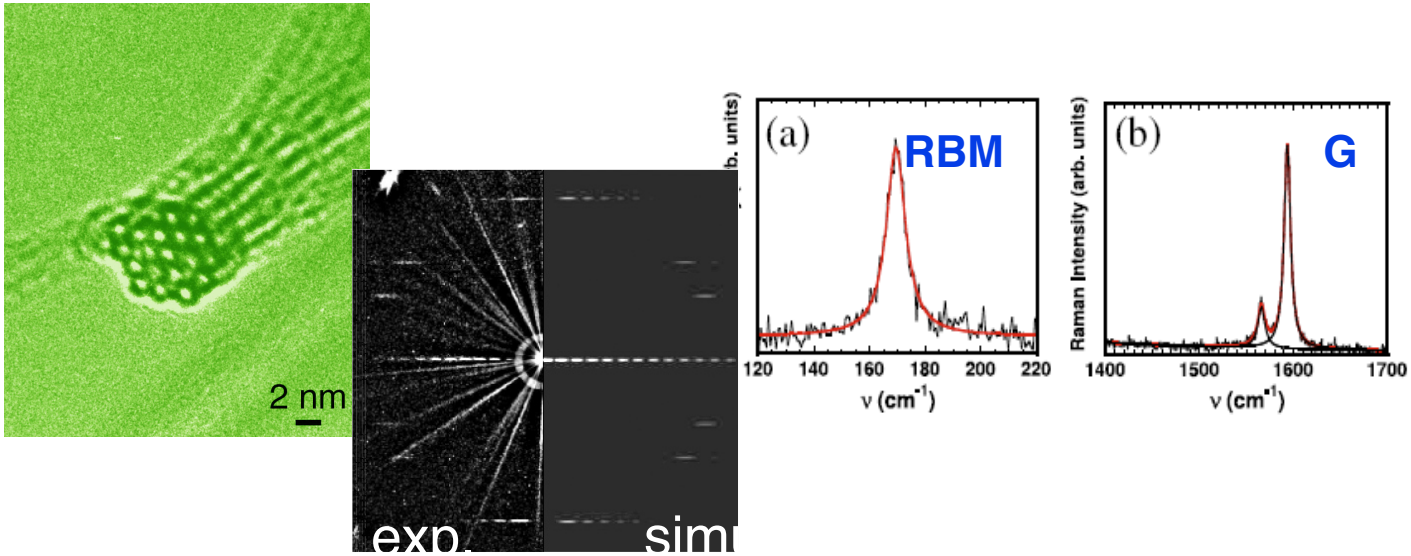
Determination of the nanotube structure :

How it can be done?



Annick LOISEAU

LEM, CNRS-ONERA (France)

ONERA

GNT Nanotubes Graphene

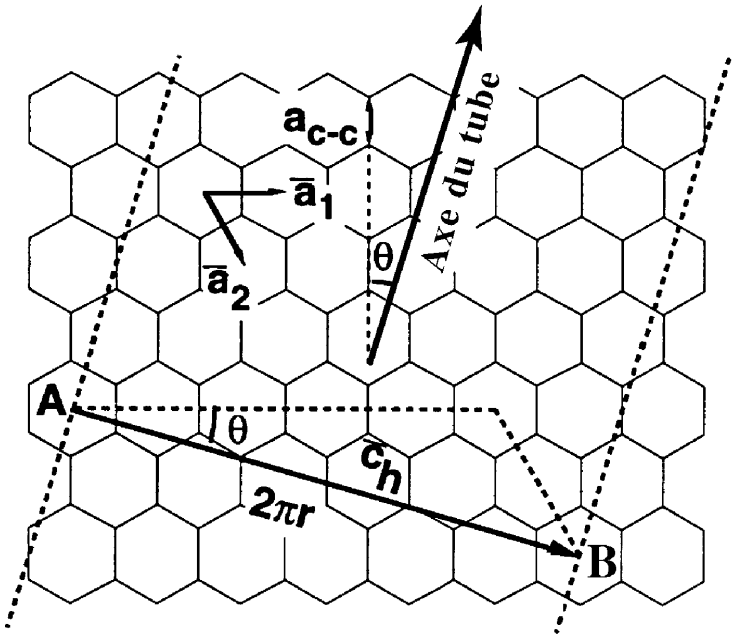
NanoSciences ILE-DE-FRANCE

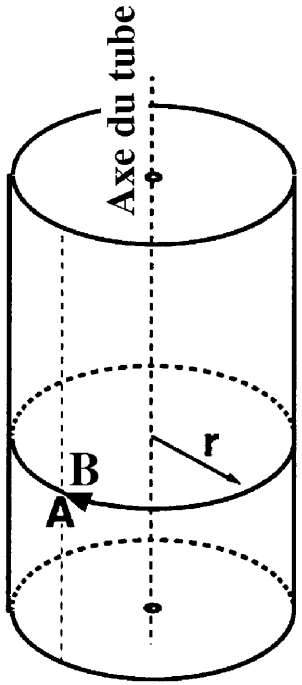
cnrs dépasser les frontières

Outline

- Forword: what is a nanotube?
- Part 1: What means characterization, what are the tools ?
  - imaging techniques versus spectroscopies
  - local techniques versus global techniques
- Part 2: Introduction to TEM and its three major modes:
  - Imaging: HRTEM, HAADF
  - electron diffraction
  - EELS
- TEM: a guide for validating spectroscopic techniques
  - TEM and Raman (T. Michel et al., PRB **80** (2009) 245416)
  - TEM and STS (H. Lin et al Nature Mat. (2010))

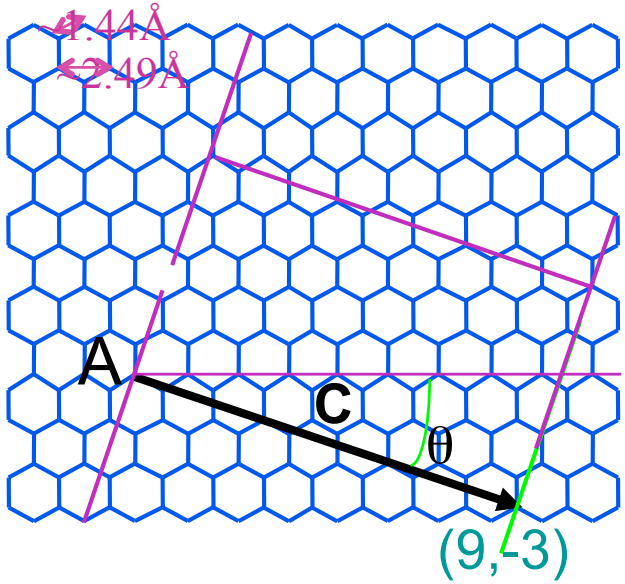
Describe a tube configuration





A given configuration is fully described by the (n, m) indices of the vector $C = n\mathbf{a}_1 + m\mathbf{a}_2$

n, m = Hamada indices



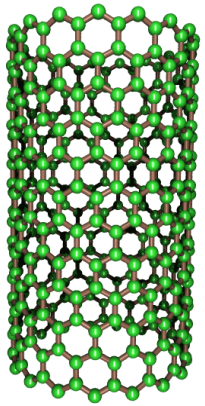
The angle θ, the tube diameter, the number of atomes can be easily deduced from n and m:

Ex tube (9, -3) : θ = - 19.1°

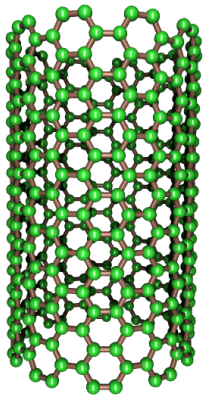
diameter = 0.63 nm

84 atoms

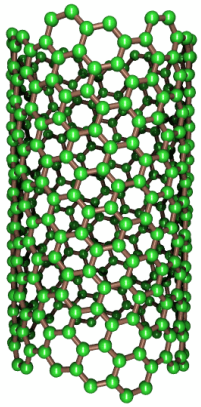
Different kinds of atomic configurations



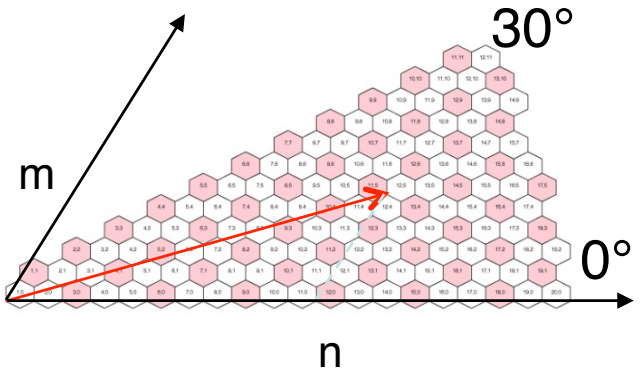
‘zig zag’
θ= 0°
(n, n)
M or SC



‘ armchair’
θ= 30°
(n,0)
Metallic

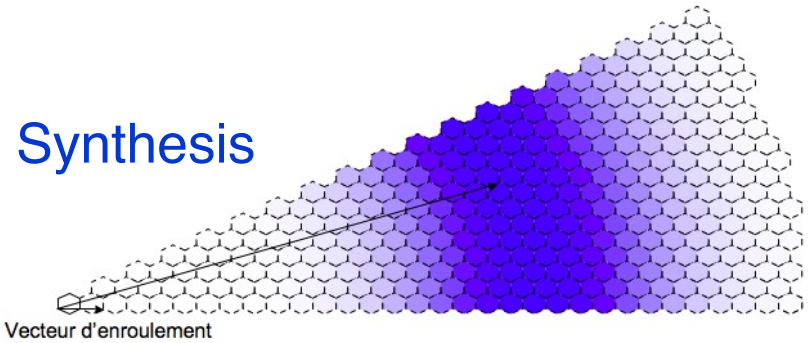


Chiral
0 < θ < 30°
(n, m ≠ n)
M or SC



n - m = 3p : metallic tube
n - m = 3p ± 1: SC tube

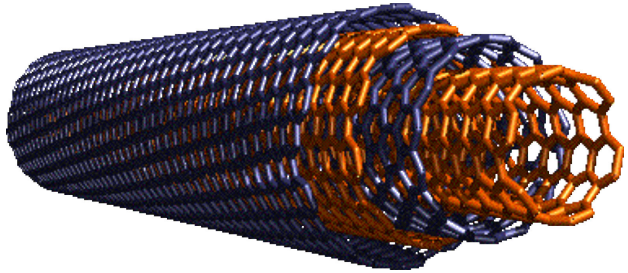
Synthesis



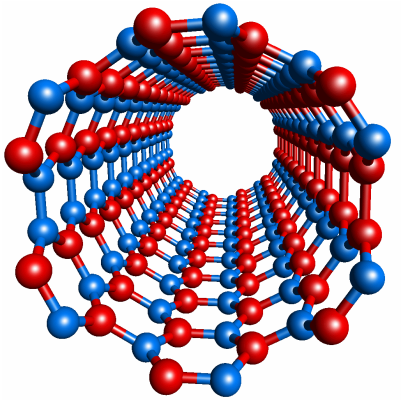
- Diameter of the tubes can be controlled to a less extent
- Very poor control of the helicity and then on the M / SC character

A sample is a mixture of configurations !

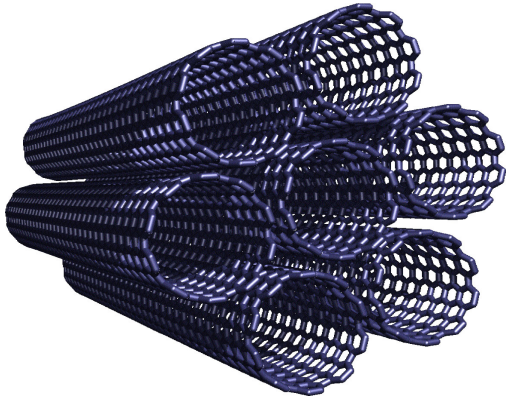
Assembling modes and compositions



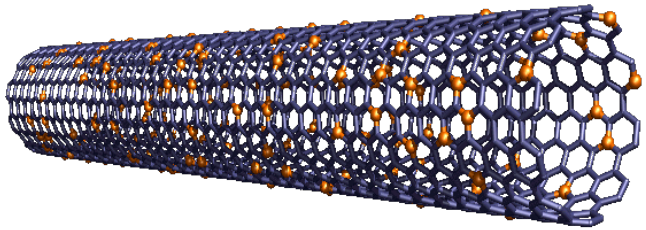
Multi-wall nanotubes(MWNT)



BN SWNT and MWNT



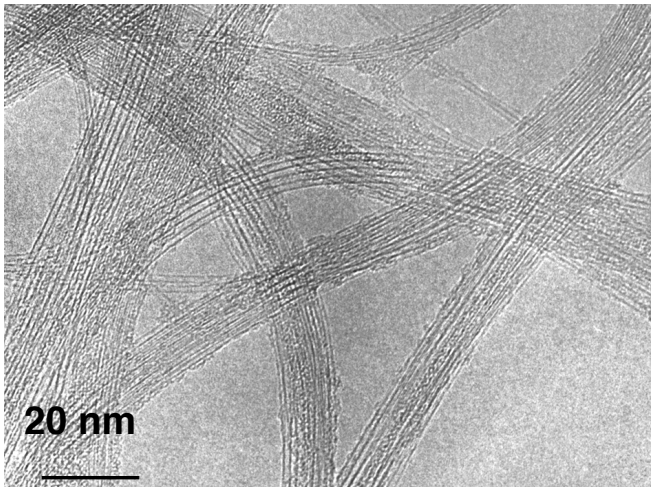
Bundles of SWNT or DWNT



C-NT with substitutional atoms
or covered with functionalizing molecules

Characterization: questions of interest

- Characterization: what for?
  - determine the structure of a tube or an assembly in order to determine, understand and use its properties



- How to determine the structure of a given tube?
  - diameter, helicity, ultimately (n,m) indices
  - assembling mode: nb of walls, bundling
  - chemistry: nature, composition and spatial distribution of hetero-atoms in substitution, inside the cavity or bound at the tube wall
  - metallic or semi-conducting character
- How to analyse a macroscopic tubes assembly ?
  - distinction between the mean tube structure and its distribution
- How to determine the tube environment and its effect on the structure ?
  - environment due to other tubes
  - chemical environment: functionalisation, surfactant, substrate...

Part 1

Characterization : approaches and tools

- Direct methods : based on structure imaging and diffraction

  Transmission electron microscopy (TEM)

  Local microscopies (AFM, STM)

- Indirect methods: spectroscopic measurements of a physical property linked to the structure

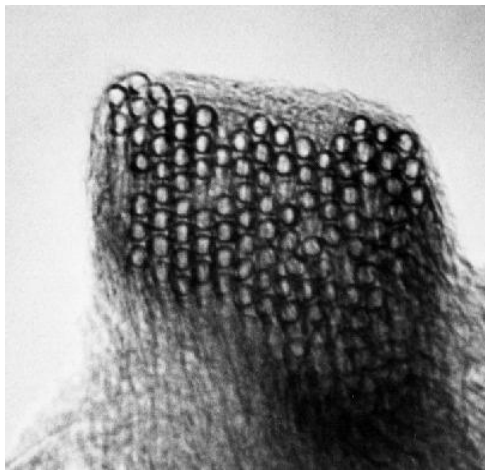
  Raman spectroscopy

  Optical UV-vis-IR absorption, Photoluminescence,

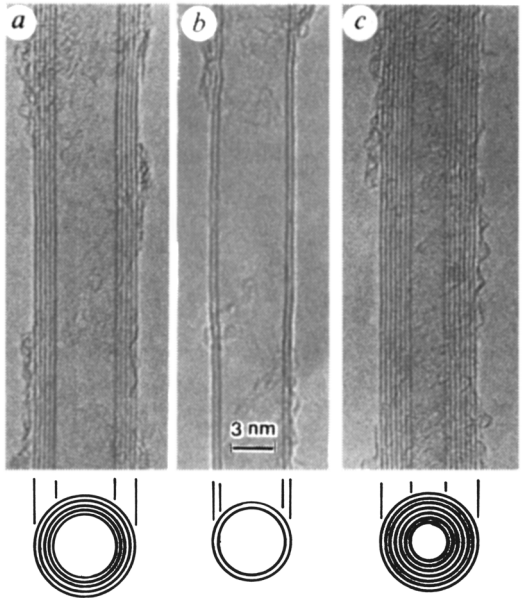
  EELS, STS….

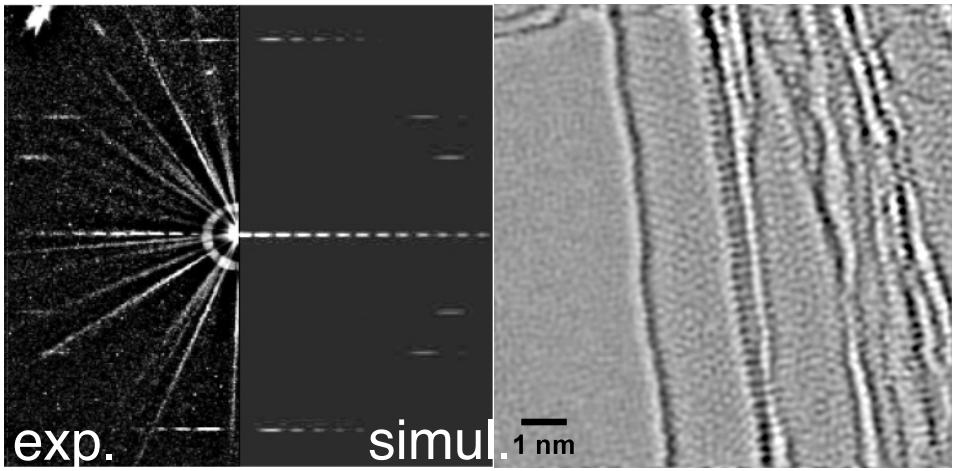
Direct methods - TEM

TEM: imaging of elastic or inelastic scattering atoms



TEM



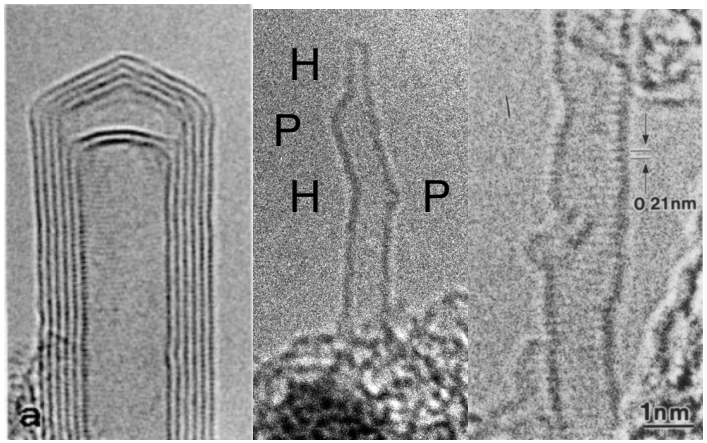


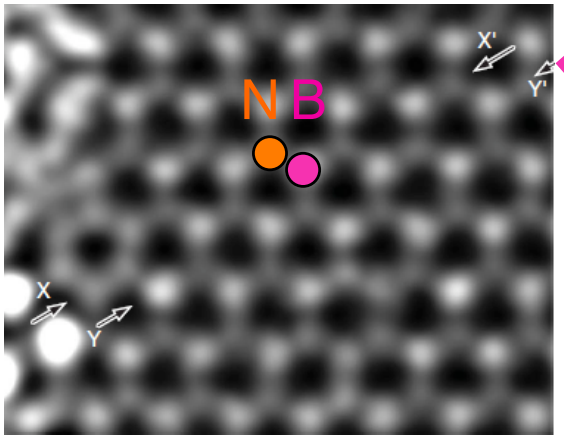
Electron diffraction

HRTEM

Assembling mode, diameter, defects

helicities, (n,m) indices



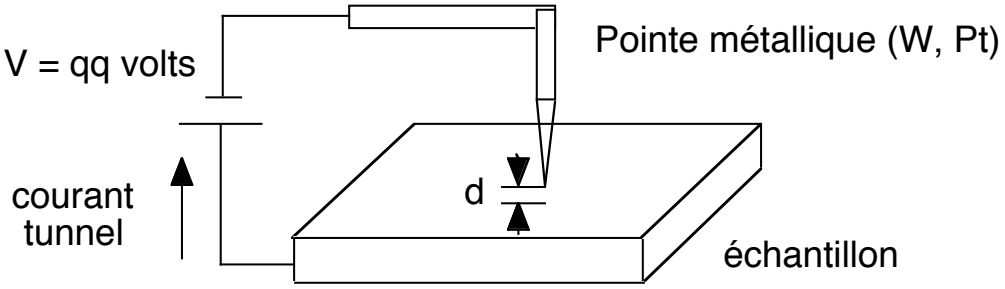


Chemical analysis

BN sheet

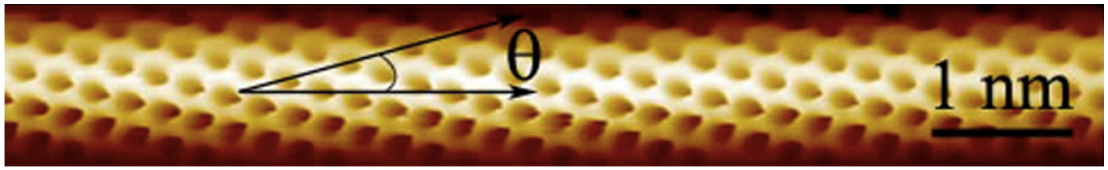
Direct methods: STM

STM: imaging of electron density close to E_f



Topographic mode

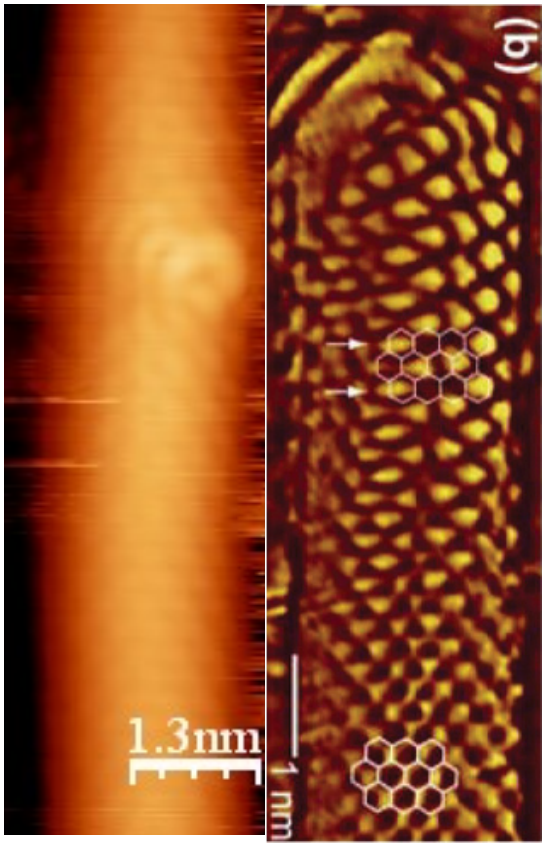
Map of the tunneling current between one atom of the tip and atoms of the tube integrating on applied tension



helicities, (n,m) indices

H.Lin et al Phys.rev. B (2010), V. Meunier et al (2000)

Pentagon Tube end



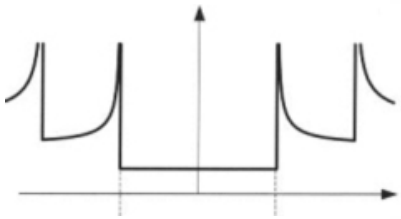
defects

Furuhashi et al PRL (2008)

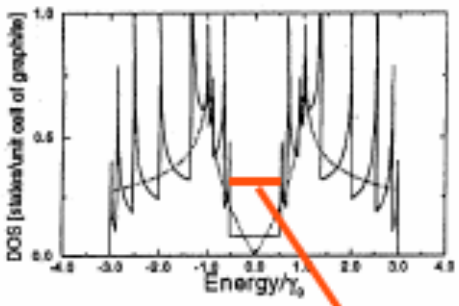
Spectroscopies based on electronic excitations

Electron density of states

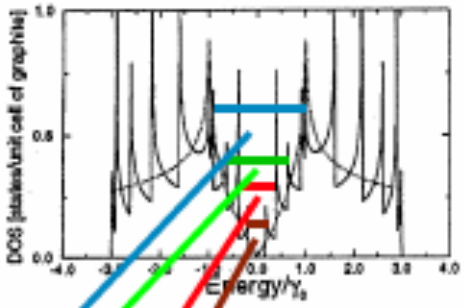
metallic case



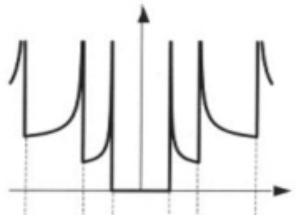
(9,0) (métallique)



(10,0) (semi-conducteur)



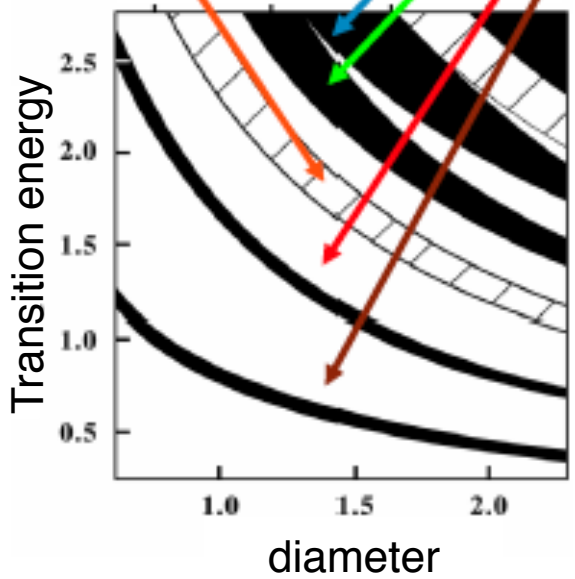
S.C. case



(after Saito)

'Kataura' plot relating inter-band energies E_{nn} to the tube diameter and M/SC character

(Kataura et al, Synthetic Met.103, 1999)



M

SC

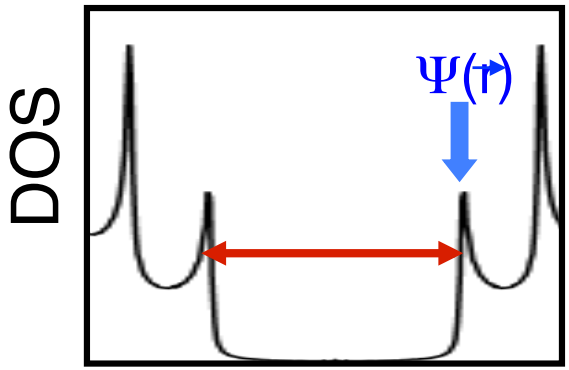
in Tight Binding approach

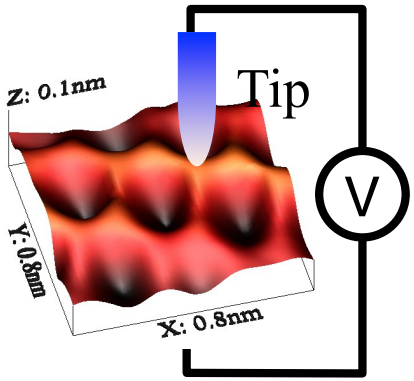
$E_{11}^{SC} = 2\,\gamma_0\,a_{C\text{-}C} / d$

→ Probing interband transitions and electronic excitations

→ Needs to know the link transition – atomic structure

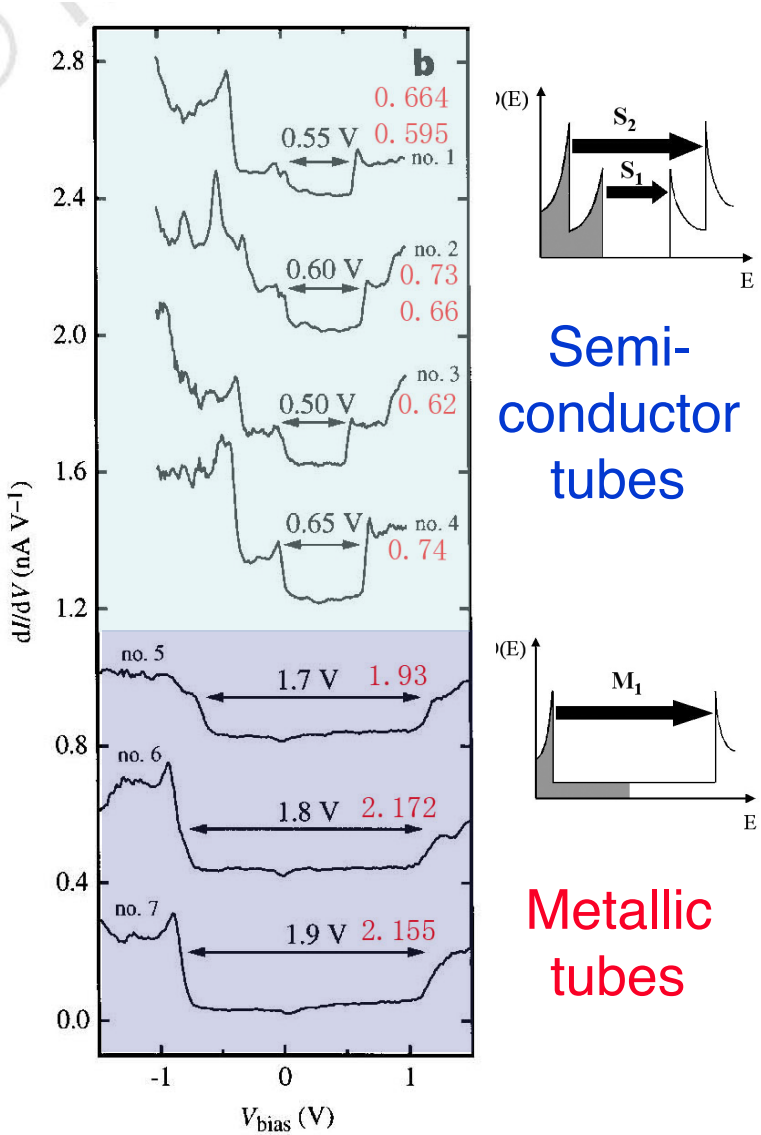
Electronic spectroscopy (STS)





Recording I(V)
at a given z
as a function of:
- position (x,y)
- tension V

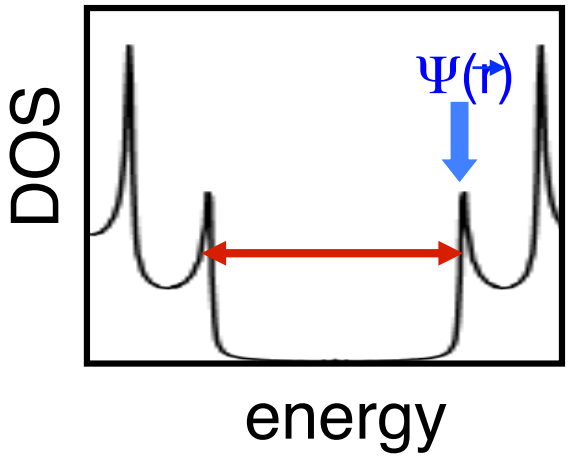
- At a given (x,y):
  dI/dV (V) = local DOS
- At a given V:
  map (x,y) of dI/dV = LDOS map at V

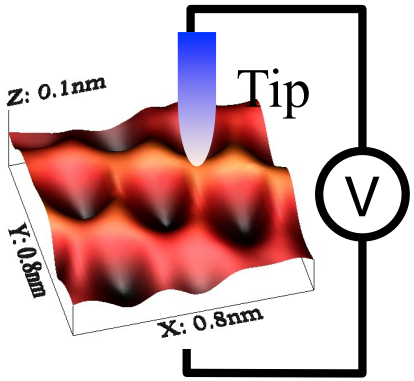


DOS of different C-SWNT

J.W.G. Wildöder et al., Nature 39, 59 (1998)

Electronic spectroscopy (STS)



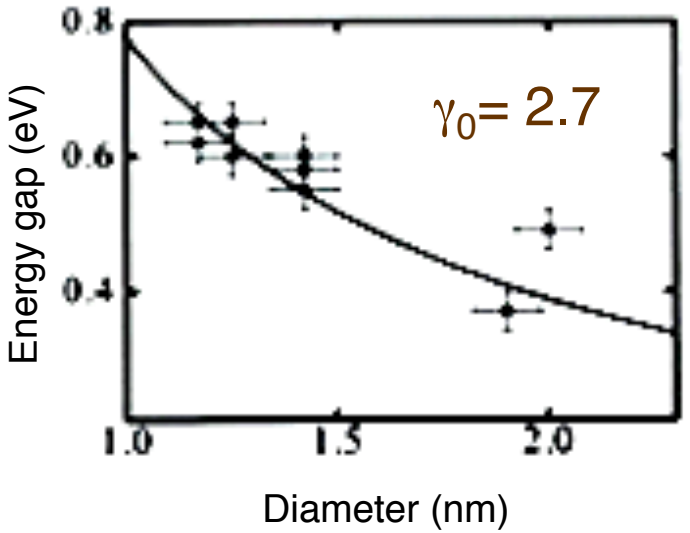


Recording I(V)
at a given z
as a function of:
- position (x,y)
- tension V

Local DOS + STM image:

→ M / SC character

→ Tube diameter d



Variation of $E_{11}^{SC} = 2\,\gamma_0\,a_{C\text{-}C} / d$

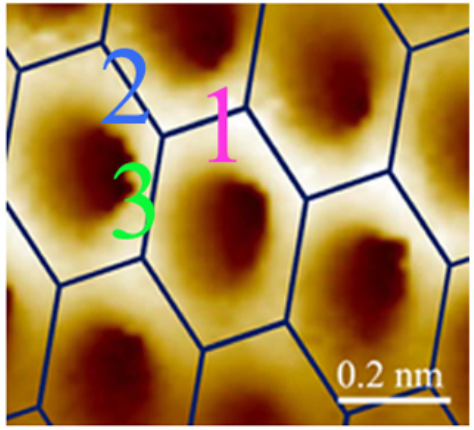
- At a given (x,y):
  dI/dV (V) = local DOS
- At a given V:
  map (x,y) of dI/dV = LDOS map at V

J.W.G. Wildöer et al., Nature 391, 59 (1998)
T.W. Odom et al. Nature 391, 62 (1998)

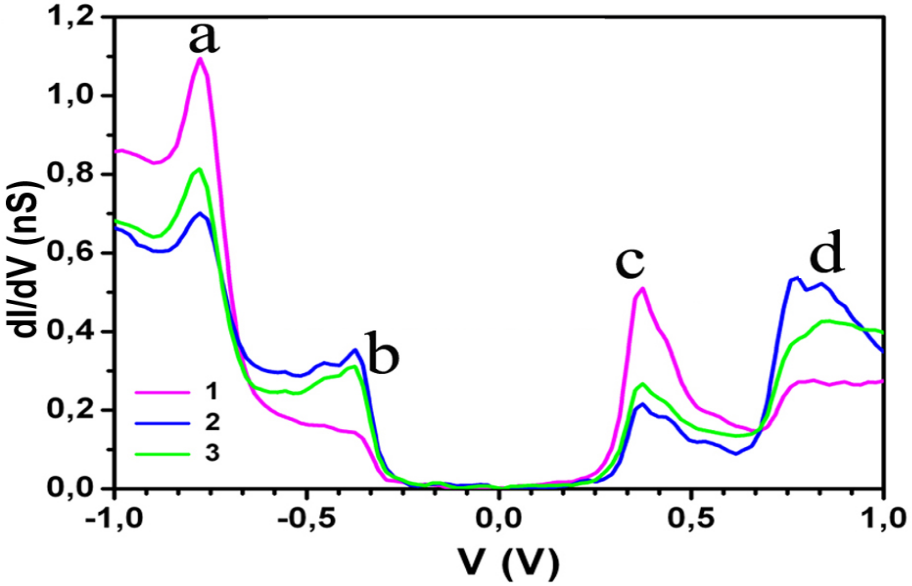
H. Lin et al
PRB (2010)
Kane & Mele (2000)

Electronic spectroscopy

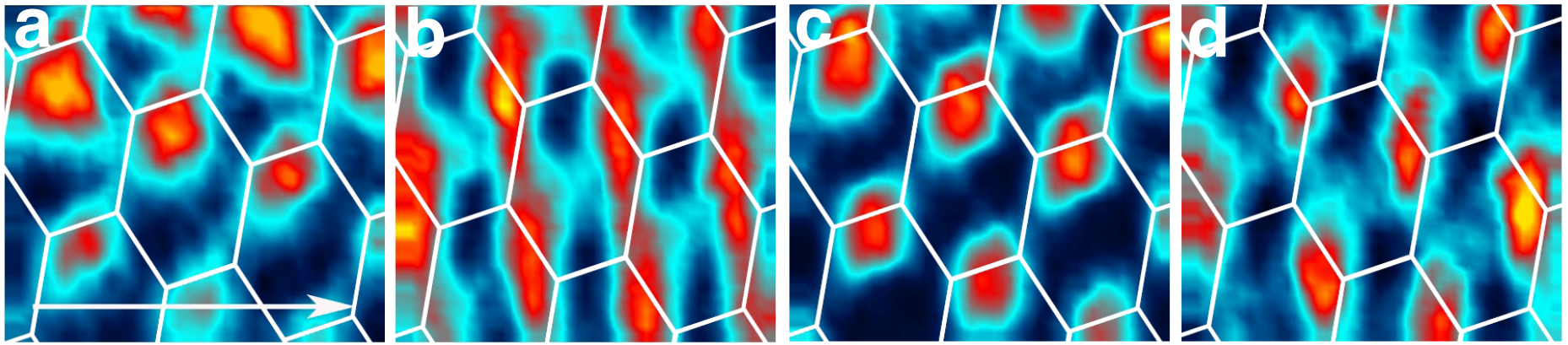
STM topography



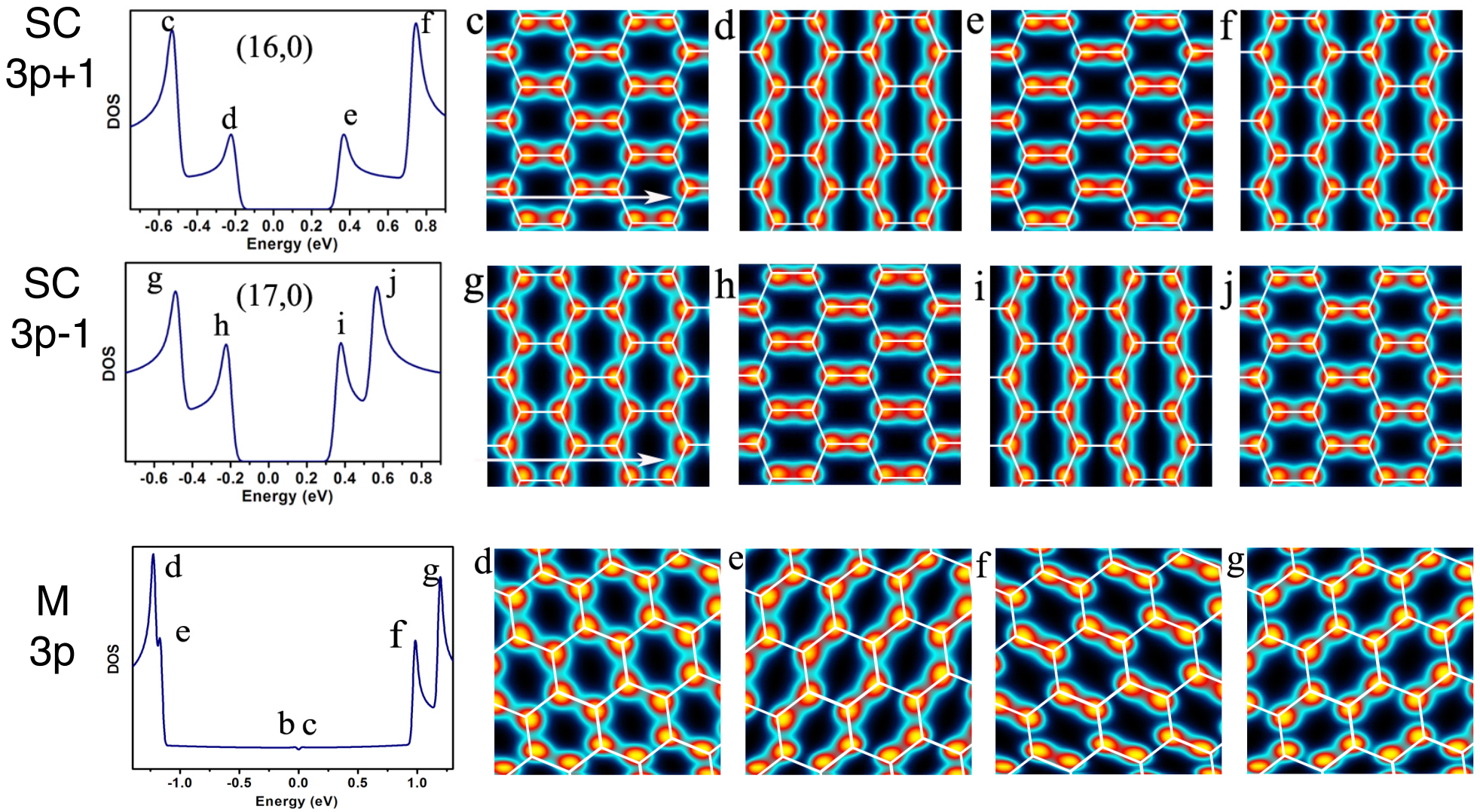
dI/dV = local DOS → M / SC



dI/dV maps = image of wave functions Ψ(r) at successive VHS → helicity



DFT simulation of VHS conductance maps

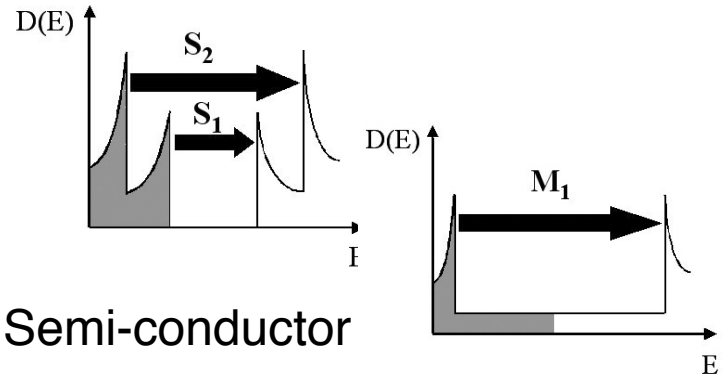


Helicity identified from broken symmetry sequence of VHS conductance maps

H. Lin et al PRB (2010)

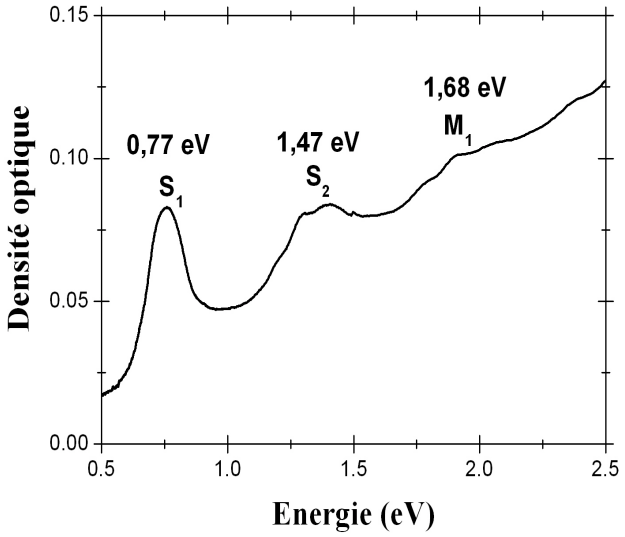
Optical spectroscopies

Absorption



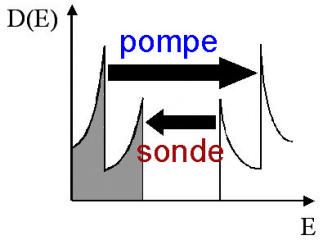
Semi-conductor

Metallic

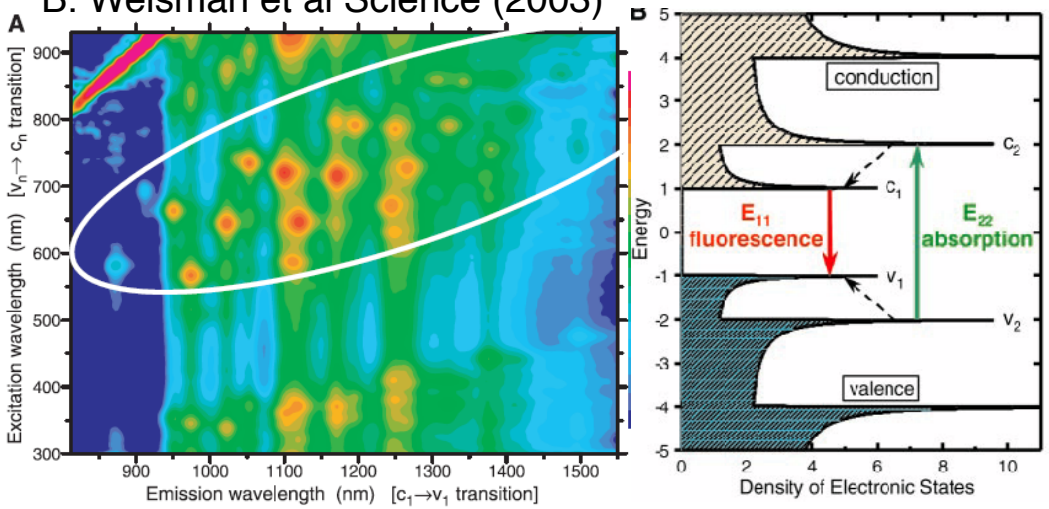


J.S. Lauret et al PRL 90, 57404 (2003)

Induced photoluminescence (PL) from semi-conducting tubes



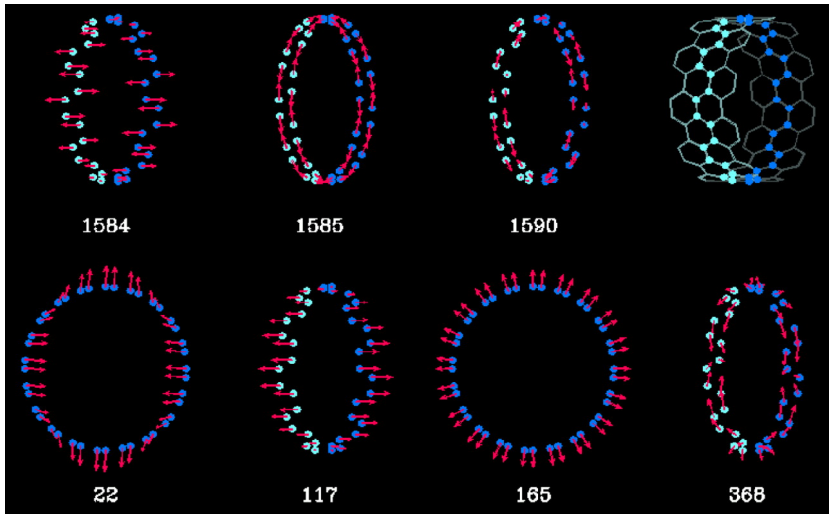
B. Weisman et al Science (2003)



- possible identification of {(n,m)} in sample
- identification restricted to SC tubes in PL
- workable only for narrow diameter distribution

Raman spectroscopy

Principle: investigation of the vibration modes (phonon) with a laser (visible light)



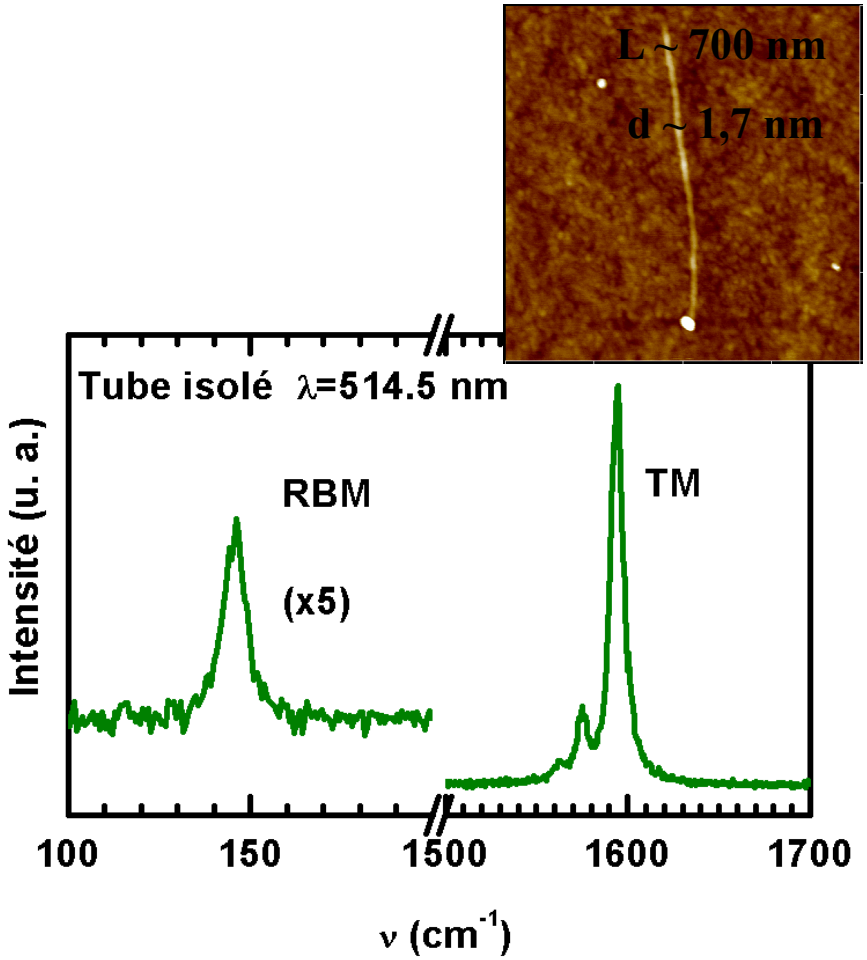
Vibration modes of carbon nanotubes

Radial mode at low frequency (RBM)

→ tube diameter : RBM ~ 1/d

Tangential modes at high frequency (TM)

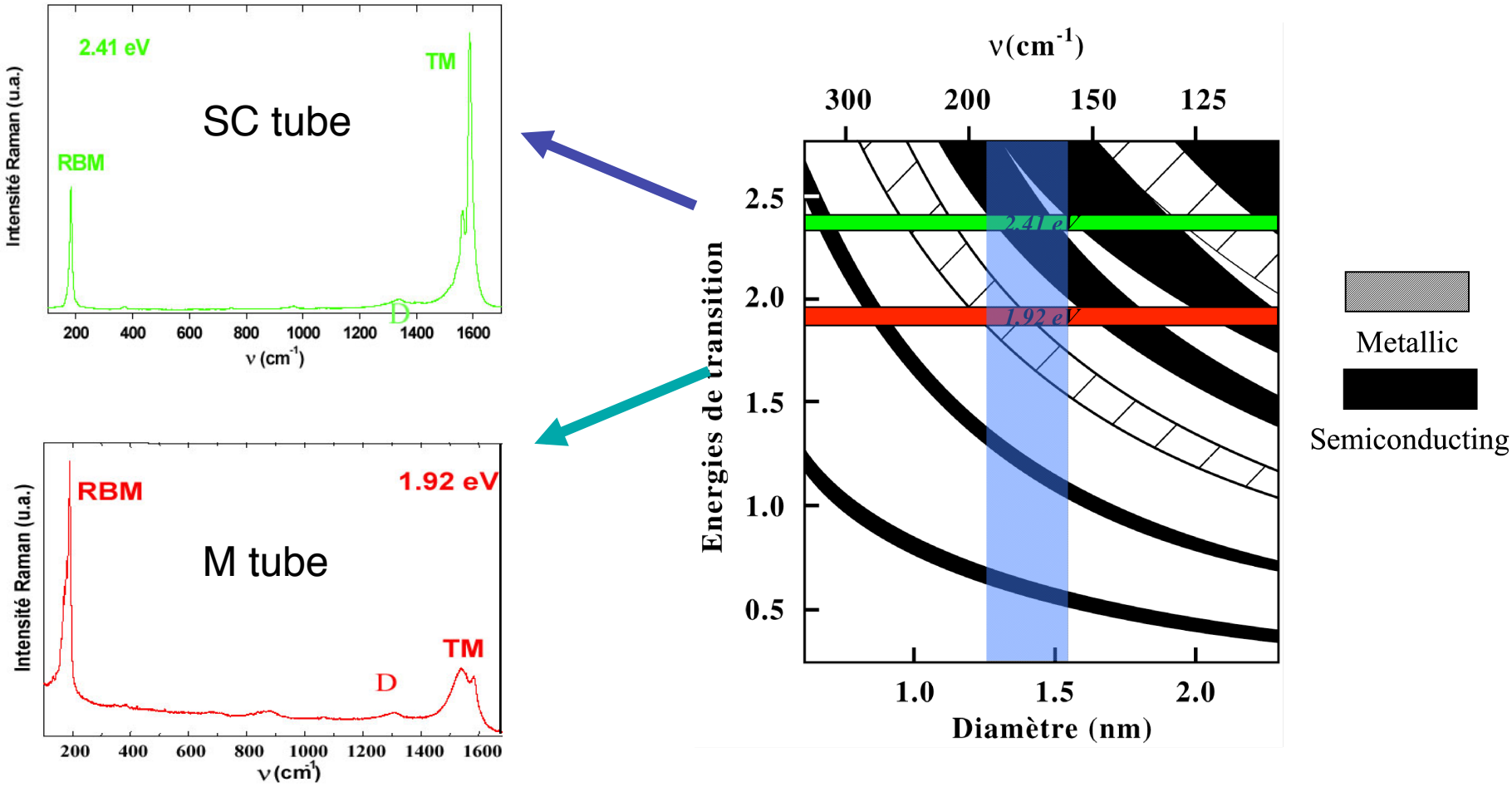
→ disorder, M / SC character



Raman spectrum of a given tube
(M. Paillet, PHD thesis)

Resonant conditions required

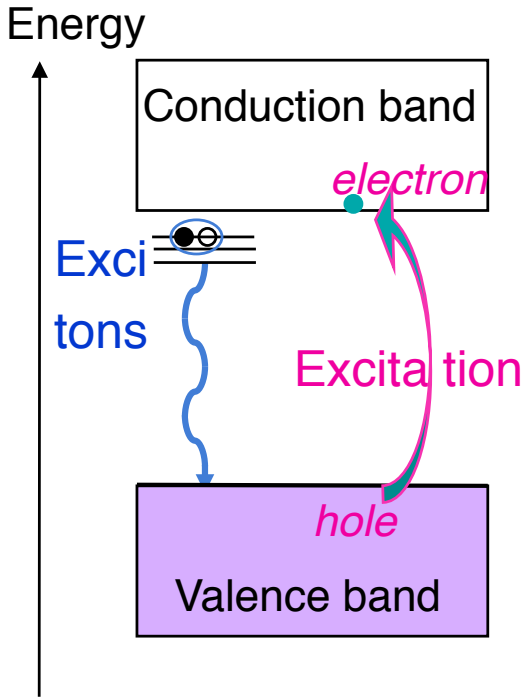
Energy of excitation laser = energy of an electron transition



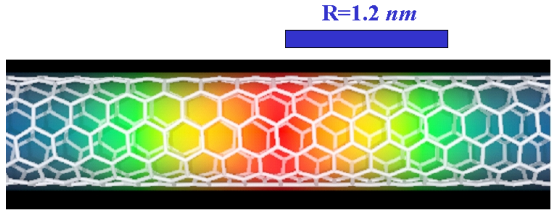
- Complete characterization of a sample needs extended range of energies
- Probe of metallic – semiconducting character
- Complete (n,m) identification possible knowing (d, M/SC, transition energy)

Optical spectroscopies versus STS

Excitonic effects



- Exciton = pair of electron - hole with Coulomb interactions
  = quasi-particle with 1s, 2p… energy states



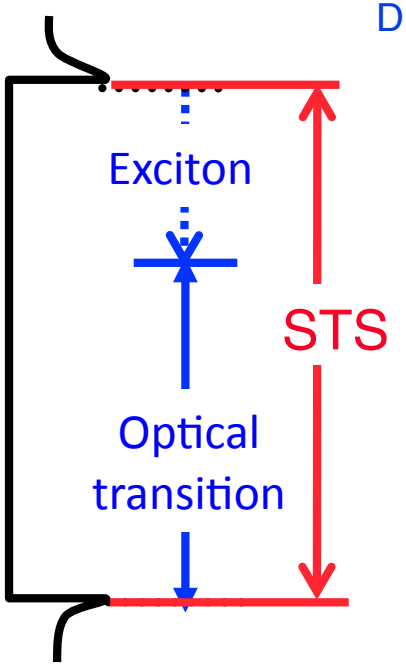
F. Wang et al., Science 838, 208 (2005)

Localized exciton in C-NT:

- e-h correlation length ~ 1- 2 nm
- binding energy ~ 300 – 400 meV

for 1 nm diameter SWNT

Dukovic et al , nano lett. (2005)



Optical spectroscopies and STS do not probe the same transitions !

H. Lin et al Nature Mat. (2010)

Advantages and difficulties

- Different scales:
  - local scale: study of individual objects
  - ➡ necessity of statistical analysis for a characterization at macroscopic scale
  - large scale: study of macroscopic samples
  - ➡ to be able to distinguish between an average and a distribution
- Direct tools are most often local techniques
- Spectroscopic techniques are widely used as they can work at large scale
- Different problems of spectroscopies:
  - 1) needs a modelization of the link property - structure
  - 2) cannot detect all the possible configurations
    - UV-vis-IR absorption: suited to narrow diameter distributions
    - Photoluminescence: detects semi-conducting tubes only
    - Raman: need of resonant conditions

Interpretation of the signal needs to be validated

➡ Measurements need to be cross-checked

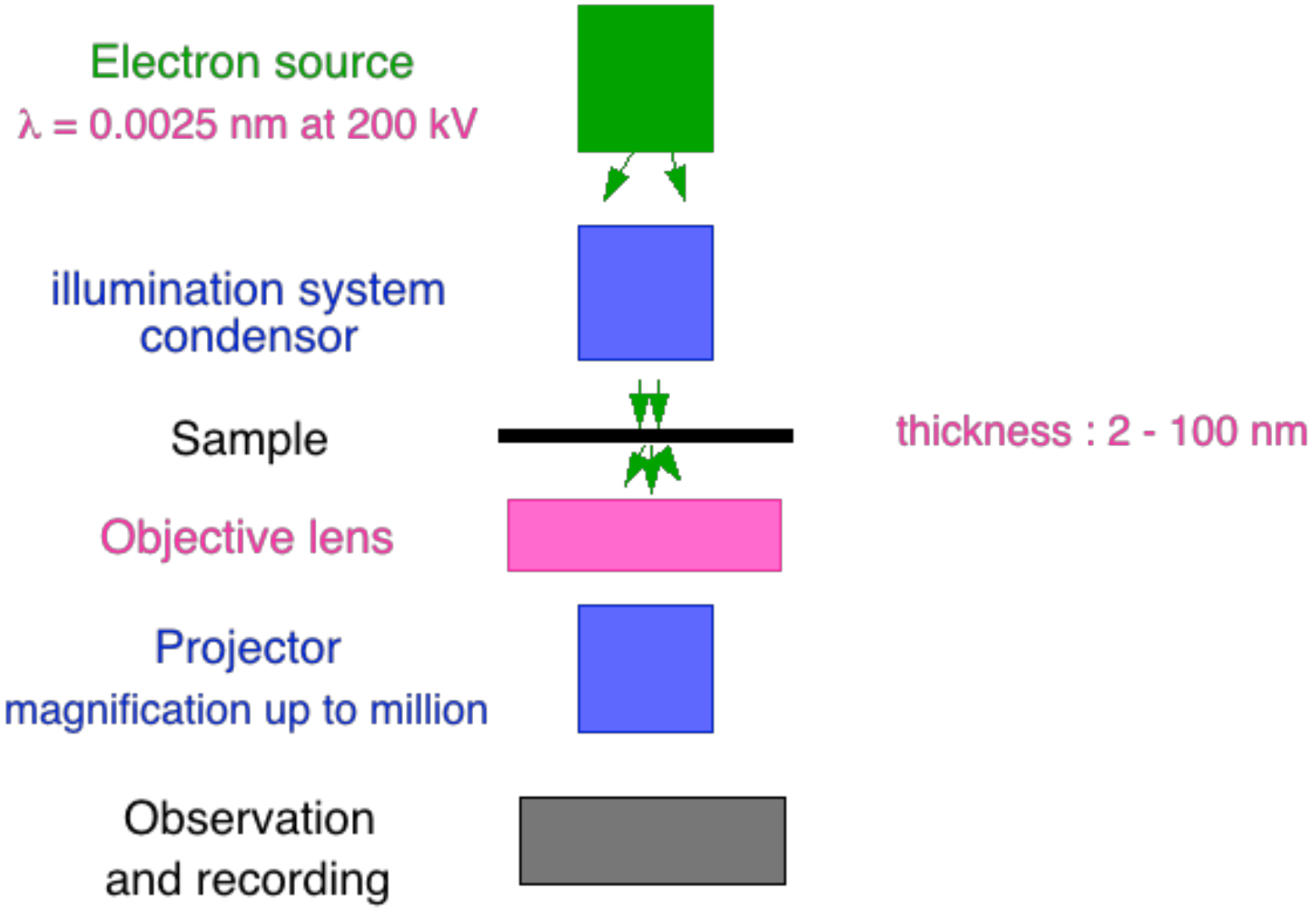
TEM : a guide for solving these problems

Second part

Transmission Electron Microscopy

- Introduction to TEM and its three major modes:
  - HRTEM
  - HAADF
  - Electron diffraction
  - EELS

A TEM: first approach



Which kind of information can we get ?

Interaction energetic electrons - matter

k_0 = de Broglie wave vector

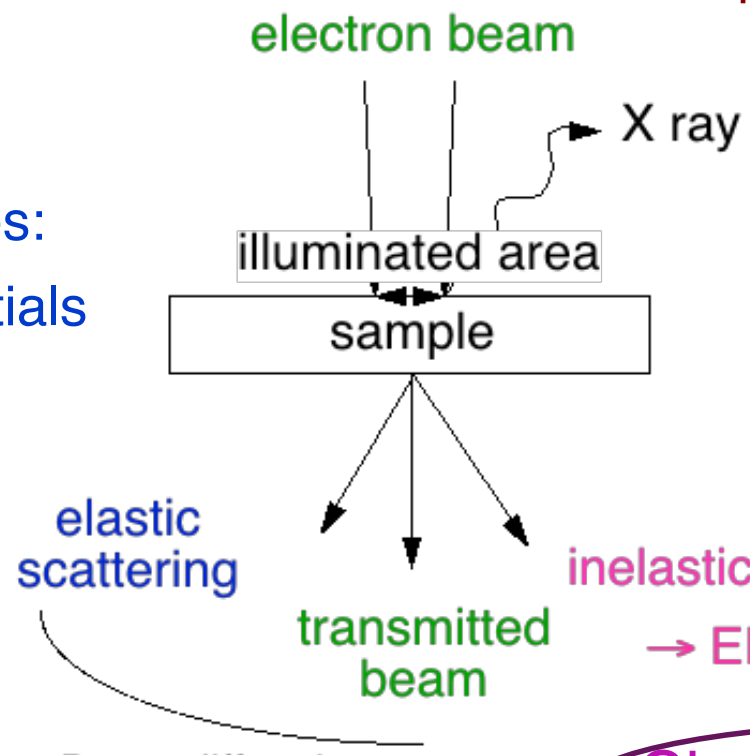
$\lambda_0 = 2\pi / k_0$

$E_0 = h^2 k_0^2 / 2m$

Scattering centres:

electrostatic potentials

of the atoms



Excitations of electron states in the sample

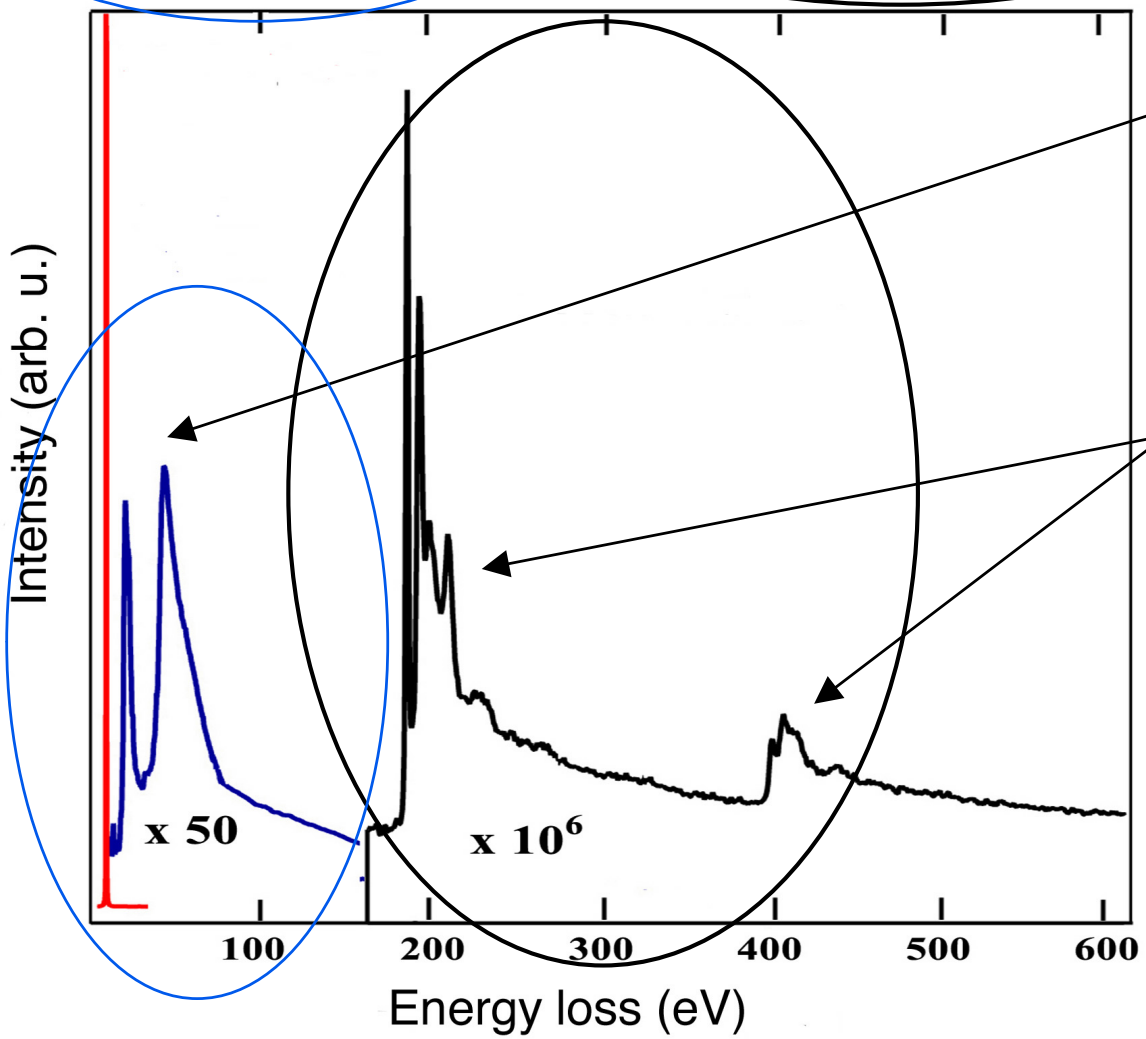
Chemical information

Structural information

Chemical information in EELS

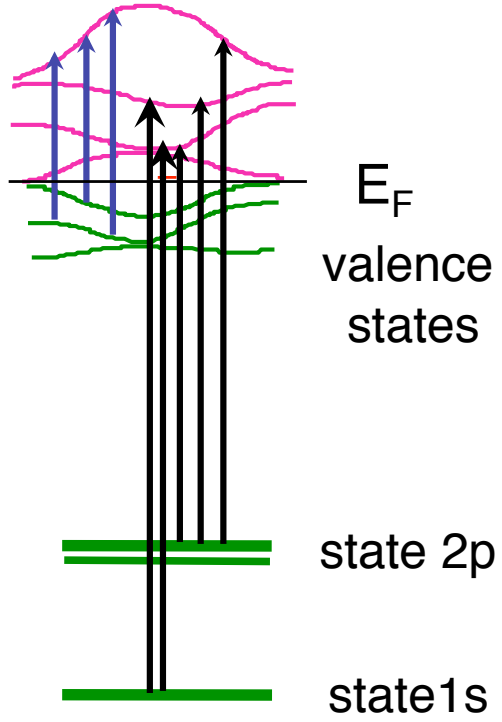
Low losses
Interband transitions
Optical gap

Core absorption edges
Elemental analysis
Chemical bonding



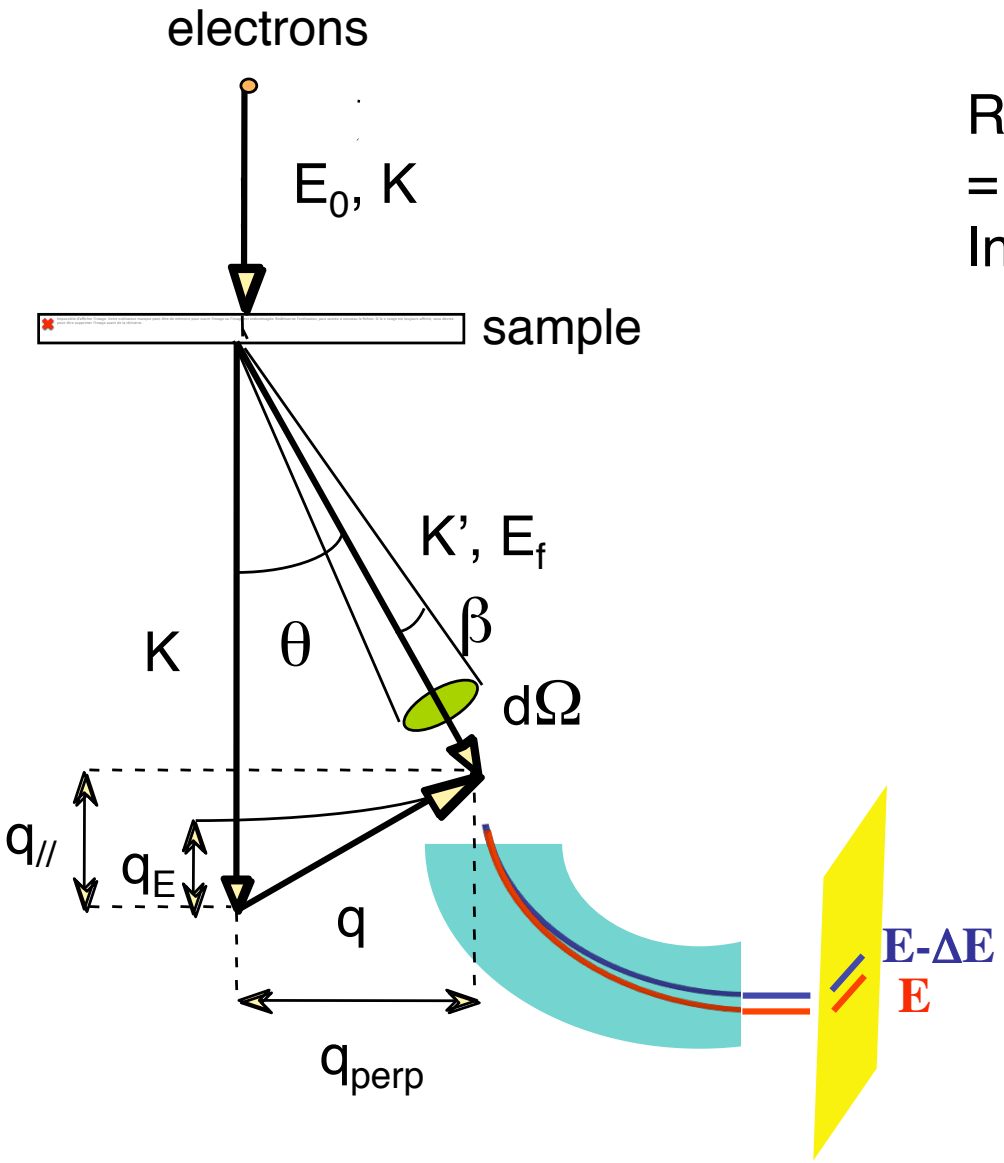
low losses

core losses K, L,… edges



- zero loss: elastic peak (> 90%)
- low losses: 0 - 50 eV
- core losses : 50 - 2000 eV or more

How to record EELS ?



Response of the material (spectrum)
=
Inelastic cross section:

$$\frac{d^2\sigma(\Delta E,\bar{q})}{dE\,d\Omega}$$

q = K' - K = transferred moment
$\Delta E = E_f - E_0$ = energy loss

Double selection:

- energy dispersion prism

→ analysis of ΔE

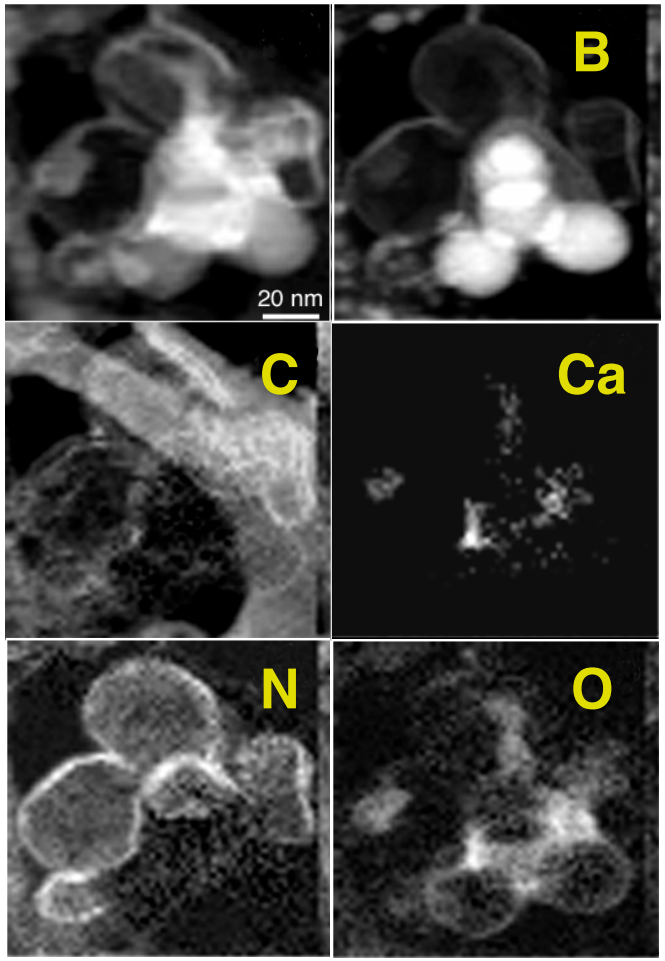
- solid angle of collection dΩ

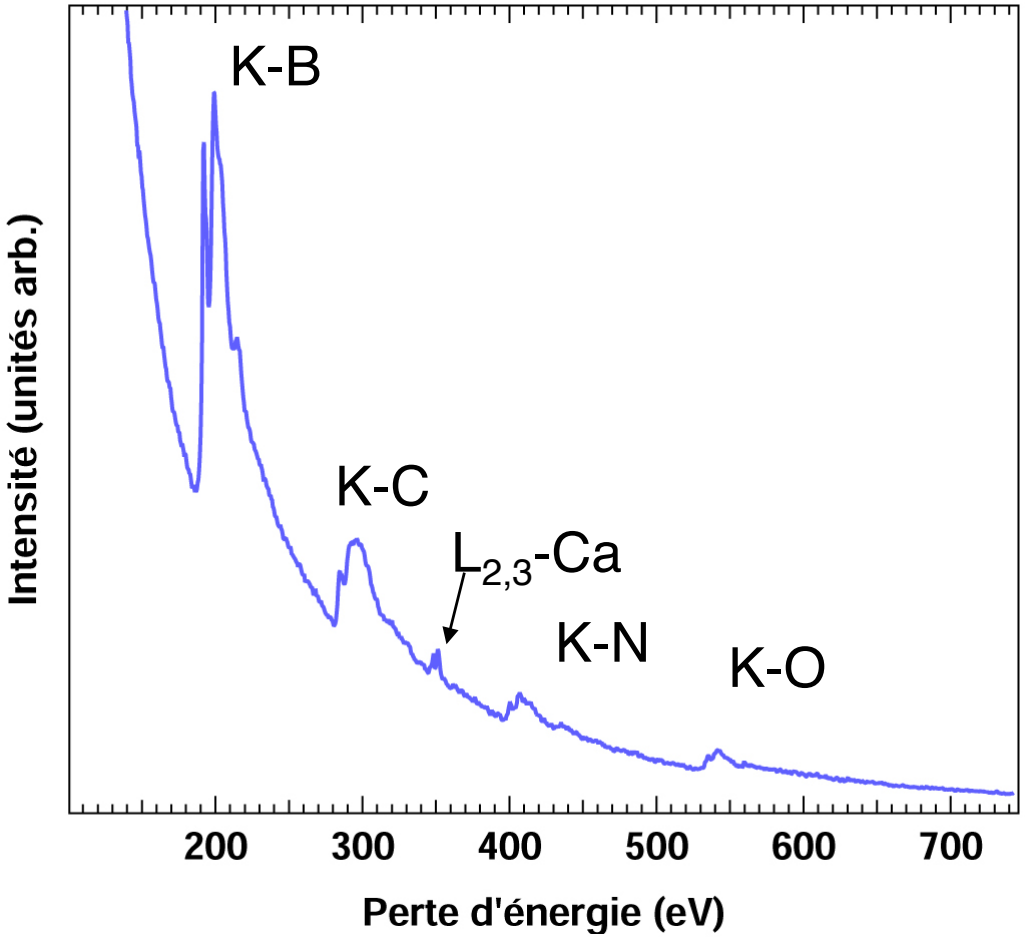
with 2β acceptance angle

→ energy resolution

Two data modes:

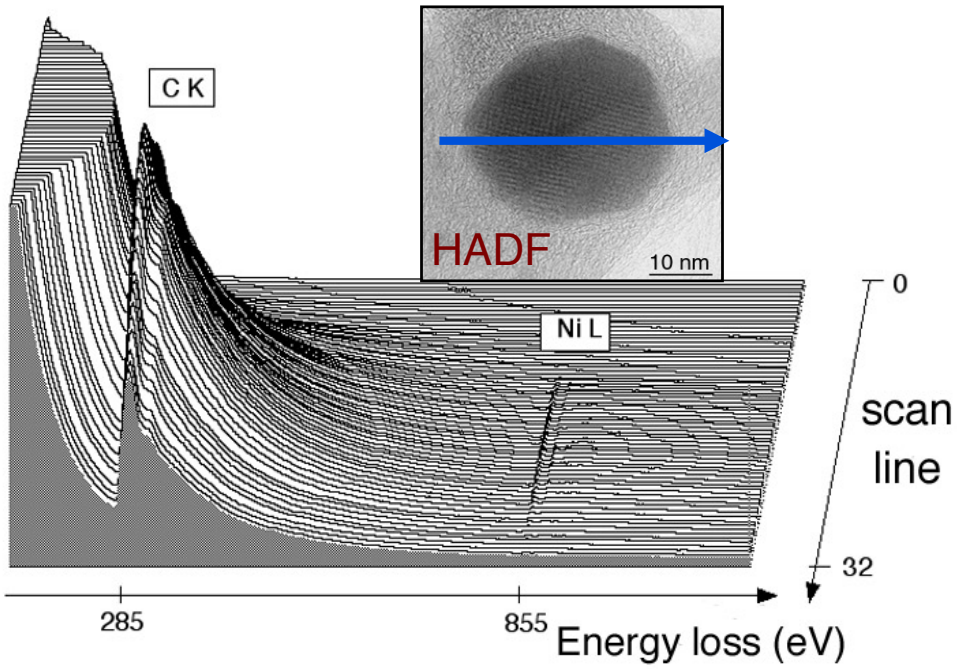
- spectrum
- mapping

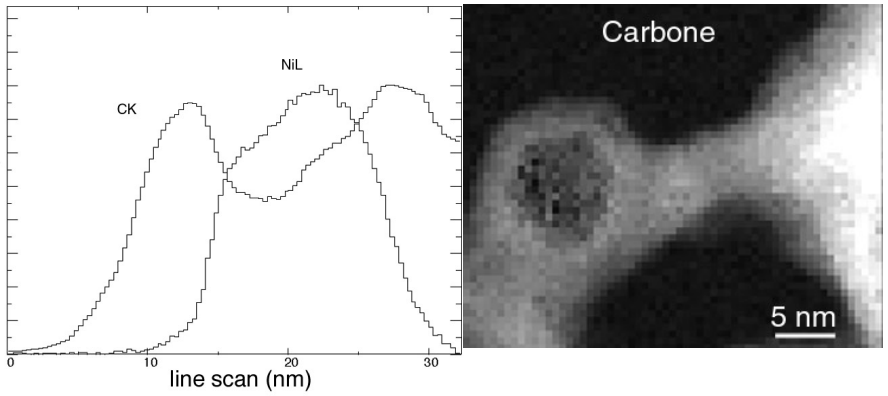


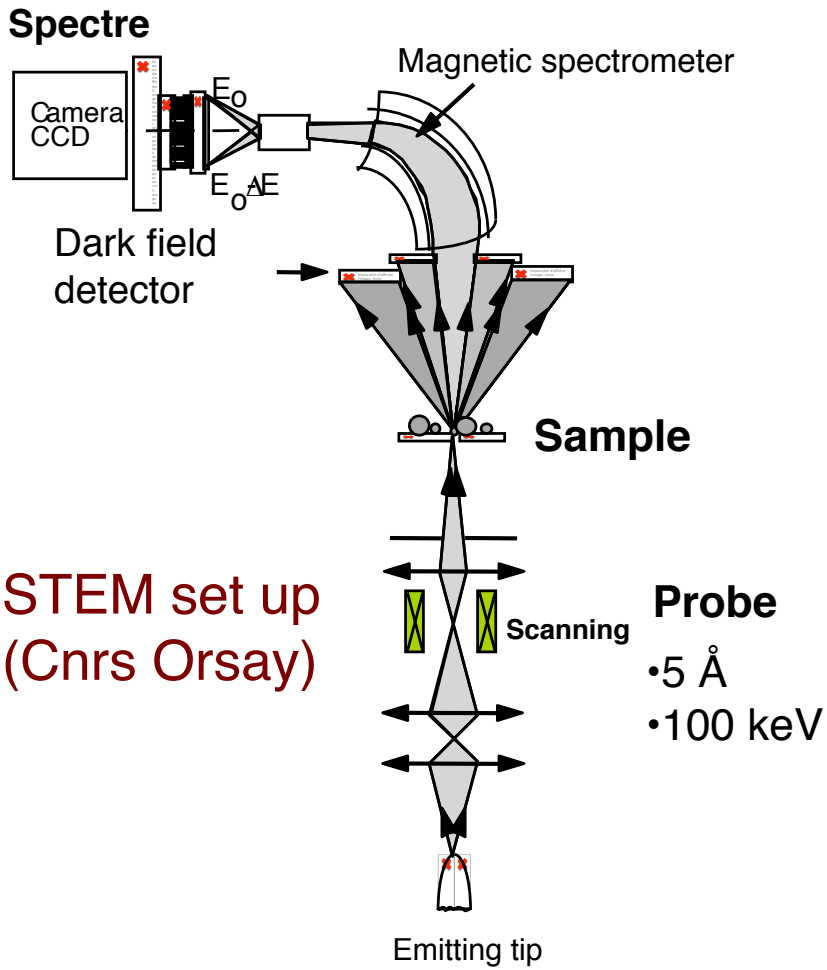


R. Arenal, pHD thesis 2005

Mapping in STEM: spectrum-imaging





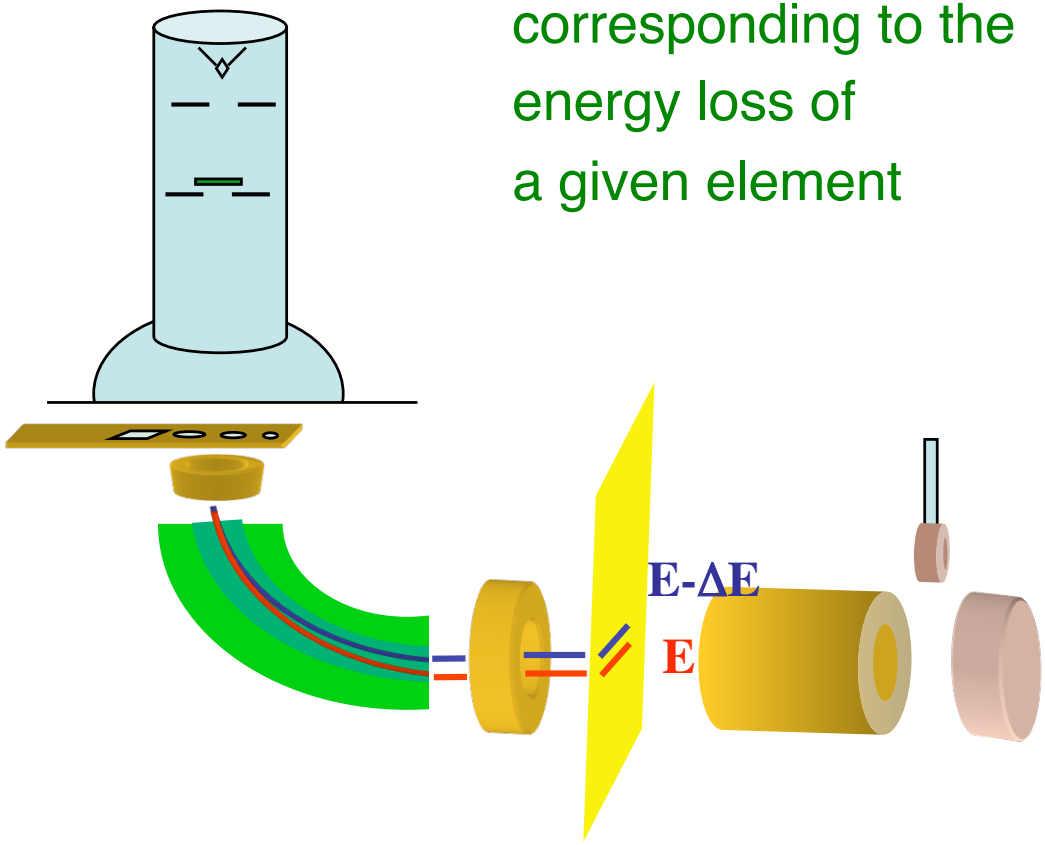


STEM set up
(Cnrs Orsay)

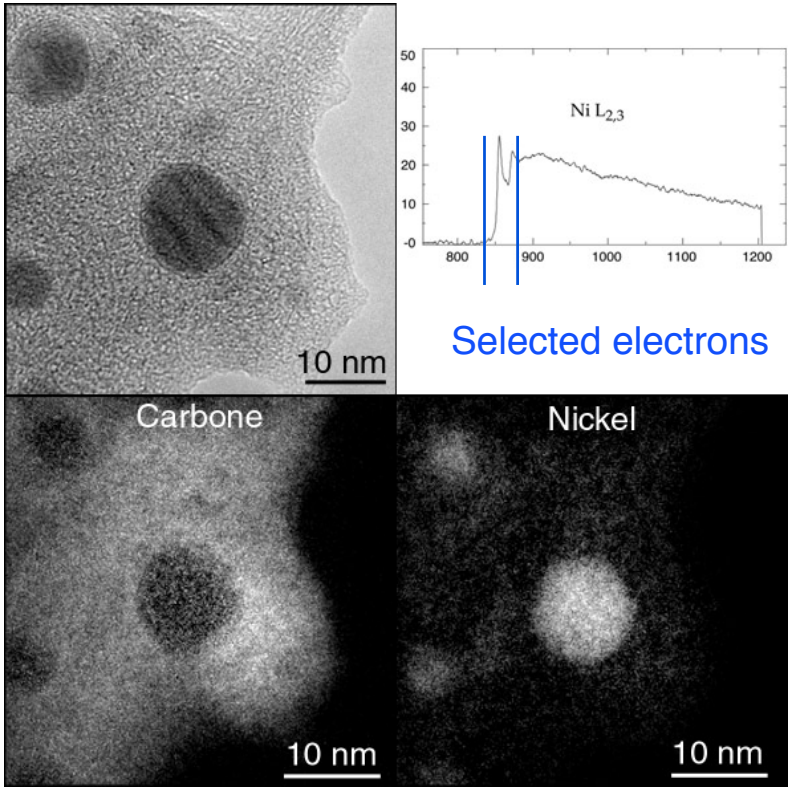
1D or 2D scanning of a sub nm probe
Acquisition in parallel of the HADF image and of the spectra

EELS and mapping in TEM

Image obtained with
the inelastic electrons
corresponding to the
energy loss of
a given element



TEM equipped with an energy filter
(in or post column)

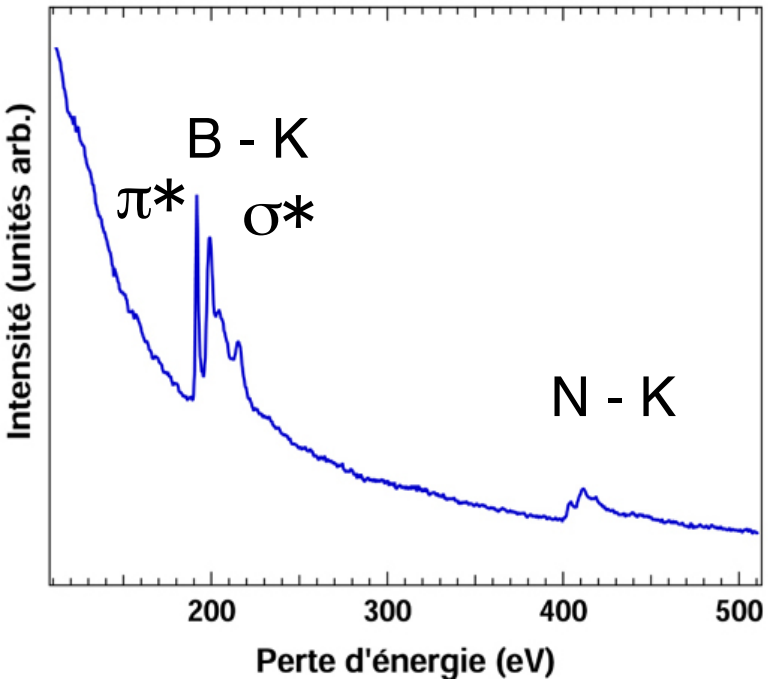


Selected electrons

J. Gavillet LEM

Elemental mapping
in energy filtered mode (EFTEM)

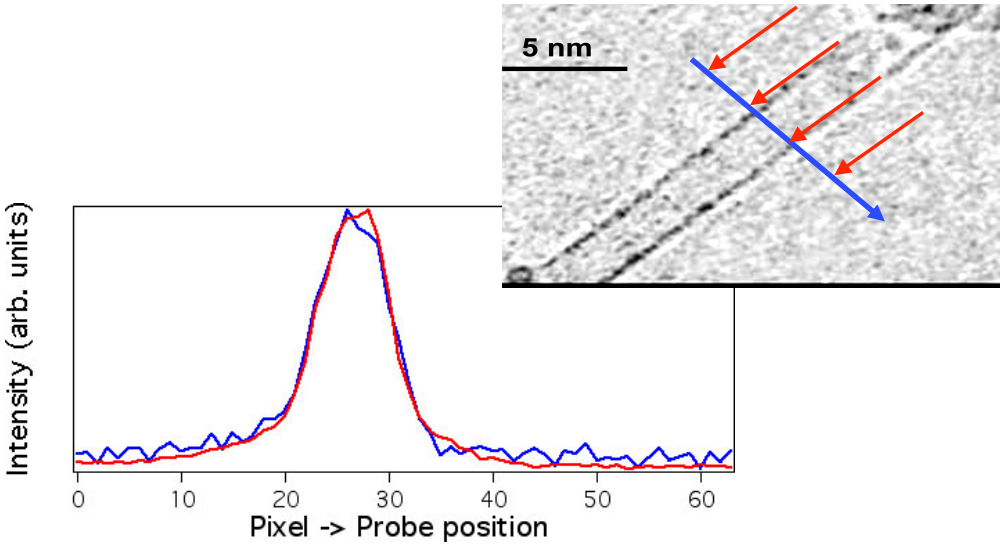
Example 1: BN - SWNT in STEM



EELS spectrum

B-K and N-K edges have very different cross sections

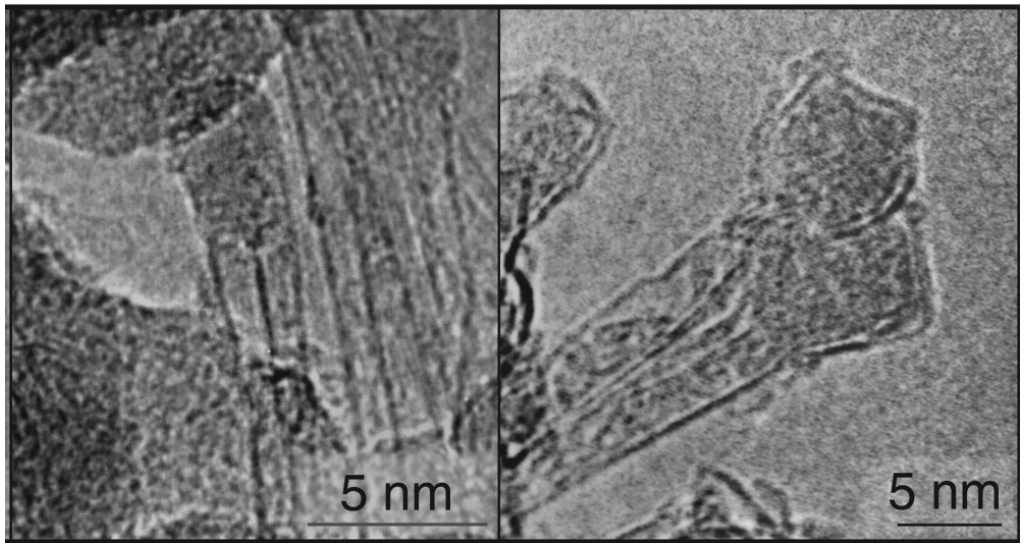
Fine structures: π* and σ* peaks characteristic of the sp^2 bonding

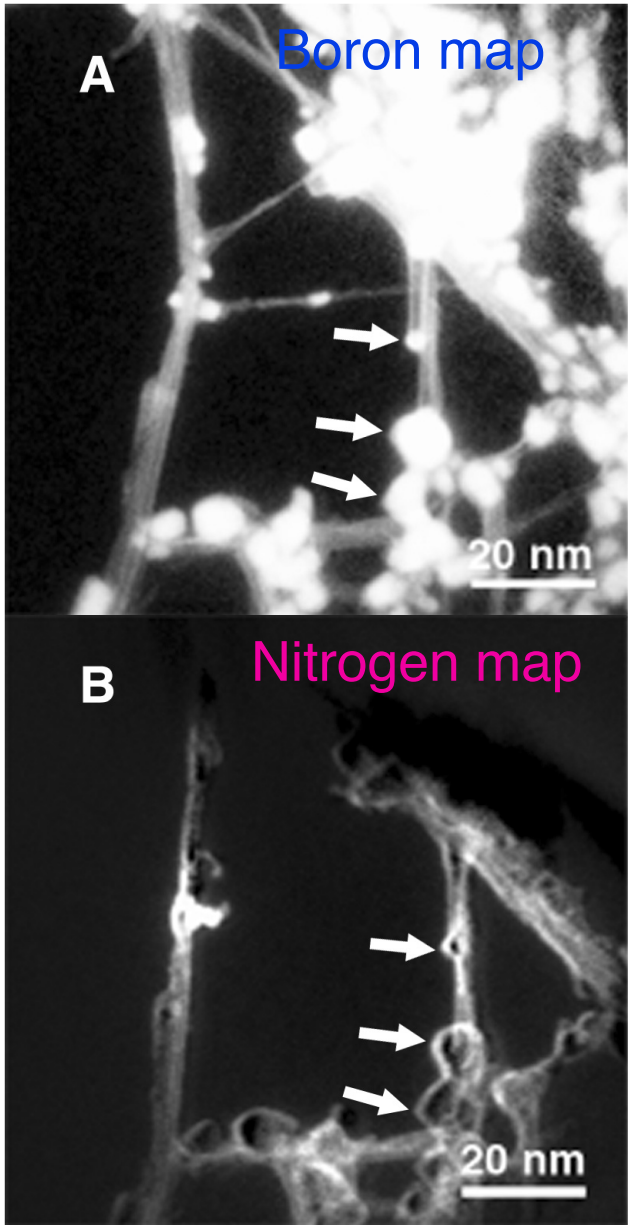


- B and N profiles across a tube recorded in line scanning mode with a STEM
- stoichiometry B:N = 1:1, determined from peak intensities

PhD thesis R. Arenal, 2005

Example 1: BN - SWNT in EFTEM





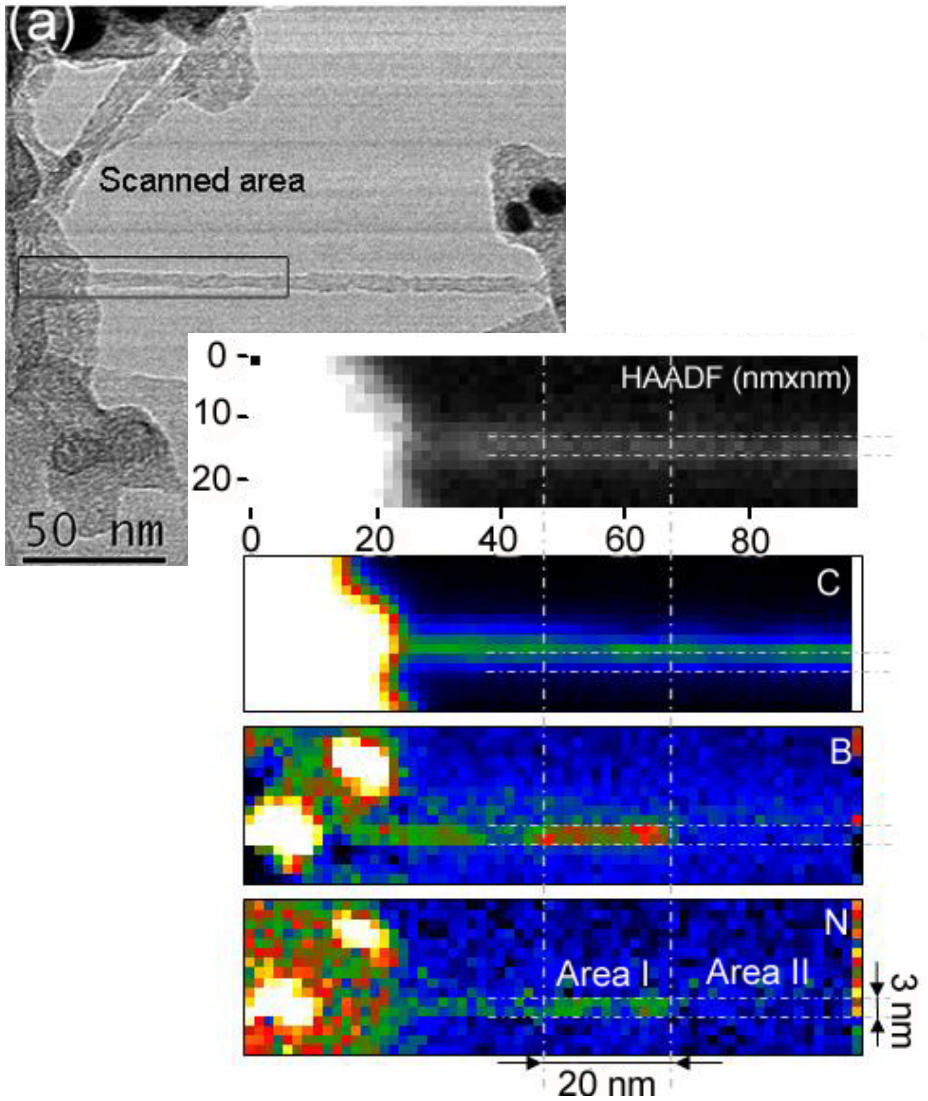
- BN - tubes are capped by a pure boron particle encapsulated at the tip

- B and N chemical maps recorded with a EFTEM

(Lee et al, Phys Rev Rapid Comm 2001)

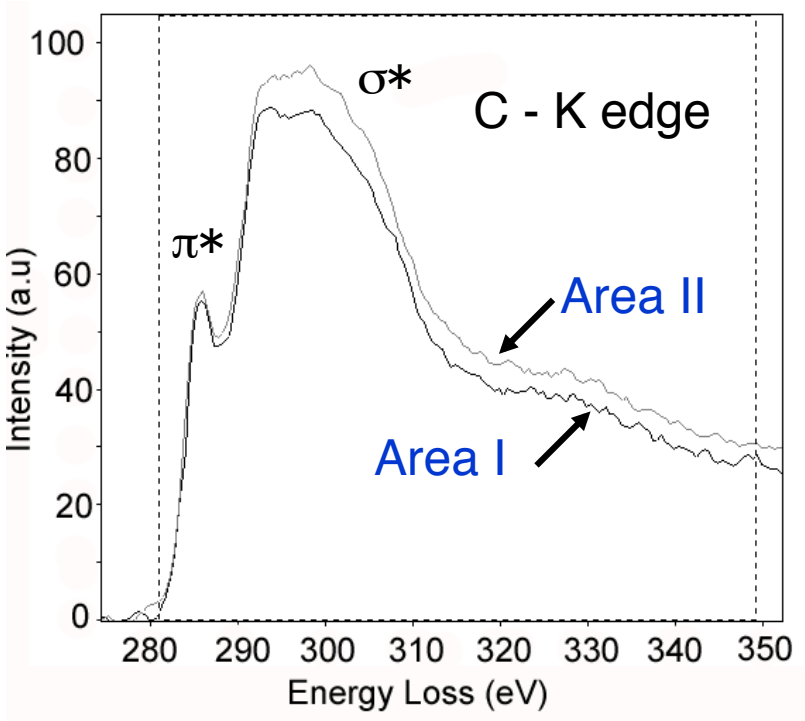
Example 2: patterned BN - C SWNT

S. Enouz et al , NanoLett. 2006



Chemical maps of a bundle

(2D scan in a STEM)



Area II: pure C

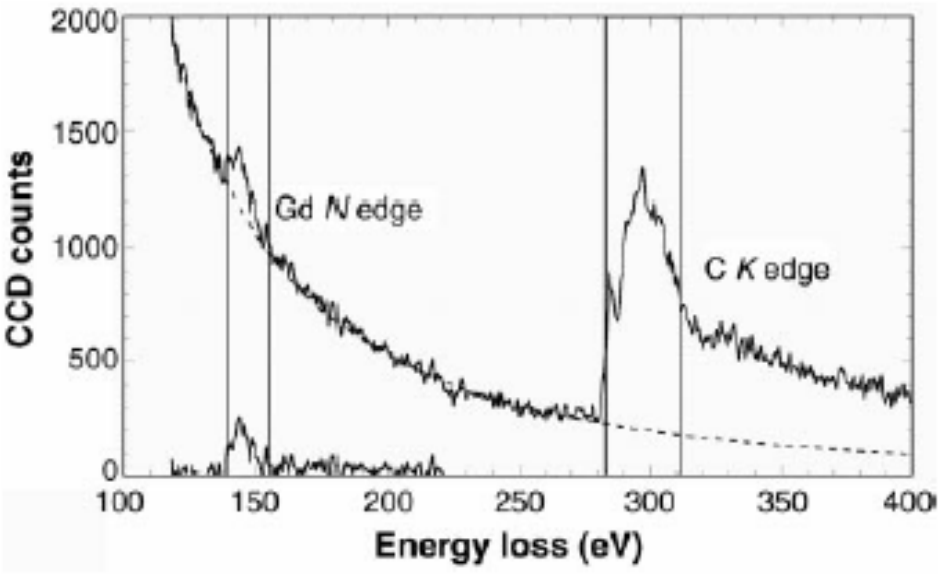
Area I: made of C, B, N

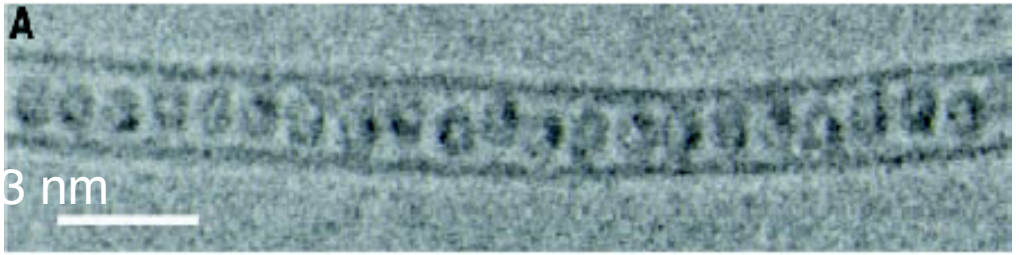
Depletion of C in area I = 10 at. %

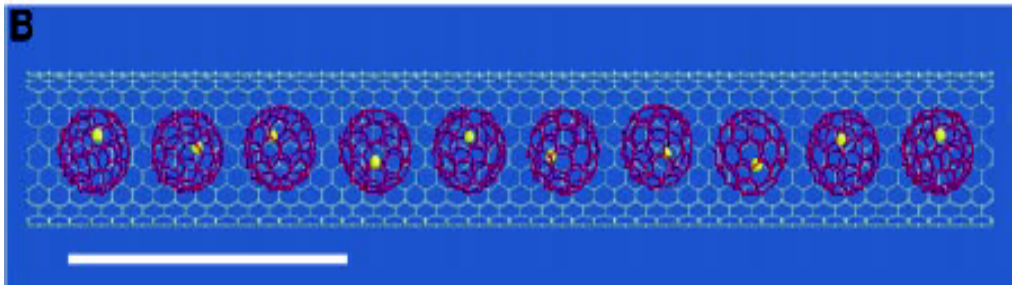
BN concentration in area I = 10 at.%

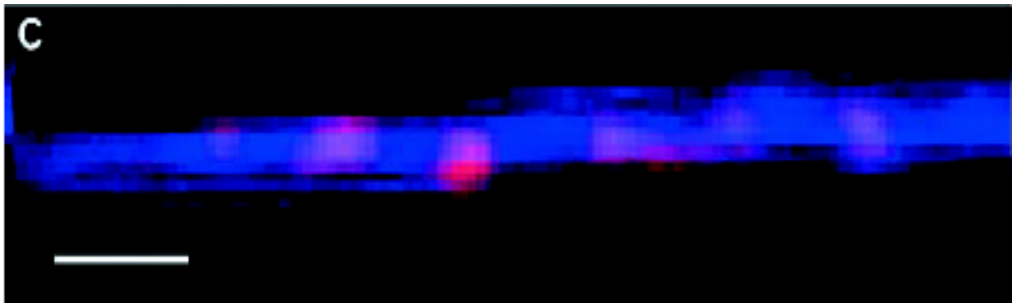
BN in partial substitution of C over 20 nm

Example 5: Gd@C82@C-SWNT









Chemical mapping of

Gd (N_{45} edge) and of C (K edge)

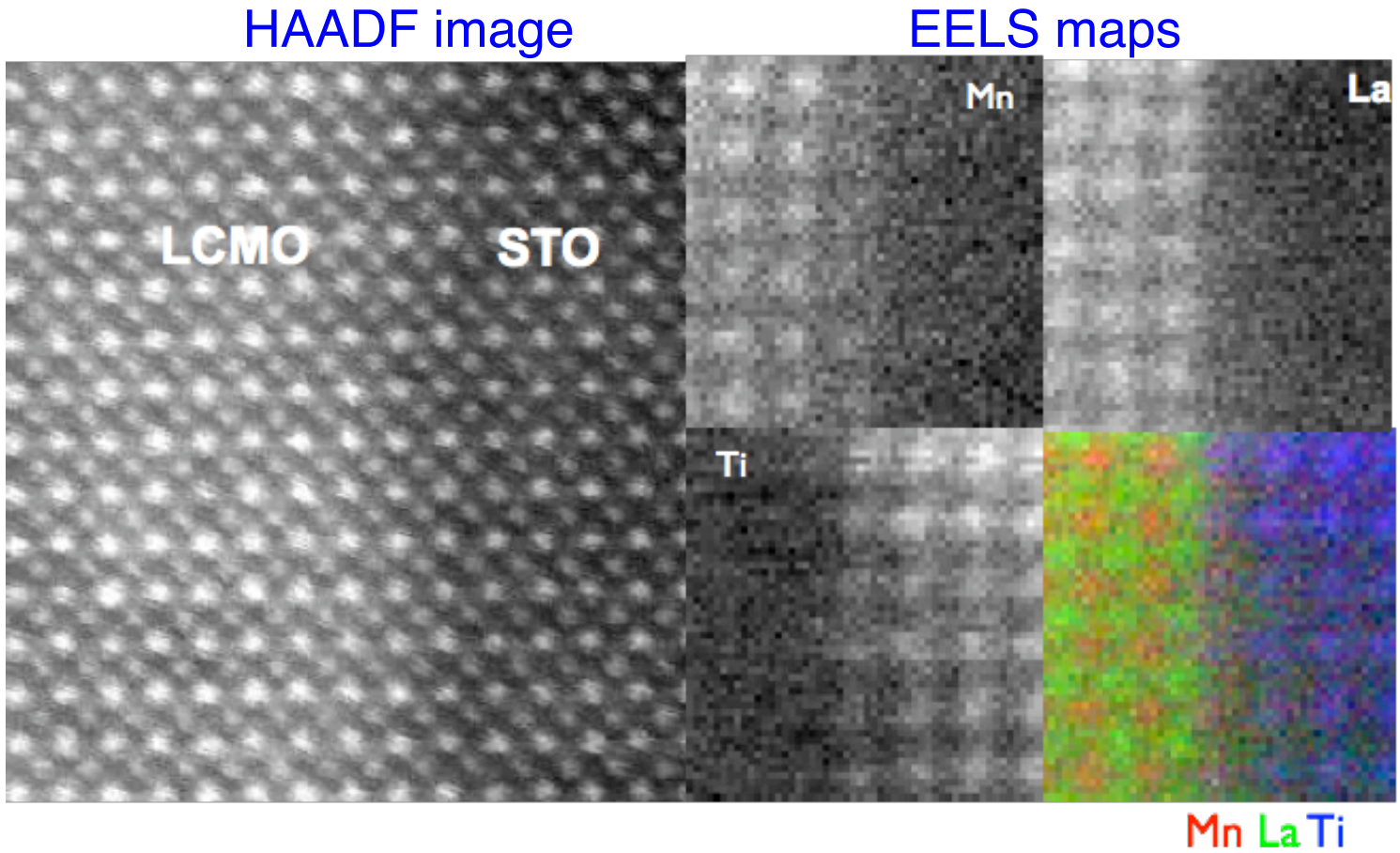
(2D scan in STEM)

Detection of one atom !

Suenaga K. et al. *Science* 290 (2000) 2281

Atomically resolved chemical maps

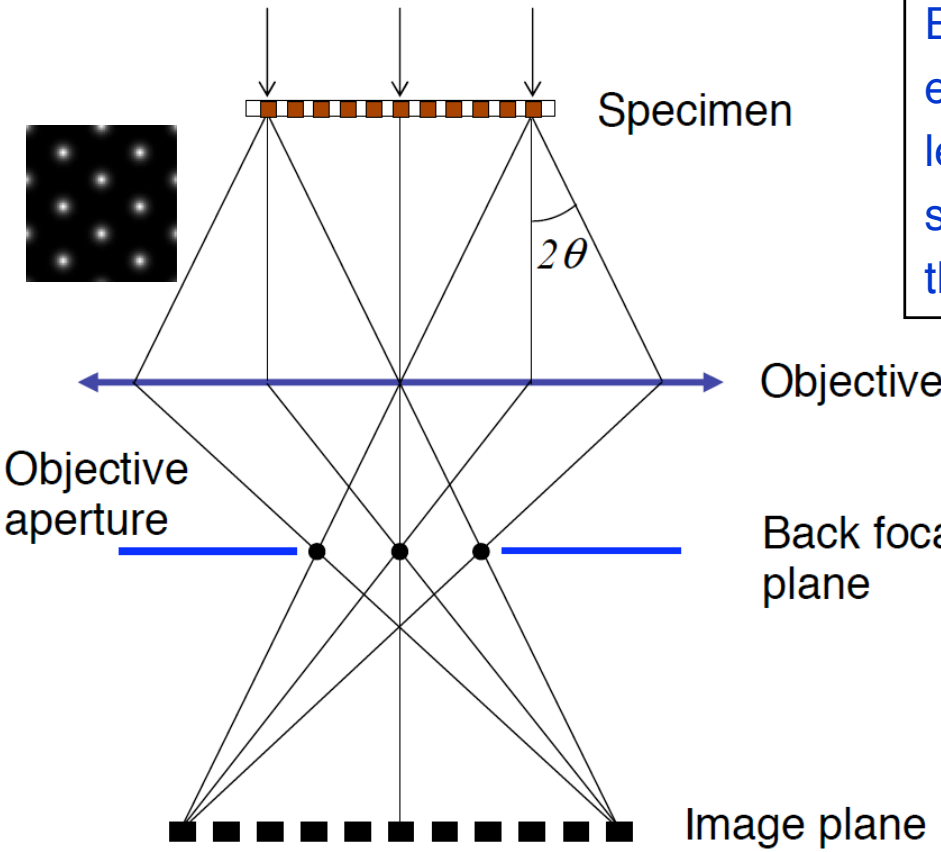
Now available with the new generation of STEM equipped with corrections of optical aberrations of the condensor stage



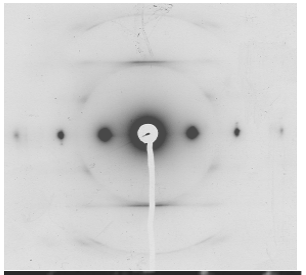
Structural information

- HRTEM
- HAADF
- diffraction

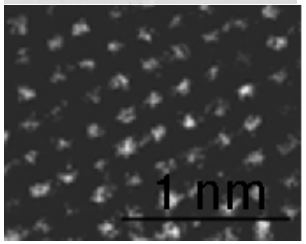
Structural information



Electrons of the beams are scattered by the electrostatic potentials of the atoms in the sample leading to their channeling. At the exit of the specimen, electron wave function is maximum at the apex of atomic scattering centres



1) Diffraction pattern of sample atomic structure



2) Image of the atomic scattering centres of the structure

Image = interference figure formed from the phases differences between the transmitted and diffracted beams

= phase contrast image

Information in image mode vs diffraction

- The image of the atomic centres reconstructed in the image plane of the objective lens is convoluted with the instrumental response of the microscope mainly depending on the aberrations of the objective lens

- Several consequences:
  - lack of resolution since large q scattered beams are not well transferred
  - phase contrast depends on the focusing conditions of the objective lens

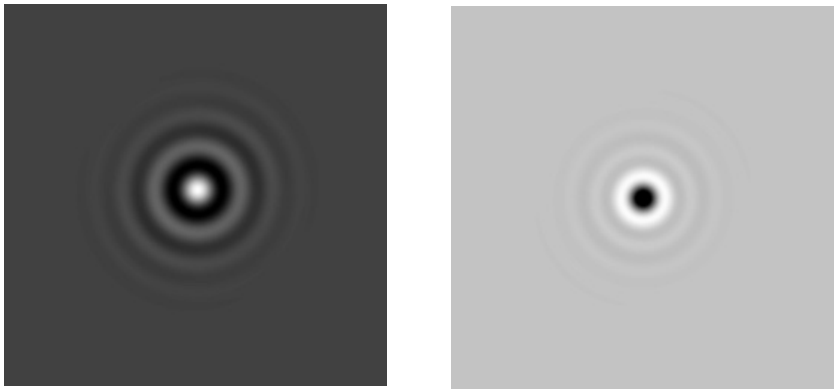


Image of a carbon atom
as a function of
the defocus of the objective lens

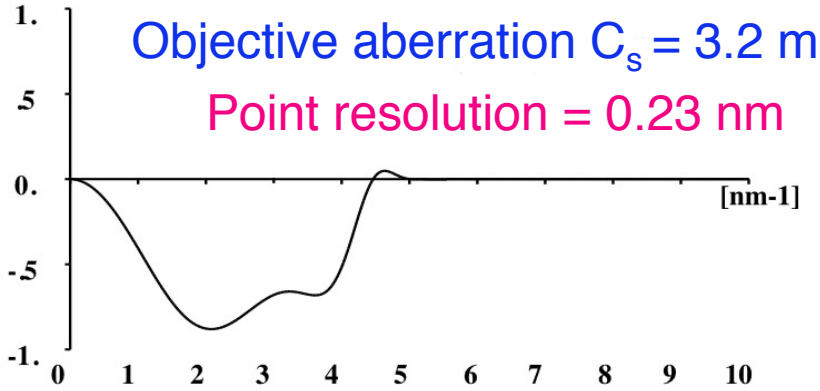
- Image mode: limitations in the structure identification depending on the microscope
- Diffraction mode: no effect of the instrument, direct structure identification

Comparison of different transfer functions

TEM 1: electron source is a filament

Objective aberration C_s = 3.2 mm

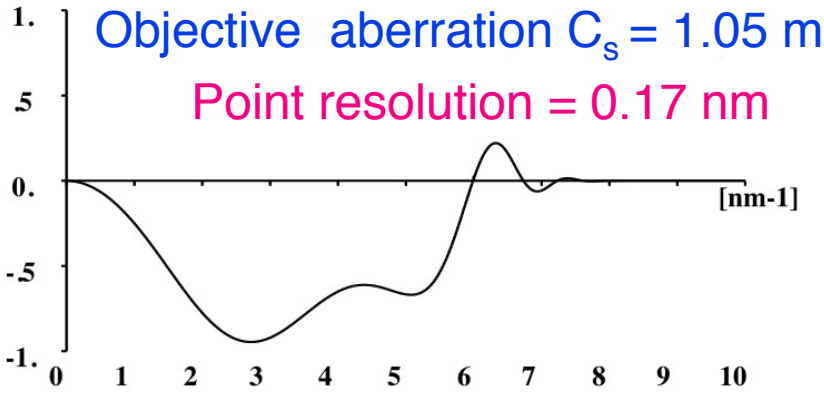
Point resolution = 0.23 nm

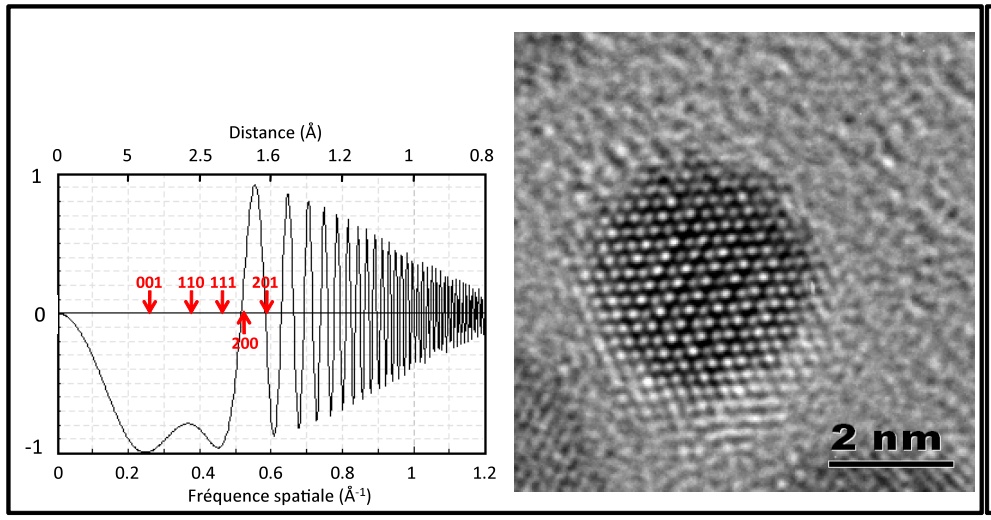


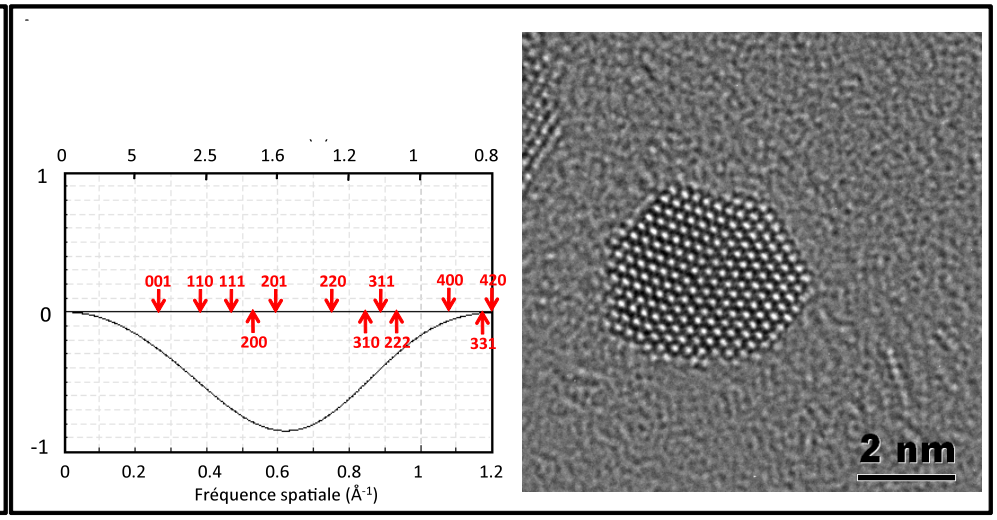
TEM 2: electron source is a filament

Objective aberration C_s = 1.05 mm

Point resolution = 0.17 nm







TEM 3: electron source is a FEG

Objective aberration C_s = 0.5 mm

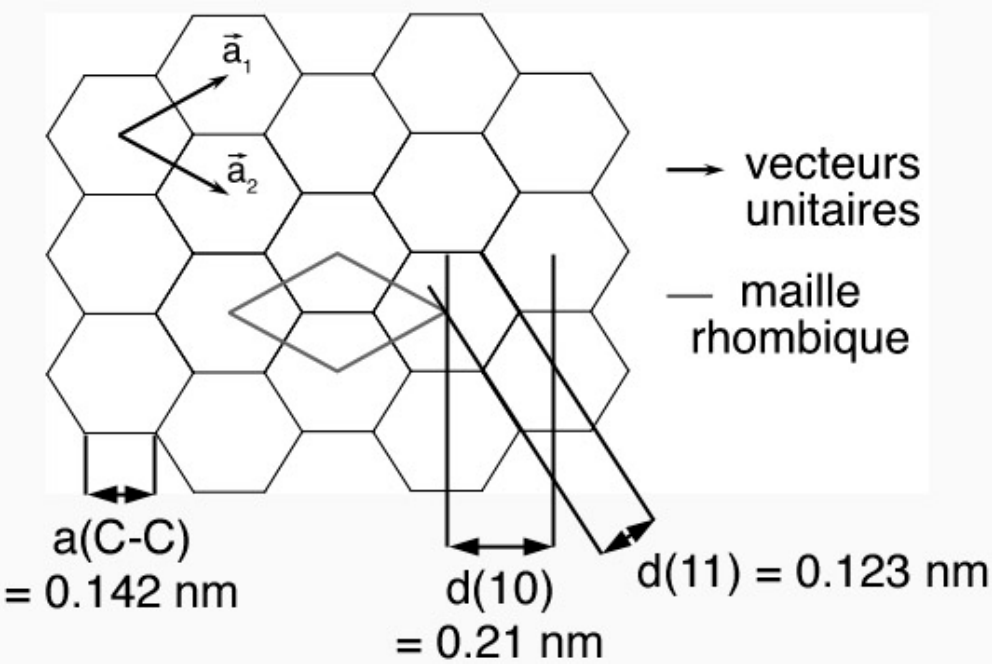
Point resolution = 0.17 nm

TEM 4: electron source is a FEG

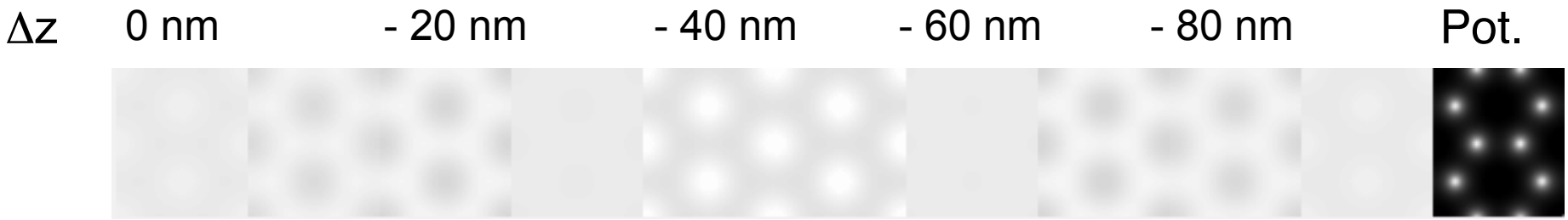
NO objective aberration C_s = 0.05 mm

Point resolution = 0.08 nm

Contrast of a graphene sheet

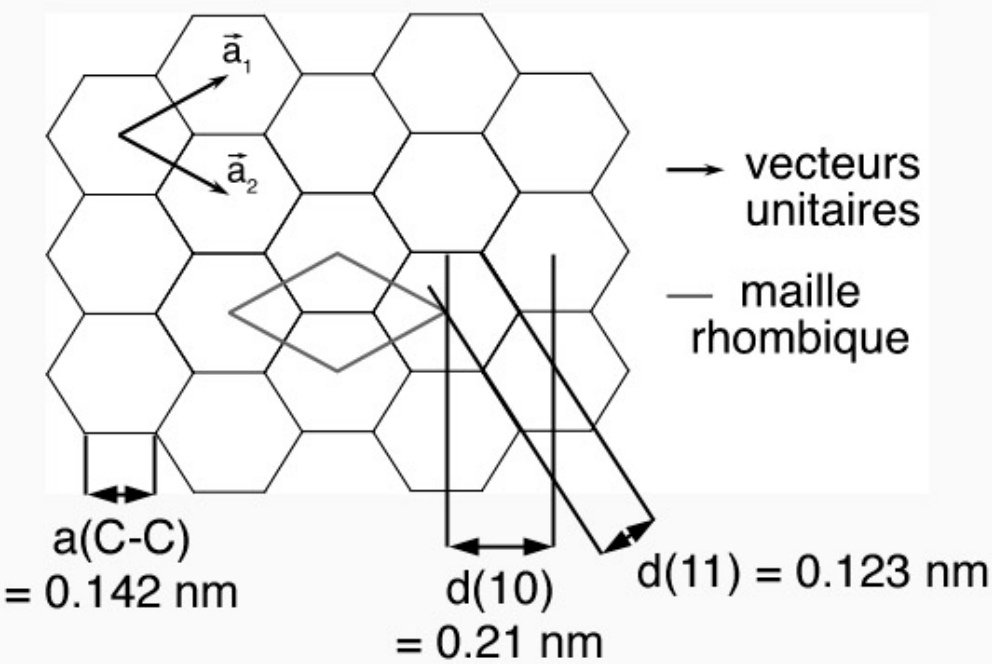


- It is not possible to image carbon positions if objective lens aberrations are not corrected
- Phase contrast is the image of the rhombic lattice

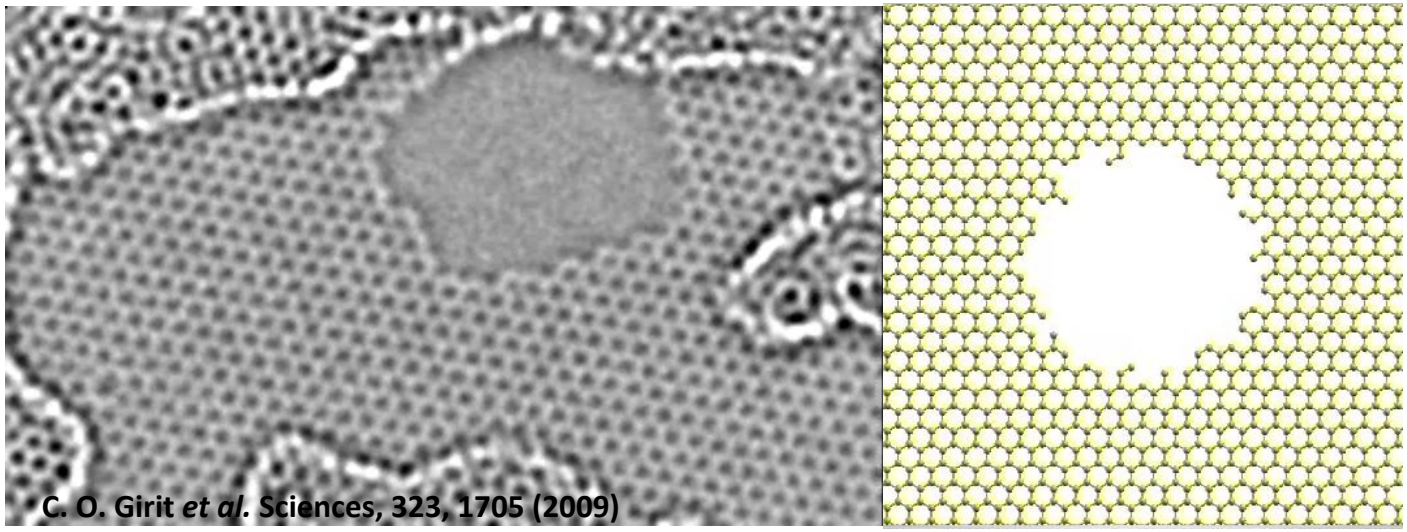


Calculated image of a graphene sheet for a non corrected microscope
Maxima of intensity located at the hexagon centers

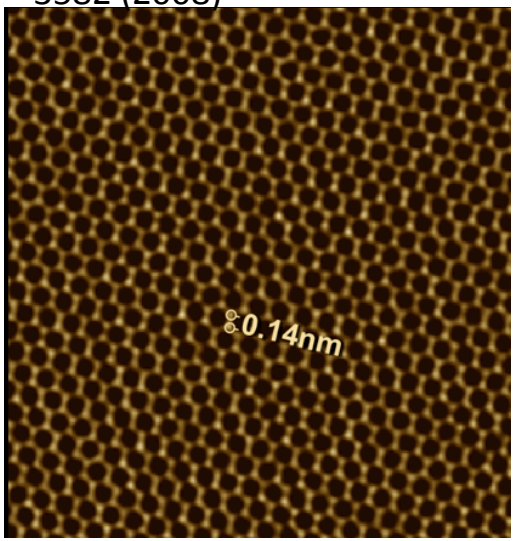
Contrast of a graphene sheet



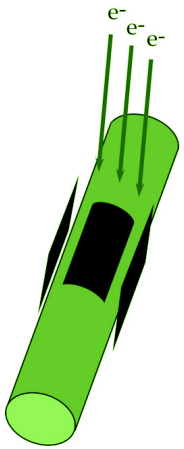
- Correction of the objective aberrations restitute a phase contrast where intensity maxima are located at the carbon scattering centers
- Image is a direct image of the carbon network !



J. C Meyer *et al.* Nano letters 8, 3582 (2008)

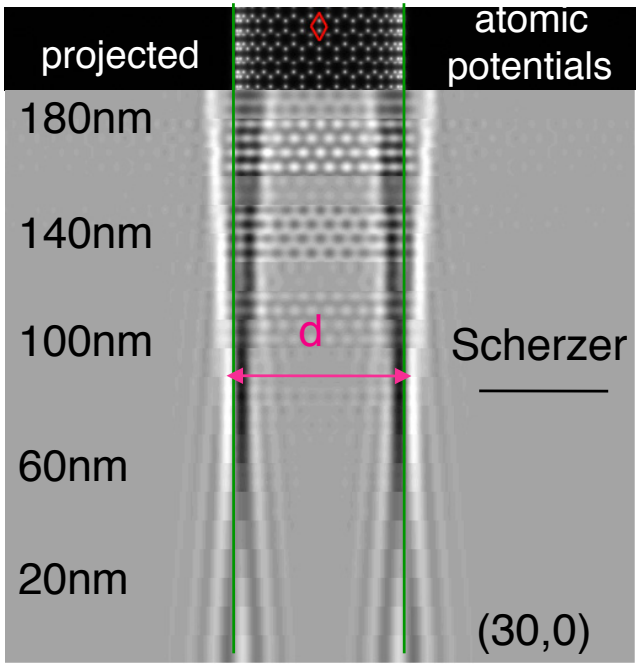


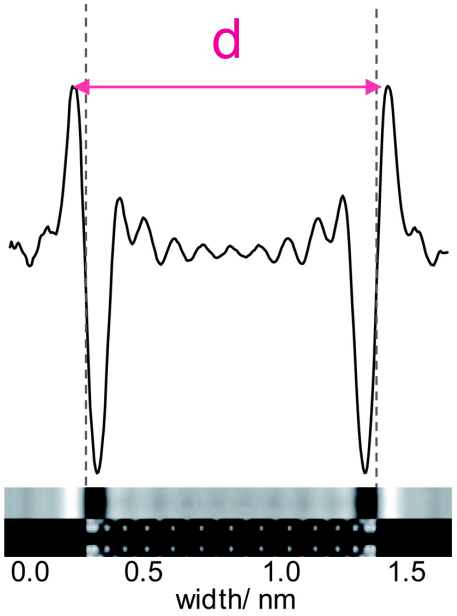
Diameter measurement - SWNT

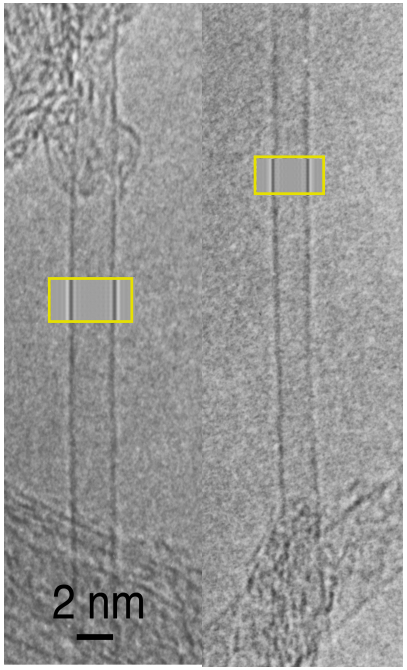


Non corrected microscope (TEM 1)

Focus series





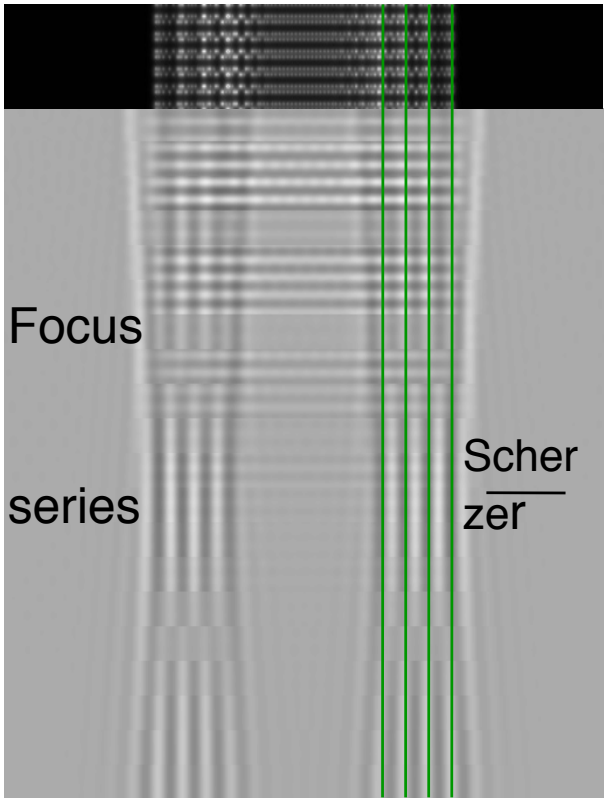


- Special focus (Scherzer) for which contrast is the finest and the highest
- Unique contribution of the tangential part
- Image consists of two black fringes with a spacing equal to the tube diameter
- Accuracy of the measurement: ± 0.05 nm

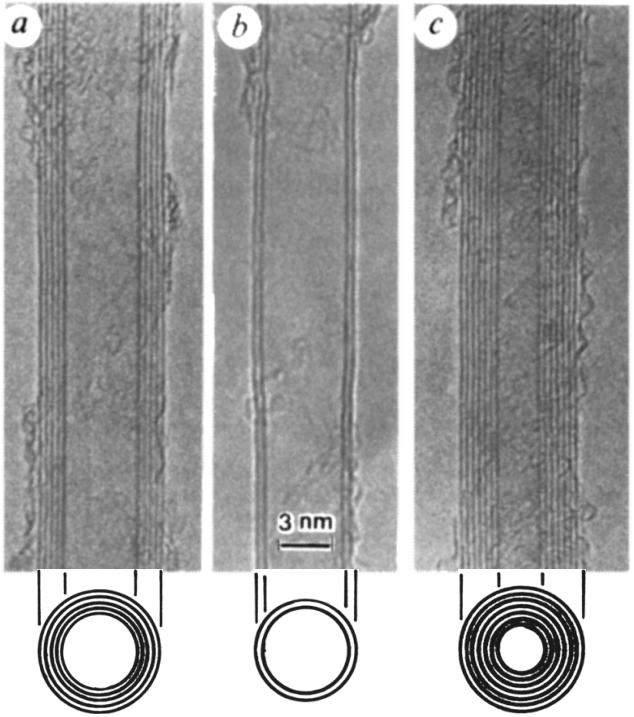
Loiseau et al Springer (2006)
Fleurier et al Adv Func Mat, (2009)

Diameter measurement - MWNT

Non corrected microscope (TEM 1)

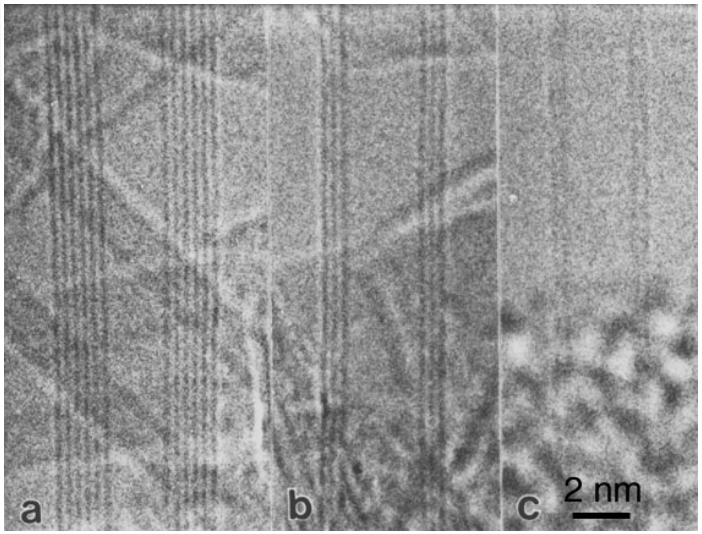


At Scherzer focus,
fringe Nb = layer Nb



Carbon tubes

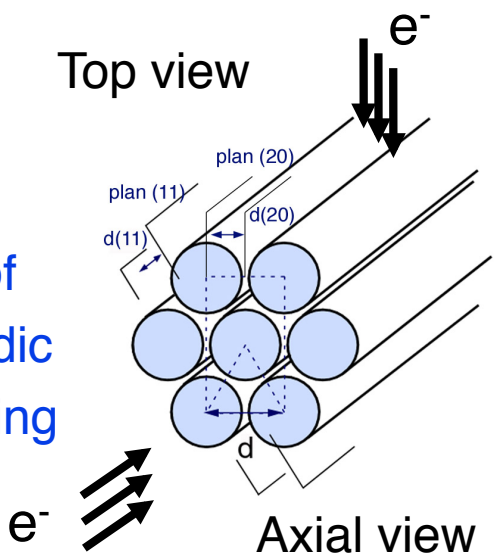
BN tubes



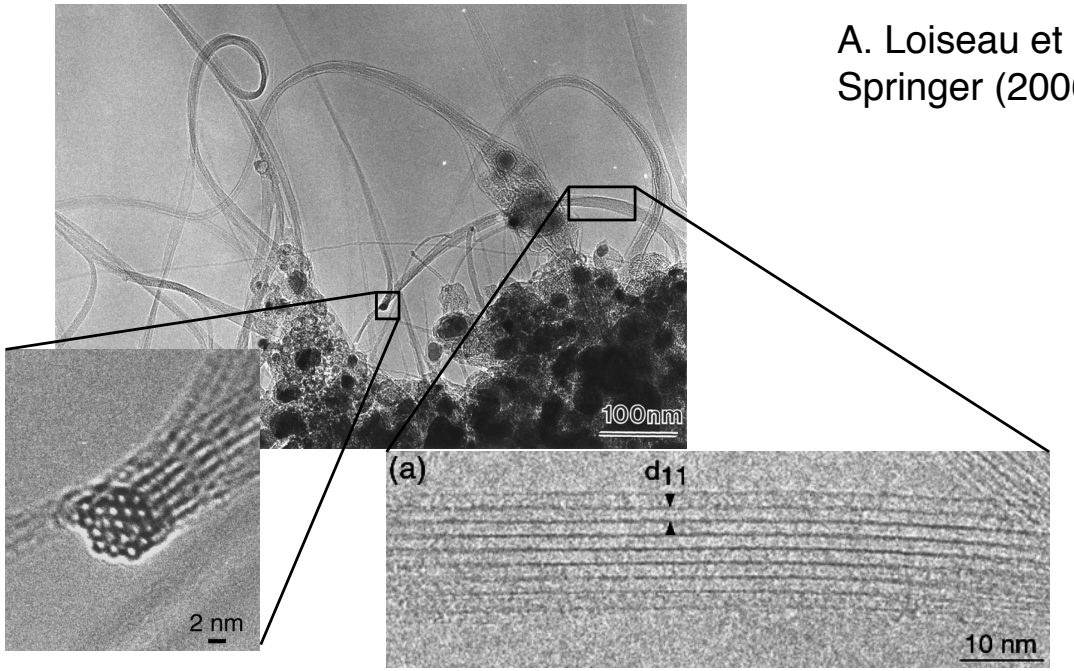
No chemical contrast !

A. Loiseau et al
Springer (2006)

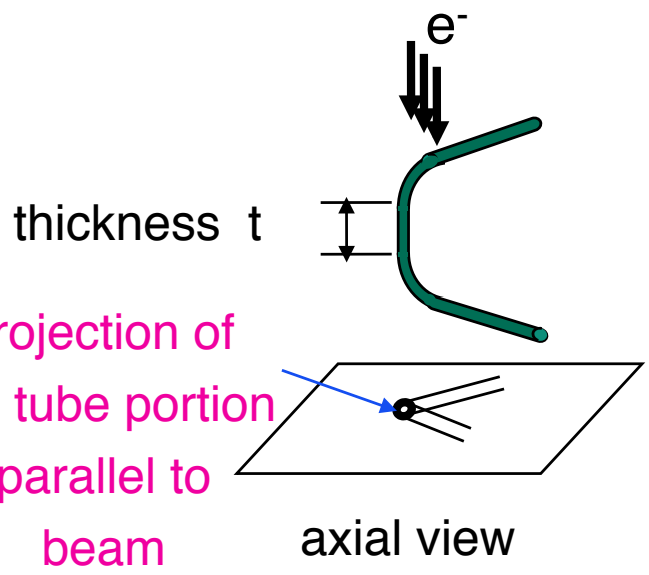
Special case of SWNT bundles



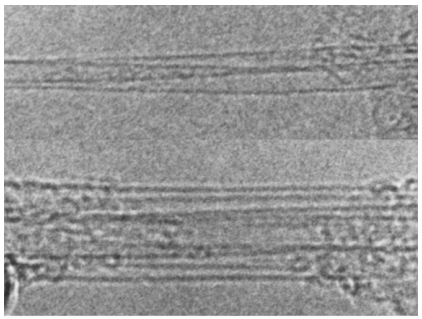
Lattice of the periodic tube packing



A. Loiseau et al
Springer (2006)



- Top view: interference fringe contrast is the image of the lattice built by SWNT
- Fringe spacing is NOT the tube diameter BUT that of lattice planes parallel to the beam

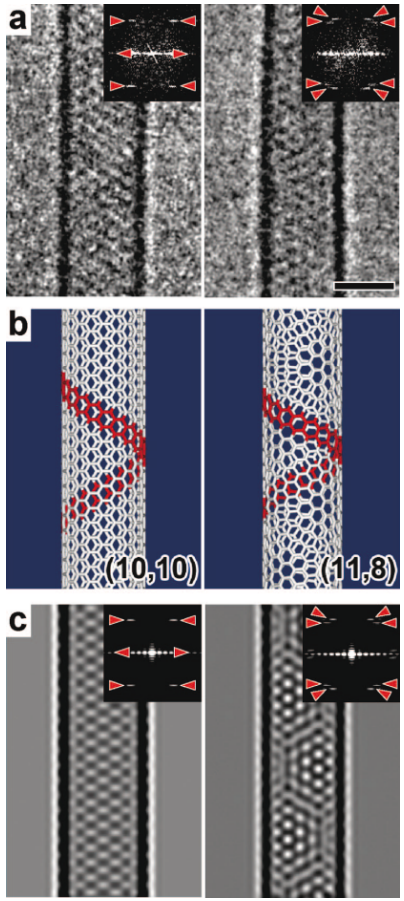


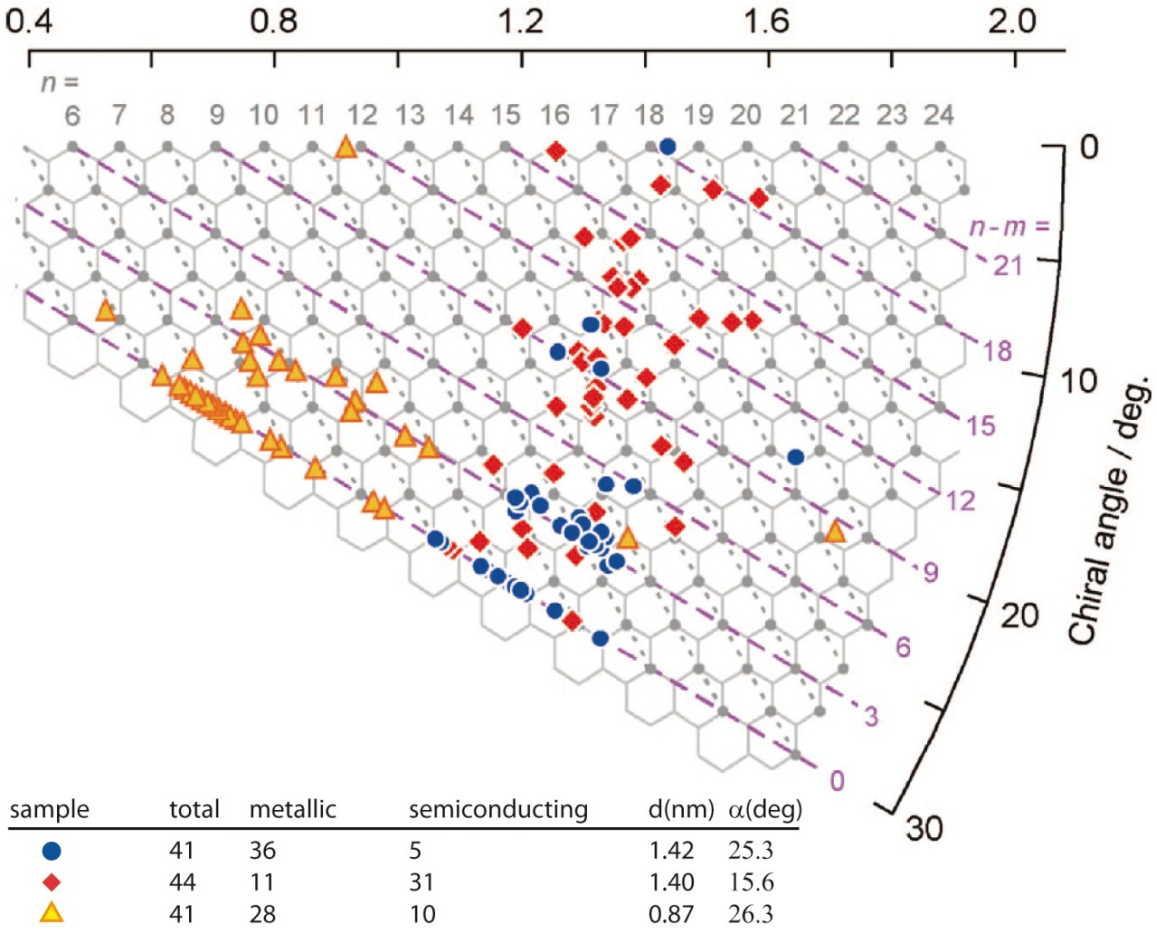
If no periodic packing, superimposition of contrasts of individual tubes

Structure analysis with a corrected TEM

Sato et al. Nano Letters 2008

corrected objective

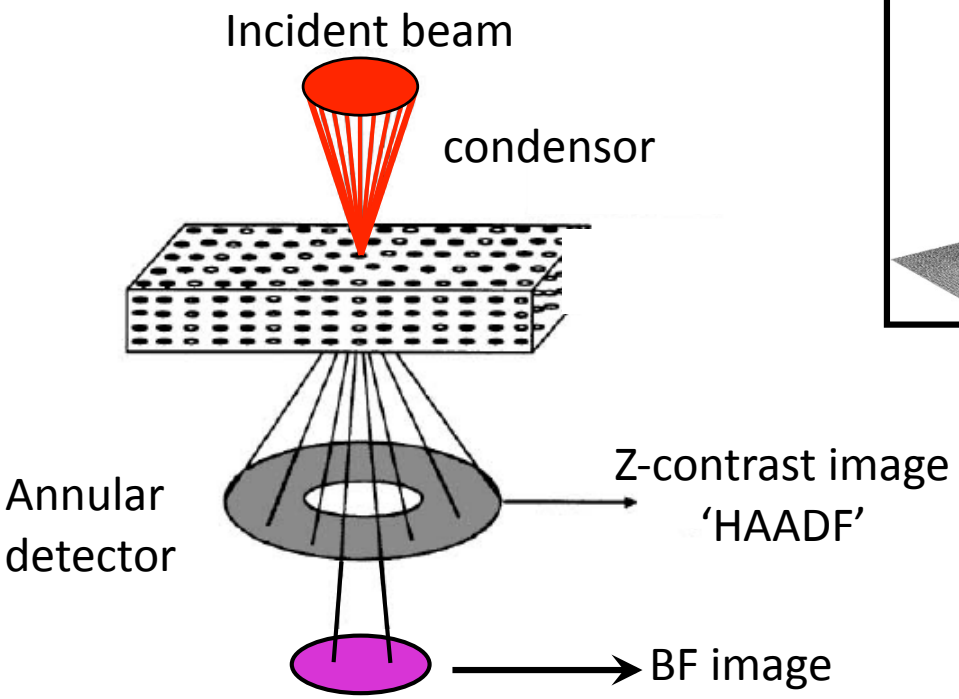


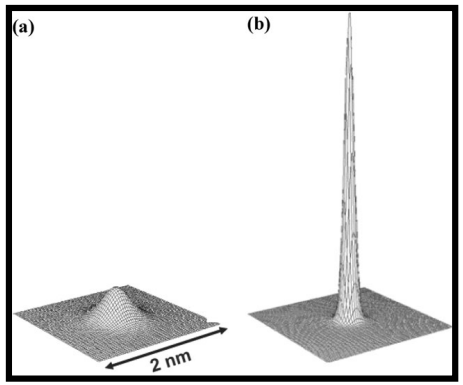


- Complete structure (d, θ) determination but very time consuming

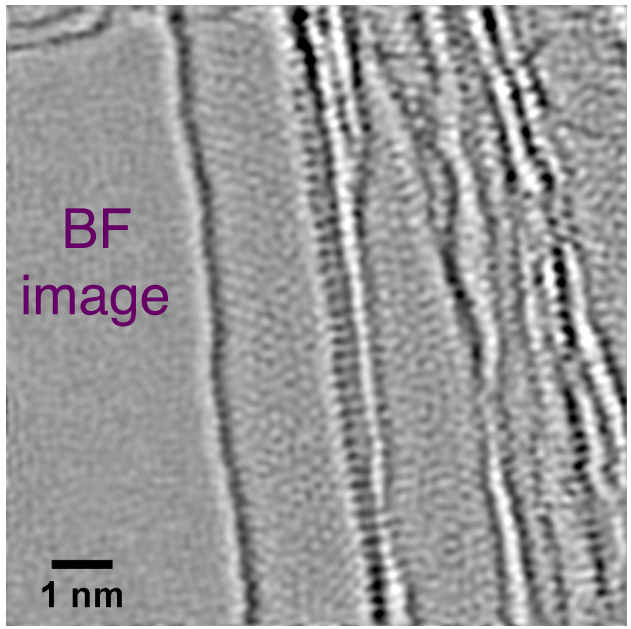
Atomic imaging with a corrected STEM

An imaging mode alternative to phase contrast HRTEM imaging





Very thin (0.1 nm) and intense electron beam thanks to aberration correction of the condensor

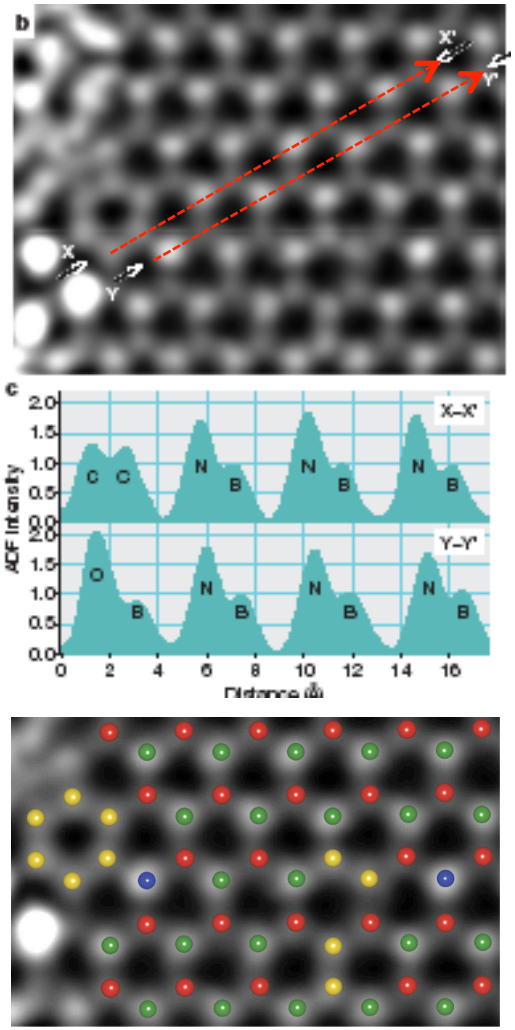


J.-A. Rodríguez-Manzo & F. Banhart, *Nano Lett.* **9**, 2285 (2009)

HAADF: image formed from electrons scattered at high angle by atoms nuclei

Contrast is $\approx Z^{\alpha}$ with $\alpha \approx 2$

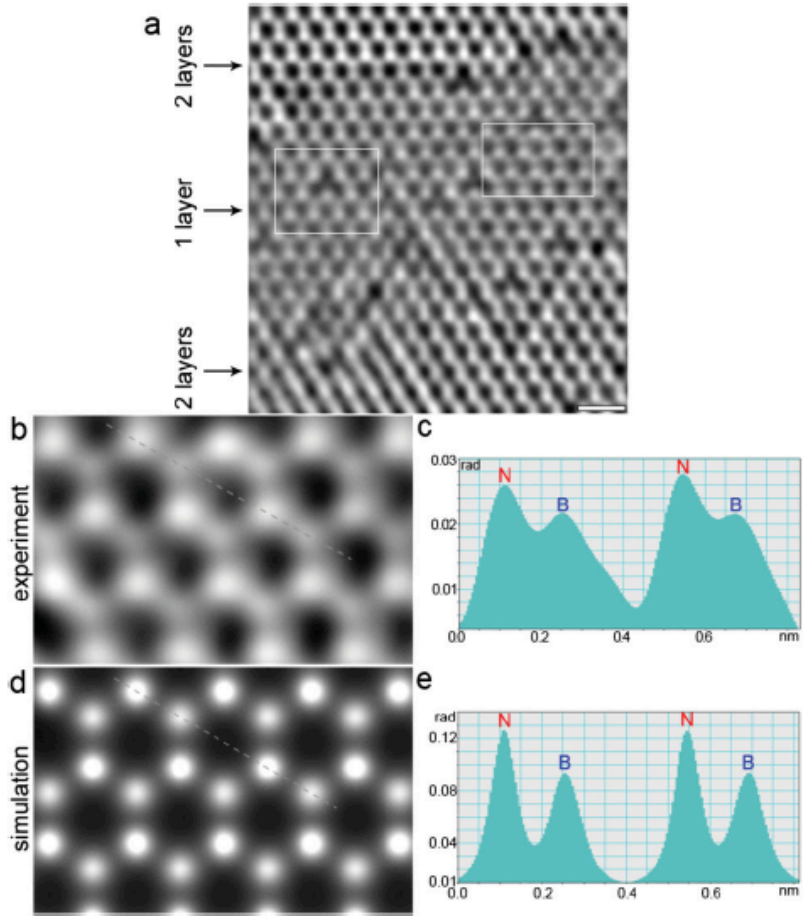
Atomic imaging of a BN single layer



HAADF image recorded with
a corrected STEM at 60 KeV

O. Krivanek et al, Nature 464 (2010)

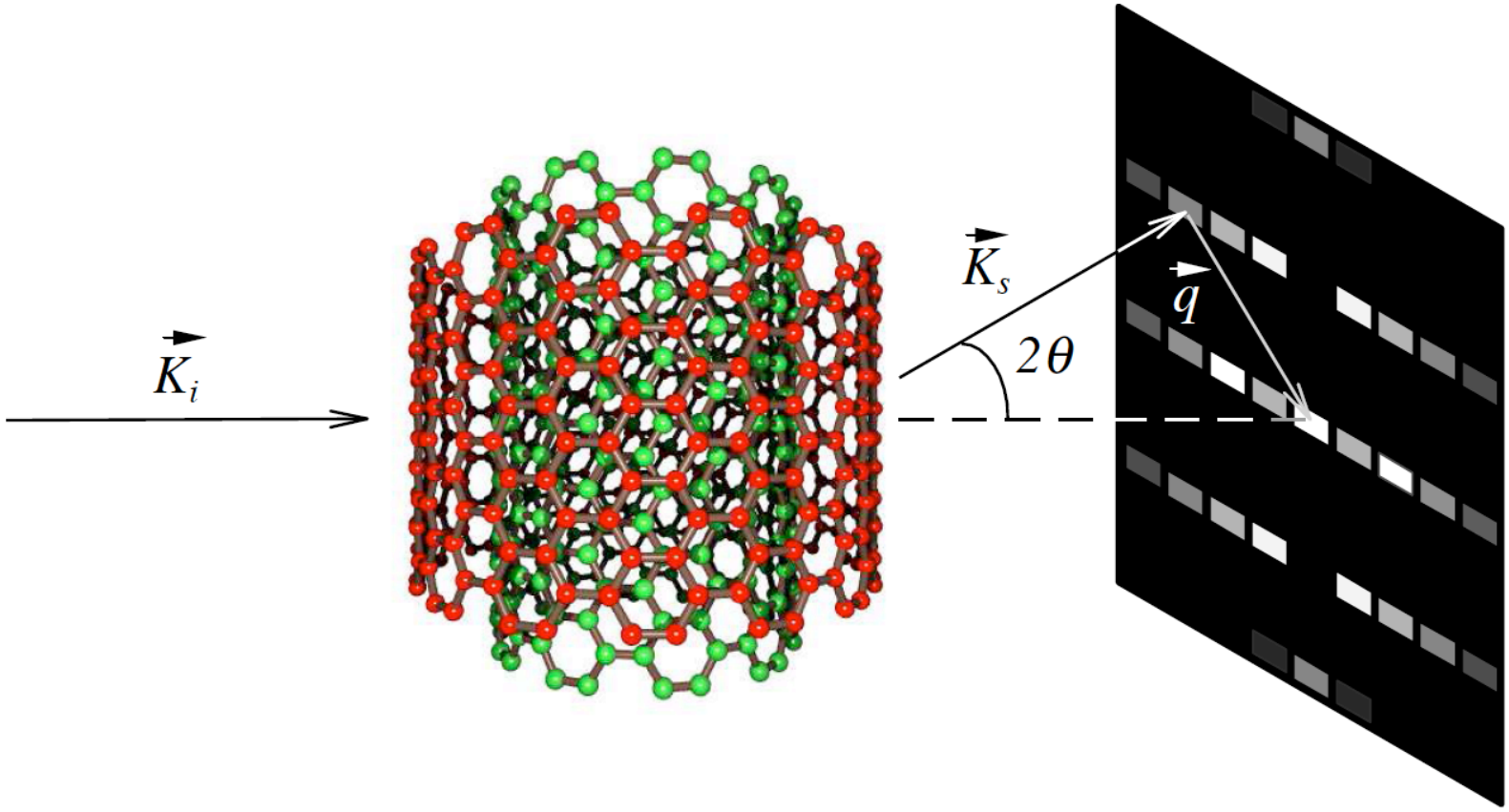
Two
strategies
TEM
or
STEM



HRTEM image recorded with
a corrected TEM at 120 KeV

C. Jin et al, PRL 102, 195505 (2009)

Electron diffraction:
a route to determine (n,m)

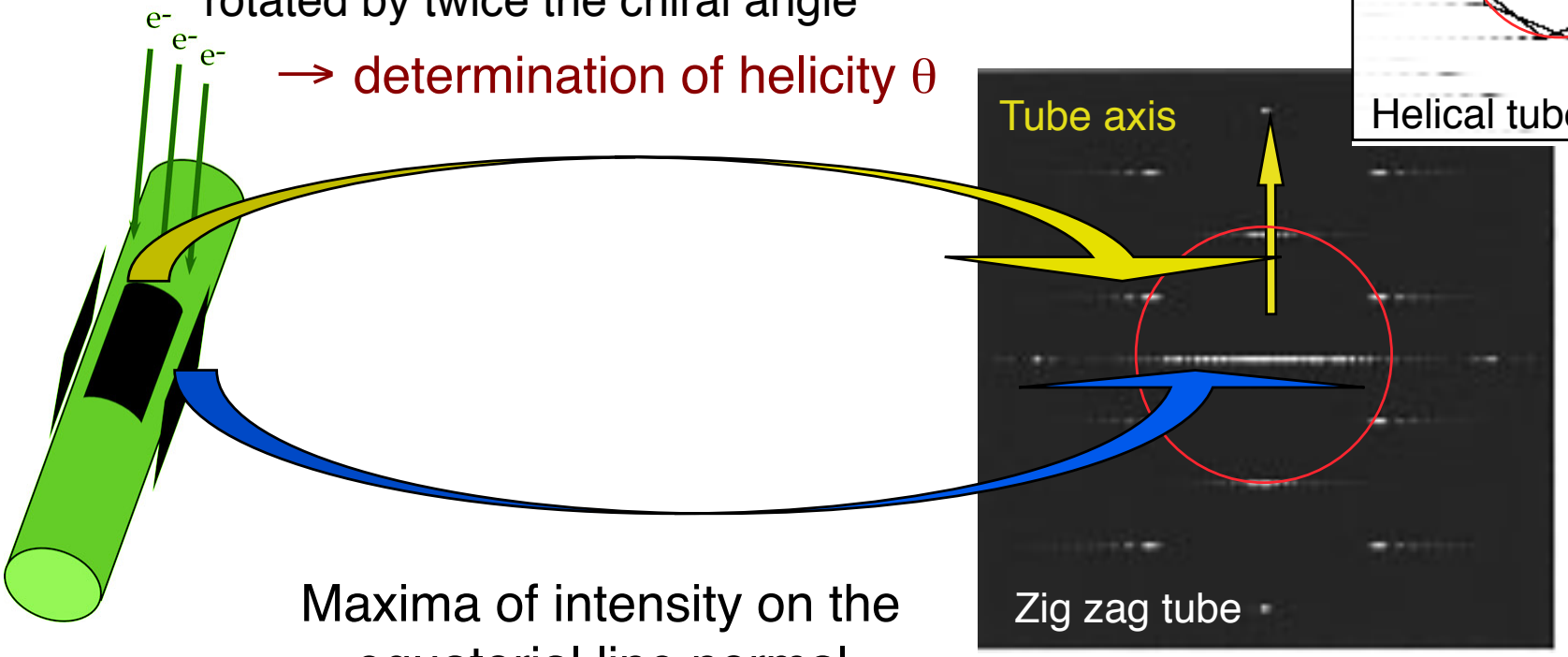


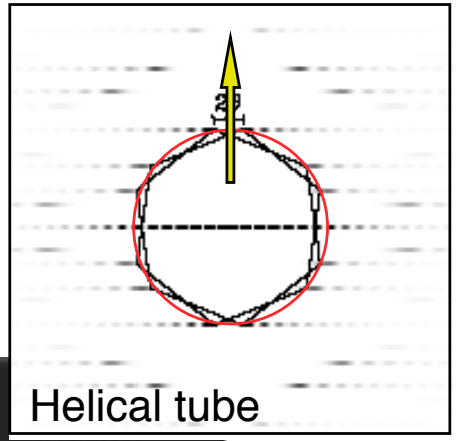
Geometry of the diffraction

Diffraction of a nanotube

Set of layer lines perpendicular to the axis
First order spots form 1 or 2 hexagons
rotated by twice the chiral angle

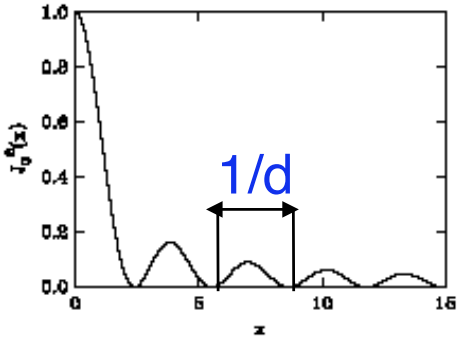
→ determination of helicity θ





Maxima of intensity on the
equatorial line normal
to the tube axis

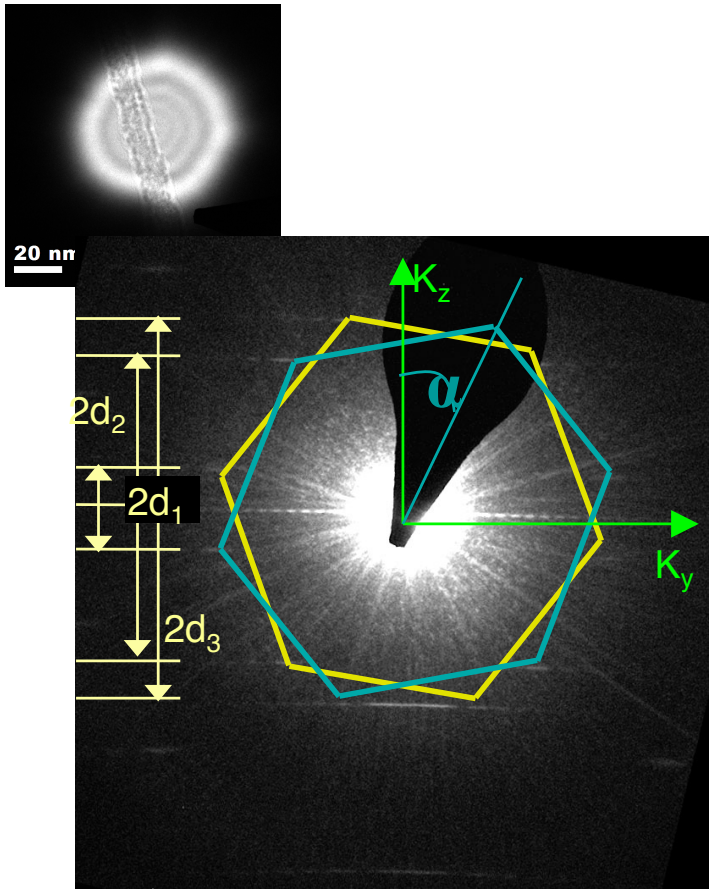
→ determination of diameter d



(Code P. Lambin, Namur)

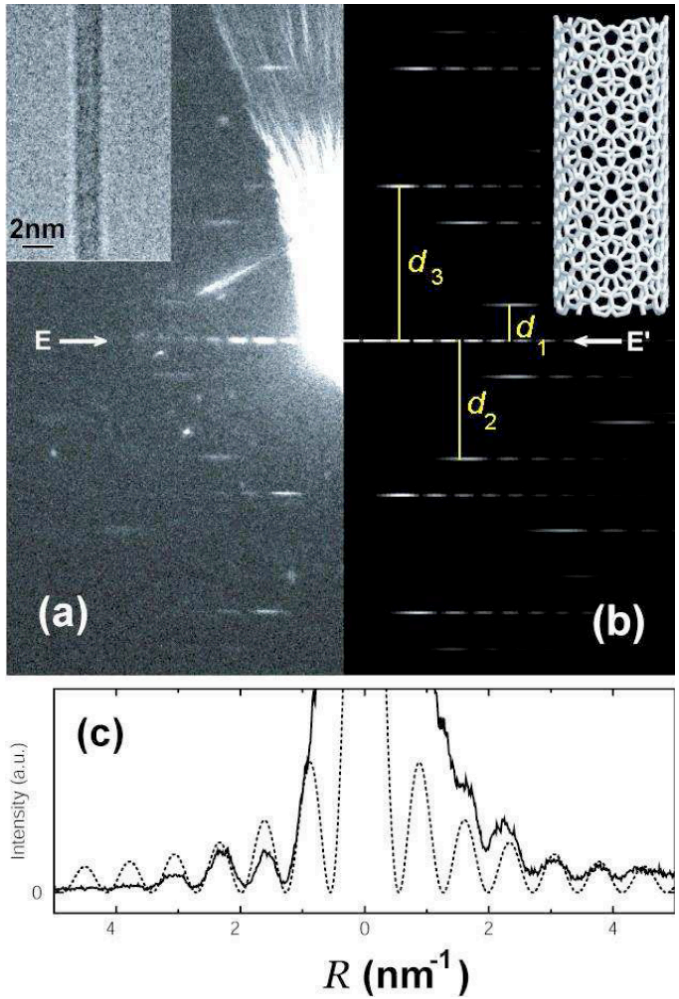
Pattern recording and analysis

M. Gao et al.
APL 82, 2703
(2003)



Nanobeam mode (40 - 50 nm)
in parallel illumination
Recording with a CCD camera

R. Arenal et al APL **89**, 073104. (2006)



• 1) Helicity θ is given by

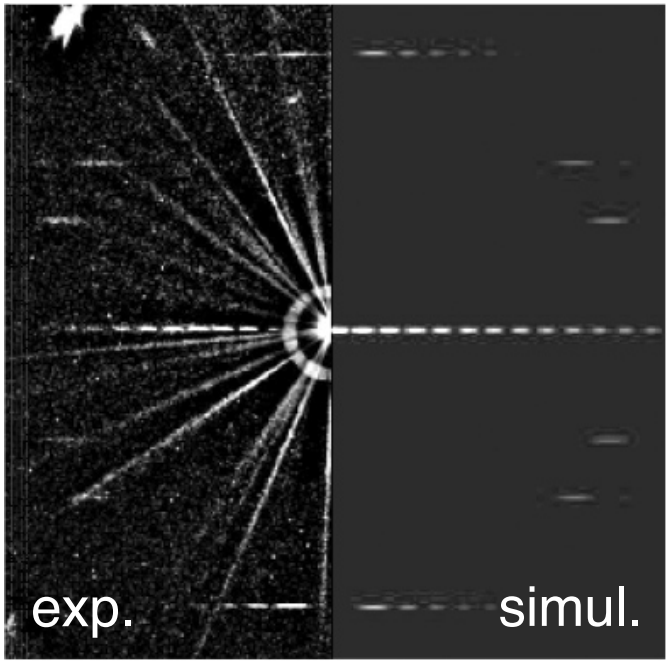
$$\Theta = \text{arctg}\left[\frac{(2\,d_2 - d_3)}{d_3\sqrt{3}}\right]$$

• 2) Tube diameter d is determined as the best fit of the intensity profile of the equatorial line

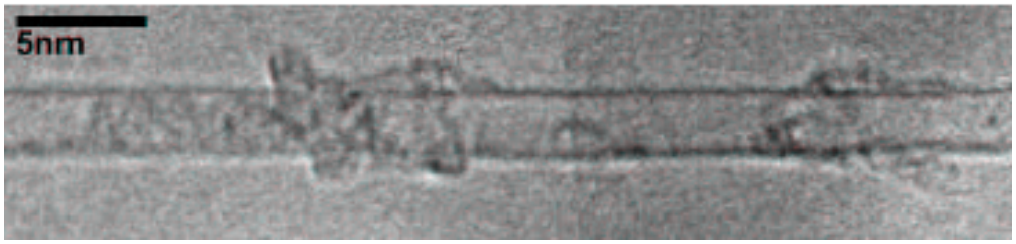
• 3) simulation of the diffraction pattern of the tube defined by d =1.39 nm and θ = 17°: tube is (14,6)

J. Meyer et al, J. Cond Matter (2005)

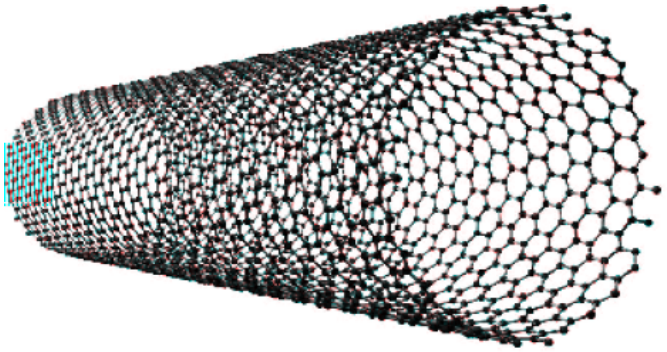
Analysis of a SWNT



Diffraction pattern :
d= 2.29 ± 0.03 nm,
θ = 6.8°



HRTEM image : d= 2.3 nm

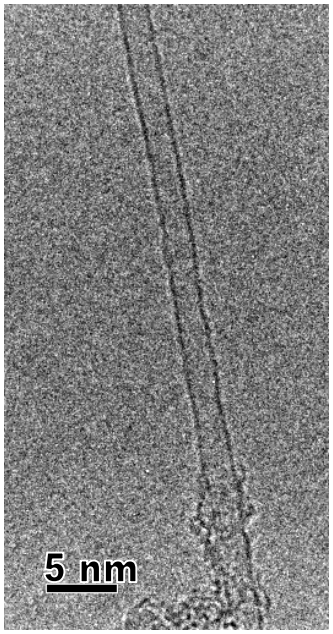


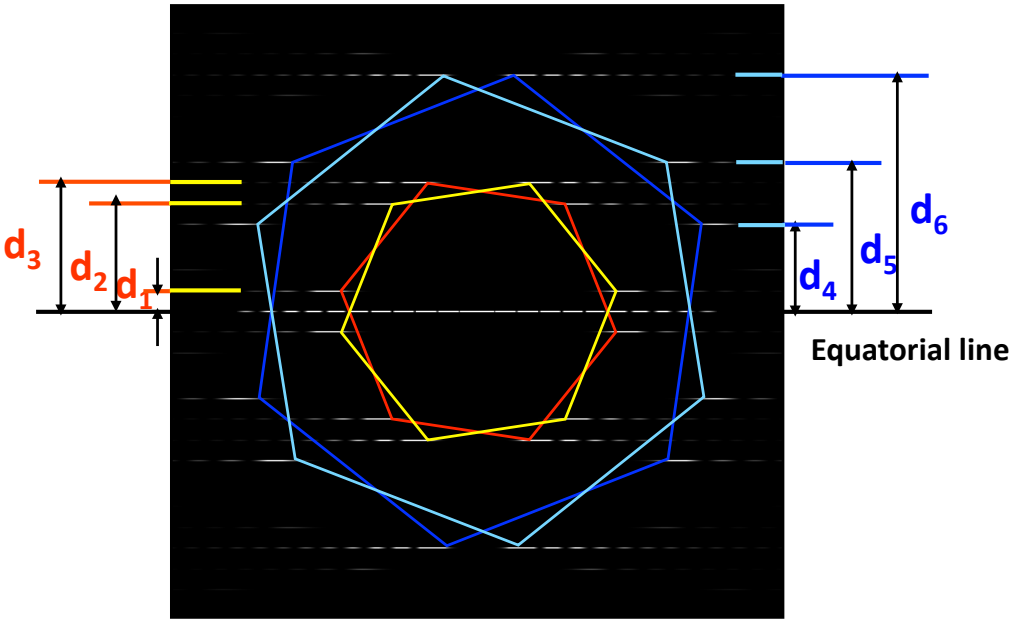
Configuration is (27, 4)

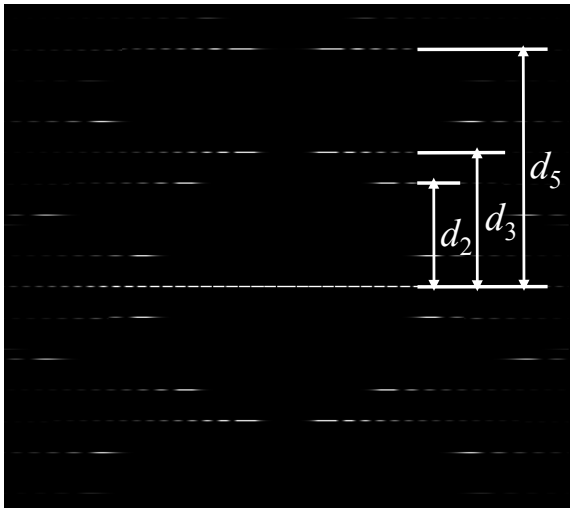
- The most reliable method to a direct determination of a configuration
- Any configuration (d, θ) can be identified provided the tube is isolated
- Technique does not need a corrected TEM as in imaging approach

More refined analysis method

H Jiang et al, CARBON 45 (2007), 662



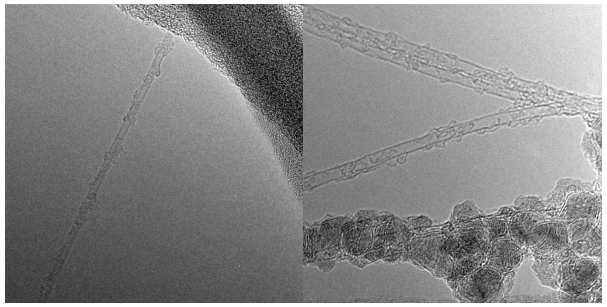




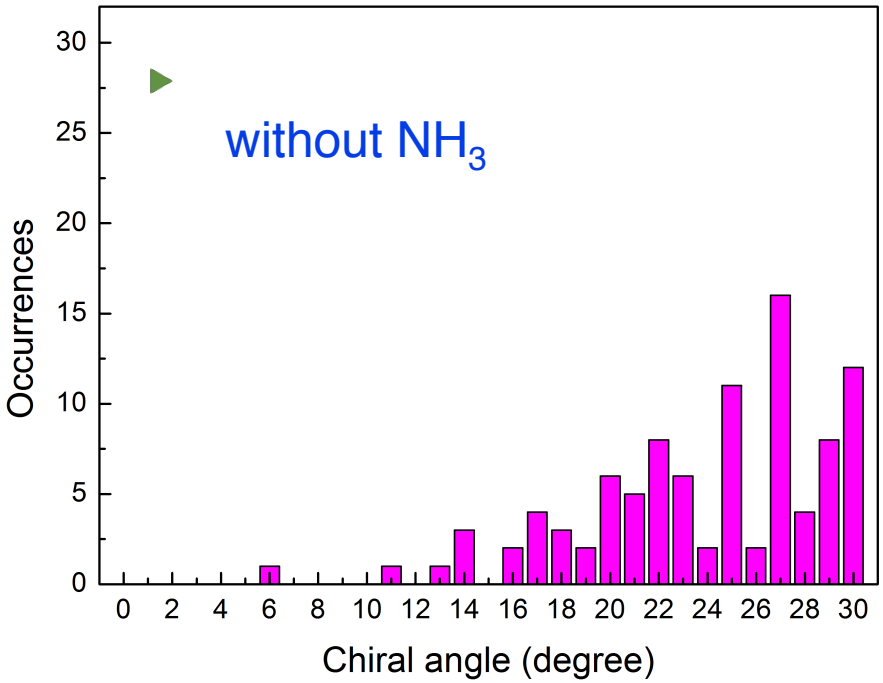
Simulation of (23,10) at $\tau = 10°$

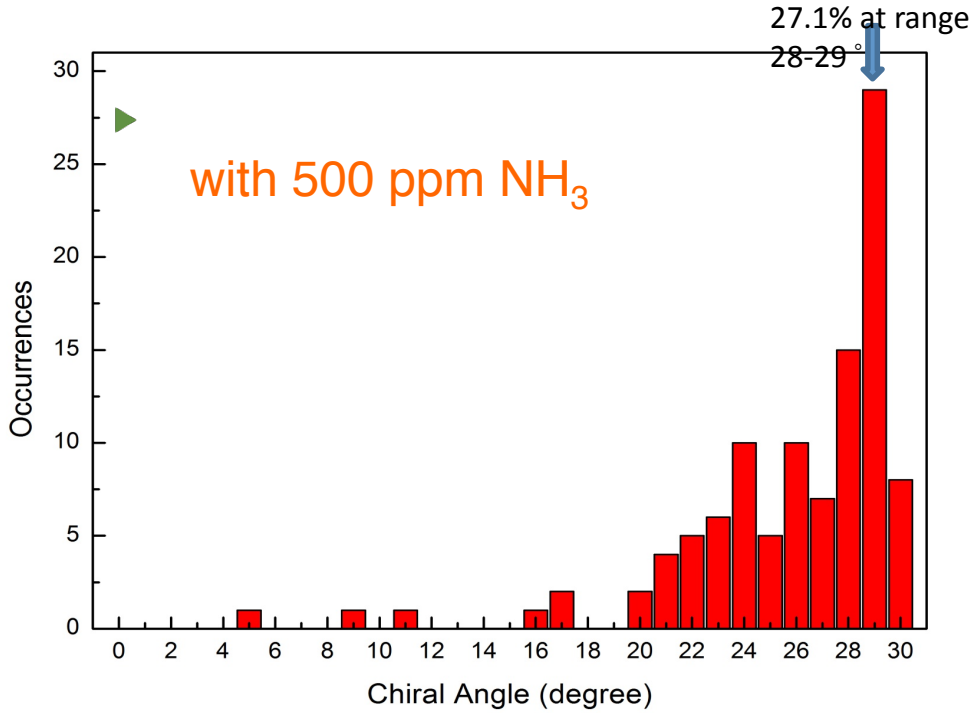
- 1) Use 6 layer lines distances measured on the pattern
- 2) Deduce non-dimensional parameters uniquely defined by (n,m)
- 3) Determination of (n,m) from these parameters
- 4) Check with simulations

Statistical analysis of helicity distribution



Statistical analysis of chiral angles of 97 SWNT synthesized by CVD at 890°C with and without NH_3





NH_3 favors armchair configurations

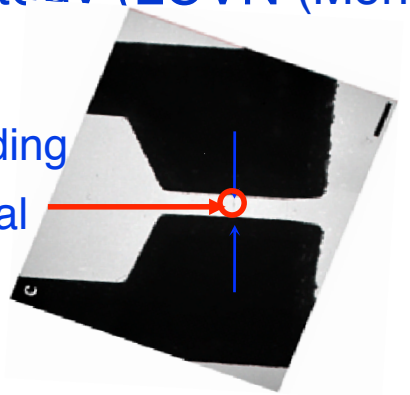
T. Susi poster 282

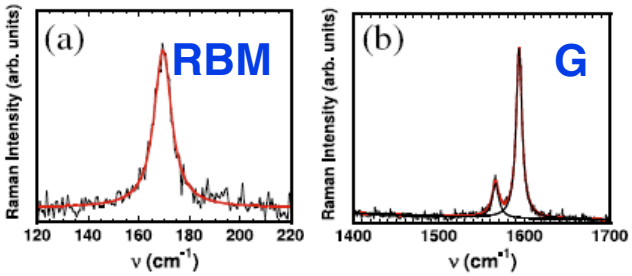
J. Meyer, M. Paillet et al.,
PRL **95** (2005) 217401.
A. Débarre et al,
PRL **101** (2008) 197403
T. Michel et al.,
PRB **80** (2009) 245416

Electron Diffraction and Raman spectroscopy

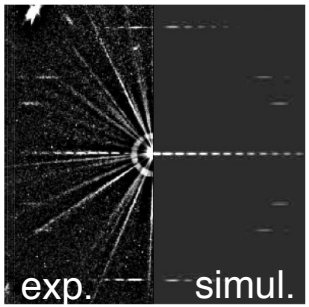
- Issue: validation of Raman modes analysis
- Strategy (LCVN (Montpellier)- MPI (Stuttgart) - LEM (Chatillon):

Free-standing individual NT





(n, m)



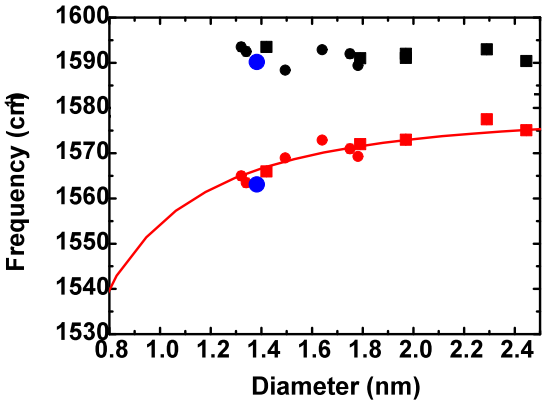
- Determination of:
  - relationship between tube diameter and RBM frequency
  - profile of G modes of metallic and semi-conducting tubes
  - relationship between resonance energy E_{ii} and diameter

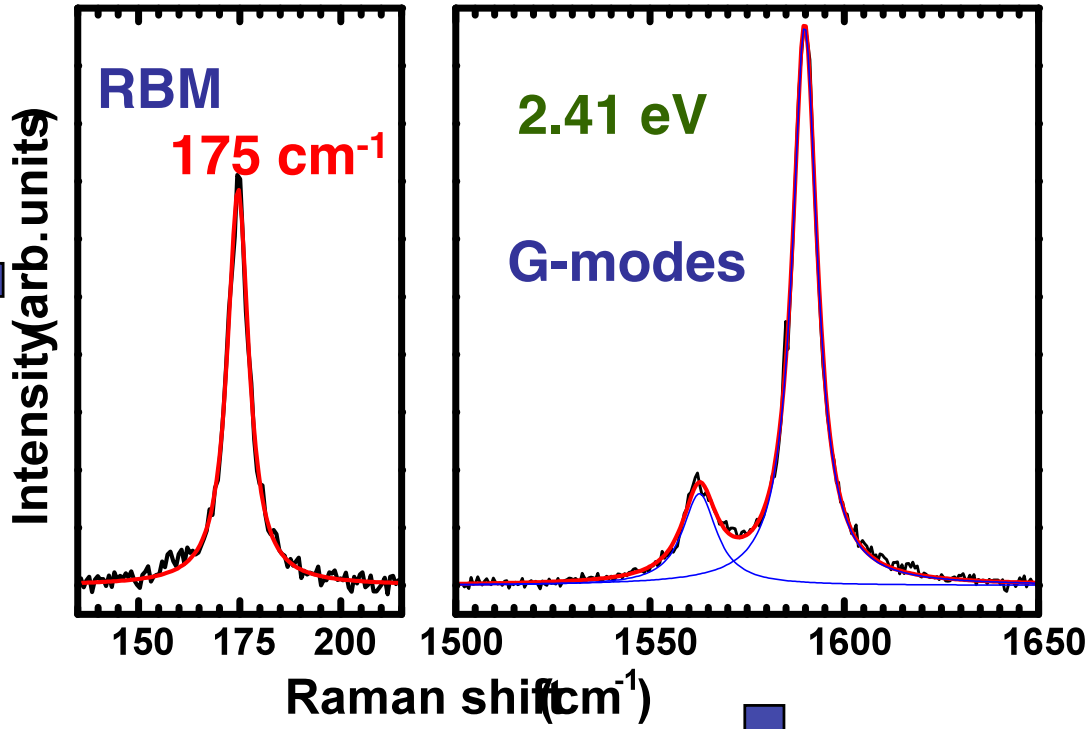
procedure of (n,m) identification from Raman spectroscopy from (RBM, E_{ii}, G profile)

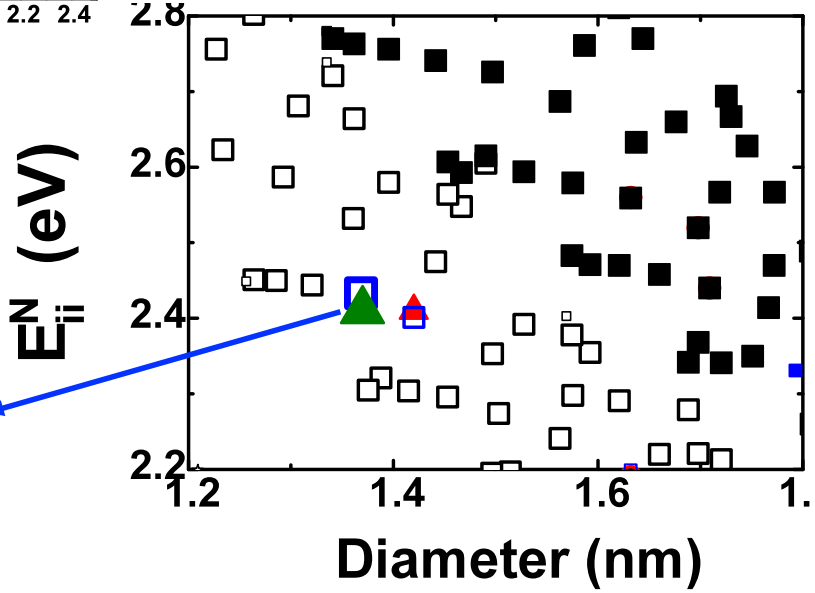
Ex: identification of a chiral SC SWNT

$$\omega_{RBM}(cm^{-1}) = \frac{204}{d(nm)} + 27\ cm^{-1}$$

Diameter =1.38 nm







(12,8)

Chiral
and
semiconducting

Conclusion

1) Different characterization techniques

- Direct: imaging, diffraction
- Indirect : electronic and optical spectroscopies

2) TEM is an unique technique combining structural and chemical analysis

- (n,m) assignment:
  - diffraction is the most reliable way but needs individual and isolated tubes
  - statistical analysis of the helicity is achievable
- corrected TEM and STEM:
  - provides chemical imaging at the atomic level

3) TEM is a valuable reference for validating spectroscopies

- Coupled measurements on individual tubes
- Crosslinked statistical analyses of assemblies