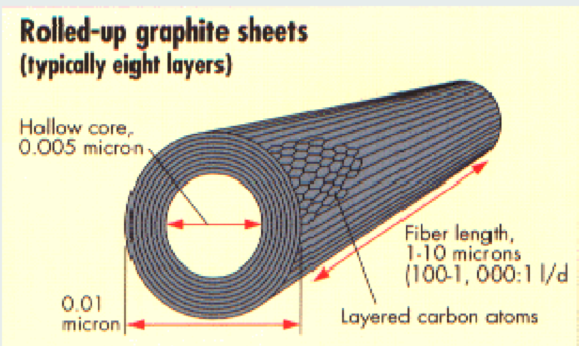

# C-Nanotubes - Forms

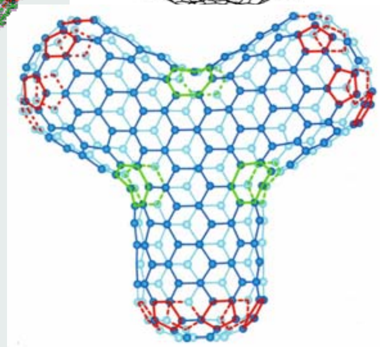








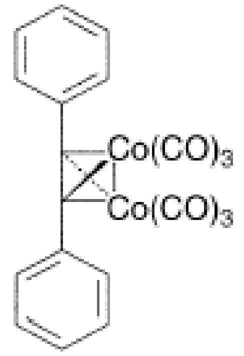


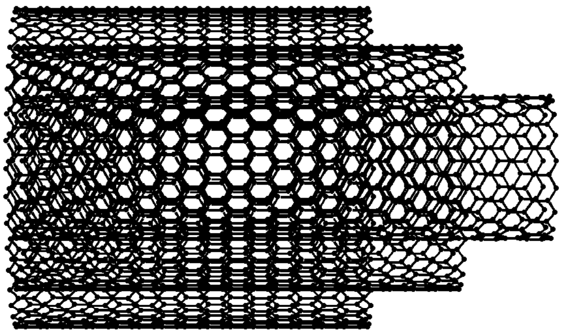



# Multiwalled Carbon Nanotubes



Synthesis below 500 °C



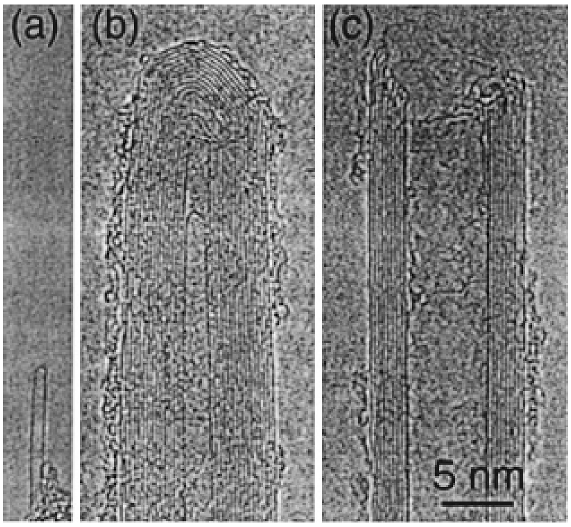


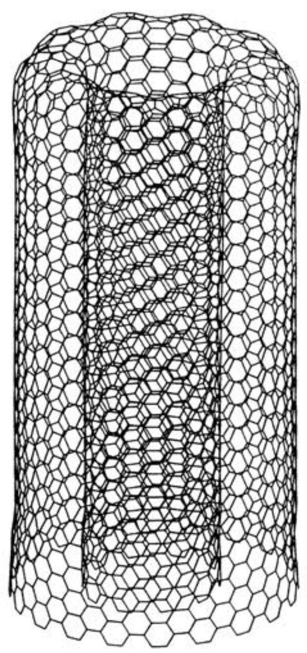

Fig. 2. TEM pictures of the ends of (a) a SWNT, (b) a closed MWNT, and (c) an open MWNT. Each black line corresponds to one graphene sheet viewed edge-on. The micrographs are reproduced at the same magnification.

D ~ 0.34 nm



# C-Nanotubes – Multiwall Connections





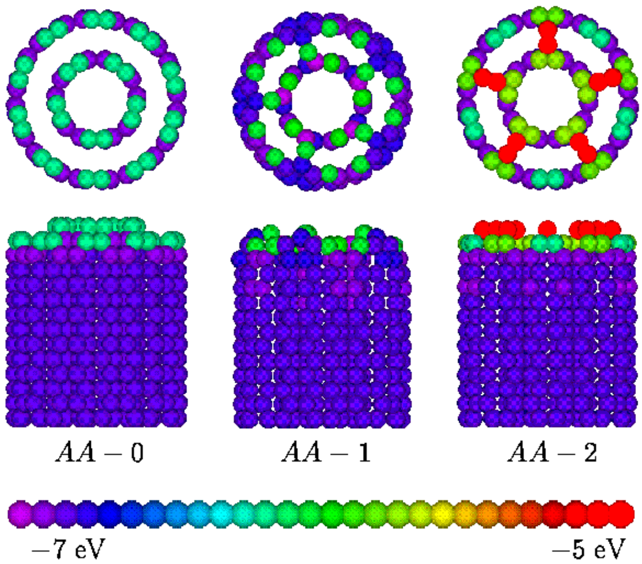




Figure 2

(Young-Kyun Kwon *et al.*, *"Morphology and stability of growing multi-wall carbon nanotubes"*)

# Helices, Springs, Actuators



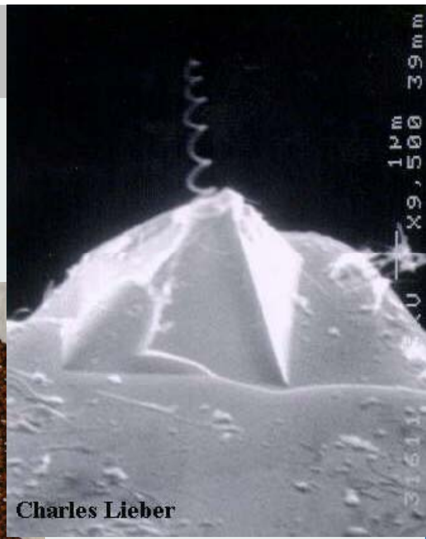




*Abb. 6. a) Rasterelektronenmikroskopische (REM)-Aufnahme mehrerer pyrolytisch synthetisierter spiralförmiger Nanoröhrchen. b) Theoretisches Modell der korkenzieherartigen Gebilde.*



# Other new CNTs ?



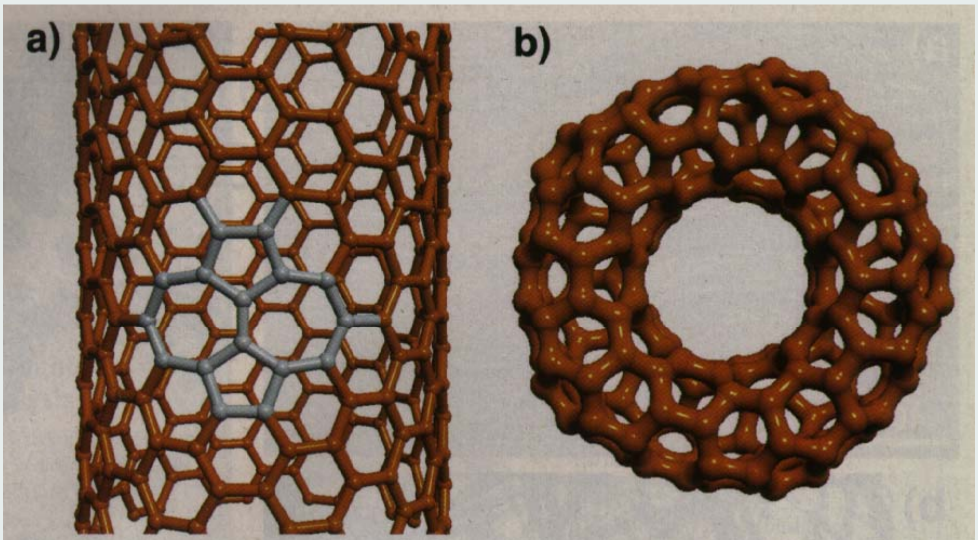
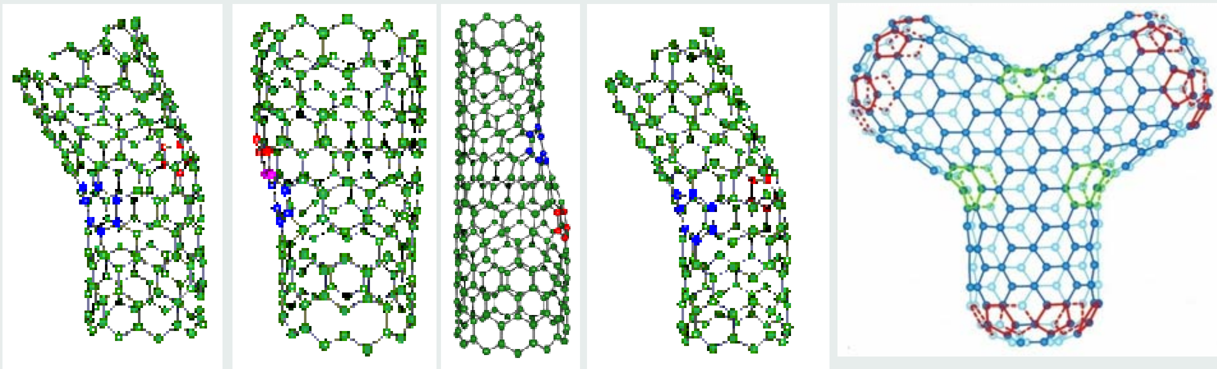
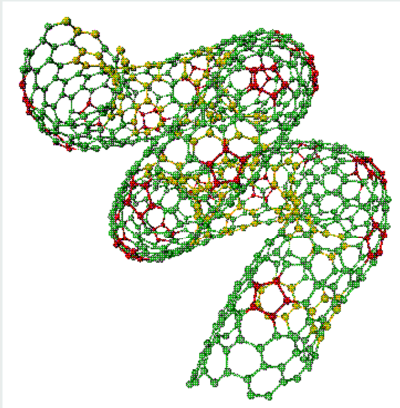



*Abb. 5. a) Modell eines einwandigen Kohlenstoff-Nanoröhrchens mit einem 5,7-Defekt, der aus vier Sechsecken über eine Stone-Wales-Transformation entsteht. b) Durch den Einbau von Fünf- und Siebenecken an bestimmten Stellen entsteht ein ringförmiges Nanoröhrchen; hier schematisch dargestellt. (Bild: Dr. H. Terrones/University of Sussex, U.K.)*

# Building Faults, Properties, Electronics





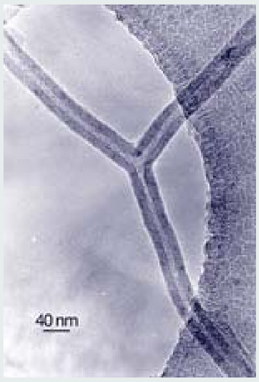


5+7 ring => Diode

But contact resistance !!

Semicond. / metallic CNT transistor

But no control on helicity!!

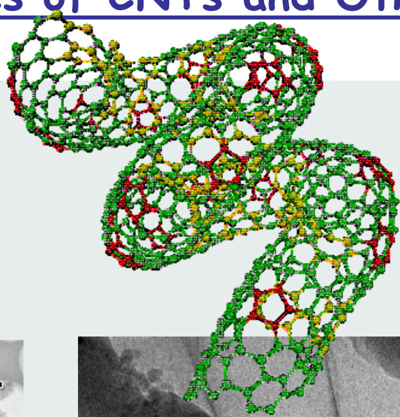


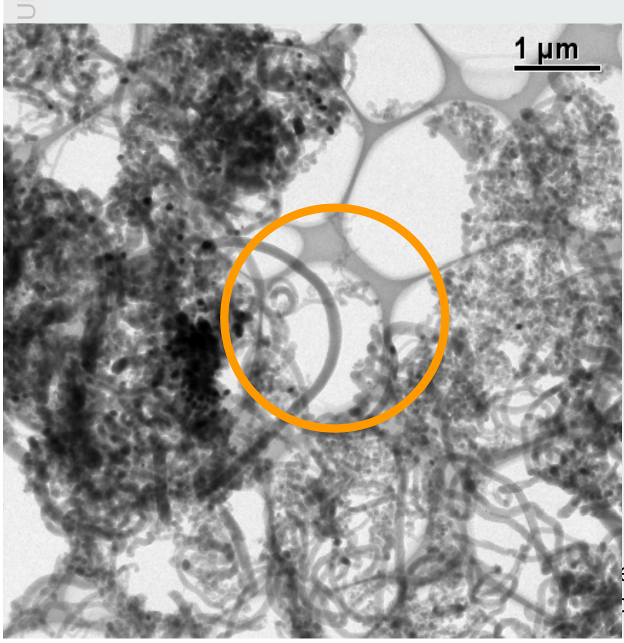


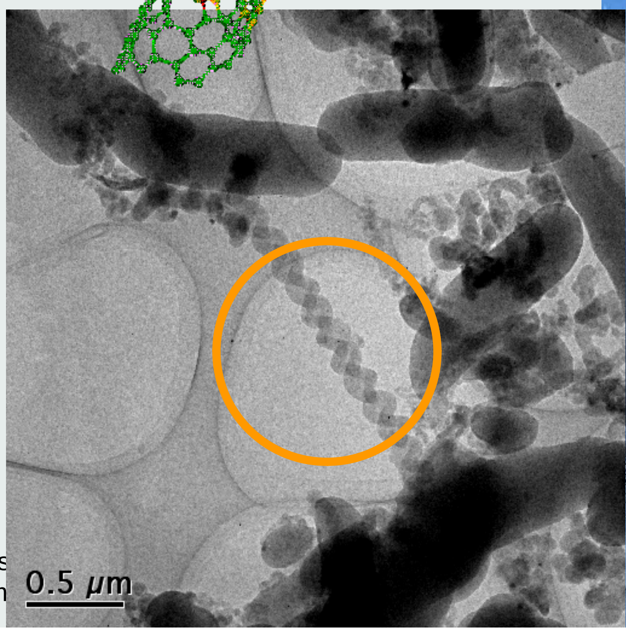

# Low Temperature Syntheses of CNTs and Other C Nanoparticles



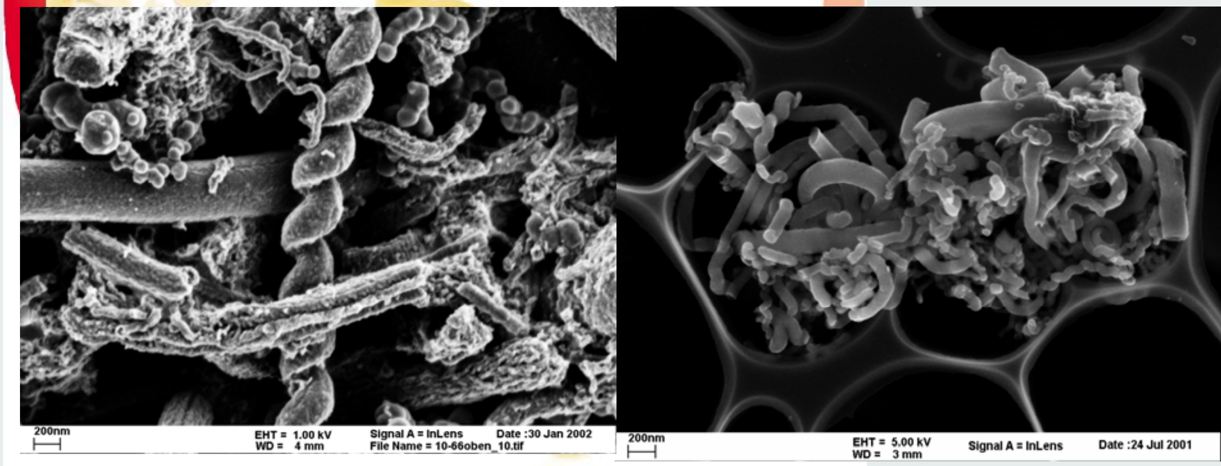
T < 500 C





# Carbons – All Pasta and Infinite Set ?

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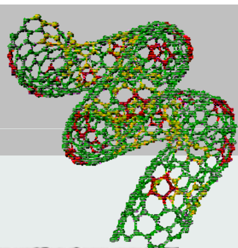
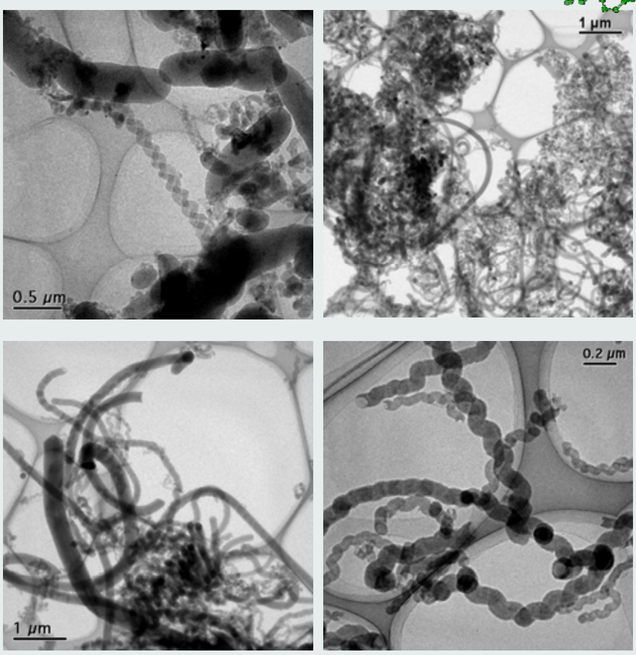
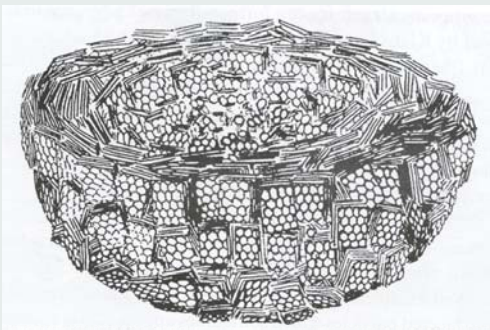
# Low Temperature Syntheses of CNTs and Other C Nanoparticles



Fish bone structures



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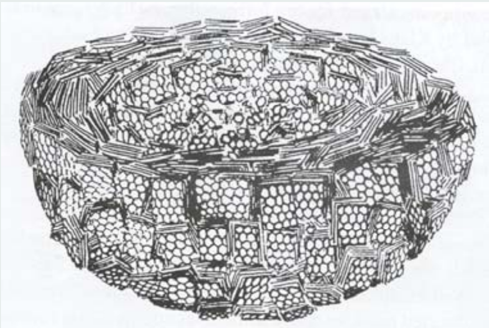
# Low Temperature Syntheses of CNTs



Fish bone structures



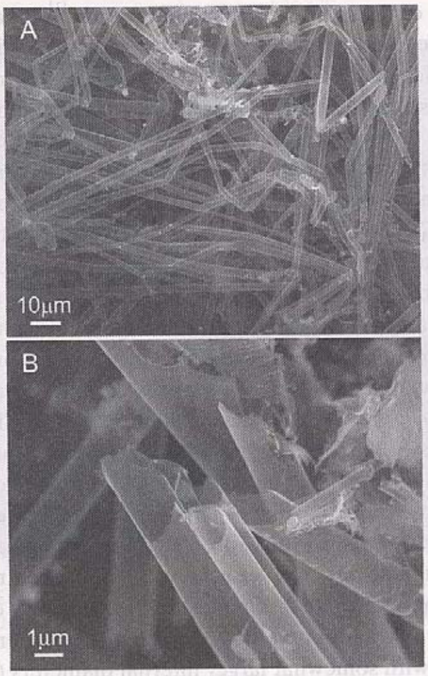


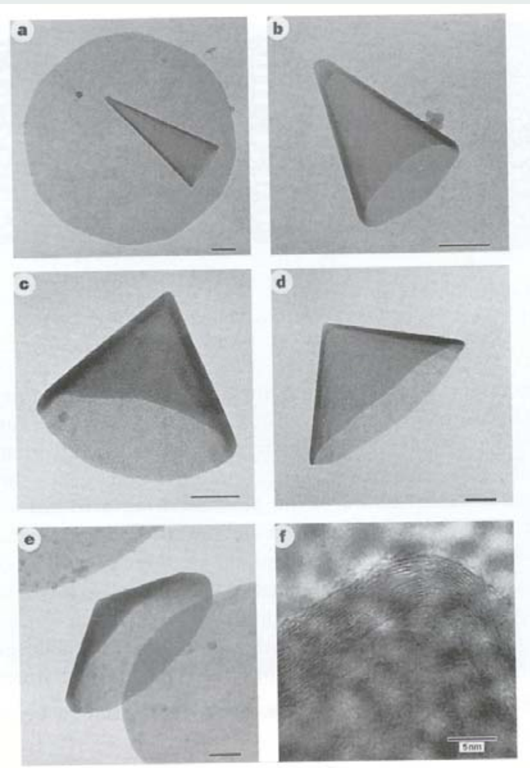

**Figure 1.** A) Low-magnification SEM image of the carbon microtubes. B) High-magnification SEM image displaying the open ends of the microtubes.



# Cones, Bamboos etc.

A. Ivantchenko, R. Nesper





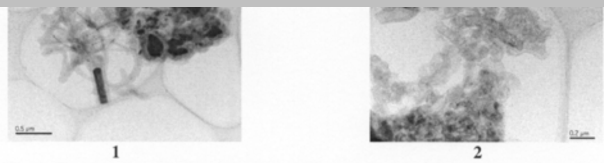




**Fig.2** Carbon microstructures obtained (1)after washing with 65% nitric acid (2)after washing with acid and heated to ~~1000~~ 1400 °C in Ar atmosphere

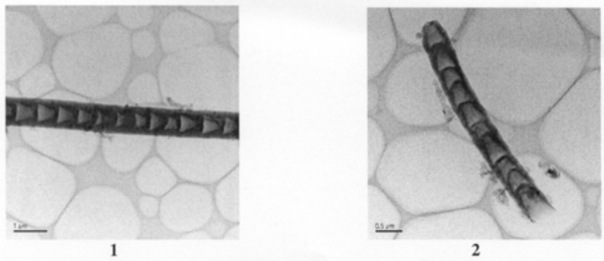


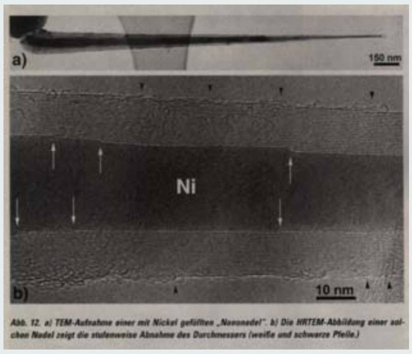

**Fig.3** Carbon microstructures obtained (1)after washing with 65% nitric acid (2)after washing with acid and heated to ~~1000~~ 1400 °C in Ar atmosphere

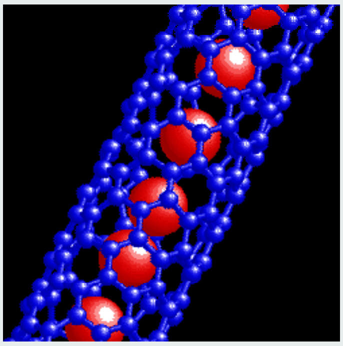

**Fig.4** Carbon microstructures obtained (1)after washing with water (2)after washing with concentrated acid

# Storage in CNTs



In a recent work of Baker and Rogriguez [1] indicate a very large specific hydrogen storage capacity in carbon nanotubes (CNT`s) and in herringbone materials. Yet, these results have not been confirmed by any research group in the world [1,2,3,6,7,8], but nevertheless they gave rise to enhanced activity in the field of carbon-based hydrogen storage on the theoretical and on the experimental side.



# $H_2$ – Storage in C-NTs ?



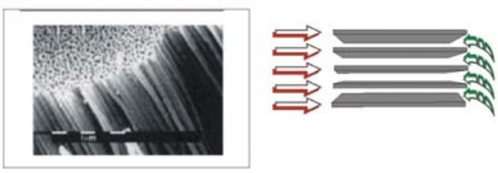
wrong !! ➔ Baker, N. Rodriguez et al., J.Phys.Chem. B 102, 423 (1998)

**Baker & Rodriguez**

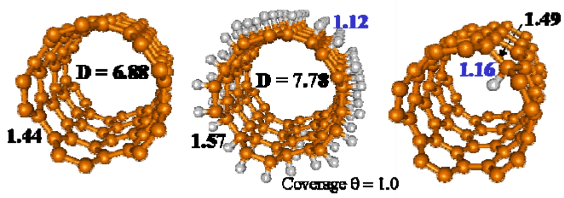
65wt% !!???

**M. Parrinello**

max. 14wt%

*Hydrogen adsorption on (5,5) SWNT*

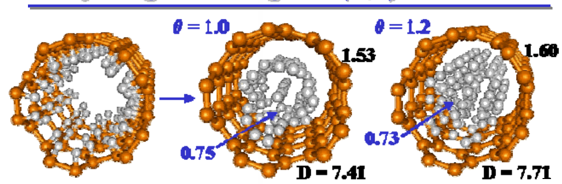



< Binding energy (eV/bond) >

| | C-C | C-H | C-H |
|---|---|---|---|
| DFTB | -9.14 | -2.65 | -0.83 |
| LDA | -8.41 | -2.10 | -1.50 |
| GGA | -7.48 | -1.75 | -1.28 |

*Nanotubes Research Lab*

*Hydrogen storage in (5,5) SWNT*




| | DFTB (LDA:GGA) | DFTB |
|---|---|---|
| • Binding energy (eV/$H_2$) | -4.57 (-3.16:-2.24) | -4.01 |
| • Wall-$H_2$ repulsive energy (eV/$H_2$) | 0.70 (0.47:0.74) | 0.78 |
| • $H_2$-$H_2$ repulsive energy (eV/$H_2$) | 0.89 (0.81:1.19) | 1.11 |

- $H_2$ molecules exist inside nanotubes.
- $H_2$ can be stored inside nanotubes with coverage > 1.0.

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# Catalyst Patterning for Growth of CNTs

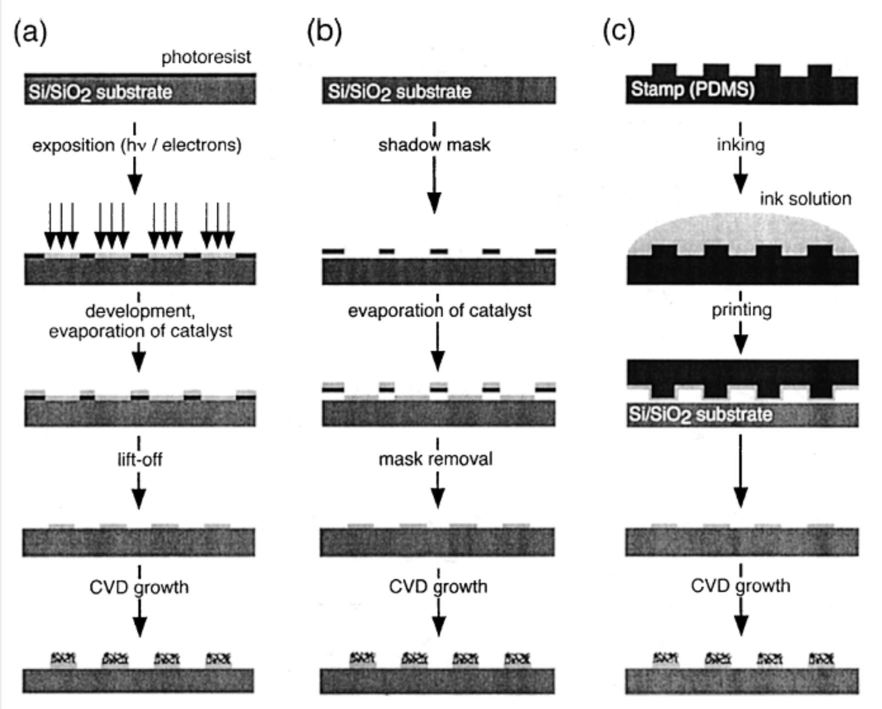



Fig. 4. Techniques to produce patterns of catalysts for the selective growth of carbon nanotubes: (a) standard lithography, (b) shadow-masking, (c) soft lithography.



# Hierarchical Order – Aggregations

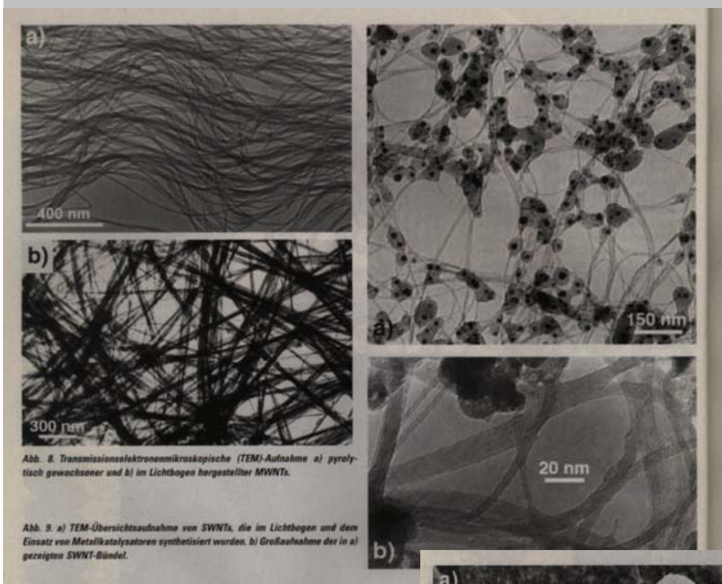



Abb. 8. Transmissionselektronenmikroskopische (TEM)-Aufnahme a) pyrolytisch gewachsener und b) im Lichtbogen hergestellter MWNTs.

Abb. 9. a) TEM-Übersichtsaufnahme von SWNTs, die im Lichtbogen und dem Einsatz von Metallkatalysatoren synthetisiert wurden. b) Großaufnahme der in a) gezeigten SWNT-Bündel.

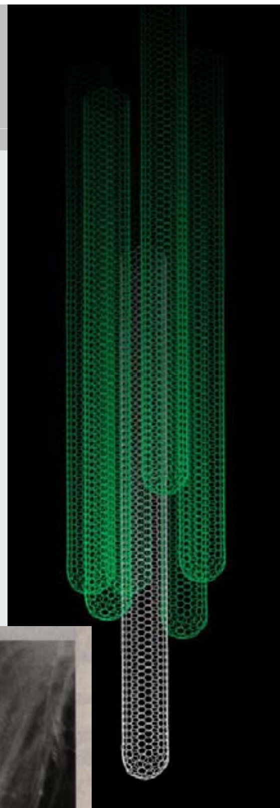
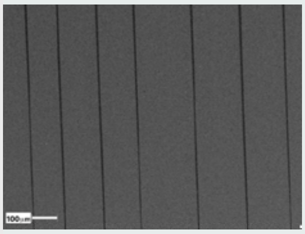
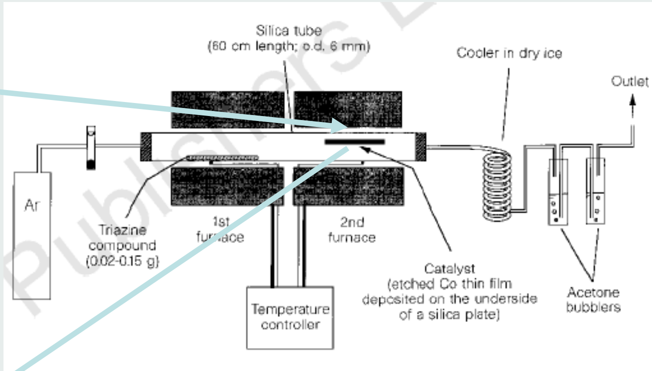


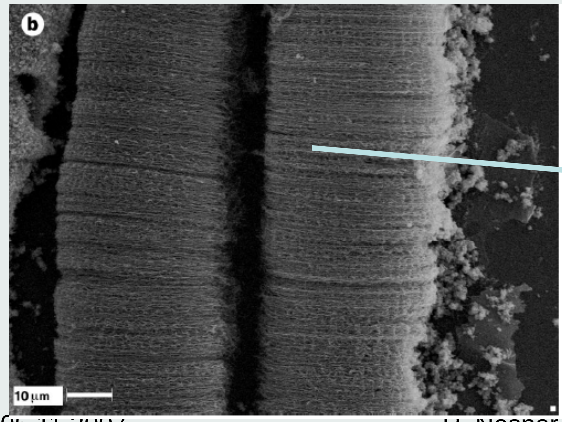

Abb. 10. a) REM-Aufnahme eines MWNT-Bündels, das während der Pyrolyse organischer Feststoffe gewachsen ist. b) Großaufnahme der ausgerichteten MWNTs dieses Bündels.

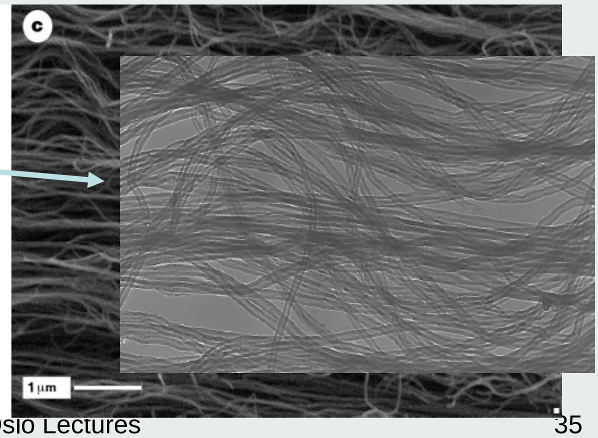
# Hierarchical Order – Carpets Predefined







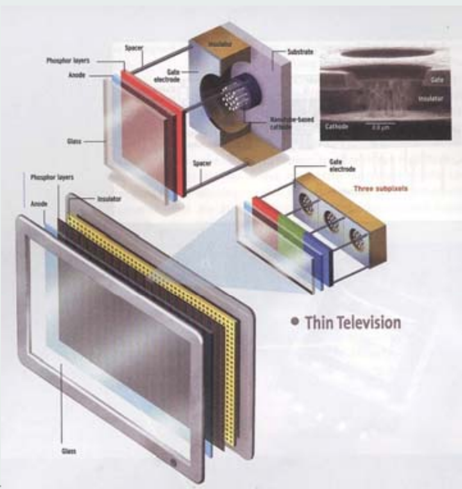



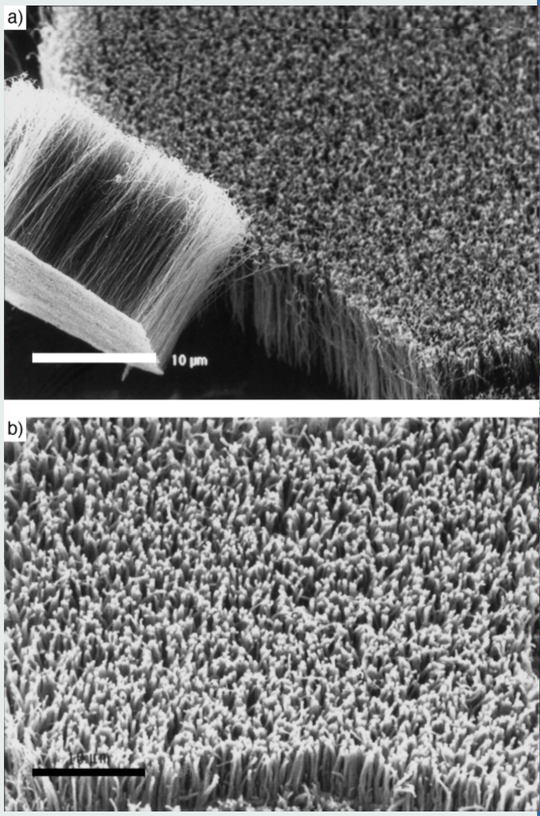



# Hierarchical Order – Carpets etc.



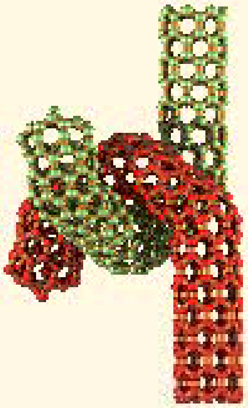

*Abb. 10. a) REM-Aufnahme eines MWNT-Bündels, das während der Pyrolyse organischer Feststoffe gewachsen ist. b) Großaufnahme der ausgerichteten MWNTs dieses Bündels.*

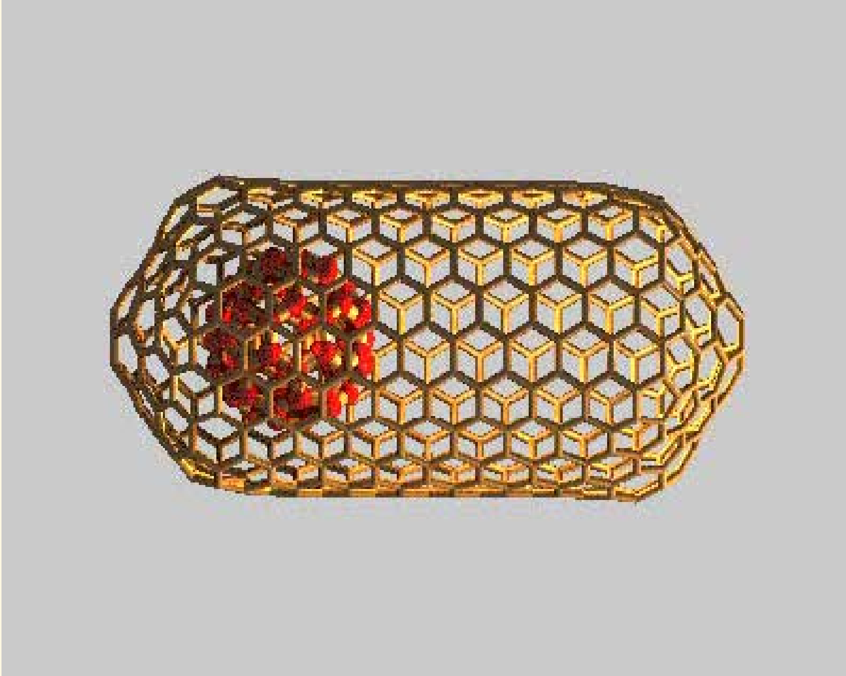


# Carbon Nanotubes Models

(http://www.pa.msu. edu/cmp/csc/nanotube.html)



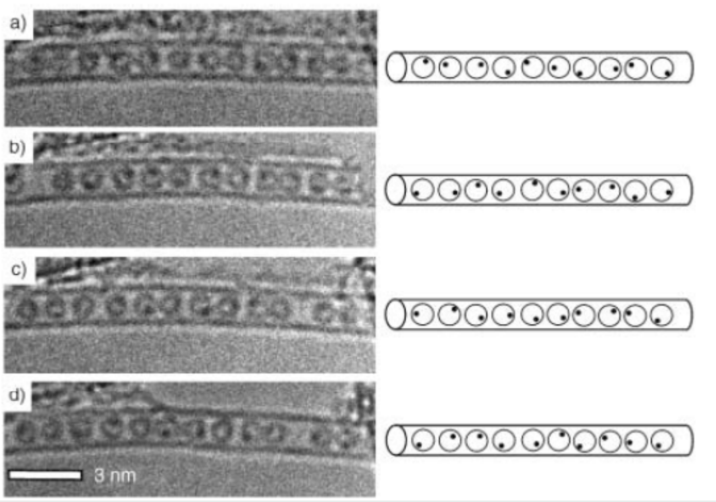


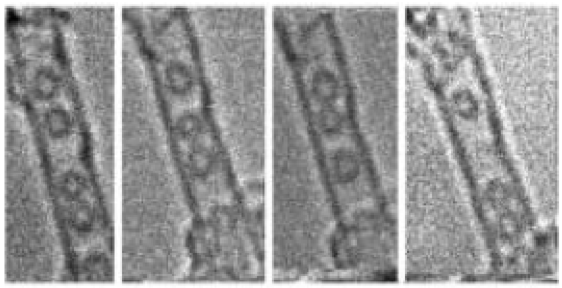


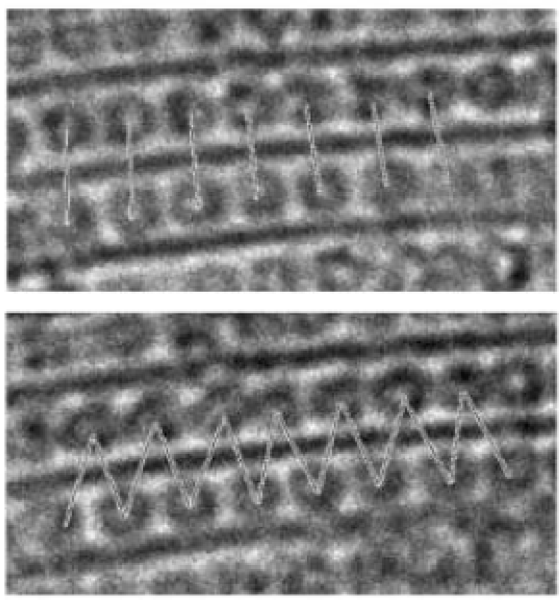
# Filling of Carbon Nanotubes



$(Ce@C_{82})@SWNTs$





# Valence & conduction bands

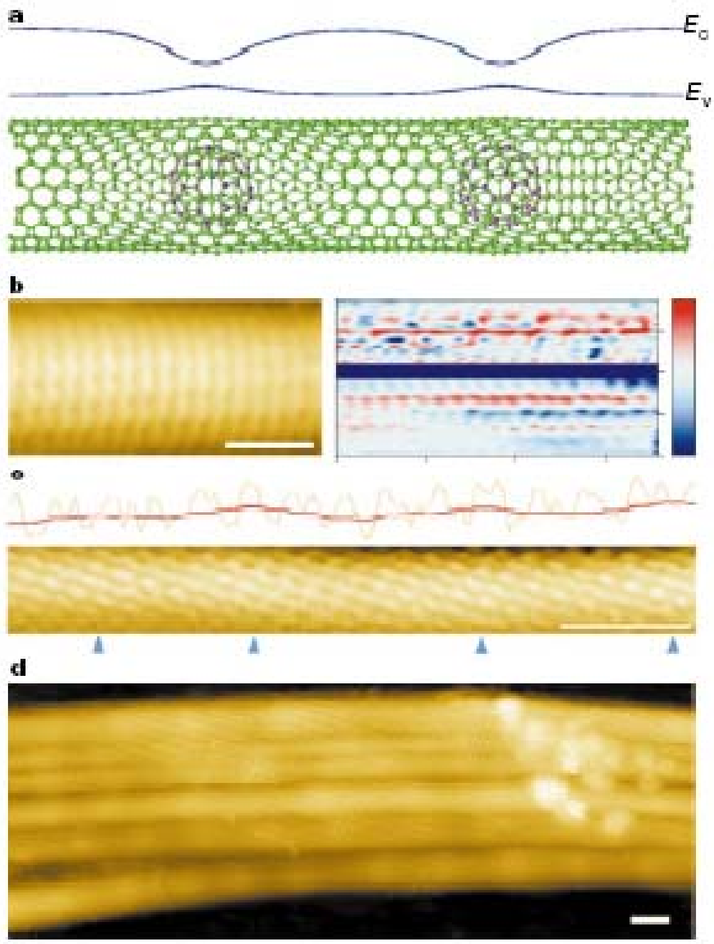


Elastic strain

STM topography

Atomic resolution

SWT bundle






# Applications of CNTs - Thermocouple



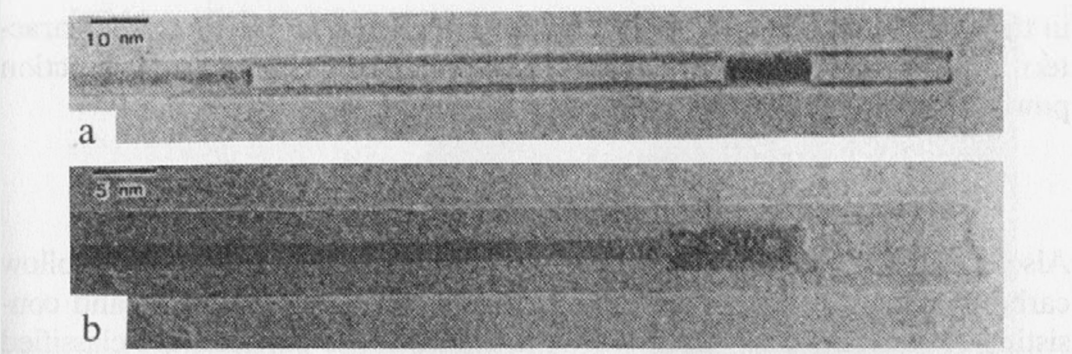
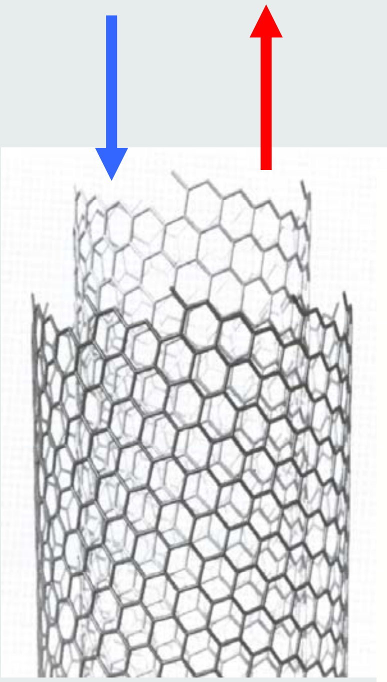
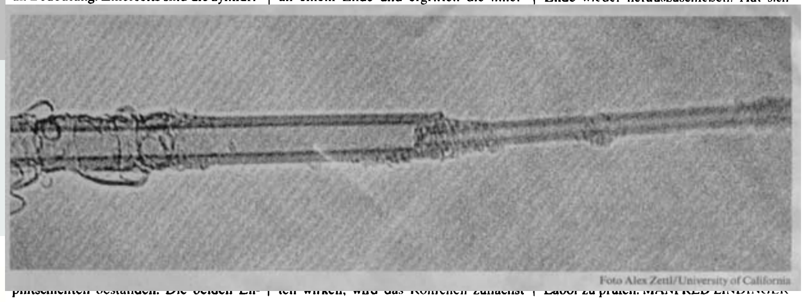



**Fig. 19.60.** TEM image of nested carbon nanotubes containing a Pb filled core [19.66].

# Tube-in-Tube



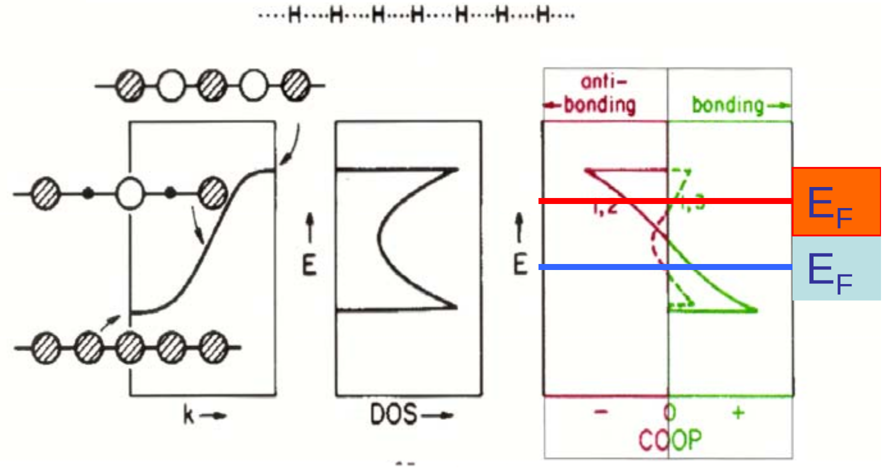




## Flinkes Nanoröhrchen schwingt wie winziges Federpendel

Nanoröhrchen aus Kohlenstoff gewinnen wegen ihrer ungewöhnlichen Eigenschaften für die Wissenschaft zunehmend an Bedeutung. Einerseits sind die zylindri- den der Röhrchen waren zunächst durch mehrlagige Kappen abgeschlossen. Zettl und seine Kollegen entfernten die Kappe an einem Ende und ergriffen die inner- wieder in das Innere der Graphithülle zurückgezogen. Dort besitzt es aber genügend kinetische Energie, am anderen Ende wieder herauszuschießen. Hat sich

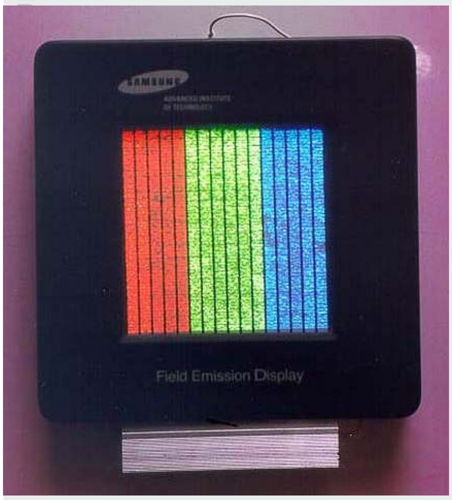
Foto Alex Zettl/University of California






# Field Emission Displays





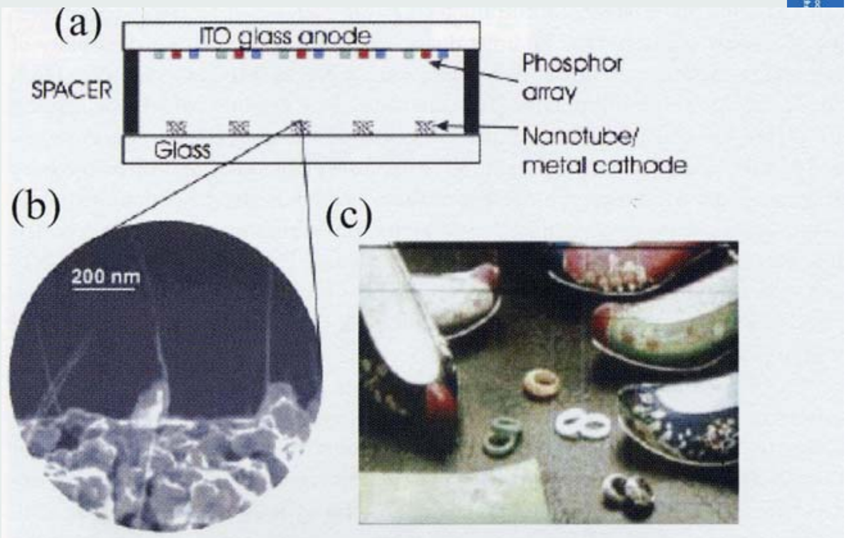
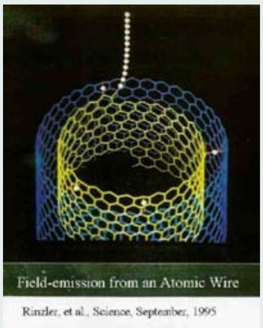




**Fig. 8.14.** (a) Schematic illustration of a flat panel display based on carbon nanotubes. ITO, indium tin oxide. (b) SEM image of an electron emitter for a display, showing well-separated SWNT bundles protruding from the supporting metal base. (c) Photograph of a 5 in (13 cm) nanotube field emission display made by Samsung. Reproduced from ref. [187], with permission.

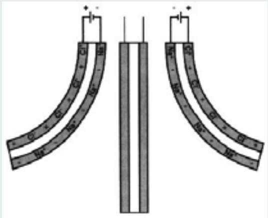
# (C)NT-Applications



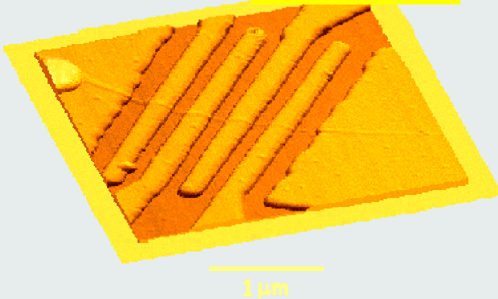
emission tip



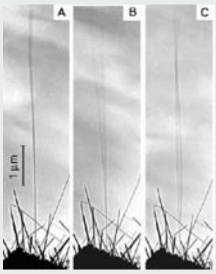

ion sensor
actuator



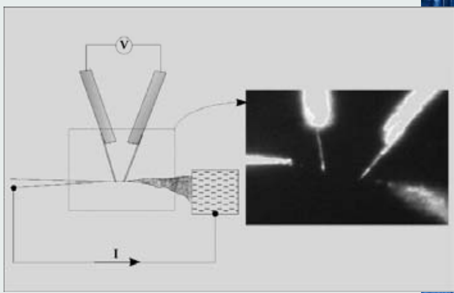
Conductor
rectifyer
transitor
sensor




??




nano tips





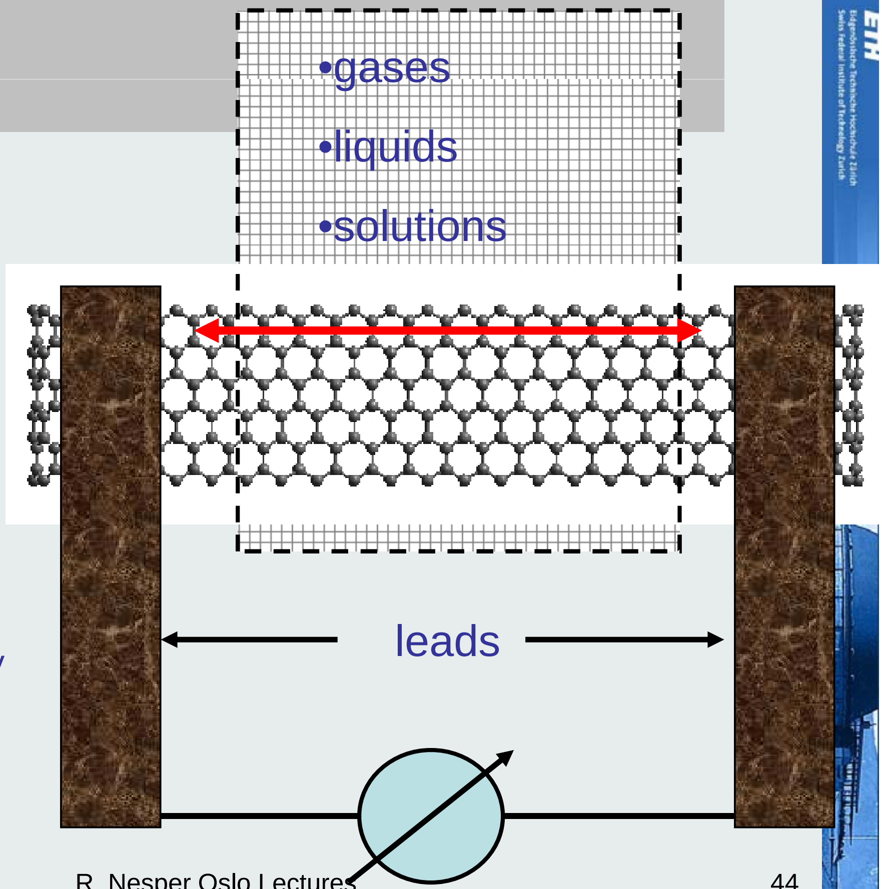

## C-NT Sensor



**Surface electron conductance**

Adsorbed species

strongly change conductivity



# Next Generation Aerospace Material

**Carbon Nanotube**

↓

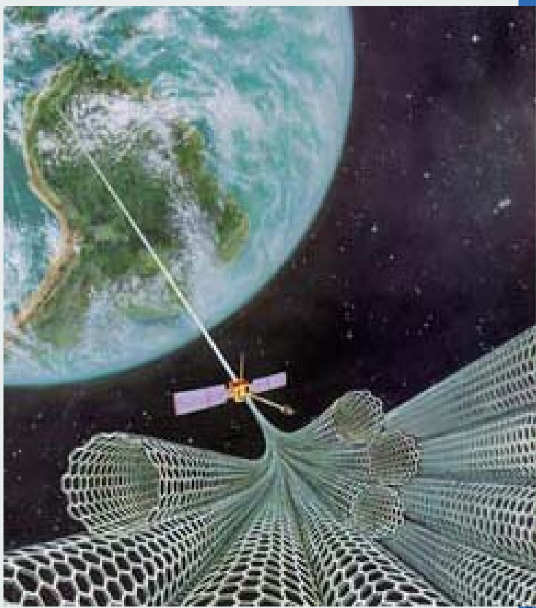
**Nanotube Fiber**

↓

**Nanotube/ Polymer**

↓

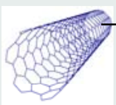
**Ultra Nanostructured Composite**



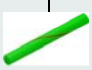




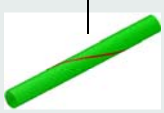
# Self Similar Helical Modeling



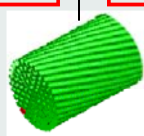
**SWCN** → **Lattice Dymanics** → **Self Similar Analysis** → **Nano-array**



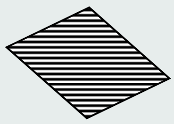
**Polymer** ↓ **Micro-Mechanics + Self Similar Analysis** → **Nano-wire**



**Polymer** ↓ **Micro-Mechanics + Self Similar Analysis** → **Micro-fiber**

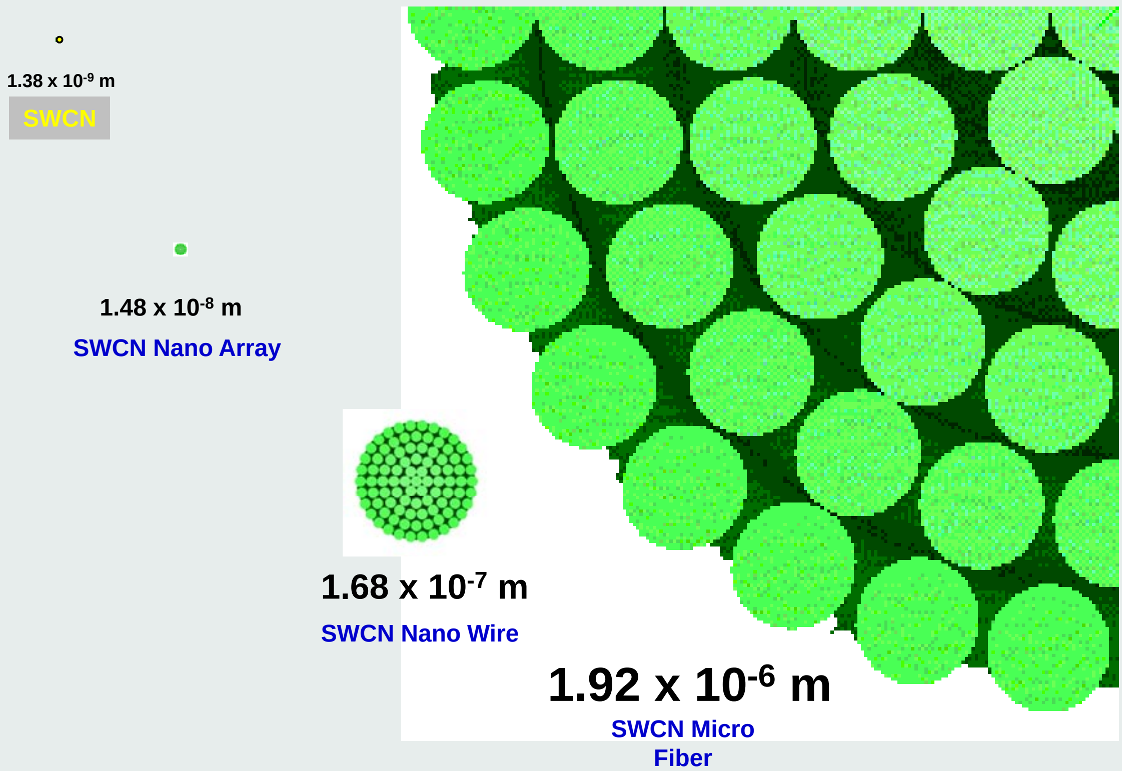


**Polymer** ↓ **Micro-Mechanics + Self Similar Analysis** → **Lamina**



# Self-Similar Scales

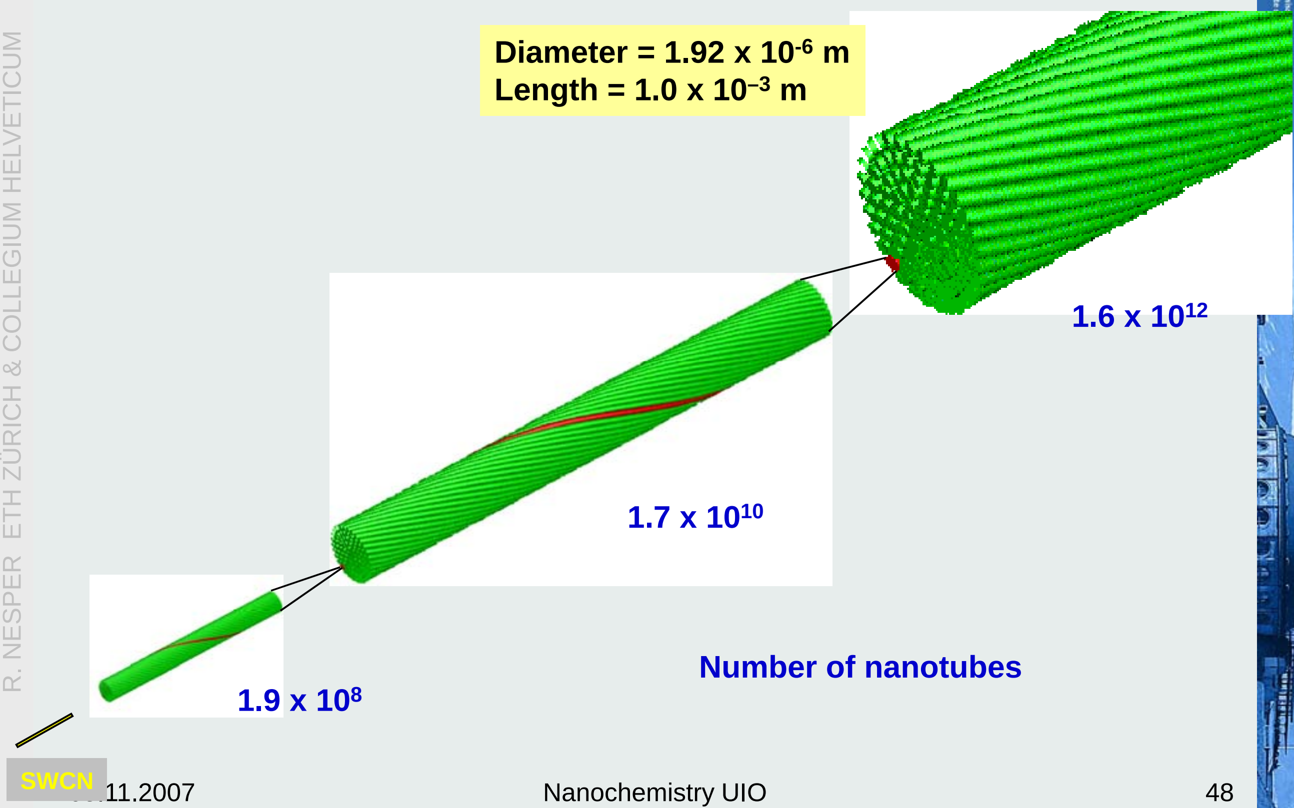
R. NESPER ETH ZÜRICH & COLLEGIUM HELVETICUM





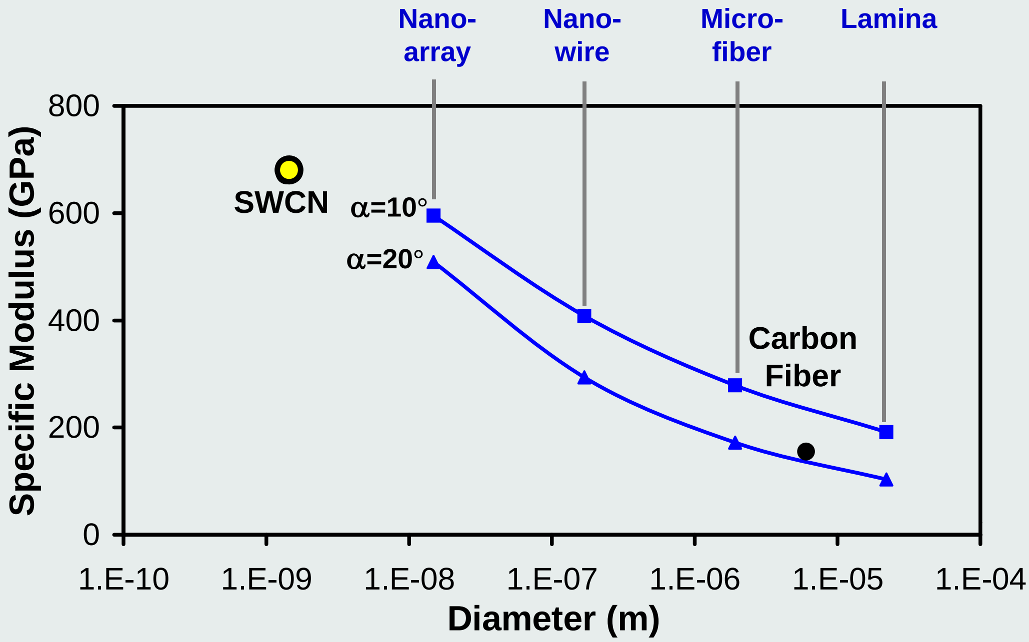

# Self-Similar Scales

R. NESPER ETH ZÜRICH & COLLEGIUM HELVETICUM



# Self-Similar Properties

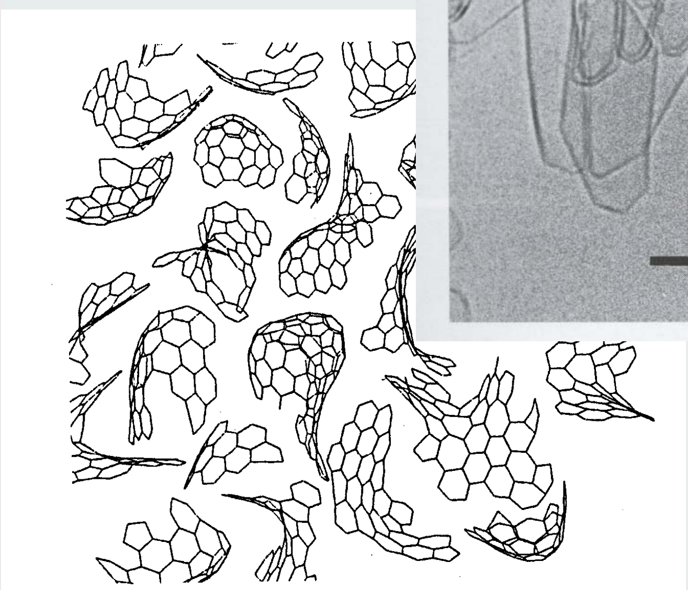


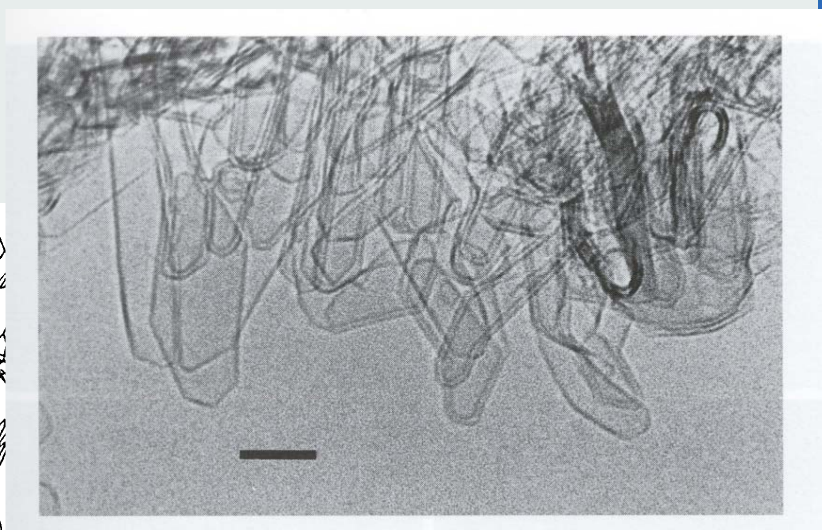





# New Carbons ?

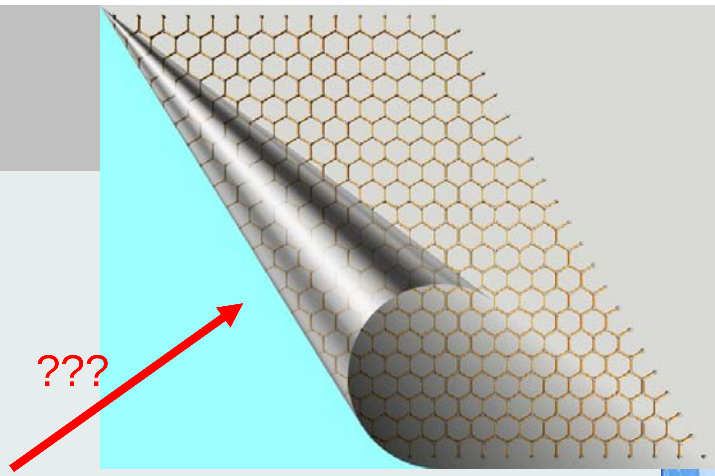




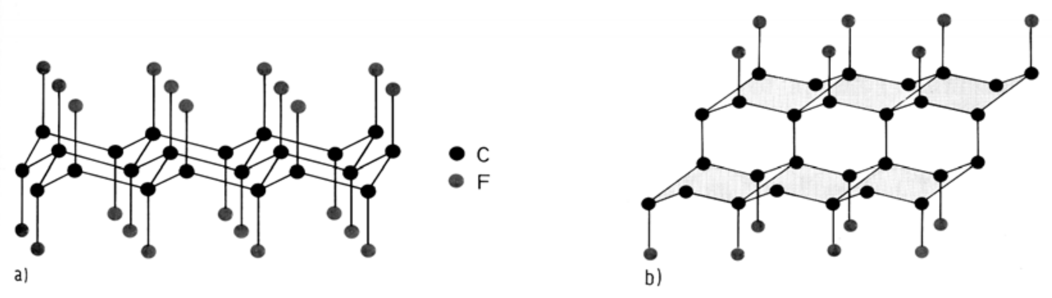


# Derivates of Graphite






$$\text{Graphit} \xrightarrow{T\,=\,350\,-\,600^{\circ}C} [CF]_x,\ x=0.5 - 1$$






# Exfoliate Graphite Intercalation Compounds?



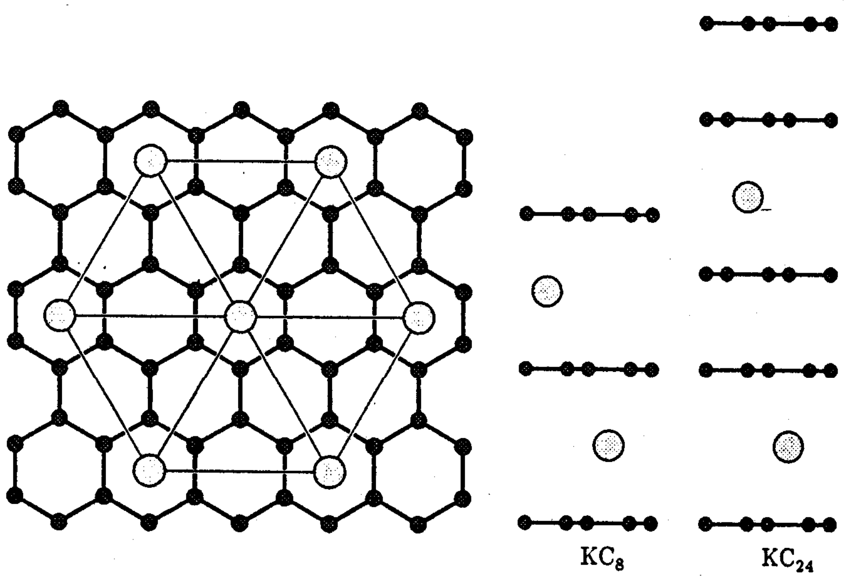
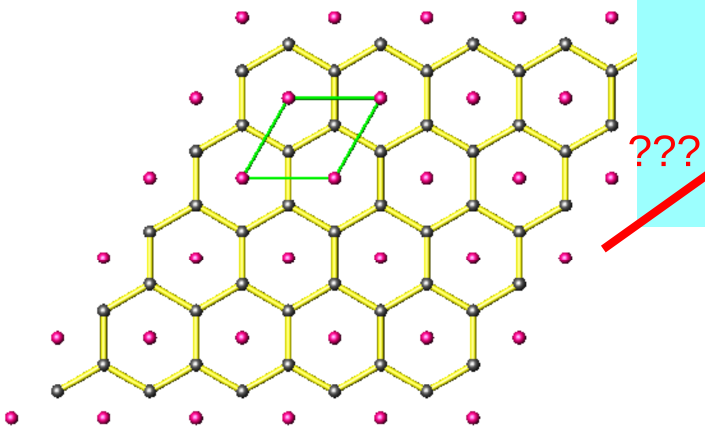
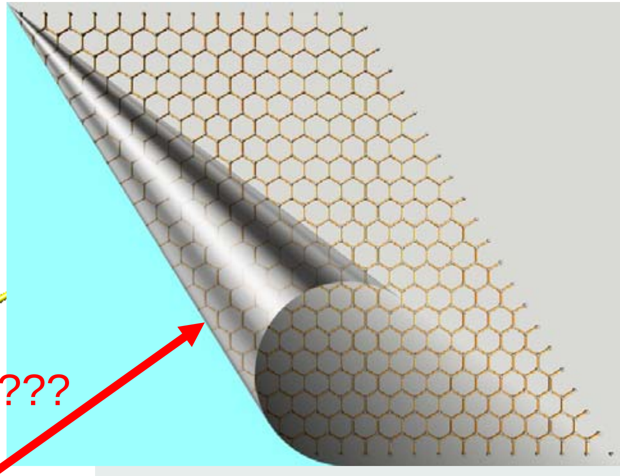



**Abb. 52:** Links: Anordnung der $K^+$-Ionen relativ zu einer benachbarten Graphitschicht im $KC_8$; im $KC_{24}$ enthält eine $K^+$-Ionenschicht nur $\frac{2}{3}$ so viele Ionen indem jedes $K^+$-Ionen-Sechseck in seiner Mitte leer ist. Rechts: Stapelfolge von Graphitschichten und $K^+$-Ionen im $KC_8$ und $KC_{24}$

# Heterographites



$MgB_2$
$AlB_2$
$MgB_2C_2$
LiBC



# Graphite-related Superconductors



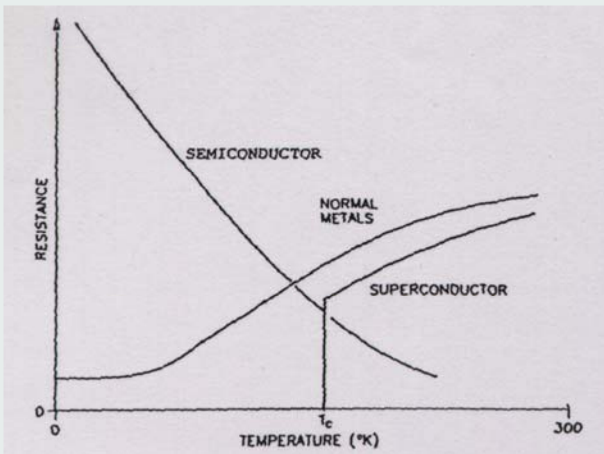
The superconducting materials demonstrate a ***zero electrical resistivity*** in a certain range of temperature, current and magnetic field.

Their maximum values are called:

*critical temperature* ($T_C$)

*critical current density* ($J_C$)

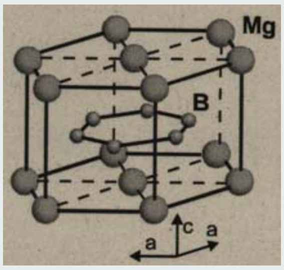
*critical magnetic field* ($H_C$)



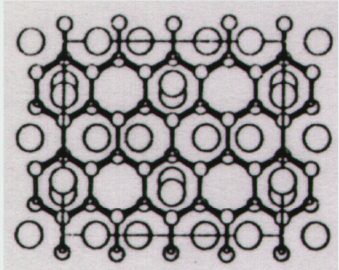

| | |
|---|---|
| $MgB_2$ | $Ca_x$-graphite |
| ~~$MgB_2C_2$~~ | $Yb_x$-graphite |
| ~~LiBC~~ | ~~„$Li_{0.5}$BC“ $T_c$=90K~~ |
| ~~$AlB_2$~~ | |

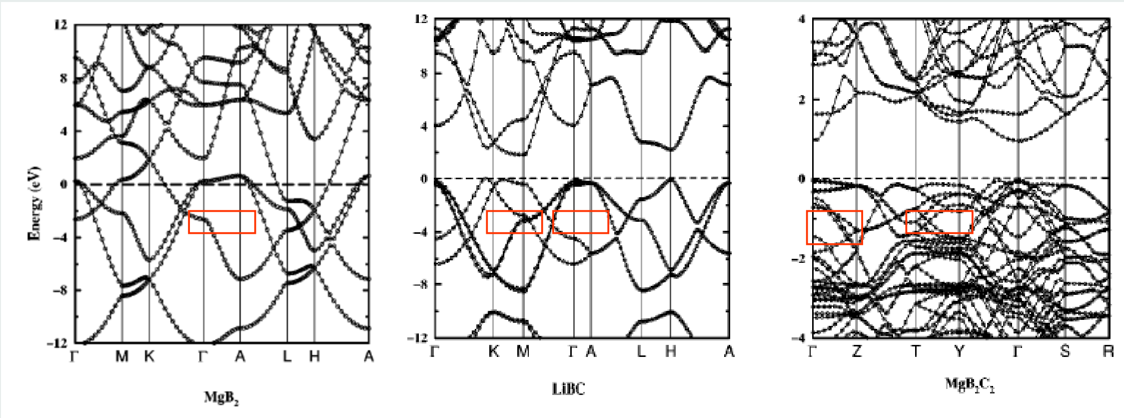
# Superconductivity - $MgB_2$ vs LiBC and $MgB_2C_2$






$MgB_2$
$MgB_2C_2$
LiBC
$Li_{0.5}BC$ $T_c$=90K

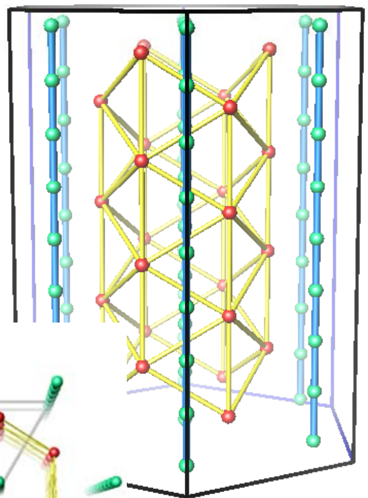


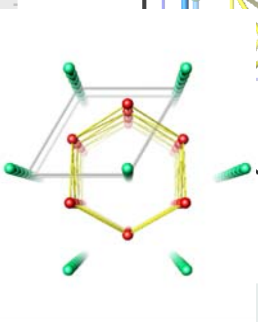


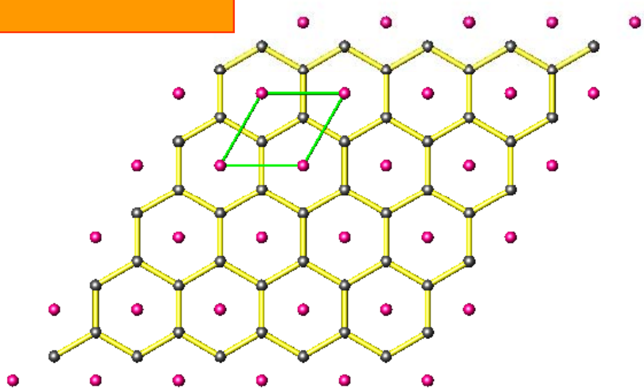



# $MgB_2$ and its Analoga *Wire Preparation ?*

LiB —Mg-Melt→ $MgB_2$







$[B=B=B=B=]_n$

**J.M. Reinoso, F. Ottinger, M. Wörle, R. Nesper, *Method for producing a super-conducting material made of $MgB_2$*, Patent No WO0207149909/2002**

# Morphologie Preserving Transformation



182 ° C

molten Litium crystalline Boron

-Under continuous stirring Boron dissolves into molten Lithium, forming an high malleable, low density, metallic solid solution

300 ° C

Li-B liquid solution

-The wire is dropped into the crucible just the time to coat it

450 ° C

$LiB_x$ formation

-The coated wire is placed into the furnace untill the metallic glittering desappears

550 ° C

$MgB_2$ formation

-The LiB wire is kept into the crucible of molten Magnesium for about 15 min.

700 ° C

- Sublimation of Mg / $Mg_xLi_y$ under High vacuum, 630 ° C, 8 h



# Preparing Wires and Rods

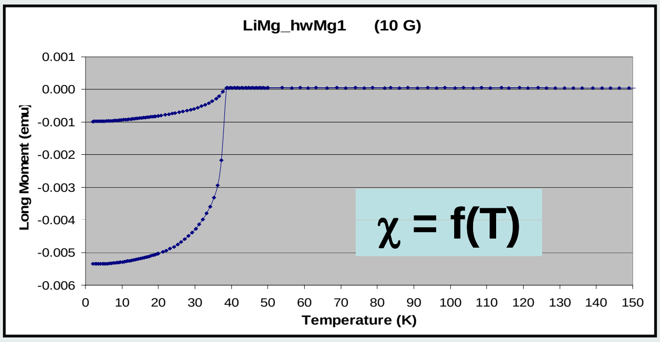


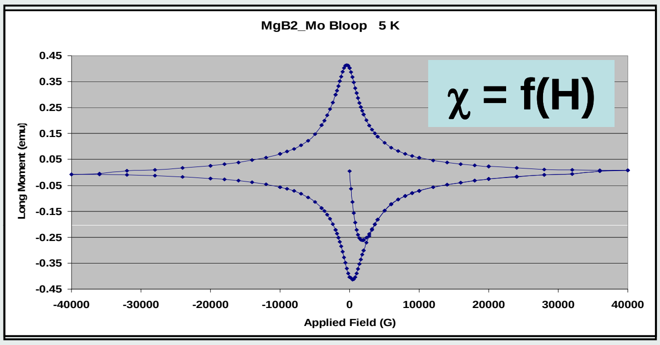
| Li-B mixture | $LiB_x$ compound | $MgB_2$ |
|---|---|---|
|  |  |  |
|  |  |  |
| - The inner part does not react completely | - The resulting coating is highly porous | - Formation of oxidic layer can occur between the wire and the coating |

# Magnetic Measurements

R. NESPER ETH ZÜRICH & COLLEGIUM HELVETICUM

**pure $MgB_2$**



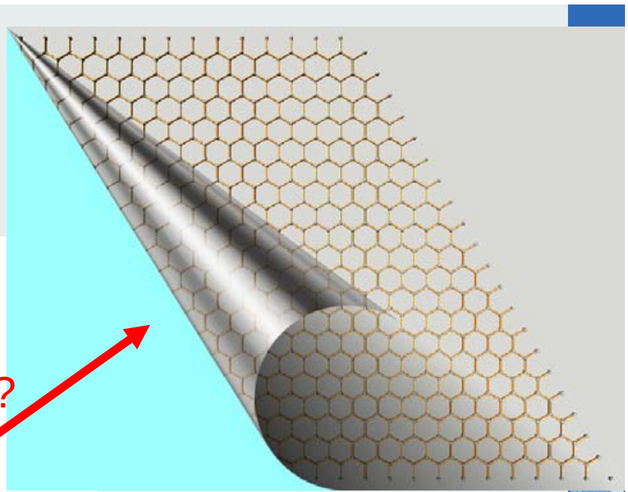


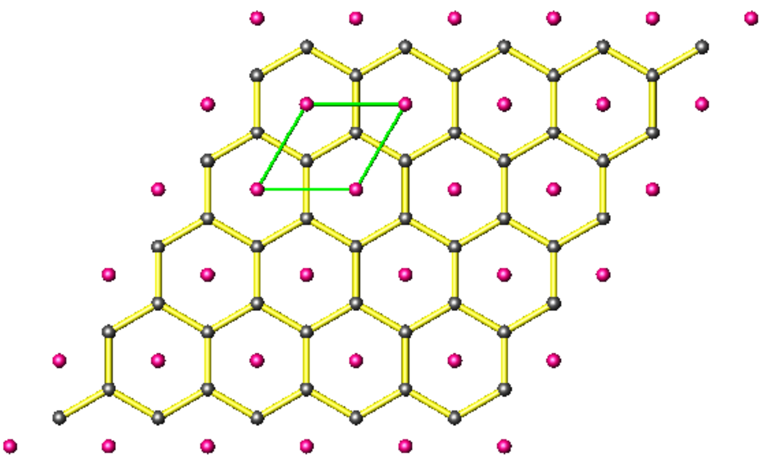

# Heterographites –

$MgB_2$
$MgB_2C_2$
LiBC

„$Li_{0.5}$BC“ $T_c$=90K

???





Scrolled Ionic Compounds ?

# Chaoite – Substitute ?

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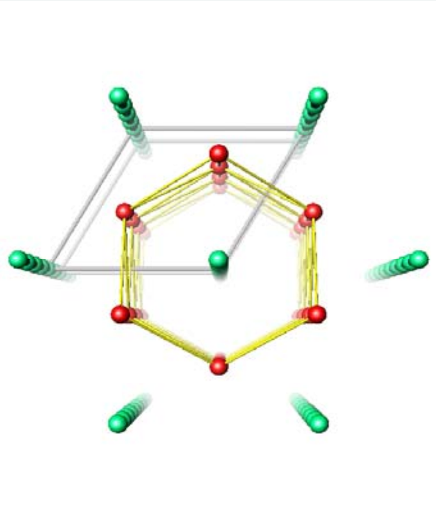
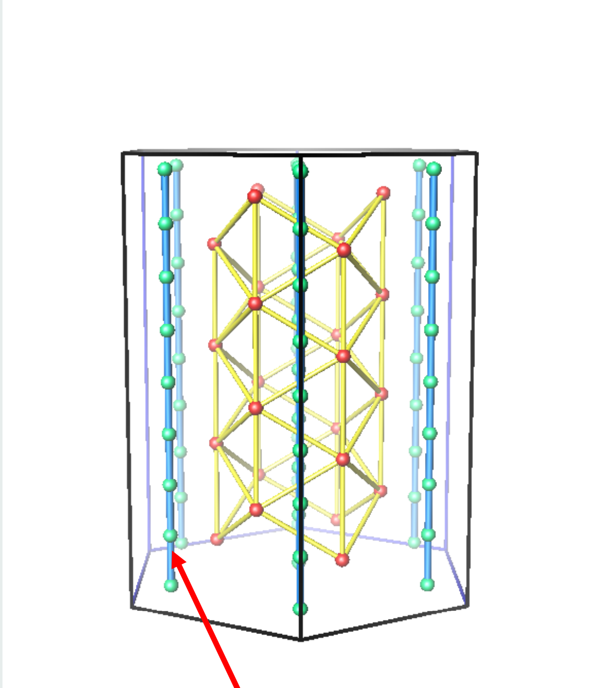
$LiB_{0.89}$





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