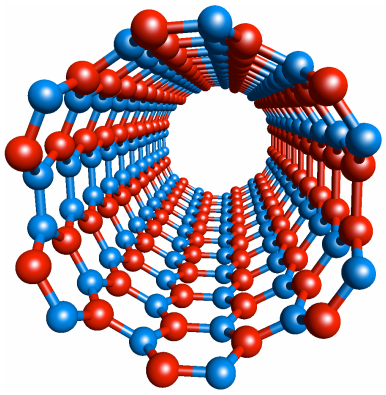
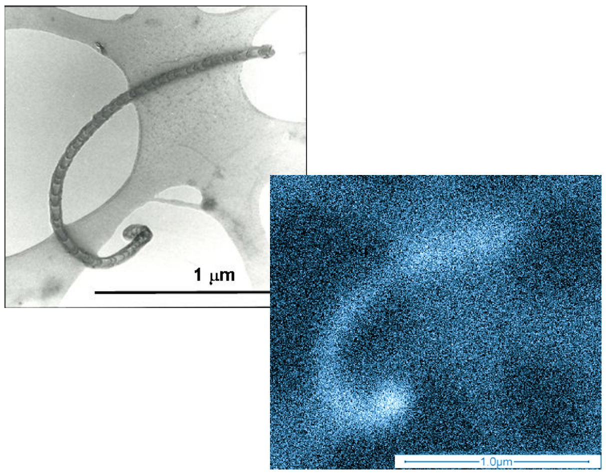
BN NANOTUBES:
growth, structure
Electronic / optical properties

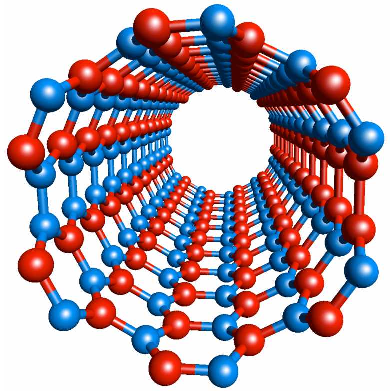




Annick LOISEAU,
LEM, CNRS-ONERA (France)

ONERA
GNT Nanotubes Graphene
NanoSciences ILE-DE-FRANCE
cnrs dépasser les frontières

BN -SWNT

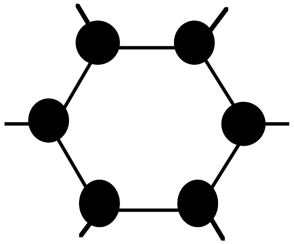


Outline

- Introduction: interest for BN nanotubes
- Synthesis of BN nanotubes: the Onera route
- Investigation of the electronic structure:
  - a good approach: optical measurements

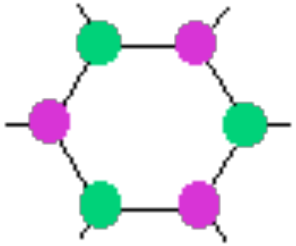
P. Jaffrennou, R. Arenal, F. Ducastelle, A. L. LEM, Cnrs-Onera
B. Trétout, DMPH, Onera J. Barjon Gemac, Cnrs Meudon
O. Stéphan, LPS, Cnrs-Univ. Orsay

Introduction



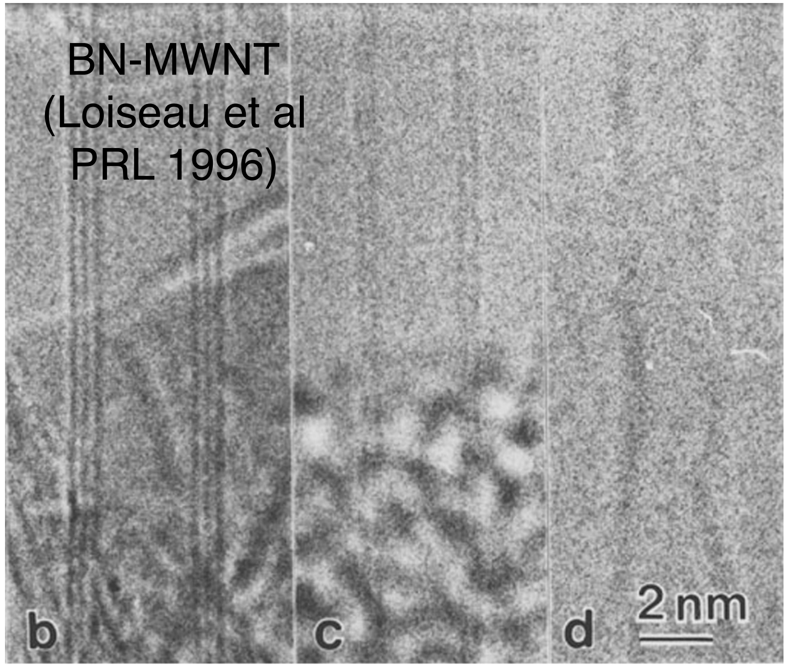
Graphite

black
semi-metal



h - boron nitride

transparent
insulating
(gap ~ 6 eV)



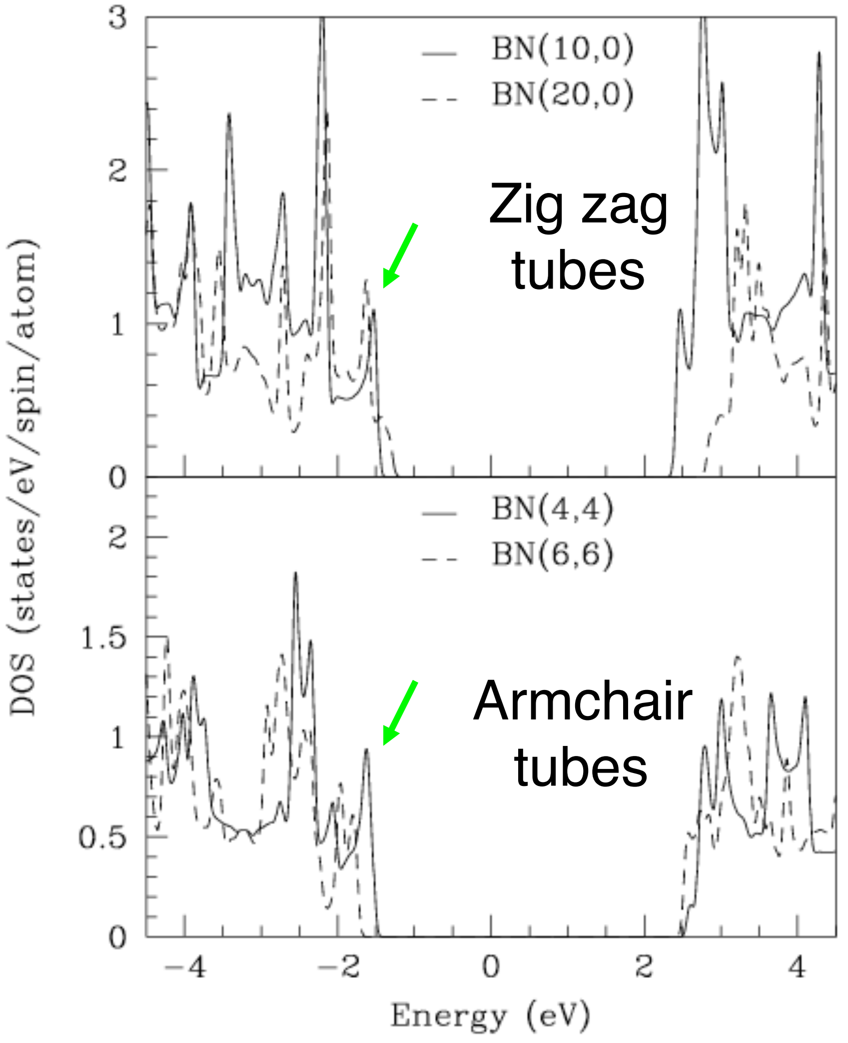
Stability of BN NTs predicted in 1994 (Blase et al, Eur. Phys. Lett.)

First syntheses of BN MWNTs and SWNTs: 1995, 1996

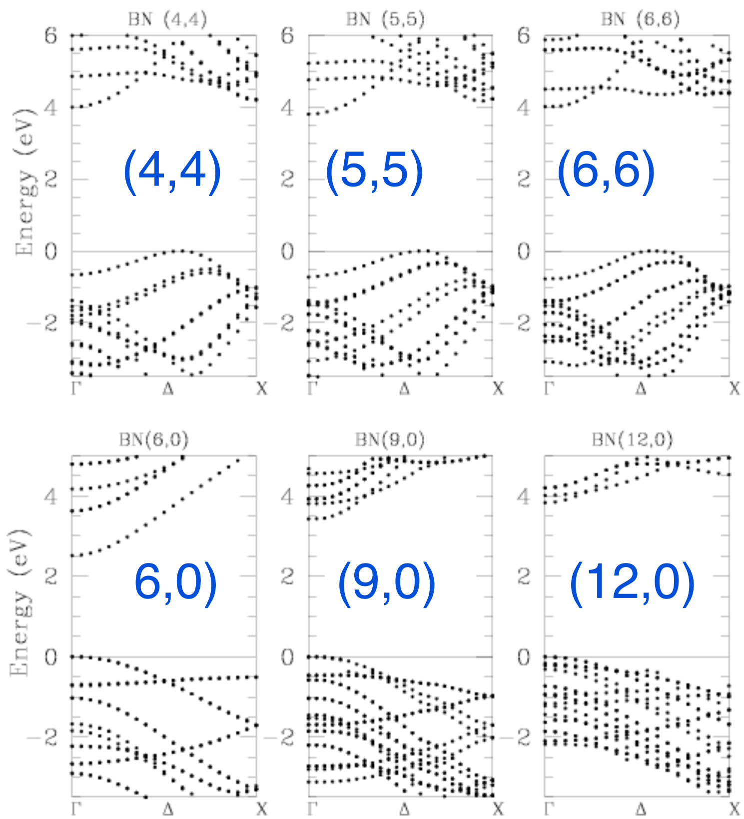
BN-NTs predicted to be large gap semi-conductors (5.5 - 6 eV)

→ interest for optics and optoelectronics in UV

Electronic structure of BN nanotubes



- Semi-conductor with a large gap
- Uniform band gap
- gap = 4 eV (LDA) - 6 eV (GW)
- 1D features of the DOS



LDA calculations (A. Rubio)

Synthesis of BN nanotubes

- Different methods of synthesis of MWNTs developped since 1995:

  electric arc, laser ablation, substitution reaction, ball milling, CVD…

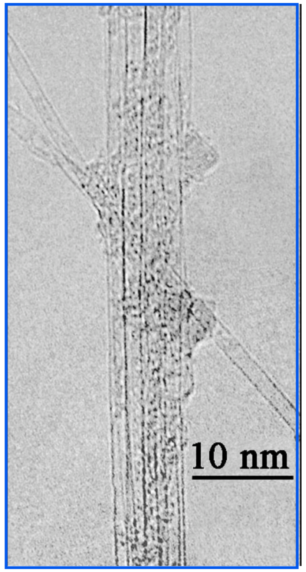
  → different kinds of MWNTs available for measurements

- A unique route to the selective synthesis of SWNTs:

  The CO_2 continuous laser vaporization of a BN target under N_2

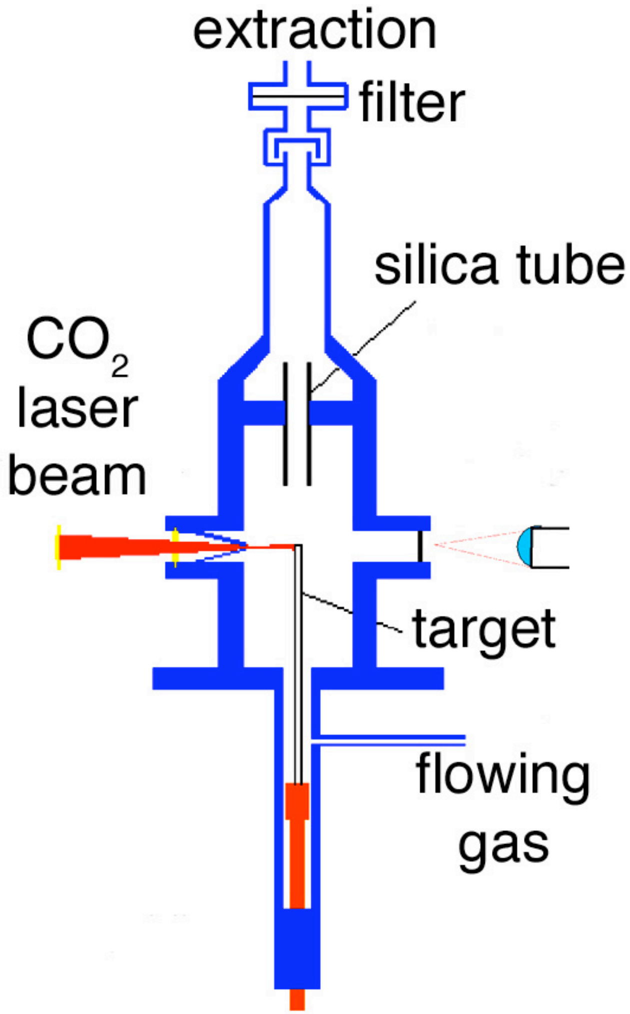
  (Lee et al, Phys. Rev B **64** (2001))

  → access to the intrinsic properties



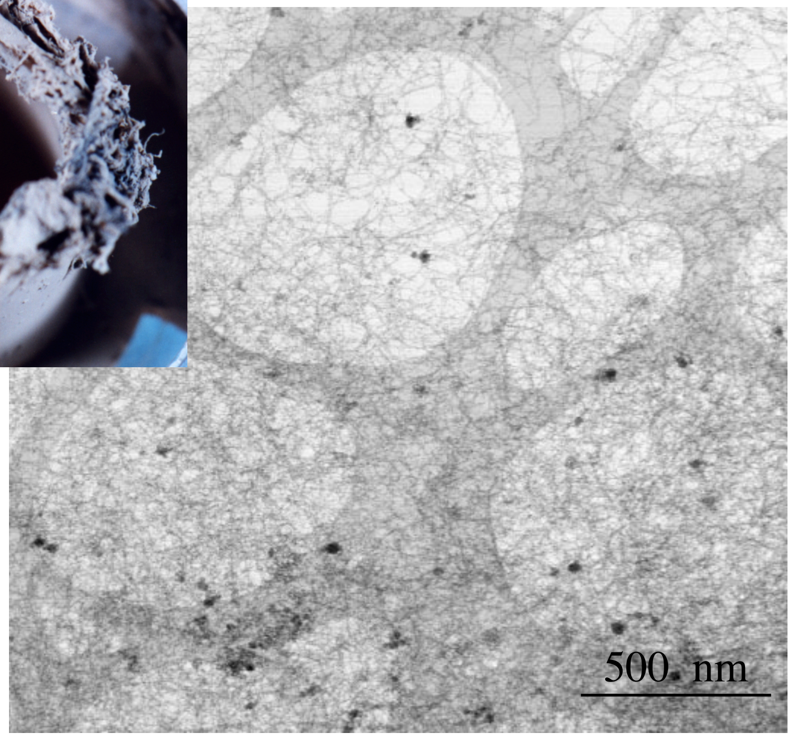
Synthesis of BN-SWNT via laser vaporization

(Lee et al, Phys Rev Rapid Comm 2001)

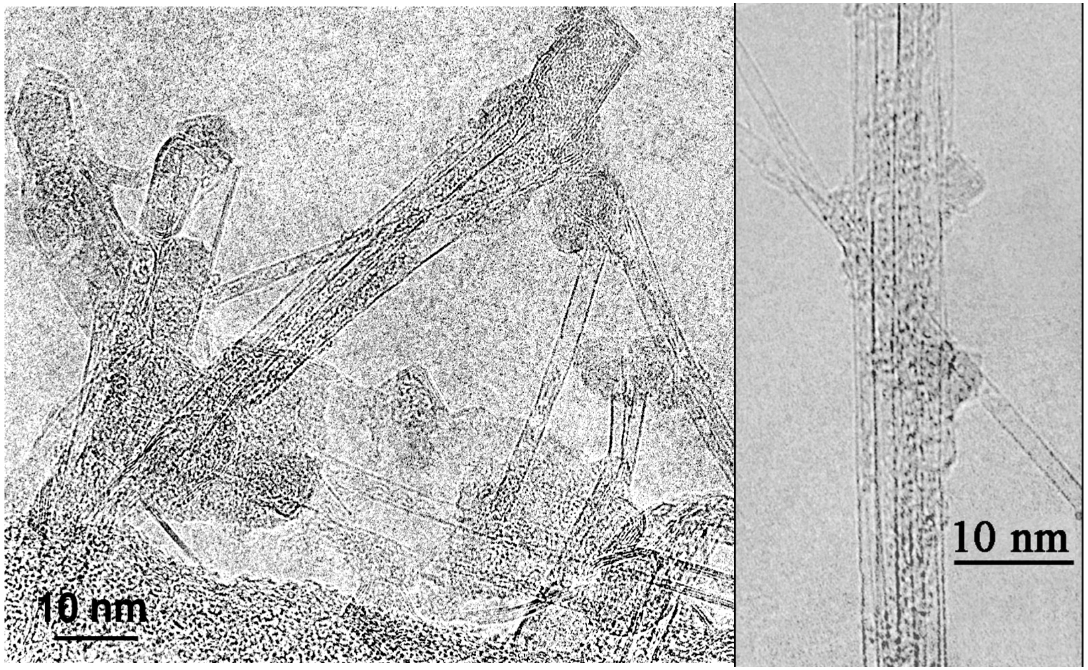


Decomposition ad vaporization under nitrogen of a h-BN targed pressed with a B_2O_3 binding

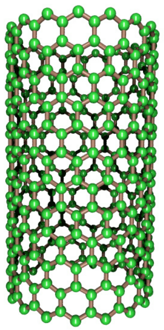
No use of a metal catalyst



Characteristics of BN - SWNT

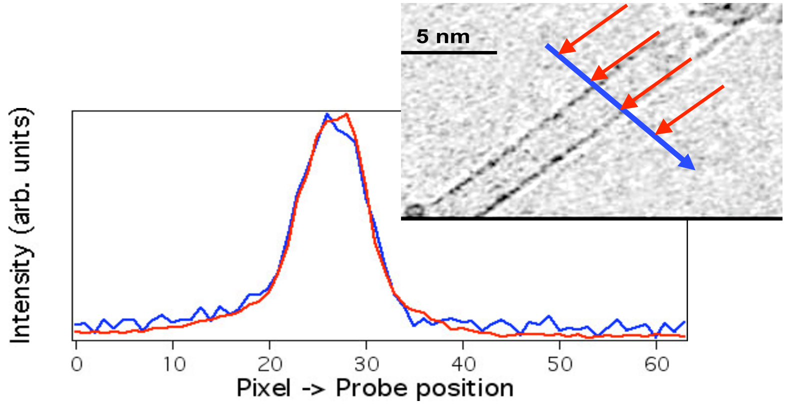


- Structure of SWNT (TEM):
  - length 200 - 1000 nm
  - diameters 1.5 - 2.5 nm
  - dominant zig zag character
    - * high resolution imaging
    - * electron diffraction

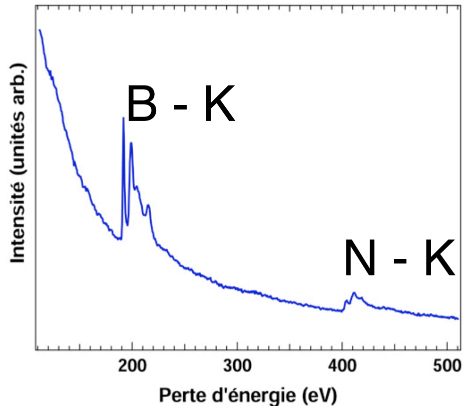


R. Arenal et al , APL **89**, 073104. (2006)

- Chemistry (EELS):
  - Stoichiometry B:N = 1:1
  - sp^2 hybridation



B and N profiles across the tube

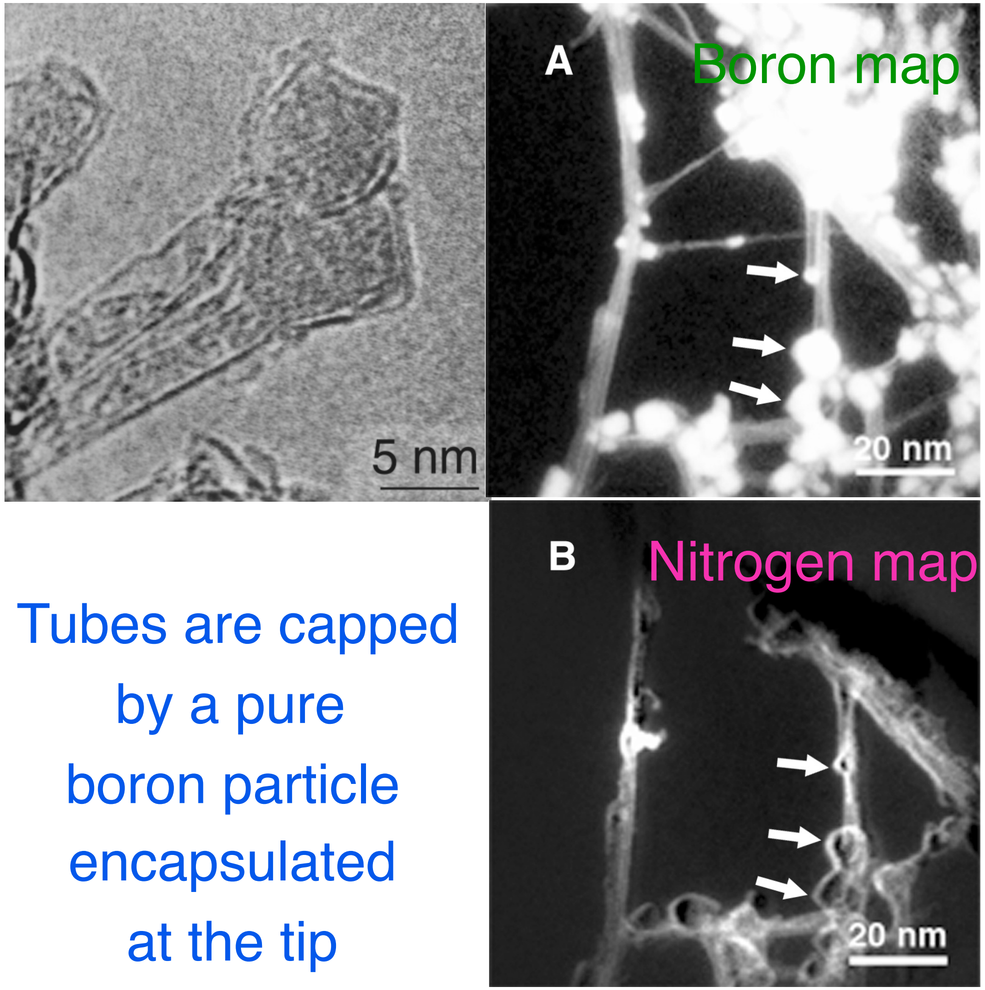


EELS Spectrum

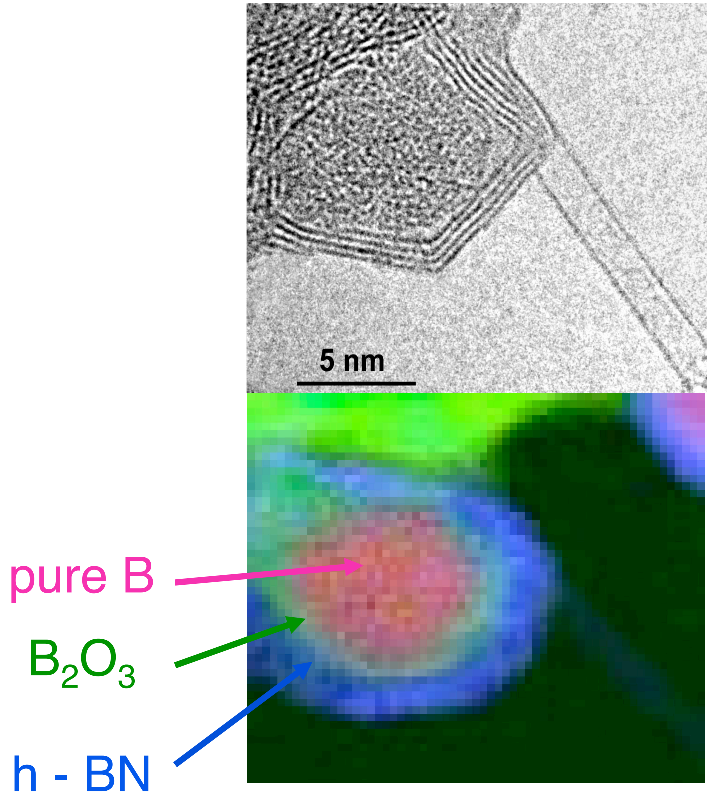
(Lee et al, Phys Rev Rapid Comm 2001)

Particles analysis using EELS

Boron particles at the tip of tubes or encaged in h-BN shells



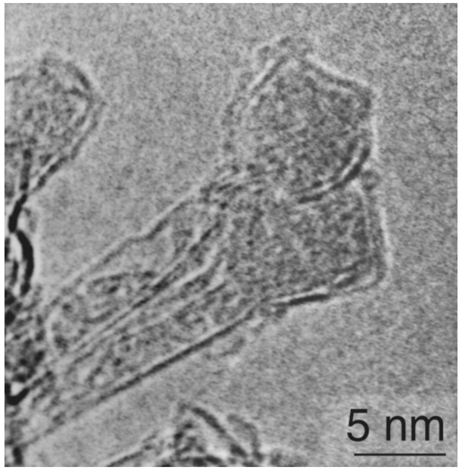
Tubes are capped by a pure boron particle encapsulated at the tip



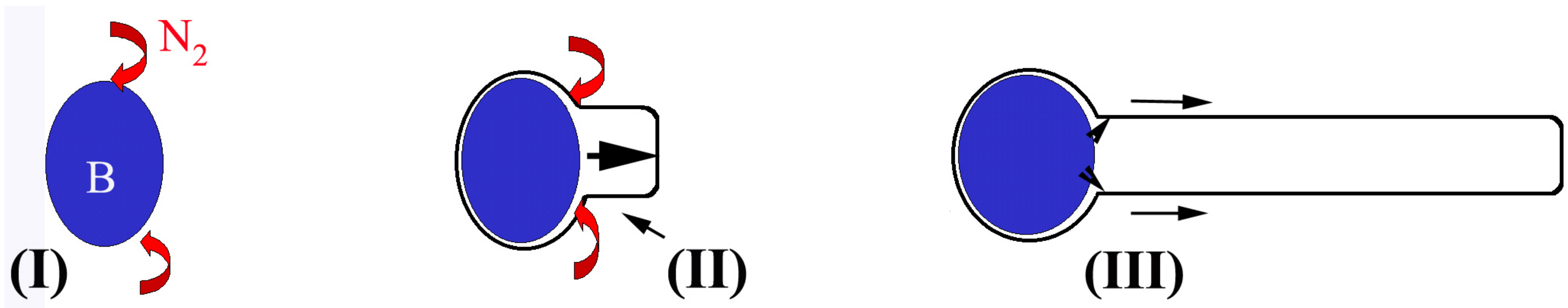
Boron encapsulated in a h-BN cage is oxydized at its surface

(Lee et al, Phys Rev Rapid Comm 2001)

Analysis of the NT formation process



- Nanotubes form and grow from a boron particle
- Synthesis proceeds via chemical reaction between B droplet and nitrogen
- Direct solidification of B droplet gives rise after contact with air to H_3BO_3
- O dissolved in B droplet inhibits the reaction B-N_2



T≤ 2700K
Reaction of B with N_2

Incorporation of N in active sites

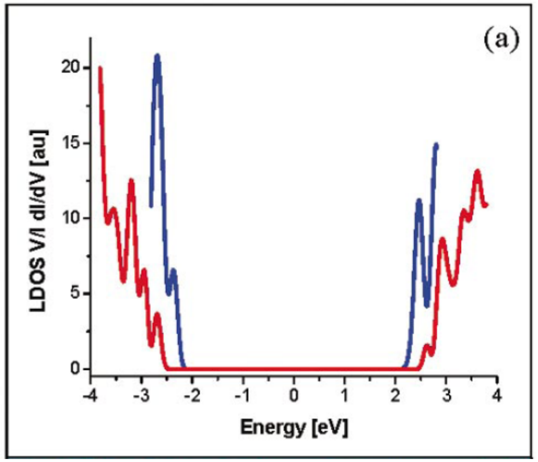
T < 2100K
Growth until B solidification

(R. Arenal et al, JACS (2007))

How to investigate electronic properties?

- Problems of interest:
  - gap determination (~ 6 eV)
  - study of the characteristics due to the 1D character of the electronic structure

- Difficulties:
  - energy of the gap
  - lack of reliable data on h-BN due to the paucity of large crystals
  - techniques used for C nanotubes are not suitable (Raman, STM/STS …)



Scanning tunneling spectroscopy on BN-MWNTs

R. Czerw *et al* APL **83**, 1627 (2003)

Important Stark effect

M. Ishigami et al PRL 94, 056804 (2005)

Our Approach

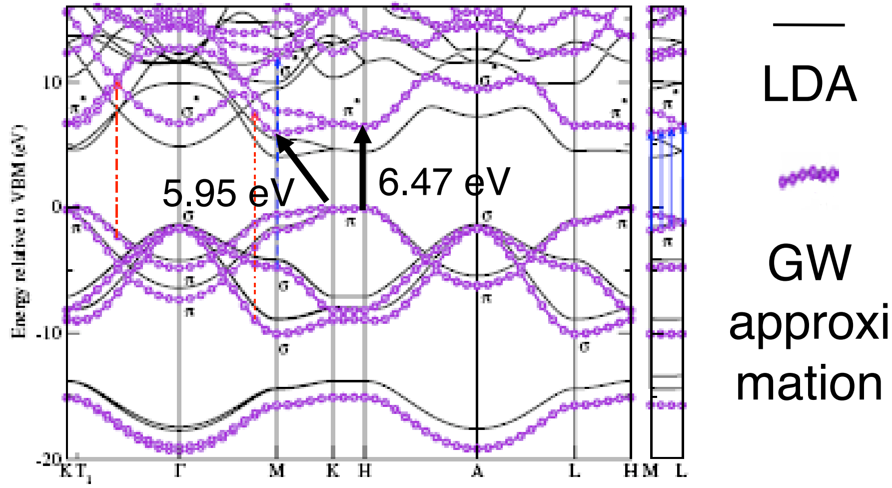
- Experimental approach:
  - study of the optical properties in the UV range
    BN-SWNTs and MWNTs of different kinds
    h-BN as reference material

- Techniques:
  - low-loss EELS of individual tubes
  - absorption of macroscopic assemblies of tubes
  - photoluminescence of macroscopic assemblies of tubes
  - cathodoluminescence of individual tubes

- Theoretical framework:
  - numerous recent ab initio studies on h-BN and BN-NTs (2006)
  - luminescence dominated by excitons of large binding energy

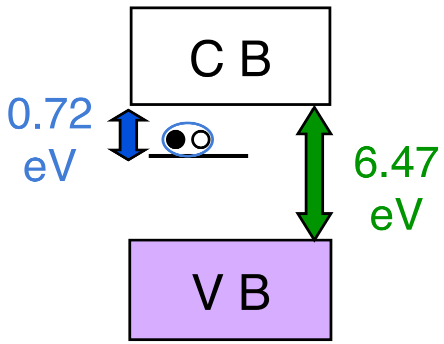
Electronic structure and excitons in h-BN

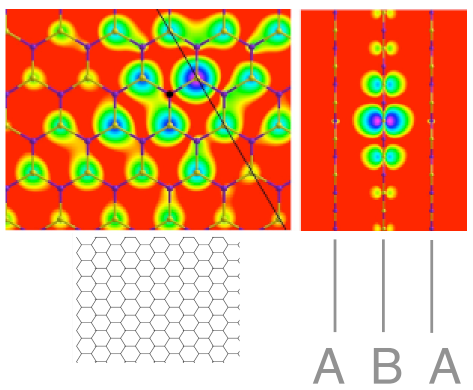
- DFT in the LDA approximation
- GW quasi particle approximation:
  - indirect gap = 5.95 eV / 4.46 eV (LDA)
  - direct gap = 6.47 eV / 4.02 eV (LDA)
  ($\pi - \pi^*$ transitions)



Band structure of h-BN

- Bethe Salpeter equation:
  - calculation of optical response $\varepsilon(\omega)$ with electron-hole interactions
  - localized excitons (Frenkel) 5.78, 5.78, 5.82, 5.85 eV
  - binding energy = 0.72 eV





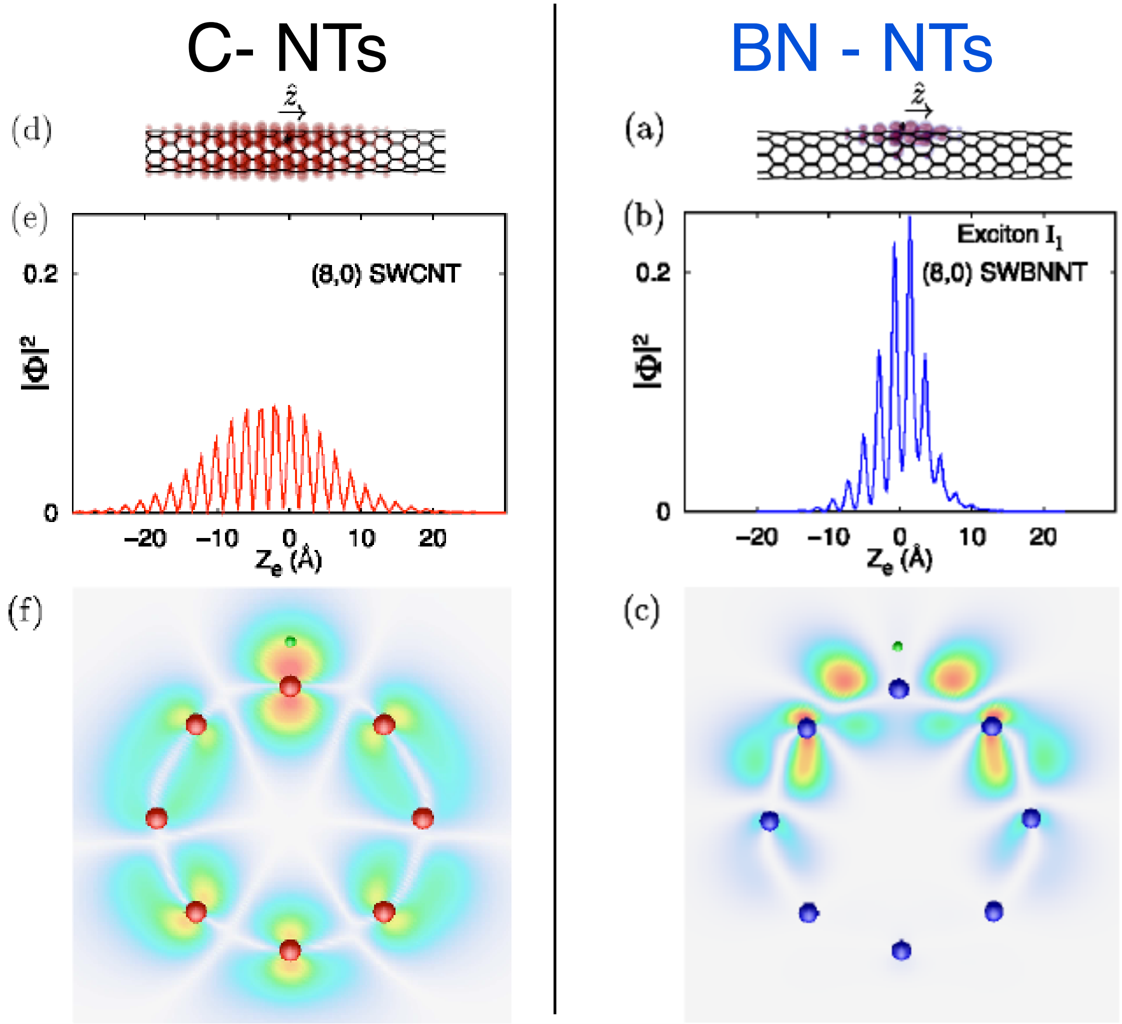
Electron - hole pair density probability in h-BN

X. Blase et al, Phys. Rev. B 51, 6868 (1995)
B. Arnaud et al, PRL 96, 026402 (2006)
L. Wirtz et al, Cond. Mat., 0508421 (2005)

Electronic structure & excitons in BN-NT

- DFT - LDA + GW
- Bethe Salpeter equation

  - larger gap
  - stronger excitonic effects
  - very localized excitons (Frenkel class)
  - binding energy = 2.1 eV



C-H Park et al, PRL 96, 126105 (2006)
L. Wirtz et al, PRL 96, 126104 (2006)

Electron - hole pair density probability in C & BN (8,0) SWNT corresponding to the lowest exciton energy

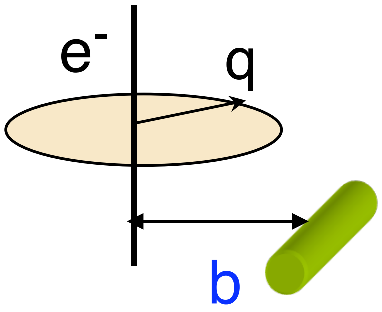
Optical measurements

- Electron energy loss spectroscopy
- Absorption in UV
- Luminescence in UV

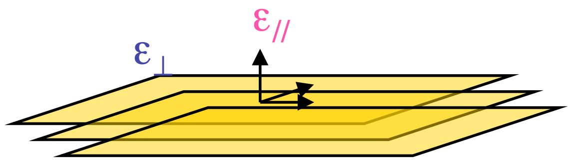
1 - Electron energy loss spectroscopy

- Low-EELS: excitation of electronic states close to the Fermi level
- EELS-Low loss signal is a polarisability P(ω)

(A.A. Lucas et al PRB 49 (1994)



- In non penetrating geometry, exalted response of the surface
- At low energy (< 10 eV) for a SWNT:



$$P(\omega) \sim \mathrm{Im}(\varepsilon_{\perp}(\omega))$$

where $\varepsilon_{//}$, $\varepsilon_{\perp}$ are dielectric constants of bulk h-BN

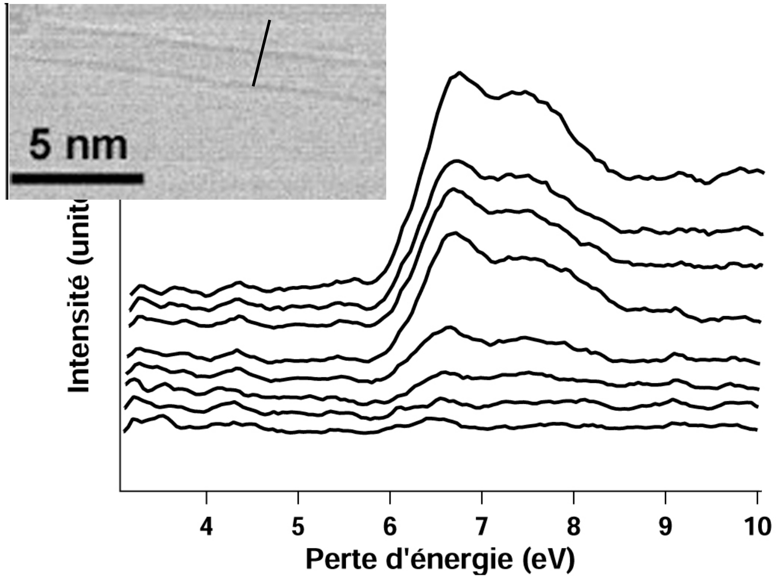
- Possible observation of optical transitions

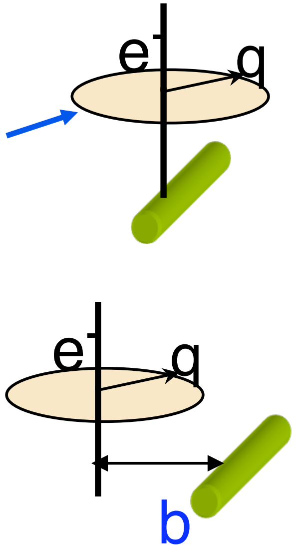
  $\pi\ \pi^*$ transition onset = optical gap

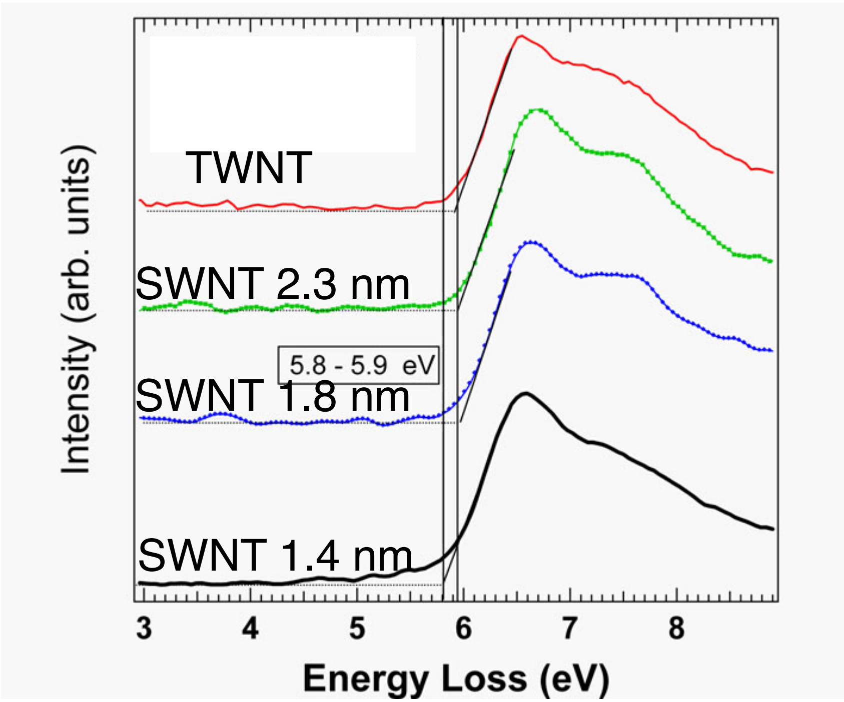
M. Kociak et al.
PRL **87**, 75501 (2001)
O Stephan et al. PRB **66**, 155422 (2002)

- Method: scanning of a nm probe across the NT in a STEM

Results







- Recording of spectra on individual tubes with a STEM (LPS Orsay)
  probe 0.5 nm, step 0.125 nm
- Simultaneous recording of the image

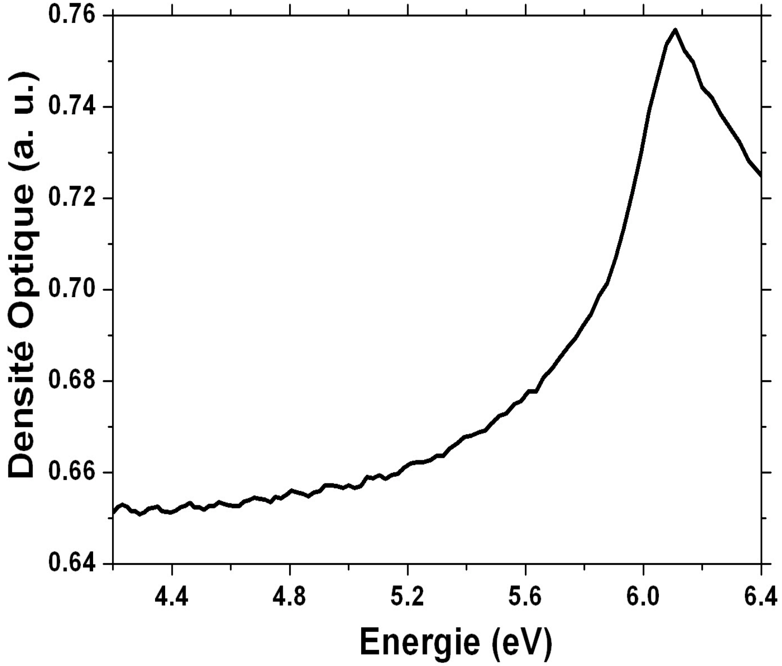
- Excitation onset :
  optical gap = ~ 5.8 - 5.9 eV

R. Arenal, O.Stéphan, M. Kociak, D. Taverna, A. Loiseau, C. Colliex, Phys. Rev. Lett.. 2005

2 - Optical absorption

<u>h - BN</u>

Microcrvstallites

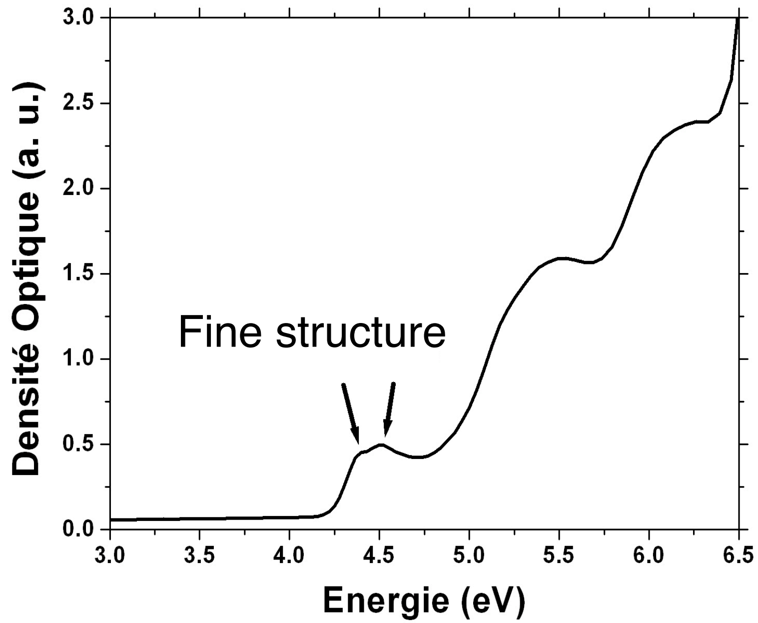


Band centered at 6.2 eV

Optical gap ~ 6 eV

<u>BN -SWNTs</u>

Partially purified macroscopic films



Two new bands: nature?

- 4.5 eV
- 5.5 eV

(A. Zunger *et al*, PRB, **13**, 5560, (1976))

J.S. Lauret, R. Arenal et al Phys. Rev. Lett. (2005))

2 - Luminescence experiments

- Photoluminescence (PL)
- Cathodoluminescence (CL)

ONERA dedicated set up

Excitation : photons

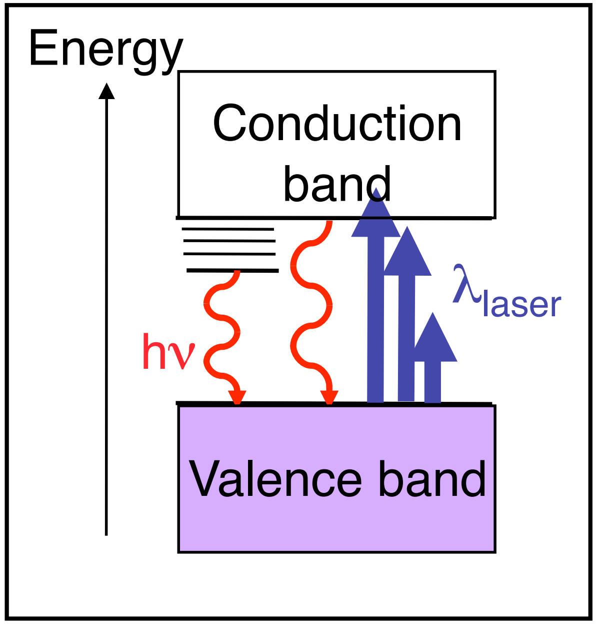
laser Nd:Yag

532 - 213 nm

laser excimer

248 and 193 nm

Temperature: 10 - 293 K



GEMaC (CNRS) set up

Excitation : e^- at 20 keV

- imaging in a MEB
- Temperature: 4 - 293 K
- Time-resolved experiments at EPFL Lausanne

☹ No imaging capability
Study of macroscopic samples

☺ Selective excitation

☺ Selection and imaging of individual objects

☹ Full excitation of the conduction band

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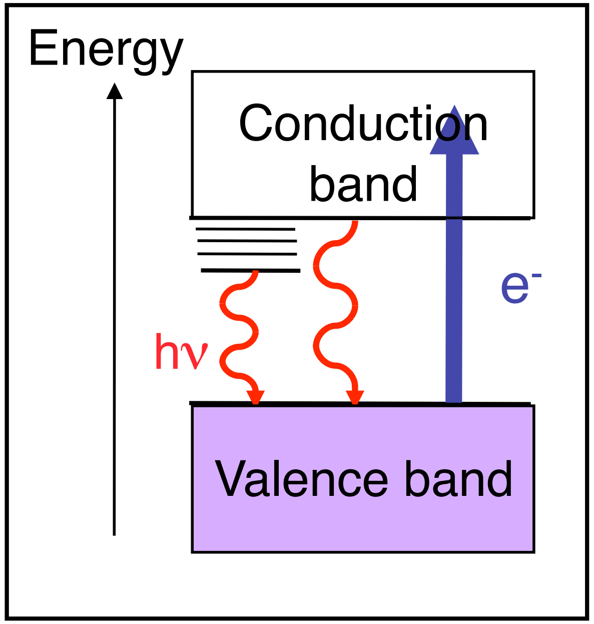

- Cathodoluminescence (CL)

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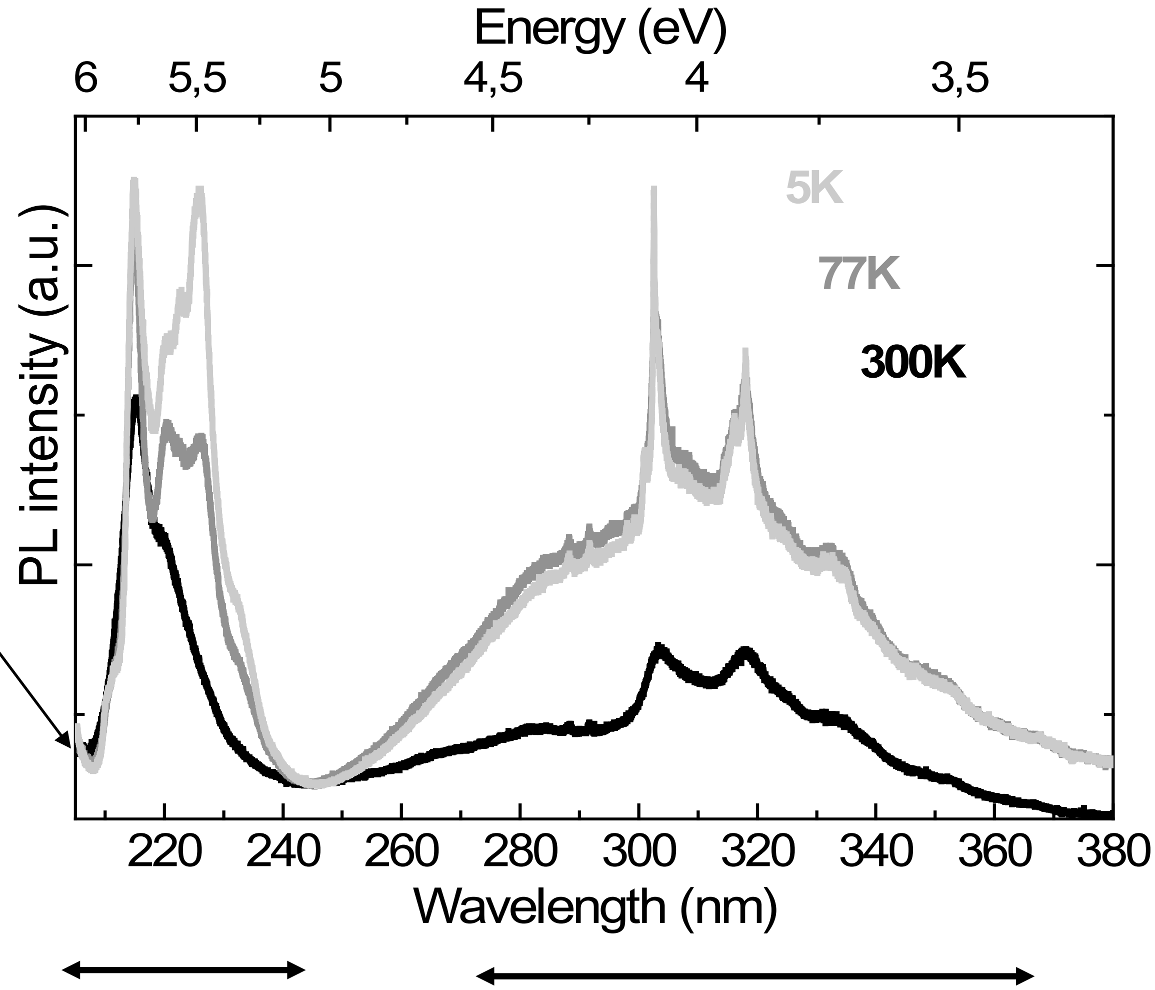
Full excitation of the conduction band

M. Silly et al
PRB, **75**,
085205 (2007)

Luminescence of h-BN



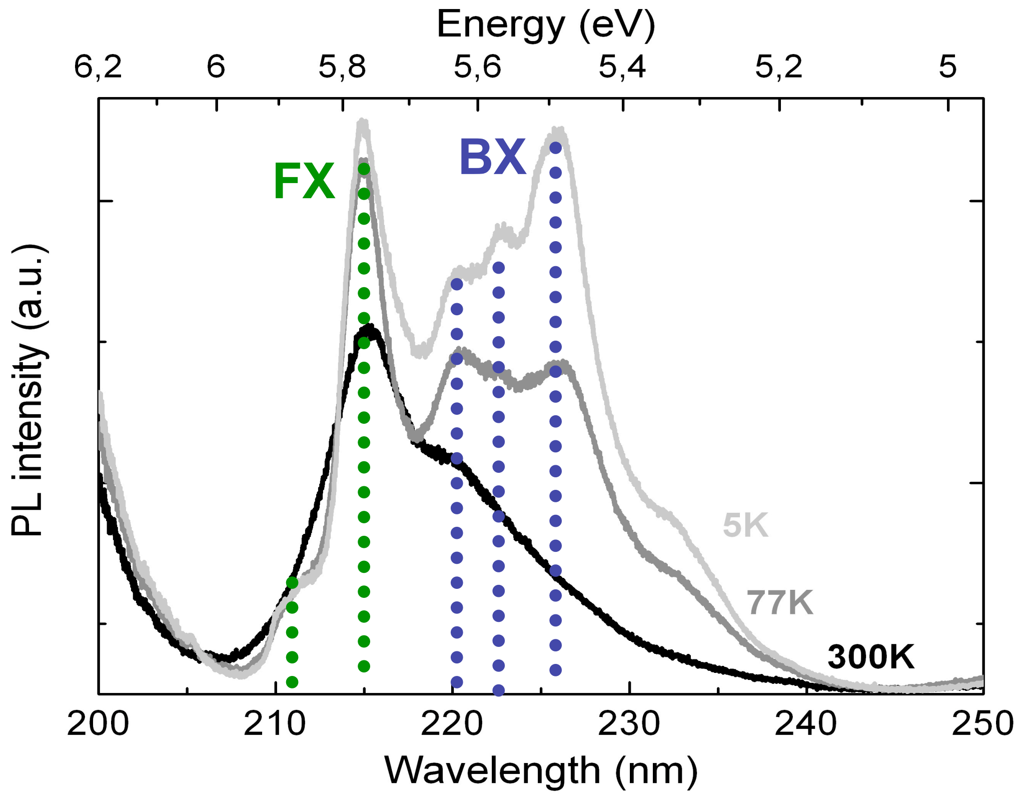
Optical gap ~ 6 eV

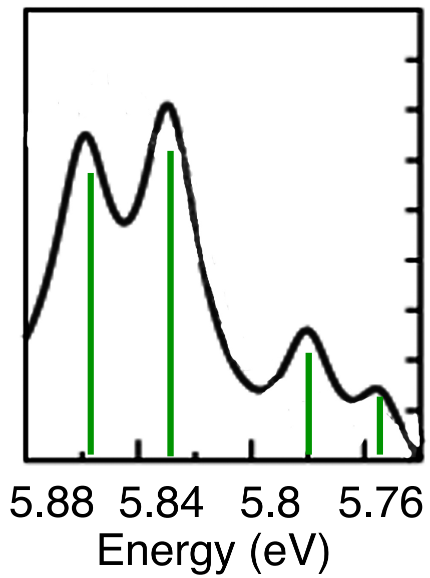
PL (193 nm) (6.42 eV) as a fn of temperature

Excitonic band related to the gap
Life time τ = 50 ps

Blue band due to defects with phonon replica: not the gap !
Life time τ = 1 ns

Analysis of the excitonic band





Calculated absorption
(Arnaud et al PRL (2006))

- Free excitons (FX):

  215 nm (5.77 eV), 211 nm (5.85 eV)

  life time $\tau = 50$ ps

  → agreement with calculations

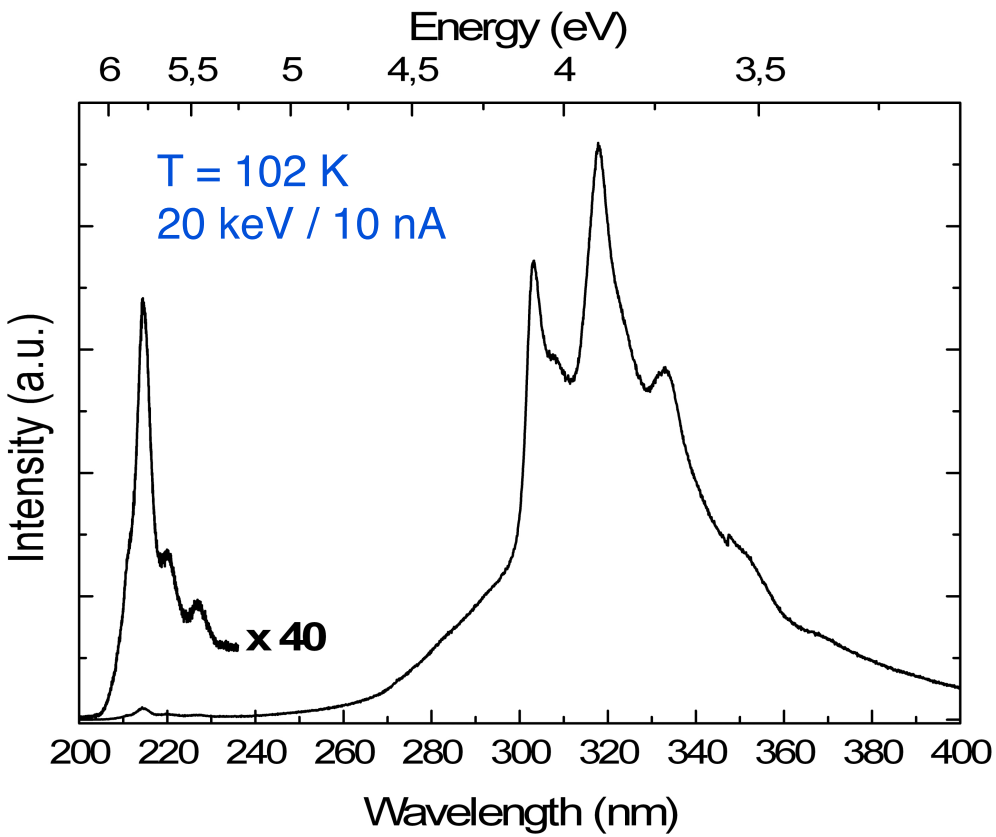
- Bound excitons (BX):

  220 nm (5.63 eV), 222.5 nm (5.57 eV),

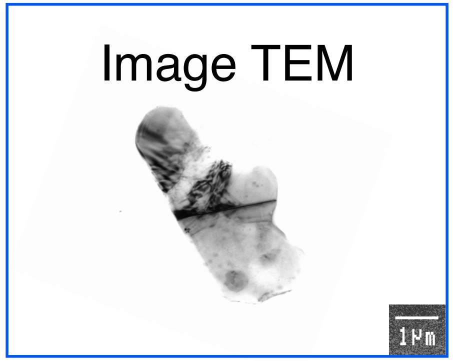
  226.5 nm (5.47 eV)

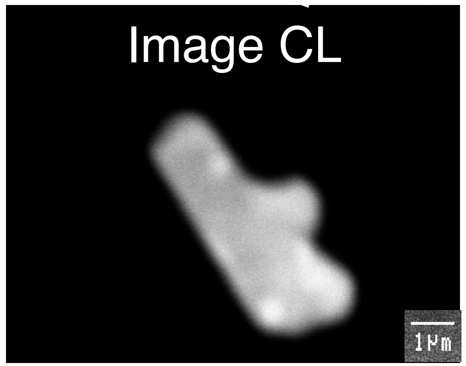
  → origin of these excitons?

Luminescence of a h-BN crystallite



Cathodoluminescence spectrum of the crystallite

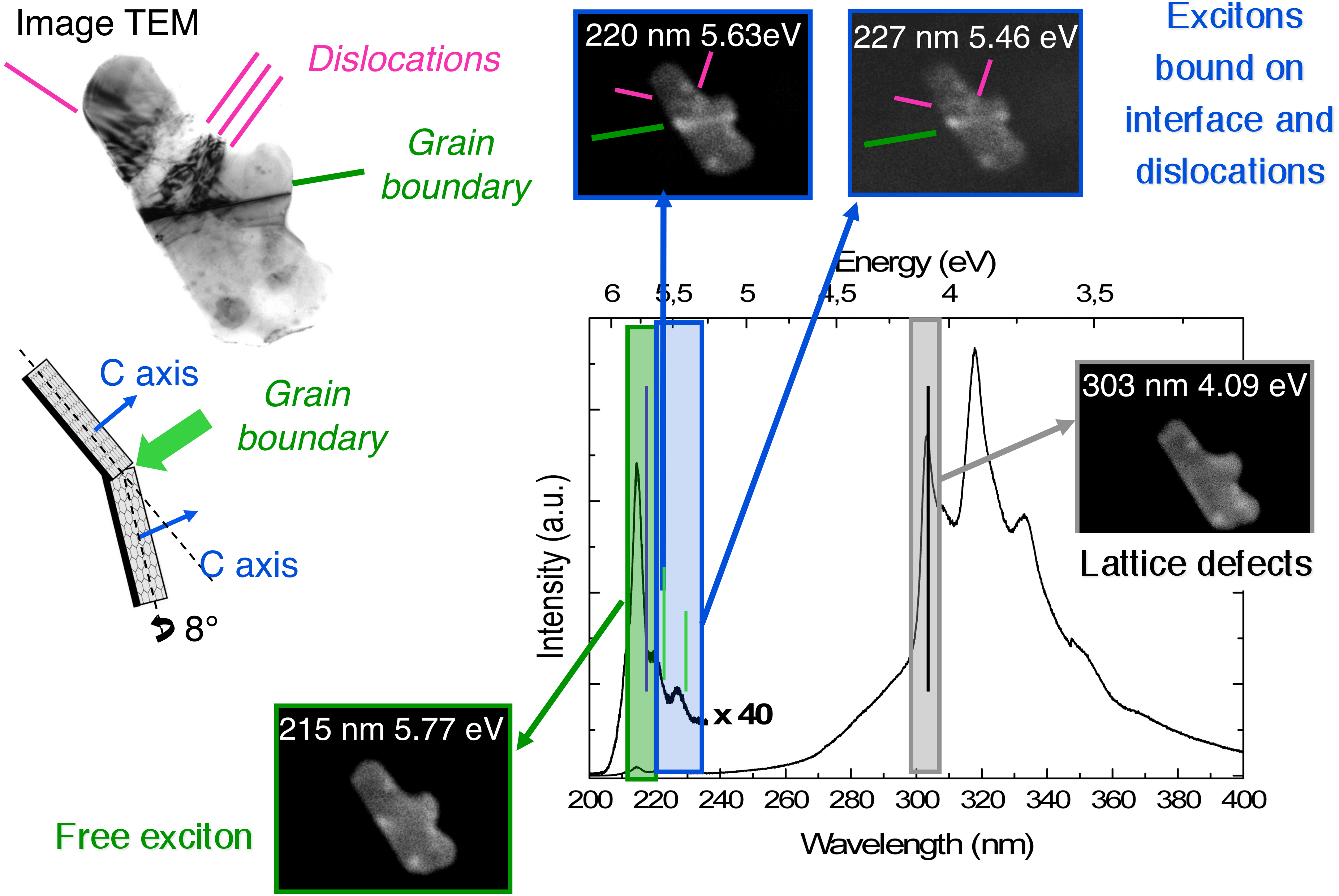




TEM and CL images

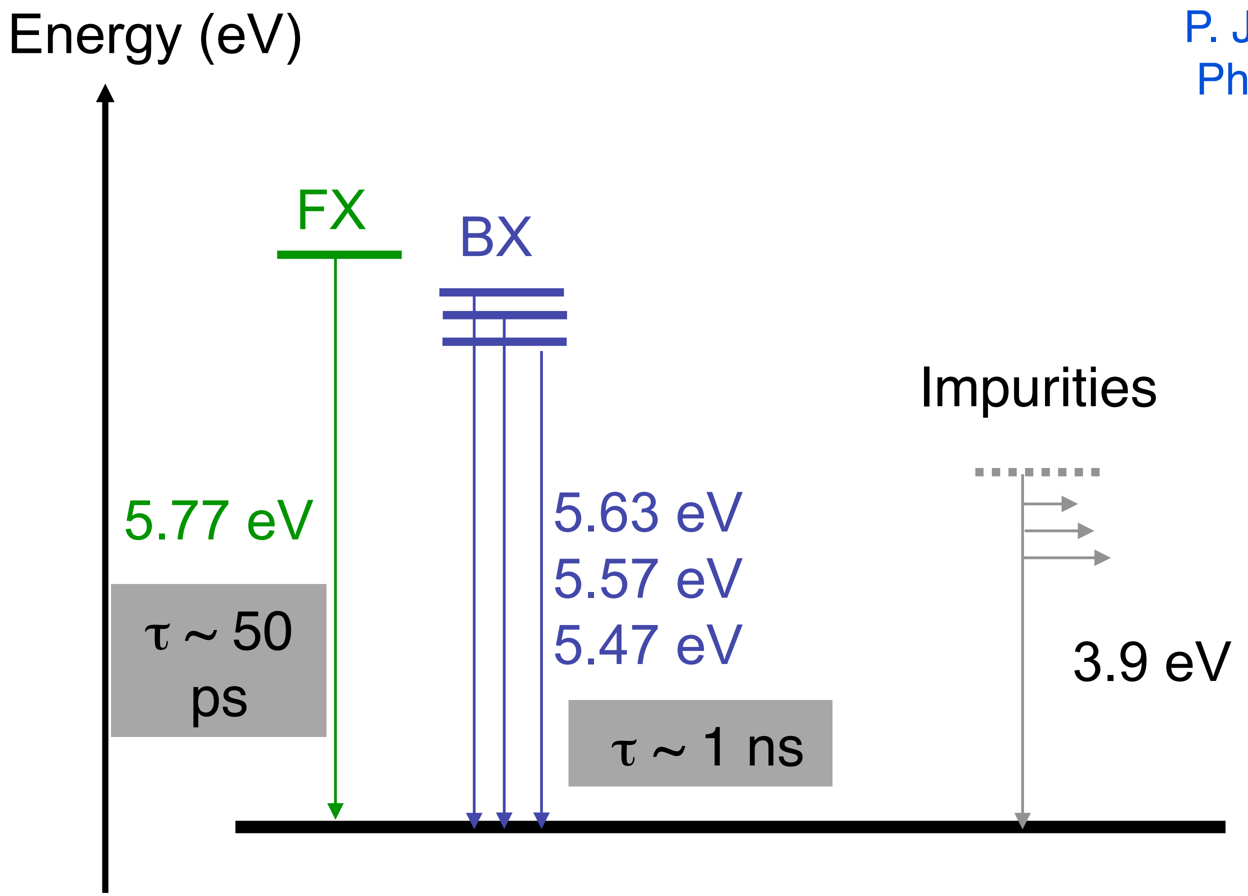
(P. Jaffrennou et al, J. Appl. Phys.(2007), PSS (2008))

Luminescence of a h-BN crystallite



Conclusion on h-BN

P. Jaffrennou et al,
Phys. Rev B (2008)

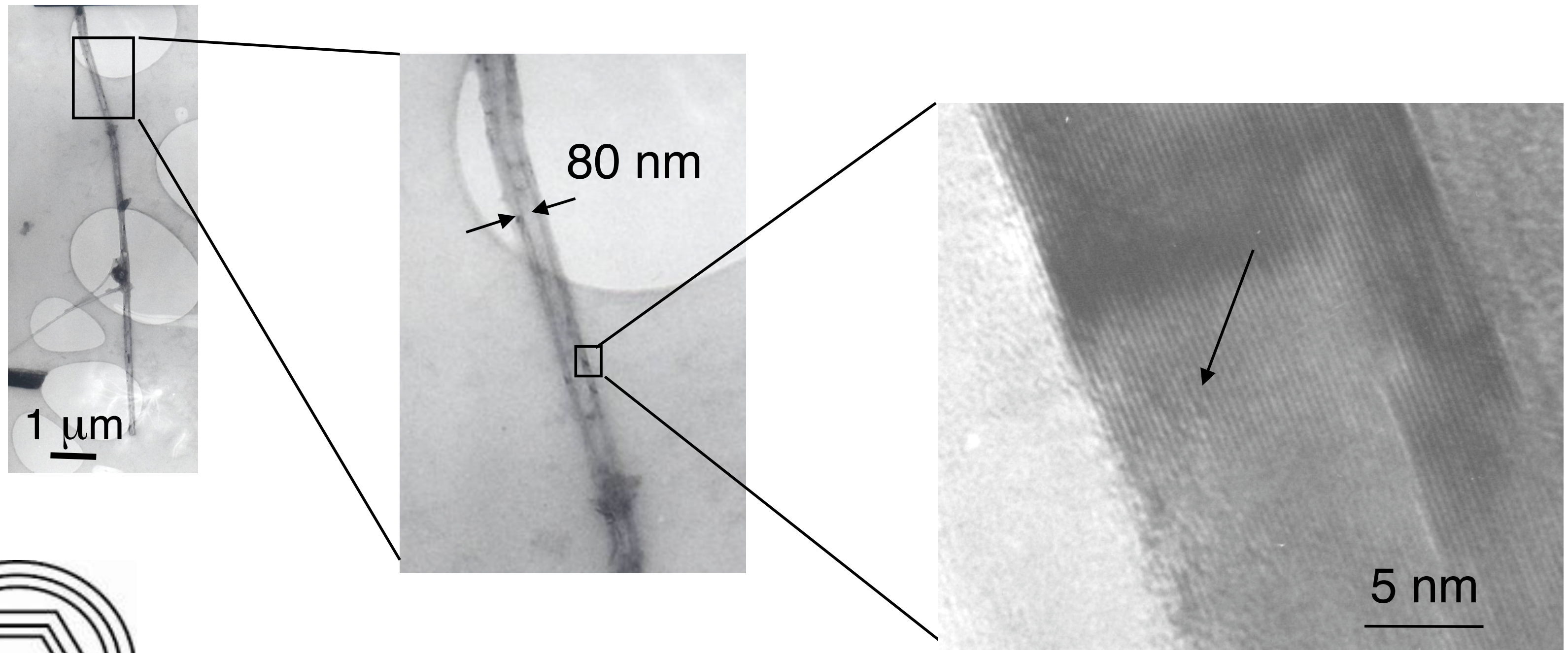


BX : binding to grain boundaries, dislocations

Existence of BX recently confirmed by PLE experiments on synchrotron (Museur et al, P. Appl. Phys. (2008)

Luminescence of MWNTs

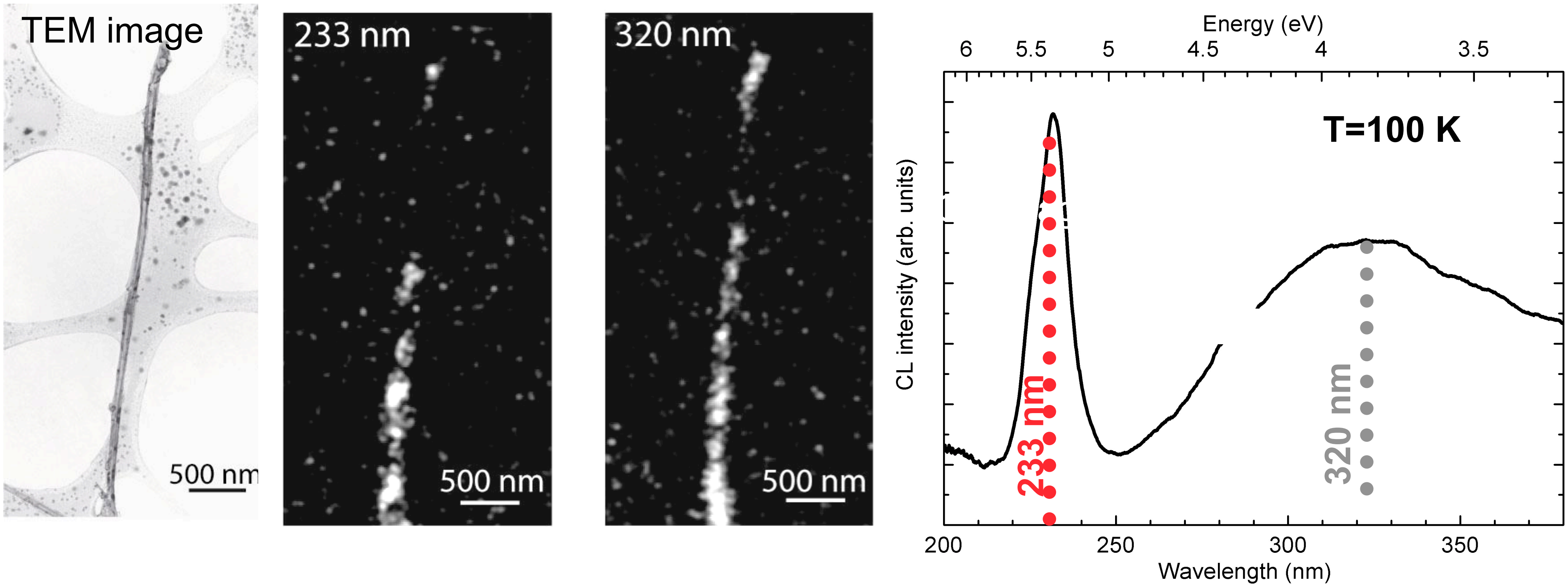
(NIMS Japan)



- About 50 walls
- Faceting, stacking faults and dislocations

Cathodoluminescence of a MWNT

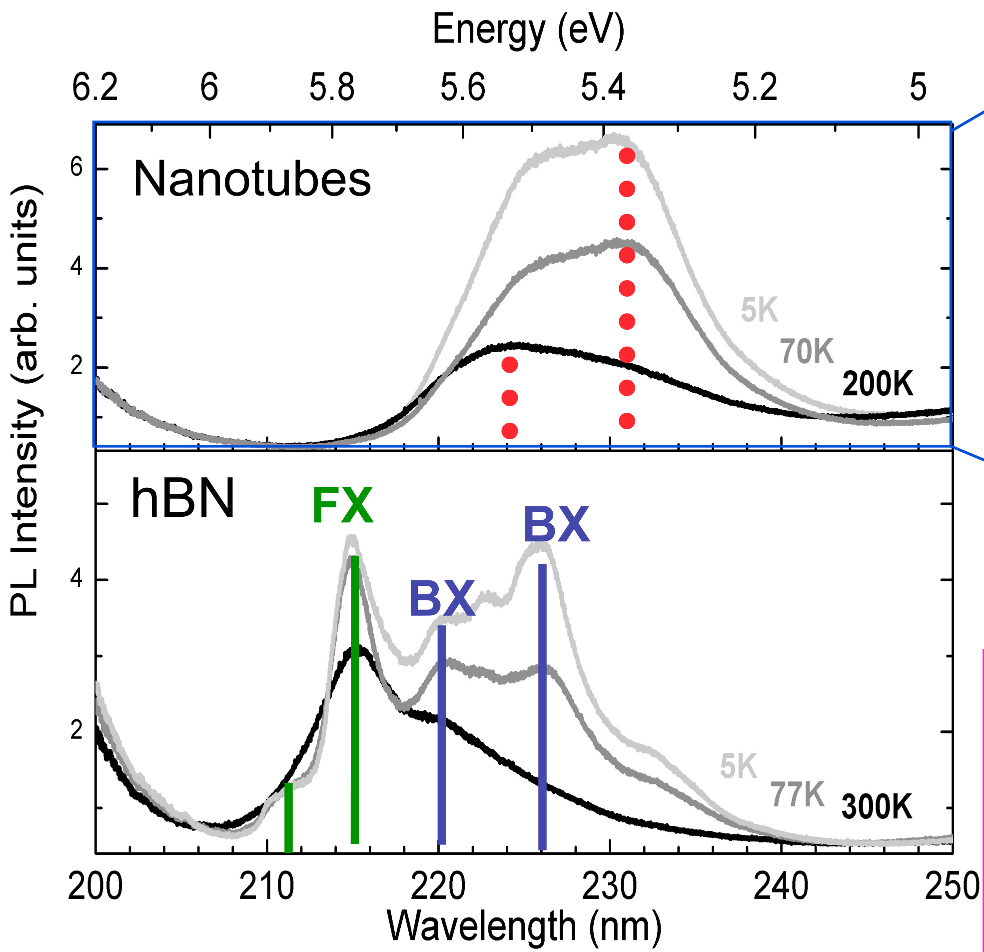
P. Jaffrennou et al, CPL (2007).

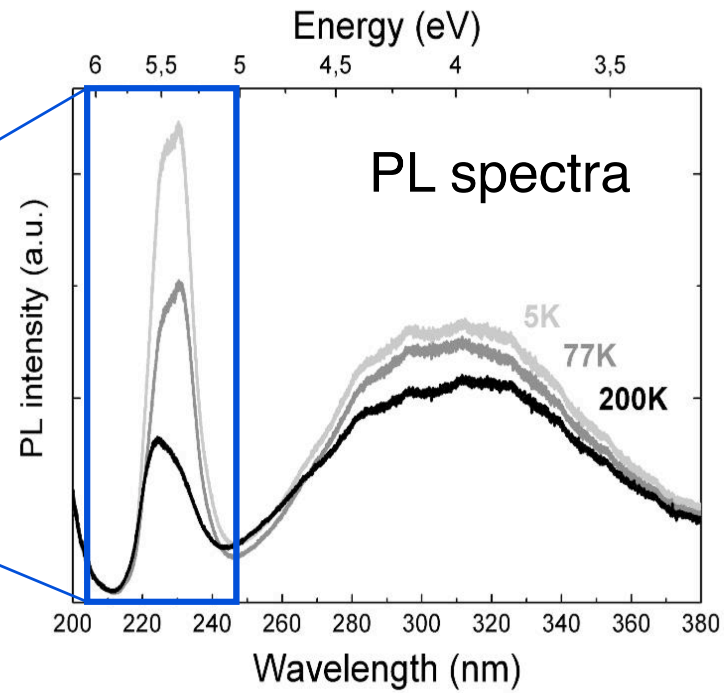


CL spectrum of individual tubes:

- blue band of defects at 320 nm as for h-BN
- excitonic band centered at 233 nm instead of 220 nm

PL (193 nm) : BN - MWNTs versus h-BN





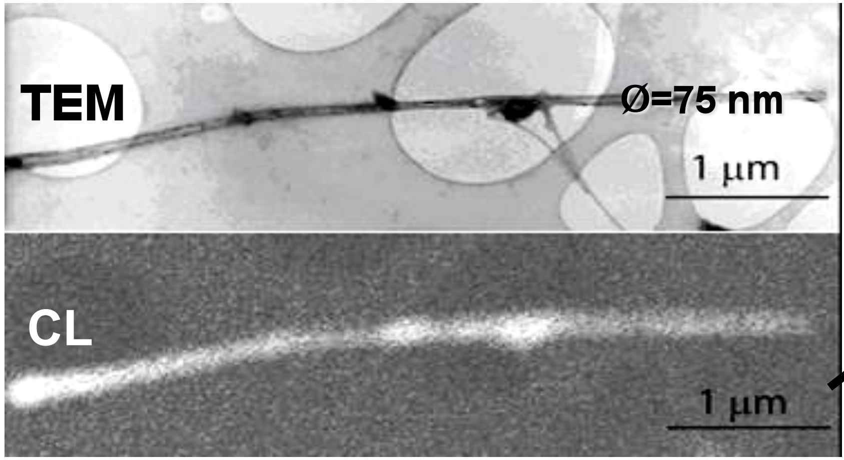
- No shift of the band of defects
  - Excitonic band is red shifted:
    - two emissions at 224 and 230 nm with variable intensities

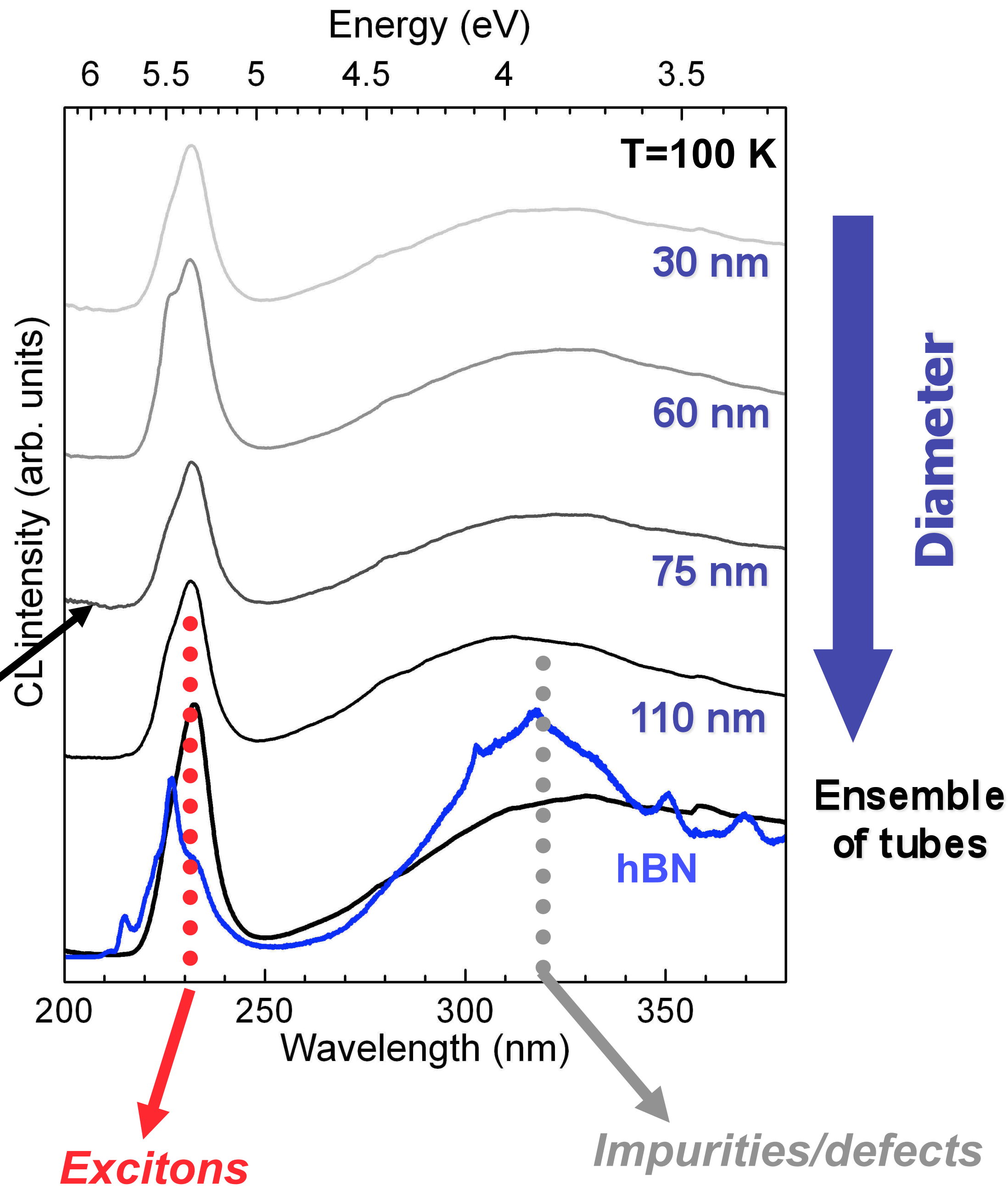
Origin of the shift?

- Red shift of the free exciton with respect to h-BN?
- Nature of the excitons?

Effect of diameter on CL spectra

Images and spectra of individual
multiwall BN nanotubes
with various diameters



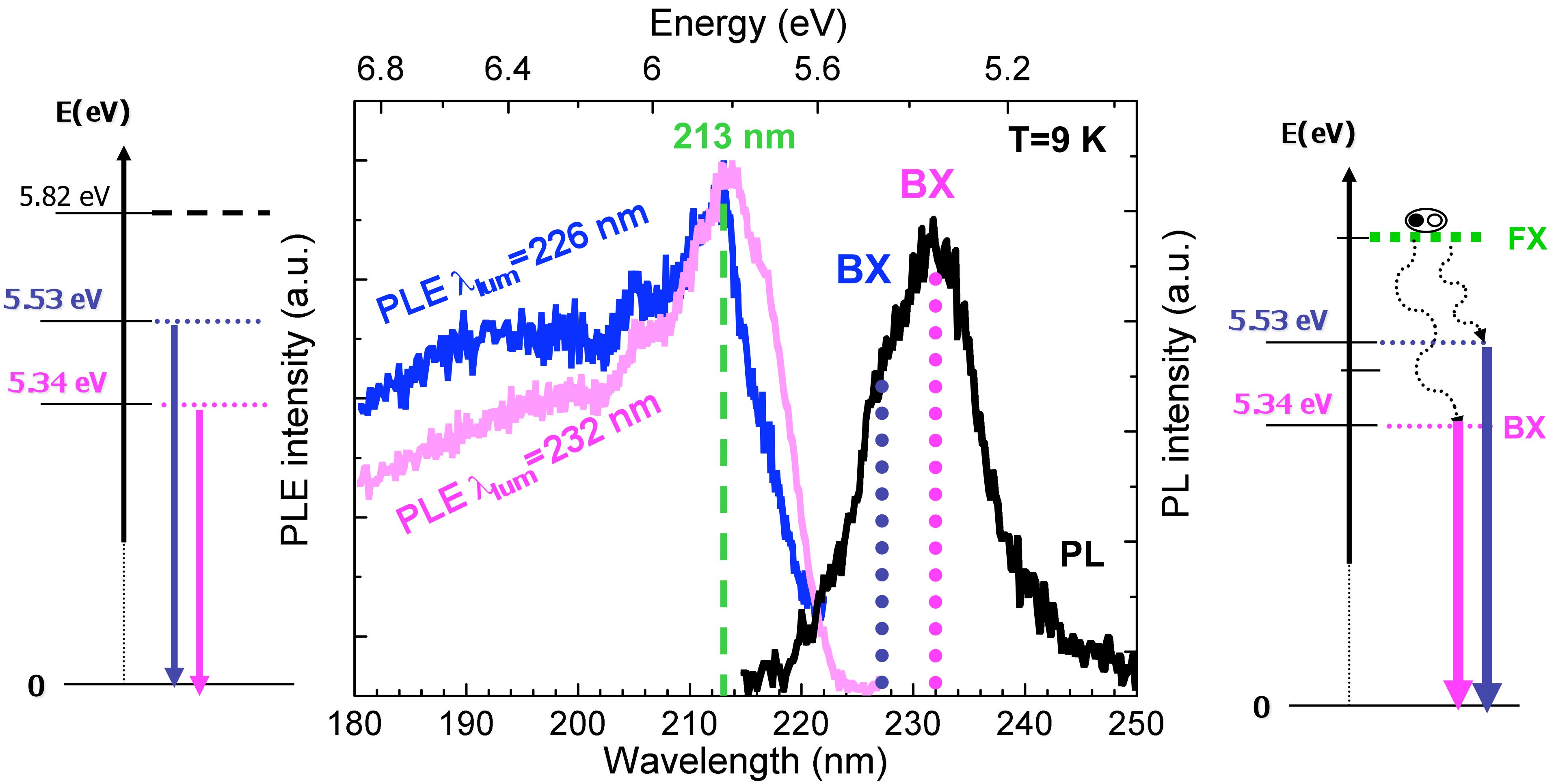


- No influence of the diameter within the range 30 - 110nm
- No confinement effect can explain the red shift

Museur *et al.*,
J. Appl. Phys. (2008)

PLE experiments

Synchrotron source
Hasylab Hambourg

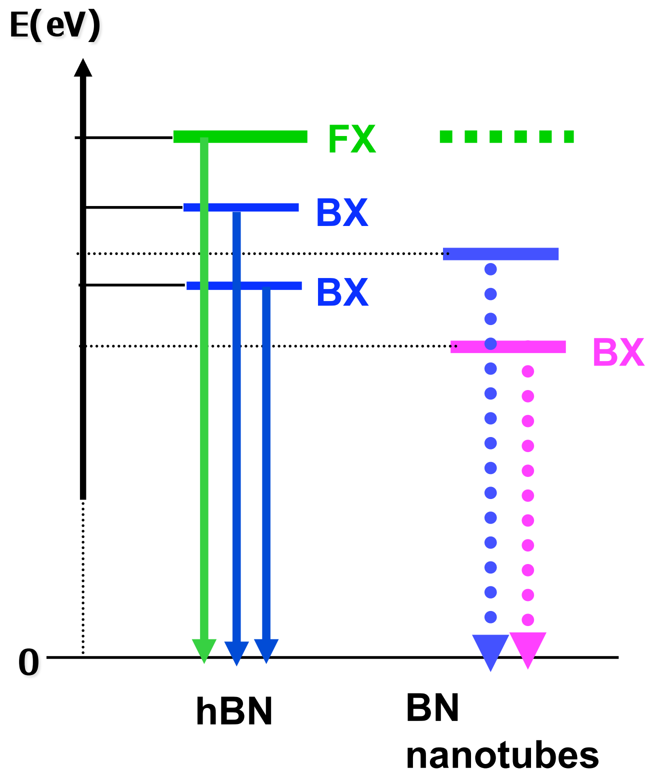


Maximum of PLE spectra at 213 nm (5.82 eV) = FX

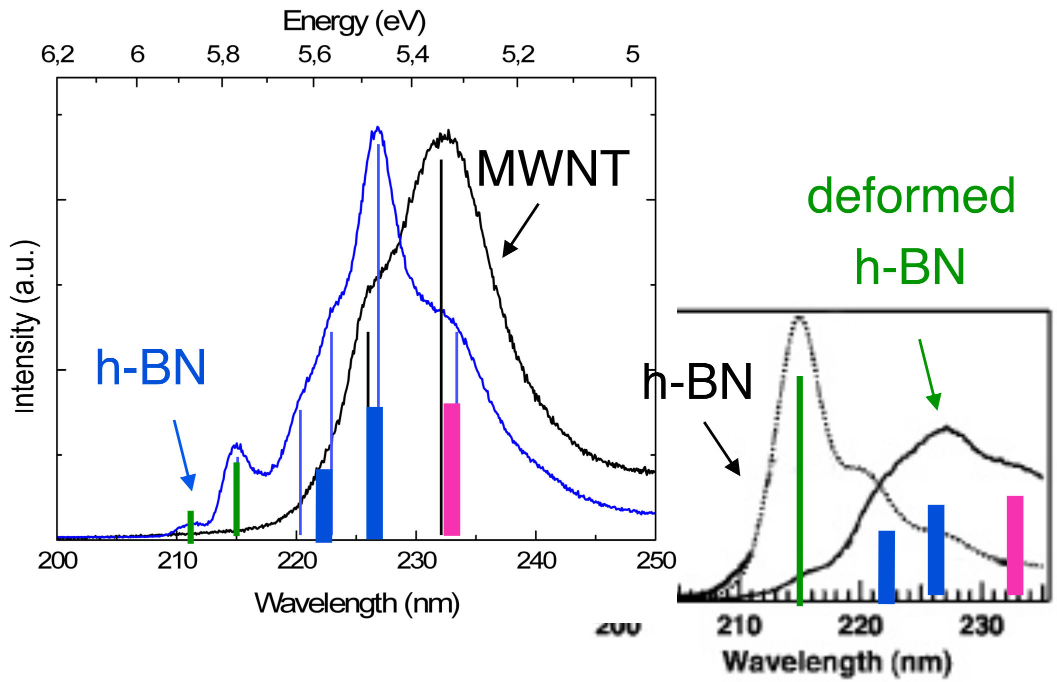
Similar spectra as the ones of BX of hBN (227 nm/5.46 eV)

Nature of the excitons in MWNT

- PLE evidence of free excitons of same energy than in h-BN
- Free excitons in MWNTs are not radiative
- Emission is favoured on excitons bound to defects
- Emission of MWNT is similar to that of deformed h-BN



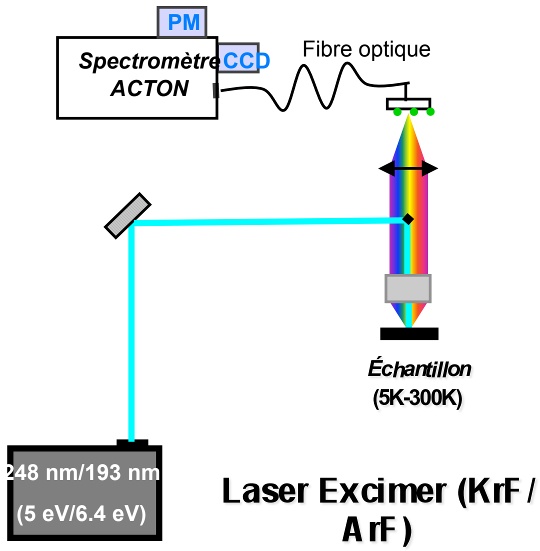
Jaffrennou *et al*., Phys. Rev. B. (2008)



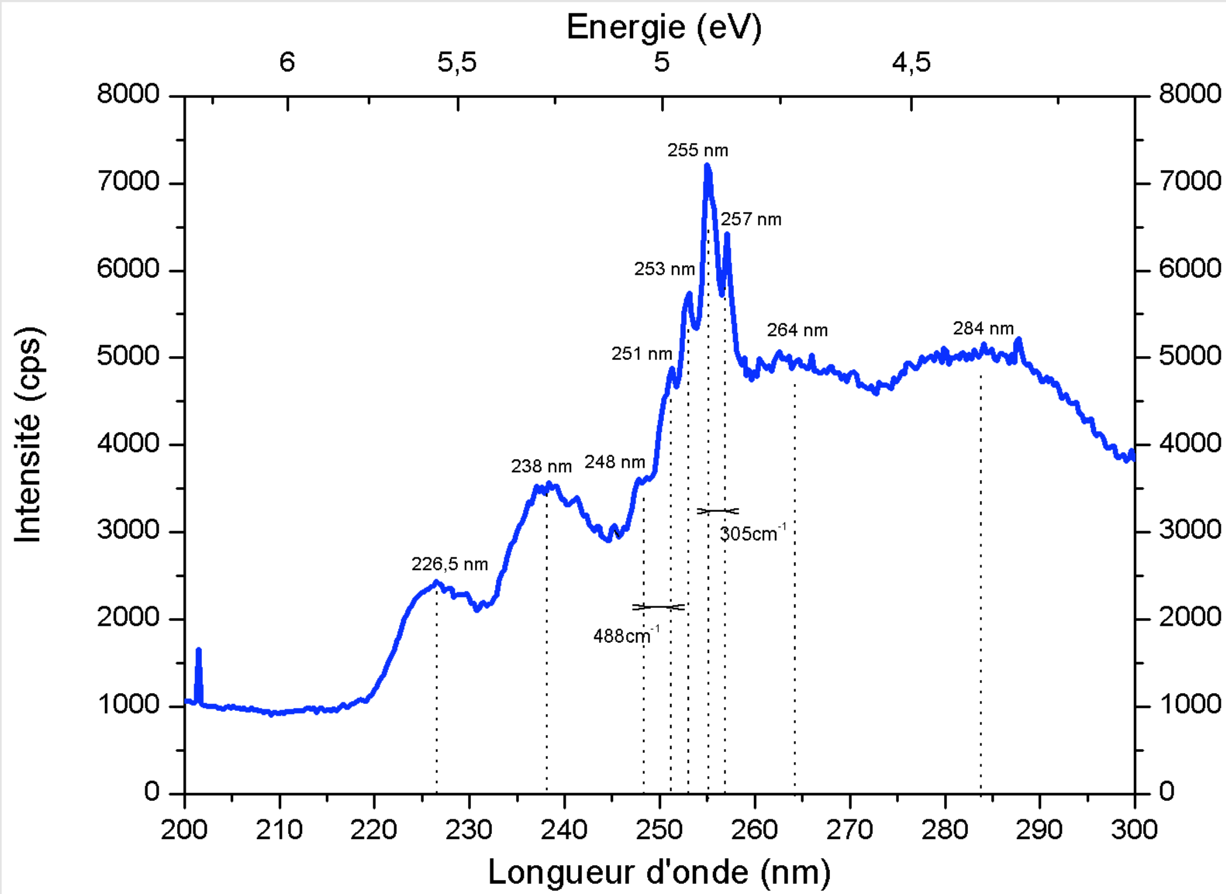
Watanabe et al APL 2006

Micro-PL on BN SWNTs

Preliminary results



Experimental set up



Conclusion and perspectives

- Large electronic gap in BN structures makes difficult its experimental determination and the study of the electronic properties:
- Good approach: combined measurements in absorption, photoluminescence, cathodoluminescence and TEM
  - study of SWNT and MWNT
  - reference material: h-BN crystallites

- Two luminescence bands identified in h-BN at:
  → 3.9 eV due to defects and 5.77 eV due to free Frenkel excitons
  → existence of both free and bound excitons

- Strong excitonic luminescence of large BN MW tubes at ~ 5.5 eV
  → no confinement effect
  → emission is due to bound excitons, free excitons are non radiative

- Next:
  - Microphoto- and cathodo- luminescence on SWNT