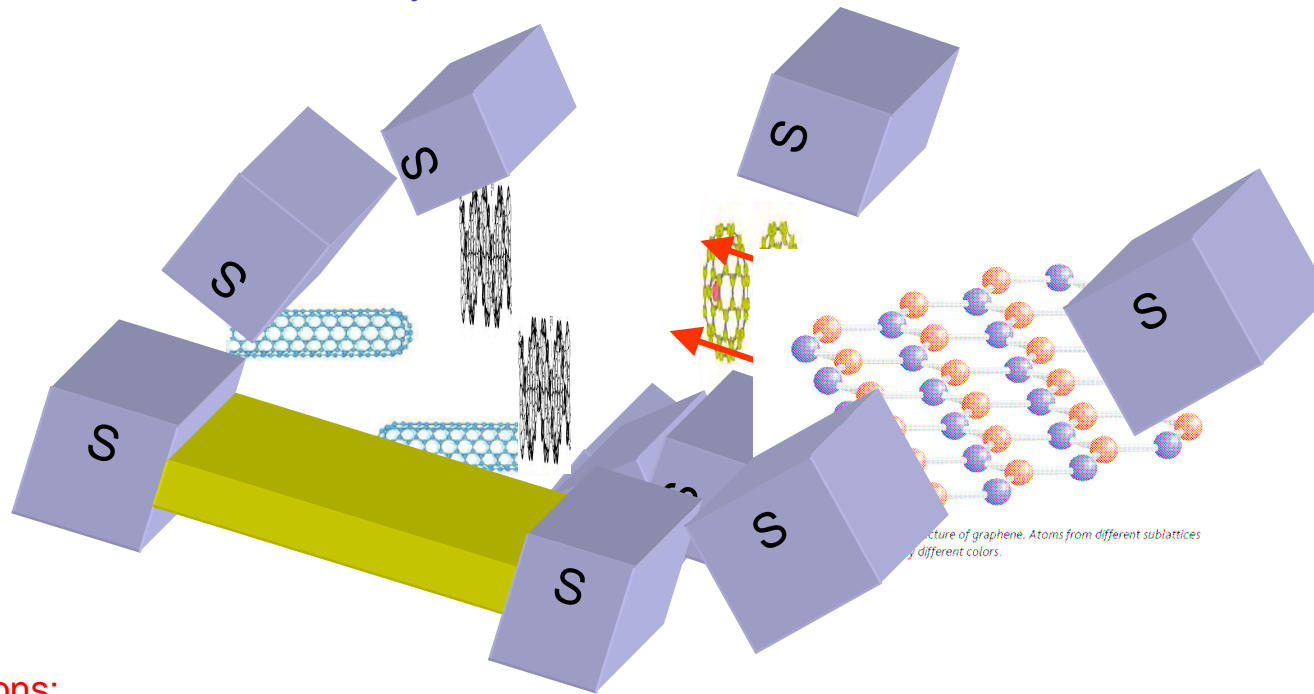


# Supraconductivité induite dans des fils métalliques et des molécules

L. Angers, F. Chiodi, A. Chepelianskii, C. Ojeda, A. Shailos, M. Kociak, P. Roche, M. Ferrier, R. Deblock, S. Guéron, A. Kasumov, B. Reulet, H. Bouchiat,

Laboratoire de Physique des Solides  
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L. Buchailot, V. Agache, A-S. Rollier (IEMN Lille)

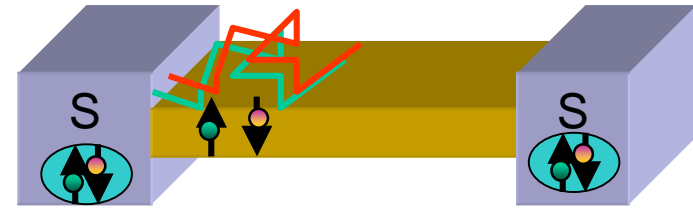
A.M. Bonnot (Grenoble)

O. Pietrement, E. Le Cam (IGR Villejuif); S. Lyonnais, J-L. Mergny (MNHN Paris)

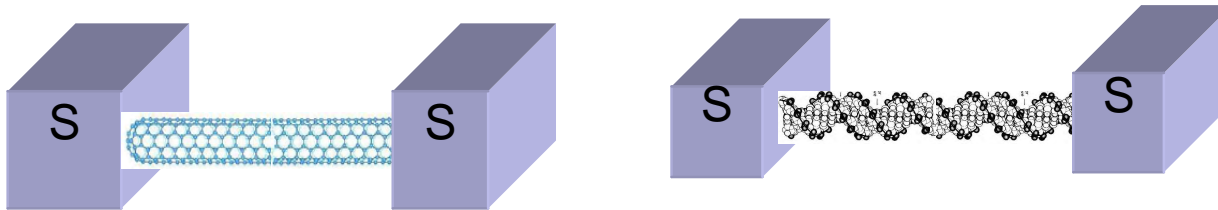
## The superconducting proximity effect in metals and molecules

- What is the superconducting proximity effect?

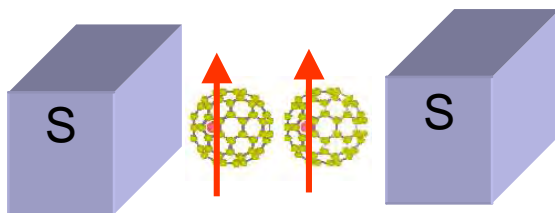
- The classical proximity effect: dc squids made of long SNS junctions, where N is a metal ( $\mu\text{m}^3$ )



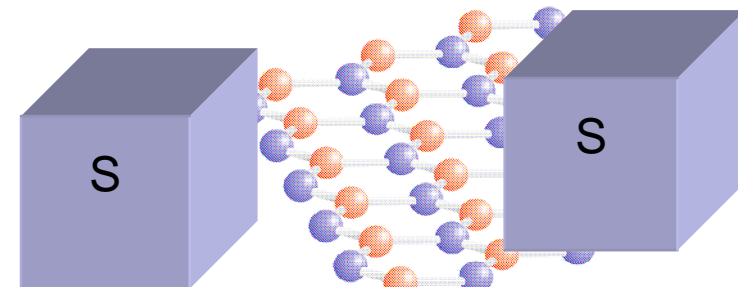
- S-Molecular wire-S junctions ( $\mu\text{m} \times \text{nm}^2$ ):  
suspended carbon nanotubes, DNA molecules



- S-Molecule-S junction ( $\text{nm}^3$ ): métallofullérène (molecule with spin)



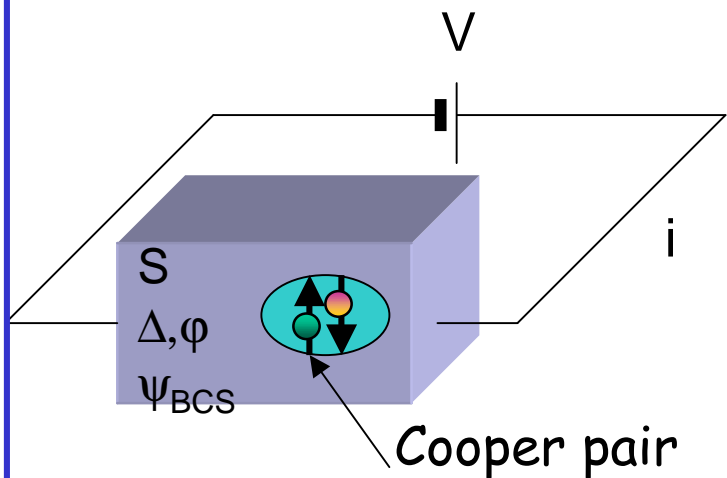
- S-Molecular plane-S junctions ( $\mu\text{m}^2 \times \text{\AA}$ ):  
graphene (several layers)



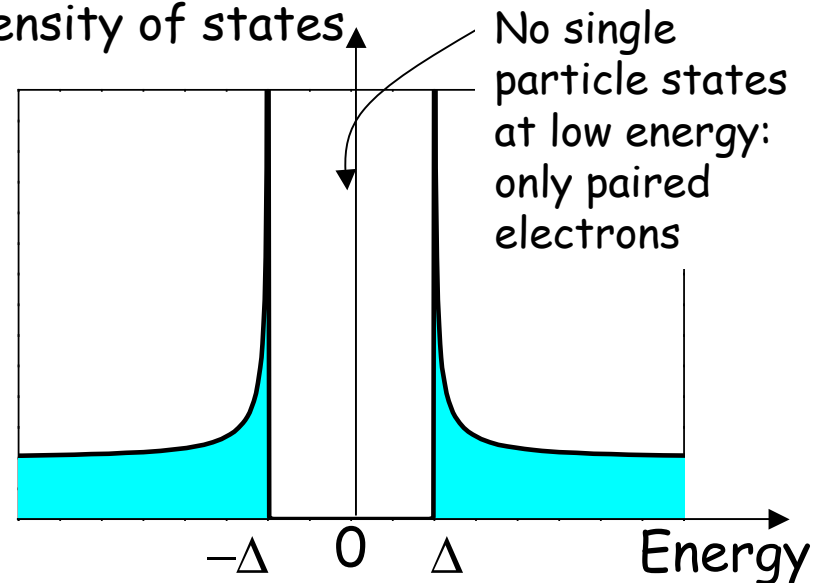
**What is the superconducting proximity effect ?**

# Ingredient number 1: Superconducting electrodes

What is a superconductor?

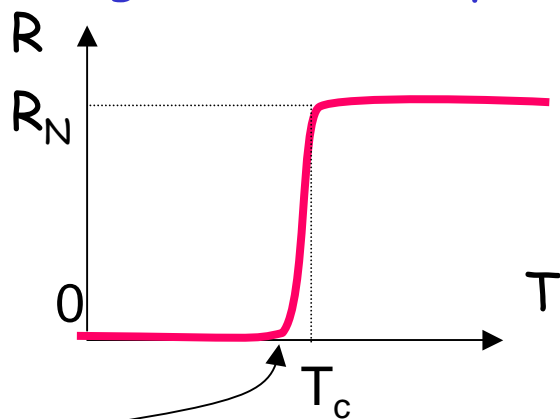


Density of states

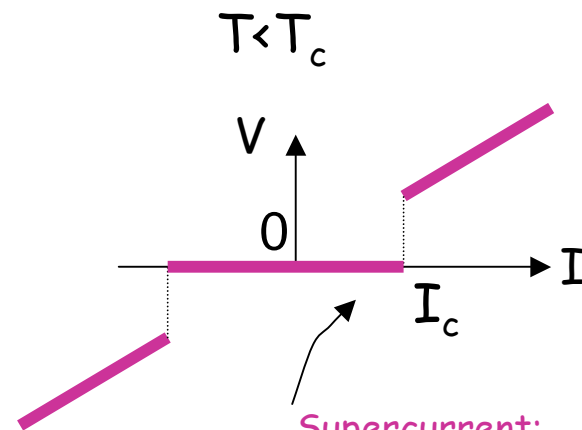


$\Delta$  = gap in the excitation spectrum, proportional to  $T_c$

Electrical signatures of superconductivity



Zero resistance state for  $T < T_c$

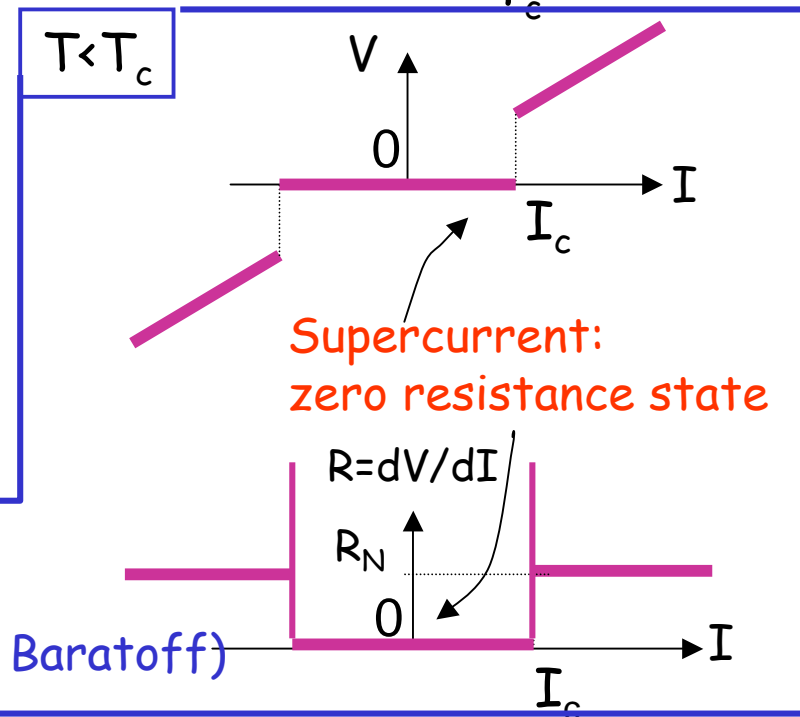
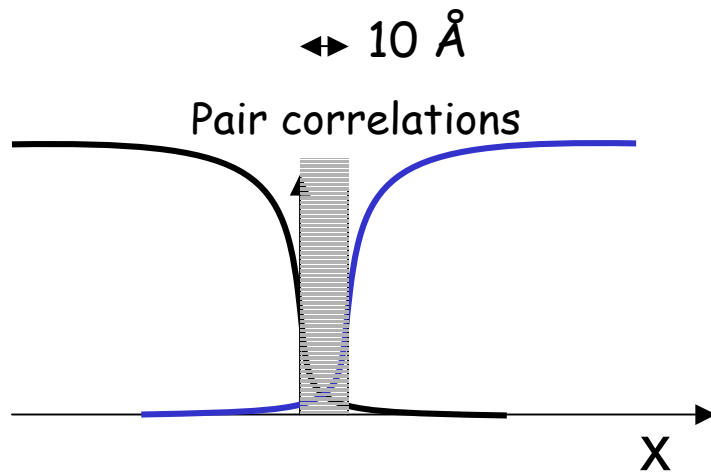
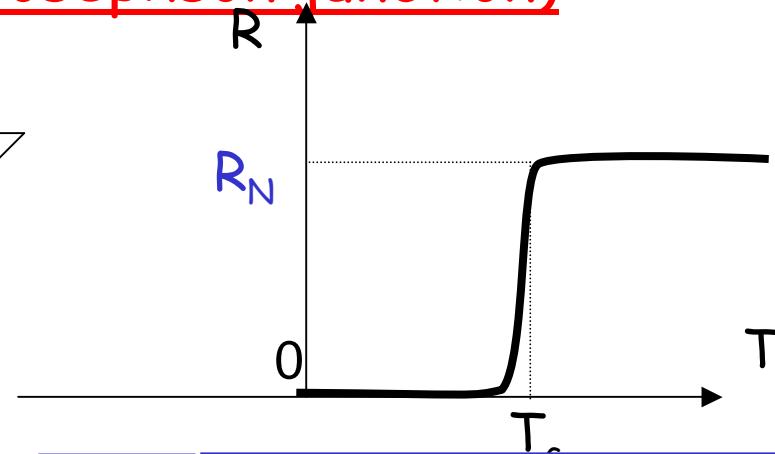
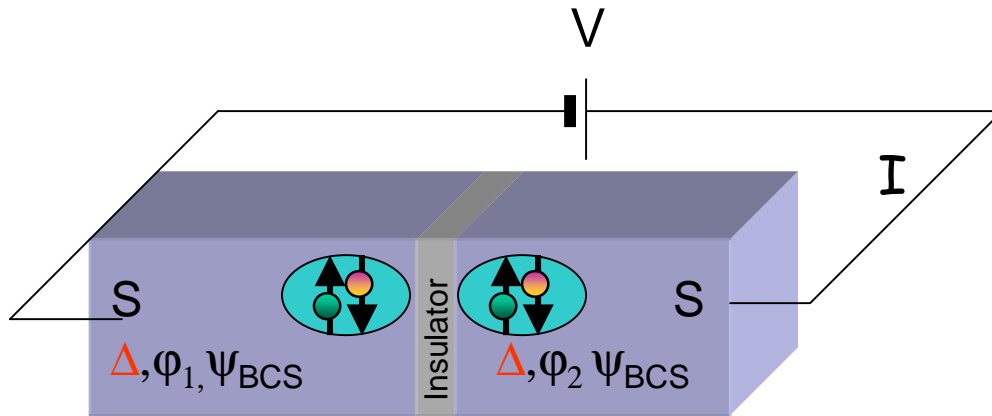


Supercurrent:  
zero resistance state

Example amongst metals: Al, Ta, Re,  $T_c \sim 1-5$  Kelvin

# Ingredient number 2: a non-superconductor

## Case 1: Insulator (the classical Josephson junction)

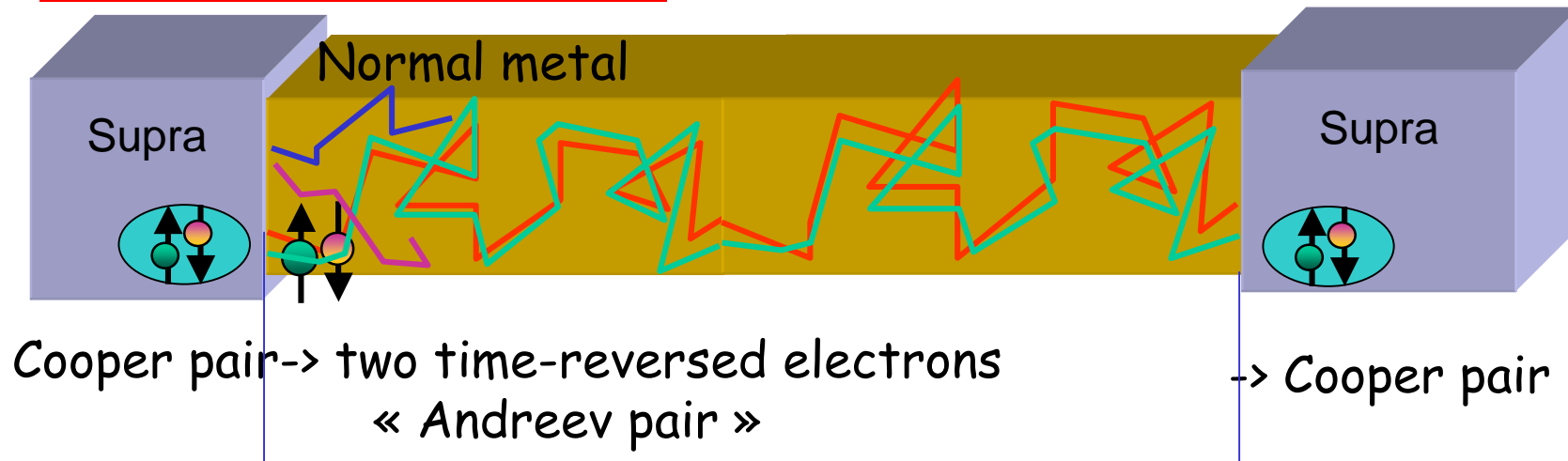


$$I = I_c \sin(\phi_1 - \phi_2)$$
$$I_c = \frac{\Delta}{e R_N} \text{ the big rule (Ambegaokar Baratoff)}$$

Pairs tunnel from one superconducting electrode to the other

## Ingredient number 2: a non-superconductor

### Case 2: a normal metal



Supercurrent if normal metal is quantum:

No change of state during diffusion from one S to other:

No spin flip, no e-phonon collision, no thermal fluctuations...

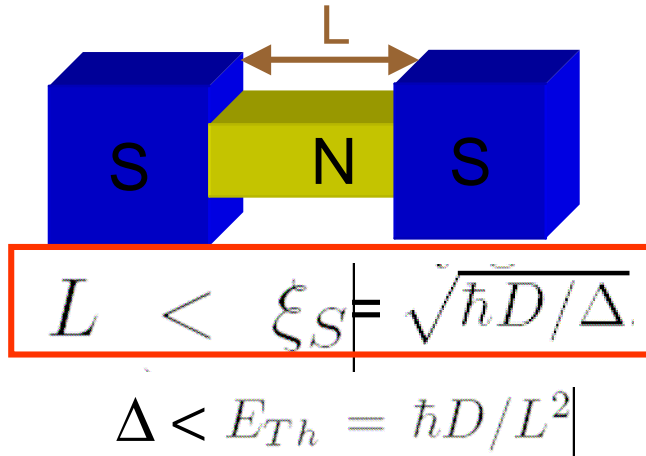
In practice: at low temperature S correlations can extend to microns in normal metals. The proximity effect probes quantum coherence and electron pair correlations.

### Case 3: a molecule

Superconducting proximity effect probes electronic properties of molecules (ground and excited states).

# Proximity effect in short junctions Vs long junctions

Short



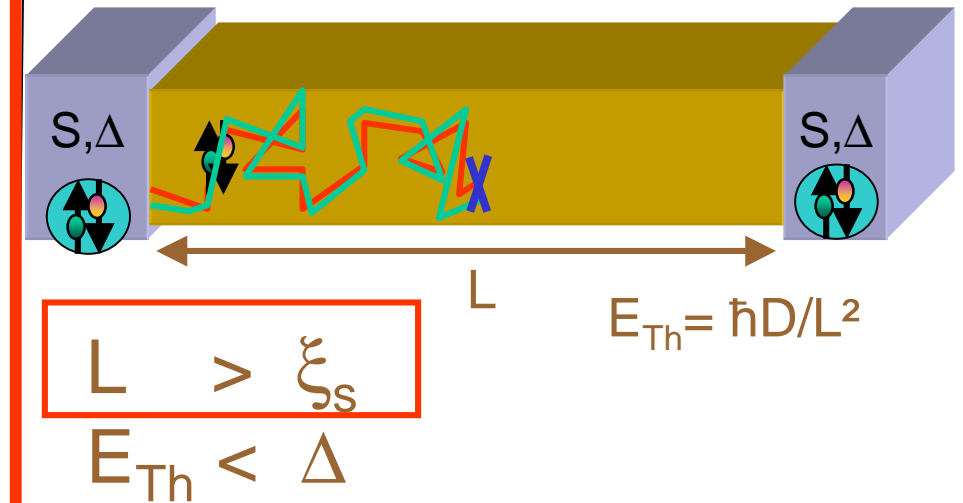
Induced gap in N  $\sim \Delta$

Critical current through N :

$$eR_N I_C(T = 0) = 2.07 \Delta$$

Learn about S

Long



Induced gap in N  $\sim E_{Th}$

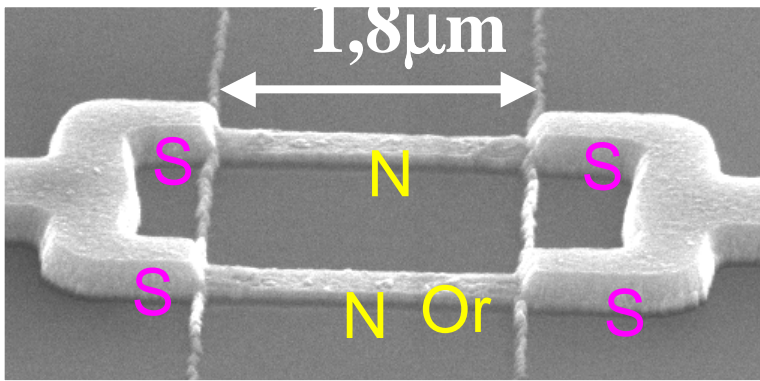
Critical current through N :

$$eR_N I_C(T = 0) = 10.82 E_{Th}$$

Dynamics of propagation in N

Learn about N!

# Effet de proximité « classique » dans des fils métalliques

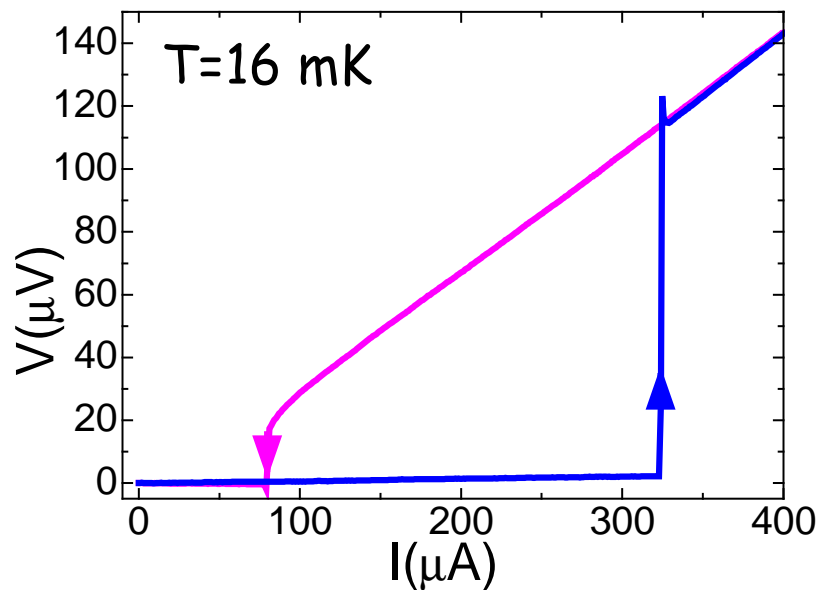
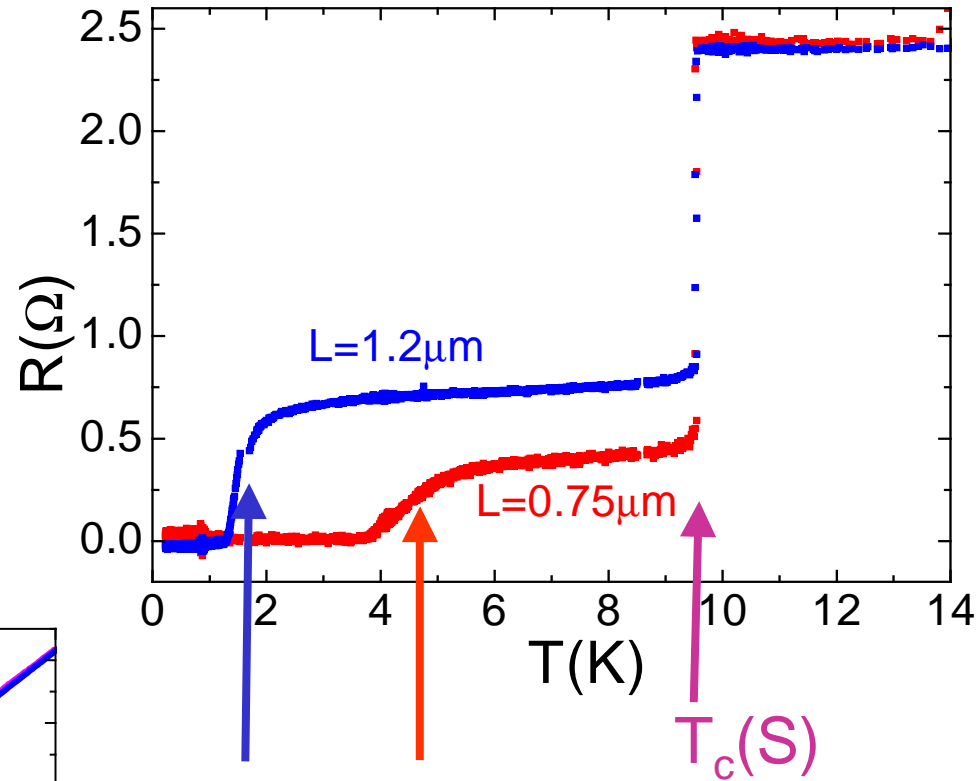
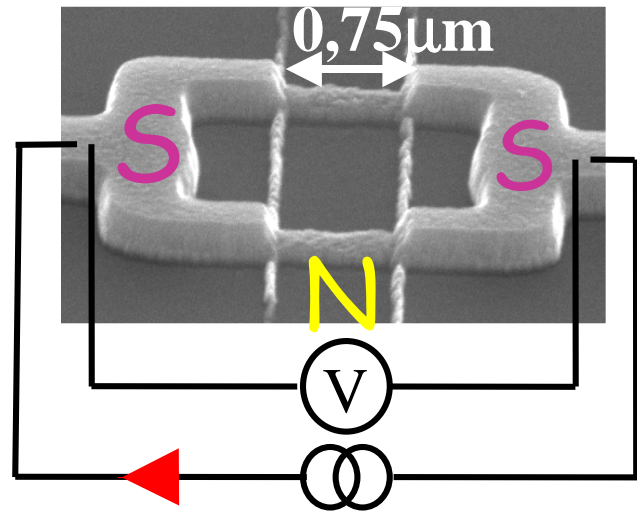


Supraconducteur= bicouche Niobium/or,  $T_c=9\text{ K}$

Métal normal=or très pur



# Effet de proximité dans des fils métalliques

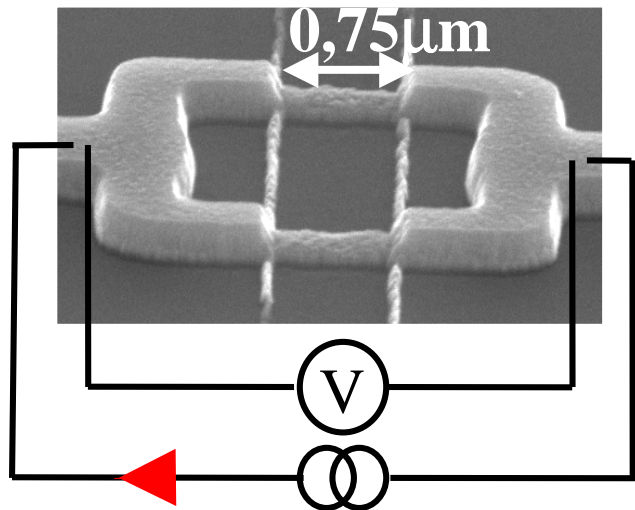


Résistance tombe à 0 quand le fil normal devient quantique.

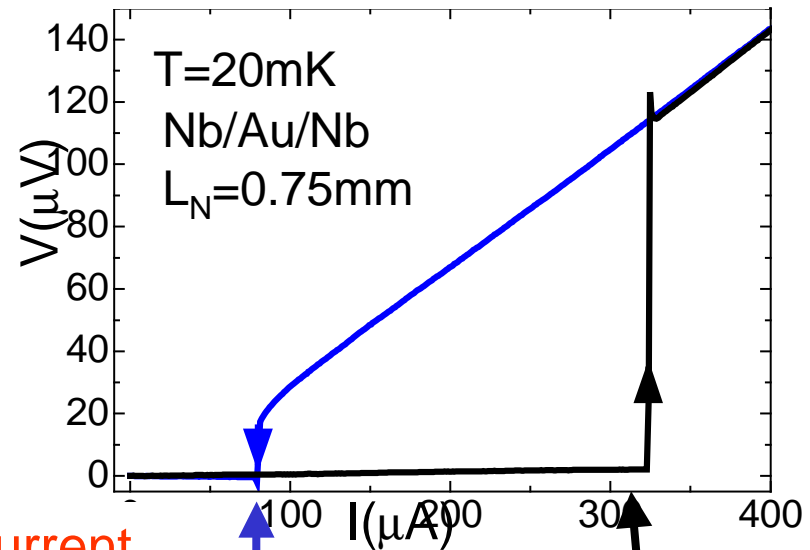
$$L < \{L_T, L_{\text{cohérence quantique}}\}$$

$$L_T = \sqrt{\hbar D / k_B T}$$

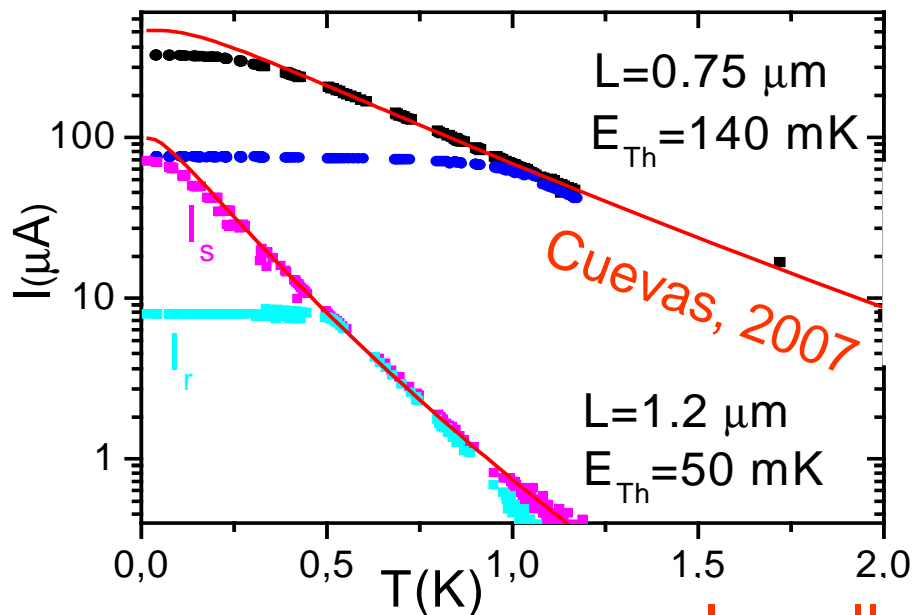
# Classical proximity effect



## Switching out of the S state



## Temperature dependence of switching current



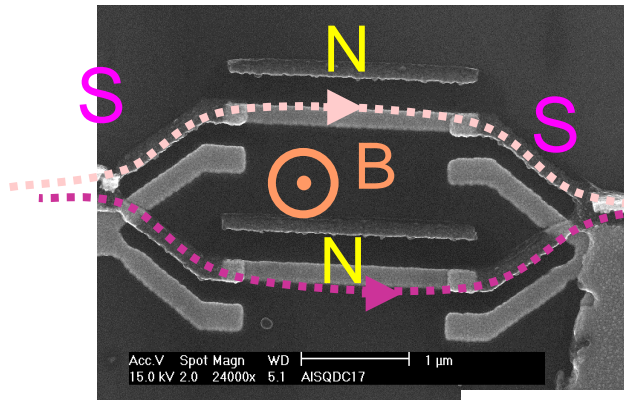
$$I_s \approx \frac{11E_{Th}}{eR_N} \approx 320 \mu\text{A}$$

$$I_c \propto T^{3/2} \exp(-L/\hat{L}_T) \sim \exp(-T/E_{Th})$$

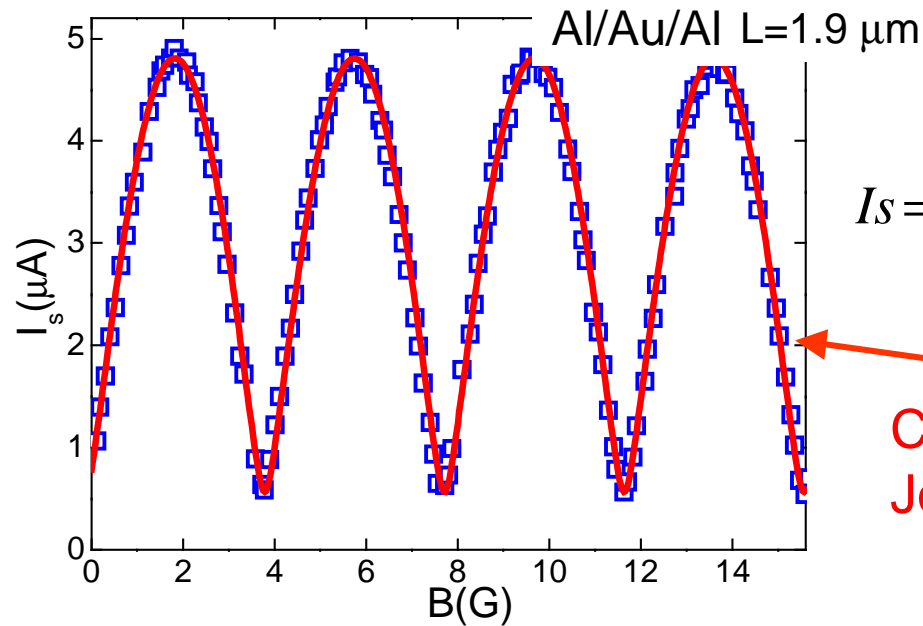
Cf. Dubos 2001 PRB

Is well described with Usadel equations

# Nouveau: un squid dc SNS



Interférence entre deux courants

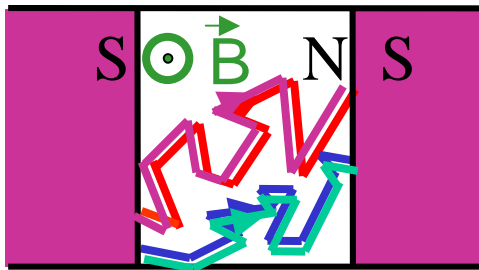


$$I_s = \sqrt{(i_{c1} - i_{c2})^2 + 4i_{c1}i_{c2} \cos^2\left(\frac{2\pi\Phi}{\Phi_0}\right)}$$

Comme un squid SIS fait de jonctions Josephson habituelles où  $I = I_c \sin(\Delta\phi)$ ?

En fait, caractère diffusif change relation  $I(\phi)$ . Mais géométrie de squid dc pas adaptée pour mesurer.

# At high field: flux quantum in the junction area?!

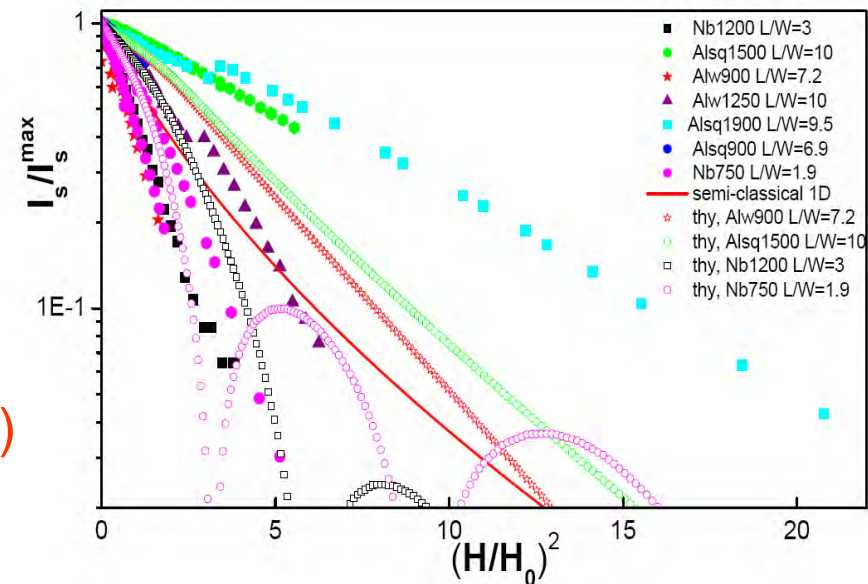
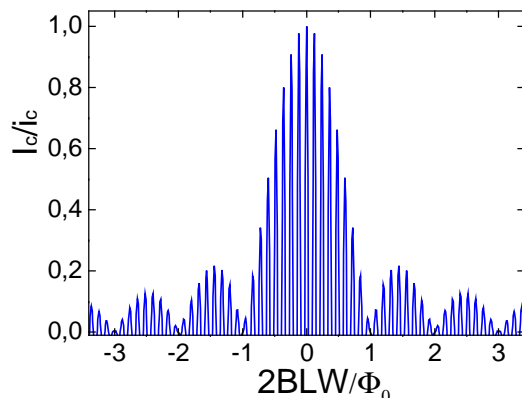


Field destroys interference between Andreev pairs  
 G. Montambaux, JC Cuevas (2007):  
 Decay depends on aspect ratio of the junction

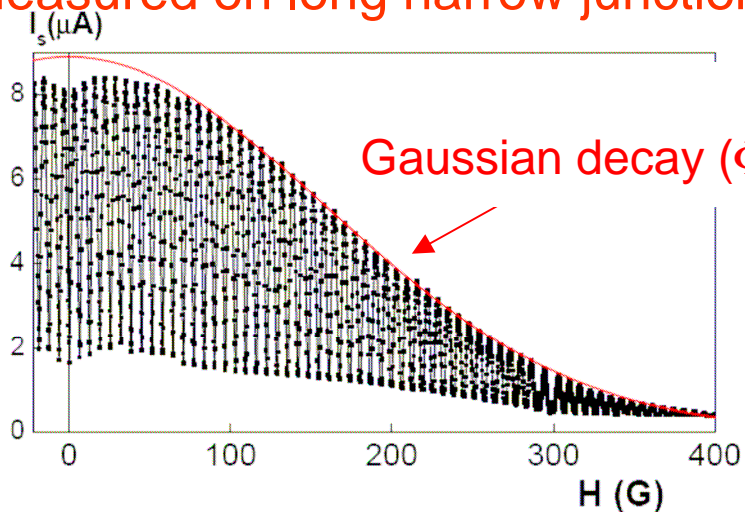
$$I_C = i_c^0 \left| \left\langle e^{-i \frac{4\pi}{\Phi_0} \int \bar{A} d\vec{l}} \right\rangle_c \right|$$

Expected for wide junction (SIS squid):

## Comparison theory/experiment



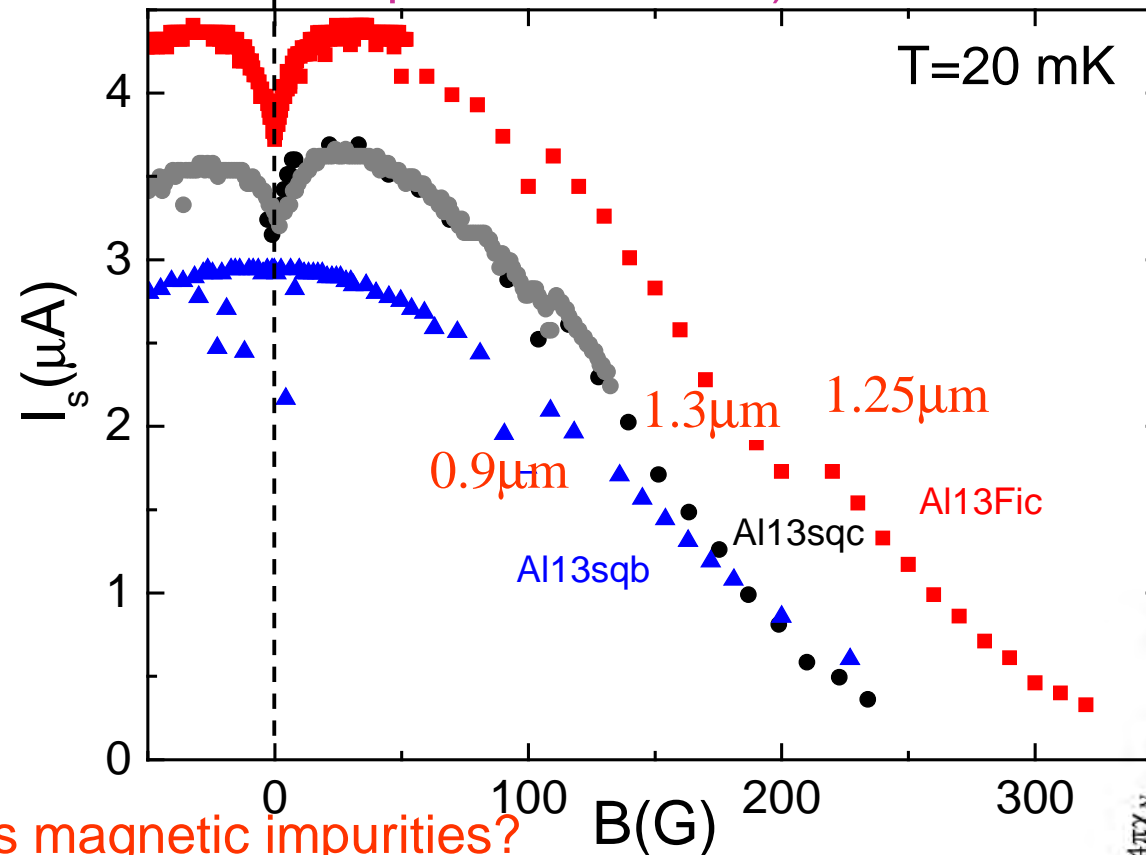
Measured on long narrow junction (SNS)



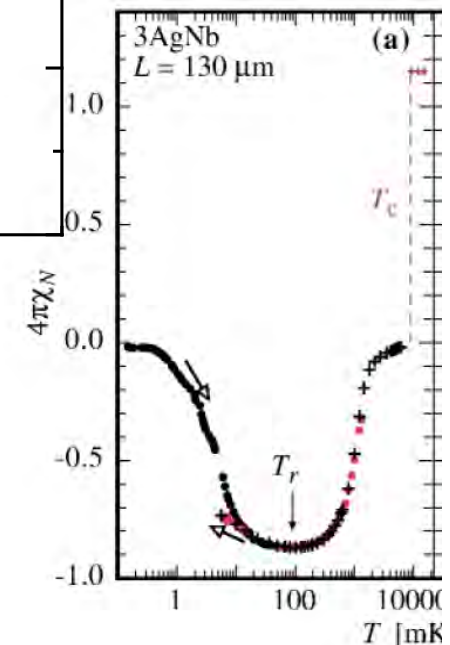
Not full agreement yet:  
 field focusing and screening?

# Some mysteries remain: field reentrance

Critical current enhanced by magnetic field!  
(Only in Al/Au/Al wires and squids, but not all)



- Field freezes magnetic impurities?  
Should happen at higher fields
- Amplified weak localization?  
20% effect!: not weak enough!
- Paramagnetic orbital contribution? (Cf Mota, 1990)



Vers la relation courant phase  
et la dynamique des paires d'Andreev

# Can we take a snapshot of the Andreev states ?

Current phase relation in a Josephson SIS junction

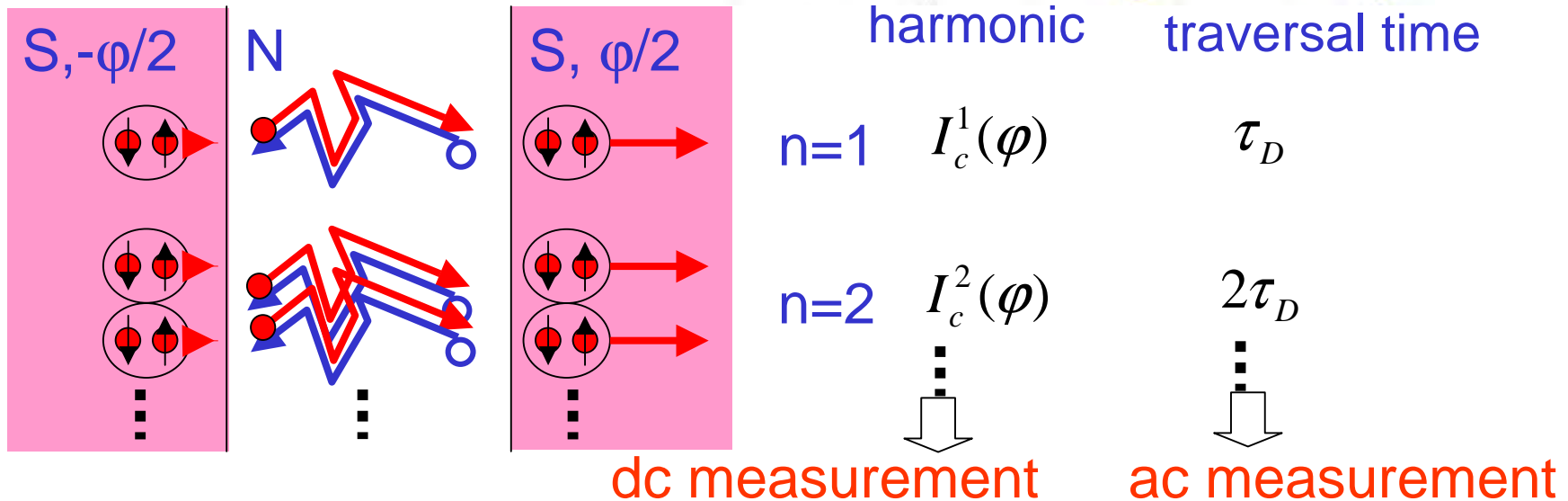
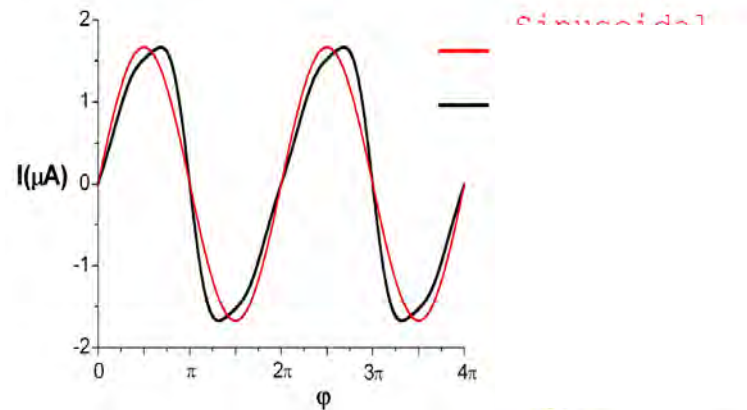
$$I = I_c \sin \phi$$

Current phase relation in a diffusive SNS junction

$$I_C(\phi) = \sum_{n=1}^{\infty} I_C^n \sin(n\phi),$$

$$I_C^n = \frac{33}{R_N} \frac{(-1)^n e E_{Th}}{(2n+1)(2n-1)}$$

Heikkila, Sarkka, Wilhelm PRB 2002

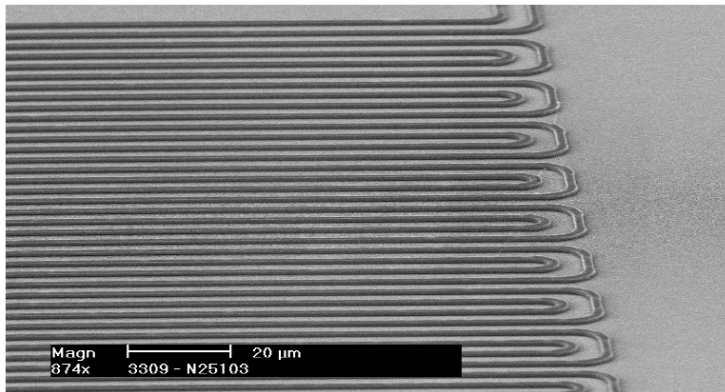


# Relation courant phase dans une mesure ac

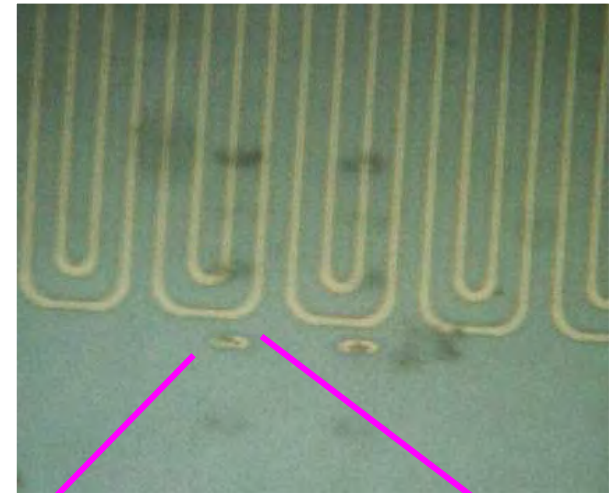
(Bouchiat, Reulet, 1995)

## Squid ac SNS sur un résonateur haut facteur de qualité

Résonateur LC multimode Nb  $Q \sim 10^3 - 10^4$

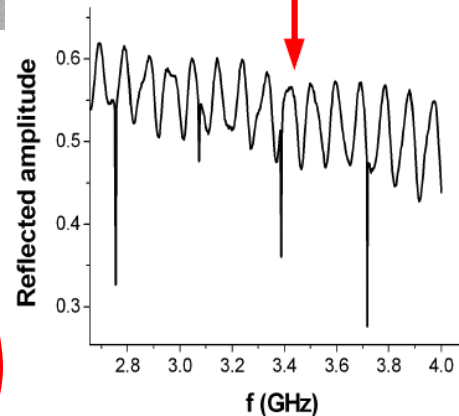


Résonateur LC multimode Nb



$$f_1 = \frac{1}{\sqrt{LC}} = 380 \text{ MHz}$$

$$f_n = n f_1$$



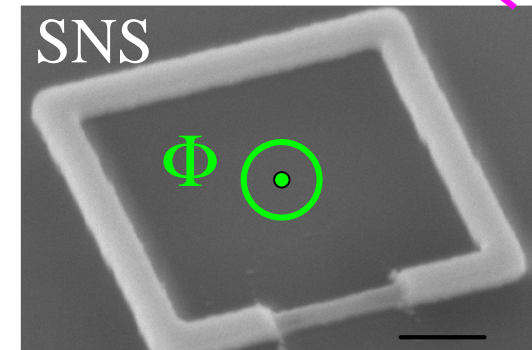
f: 300 MHz to > 8 GHz

$$f_1 = \frac{1}{\sqrt{LC}} \rightarrow \frac{\partial f}{f} = -\frac{1}{2} \frac{\partial L}{L}$$

$$\left. \begin{aligned} \delta \Phi_A &= M i_R \\ \delta i_A &= \frac{\partial i_A}{\partial \Phi_A} \delta \Phi_A \end{aligned} \right\} \Phi_R = L_R i_R + M \delta i_A$$

$$\Phi_R = \left( L_R + M^2 \frac{\partial i_A}{\partial \Phi_A} \right) i_R$$

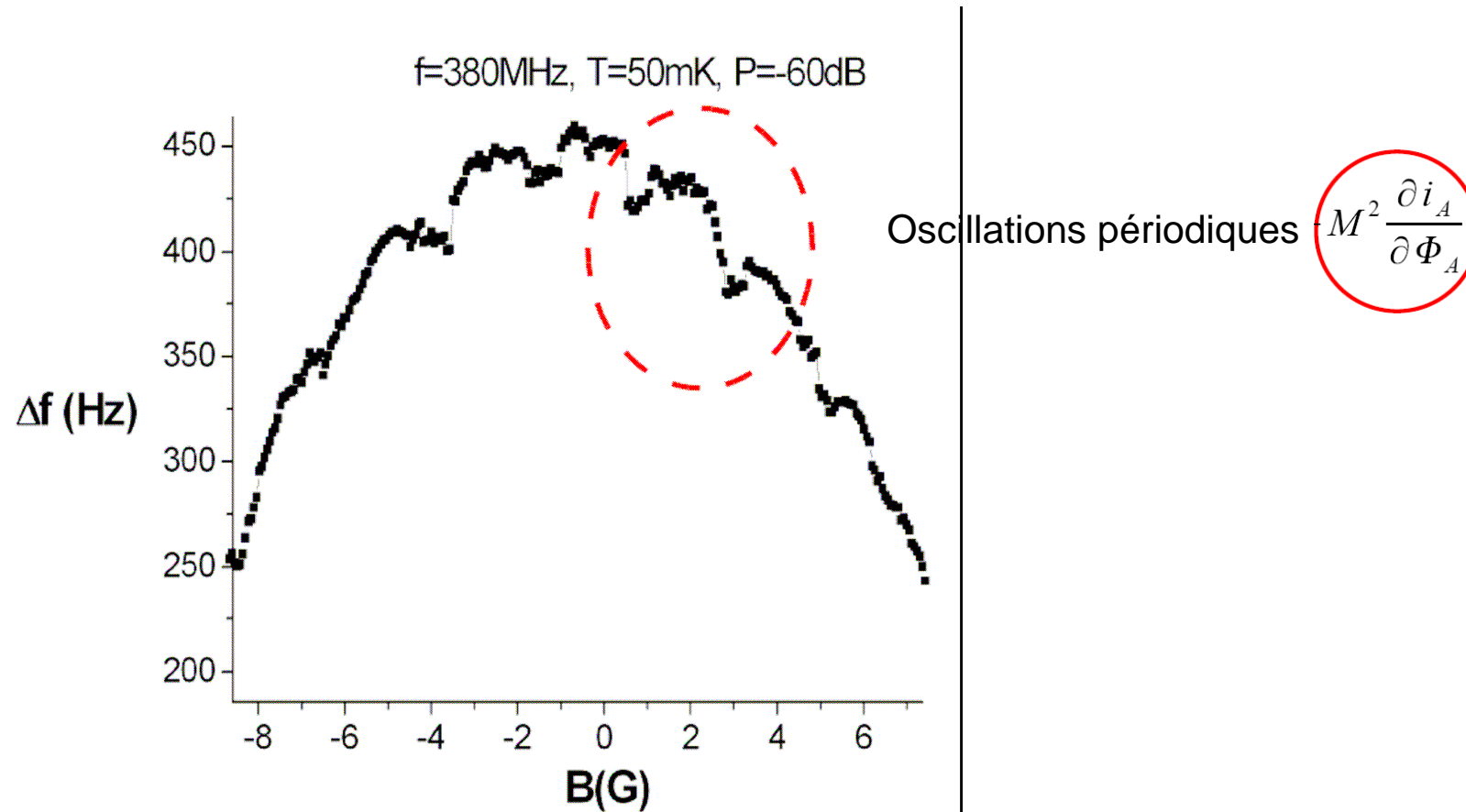
Inductance cinétique anneau  $L_A$



Squid ac SNS (Nb/Au)



# Résultats préliminaires



Accès à  $I(\varphi)$  jusqu'à 8 GHz... en cours

# The classical proximity effect in long junctions:

Still need to:

Understand the role of magnetic field in the proximity effect;  
Geometry can be varied at will (aspect ratio)

Grasp the dynamics of the diffusing pairs:

IV curves,

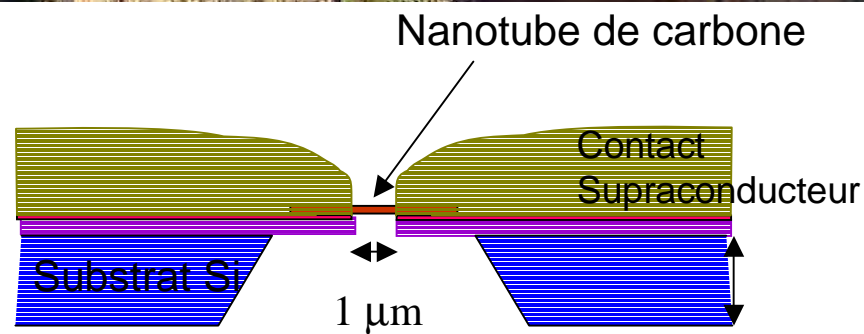
Distribution of switching current,

ac measurement of the current Vs phase relation, as a  
function of frequency (conversion time, diffusion time, coherence  
time...)

Et les molécules?

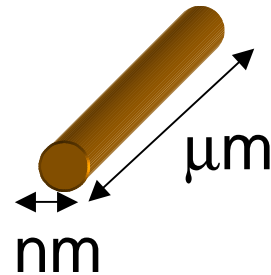
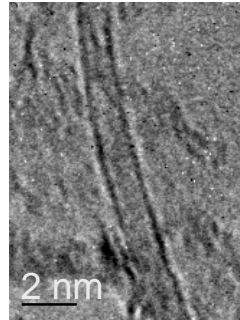
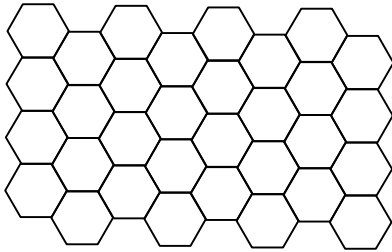
# Supraconductivité induite à travers des nanotubes de carbone suspendus

Constantine, Algérie

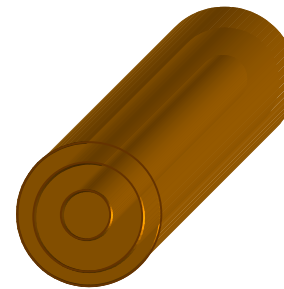
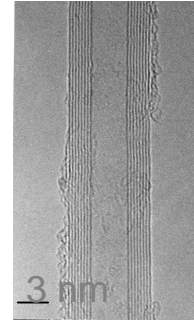


# Qu'est-ce qu'un nanotube de carbone?

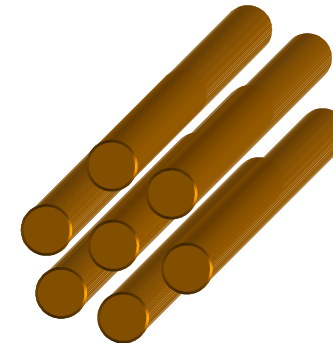
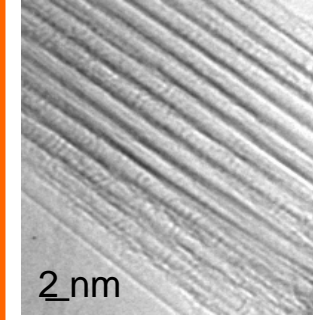
Un plan de graphène enroulé sur lui-même



Individuel



Multiparoi

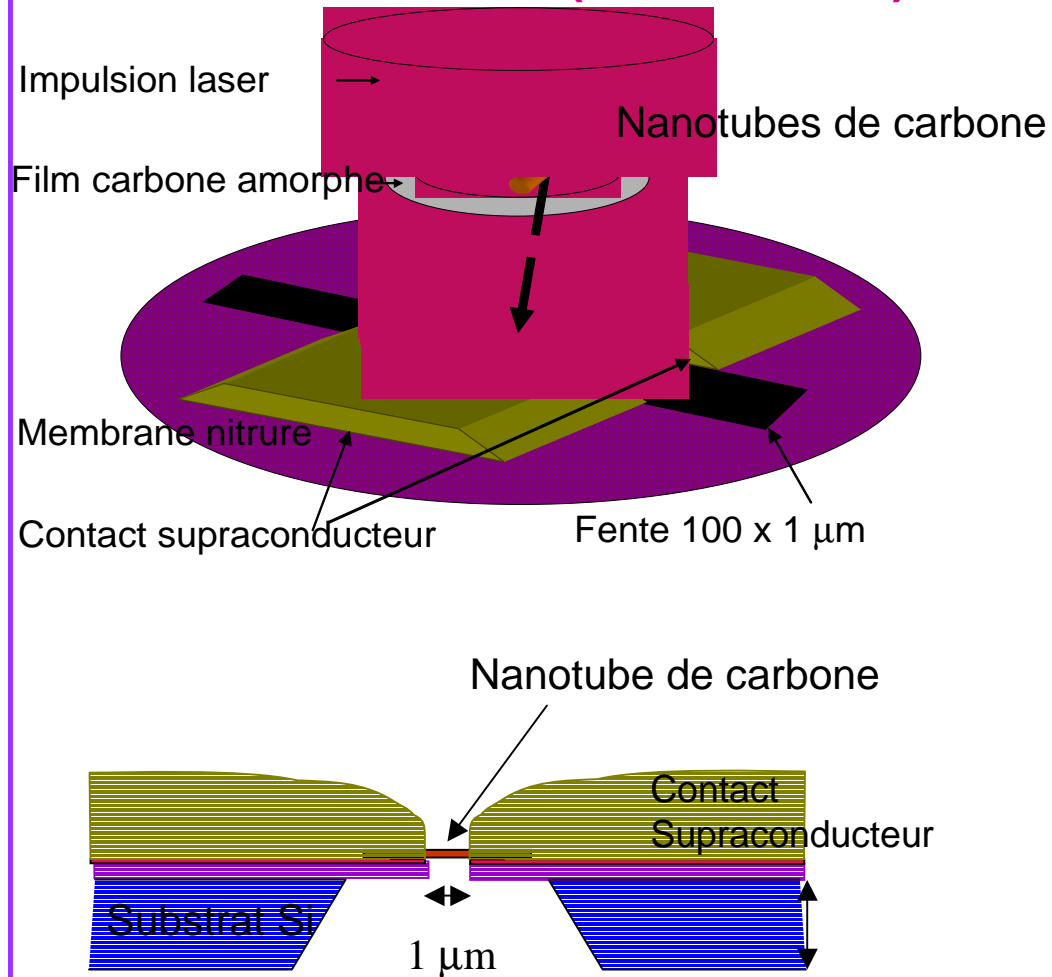


cordes

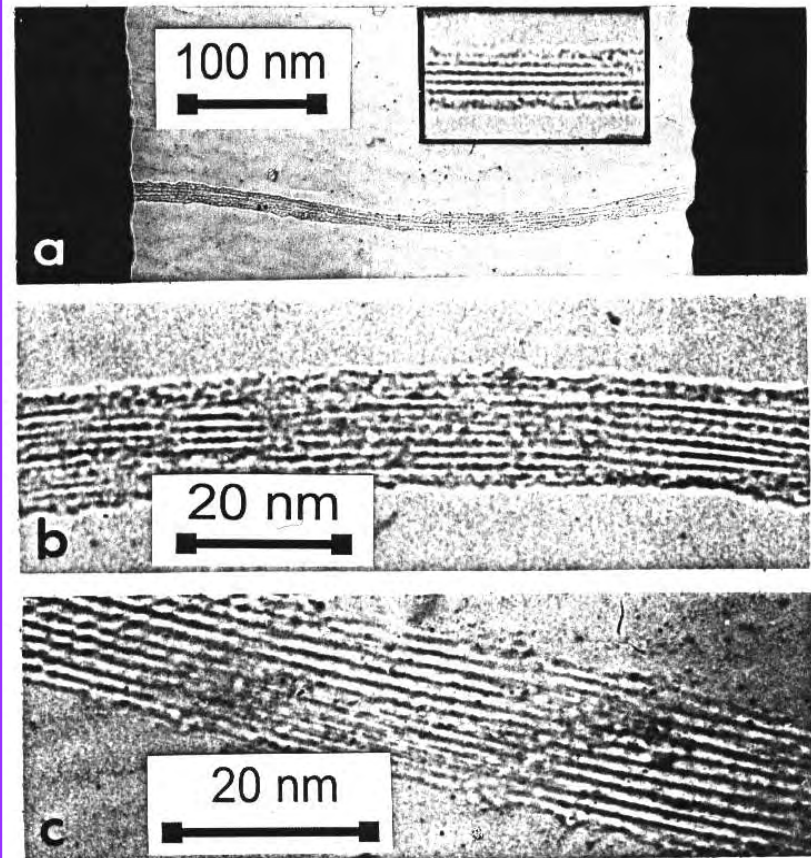
- **Structure électronique particulière:**
- **1/3 nanotubes sont très bons conducteurs**
- **Un fil moléculaire!**

# Connecter les nanotubes et les observer

## Nanosoudure laser (A. Kasumov)

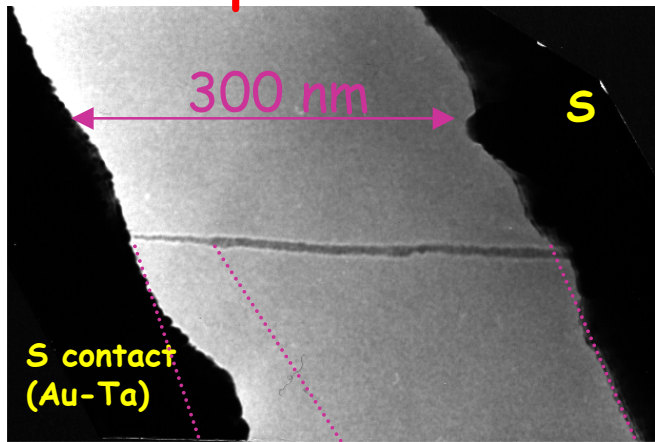


## Caractérisation au microscope électronique à transmission

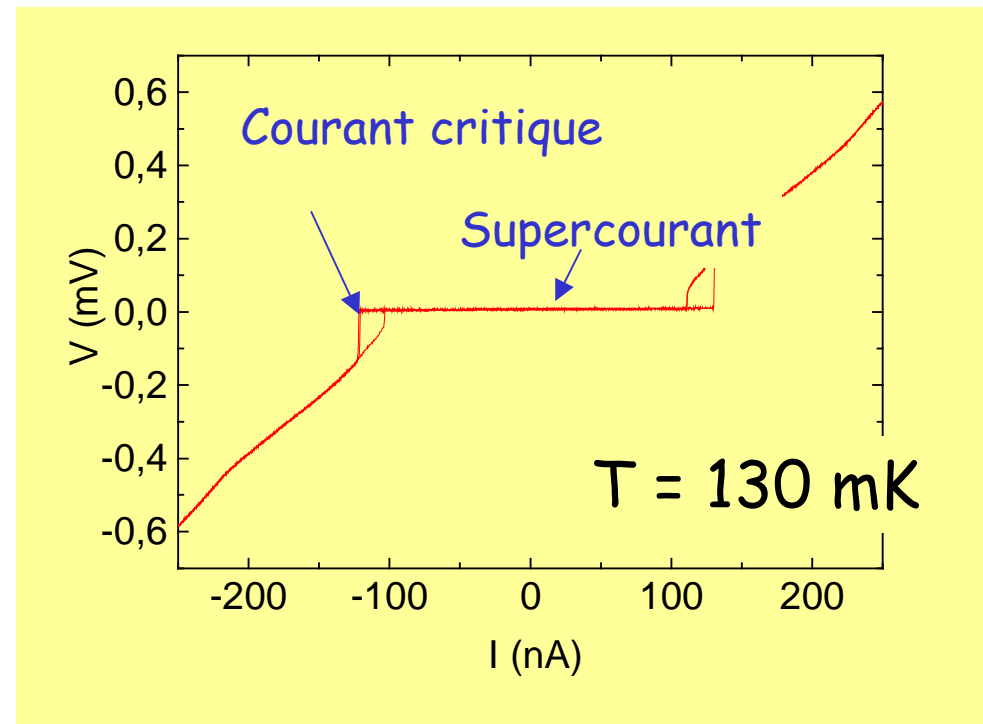
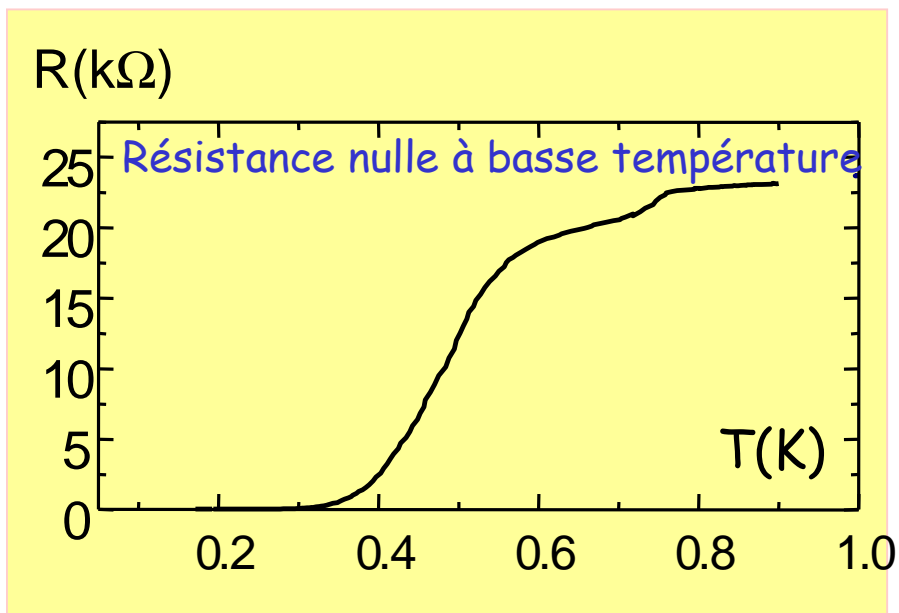
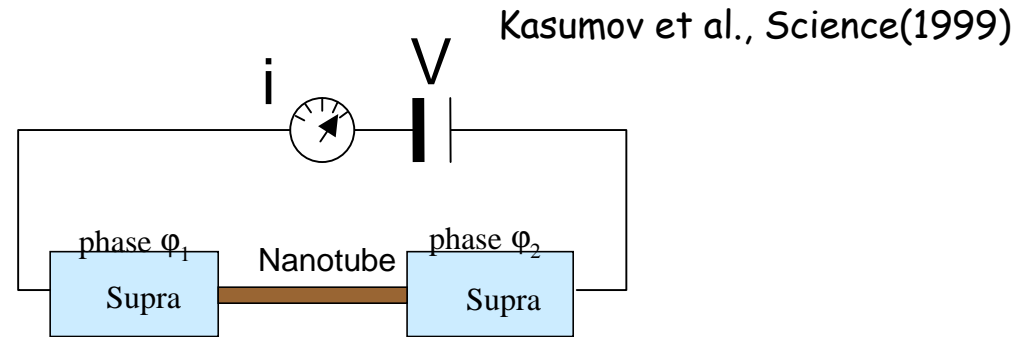


## Refroidir les nanotubes sélectionnés

# Supercourant à travers un nanotube de carbone

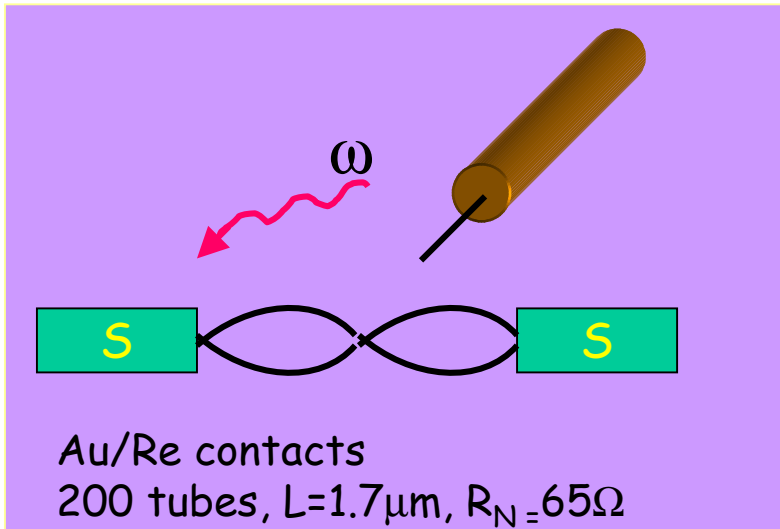


1 tube    7 tubes



Courant critique trop élevé! ( $R_N I_c > \Delta_{\text{contact}}$ )  
Les nanotubes sont eux-mêmes supraconducteurs!

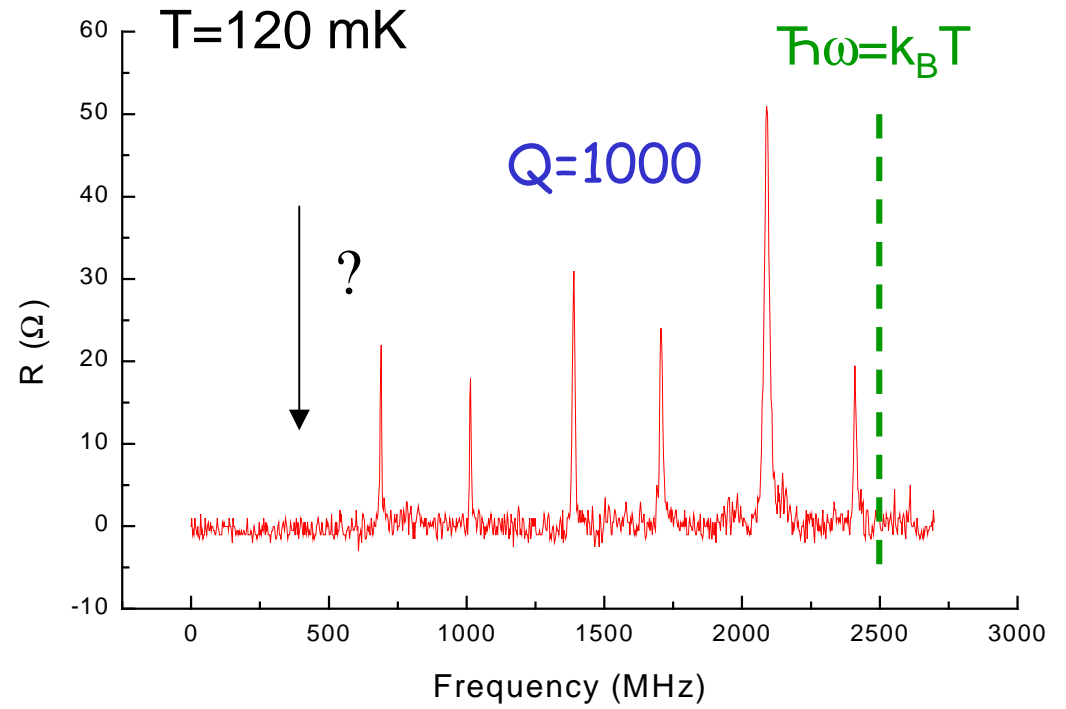
# Use the proximity effect to detect mechanical vibrations



Fundamental transverse mode  
of a clamped rod

$$f_T = 22.4 \frac{R}{2L^2} \sqrt{\frac{E}{\rho}} \approx 276 \text{ MHz}$$

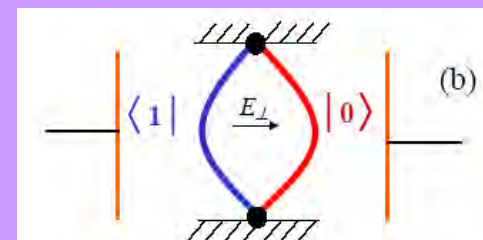
E Young modulus  $\sim 1\text{TPa}$



Reulet et al. PRL 2000

• Detection: Heating or phase coherence breaking at resonance

• Possible Qbit candidate (F. Nori, 2004):

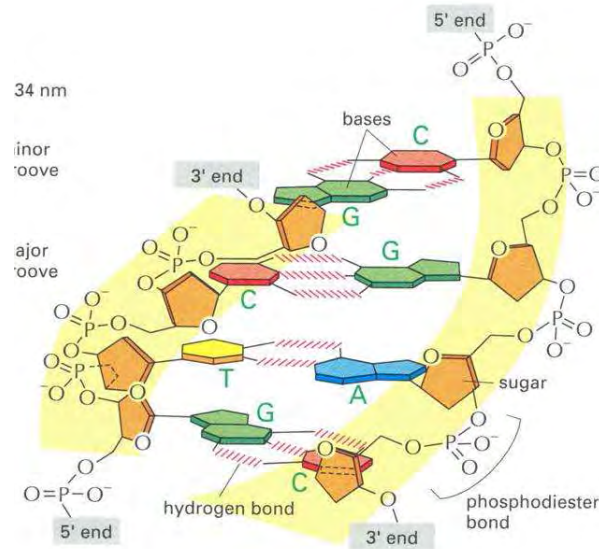
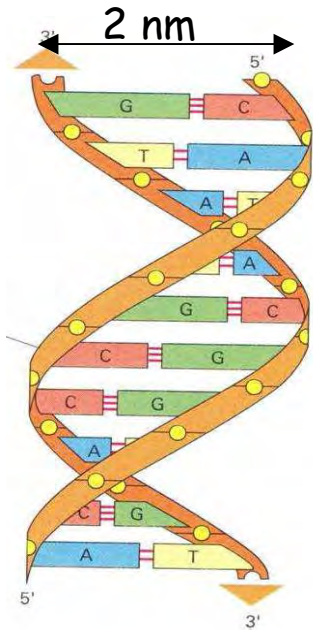




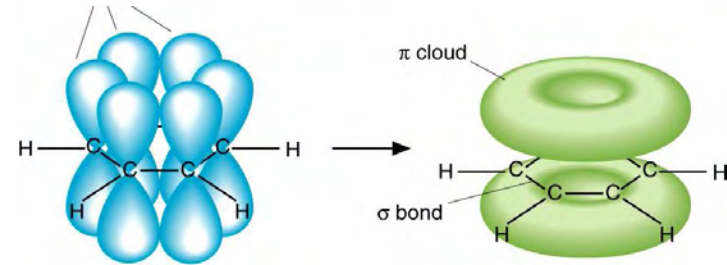
Un autre fil moléculaire: l'ADN

# Why would DNA conduct electricity?

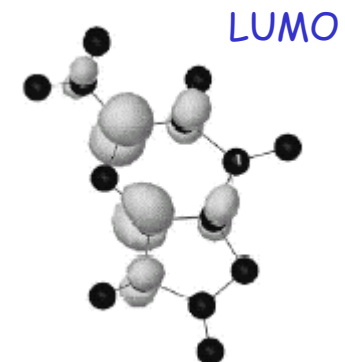
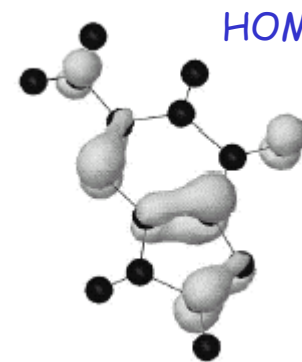
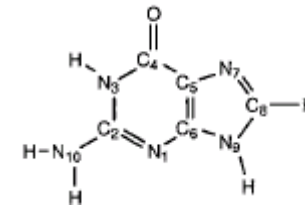
Base pairs resemble benzene molecules



Benzène:



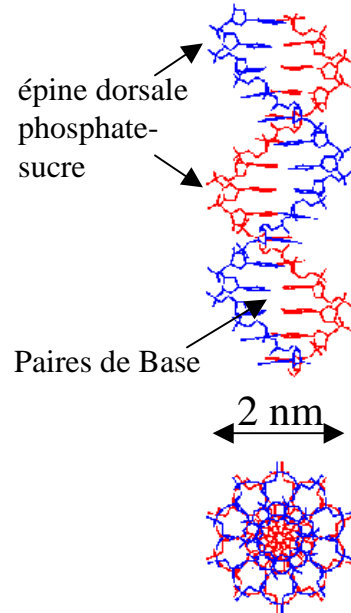
Guanine:



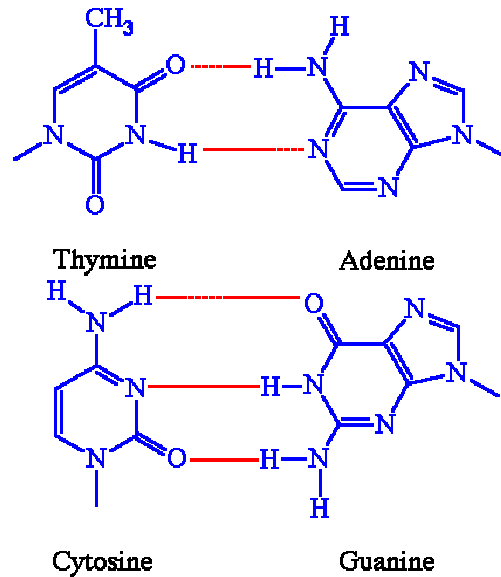
- Delocalized orbitals (in the base planes and along the helix)
- Calculations predict semi-conducting band structure
- Random base sequence
- Disordered wire? Localized? Doping?

# Pourquoi l'ADN conduirait-elle?

## ADN-B (standard)



## Bases Aromatique



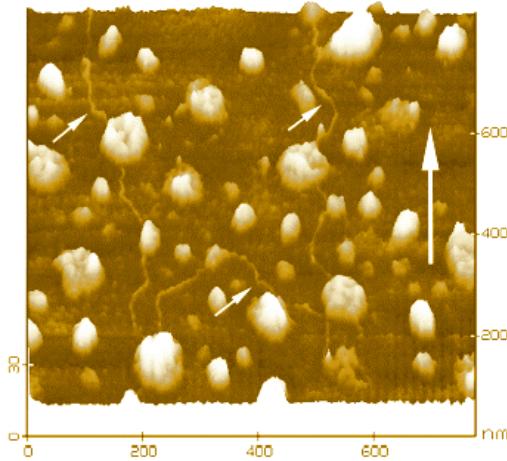
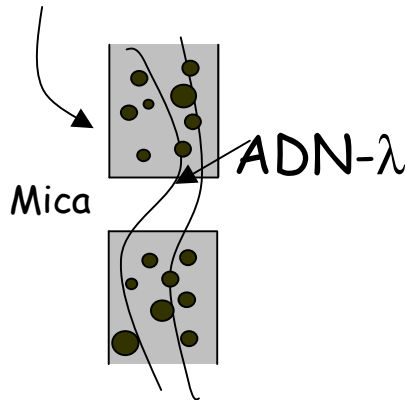
- Electrons délocalisés sur les bases et le long de l'hélice
- Calculs prédisent semi-conducteur
- Mais désordre dû à séquence aléatoire de paires de bases.

→ Fil désordonné, peut-on le doper?  
Peut-on voir la signature de sa structure hélicoïdale?

# Supraconductivité à travers des molécules d'ADN

Electrodes: Rénium/Carbone  
Supraconducteur sous  $T_c=1$  K

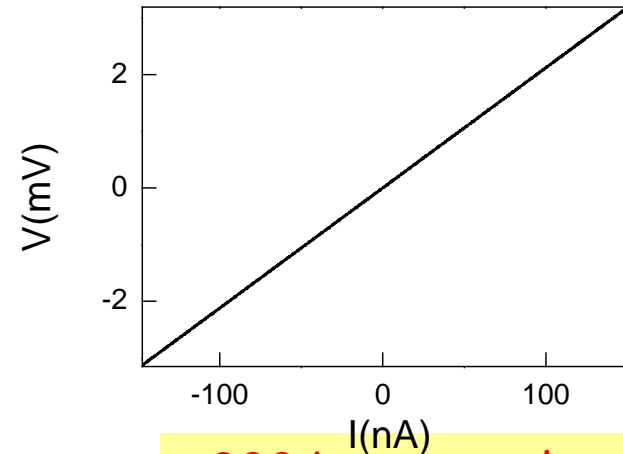
Image AFM



Kasumov et al, Science 2001

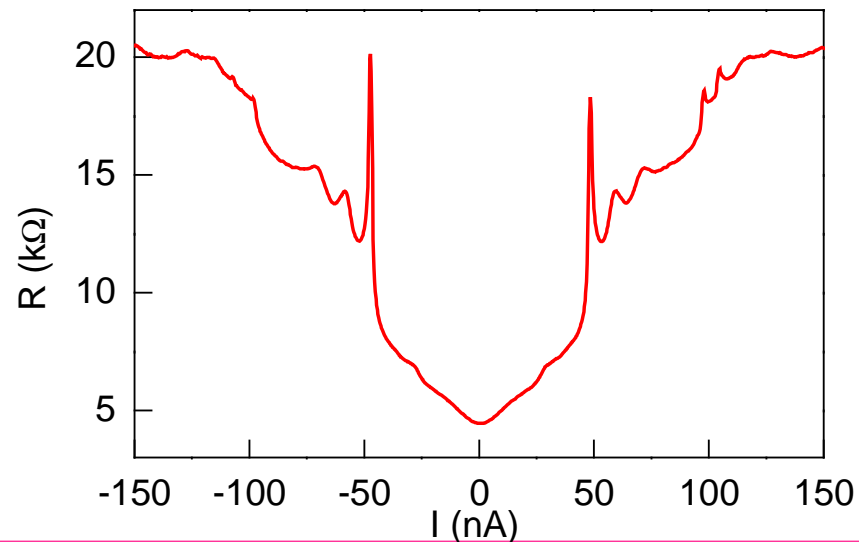
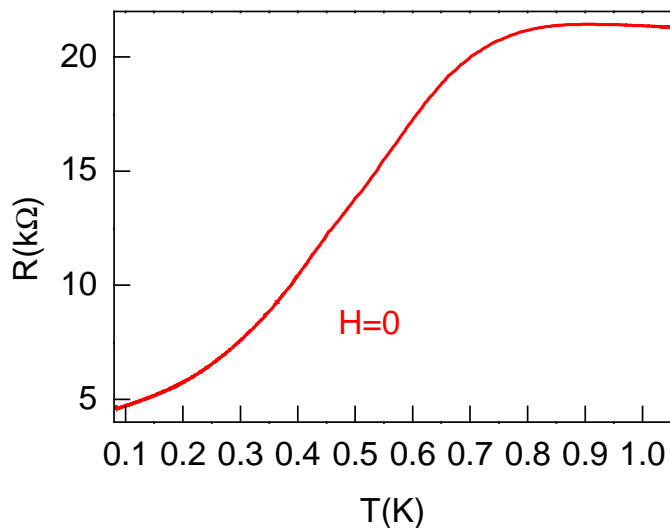
Loi d'Ohm à 1 Kelvin!

10 brins d'ADN



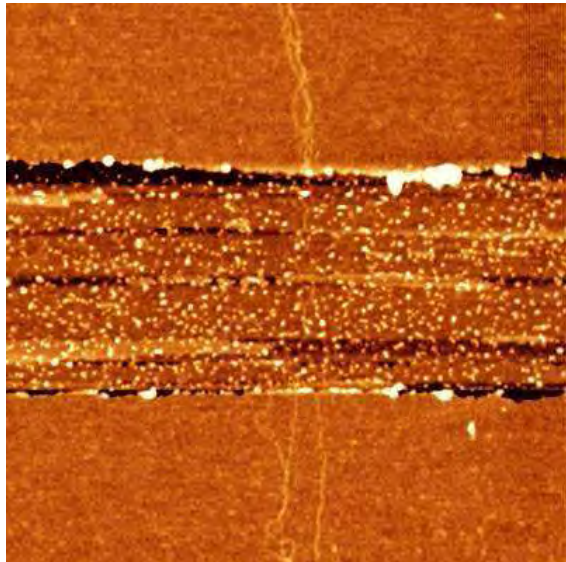
~200 kΩ per molecule

## Supraconductivité (partiellement) induite à basse température



Les paires supraconductrices peuvent se propager sur ~200 nm à T= 0.1 Kelvin

## ADN conduit aussi entre des électrodes de Platine Carbone



(Kasumov et al, APL 2004)

Mais:

Expérience difficile à reproduire:

ADN est une molécule fragile!

Contrôler la surface et les interactions

Les électrodes

Le rôle de la solution tampon

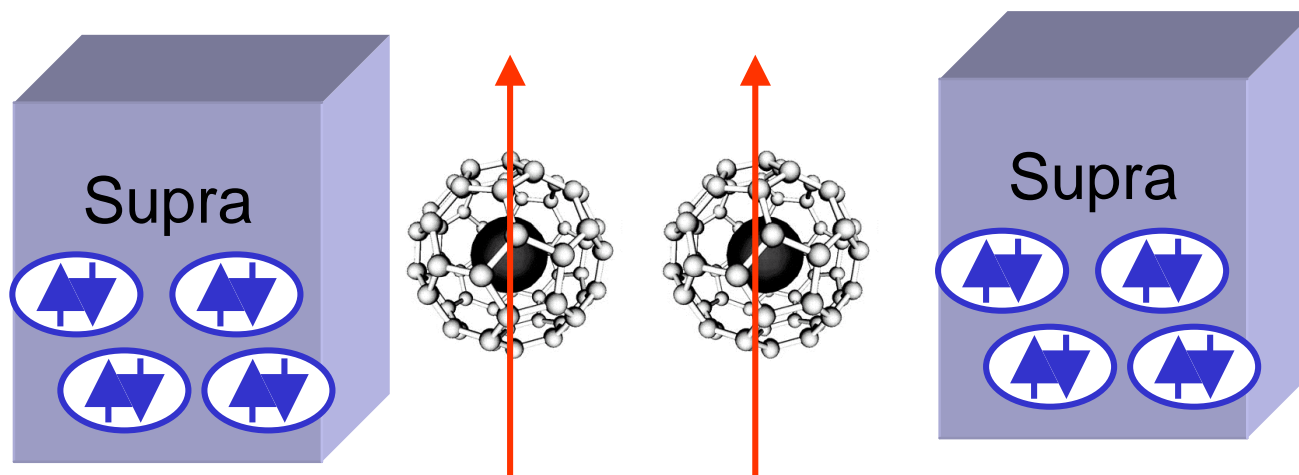
Le dopage éventuel par les contacts...

thèse A. Chepelianskii

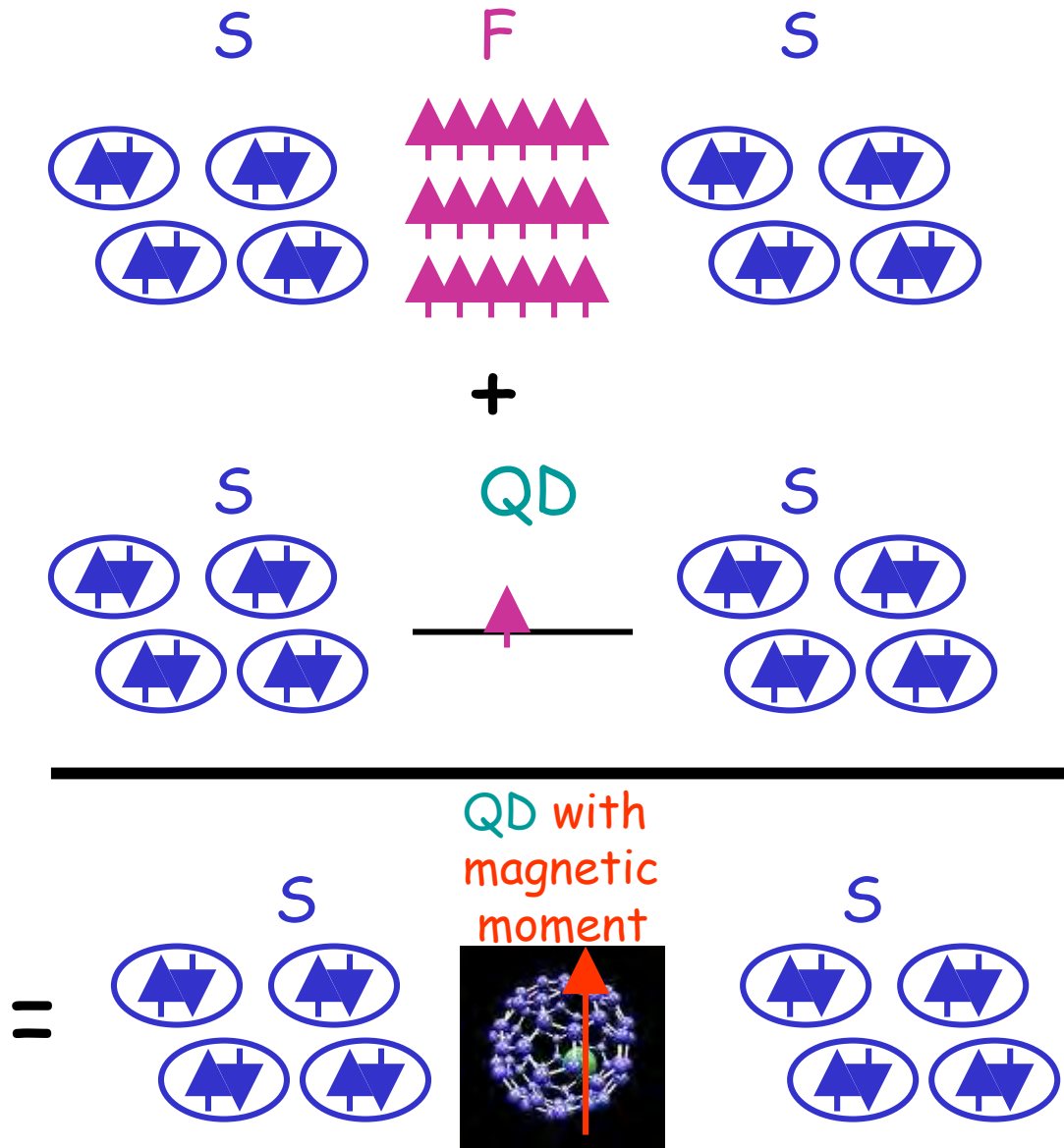
De plus en plus petit...

# Junction Supra-metallofullerene-Supra

A. Kasumov, R. Deblock, S. Guéron, H. Bouchiat (LPS Orsay);  
K. Tsukagoshi, M. Kawamura, T. Kobayashi, Y. Aoyagi (RIKEN, Japan)  
K. Senba, T. Kodama, H. Nishikawa, I. Ikemoto, K. Kikuchi,  
(Department of Chemistry, Tokyo Metropolitan University, Japan)



# Why S-metallofullerene-S junctions ?



Superconductivity and ferromagnetism?

Superconductivity and a quantum dot with one unpaired spin? (Superconductivity and Kondo.)

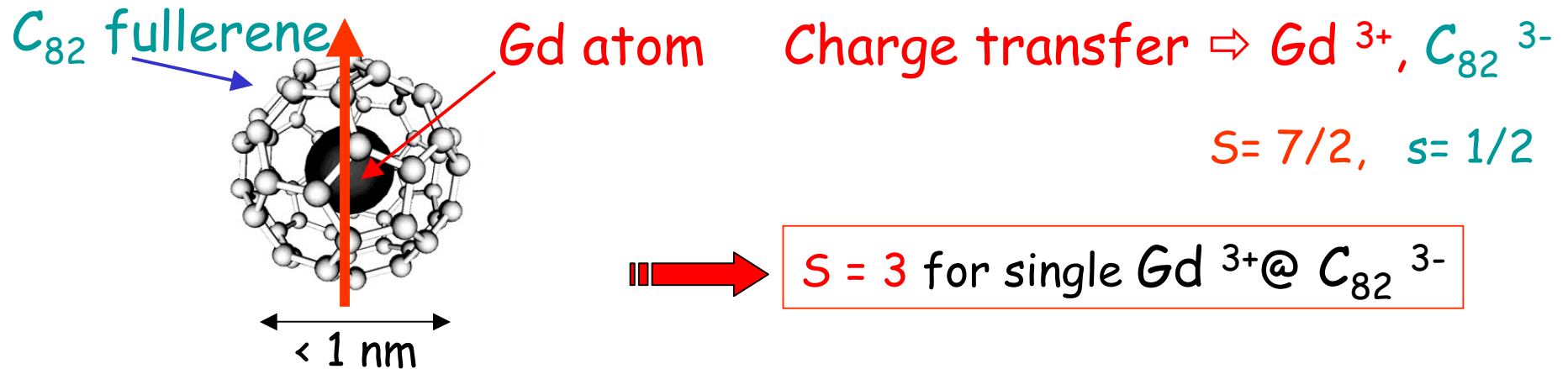
S-metallofullerene-S !



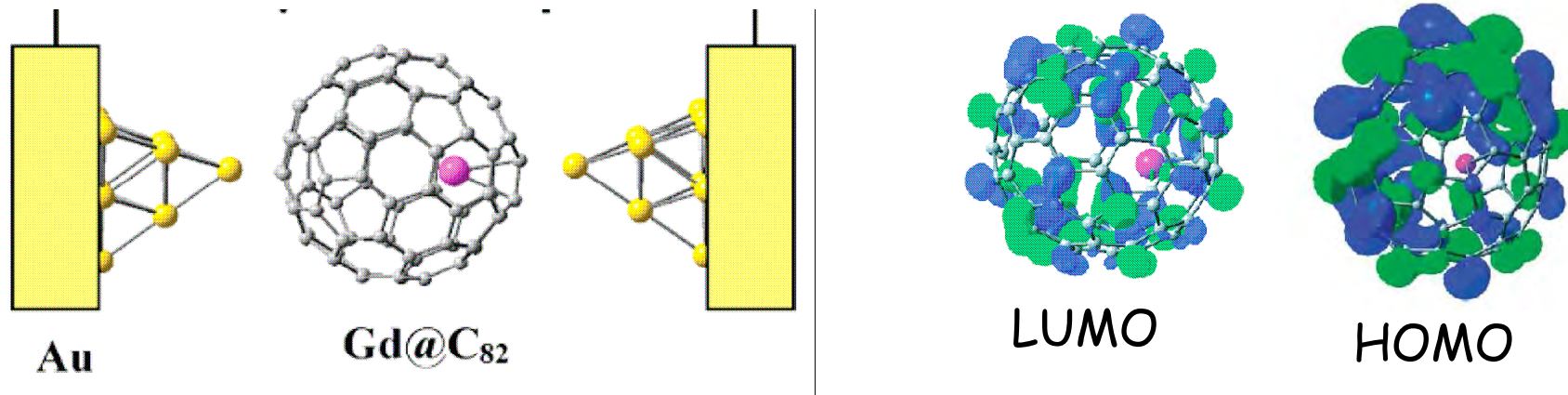
# What is a metallofullerene ?



A fullerene molecule with an metal atom inside.



Does it conduct? Senapati et al, Nanolett (2004)

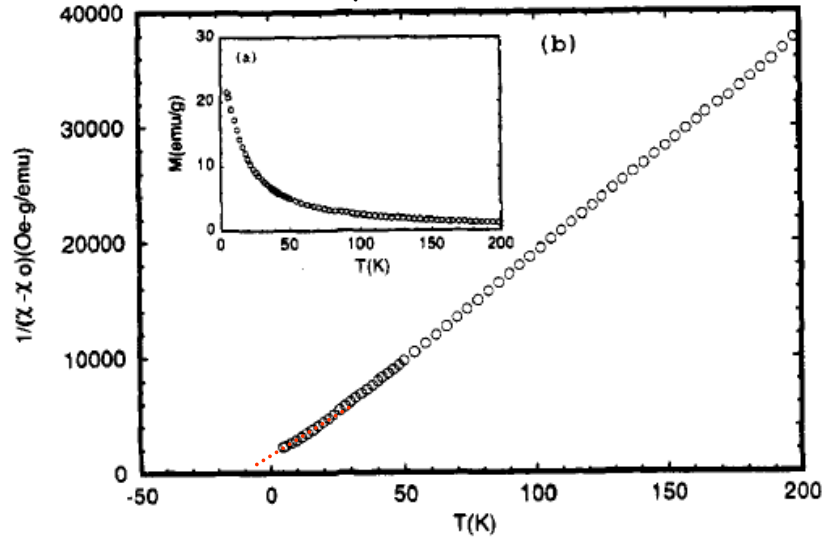


Estimate  $R < 6 \text{ k}\Omega$ , and (but) Gd plays no role!

# Magnetic properties of $Gd@C_{82}$ dimers and clusters ?

## Susceptibility on powder (dimer), at 5 T

(Funasaka et al, J. Phys. Chem. 1995)

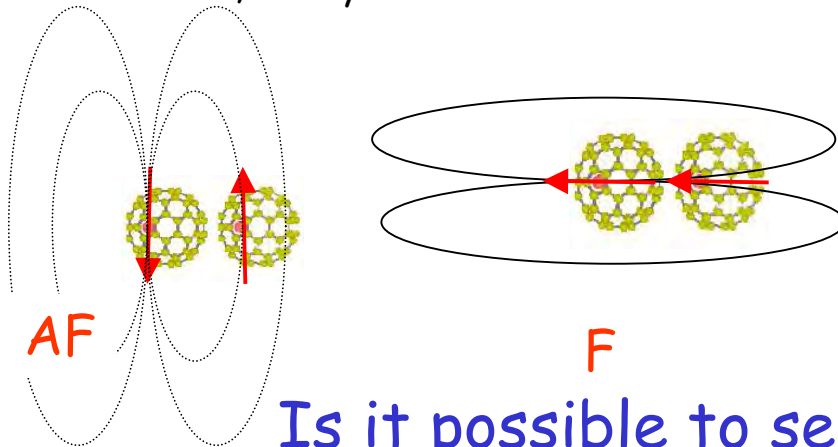


Paramagnetic above 3 K  
Extrapolation to 0 K:

Antiferromagnetic,  $J=0.7$  K

## Magnetism of $Gd@C_{82}$ dimer: 2 coupled spins $7/2$

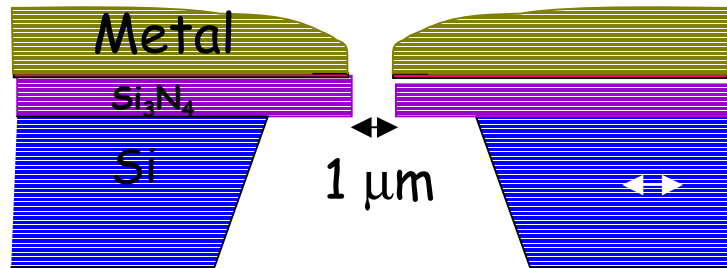
Furukawa *et al.*, J. Phys. Chem. A 2003 : Dimerisation in condensed solution



Weak dipolar coupling (0.1 K):  
Antiferromagnetic or ferromagnetic

Is it possible to see these magnetic states?

# Fabrication d'électrodes pour mesurer et visualiser des molécules de quelques nanomètres



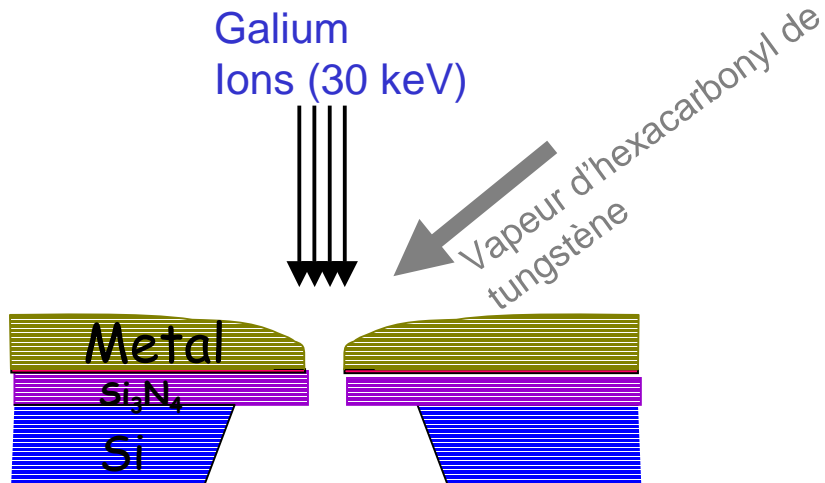
Trop gros!

Il faut diminuer l'écartement entre électrodes

# Electrodes pour mesurer une molécule...

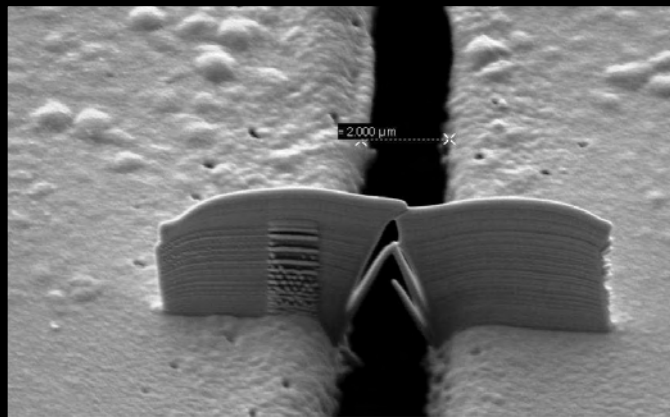
Alik Kasumov: Japon, Orsay!

Faisceau d'ions focalisé



Imaging = SEM 200 $\mu\text{m}$  WD = 5 mm EHT = 5.00 kV Signal A = SE2 Date :27 Jun 2005 Time :16:50:25  
XB-27-01 Mag = 59 X FIB Lock Mags = Yes FIB Probe = 10 pA System Vacuum = 8.30e-007 Torr

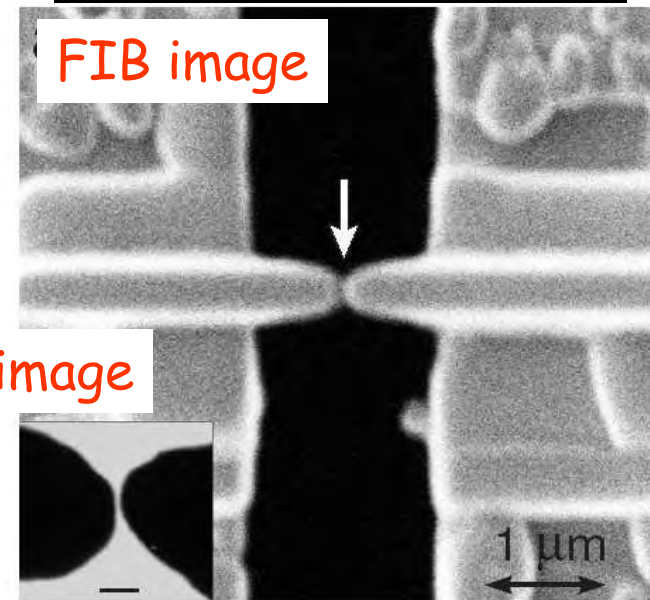
W. Nativel, C. Collet, Thalès



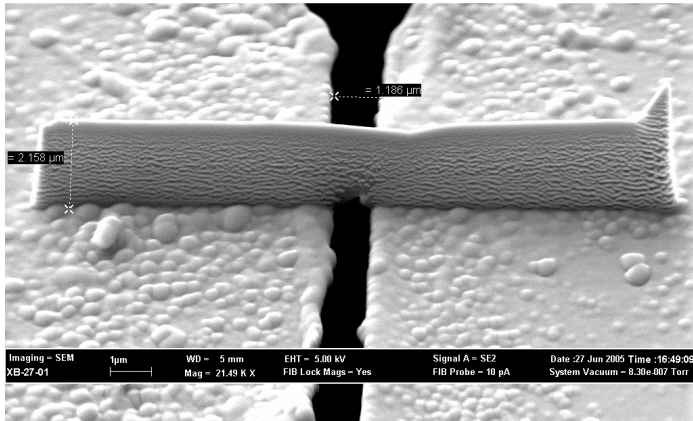
EM 1 $\mu\text{m}$  WD = 5 mm EHT = 5.00 kV Signal A = SE2 Date :3 May 2006 Ti  
Mag = 20.00 K X FIB Lock Mags = Yes FIB Probe = 20 pA System Vacuum = 8.30e-007 Torr

FIB image

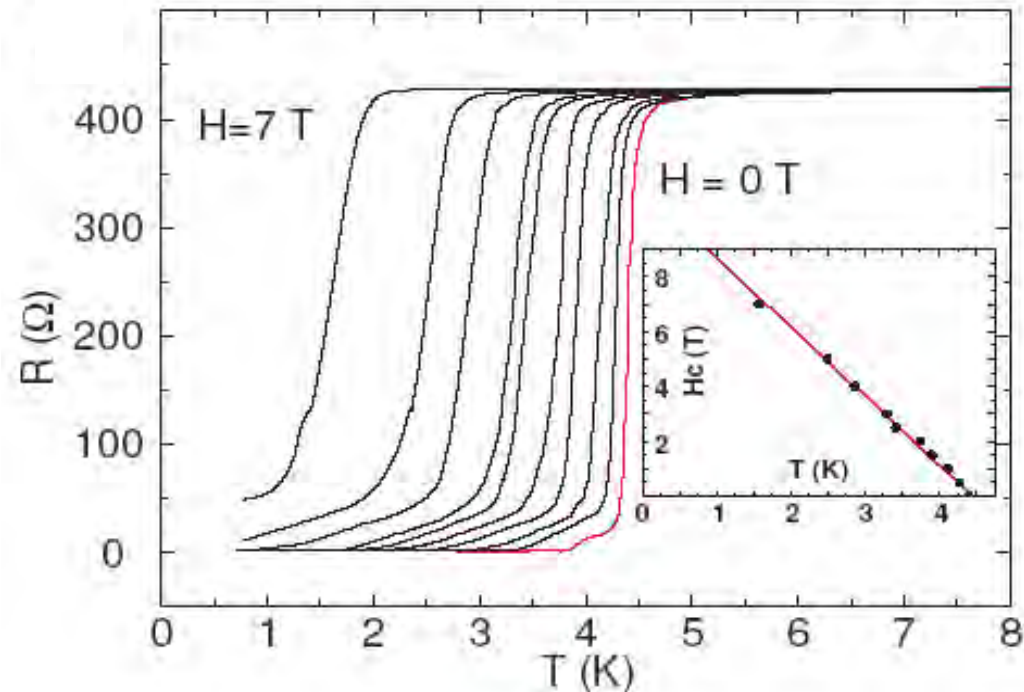
TEM image



# Properties of superconducting tungsten electrodes

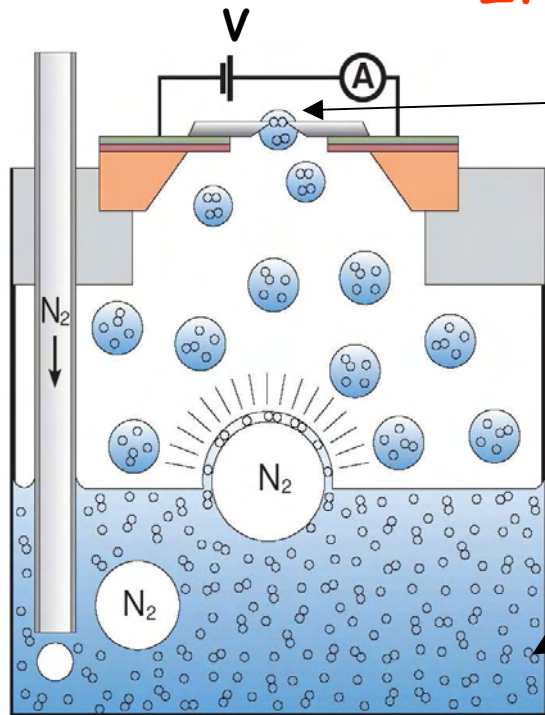


- Length = several microns, typical width = 200 nm
- Auger analysis :75% tungsten  
10 % carbon  
10 % gallium  
5% oxygen
- $R_{sq}$ : between 1 and 50 Ohm
- $T_C = 4-5$  K (pure W has  $T_C$  of less than 100 mK !)
- $H_C = 7$  T !!!



Investigate the proximity effect in high fields!

# Insertion des métallofullérènes

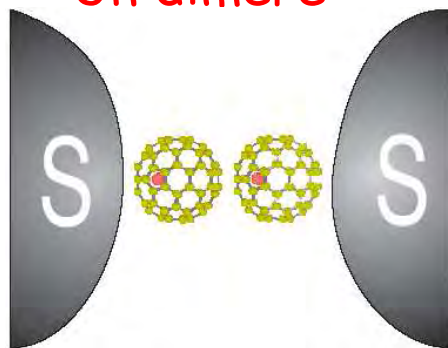


Interstice nanométrique, suspendu!

solution  $CS_2$  10  $\mu g/ml$  fullerene  
(Furukawa *et al.* J. Phys. Chem. A (2003)).

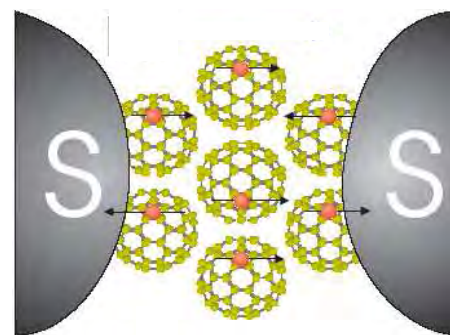
On a obtenu:

Un dimère



$$R(300\text{ K}) = 13\text{ k}\Omega$$

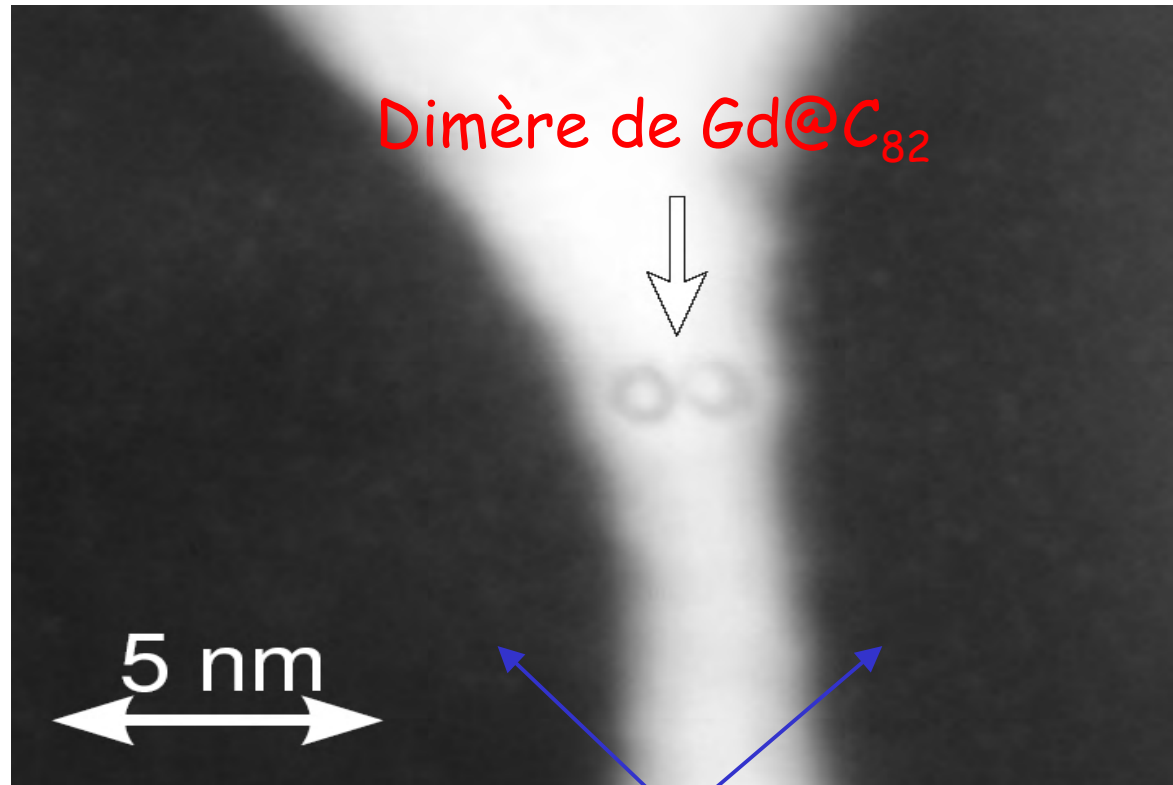
Des agrégats  
d'environ 7 molécules



$$R(300\text{ K}) = 3\text{ and }1.5\text{ k}\Omega$$

Comment le sait-on ?

On l'a vu!



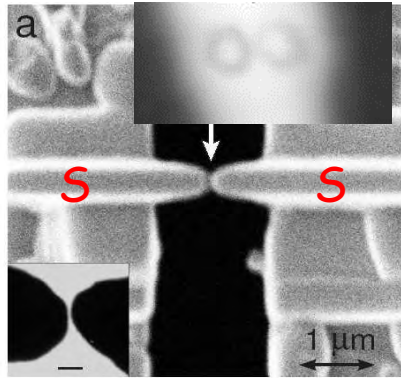
électrodes supraconductrices en tungstène

Observation dans un microscope électronique en transmission

- nombre et nature des molécules
  - rien d'autre dans l'interstice
- ... Et on mesure!

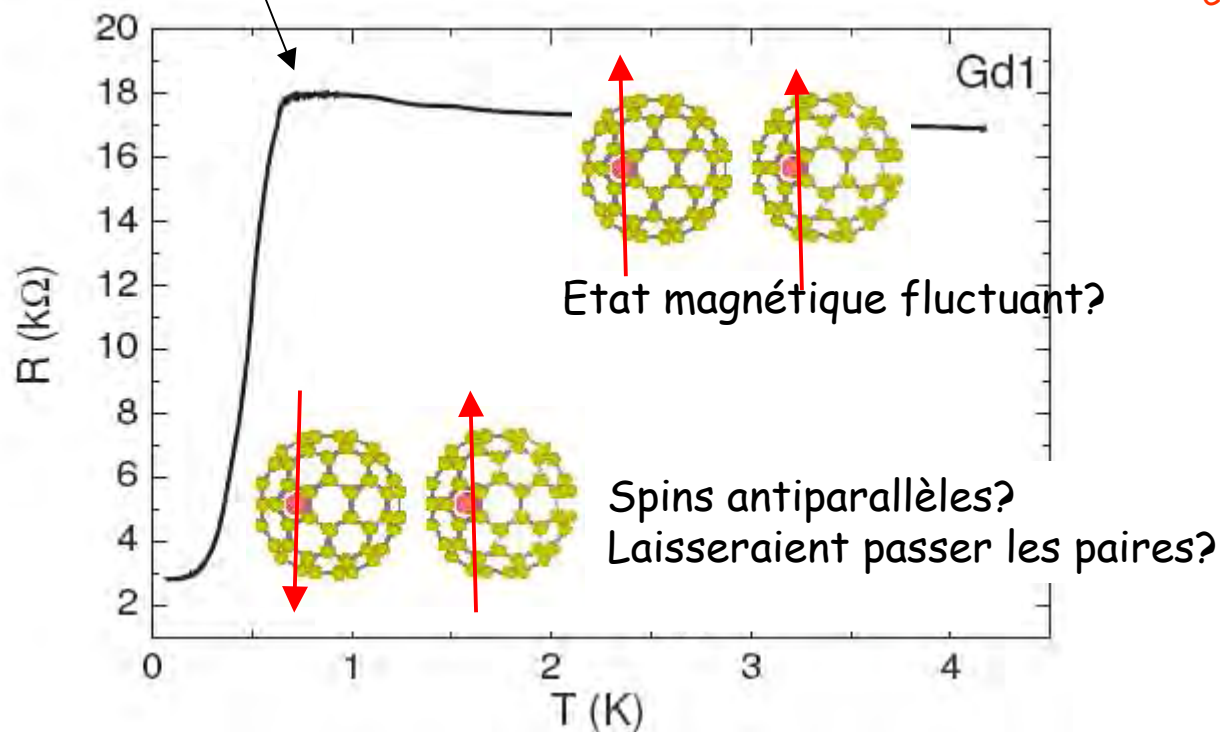
Kasumov et al, Phys. Rev. B 72, 033414 (2005)

# Les paires passent-elles à travers un dimère de métalofullérène?



Transition with  $T_C = 0.7 \text{ K}$ ,  $H_C = 1 \text{ T}$

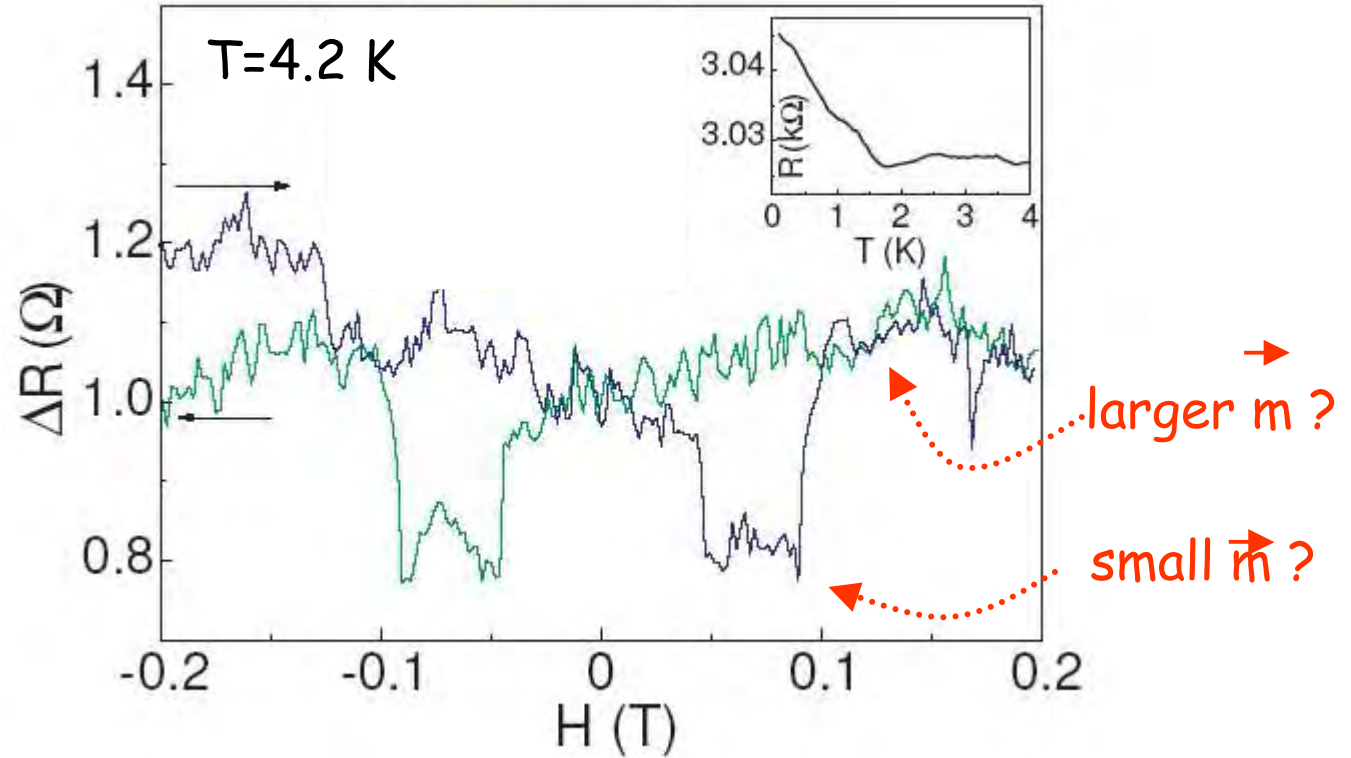
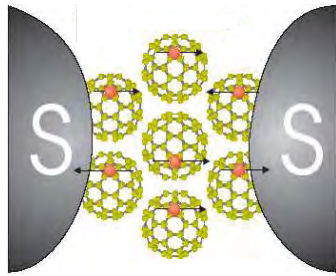
Mais la  $T_C$  des contacts est de 5K !



Selon son état, la molécule peut bloquer le passage des paires



# No proximity effect in a metallofullerene cluster (about 10 molecules)



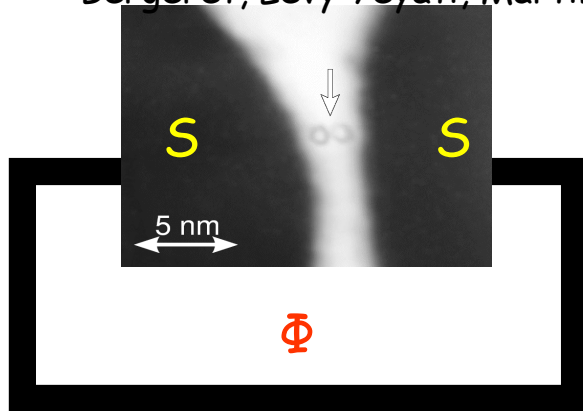
Hysteretic behavior: magnetic moment (frustrated AF grain?)

Magnetic ordering in the cluster with a magnetic moment?

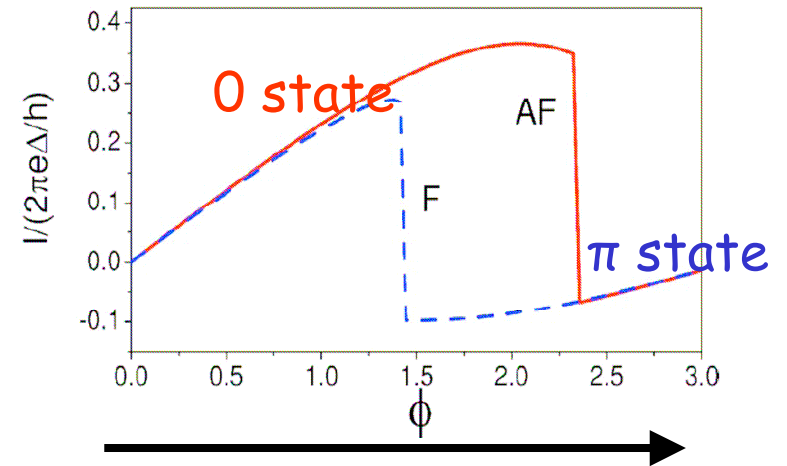
# What next?

- Prediction: electronic configuration can control relative orientation of moments

Bergeret, Levy Yeyati, Martin-Rodero, Phys. Rev. B (2006)



Need a loop to test prediction

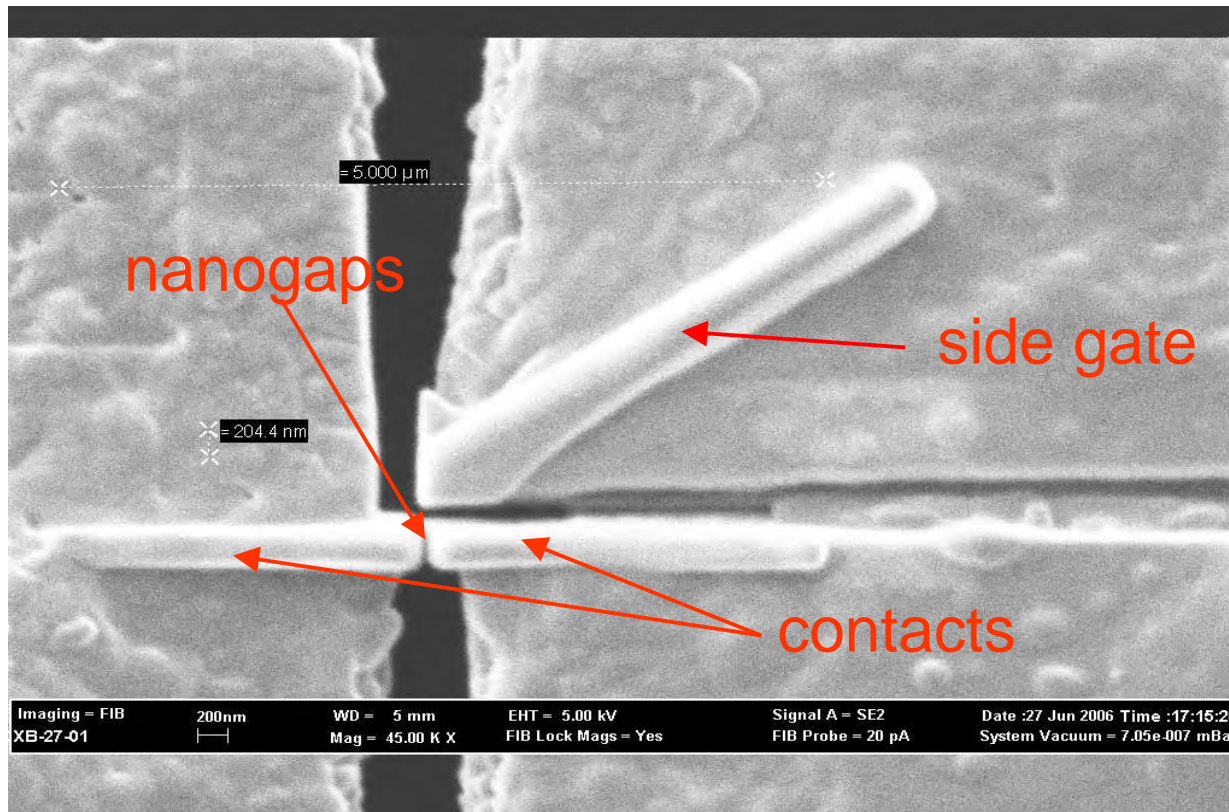


- Simplify: Monomers of metallofullerenes (La@C82)
- Other molecules (DNA quadruplexes...)
- Find a way to gate these suspended devices, and still observe them...

# Toward suspended gates on metallofullerenes...

Focused Ion Beam-assisted growth (A. Kasumov, F. Fortuna)

SEM image

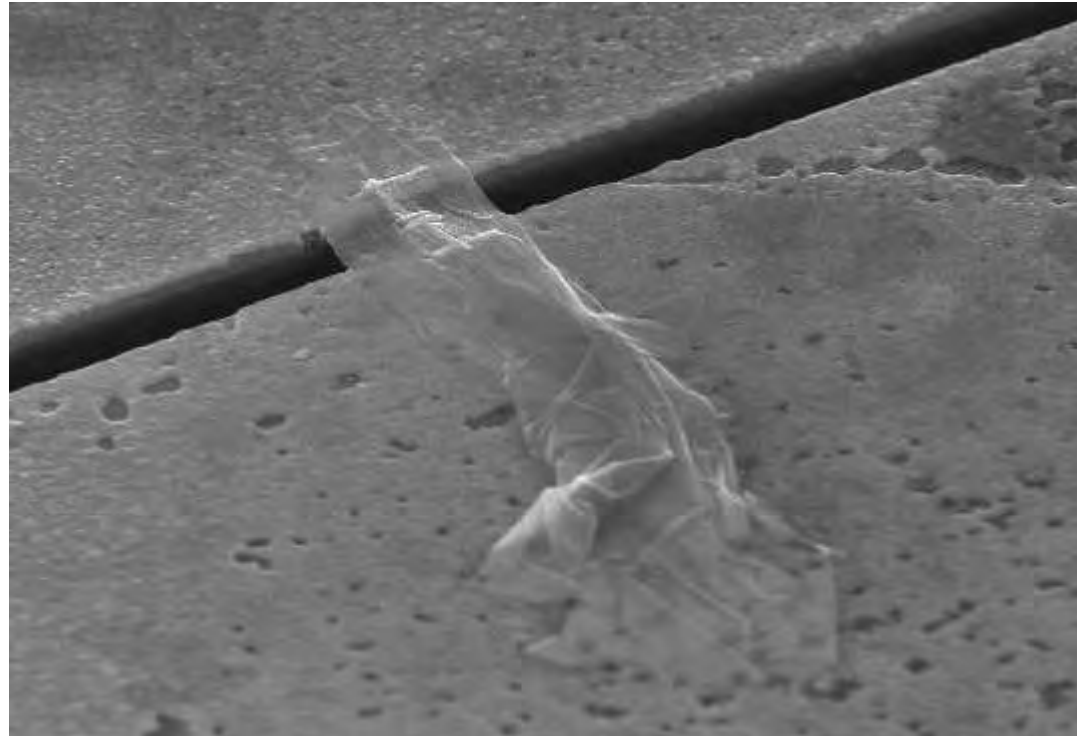
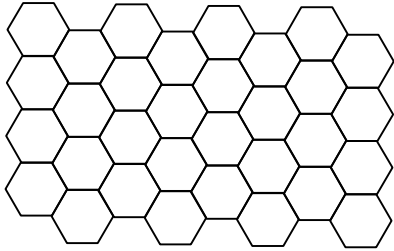


Work in progress...

# La nouvelle passion: le graphène

A. Shailos, P. Delplace, W. Nativel, C. Collet,

M. Ferrier, R. Deblock, S. Guéron, A. Kasumov, H. Bouchiat



Graphène: monoplan atomique.

Les électrons ont des propriétés très particulières:

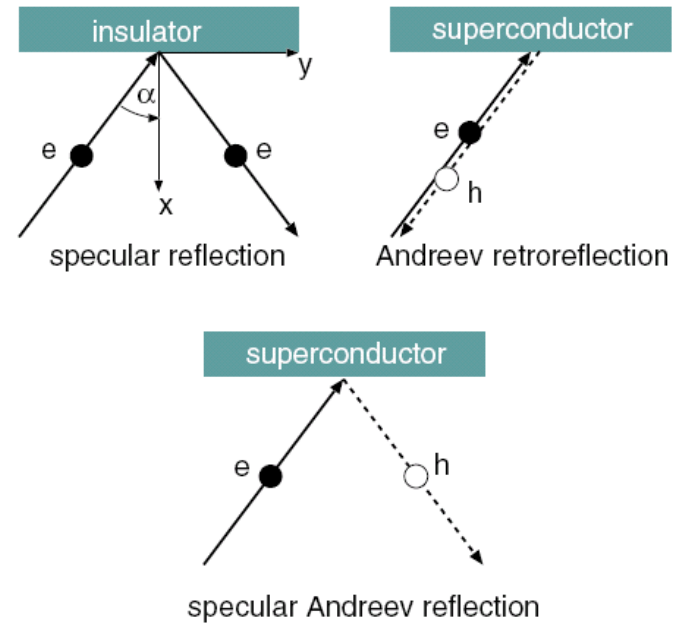
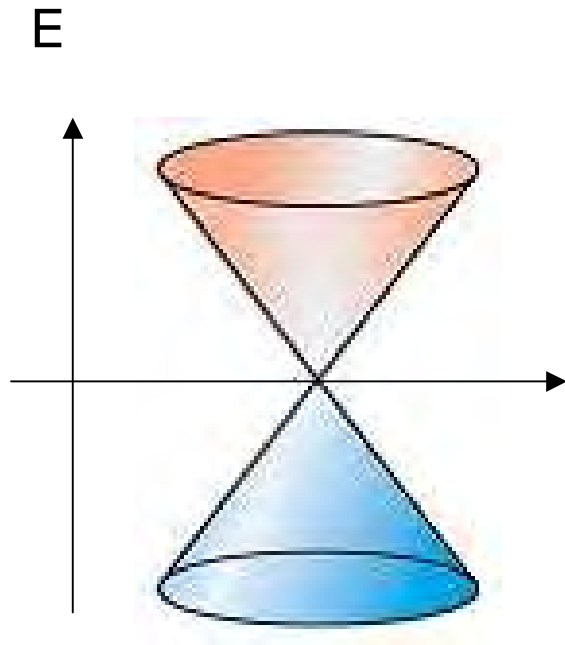
En particulier, modifie la conversion paire- $\rightarrow$  électrons conjugués (prédiction 2006).

# Use the proximity effect to probe a non superconducting sample

Graphene????

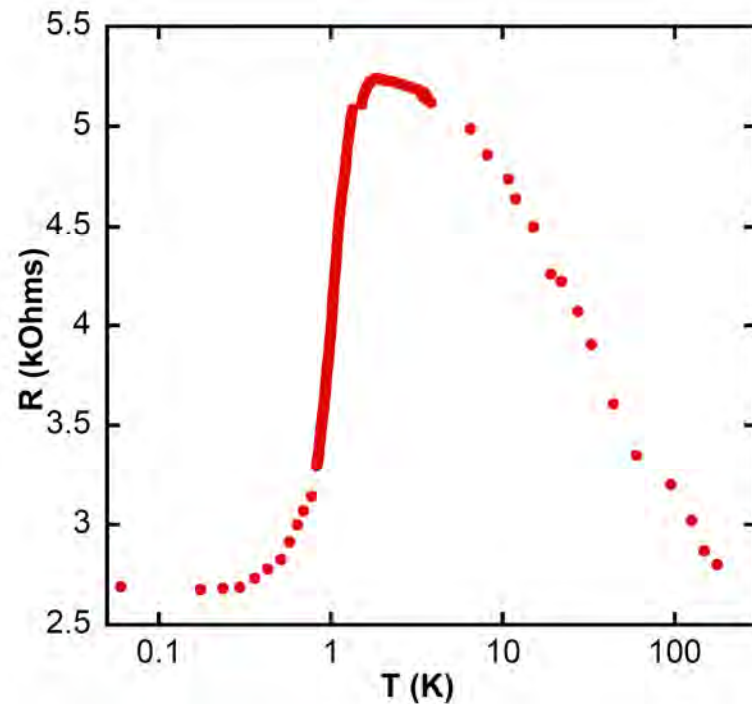
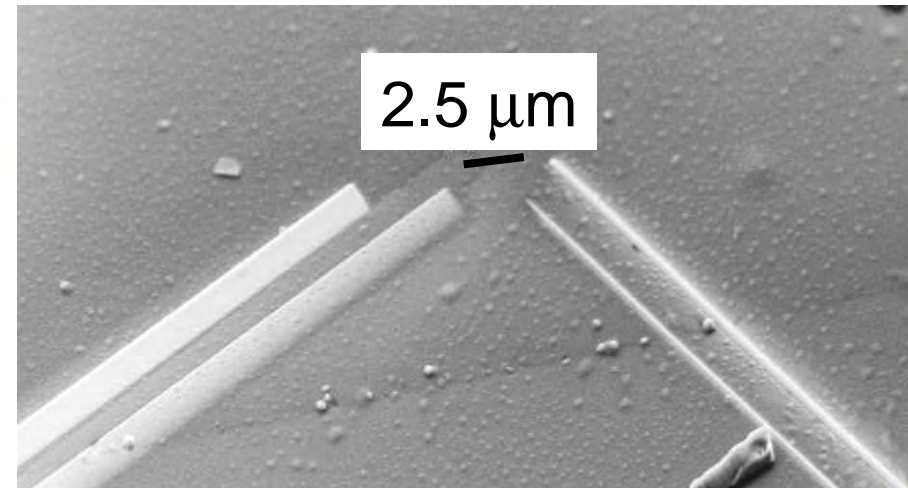
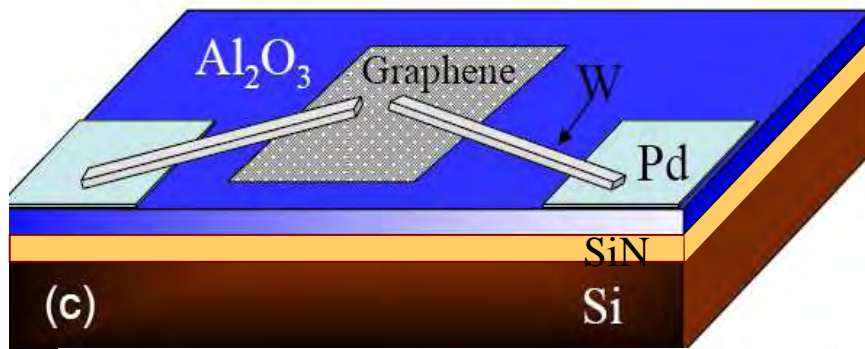
Effect of the band structure on proximity effect?

Beenakker, 2006: modified Andreev reflexion



# (Quelques couches de) Graphène connecté à des électrodes supraconductrices

Microscope électronique balayage

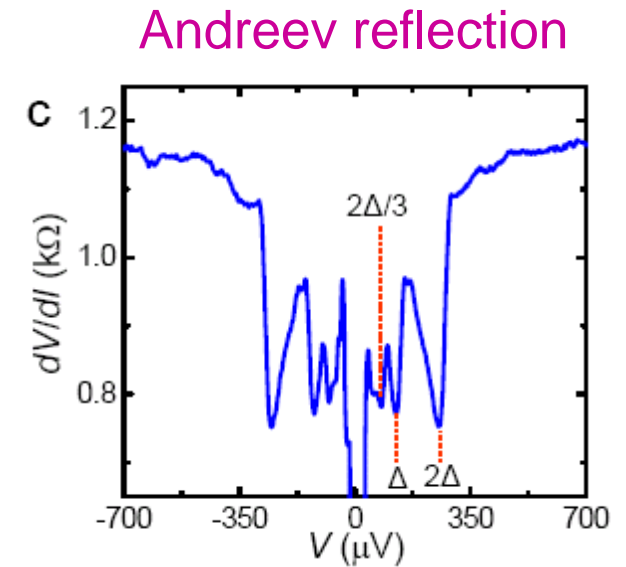
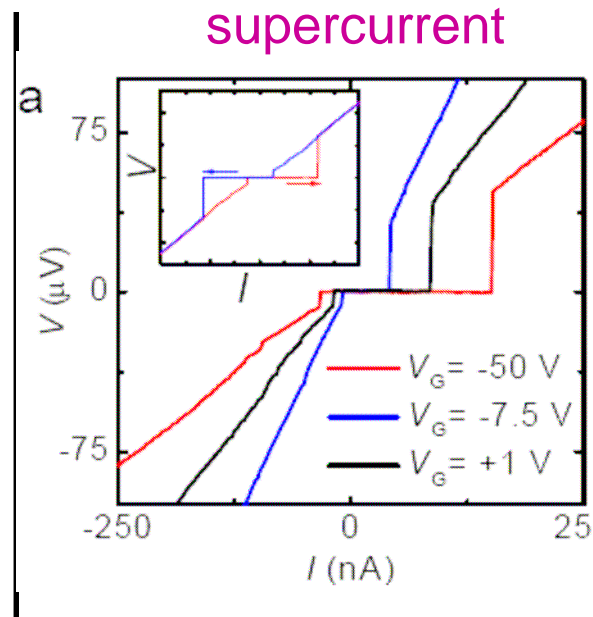
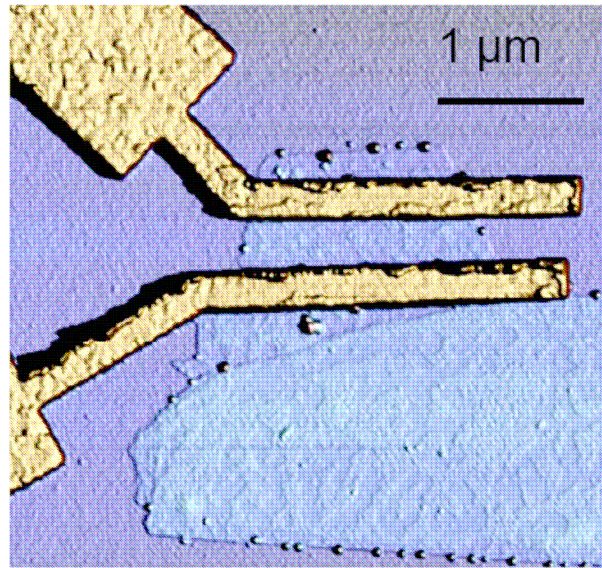


Résistance chute, mais ne tombe pas à 0: électrodes trop éloignées. D'autres ont fait mieux (U. Delft).

À suivre...

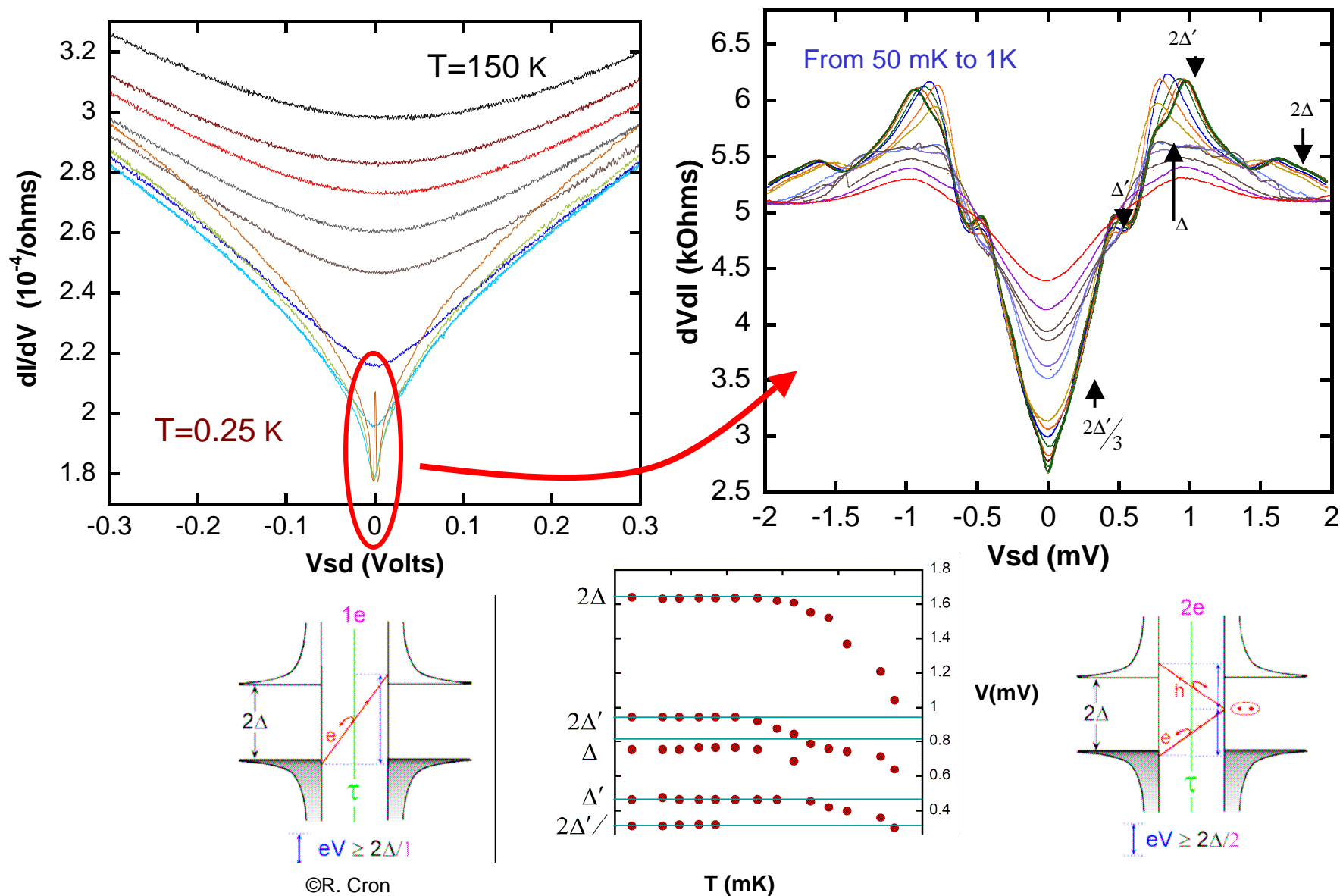
# Heersche et al, Nature 2006: gate-dependent supercurrent

S electrodes: Ti/Al,  $T_c=1$  K , less than 400 nm apart



High field behavior?

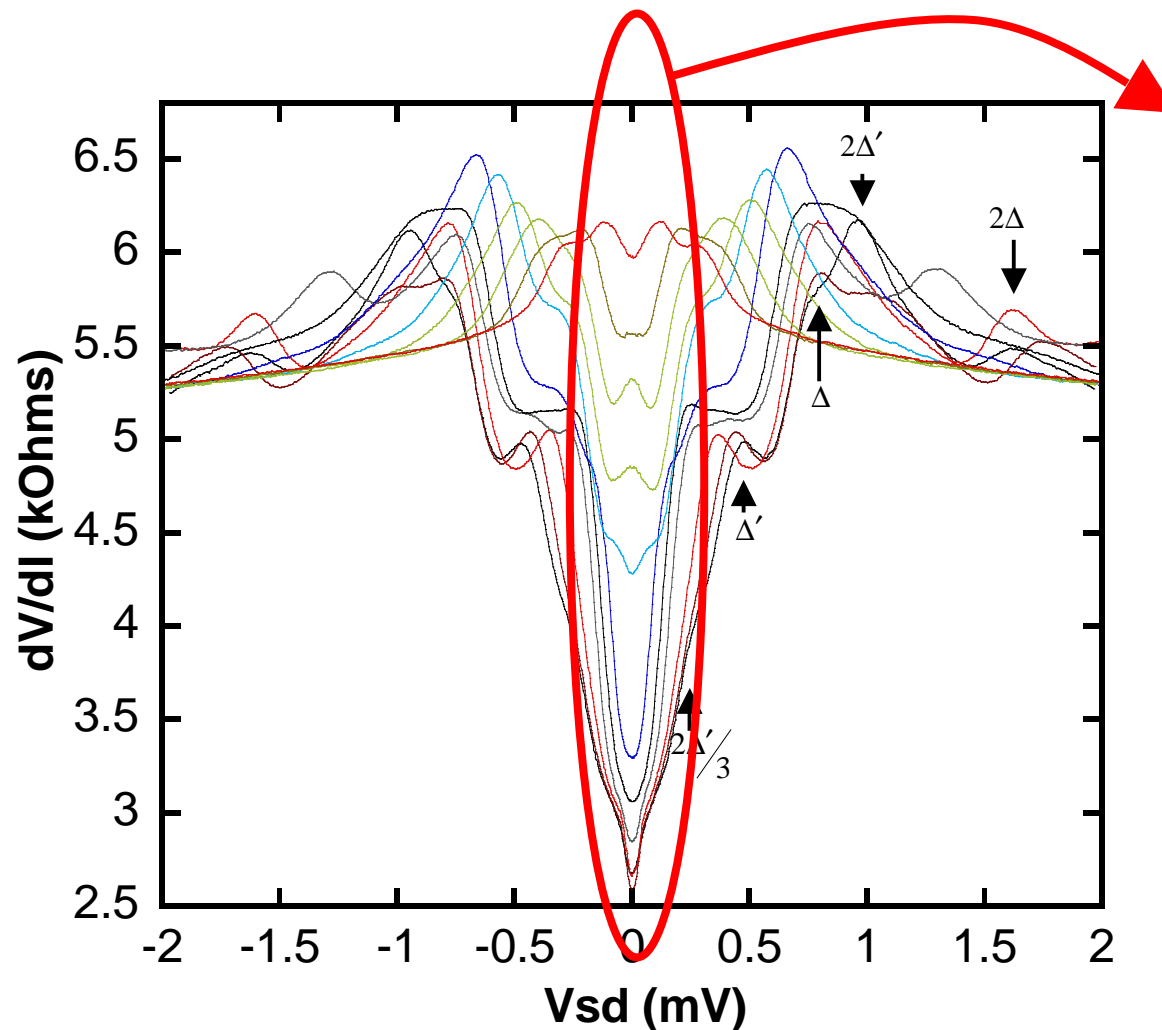
# Differential conductance in meV range : graphene/ite band structure



Multiple Andreev reflection peaks. 2 gaps due to local doping by contacts ?



## Field dependence is more complicated



Resistance alternates between local maximum and minimum:

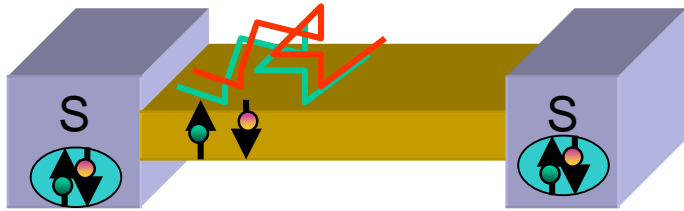
Effect of orbit focusing by magnetic field?

Could we see focusing by magnetic field ?

Shailos et al, Europhys Lett (2007)

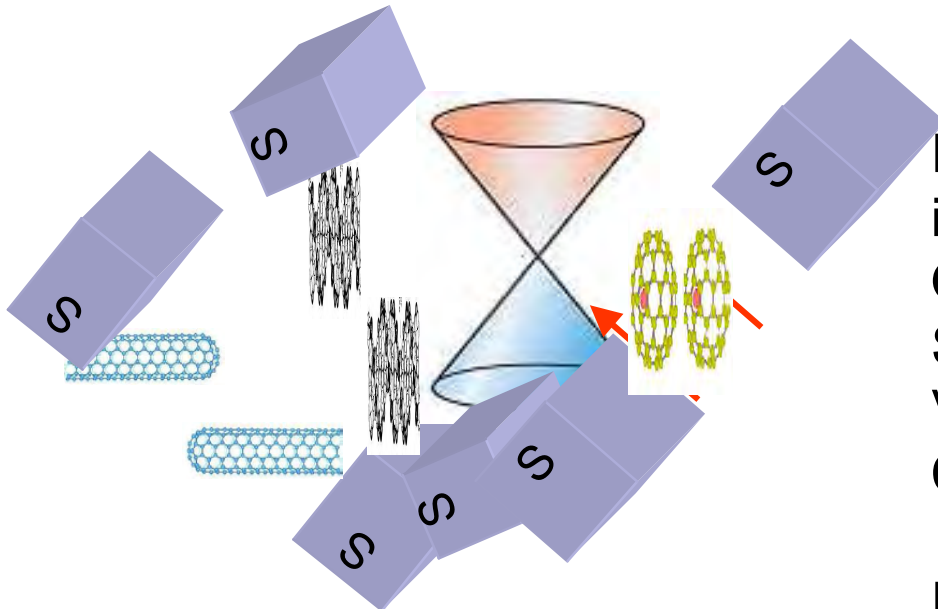
# The superconducting proximity effect in metals and molecules

## Long diffusive junctions



Still things to explore (magnetic field, dynamics):  
snapshots of diffusing Andreev pairs

## 0d, 1d, 2d « molecule »



Proximity effect singles out  
intrinsic properties of molecules:  
Orbital states  
Spin states  
Vibrational modes  
Correlated states...

Enhances contrast thanks to the  
superconducting electrodes.