united nations educational, scientific and cultural organization

international atomic energy agency

the **abdus salam** international centre for theoretical physics

ICTP 40th Anniversary

SMR 1564 - 7

SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
(24 May - 11 June 2004)

Metal Nanowires: Structure, Magnetism and Transport

Erio TOSATTI
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These are preliminary lecture notes, intended only for distribution to participants.

METAL NANOWIRES: STRUCTURE, MAGNETISM AND TRANSPORT

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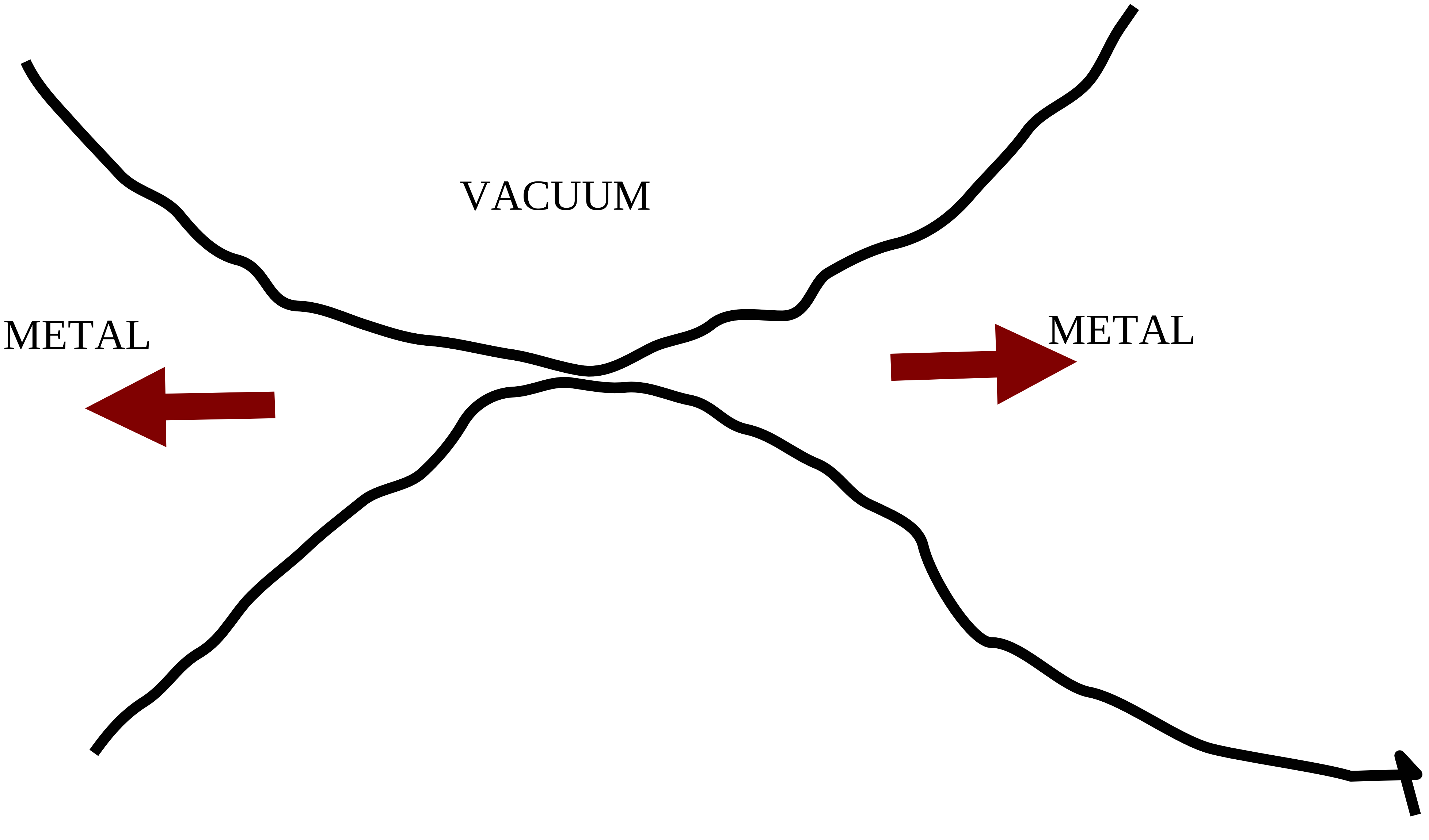
K. Takayanagi (Tokyo)
D. Ugarte (Campinas)
C. Untiedt (Alicante)

WHEN WE TURN LIGHTS OFF ....



CONTENTS

METAL NANOCONTACTS AND NANOWIRES: WHEN & WHY DO THEY FORM.

STRUCTURE: MAGIC AND WEIRD NANOWIRES

MONATOMIC NANOWIRES ARE MAGIC TOO

MAGNETISM AND TRANSPORT, NEG. BALLISTIC MAGNETORESISTANCE

NANOMAGNETISM IN 4d, 5d METAL NANOWIRES?

Rodrigues et al. (2000)

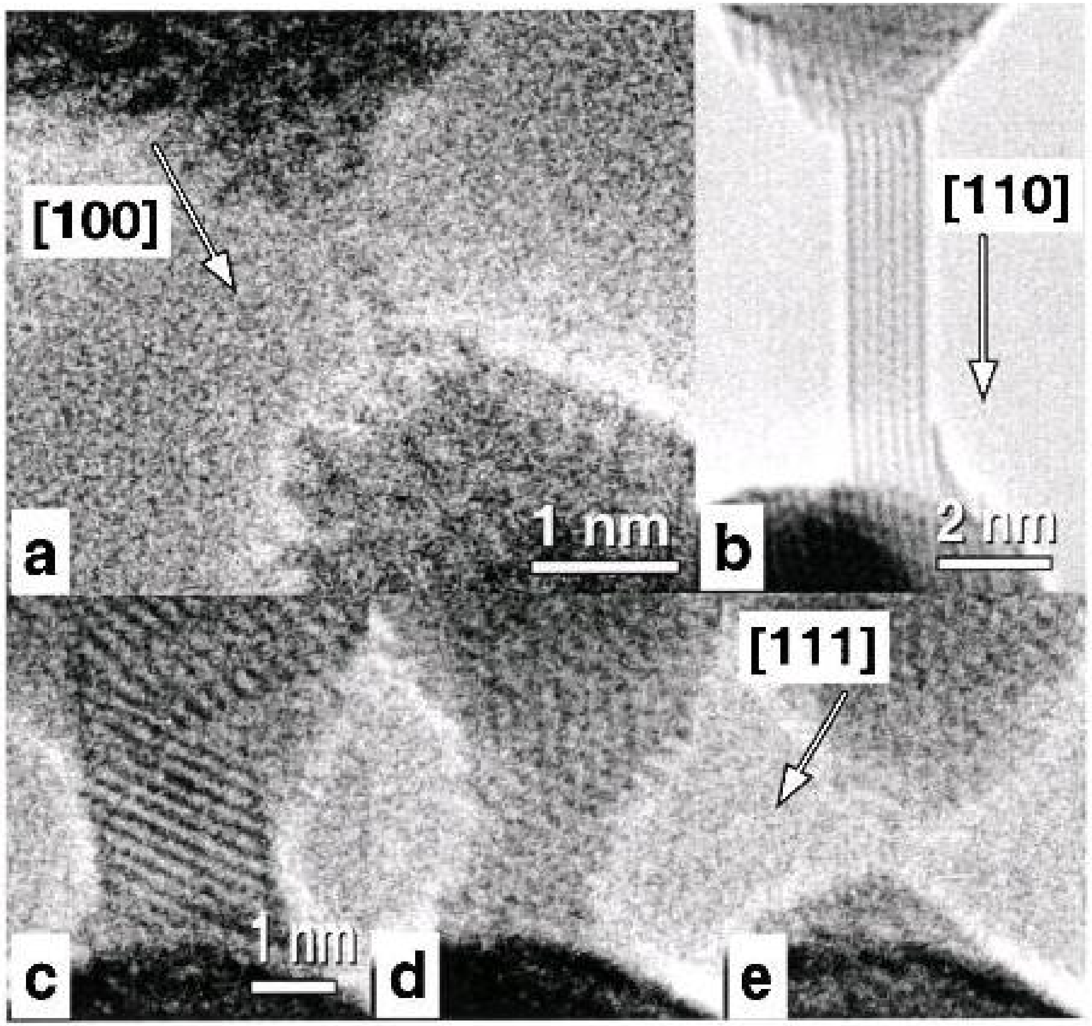


FIG. 2. HRTEM images of gold NWs; atomic positions appear dark. (a) [100] atom-chain NW; (b) rodlike [110] NW; (c)–(e) temporal evolution of a NW formed when the apexes are sliding: 0, 17:12, and 24:15 min, respectively.

Kondo, Takayanagi (2000)

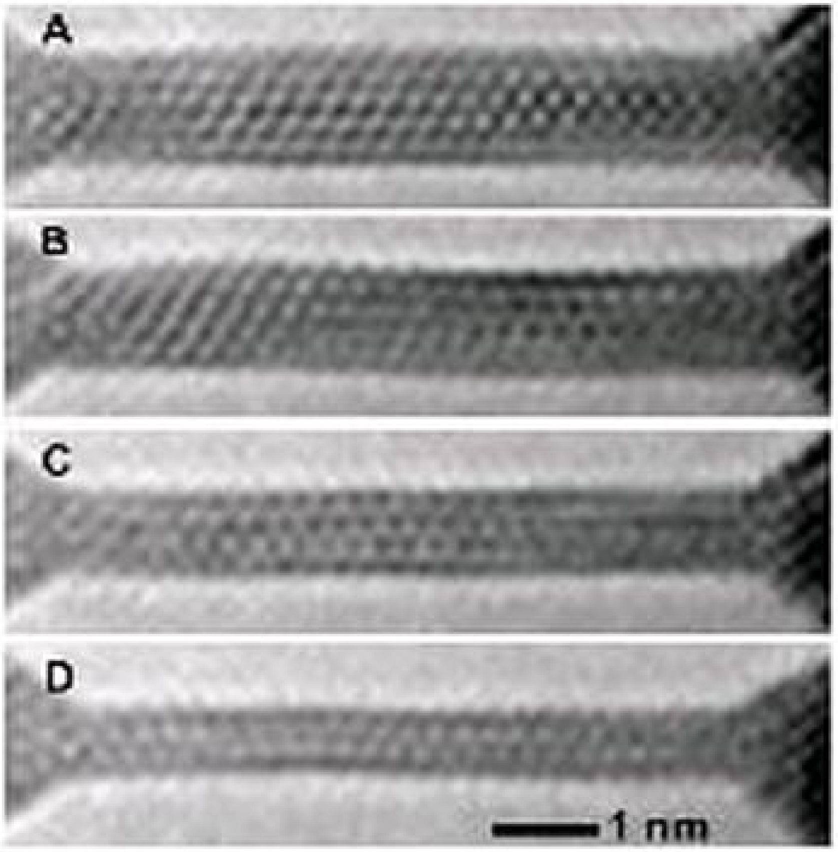


Fig. 1. TEM images of stable gold nanowires observed during one thinning process. The diameters of the wires in (A), (B), (C), and (D) are 1.3, 1.1, 0.8, and 0.6 nm, respectively. The dark dots represent positions of atoms projected on the image plane. The dark dots are aligned on atom rows along the wire axis. These wire images are wavy, particularly in (D).

UNDERSTANDING EVOLUTION AND STRUCTURE OF NANOCONTACTS

1. PLASTIC FLOW

2. QUASI-EQUILIBRIUM NANOWIRES:
   LONG LIVED MAGIC STRUCTURES

3. BREAKING

QUASI EQUILIBRIUM STRUCTURES: MAGIC NANOWIRES

a) **THICK** NWS ARE CRYSTALLINE:
MAGIC STRUCTURES DETERMINED BY GOOD FACES

b) **MODERATELY THIN** NWS:
ELECTRONIC SHELL CLOSING

c) **ULTRA-THIN** NWS (R<10 A) :
POSSIBLE NONCRYSTALLINE PACKINGS

- QUASI EQUIL. THICK WIRES:
  - CRYSTALLINE

Au

Kondo et al (1997)

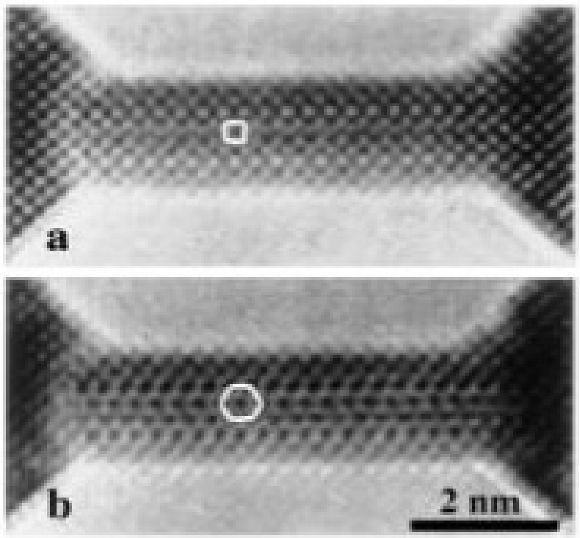
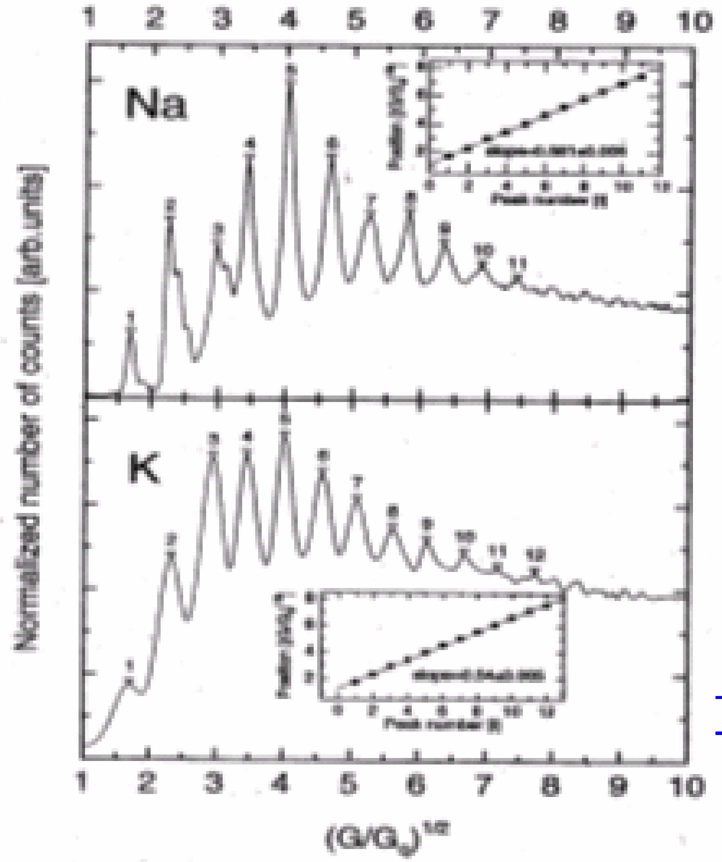
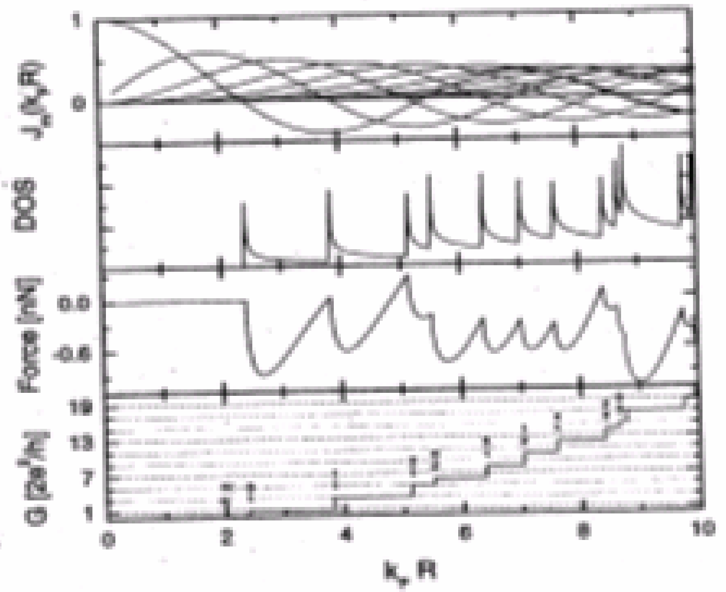


FIG. 2. Transmission electron micrographs of an NB 2 nm thick; obtained at the focuses of (a) 65 nm and (b) 55 nm. Note the square lattice in (a) and hexagonal one in (b).





PEAKS = CLOSED ELECTRONIC SHELLS

YANSON, RUITENBEEK et al (2001)

THIN WIRES: ELECTRONIC SHELL CLOSING

ULTRATHIN: PACKING INDUCED NONCRYSTALLINE Nws

GULSEREN et al (1998)

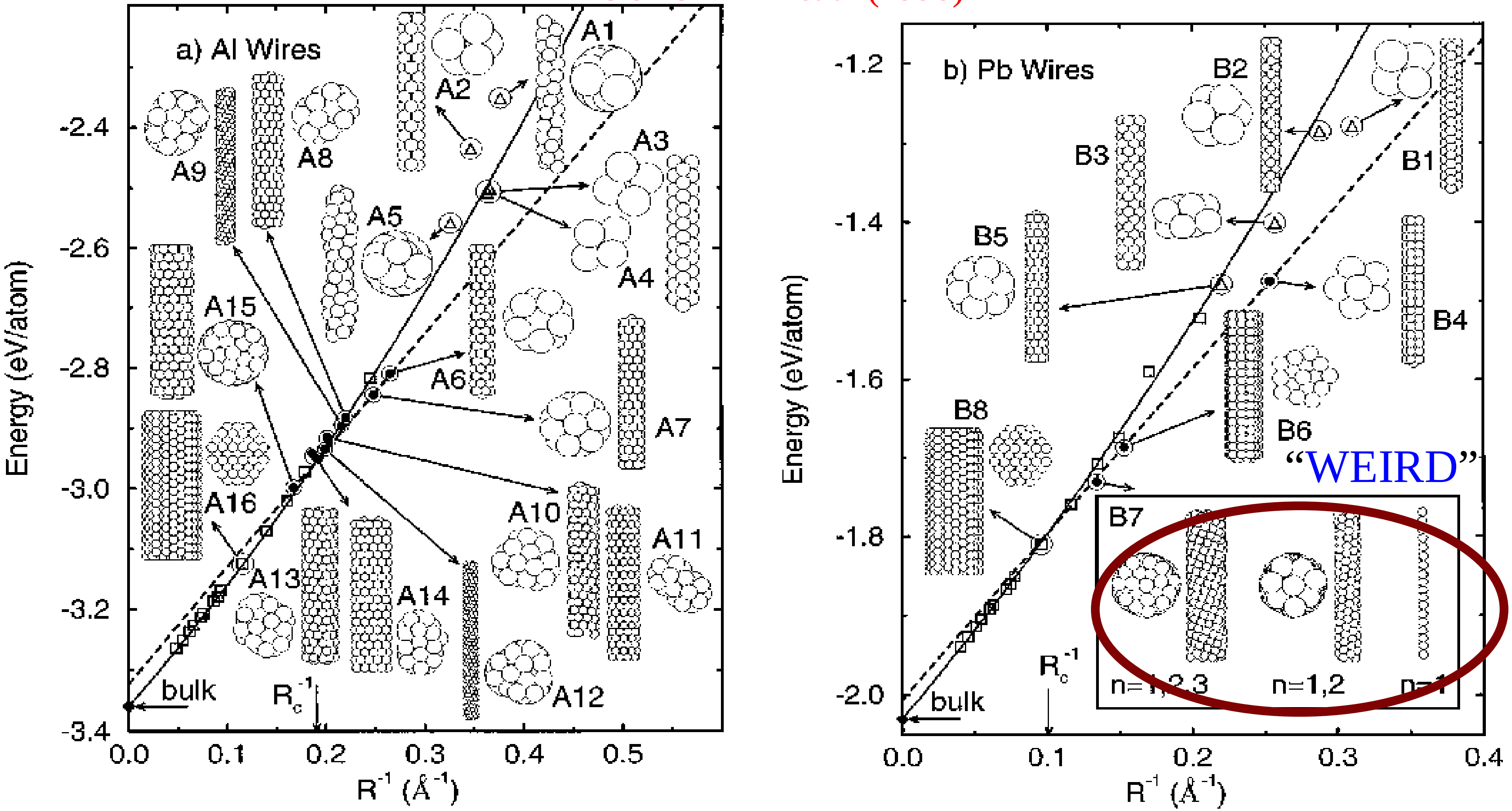


FIG. 1. Total energy per atom E vs inverse wire radius $1/R$ for the relaxed structures obtained by optimization for (a) Al and (b) Pb wires. A selection of morphologies is shown. fcc wires are represented by open squares and weird wires by full circles. Very thin wires which do not belong to either class have been marked with open triangles. Solid lines represent a fit to fcc wires using Eq. (1), and dashed lines represent a fit to weird wires using Eq. (2). Weird structures become favored for $R < R_c$. (b) Inset: structure of the helical Pb wire $B7$: complete wire ($n = 1, 2, 3$), with outer shell removed ($n = 1, 2$), and inner strand ($n = 1$). Note how the outer shell exhibits a nearly square atomic structure, while that of the second shell is nearly triangular.

(7,3)
↓
7-17

Kondo
Takayanagi
(2000)

11-4

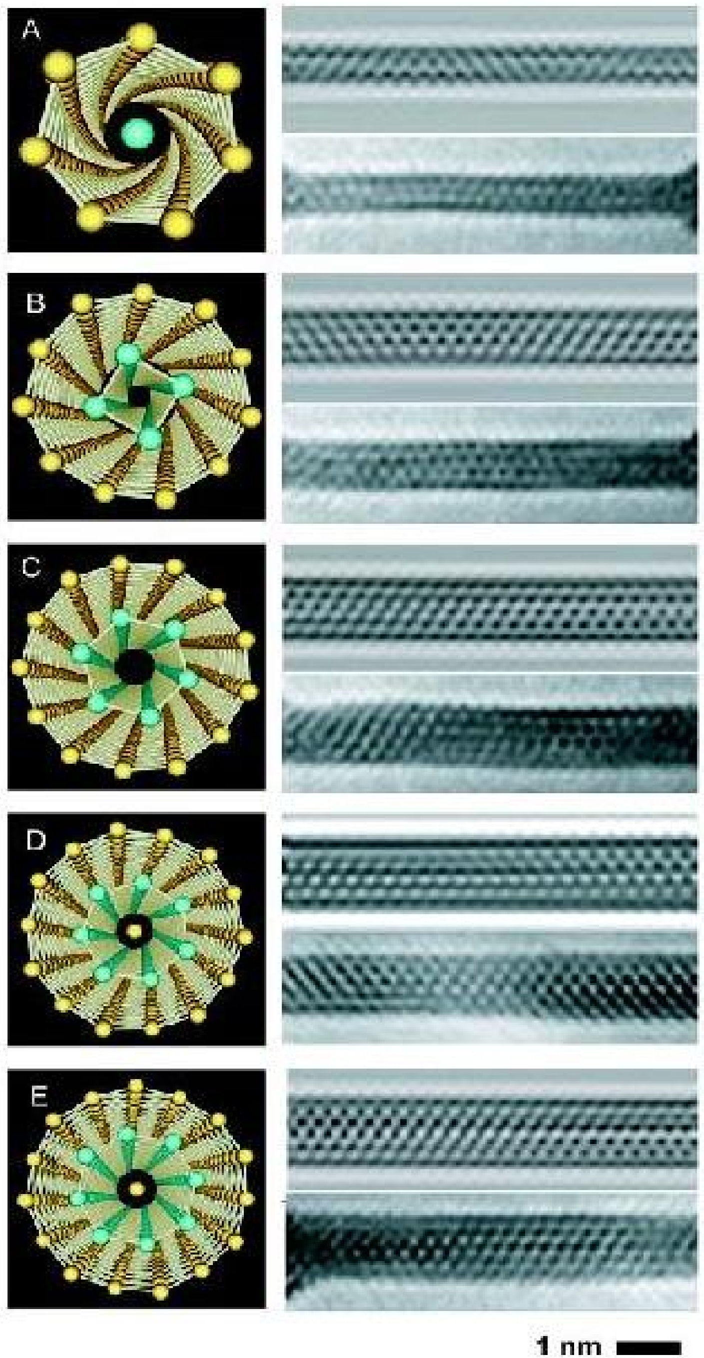
13-6

HELICAL!

Delta N = 7 !!

14-7

15-8



Prediction:
Gulseren et al (1998)

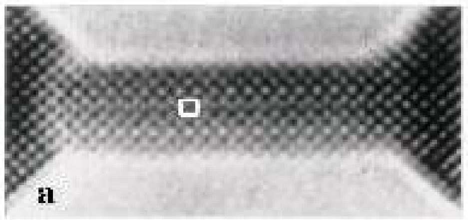
Ab initio theory:

“Weird” wires stabilized by packing

Tosatti et al. (2001)

QUASI EQUILIBRIUM MAGIC STRUCTURES: THEORY

THE CONCEPT OF STRING TENSION



Tosatti et al

Science 291, 288 (2001)

$$f = \frac{F - \mu N}{L}$$

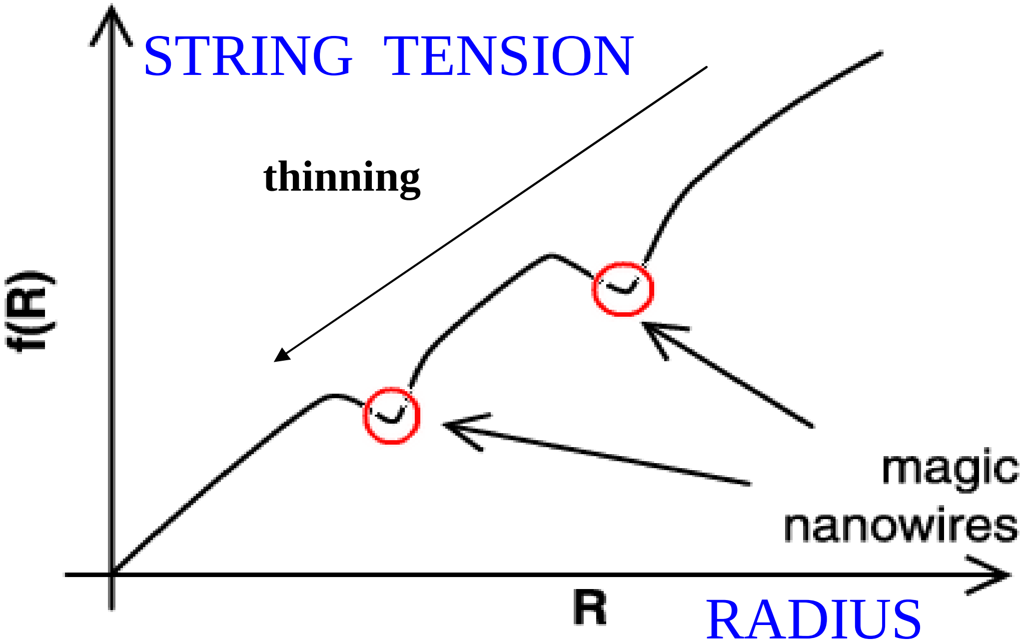


Fig. 1. String tension of a tip-suspended nanowire as a function of radius (schematic). Local minima signal long-lived magic nanowires. The wire disappears ($R = 0$) at true equilibrium.

ARY 2001 VOL 291 SCIENCE www.scienc

Ab initio theory (Tosatti et al Science 291,288(2001))

$$f = \frac{F - \mu N}{L}$$

1. BUILD CRUDE WIRE MODEL USING EMPIRICAL FORCES

2. OPTIMIZE ZERO STRESS STRUCTURE BY FIRST PRINCIPLES DENSITY FUNCTIONAL CALCULATION

3. OBTAIN F (= E AT T=0) AND L OF OPTIMAL ZERO STRESS STRUCTURE

4. OBTAIN mu FROM BULK CALCULATION

5. CALCULATE STRING TENSION f, REOPTIMIZE IN PRESENCE OF STRESS UNTIL SELFCONSISTENT

6. BUILD ANOTHER WIRE MODEL, ETC

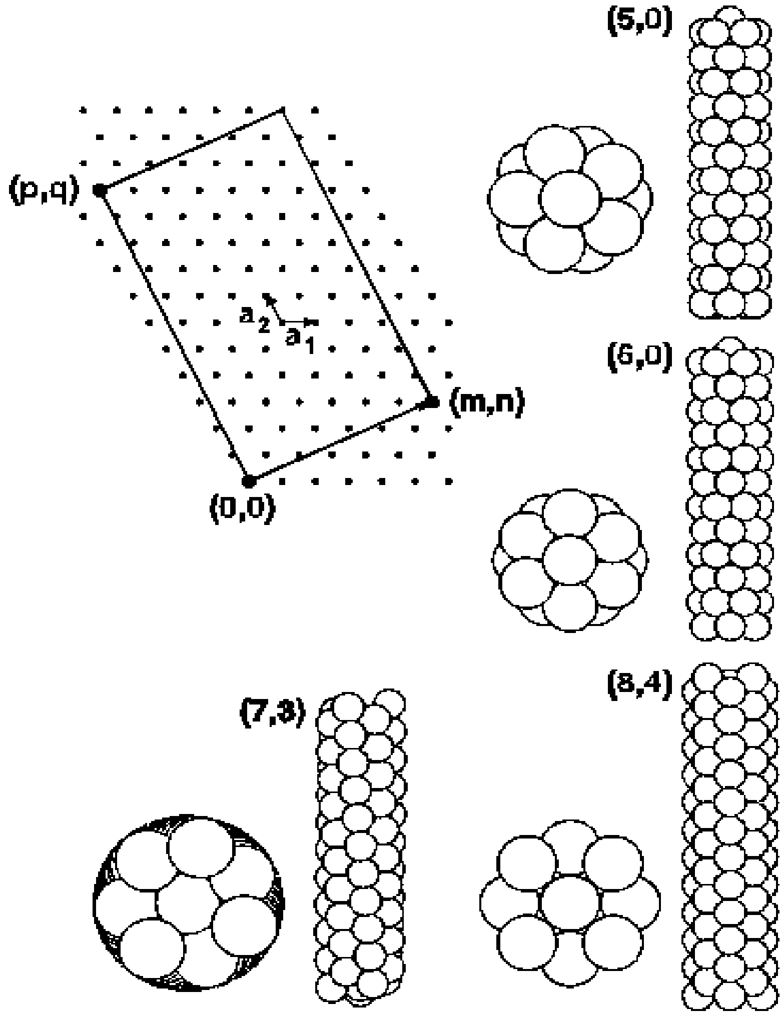


Fig. 2. Cylindrical folding of a triangular lattice for an (m, n) tube, with views of several coaxial tube nanowires. Each atom is pictured as a sphere of atomic radius. The (7, 3) gold nanowire (note its chirality) was reported to be magic in (3).

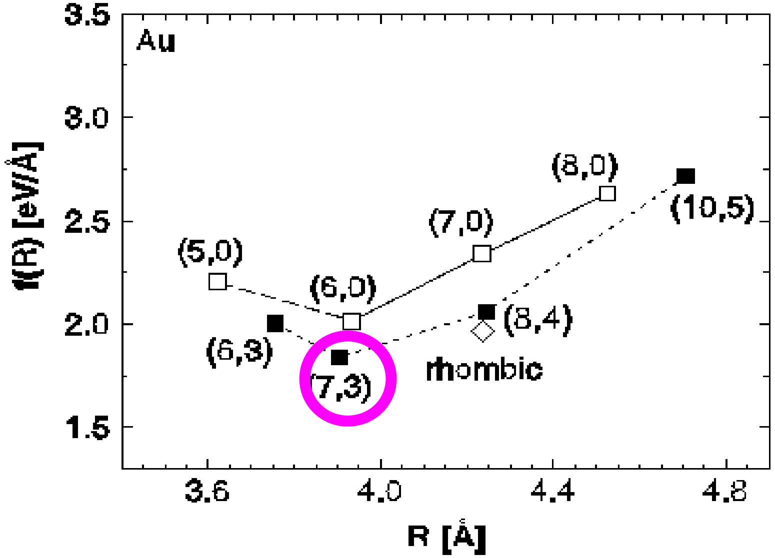


Fig. 3. Calculated (*22*) string tension (1 eV/Å = 1.6 nN) of tip-suspended gold nanowires at zero temperature (only the largest and smallest *n* values are shown). The minimum demonstrates why the (7, 3) nanowire is magic. The calculations were carried out for infinite tip-free wires, with structure relaxed to minimize string tension (Eq. 1), starting from initial wire geometries obtained by Voter's potential; μ(Au) = −4.401 eV was obtained from a separate bulk calculation.

(7,3)

$7,-1^7$

Kondo
Takayanagi
(2000)

11,-4

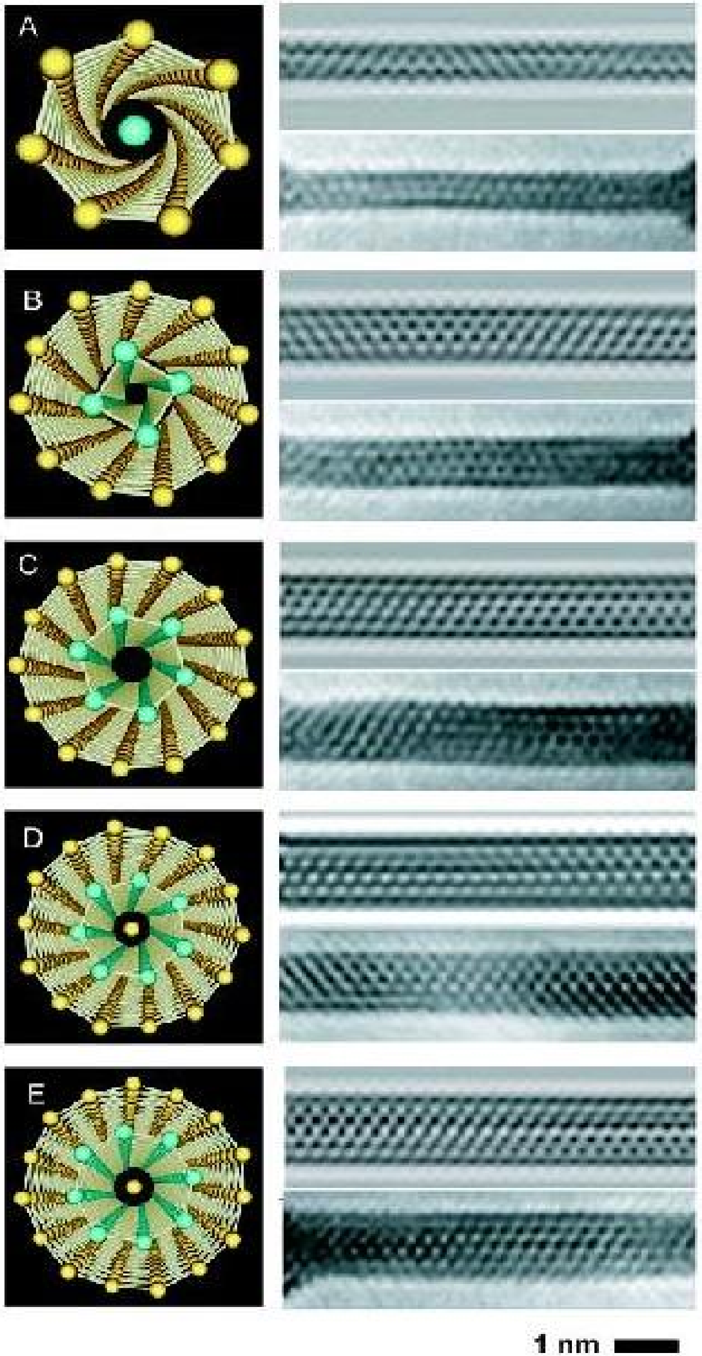
13-6

HELICAL!

14-7

Δ N = 7 !!

15-8



Prediction:
Gulseren et al (1998)

Ab initio theory:

“Weird” wires stabilized by packing

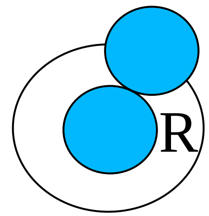
Tosatti et al. (2001)

WHY HELICAL?

$$f = \frac{F - \mu N}{L}$$

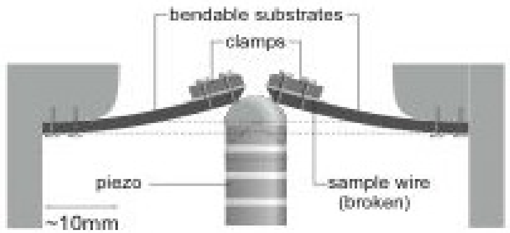
→ **HELICAL** TUBE NARROWER AND **LONGER**

WHY delta N = 7?



→ 2 pi N = 6.28 N< NR! **-->** N=7

BREAK JUNCTION
CONDUCTANCE
DEMONSTRATES
WIRES TOO



RUITENBEEK et al (2003)

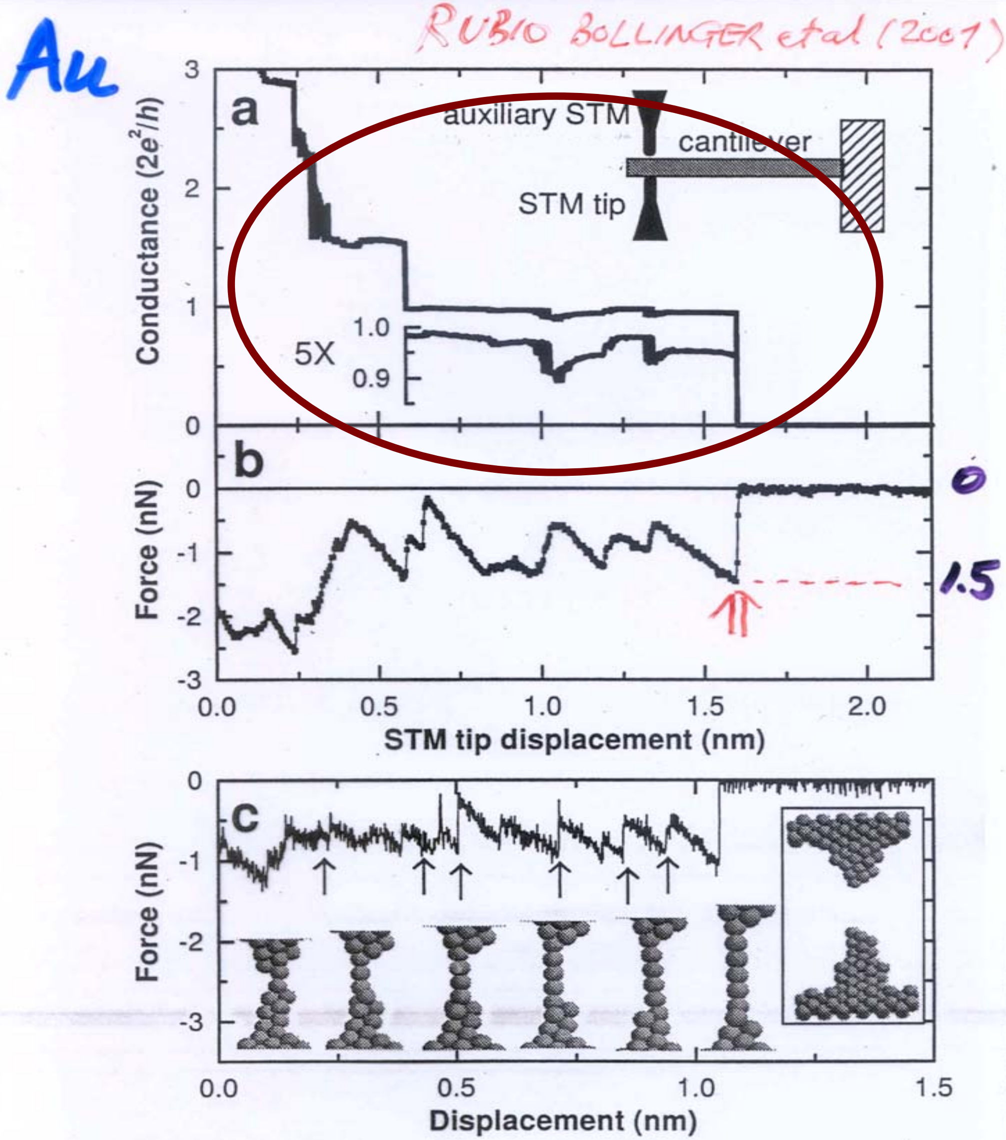
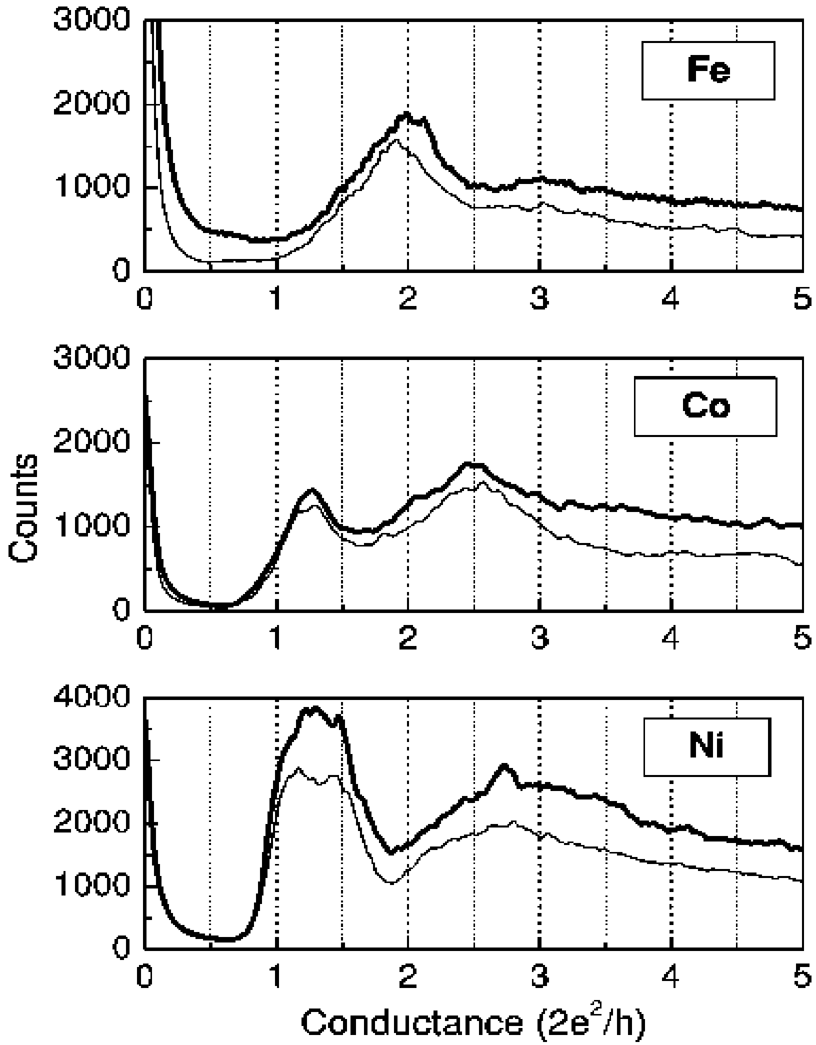


FIG. 1. Simultaneous conductance (a) and force (b) measurement during chain fabrication and breaking. The conductance in the last plateau has been zoomed to show detailed variations. Inset: schematic drawing of the experimental setup. (c) Calculated force during the MD simulation.

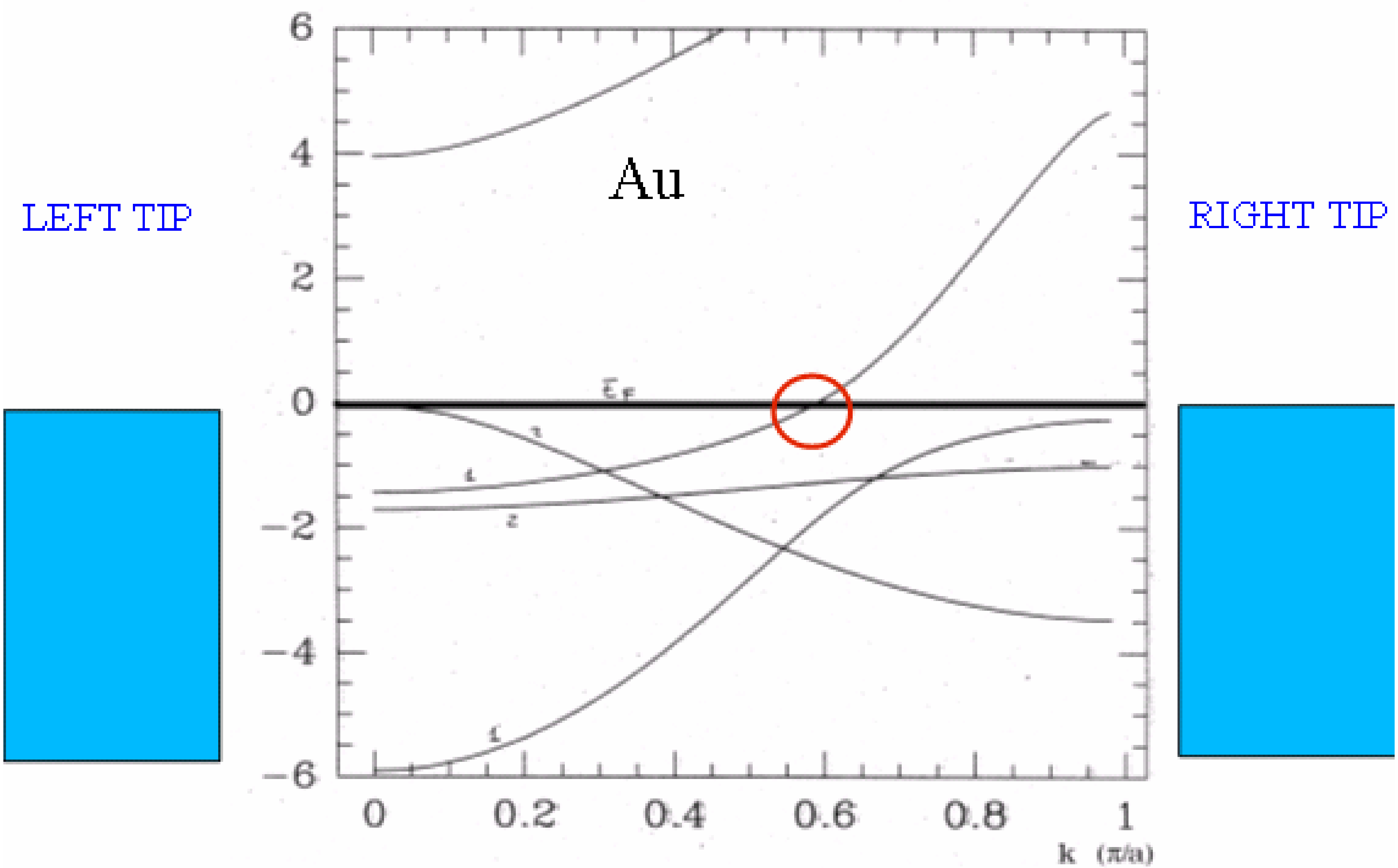
CONDUCTANCE STEP HISTOGRAMS

UNTIEDT, DEKKER, DJUKIC, AND VAN RUITENBEEK (2004)

T= 4.2 K



ELECTRONIC PROPERTIES

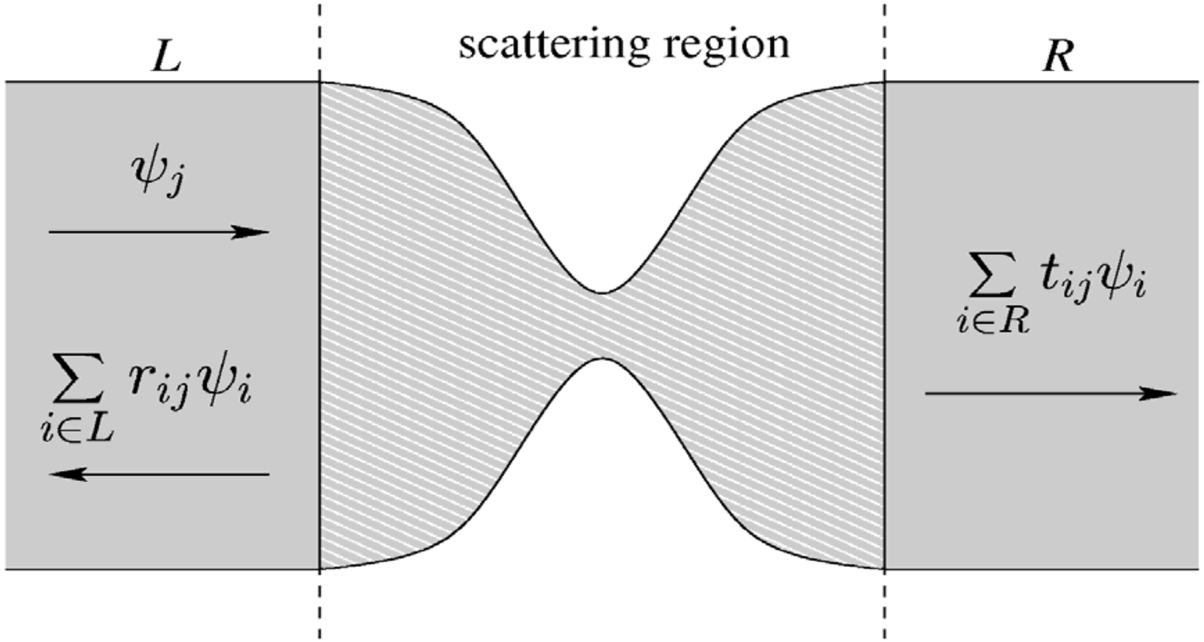


Ballistic conductance

Landauer-Buttiker formula for ballistic conductance:

$$G = \frac{e^2}{h}\mathrm{Tr}[T^+T],$$

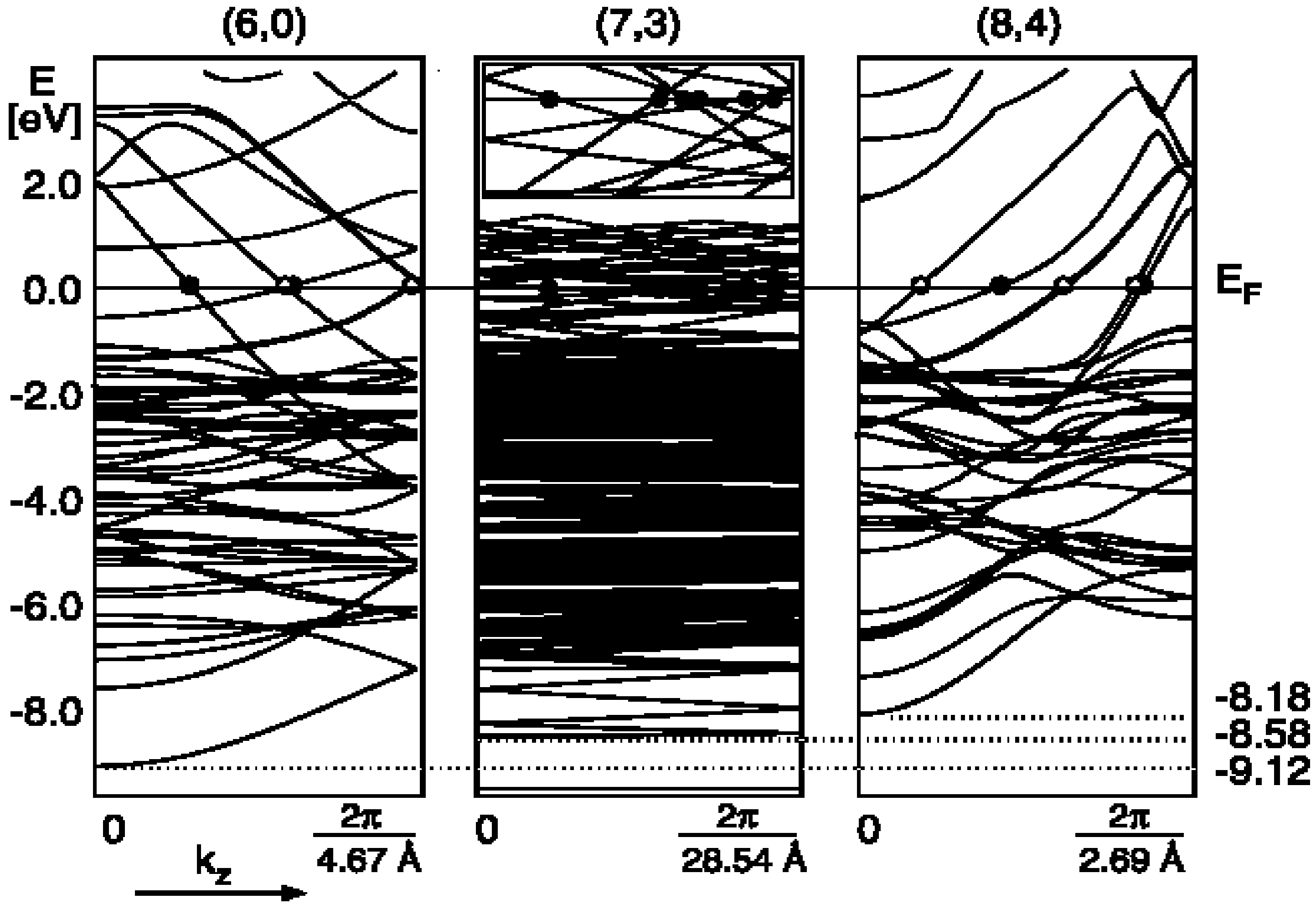
$$T_{ij} = \sqrt{\frac{I_i}{I_j}}\, t_{ij}$$



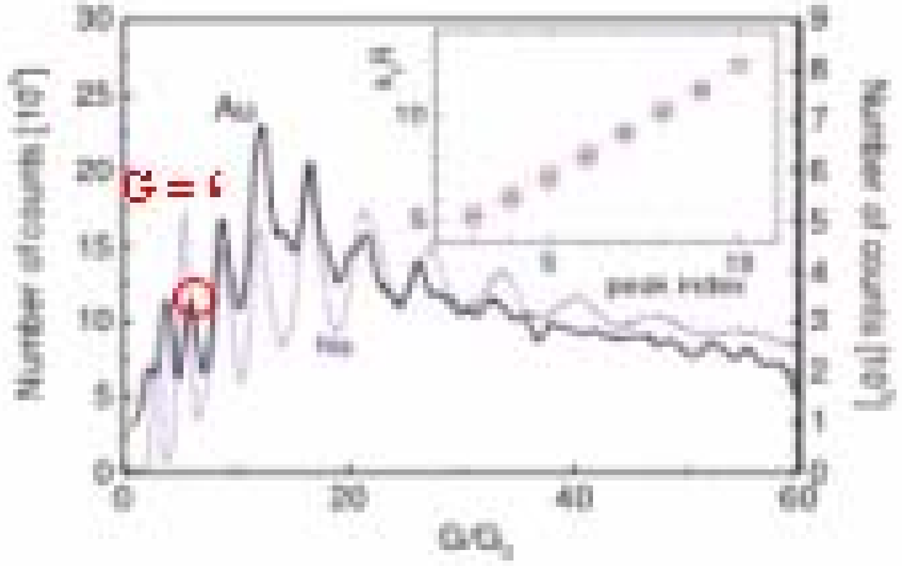
$G < G_{MAX} = (e^2/h)\,(N_{UP} + N_{DOWN})$

Au (7,3) NANOWIRE

6 channels!

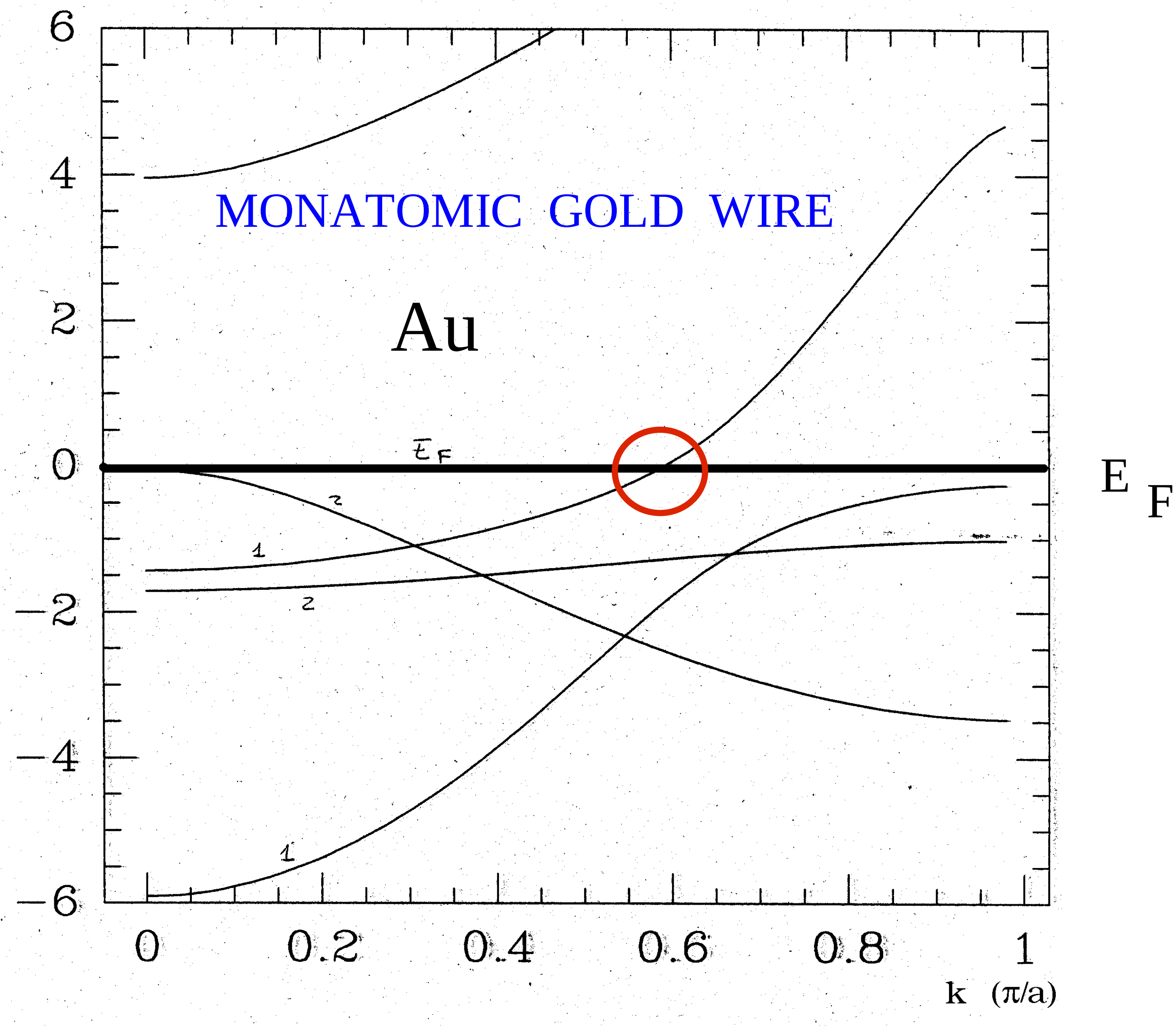


DETECTING MAGIC NANOWIRES THROUGH CONDUCTANCE



MARES et al (2004)

MONATOMIC NANOWIRES


MONATOMIC GOLD WIRE
Au
E F
6
4
2
0
−2
−4
−6
0
0.2
0.4
0.6
0.8
1
k (π/a)

A.I. Yanson
(2000)

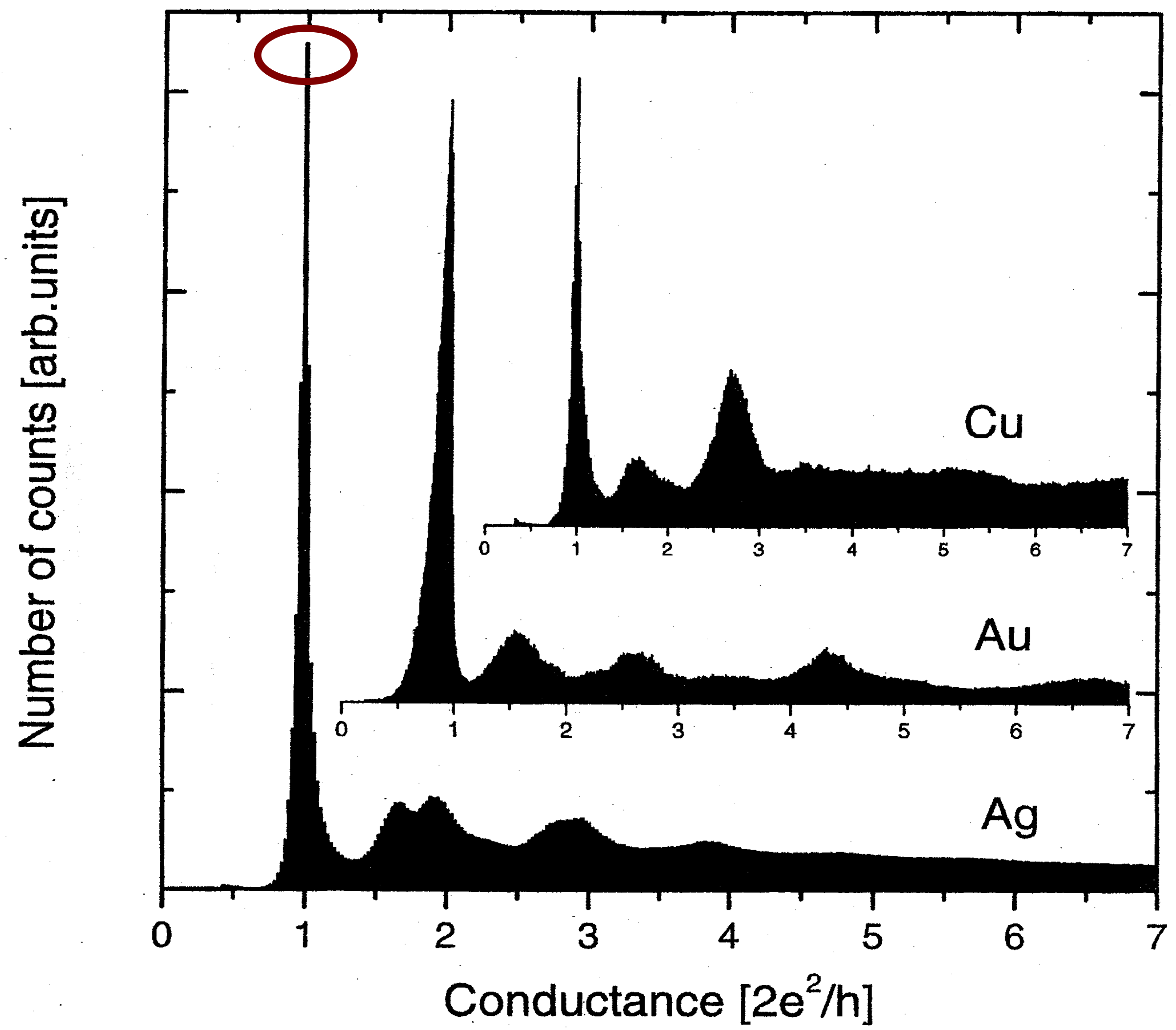


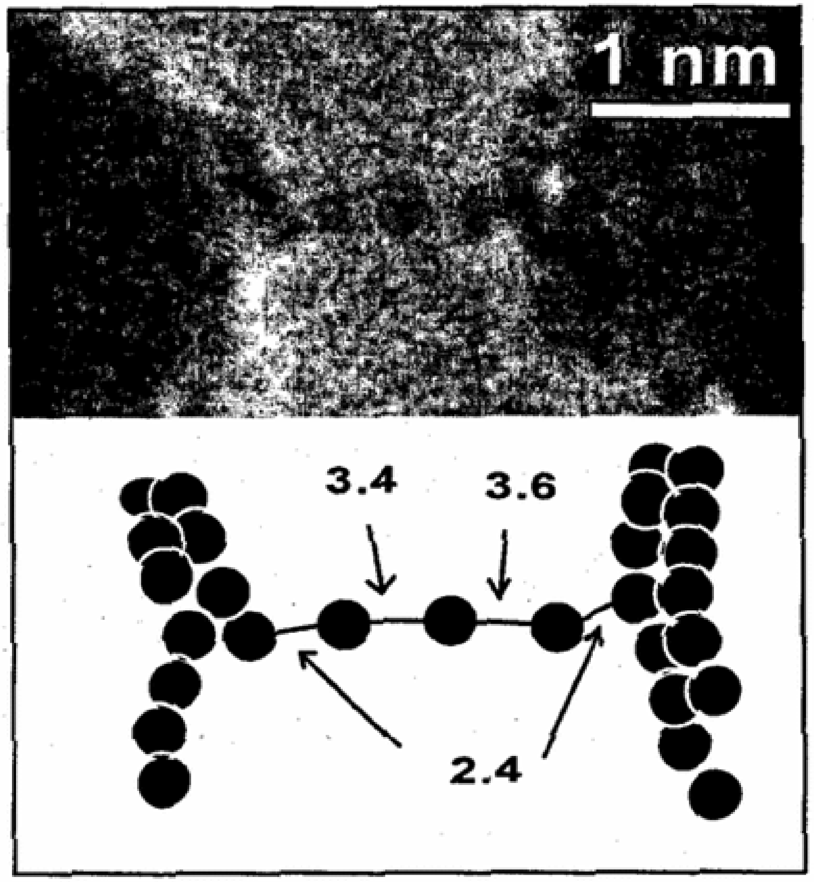
Figure 3.6: Conductance histograms for pure copper, silver and gold constructed from >1000 individual conductance traces each. The measurements were performed at 4.2 K and 100 mV bias voltage. Total amplitudes of the histograms are scaled to fit; relative amplitudes of the peaks within each histogram

Rodrigues & Ugarte

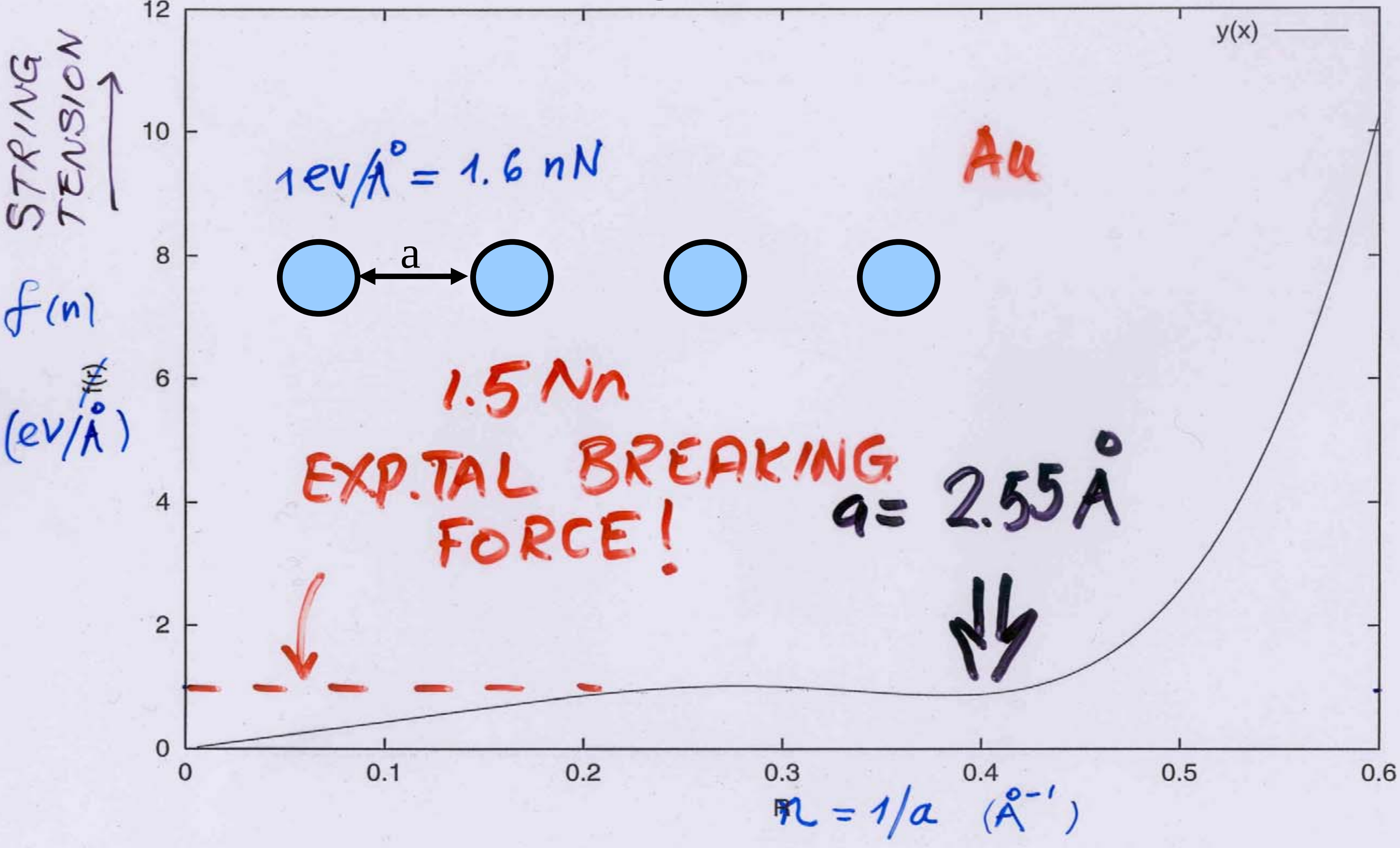
A
A

A

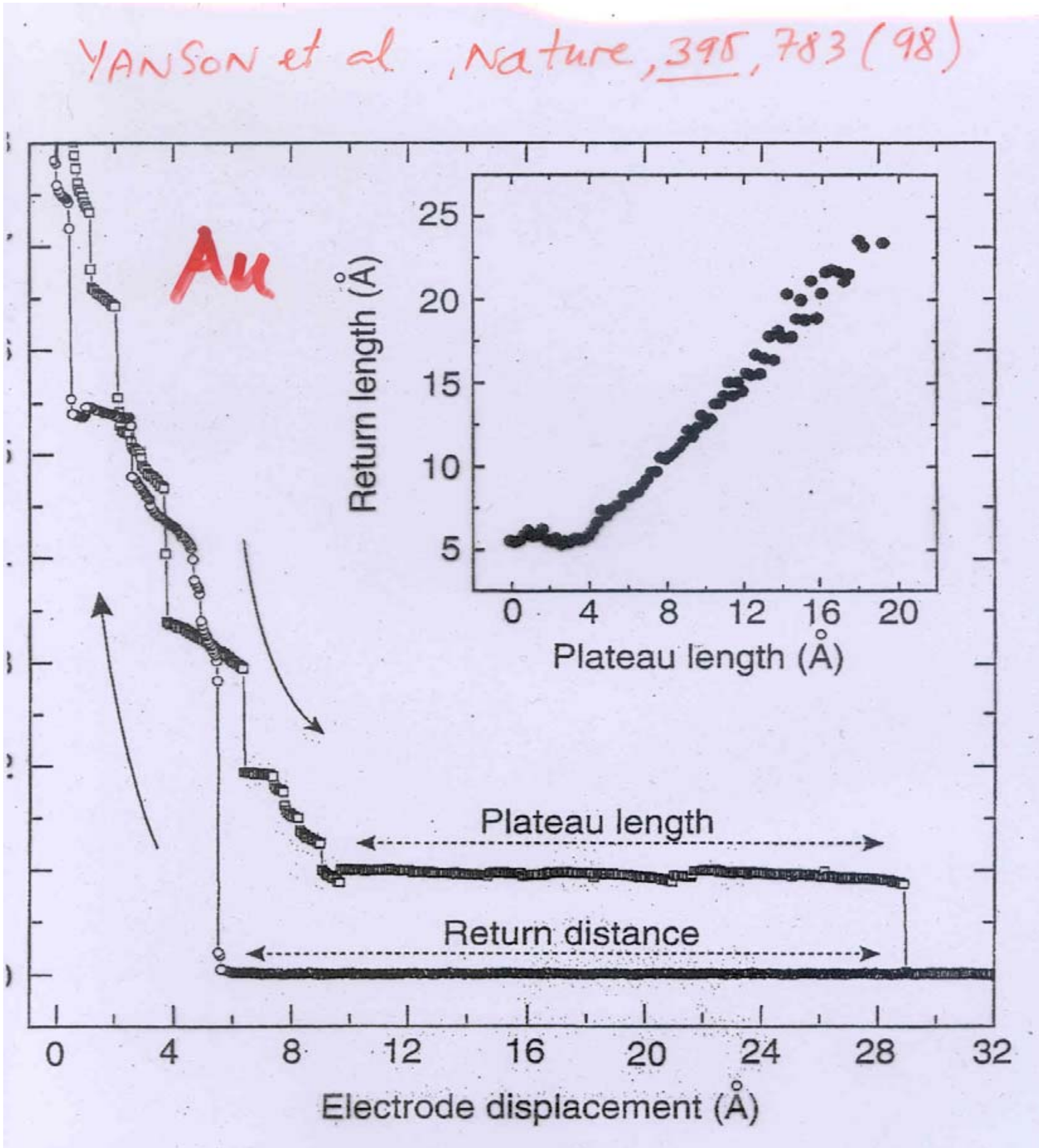
Au



Monatomic wires are **magic** too! Theory ...

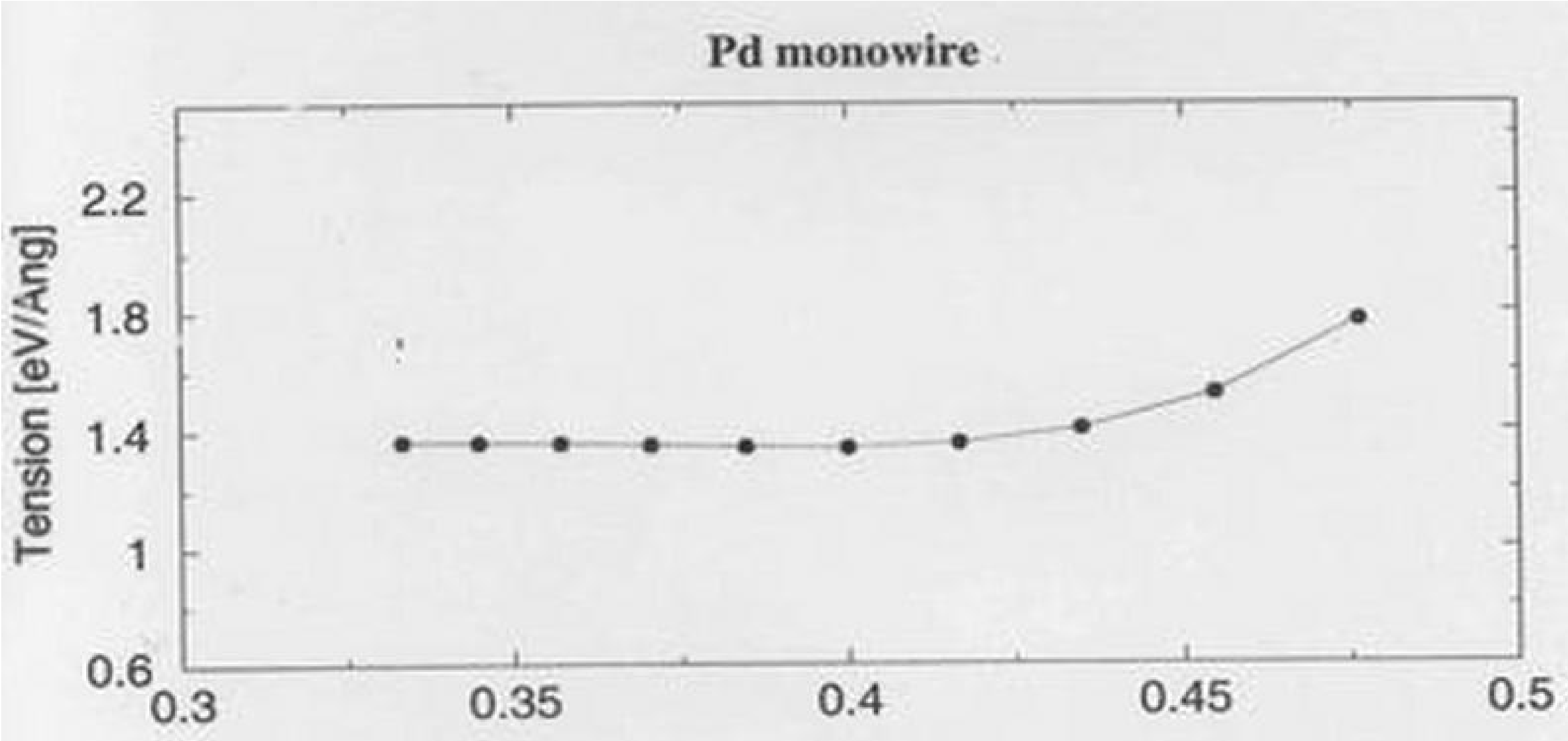


...AND IN EXPERIMENT



1 Conductance as a function of the displacement of the two gold
les with respect to each other in an MCB experiment at 4.2 K. The trace

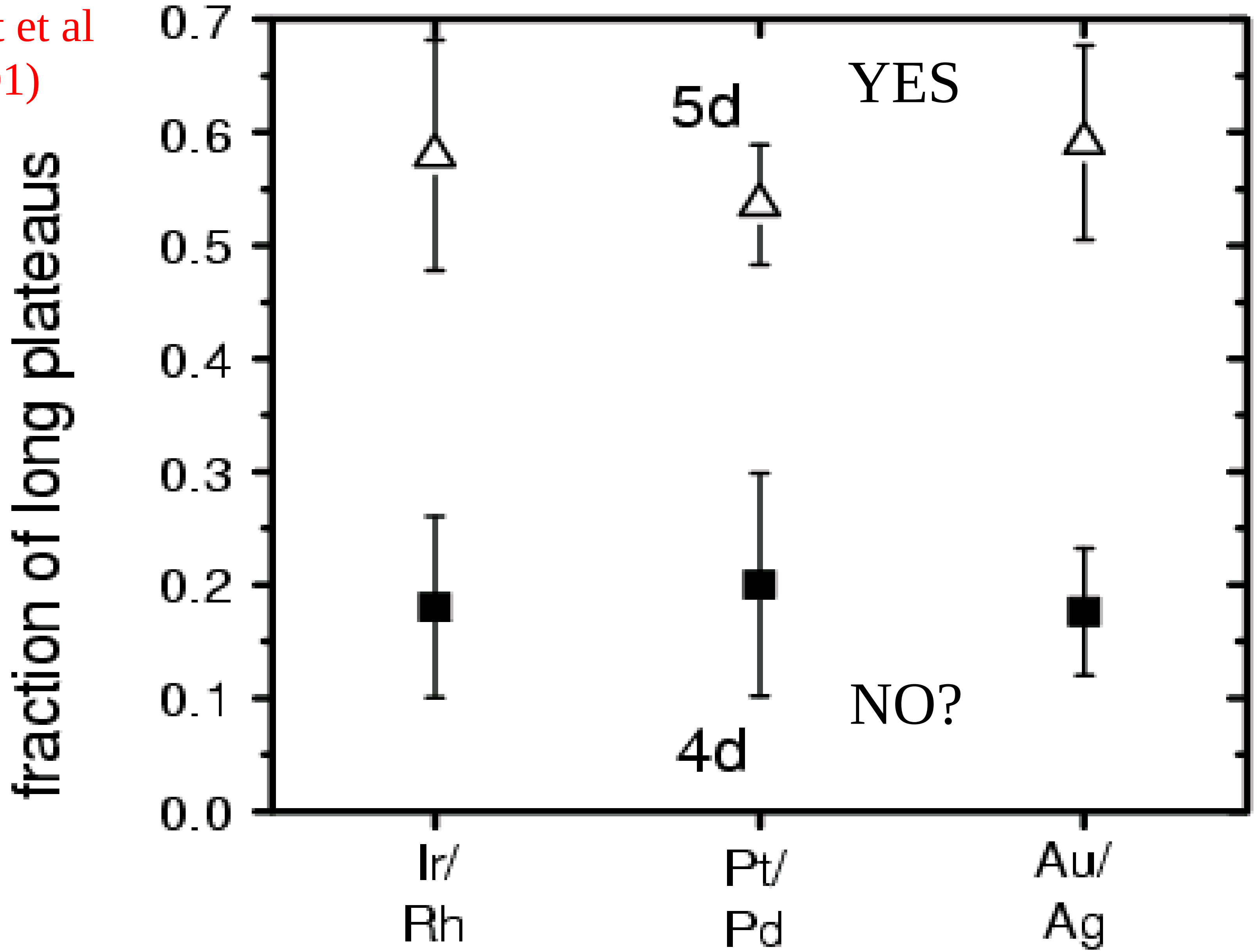
...BUT EXPECTED ONLY IN **HEAVY** METALS



1/a (Å^{-1})

...IN AGREEMENT WITH BREAK JUNCTION EXPERIMENTS

Smit et al (2001)



- ALTHOUGH THEY ARE SEEN ALSO
- IN LIGHTER METALS IN TEM DATA.
-

RODRIGUES et al
(2003)

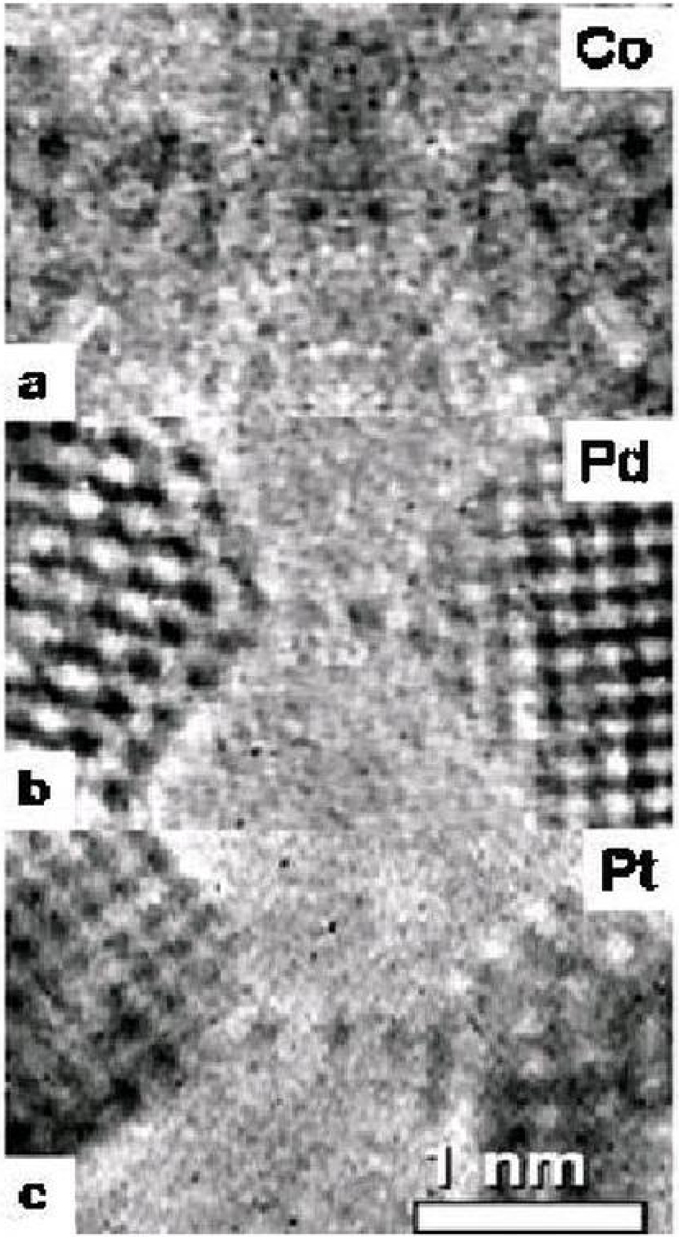


FIG. 2. HRTEM atomic resolved images showing the formation of suspended chains of atoms just before the contact rupture. (a) Co. (b) Pd. (c) Pt.

SHORT, STRESSED MONATOMIC NANOWIRES

F. PICAUD et al, Surf. Sci. 532-535, 544 (2003)

* TOO SHORT FOR PEIERLS INSTABILITY

* STRESS SUPPRESSES INSTABILITIES LIKE ZIG-ZAG

* LONGITUD. PHONON PARTLY SOFTENS WITH STRESS

* JUNCTIONS TAKE APPROX HALF THE STRAIN

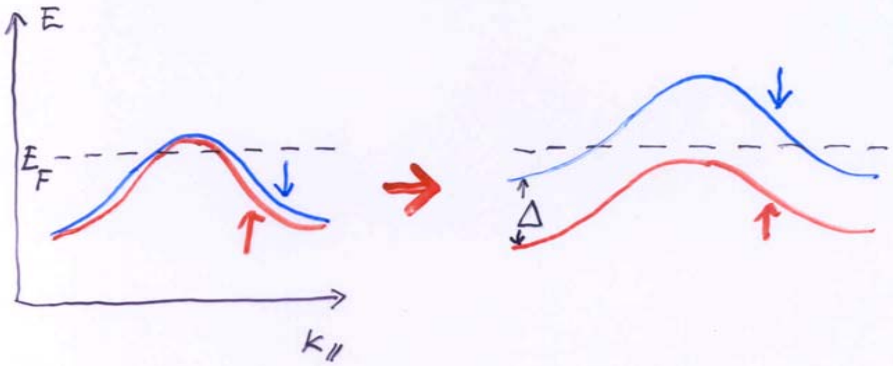
* TRANSV. PHONON FREQ. PROPORT. SQRT(STRESS) (LIKE A GUITAR STRING)

* BANDS NARROW DOWN, d-BAND MAGNETISM + CORRELATIONS STRONGER

MAGNETISM

OF NANOWIRES & EFFECTS ON CONDUCTANCE

HOW MAGNETISM INFLUENCES BALLISTIC CONDUCTANCE

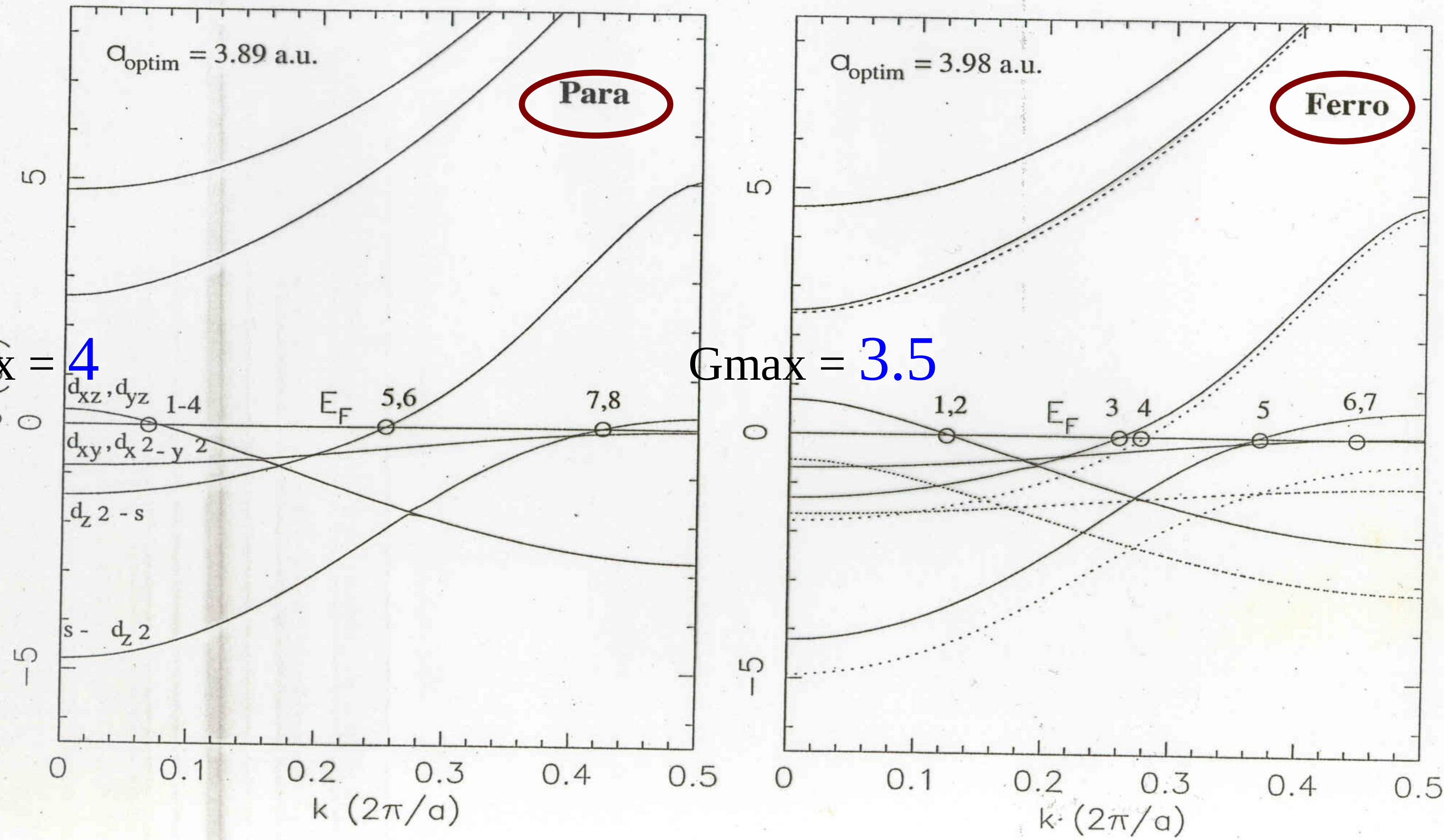


$$\frac{G}{2e^2/h} = \sum_{i\sigma} |t_{i\sigma}|^2 \lesssim N_\uparrow + N_\downarrow$$

$$G_{MAG} \leq G_{NON\,MAG} \qquad E = E_F$$

Ni

SMOGUNOV, DAL CORSO, TOSATTI (2002)



Gmax = 4

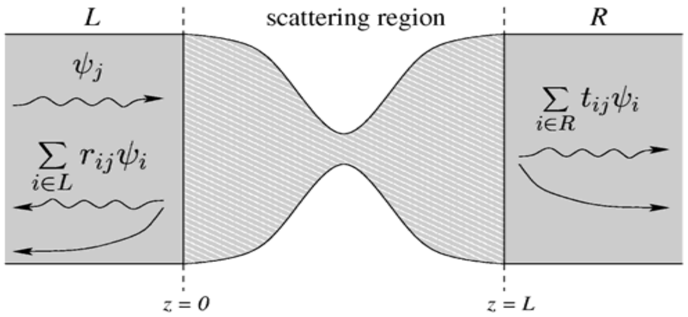
Gmax = 3.5

Ballistic conductance

Landauer-Buttiker formula for ballistic conductance:

$$G = \frac{e^2}{h}\mathrm{Tr}[T^+T],$$

$$T_{ij} = \sqrt{\frac{I_i}{I_j}}\, t_{ij}$$



- obtain both propagating and decaying states ψ_i in the electrodes (complex band structure).

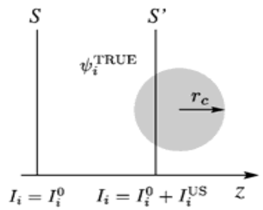
Choi, Ihm (1999)

- calculate the probability currents I_i of propagating states ψ_i in the z direction.

$$I_i^0(z_0) = \frac{\hbar}{m}\mathrm{Im}\left[\int_S \psi_i^*(\mathbf{r})\frac{\partial\psi_i(\mathbf{r})}{\partial z}\bigg|_{z=z_0} dS\right]$$

$\Downarrow$ ψ_i are *pseudo* wave-functions

$$I_i(z_0) = I_i^0(z_0) + I_i^{\mathrm{US}}(z_0)$$



Smogunov, Dal Corso
Tosatti (2003)

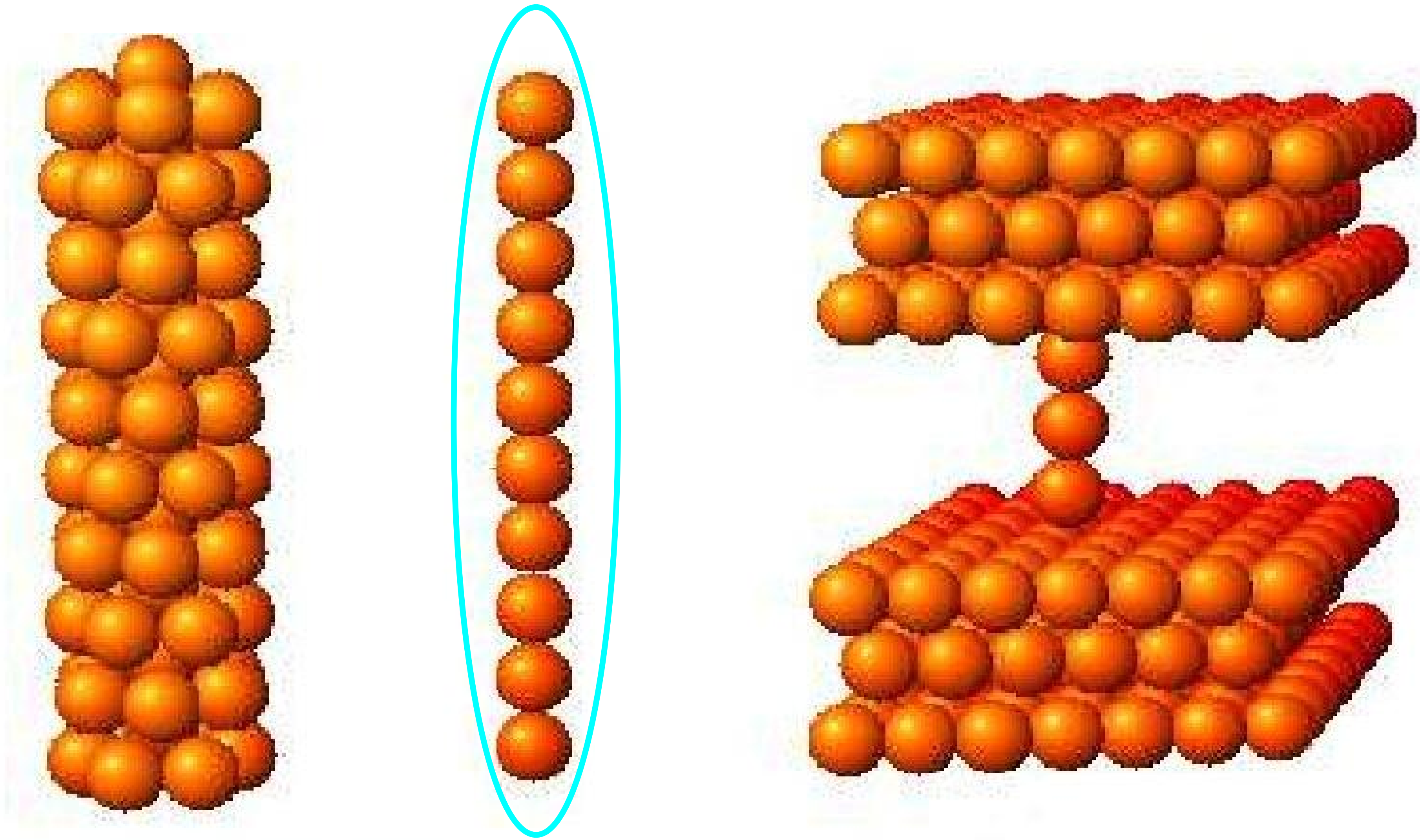
Expression for augmentation part $I_i^{\mathrm{US}}(z_0)$ is found by requiring:

a) $I_i(z_0)$ *does not* depend on z_0;
b) if the plane $S = z_0$ does not intersect core spheres $I_i^{\mathrm{US}}(z_0) = 0$

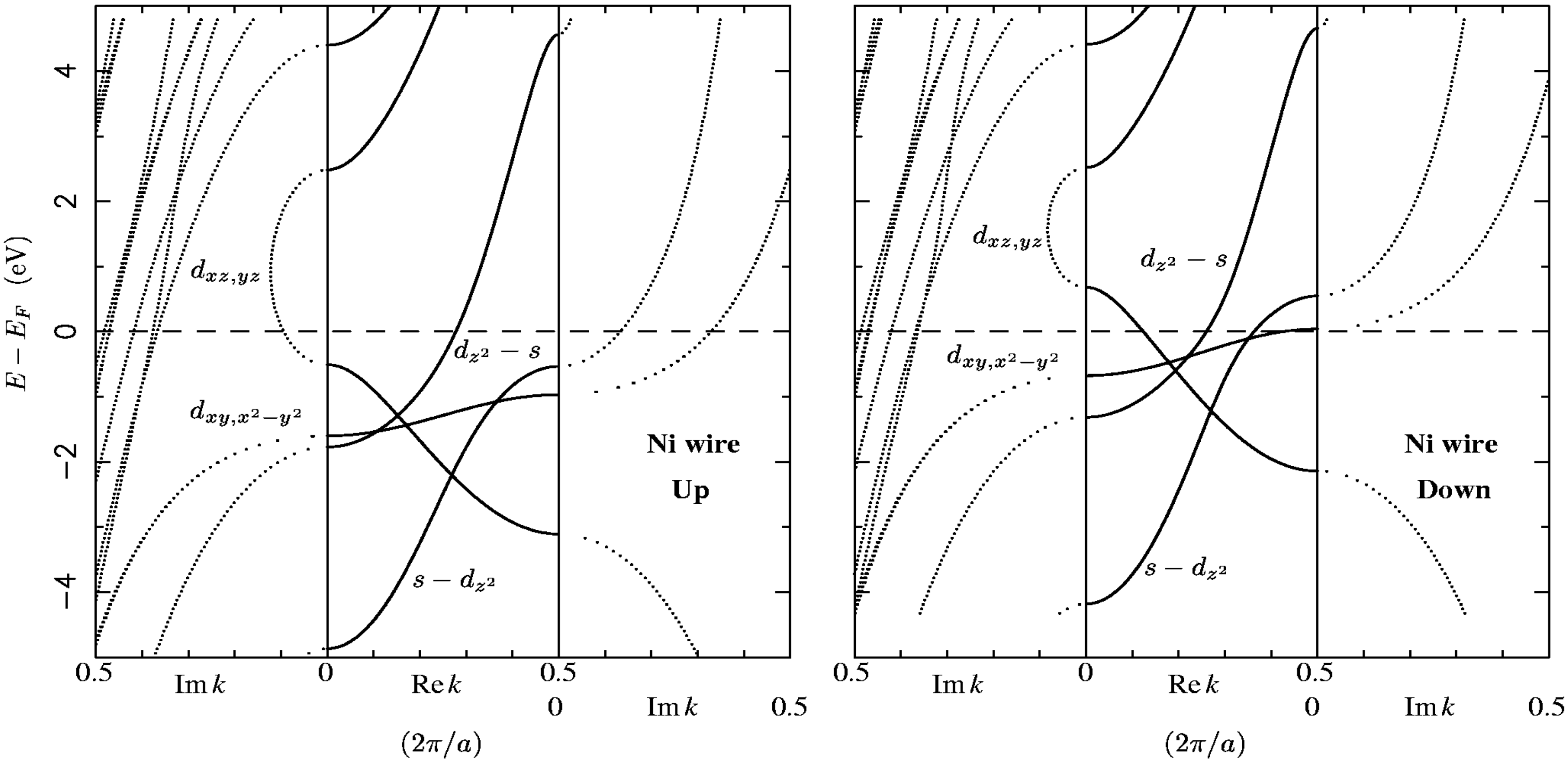
- use matching conditions on the two boundaries $z = 0$, $z = L$ to calculate coefficients r_{ij}, t_{ij}.

$\downarrow$

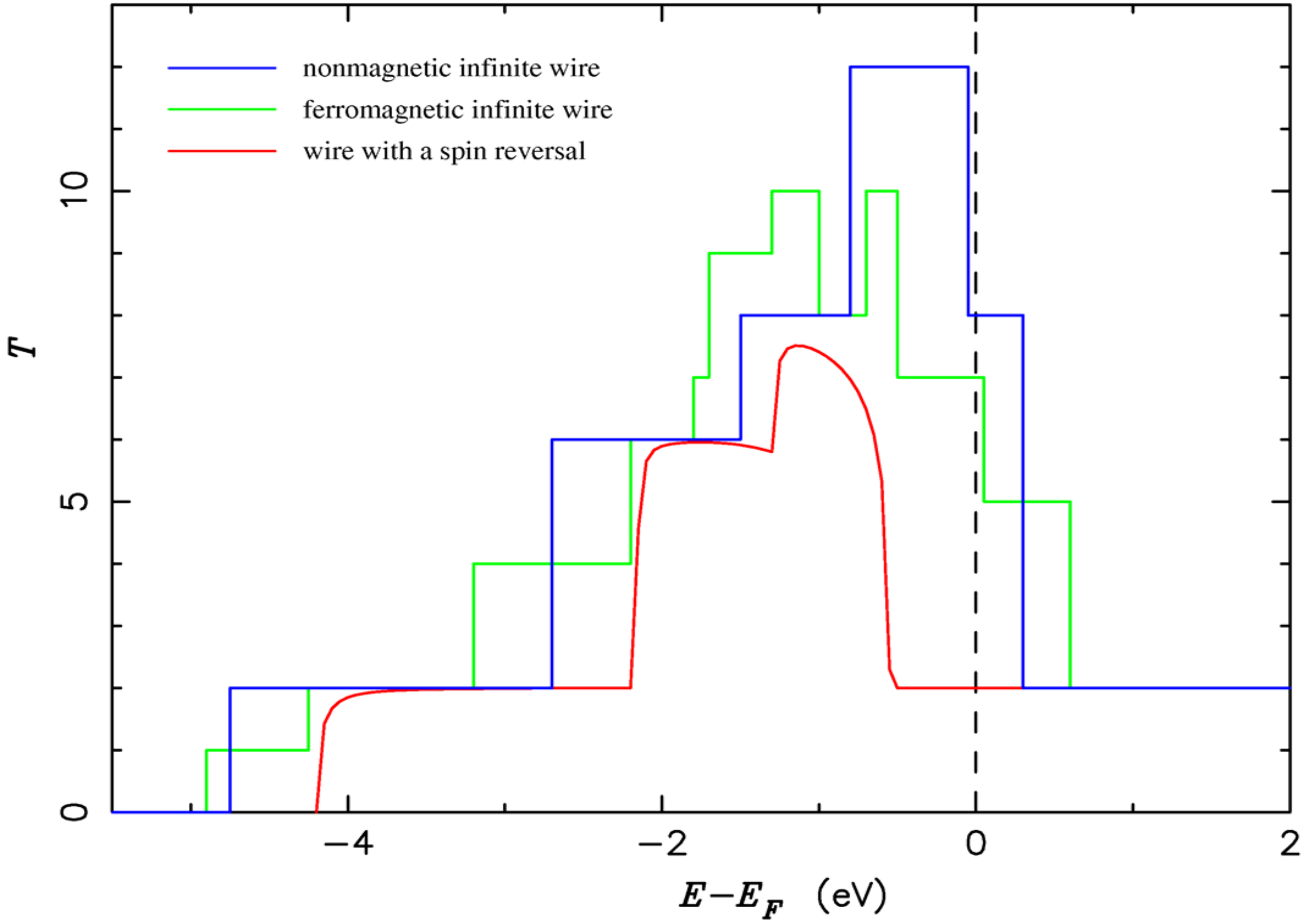
T_{ij}, G



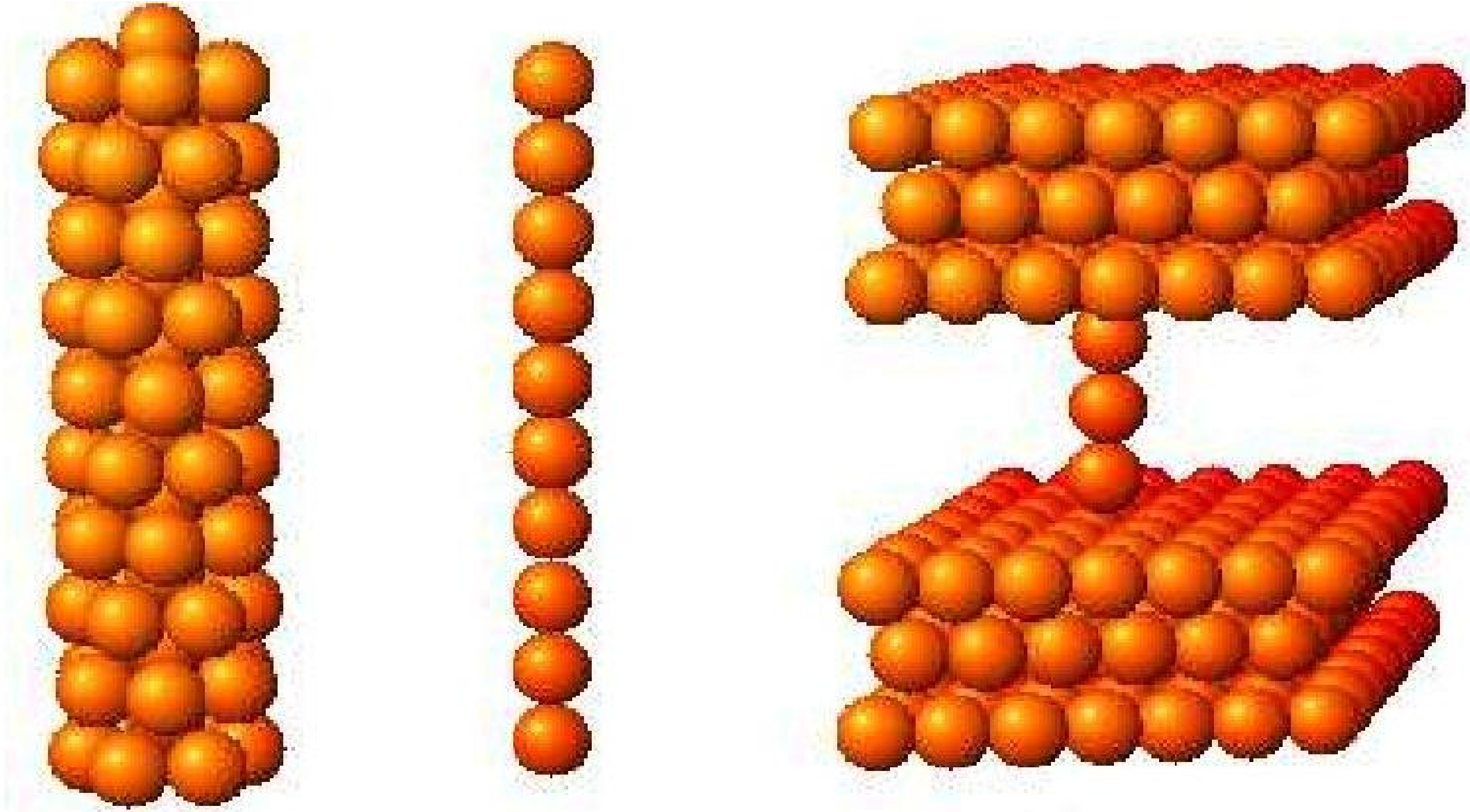
Complex band structure of monatomic Ni wire



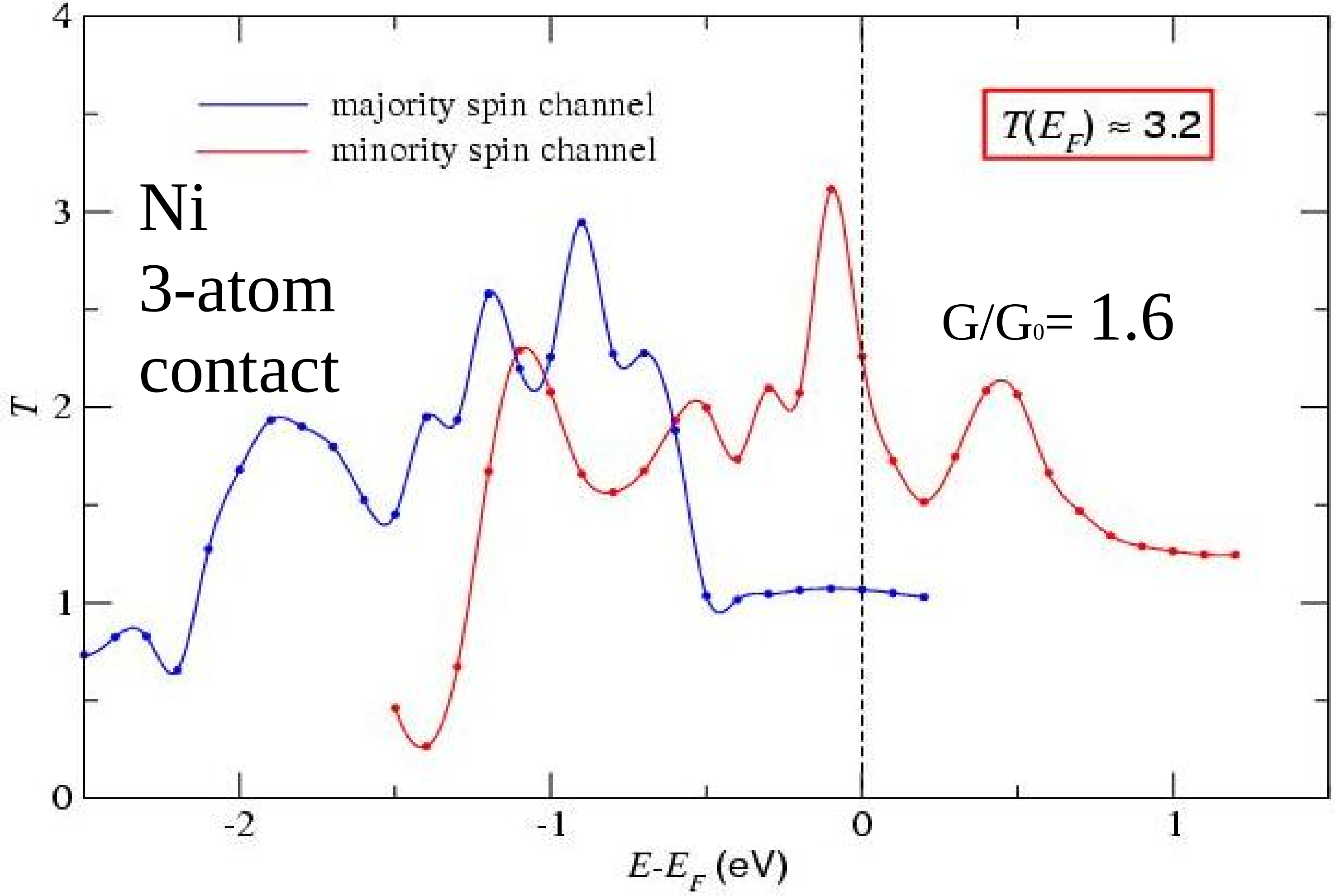
Transmission coefficient for monatomic Ni nanowire



NICKEL , DFT CALCULATIONS



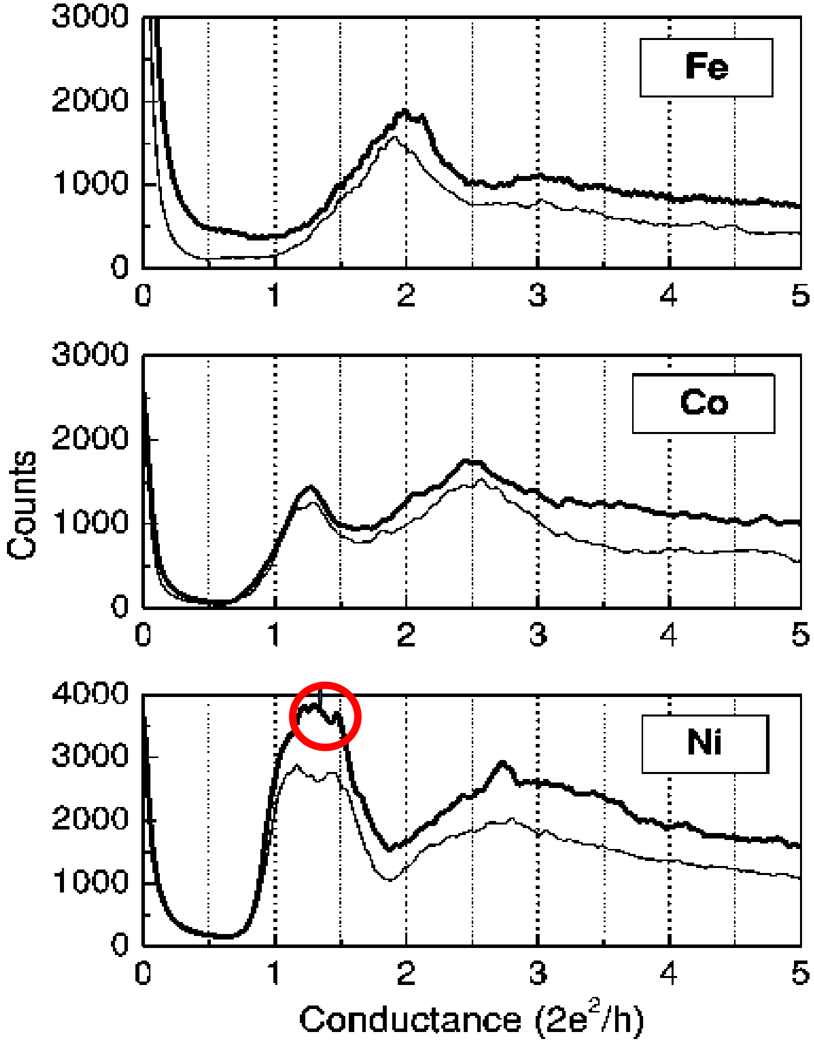
SMOGUNOV, DALCORSO, ET
(2004)



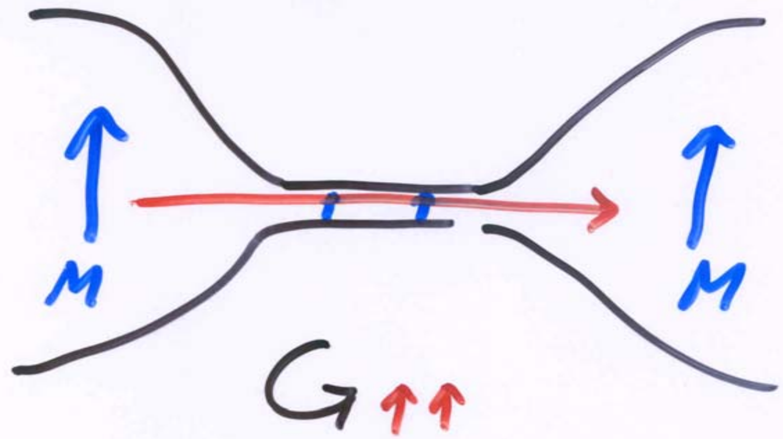
A. Smogunov et al (2004)

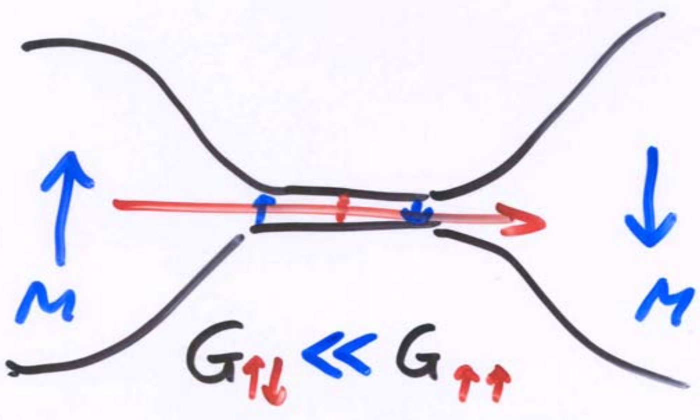
UNTIEDT, DEKKER, DJUKIC, AND VAN RUITENBEEK **(2004)**

T= 4.2 K



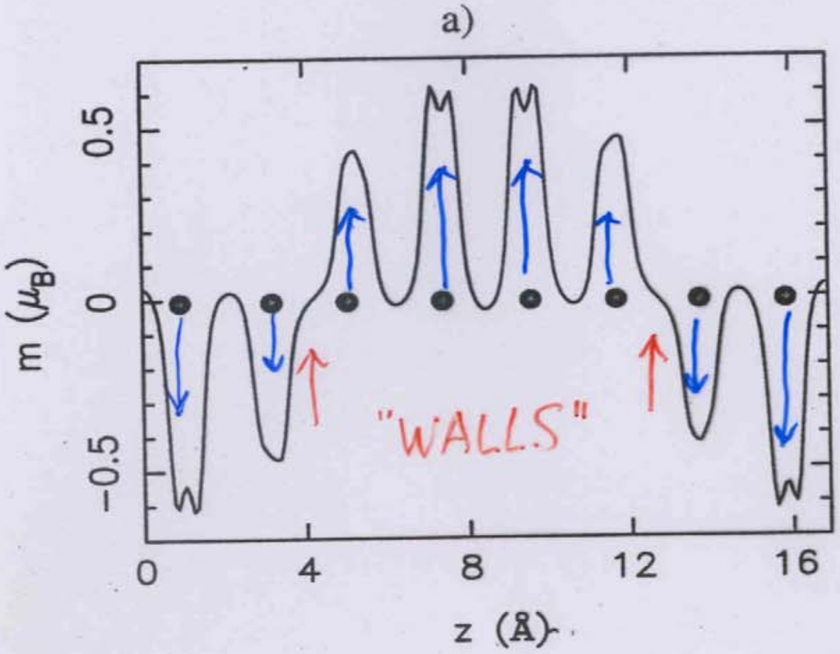
"BALLISTIC MAGNETORESIST."

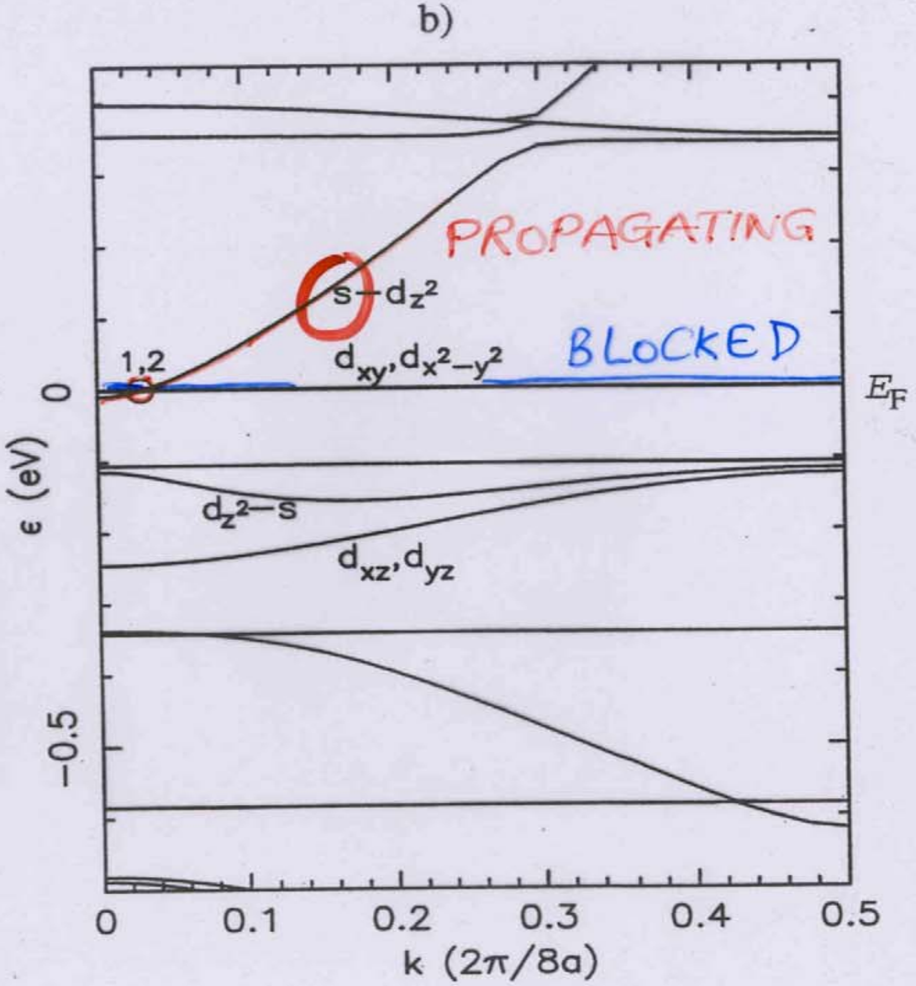




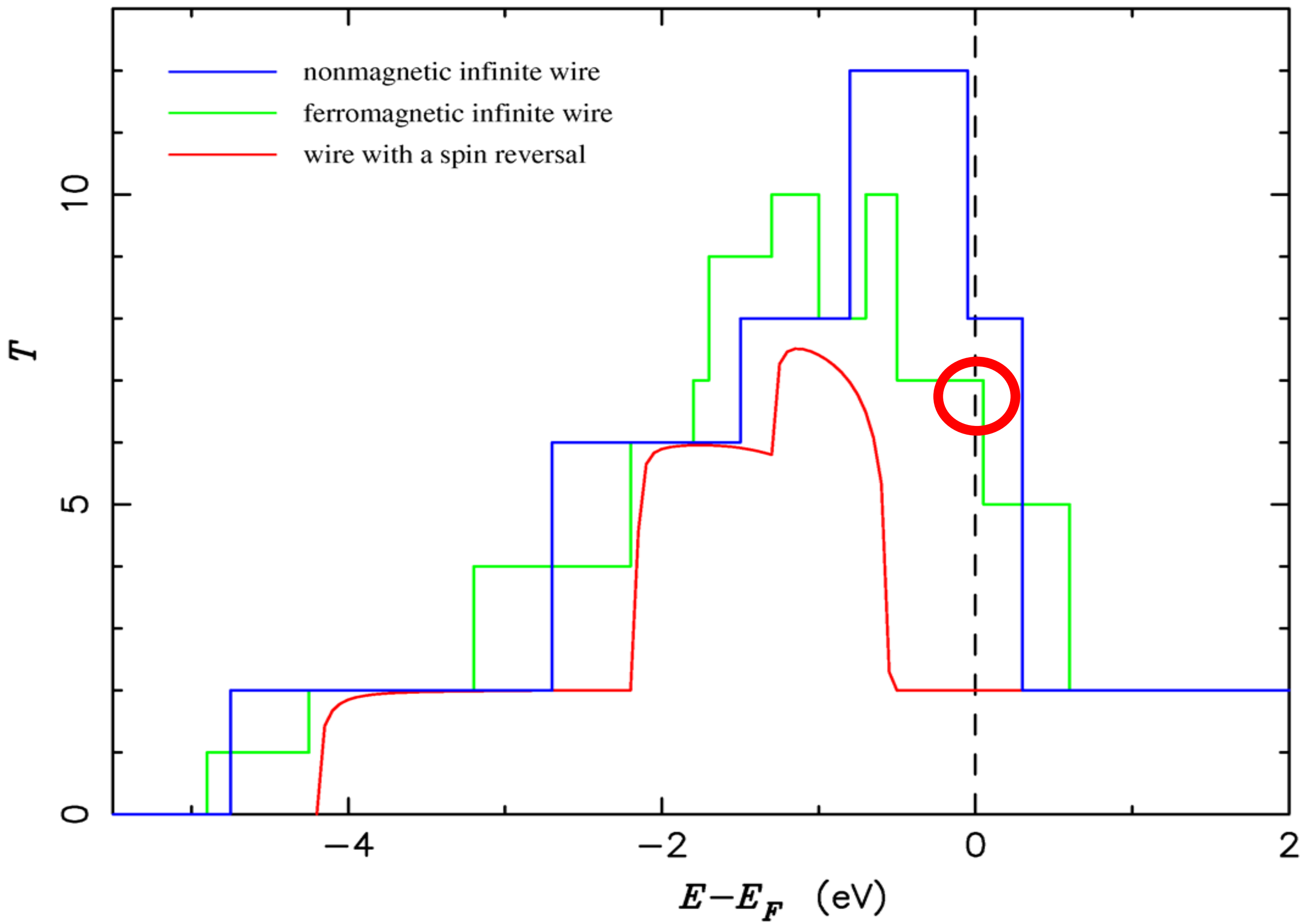
A. SMOGUNOV, A. DAL CORSO, E.T., SURF. SCI 507, 609 (2002)

Ni $M_z = 0$





Transmission coefficient for monatomic Ni nanowire



CAN NANOWIRES TURN SPONTANEOUSLY

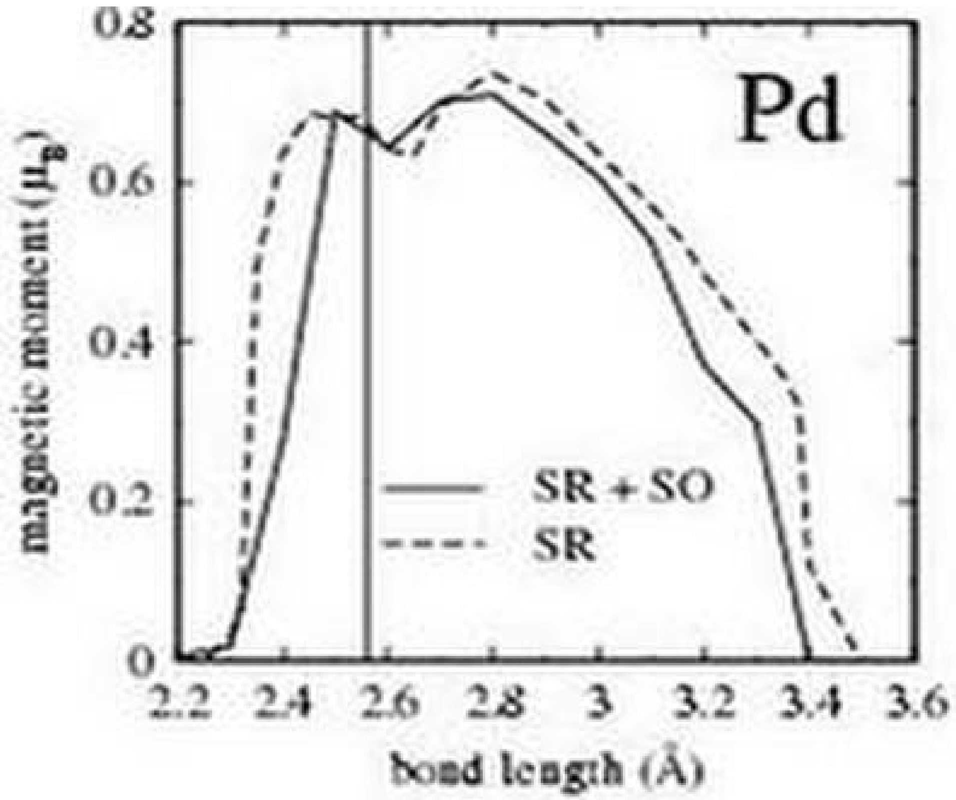
MAGNETIC ??

Recall Uzi Landman's lecture....

CAN Pd BECOME MAGNETIC IN NANOWIRES?

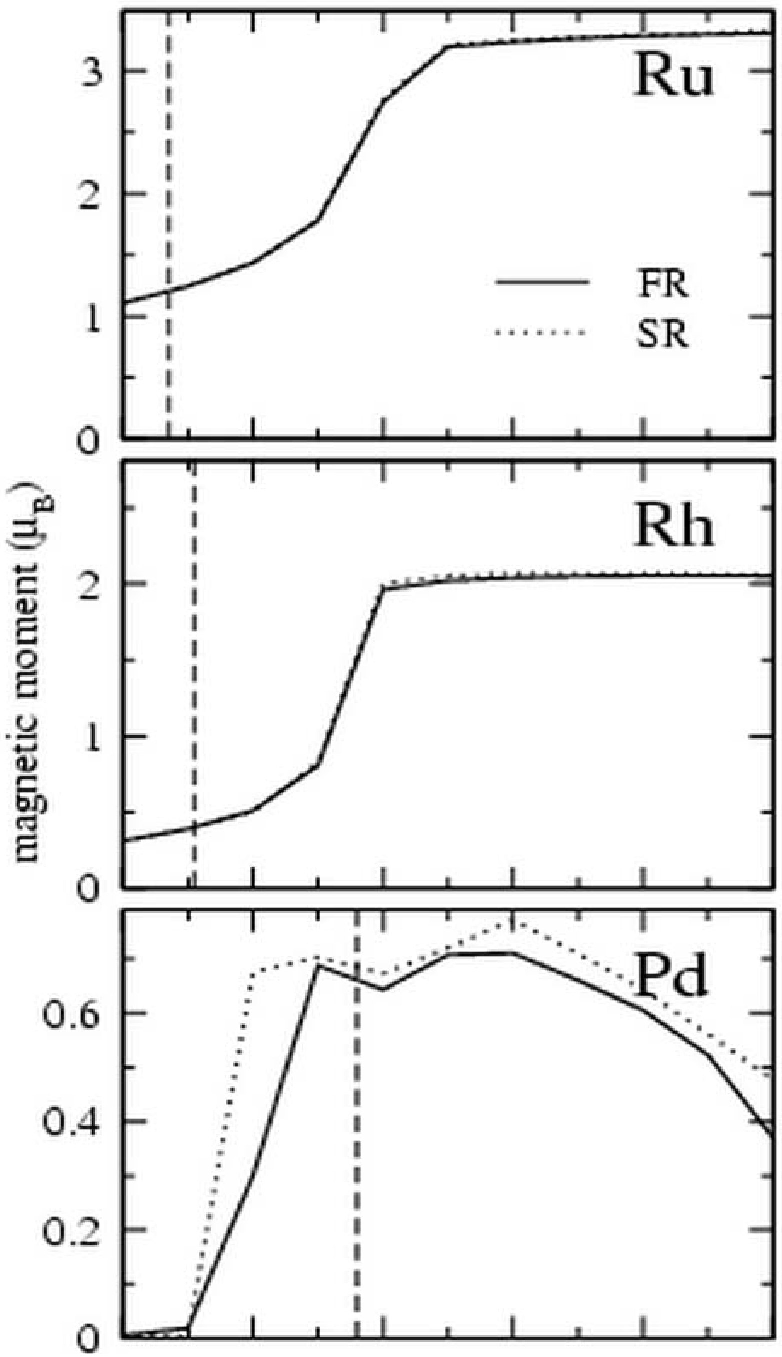
A

YES!

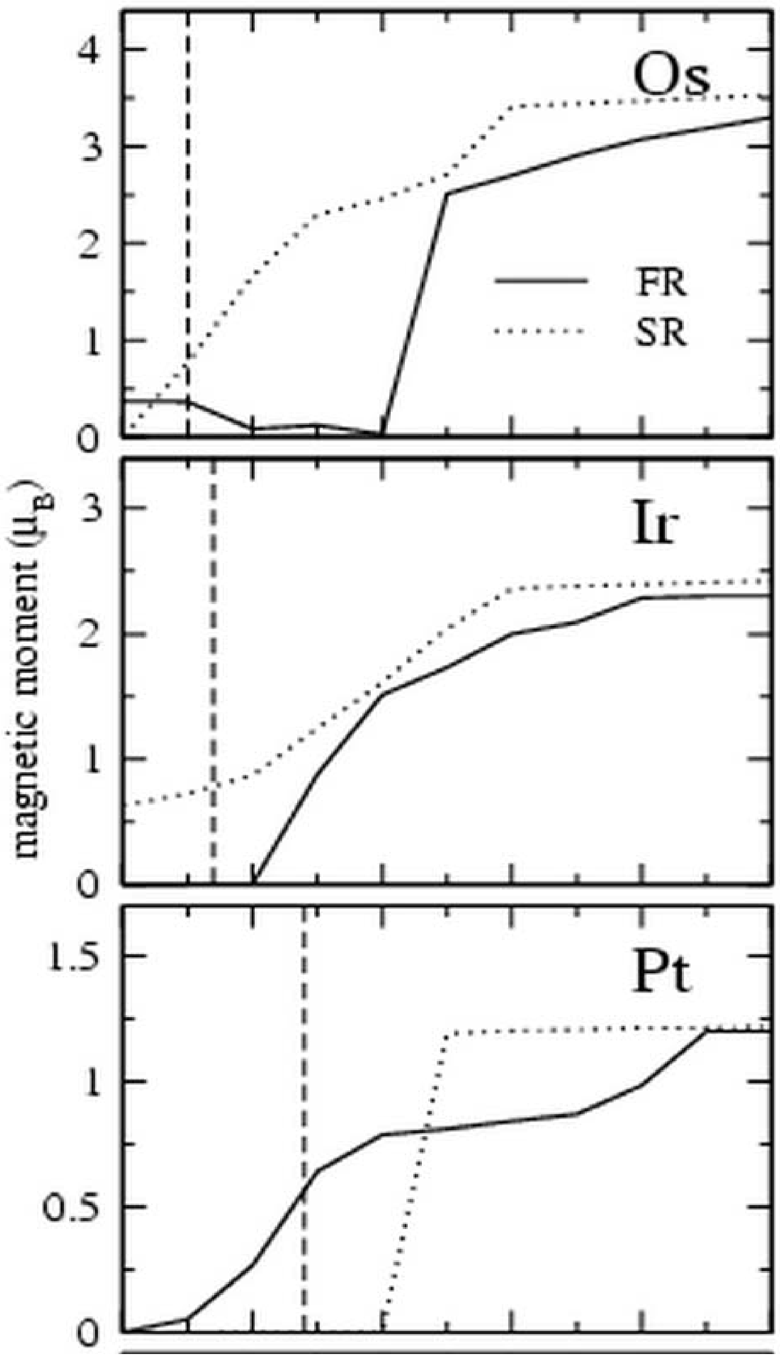


DELIN, TOSATTI
(2004)

AND SO CAN Ru, Rh; AND SO CAN EVEN Ir, Os, Pt

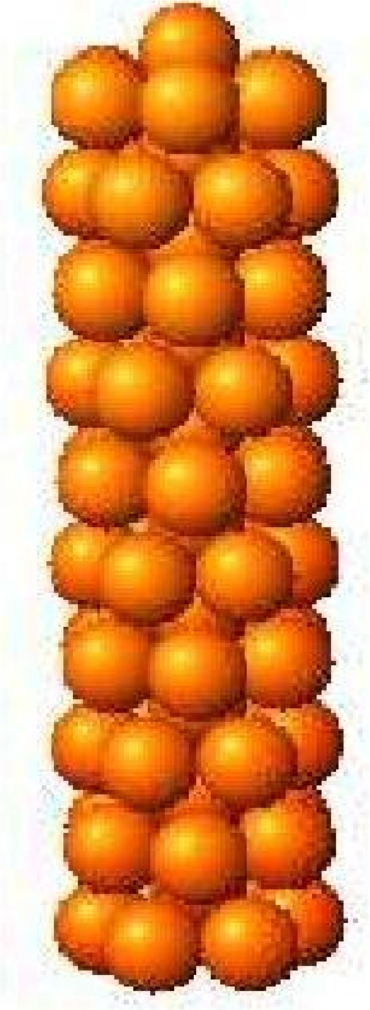


Ru
Rh
Pd
FR
SR
magnetic moment (μ_B)
0
1
2
3
0
1
2
0
0.2
0.4
0.6

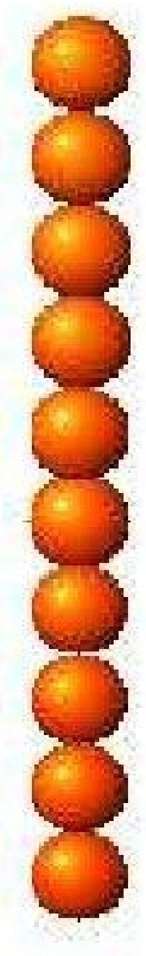


Os
FR
SR
Ir
Pt
magnetic moment (μB)
0
1
2
3
4
0
1
2
3
0
0.5
1
1.5

PALLADIUM , DFT CALCULATIONS



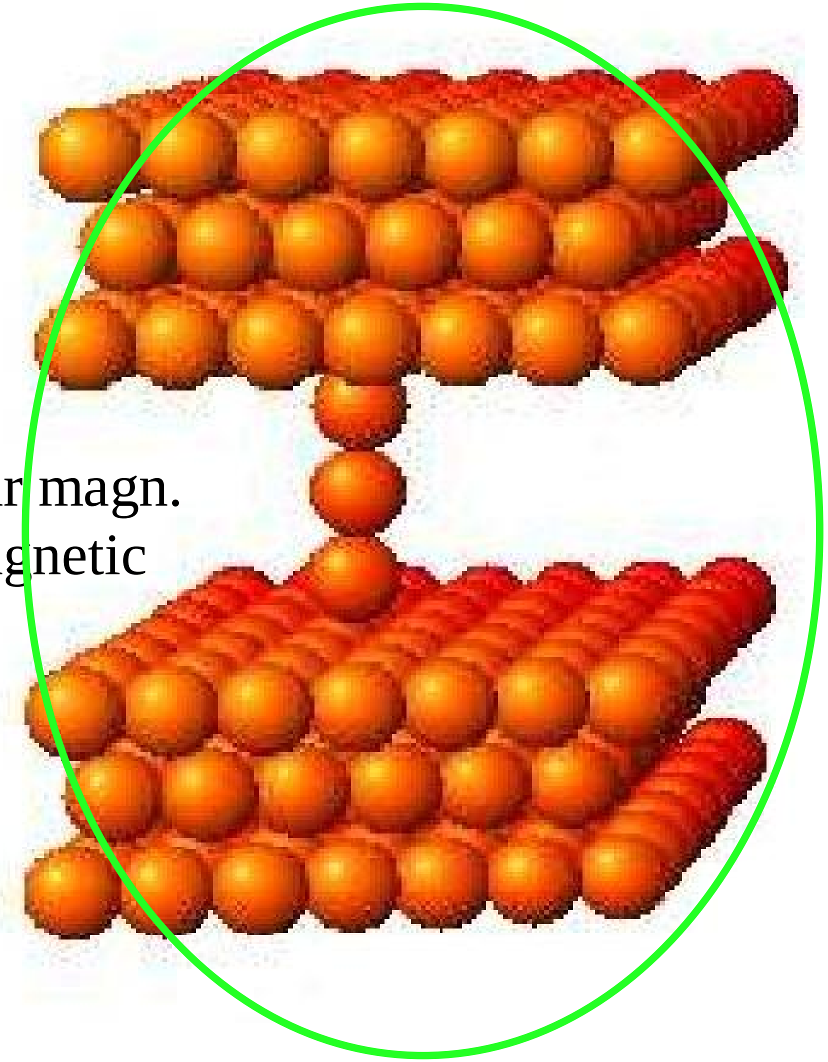
nonmagnetic



0.7 Bohr magn.

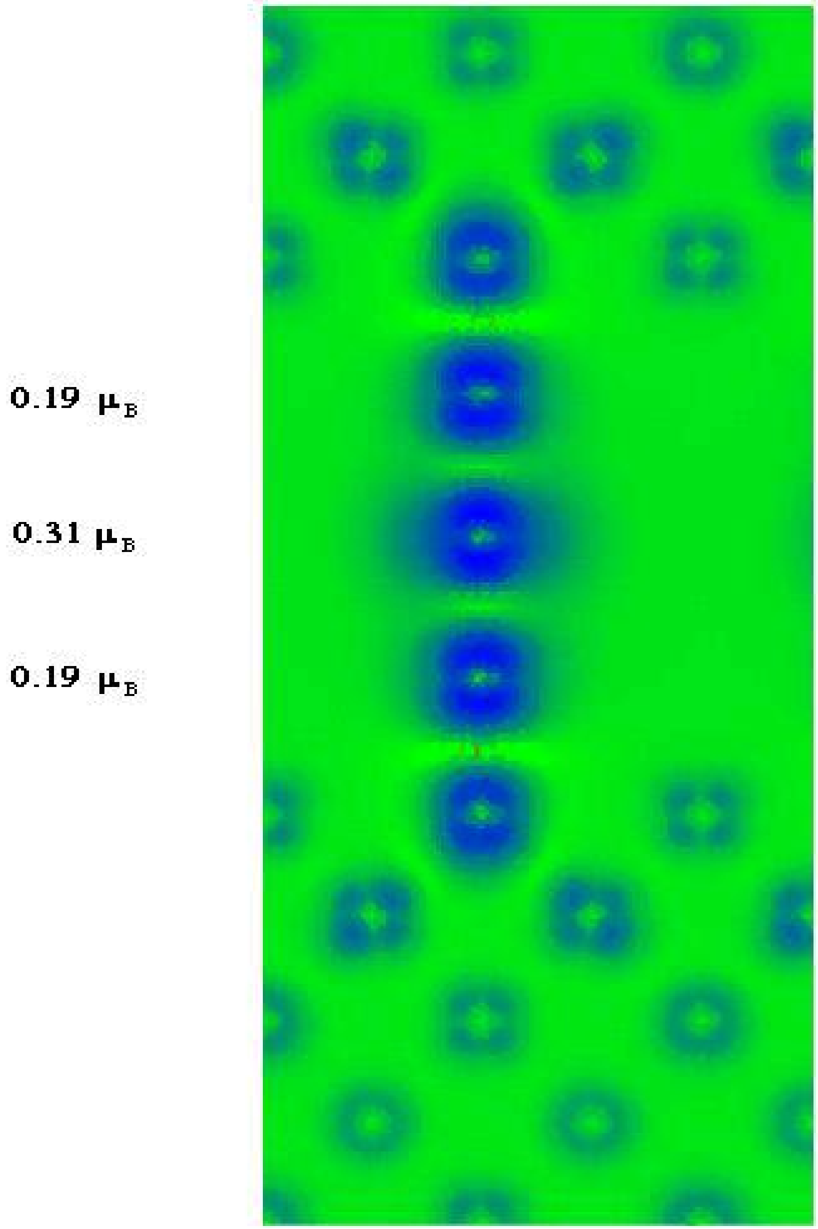
ferromagnetic

0.3 Bohr magn.
ferromagnetic



Magnetization
of Pd
3 atom
contact

P. Gava et al (2004)



NANOMAGNETISM AND CONDUCTANCE

CONDUCTANCE AND NANOMAGNETISM??

LARGE B

ZERO T

G= (e^2/h) Tr (T*T)
spin channels conduct differently

ZERO B

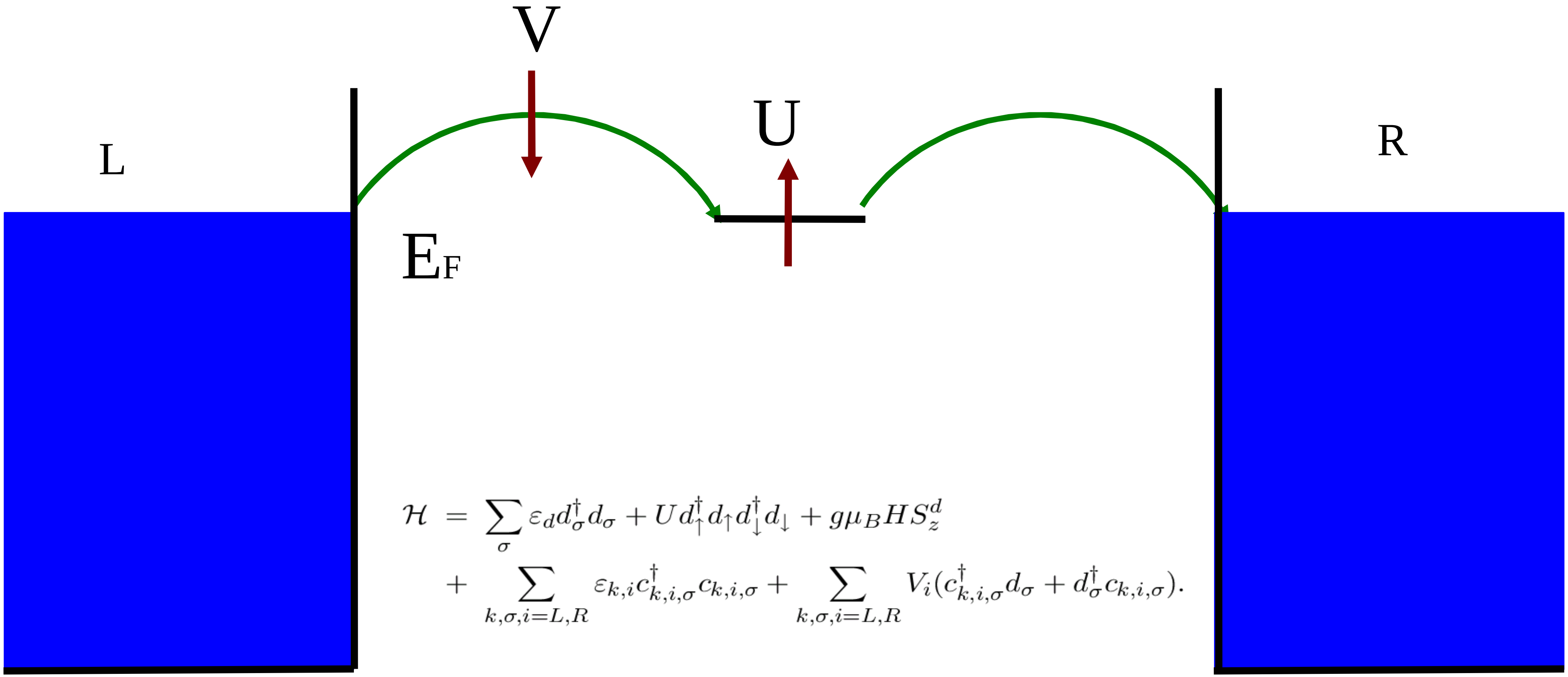
ZERO T

Kondo – like problem:
spin channels conduct identically

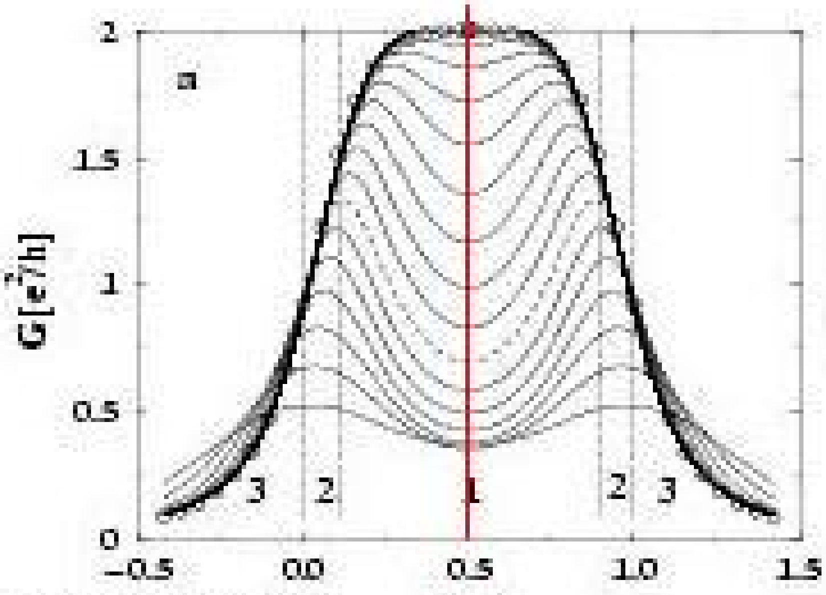
ZERO B

LARGE T

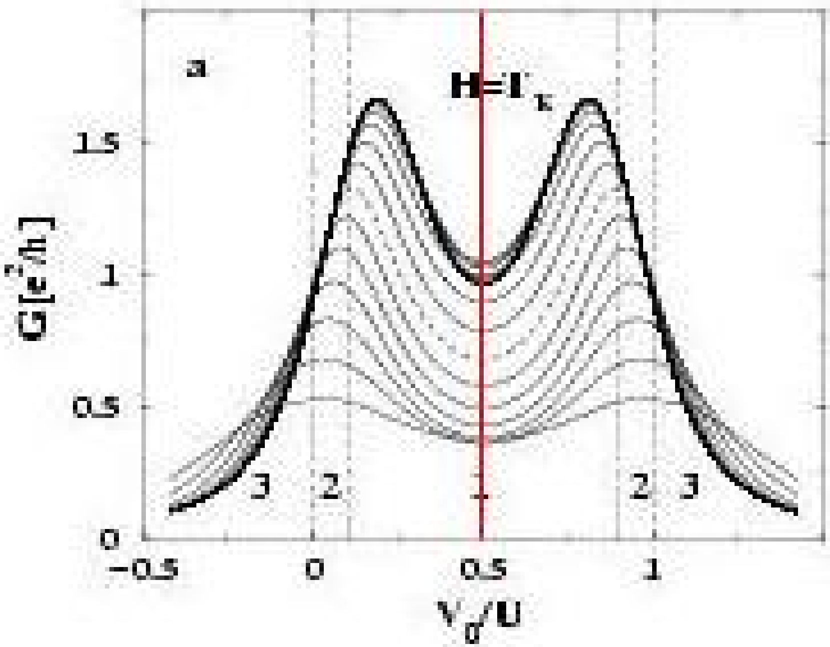
Kondo state thermally destroyed, conductance drops

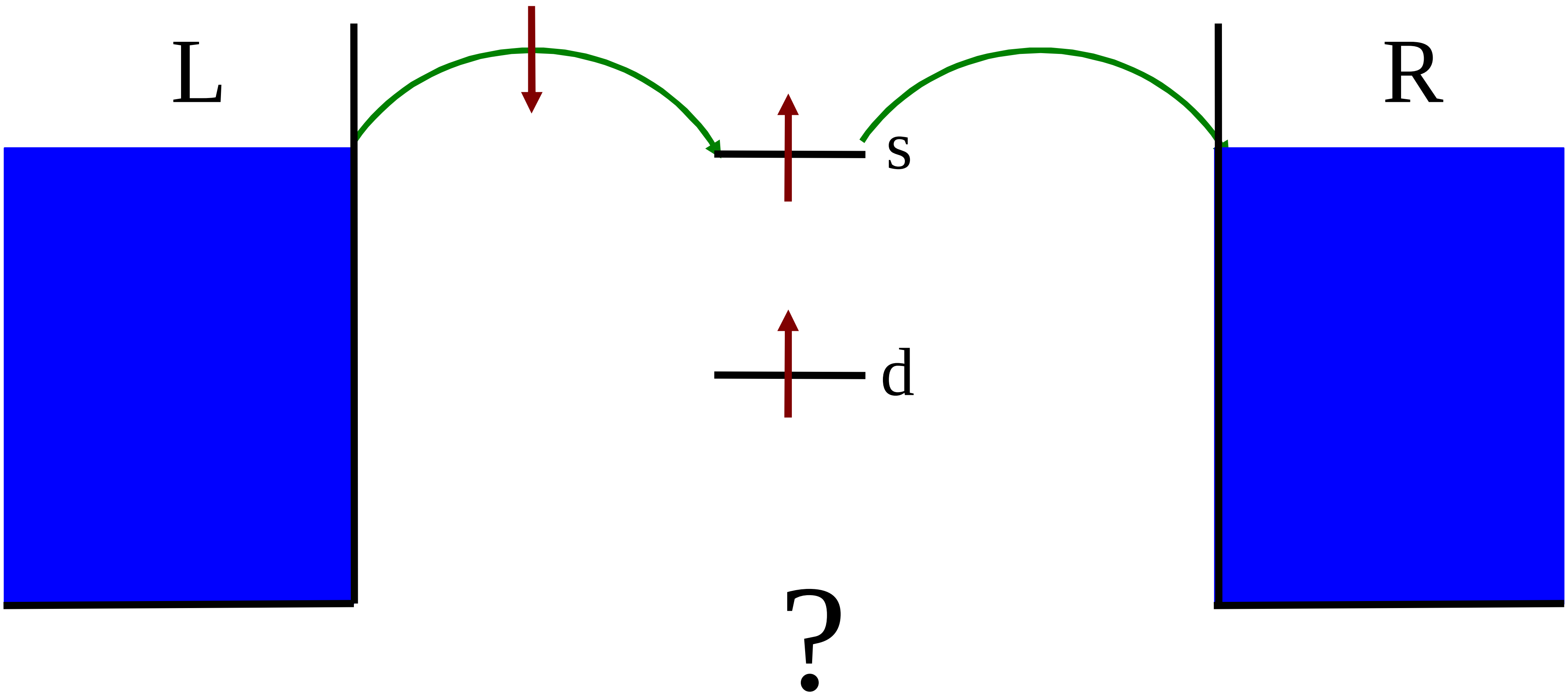


$$\mathcal{H} = \sum_{\sigma} \varepsilon_d d_\sigma^\dagger d_\sigma + U d_\uparrow^\dagger d_\uparrow d_\downarrow^\dagger d_\downarrow + g\mu_B H S_z^d$$
$$+ \sum_{k,\sigma,i=L,R} \varepsilon_{k,i} c_{k,i,\sigma}^\dagger c_{k,i,\sigma} + \sum_{k,\sigma,i=L,R} V_i (c_{k,i,\sigma}^\dagger d_\sigma + d_\sigma^\dagger c_{k,i,\sigma}).$$



Costi (2003)





L
R
s
d
?

CONCLUSIONS

NANOCONTACTS MAY THIN DOWN TO NANOWIRES

MAGIC NANOWIRES HAVE LONGER LIFETIMES

MONATOMIC NANOWIRES CAN BE MAGIC TOO

MAGNETISM VS. BALLISTIC CONDUCTANCE,
EXPECT LARGE NEGATIVE MAGNETORESISTANCE

NANOWIRES OF NONMAGNETIC TRANS. METALS
CAN TURN MAGNETIC, THAT WILL AFFECT
CONDUCTANCE