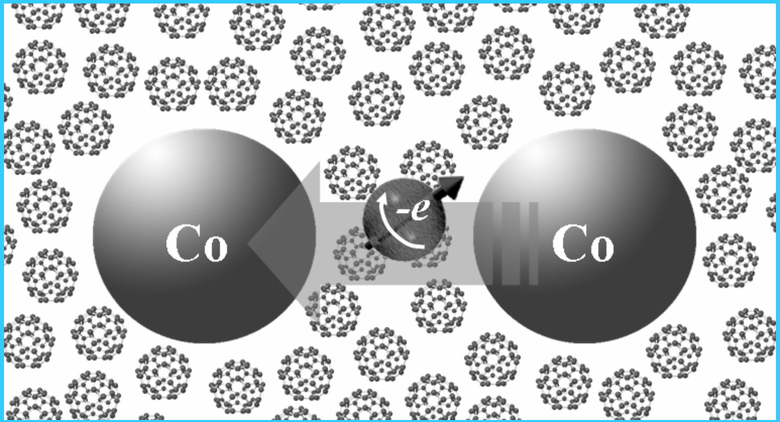
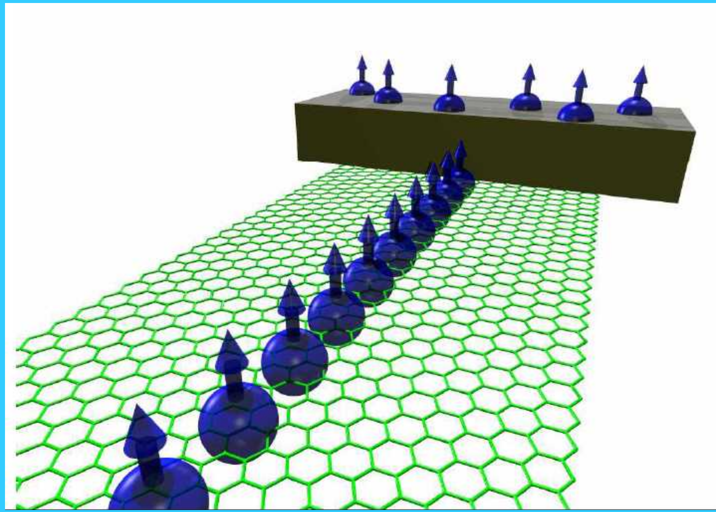
2008.12.18 TU-Dresden

Molecular Spintronics using π-Electron Molecules





Masashi Shiraishi

1. Osaka University, Japan. 2. JST-PRESTO, Japan

Co-workers in this study

Osaka University

Prof. Yoshishige Suzuki
Prof. Teruya Shinjo
Dr. Ryo Nouchi (⇒Tohoku Univ.)
Dr. Takayuki Nozaki
Dr. Masaki Mizuguchi (⇒Tohoku Univ.)
S. Miwa, H. Kusai, S. Tanabe, M. Ohishi, D. Hatanaka

Experimental Assistance

Tohoku Univ.
Prof. Yoshihiro Iwasa
Prof. Taishi Takenobu
Dr. Hidekazu Shimotani

Univ. of Tokyo
Prof. Masashi Takigawa
Dr. Makoto Yoshida

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Research direction of our Osaka Univ. Group

Molecular Science Gp. (Shiraishi's Group) belonging Prof. Y. Suzuki's Lab.

Materials

Graphene
Fullerenes
Carbon nanotubes
Organic Molecules (Rubrene, Alq_3, etc)

Research Field

Molecular Spintronics

Graphene spintronics
Organic spintronics
…..

Research Field

Molecular Electronics

CNT-FETs

Contents of my talk

Introduction :

Basic concepts of spintronics
Previous serious problems in molecular spintronics

Part I : Molecular spintronics using molecular nano-composites

Appearance of magnetoresistance (MR) effects
Background physics
What was missing?

Part II : Molecular spintronics using graphene

Spin injection at room temperature
“Local” and “Non-local” MR effects
Remaining problems in molecular spintronics

Background of this study

What is expected to molecular spintronics ?

Molecules ⇒ Carbon, Hydrogen

A small spin-orbit interaction ($\lambda \sim Z^4$)

Long spin relaxation time

Long spin coherent length ? (If high mobility…)

Molecules ⇒ Semiconductor

Gate-induced (spin) current control

Applications :

for instance,

quantum computation devices

molecular spin transistors

Spin-orbit interaction ~A relativistic effect~

Dirac Equation (4×4 matrix)

$$\begin{pmatrix} m\cdot I & \sigma\cdot p \\ \sigma\cdot p & -m\cdot I \end{pmatrix}\begin{pmatrix} \phi \\ \chi \end{pmatrix} = E\begin{pmatrix} \phi \\ \chi \end{pmatrix}$$

Positive energy solutions (2-component)

Negative energy solutions (2-component)

m : mass term, σ: Pauli's spin matrix, p : momentum

$$\sum_{i=1}^{3}\alpha_i\cdot p+\beta\cdot m \qquad \alpha_i=\begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix},\quad \beta=\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

4×4 matrix

Introduction of an electro-magnetic field (to positive energy solution)

$$ih\frac{\partial}{\partial t}\phi=[\frac{(p-eA)^2}{2m}-\frac{e\hbar}{2mc}\sigma\cdot B+e\Phi]\phi$$

$$=[\frac{p^2}{2m}-\frac{e}{2mc}(L+\underline{2s})\cdot B]\phi.$$

g-value = 2

Spin-orbit interaction ~A relativistic effect~

Diagonalization of the Dirac equation by Unitary transformation
(Excluding the mixing of positive and negative solutions)
⇒ Foldy=Wouthuysen transformation

Mass velocity term

Electrostatic dipole

Magnetic dipole

$$H = \beta\{m + \frac{(p-eA)^2}{2m} - \frac{p^4}{8m^2}\} + e\Phi - \frac{e}{2m}\beta(\sigma\cdot B)$$

$$\boxed{-\frac{ie}{8m^2}\sigma\cdot rotE - \frac{e}{4m^2}\sigma\cdot E\times p} - \frac{e}{8m^2}divE$$

Spin-orbit interaction terms

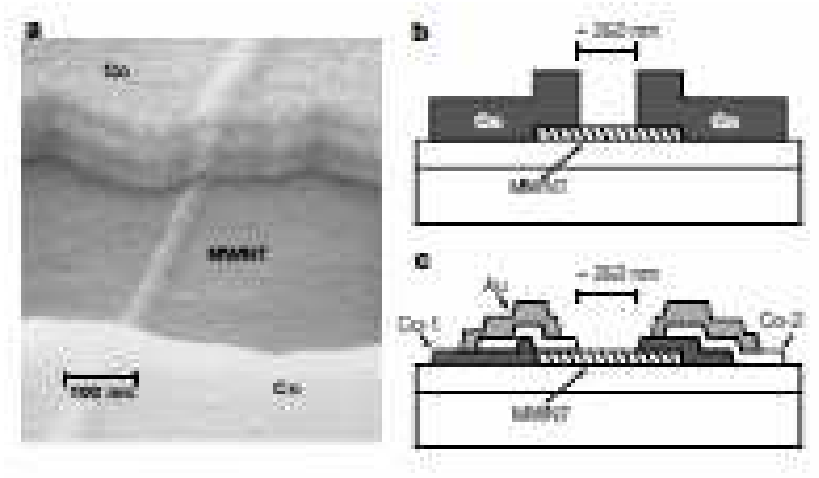
Darwin term
(Zitterbewegung)

To spherically symmetric potential, the 1st term = 0.
The 2nd term is double of that in Classical mechanics (Thomas precession).
S-O Hamiltonian is

$$H = \frac{\mu_B e\hbar Z}{4\pi m r^3}(\sigma\cdot L) \quad \Rightarrow \; Z^4$$

Serious problems in molecular spintronics

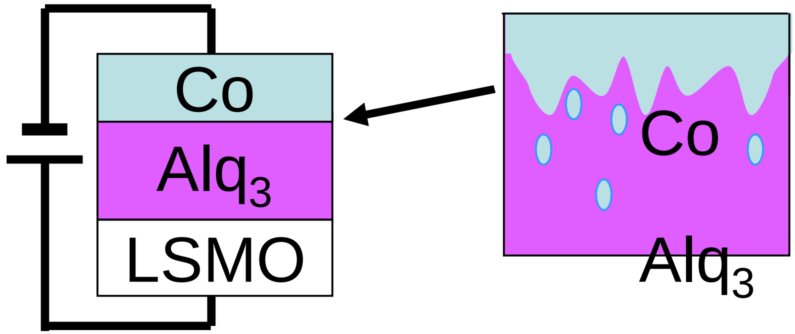
In-plane structures



Correspondence between MR effects and magnetization of FM

Spurious signals (Large R_c)

Sandwiched structures



Difficulty in obtaining a clear interface & implementing various characterizations.

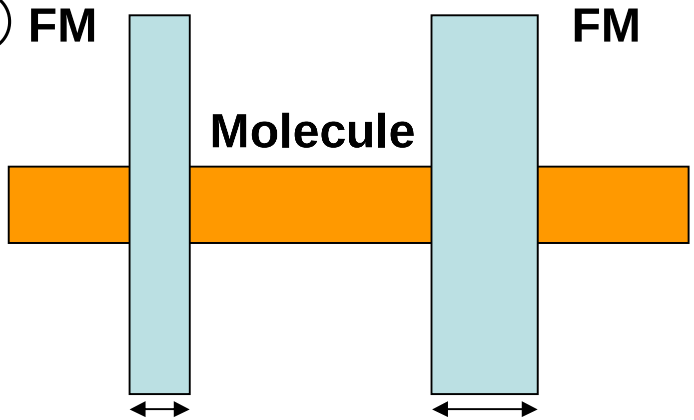
Spins were injected????

How can we reproduce them ?

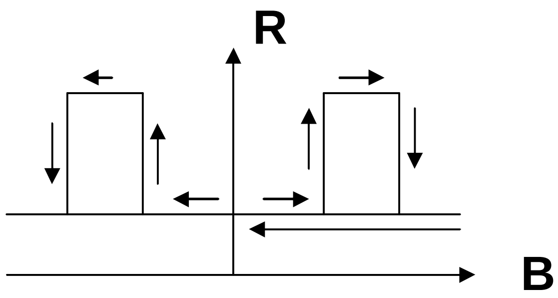
Underlying physics "?"

Serious problems in molecular spintronics

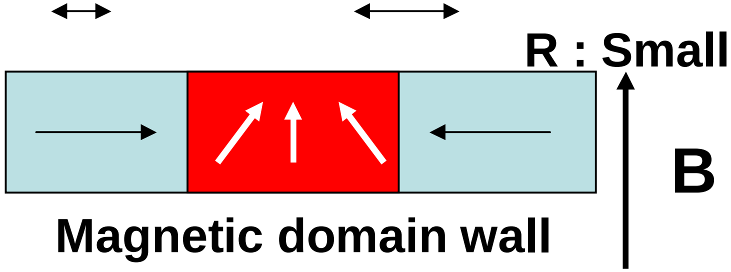
①

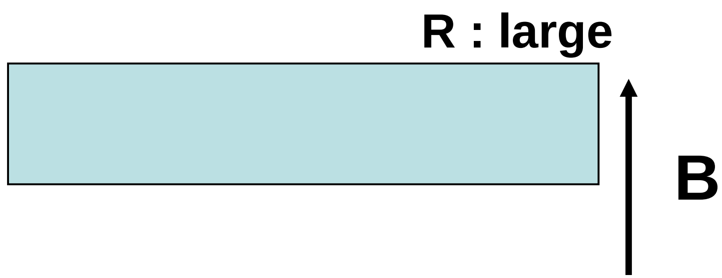


Resistance hysteresis & Magnetization Process



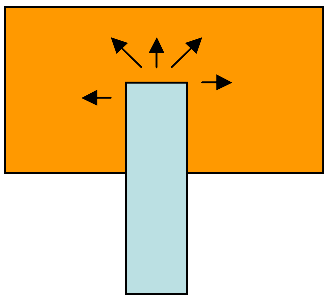
②





Anisotropic MR effect

③



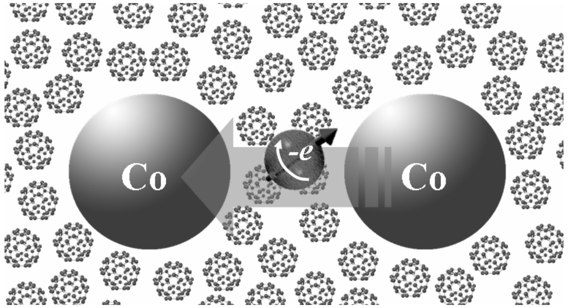
Local Hall effect

④ **Large noise (R_c)**
⇒ Spurious signal

⑤ **Reliability of a "local" scheme "?"**

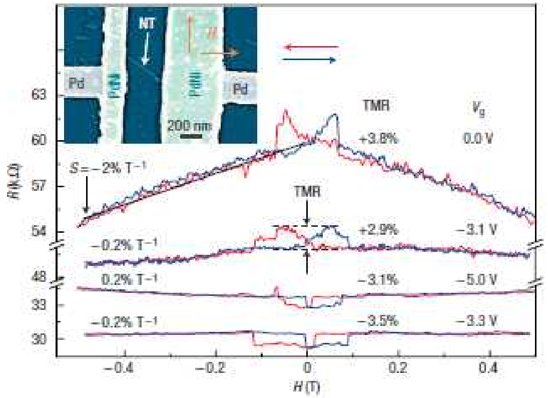
How to solve or bypass the problems?

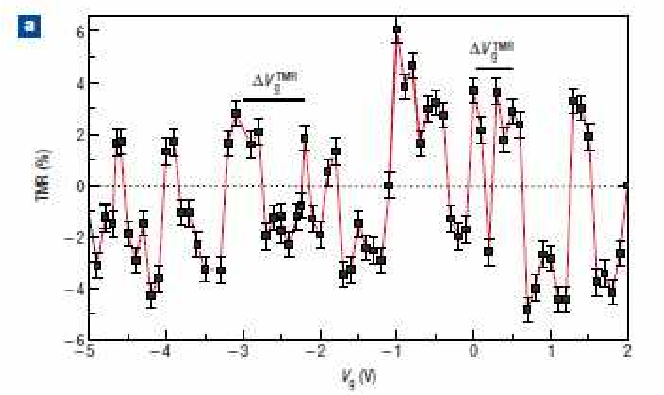
①



MR curves & Magnetization process are characterized in the same sample.

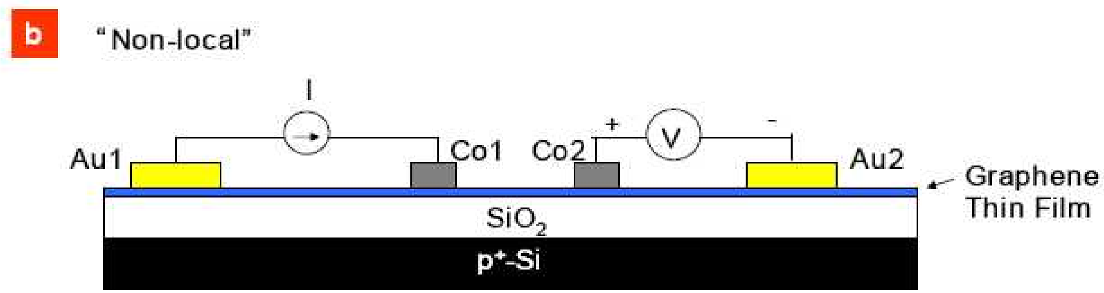
②





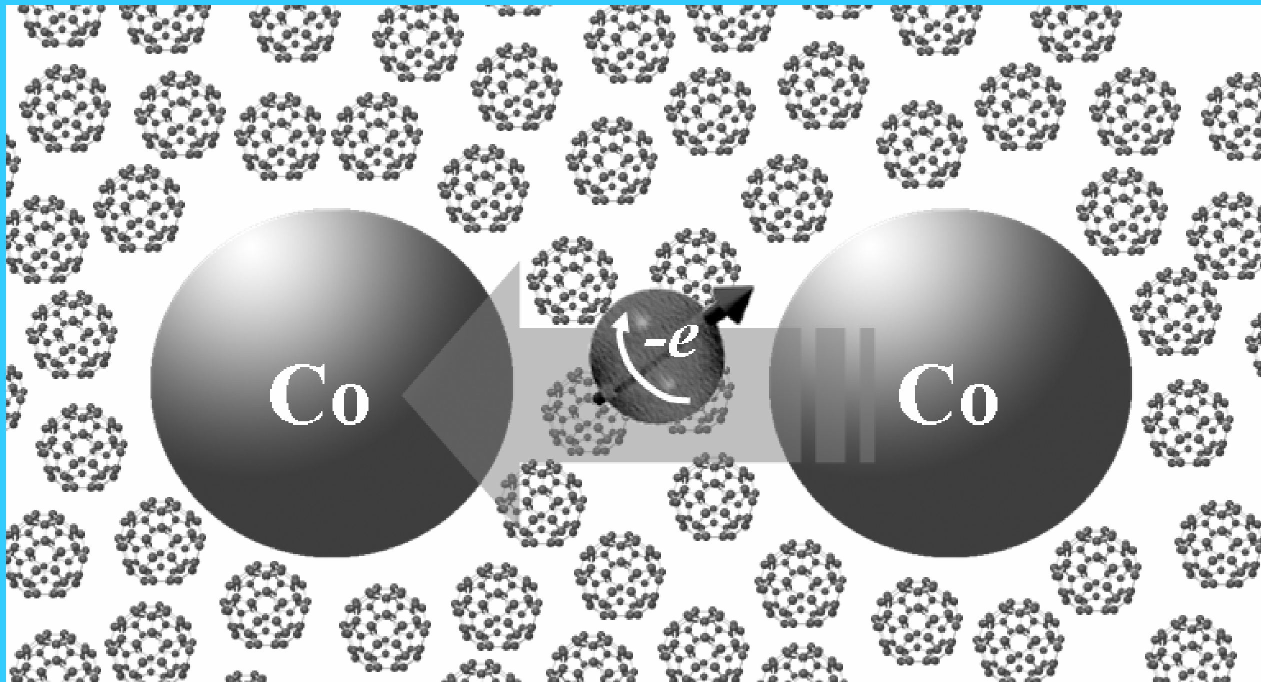
TMR oscillation

③



Non-local method (excluding spurious signals)

PART I : Molecular nano-composite spin devices



Remaining obstacles & our strategy

1. A lack of detailed analyses of magnetization processes

   (Device structures were not suitable for various characterizations.)

2. Excess contact resistance (⇒spurious signals)

3. Uncontrolled interface formations between FM/NM

should be solved for further progress
and obtaining reliable results !!

In this study…

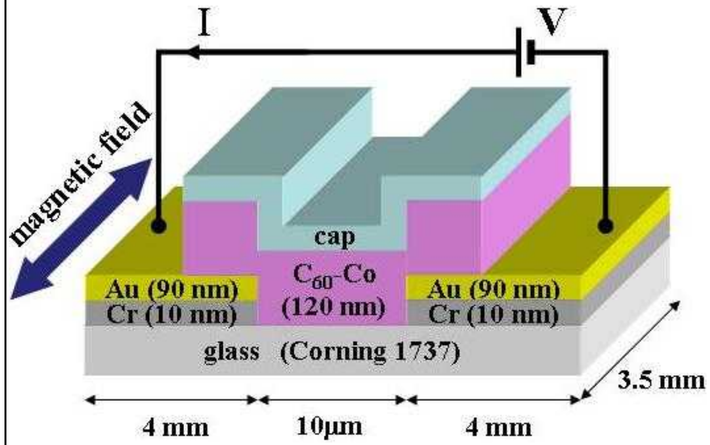
Introducing a novel system, C_{60}-Co nano-composites

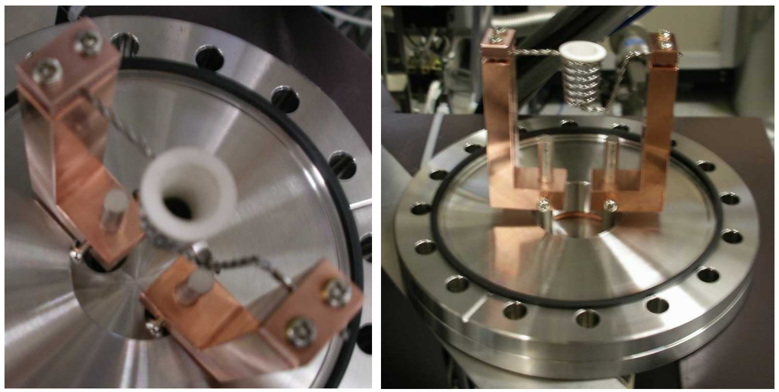
⇒ bypassing the interface problems
inducing reliable results by various characterizations

H. Zare-Korsaraki and H. Micklitz, 2004

Fabrication processes and sample structures

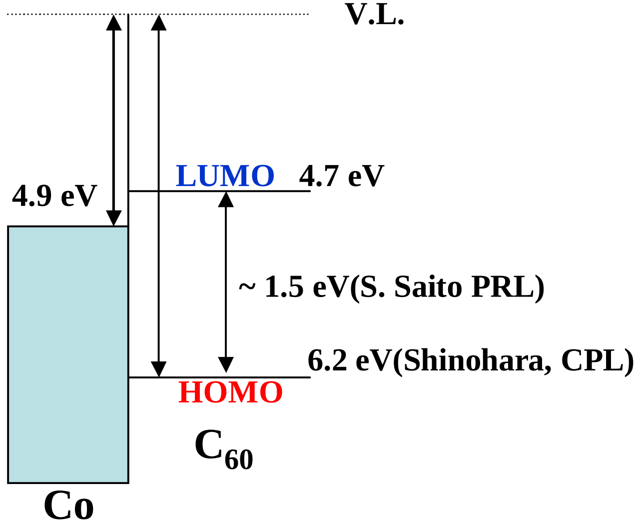
1. Using photo-lithography
2. Evaporating Cr and Au electrodes
3. Lift-off
4. Coevaporation of C_{60}-Co (10^{-6}~10^{-7} Torr)
5. Capping layers (C_{60}+SiO)
7. Coating by ZEP-520A
8. Annealing at 180 ℃, 30 min in vacuum
9. Magnetoresistance (MR) measurements





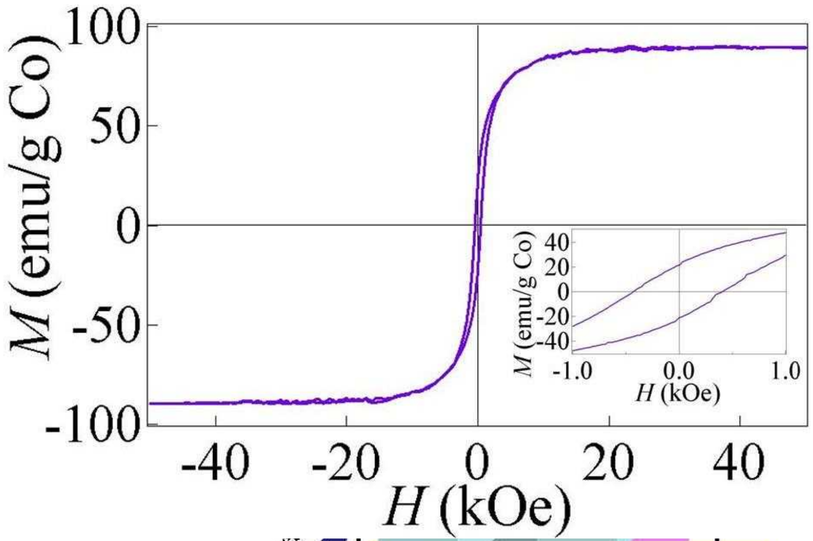
C_{60} evaporation systems

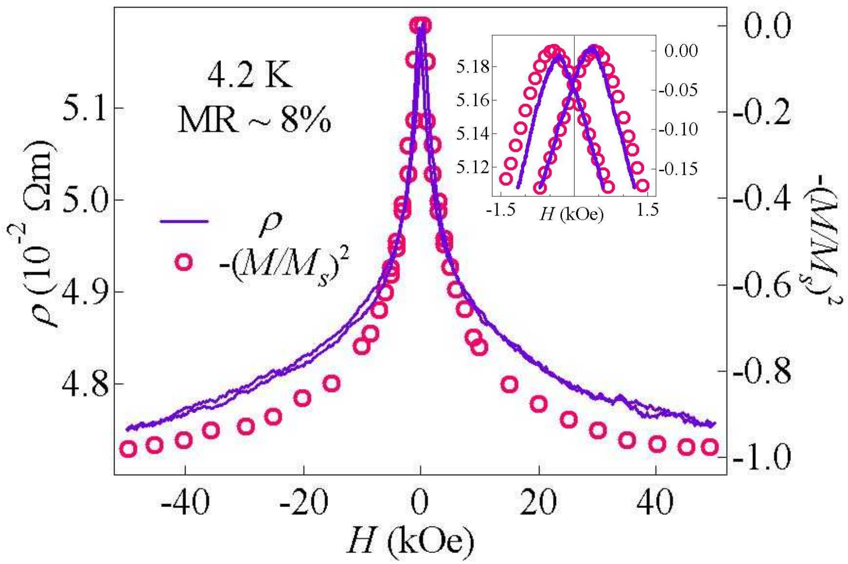
C_{60} powder

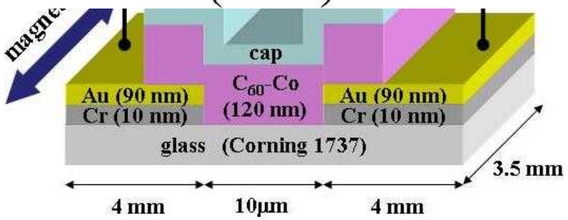


Small gap between W.F. of Co and LUMO comparing with a Alq3 case.

Introduction of C_{60}-Co nano-composites







The MR curve coincides with the magnetization of the Co.

Magnetization of the Co induces the observed MR effect.
= Reliable study !

S. Miwa, M.S. et al. JJAP 45, L717 (2006).
S. Miwa, M.S. et al. PRB76, 214414 (2007).

Structural analyses of the C_{60}-Co nano-composite

Fig. 1

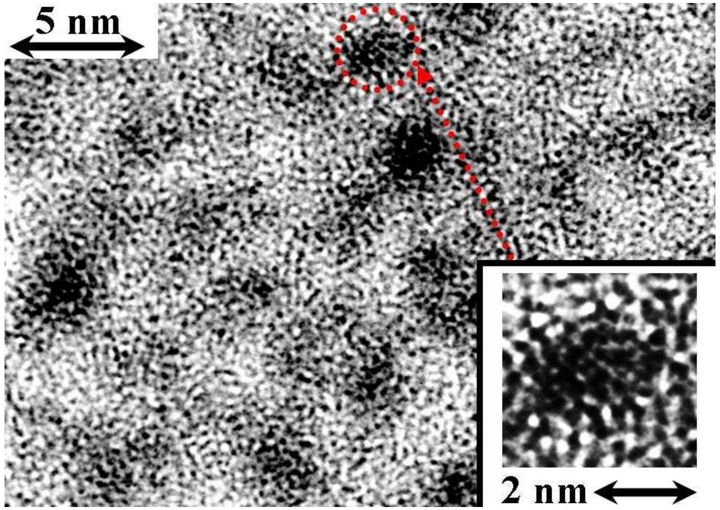
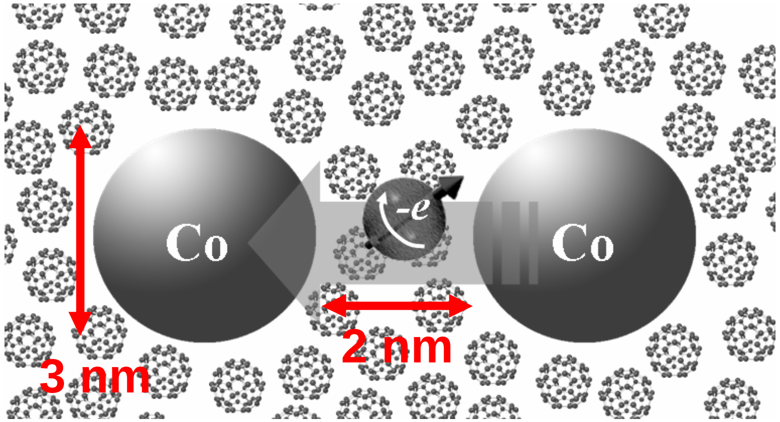
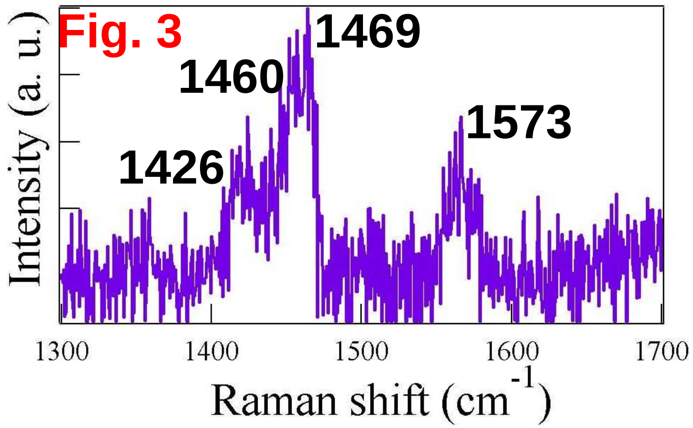


Fig. 2

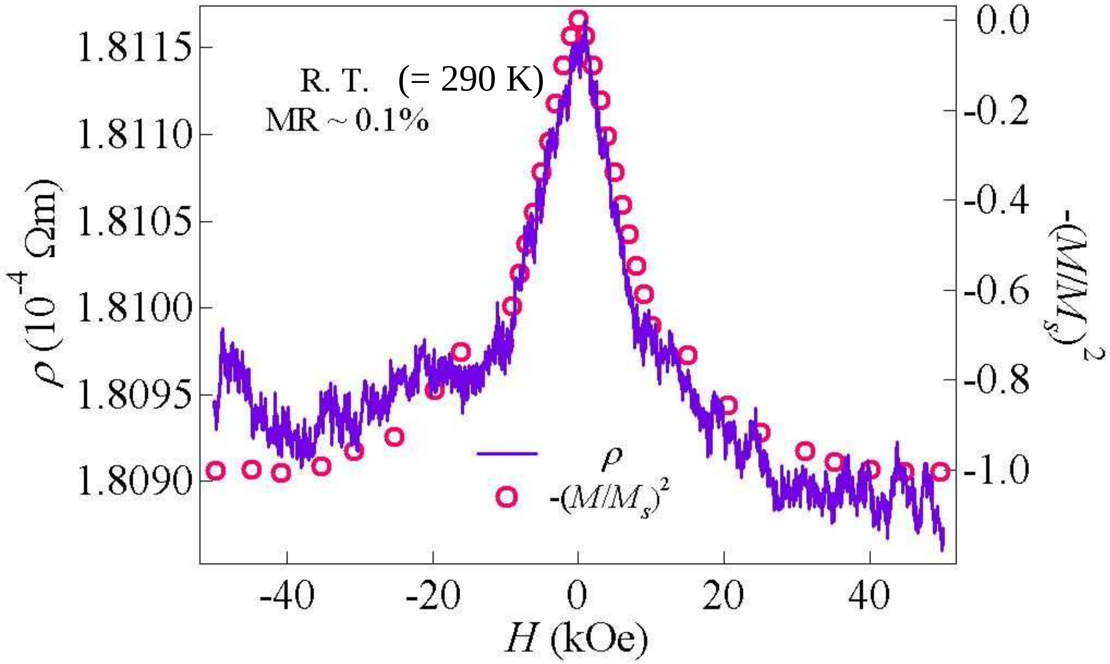


1. The Co size：2-3 nm (Fig.1,XRD：2 nm)
2. Distance ~ 1.5-2.2 nm (From XRD)
3. No percolation of the Co (Fig.1)
4. Spin dependent transport in C_{60} (Fig.2)
5. No obvious damage to C_{60} (Fig. 3)

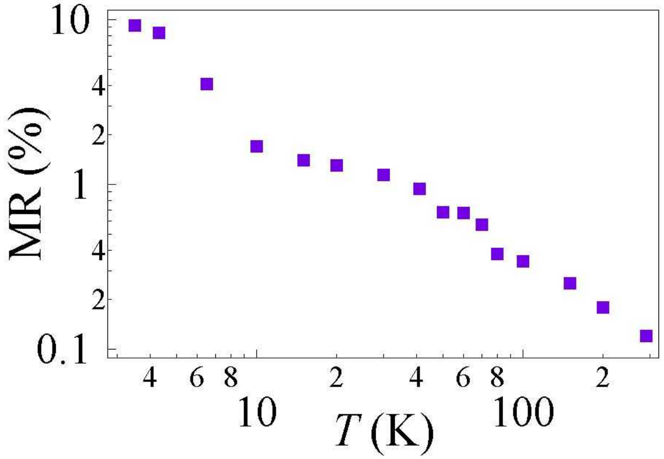
Fig. 3



An observation of the MR effect at room temperature



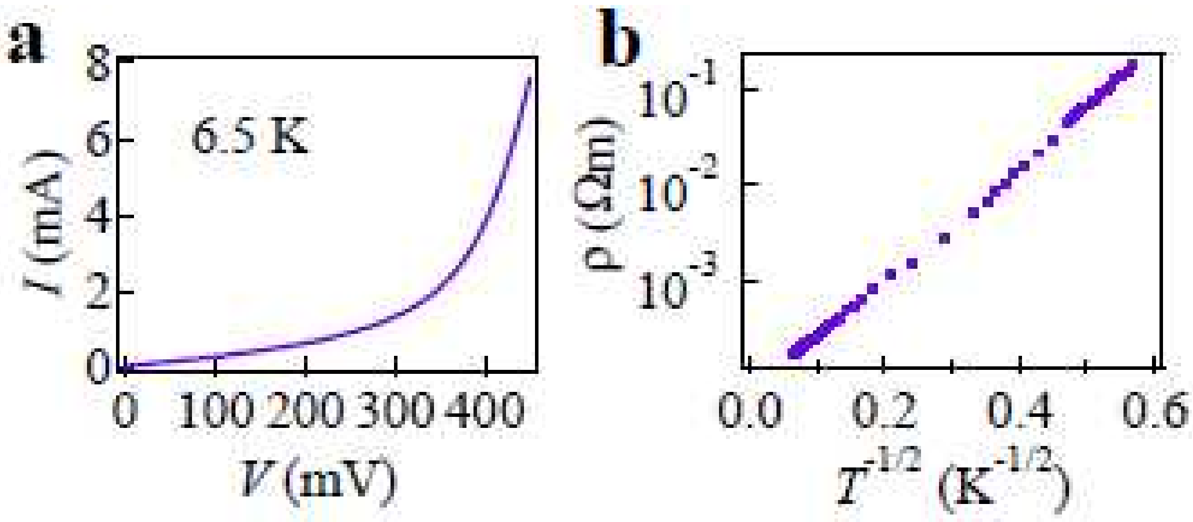
Temperature dependence of the MR ratio



The first observation of an MR effect at RT induced by spin-dependent transport in molecular spin devices !!

Recently,….
the MR ratio increased up to 300-500% at 4 K.

A role of molecules ?



$T^{-1/2}$ dep. (Hopping transport) ⇒ Coulomb interaction between conducting electrons

Coulomb energy

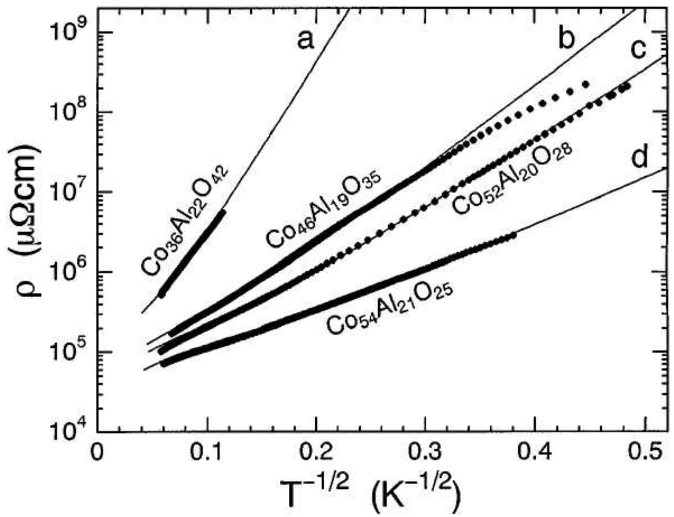
$$E_c = \frac{k_B}{2}\sqrt{TT_0},$$

When T=6.5 K, then
E_c=1.48 meV

Number of junctions :
300-400

In Co-Al-O system,

Co-Al-O granular film
S. Mitani et al., PRL 1998.



Molecules behave as a tunnel barrier ?

Replacement of molecular matrices

Rubrene

Application for field effect transistors (FETs)

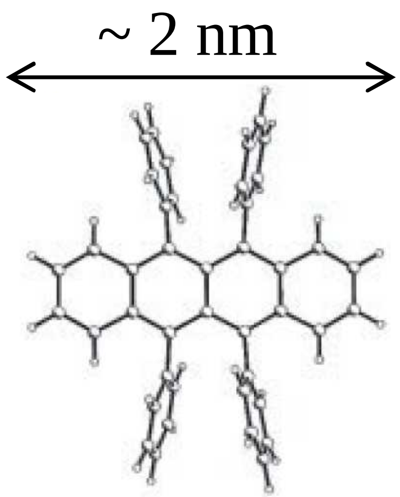
S.C. FET μ **= ~40 cm^2 V^{-1} s^{-1}**

V. C. Sundar *et al*., *Science* 3**12**, 1644 (2004).

J. Takeya et al., *Appl. Phys. Lett.* in press.

Thin film FET

S. Seo, *et al*., *Appl. Phys. Lett.* 88, 232114 (2006).



Rubrene : $C_{42}H_{28}$

Alq3

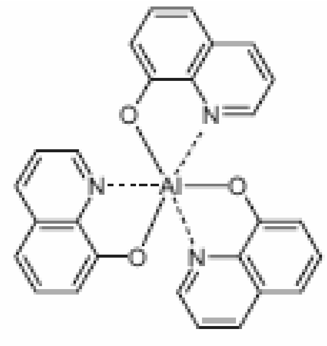
An electron transport layer of O-LED

Tang et al., Appl. Phys. Lett. 51, 913 (1987).

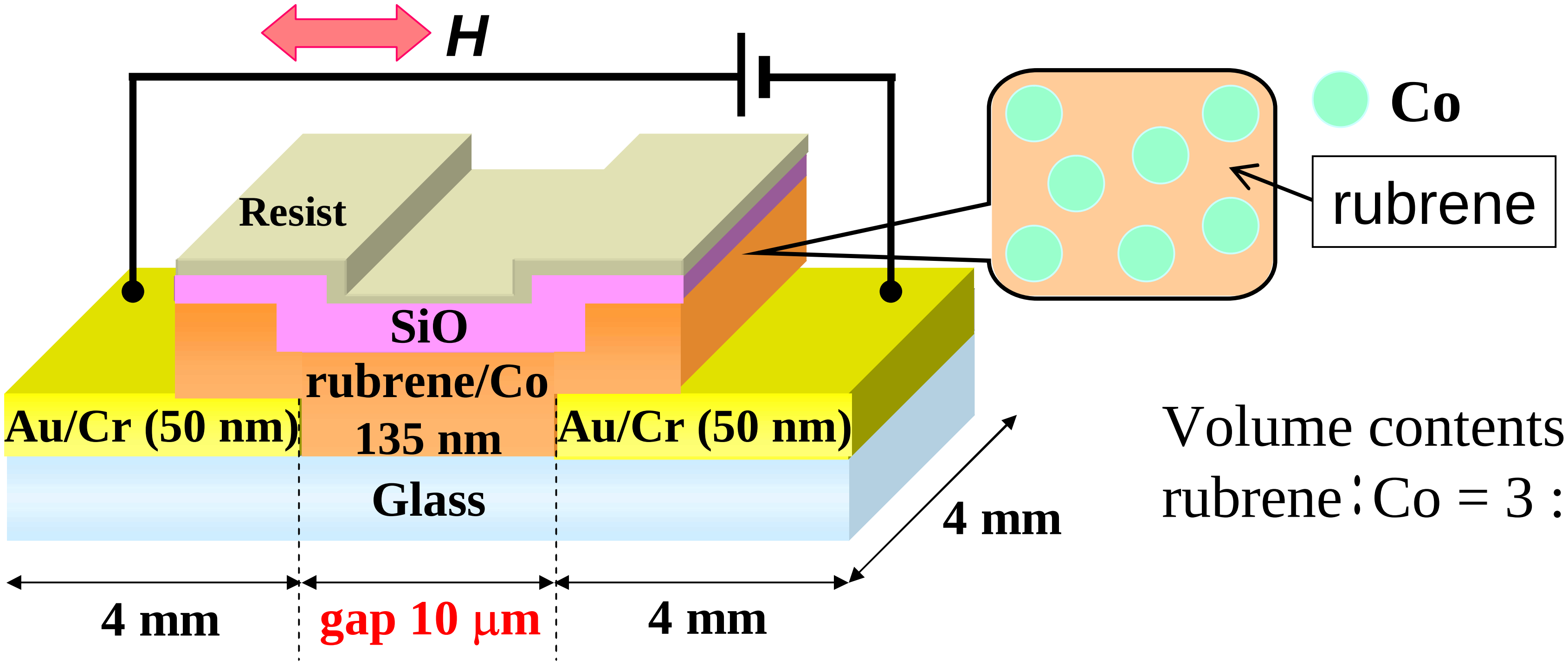
An MR effect in sandwiched devices

Xiong et al., Nature 2003

An intrinsic MR effect（Wohlgenannt et al.)



A device structure using rubrene-Co nano-composite



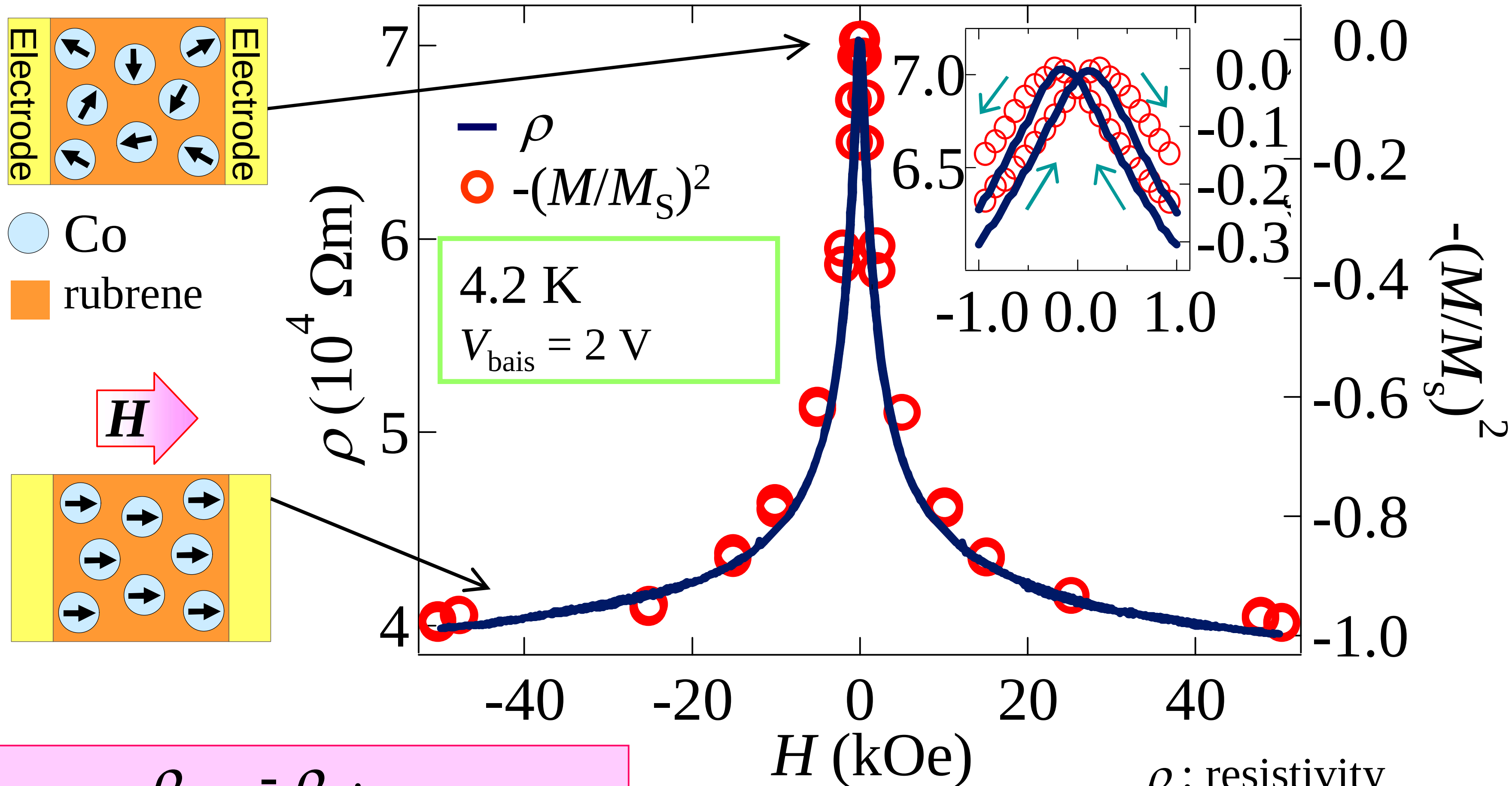
Volume contents
rubrene : Co = 3 : 1

① Fabrication of NM electrodes

② rubrene/Co co-evap.(10^{-7}~10^{-6} Torr)
- rubrene : ~ 0.3 Å /s , 1000 Å
- Co : ~ 0.1 Å /s , 350 Å

③ Capping layers [SiO (~ 500 nm) + resist]

A large MR effect in rubrene-Co nano-composite



ρ : resistivity

M_s : sat. mag.

MR ratio $= \dfrac{\rho_{max} - \rho_{min}}{\rho_{min}} =$ **78%**

H. Kusai, M. Shiraishi et al., Chem. Phys. Lett. 448, 106 (2007).

The origins of the large MR ratio

MR ratio = $\boldsymbol{P^2}$

Co spin polarization: P = 34% → MR ratio = 12%

C_{60}-Co: **MR ratio = 300%**
Rubrene: **MR ratio = 80%**

Larger than the theoretical predicted value

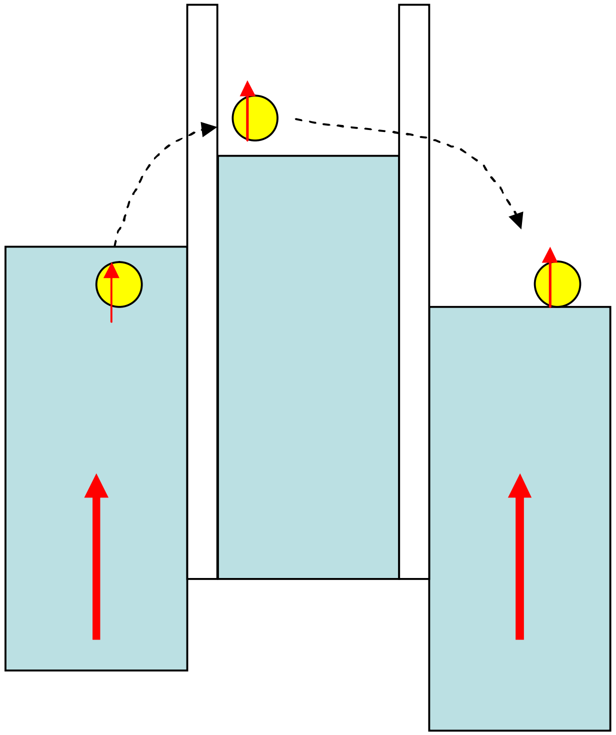
Possible reasons

1. **Enhancement of the MR ratio by Coulomb blockade ?**
   (S. Mitani et al., PRL81, 2799 (1998).)
2. **Enhancement of spin polarization of the Co at the interface ?**
   (C-K. Yang et al., PRL203 (2003).)

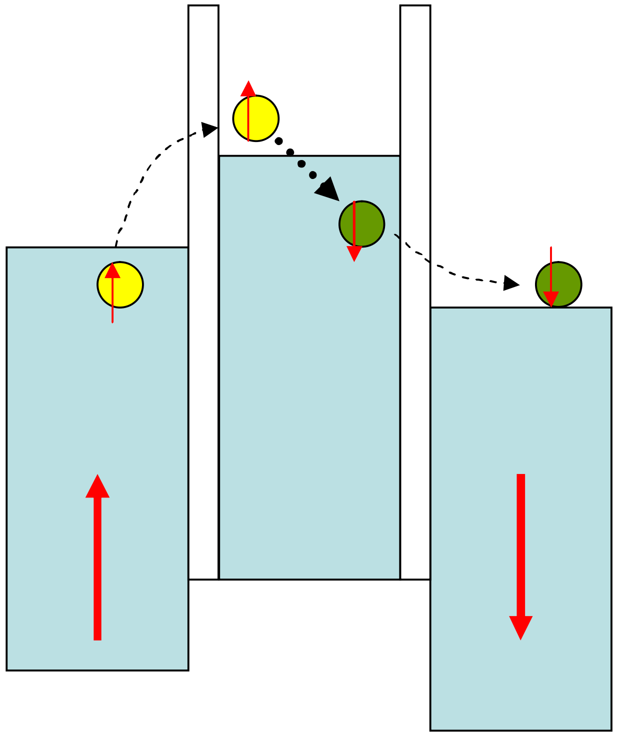
1. **Yes. Coulomb blockade and co-tunneling are important.**
2. **Yes. (M. Shiraishi et al., APL 93, 53103 (2008).** ^{59}**Co spin echo)**

Importance of surface & interface characterizations !!

Why Coulomb blockade is important?



Parallel alignment

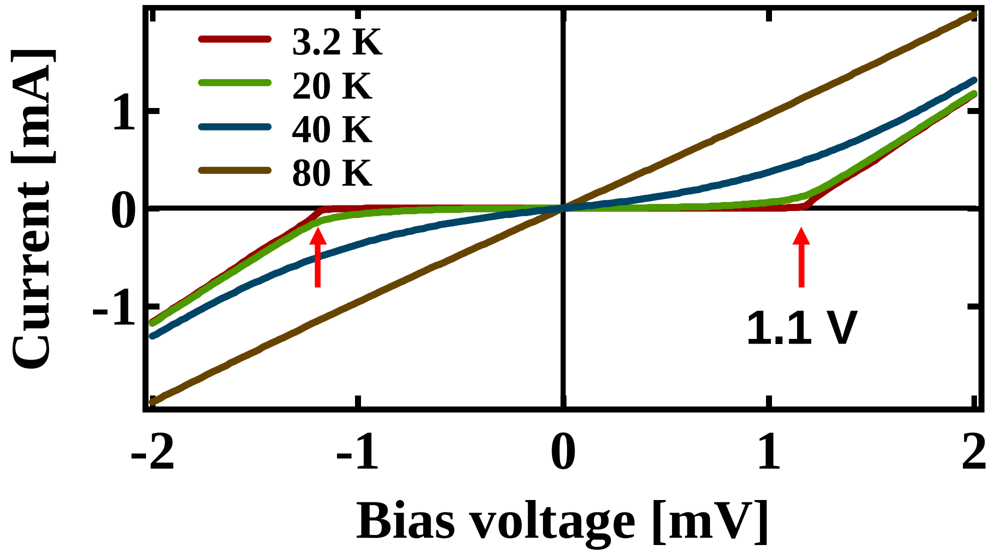


Anti-parallel alignment

A spin flip process is needed

Low conductivity !!

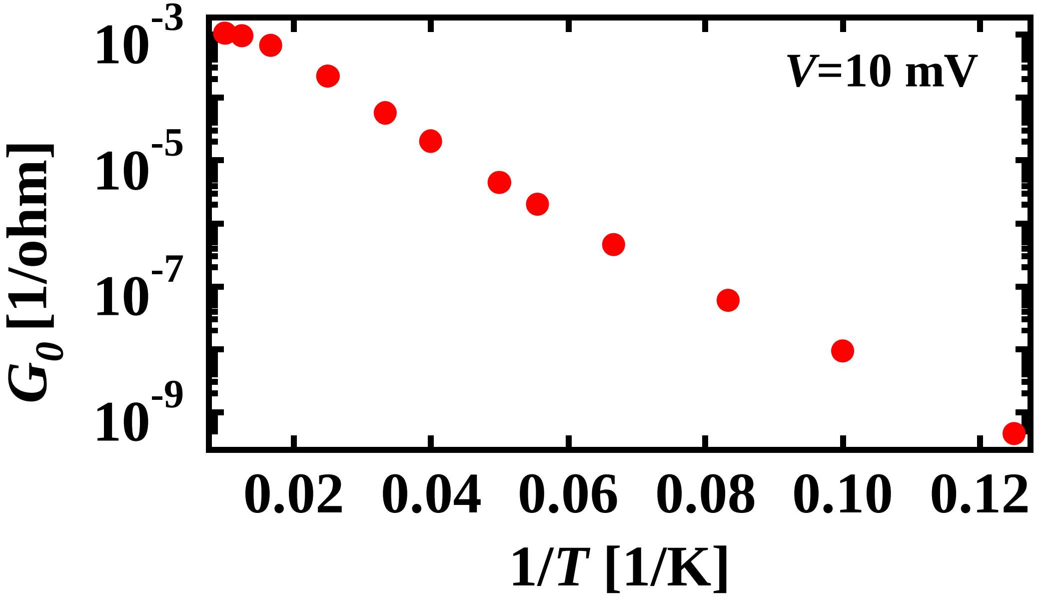
Clear Coulomb blockade



$d_{Au\text{-}Au}$=400-500 nm

NOT breakdown !

Spin (Coulomb) blockade !!



Zero bias conductance :

$$G \propto \exp\left[\frac{-U}{k_B T}\right]$$

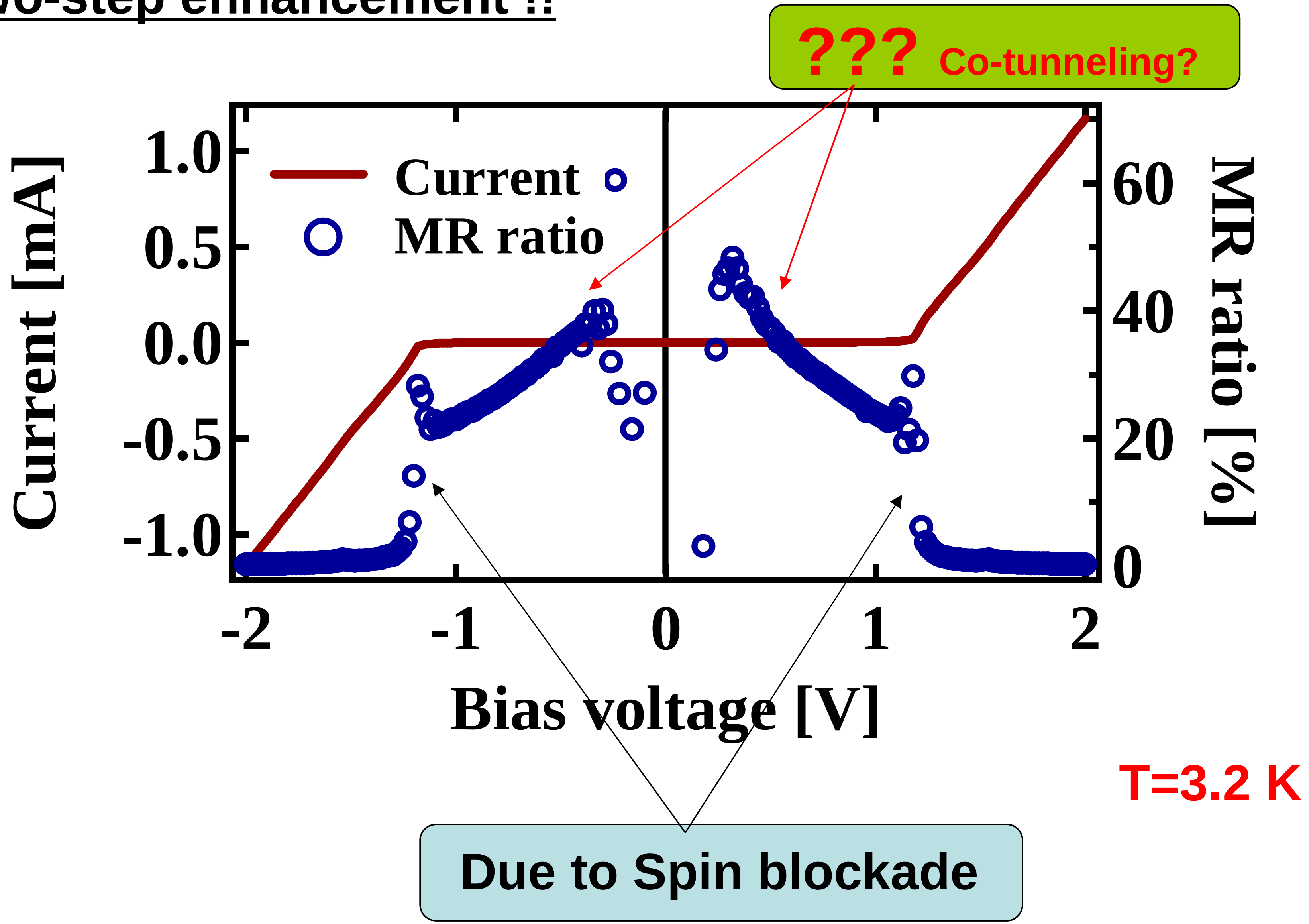
U : 12 meV

r_{Co} : 1.4 nm

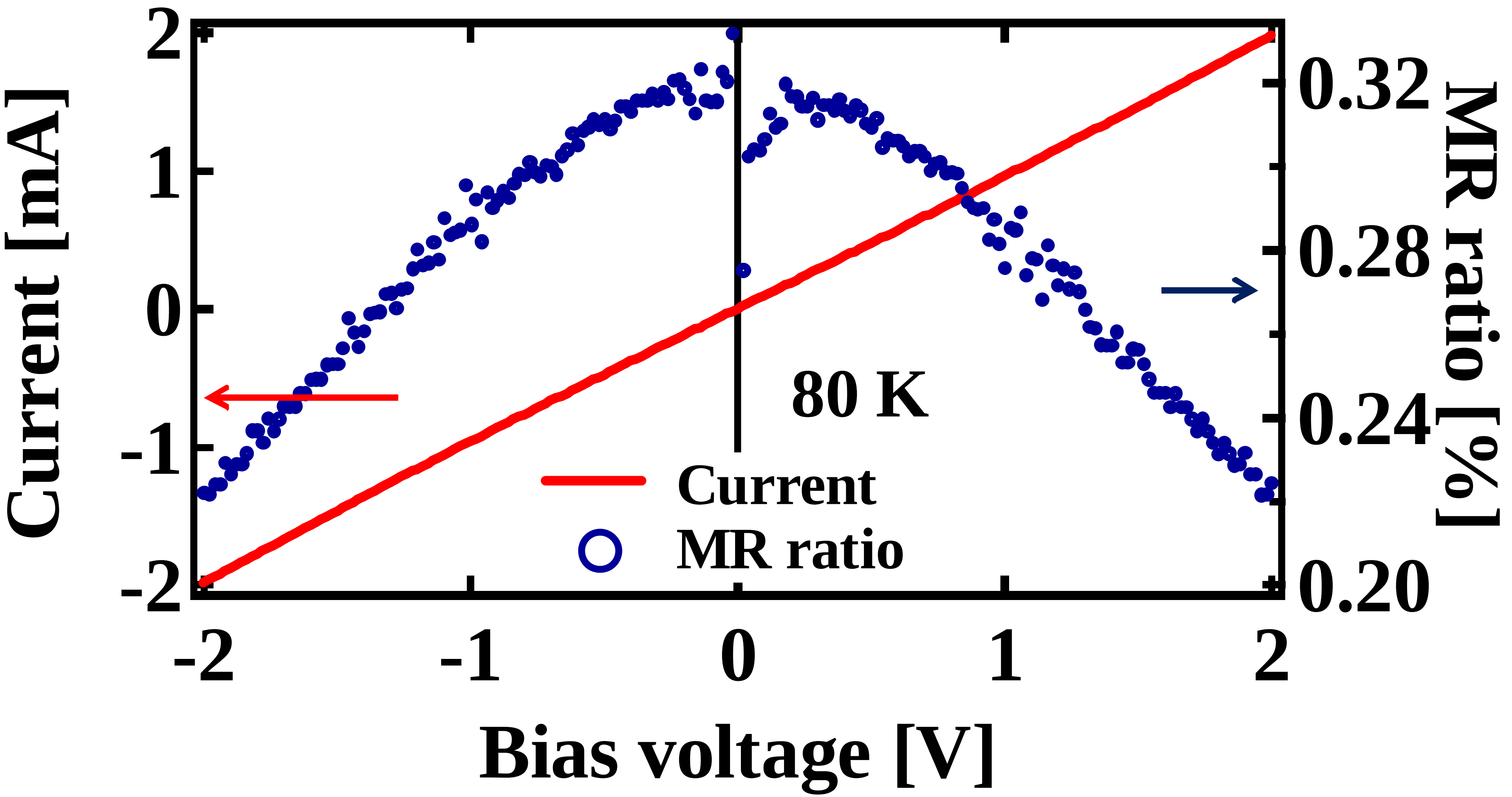
r_{Co} : 0.8-2.3 nm (by SQUID)

Correspondence between CB and MR

Two-step enhancement !!



Bias voltage dependence of MR ratio (80 K)

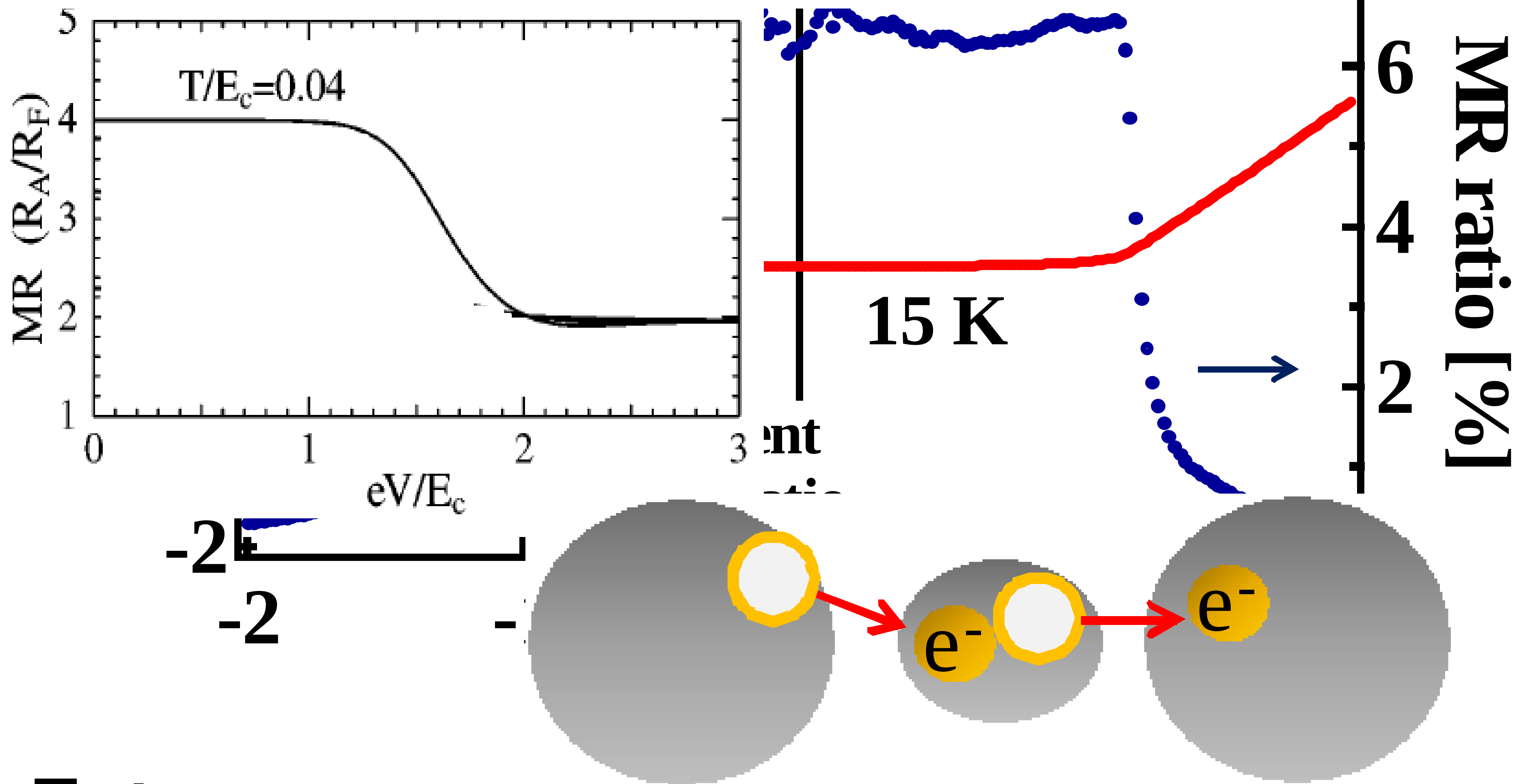


■ The *I-V* characteristic is linear, thus no CB effect.

■ The MR ratio monotonously decreases with increasing the bias voltage

Bias voltage dependence of MR ratio (15 K)

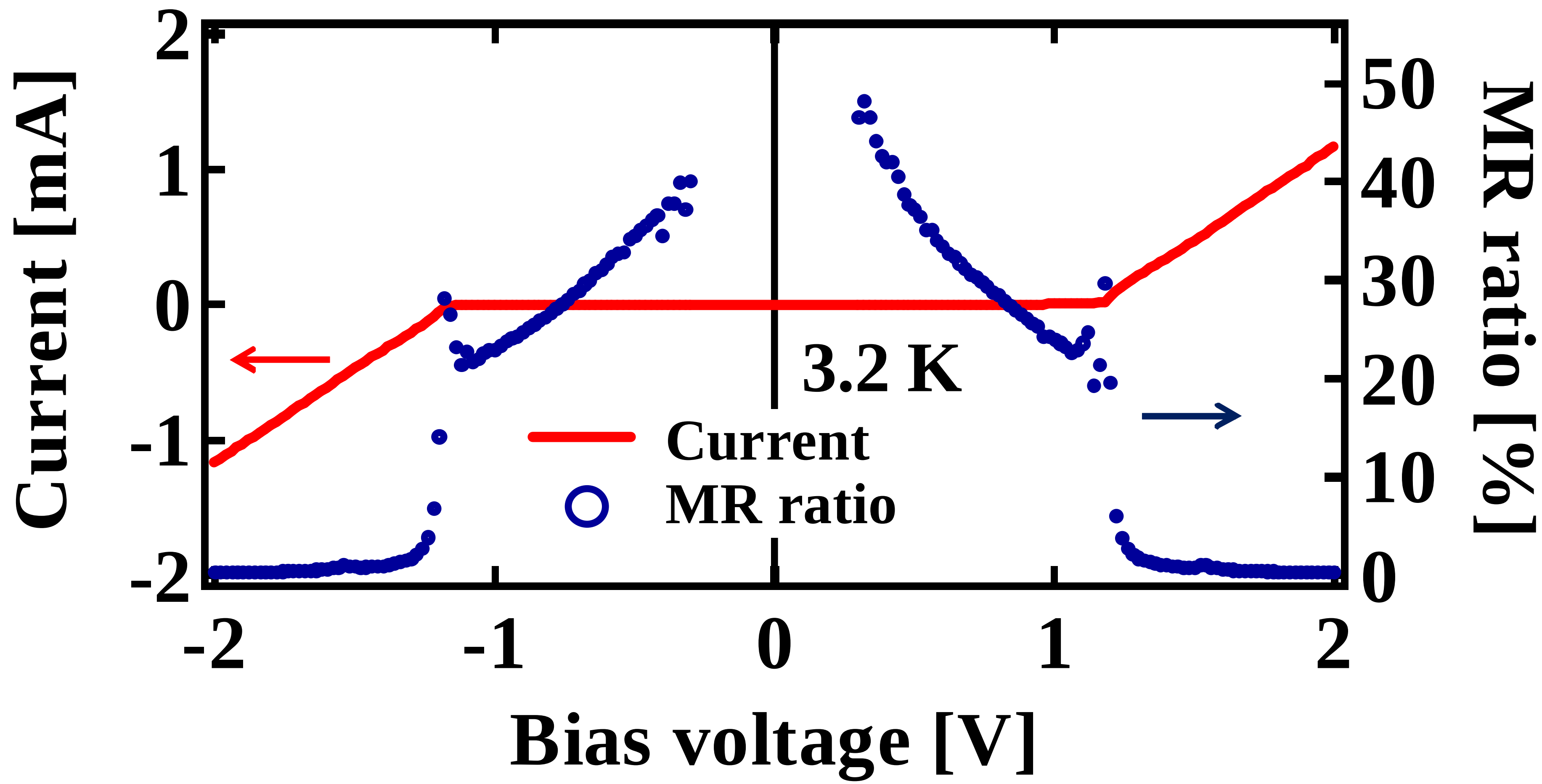
S. Takahashi and S. Maekawa, *phys. Rev. Lett.* **80**, 1758 (1998).



■ **Clear appearance of the MR enhancement by the CB effect**

■ **Constant MR ratio in the CB region**
→ **Second-order co-tunneling**

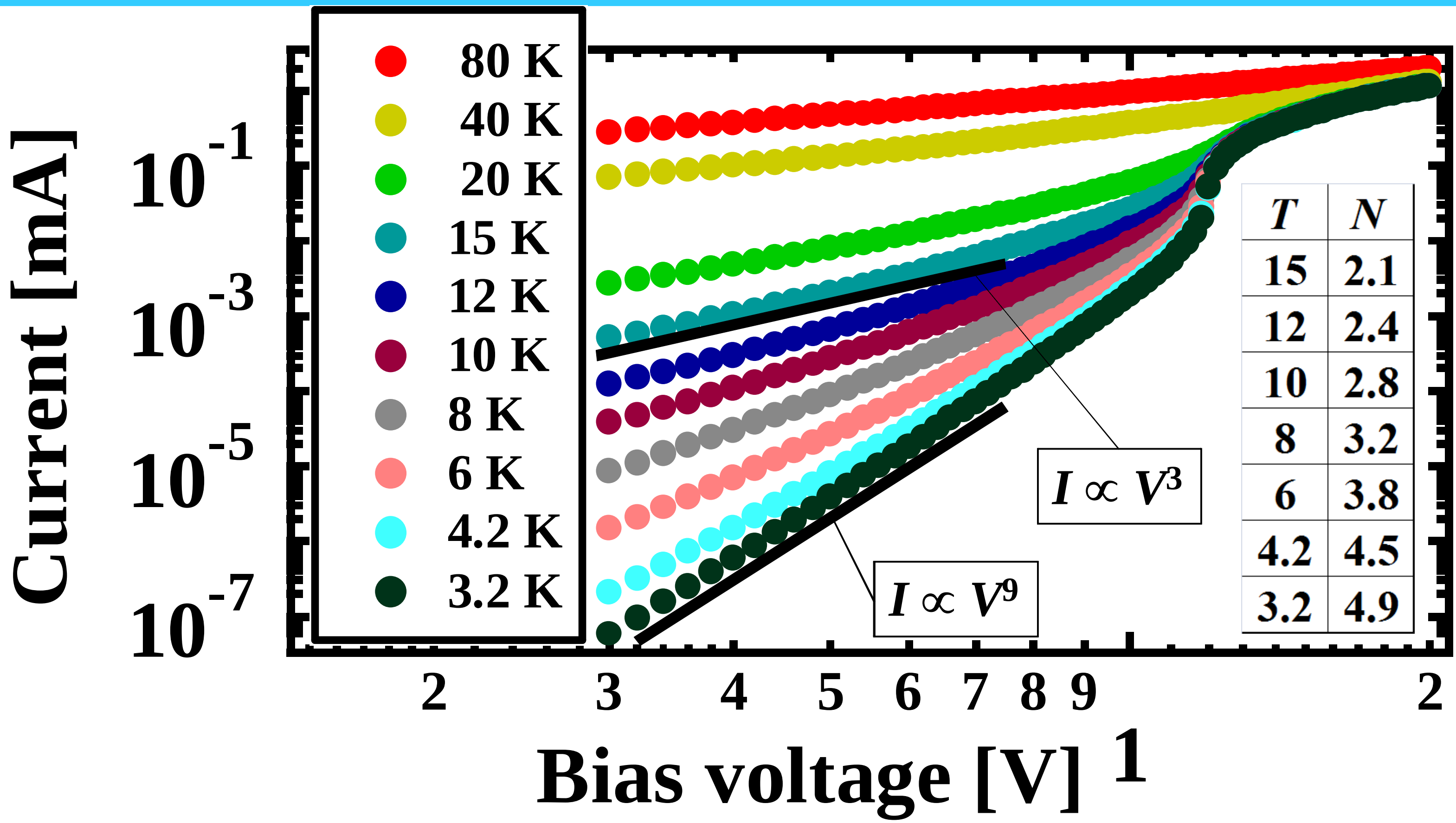
Bias voltage dependence of MR ratio (3.2 K)



■ Clearer appearance of the enhancement by the CB effect at the threshold

■ Appearance of an additional MR enhancement in the CB region

Log-log plots of *I-V* characteristics



- **Agreement with the transport property of Co-tunneling** **($I \propto V^{2N-1}$, N :the number of junctions)**
- ***N* decreases with increasing temperature.**

Dominant transport : High-order Co-tunneling

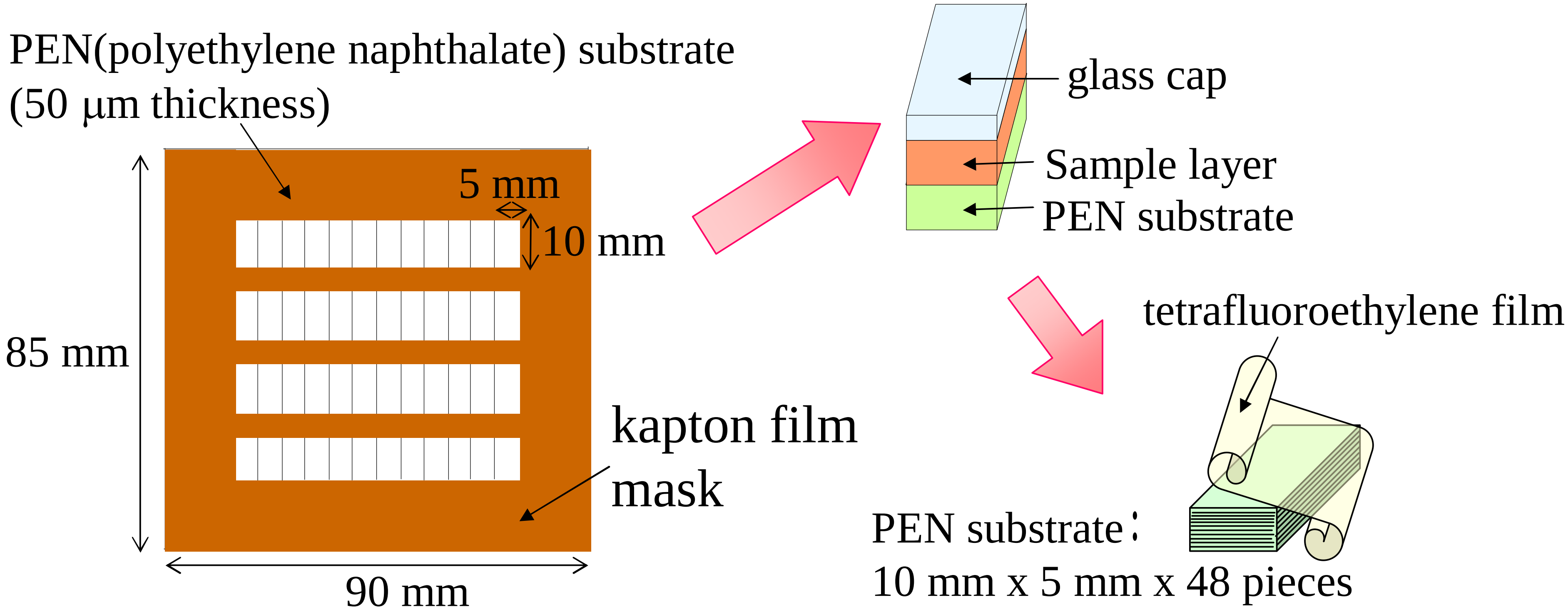
T. B. Tran *et al.*, *Phys. Rev. Lett*. **95**. 076806 (2005)

Conclusion 1 (CB & CT)

1. Clear Coulomb blockade (CB) and co-tunneling (CT) were observed.
2. Two-step enhancement of the MR ratio was observed.
3. The CB & the CT contributed to the enhancement of the MR ratio.

D. Hatanaka, M. Shiraishi et al., to be submitted.

Spin polarization characterization (NMR spin echo)



Measured Samples

- Co(~350 nm, 0.1 Å/s) + glass
- rubrene(~1050 nm) + glass
- rubrene(~1050 nm)-Co(~350 nm) + glass
- rubrene(~700 nm)-Co(~350 nm) + glass

Spin polarization characterization (NMR spin echo)

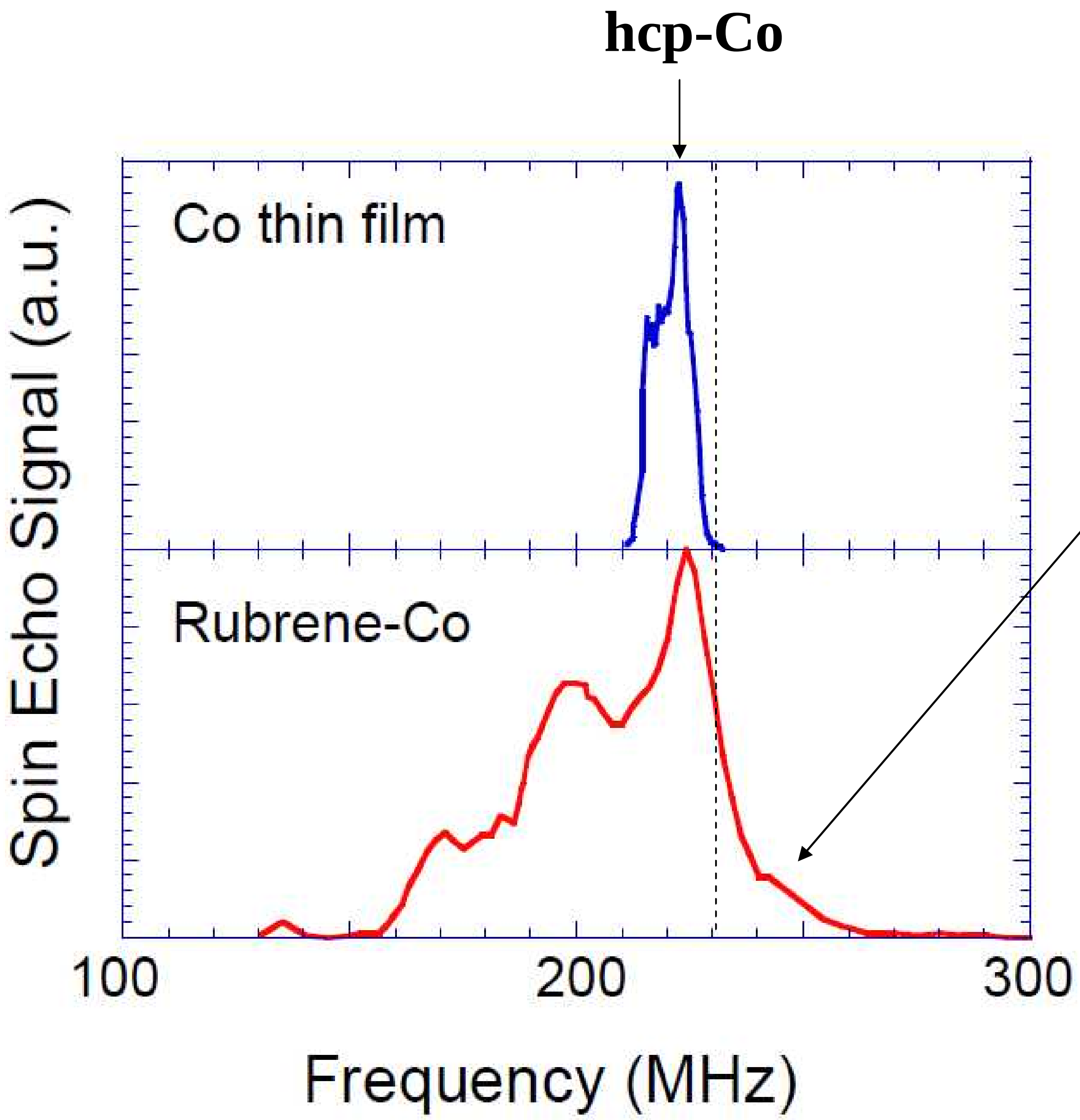
^{59}Co spin echo

Co nano-particles in the nano-composites (Diameter：0.8-2.3 nm)

No signal from rubrene

Temperature： 2 K
Frequency：100-320 MHz
Magnetic field：0-9 T

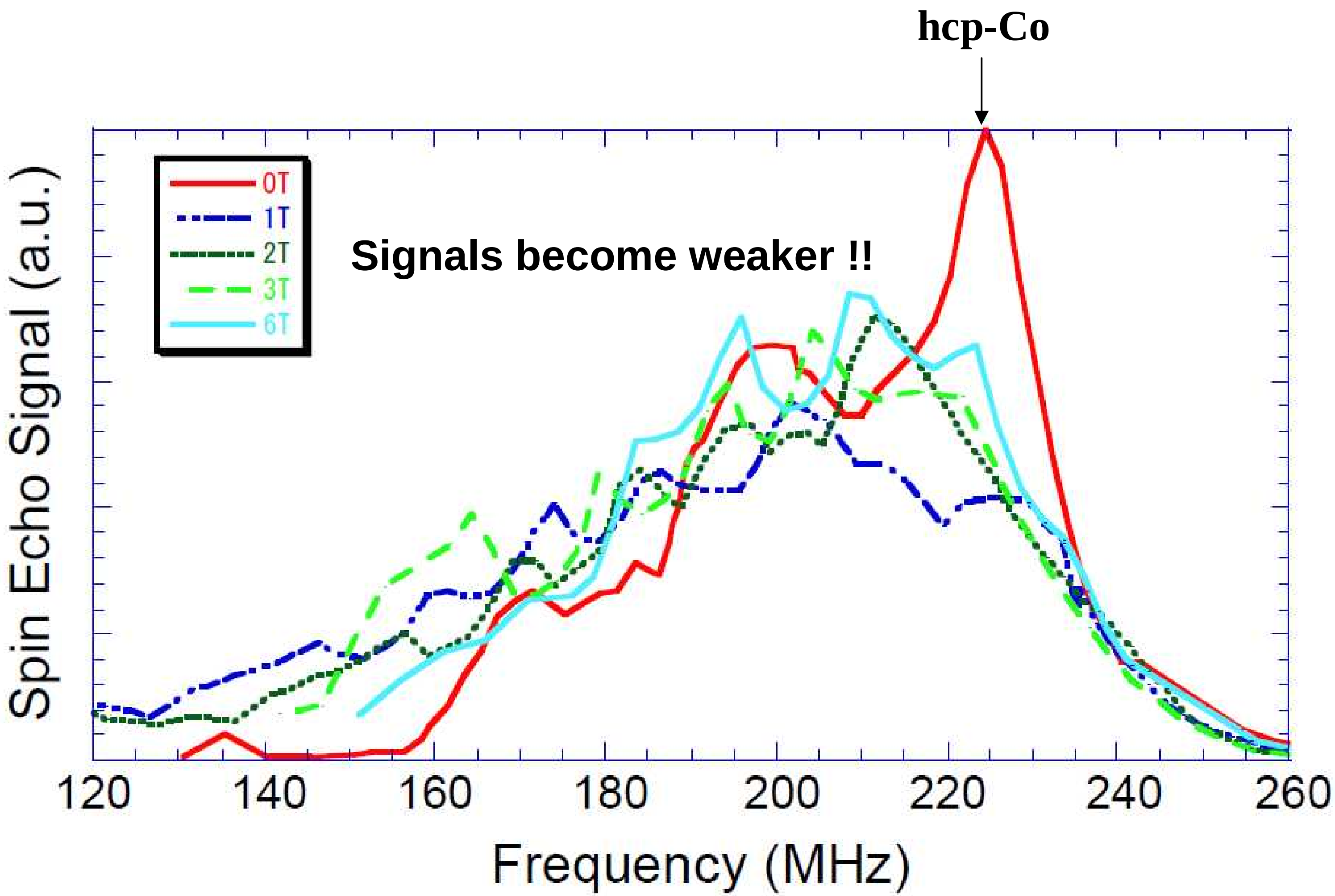
Spin echo signals (Co thin film & rubrene-Co)



Enhancement of spin polarization at the Co surface.

~ +10 %

Spin echo signals (Magnetic field dependence)



Completely different behavior in comparison with Co thin film !!

An interpretation

Important message）

Unique behavior under a magnetic field application

=A possible model=

①*B*=0 T

A hyperfine field is fully observed.

②*B* > 1 T

Parallel to the applied field,

but random to the crystal axis.

⇒ anisotropy of the hyperfine field

+

hcp-Co induced a quadrupole effect

Conclusion 2

1. **Enhancement of spin polarization was observed by NMR.**
2. **The enhancement was estimated to be ~10%.**
3. **It is not enough to explain all of the enhancement of the MR ratio.**
4. **The spin structure of molecular spin devices was firstly clarified.**

M. Shiraishi et al., Applied Physics Letters 93, 53103 (2008).

Conclusive remarks in Part I

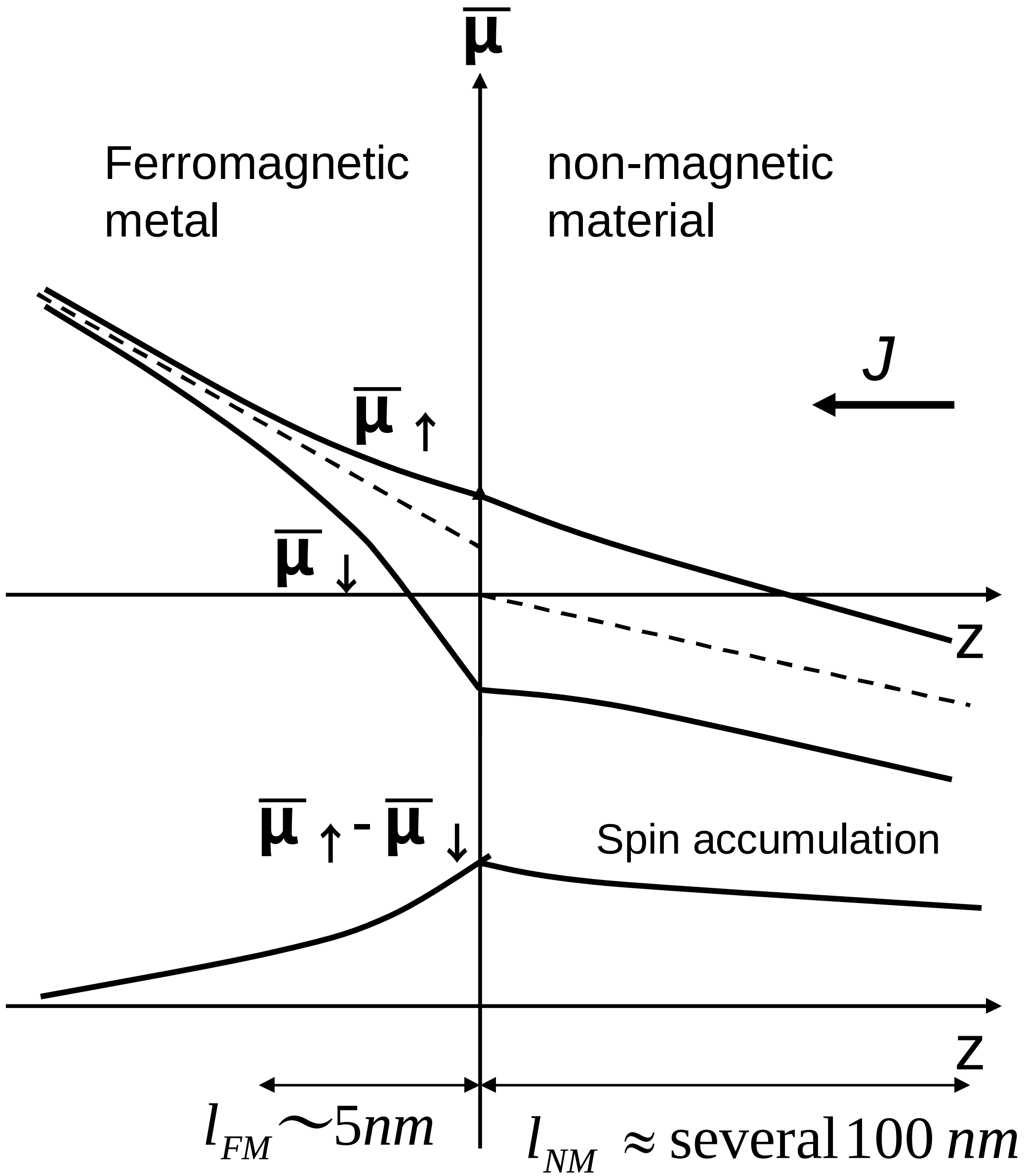
1. The first observation of a spin-dependent MR effect at RT in molecular spin devices.
2. Large MR ratio (80%) was observed in rubrene-Co nano-composites. Recently, 300-500%@4 K in a C_{60}-Co system.
3. MR ratio of 12% in Alq3-Co nano-composites. (S. Tanabe, M. Shiraishi et al., APL 91, 63123 (2007).)
4. Background physics becomes clear.

However, spin injection was not achieved !!

- **Molecules are barriers (TMR!)**
- **Conductance mismatch**

Sakai, Takanashi, et al., APL 2006. (C_{60}, 400%@4 K, TMR)
Moodera et al., PRL 2007. (Alq3, Rubrene : TMR)
Bader et al., PRB 2008. (Alq3 : TMR)

FM/NM contact
Spin-injection



Spin-polarization of the injected current

$$\frac{J_\uparrow - J_\downarrow}{J_\uparrow + J_\downarrow} = \frac{\beta}{1 + \dfrac{r_{NM}}{r_{FM}}}$$

$\beta = (\sigma_\uparrow - \sigma_\downarrow)/(\sigma_\uparrow + \sigma_\downarrow)$ **:Spin-asymmetry**

$r_{FM} = l_{FM}\left(\sigma_\uparrow^{-1} + \sigma_\downarrow^{-1}\right)/4$ **:interface effective resistance**

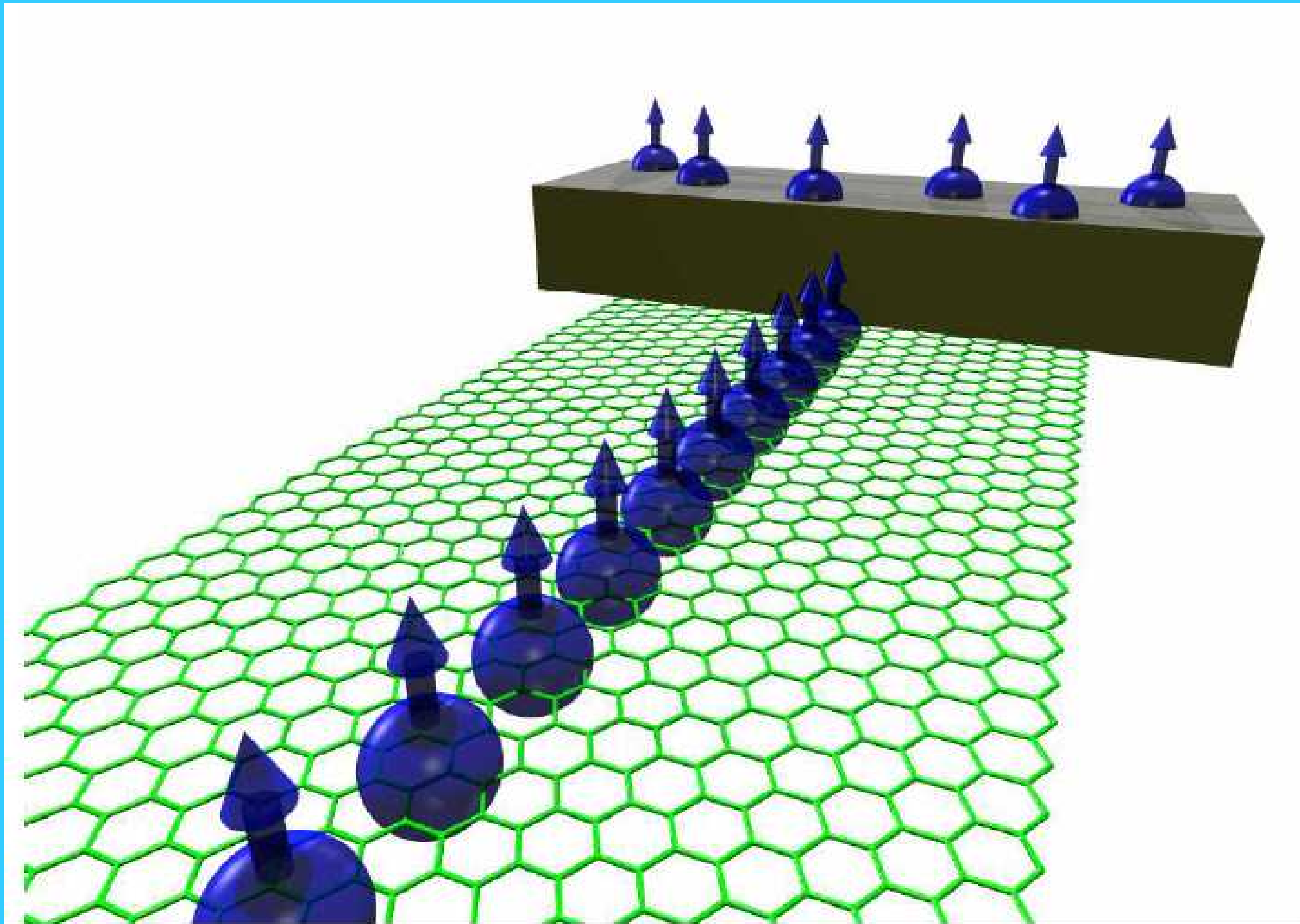
$r_{NM} = l_{NM}\sigma_{NM}^{-1}/2$

We cannot inject spin for the case;

$$r_{NM} >> r_{FM}$$

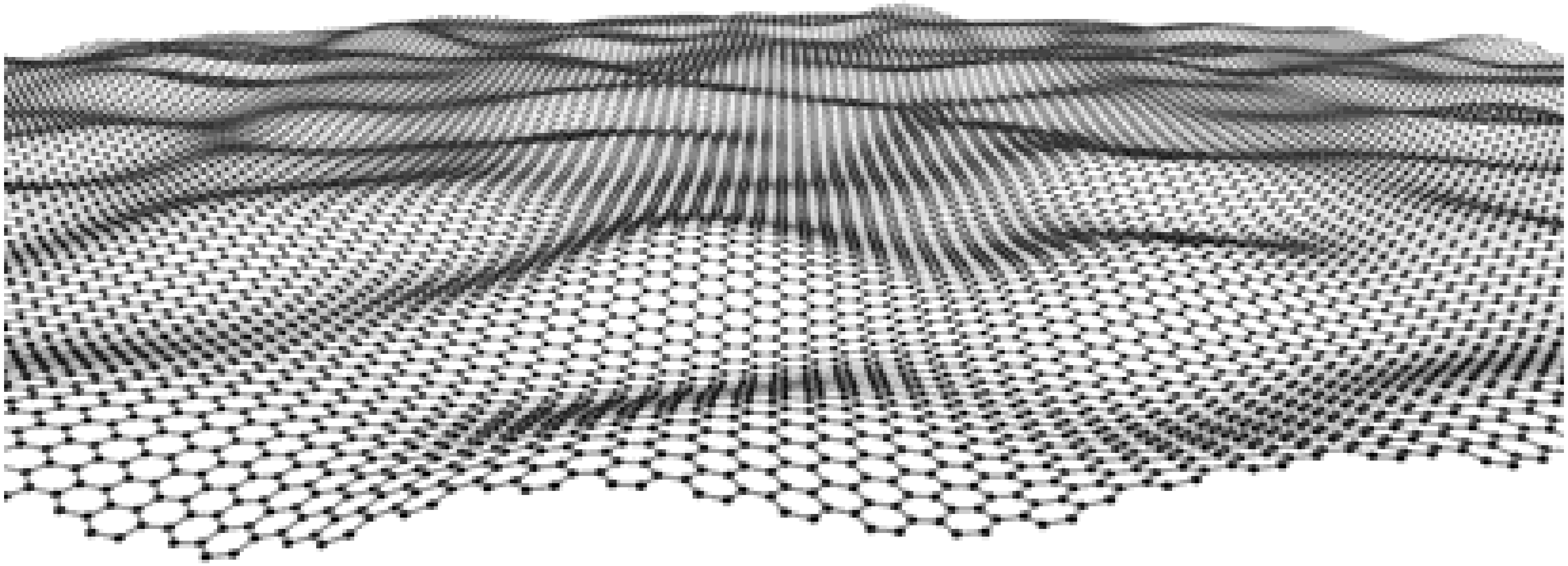
A. Fert et al., PRB 2001.

PART II : Spin injection into graphene at room temperature



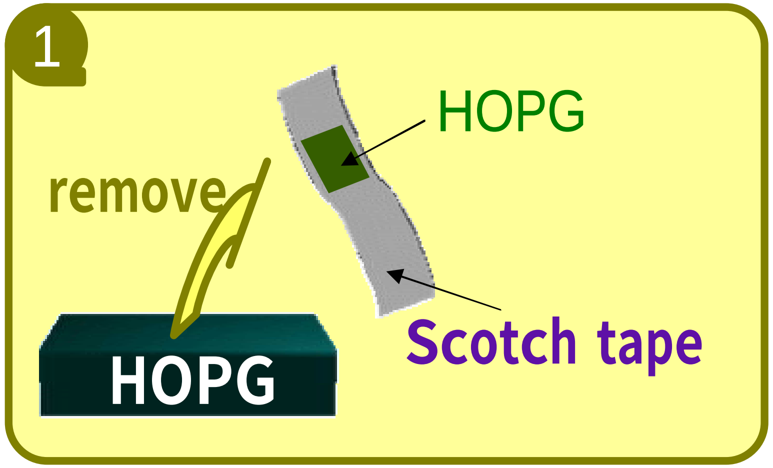
How to inject spins into molecules ?

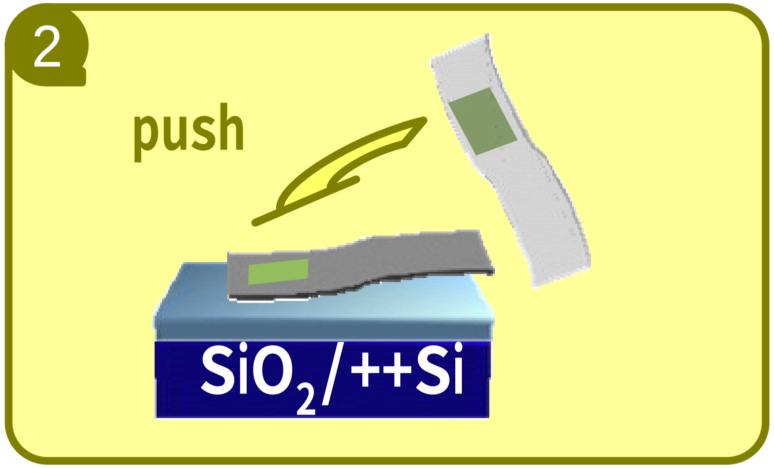
The answer is….

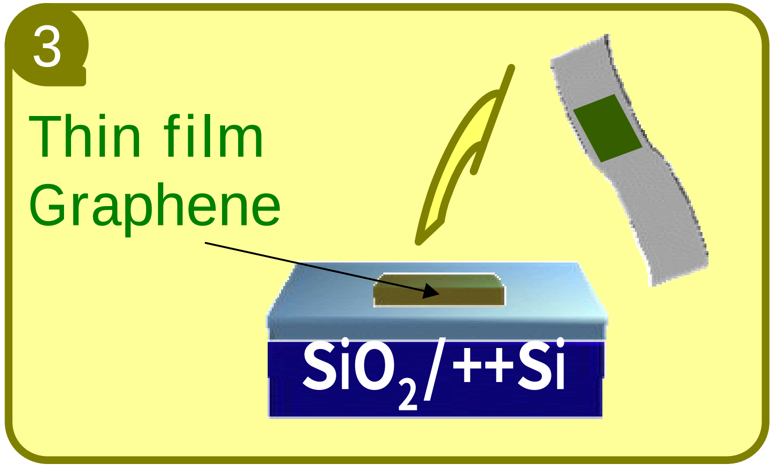


Graphene

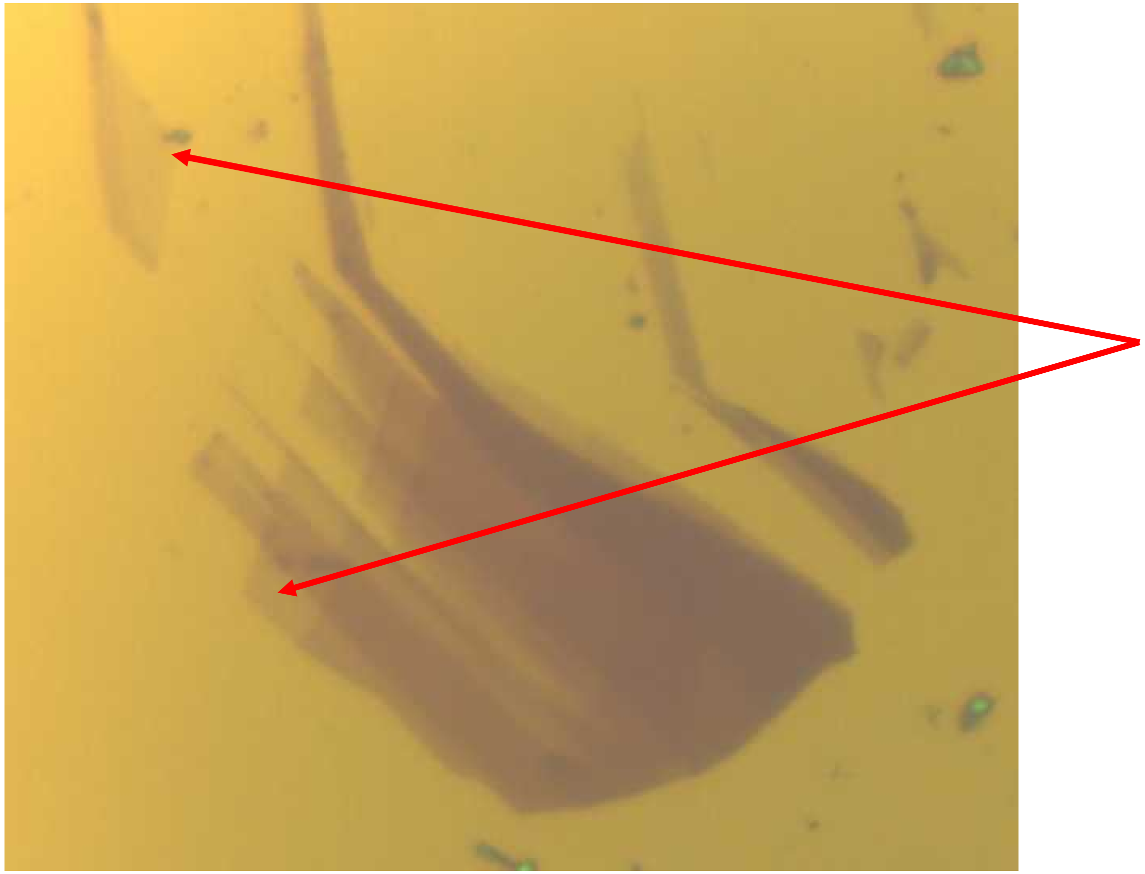
Fabrication process (Scotch tape peeling)







Graphene (Single- & Multi-layered, Optical microscopic image)



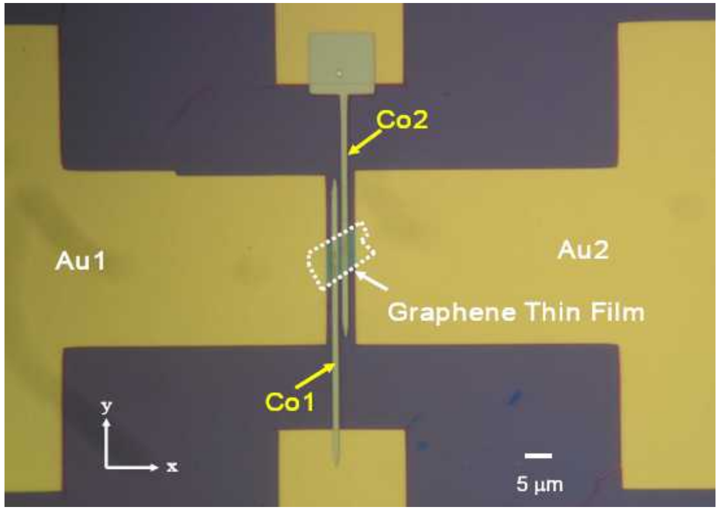
Sample geometry and measurement techniques

Local 2-T & Non-local 4-T

DC measurements

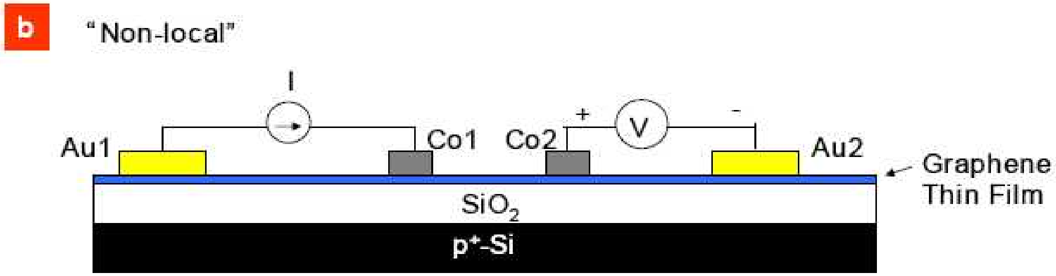
Room temperature

No tunneling barrier

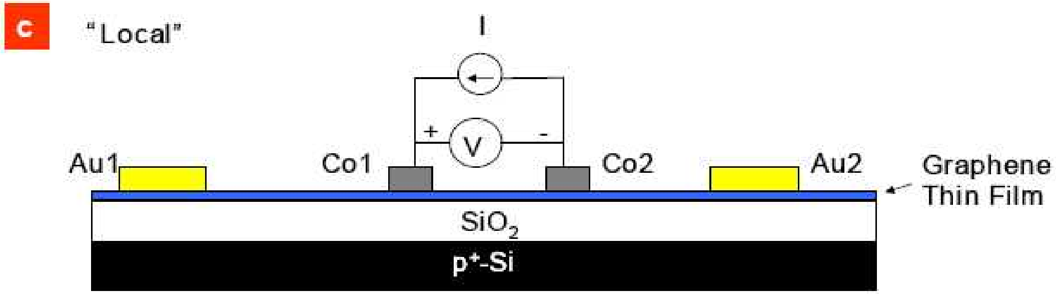


$R_{Co1\text{-}Au1}$ ~ 110 Ω

($R_{Co\text{-}wire}$ ~ 50 Ω)

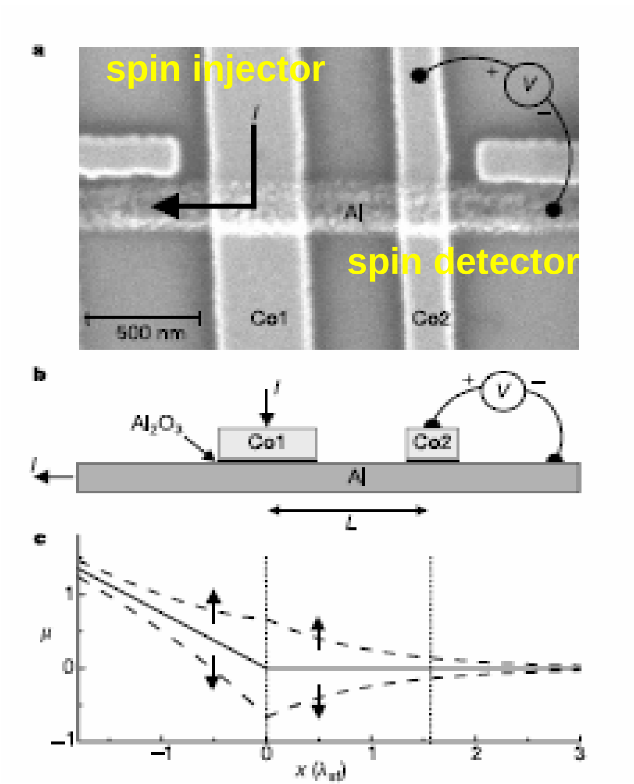


$R_{Co1\text{-}Co2}$ ~ 205 Ω



A concept of "non-local" measurements

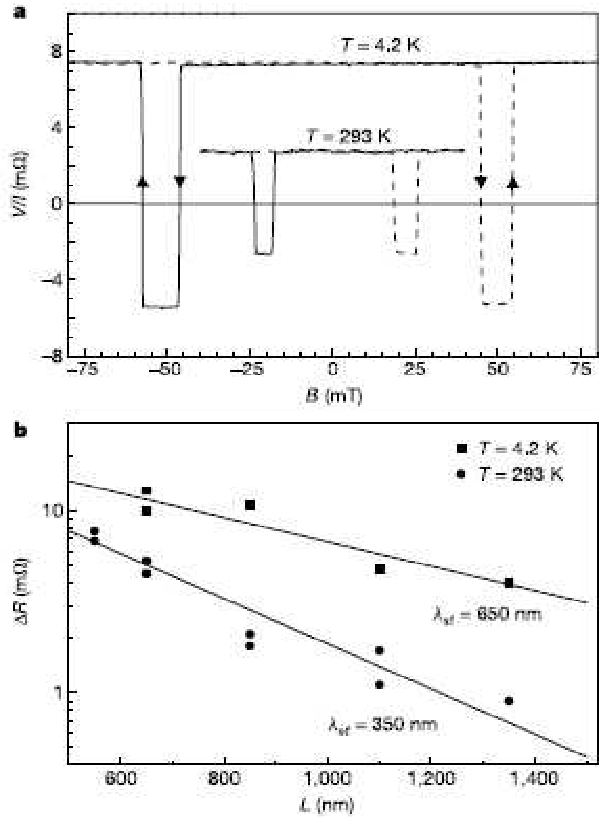
The basic concept



An electric current : anisotropic
A spin current : isotropic

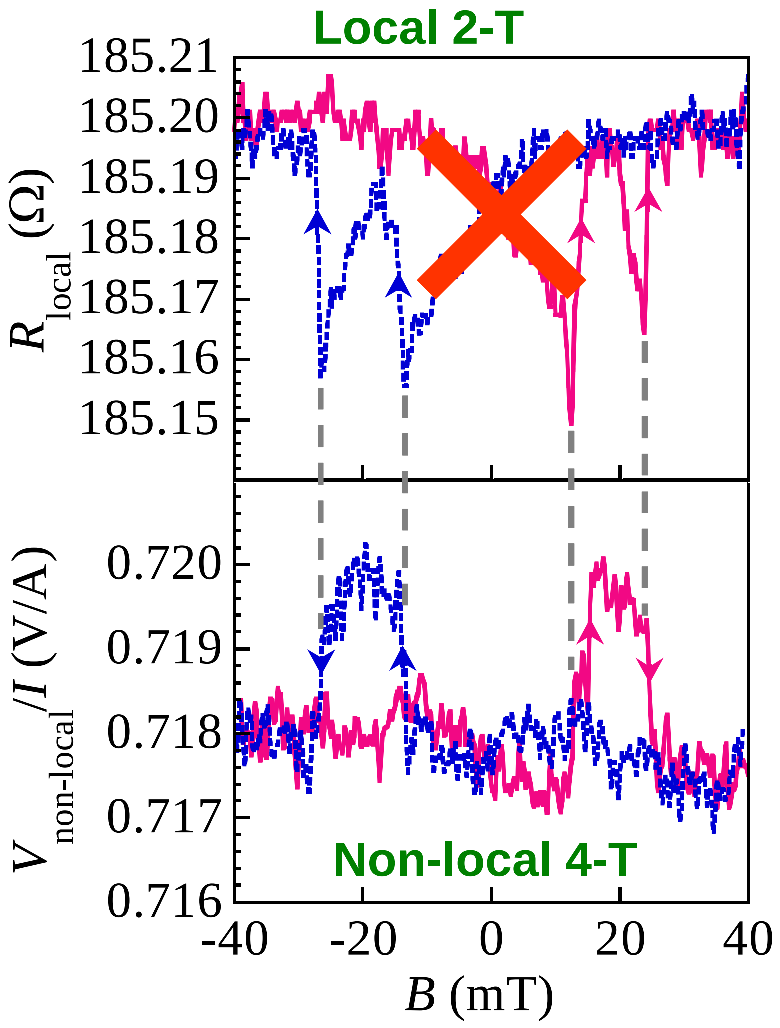
Al nanowire: non magnetic

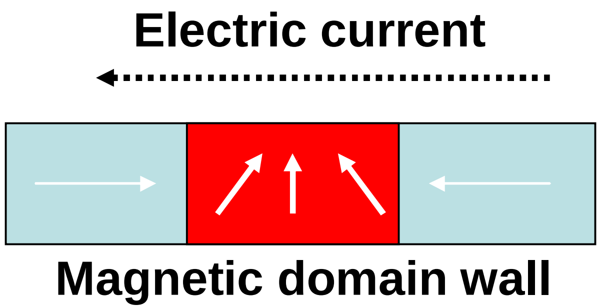
A proof of spin injection into the Al nanowire using difference of electrochemical potential of spins



F.J. Jedema *et al*., Nature 416, 713 (2002).

Observation of spin injection signals





AMR effect

Local 2-T : AMR-induced signals
Non-local 4-T : Spin injection signals

⇒ Detection of spin current in graphene at room temperature

Jpn. J. Appl. Phys 46, L605 (2007). (Express Letter)

Clear proof of "spin injection" into graphene !!

Spintronics using graphene

2007.06.22
Our paper was published !!
Cond-mat) 0706.1451
Multi layer graphene (Graphene Thin Film, GTF) W/O tunneling barrier

Japanese Journal of Applied Physics
Vol. 46, No. 25, 2007, pp. L605–L607
JJAP Express Letter

Spin Injection into a Graphene Thin Film at Room Temperature

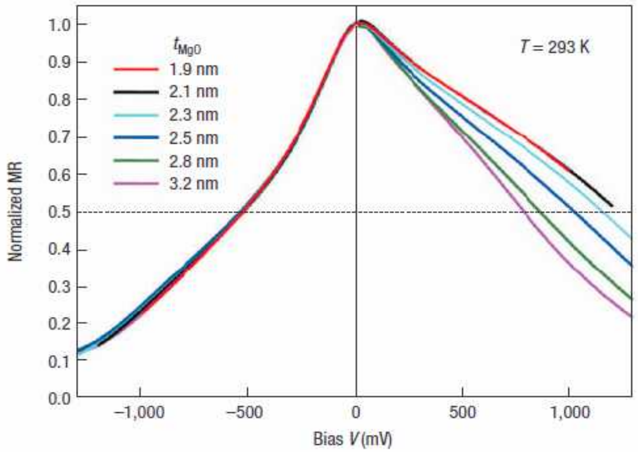
Megumi OHISHI, Masashi SHIRAISHI*, Ryo NOUCHI, Takayuki NOZAKI, Teruya SHINJO, and Yoshishige SUZUKI
Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan
(Received June 2, 2007; accepted June 6, 2007; published online June 22, 2007)

2007.07.15
Groningen Univ., Nature 448, 571 (2007).
Cond-mat) 0706.1948
Single layer graphene WITH tunneling barrier

2007.09.19
Univ. of Maryland, APL 91, 123105 (2007).
Cond-mat) 0706.1597
Single layer graphene W/O tunneling barrier

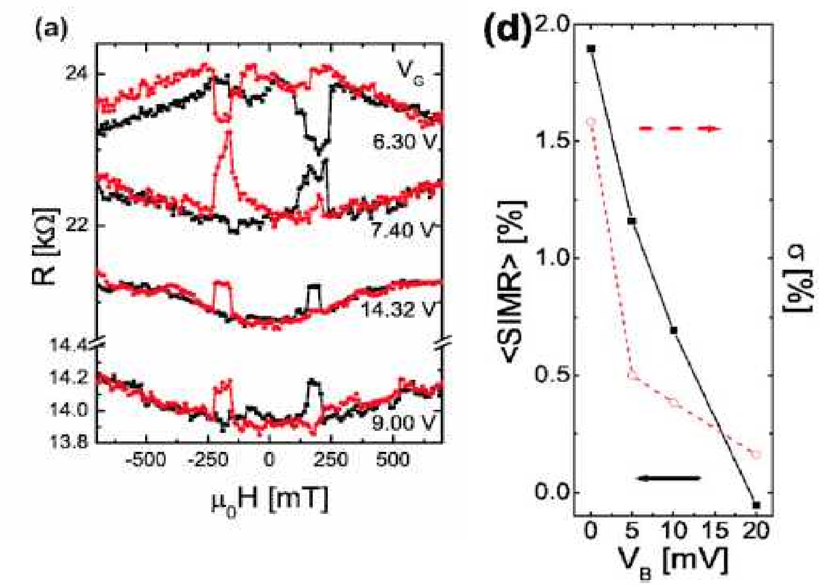
The other repots
by M. Nishioka et al. (in APL)
by R.K. Kawakami et al. (in PRB) and more…

Inferiority of molecular spintronics (1)



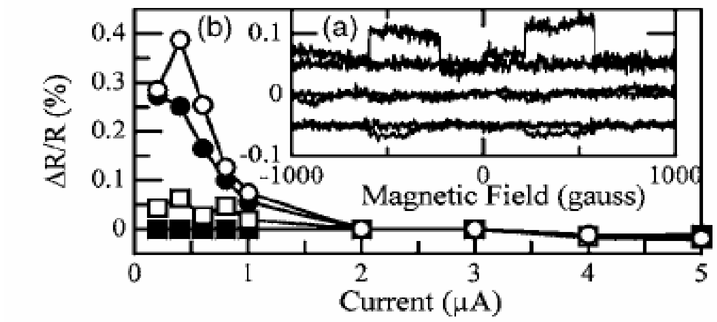
MgO-based TMR : ~1 V (RT)
S. Yuasa et al., Nature Mat. 2004.

V_{half} : MR ratio becomes a half of max.
The decrease : spin scattering = loss of P
(magnon/phonon…)



SWNT spin valve : ~10 mV (4 K)
MR ratio ~ 2 %
H.T. Man et al., PRB 2006.

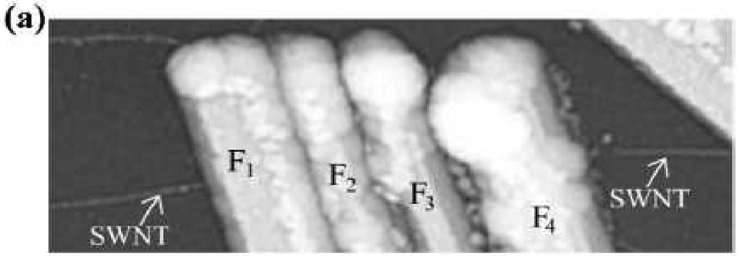
Poor bias voltage dependence

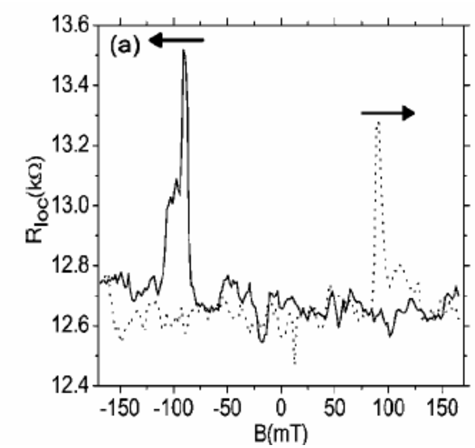


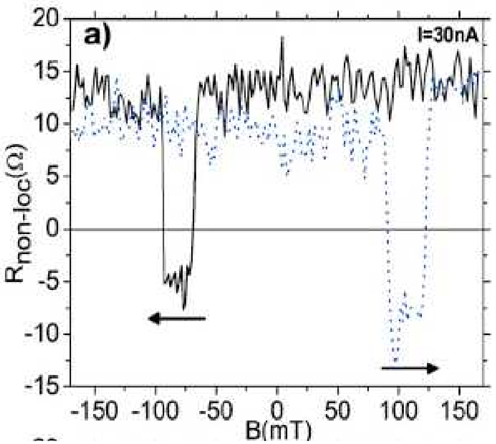
graphene spin valve : ~ 5 mV (2 K)
MR ratio ~ 0.4%
M. Nishioka et al., APL 2007.

Inferiority of molecular spintronics (2)

No accordance between “Local” & “Non-local” results







“local” Δ*R*~700 Ω **“non-local” Δ*R*~20 Ω**

N. Tombros, B.J. van Wees et al., PRB 2006.

T=4.2 K

2× (Non-local ΔR) ＝(Local ΔR)

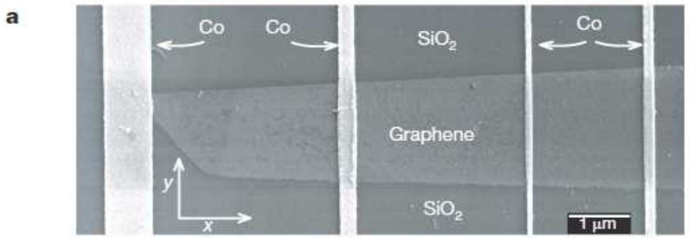
F.J. Jedema et al., PRB 2003.

“…90% of local signals are not due to spin accumulation….”

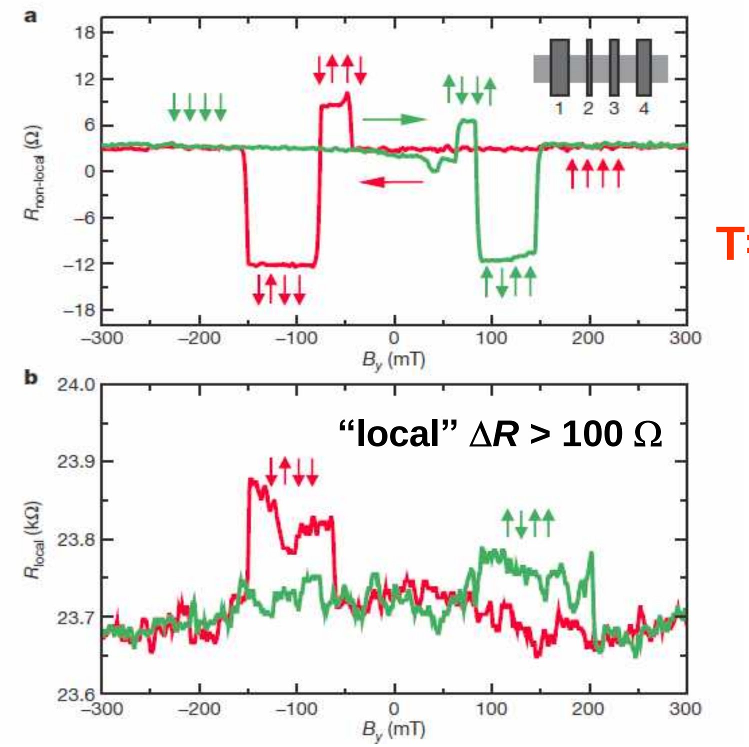
The missing part in molecular spintronics
(Underlying physics cannot be discussed.)

Inferiority of molecular spintronics (3)

Molecule | **Metal**



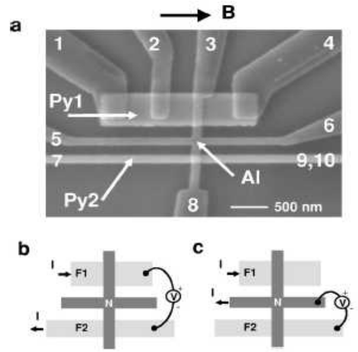
“non-local” ΔR~12 Ω



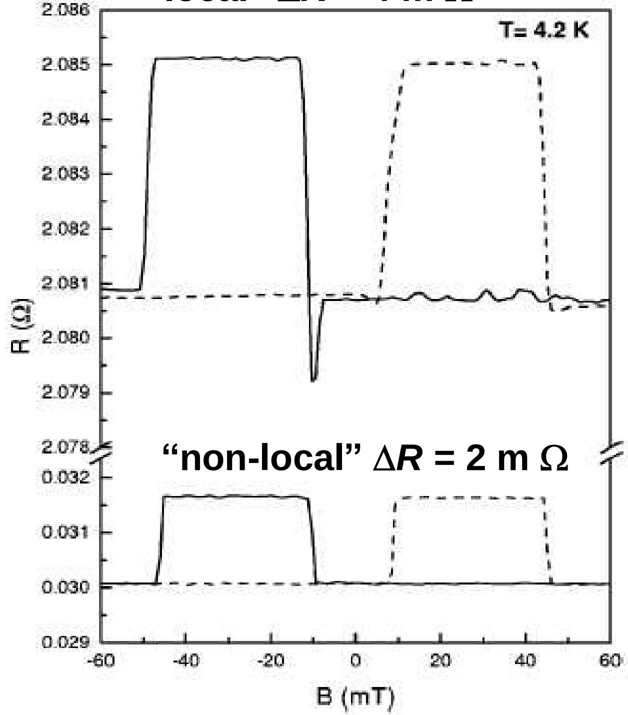
“local” ΔR > 100 Ω

T=5 K

Tombros, van Wees et al., Nature 2007.



“local” ΔR = 4 m Ω



“non-local” ΔR = 2 m Ω

Jedema, van Wees et al., PRB 2003.

Next milestones

Solving the two important problems in molecular spintronics;

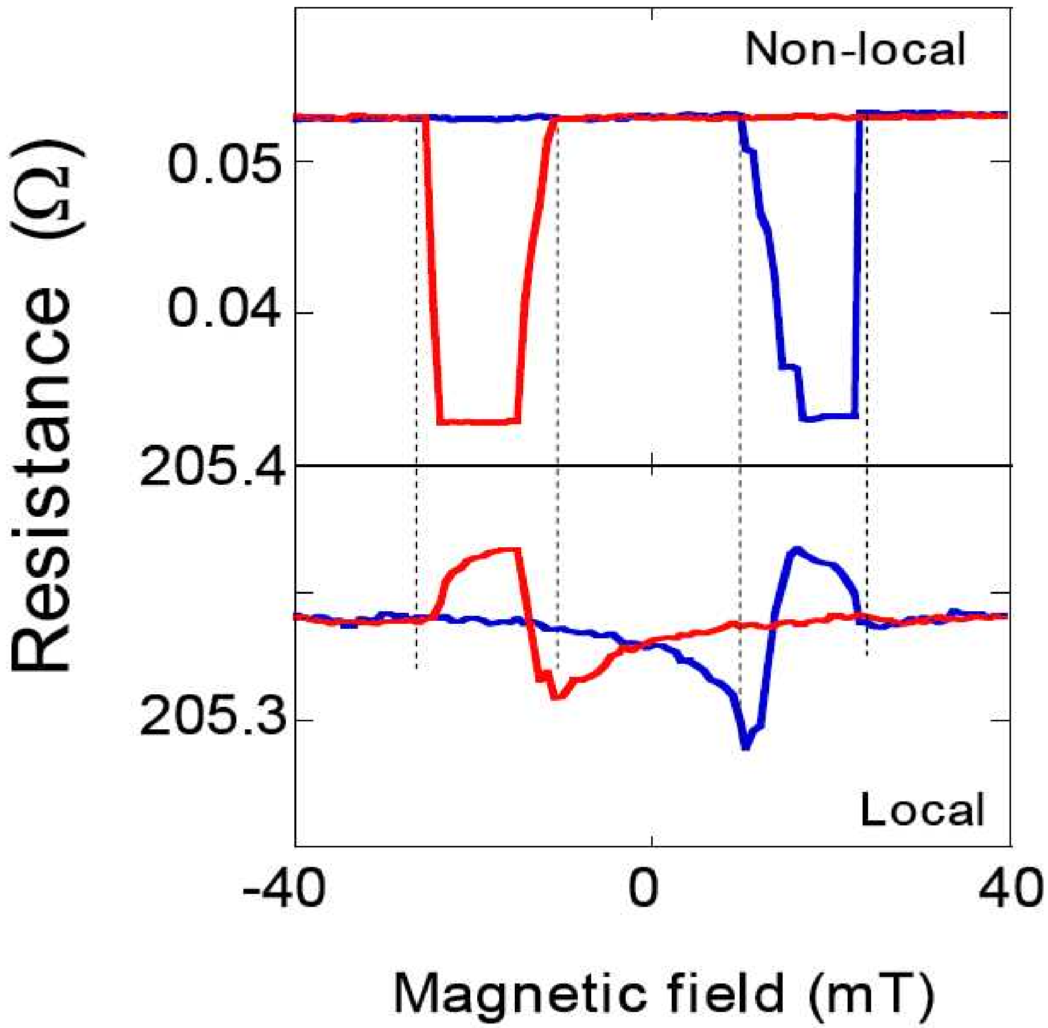
1. Poor bias voltage dependence of spin polarization
2. Missing accordance between "local" & "non-local" results

by using our graphene-based spin valves.

The milestone ;

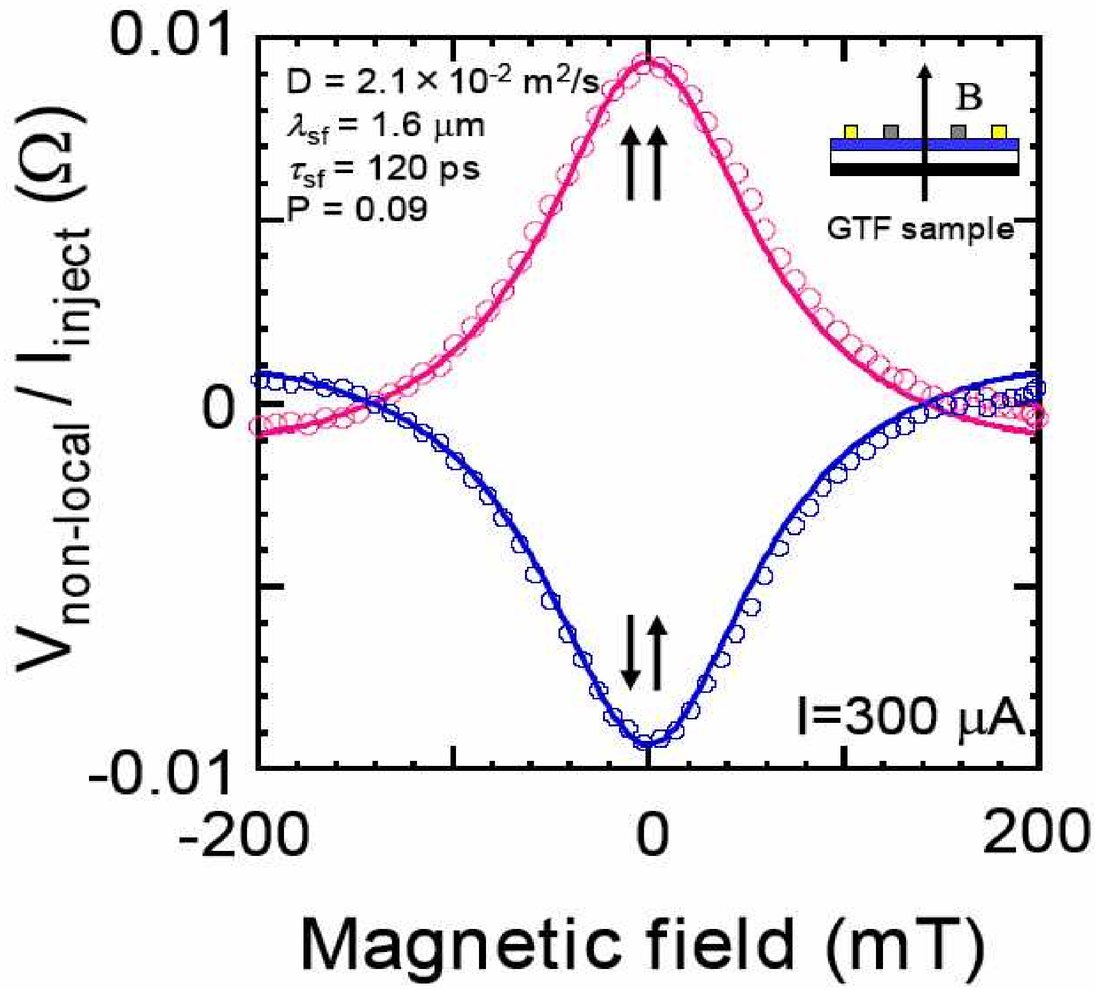
Constructing a steadfast basis of molecular spintronics

Local magnetoresistance at room temperature



M. Shiraishi et al., cond-mat 0810.4592.

Spin precession and spin coherence in "non-local"

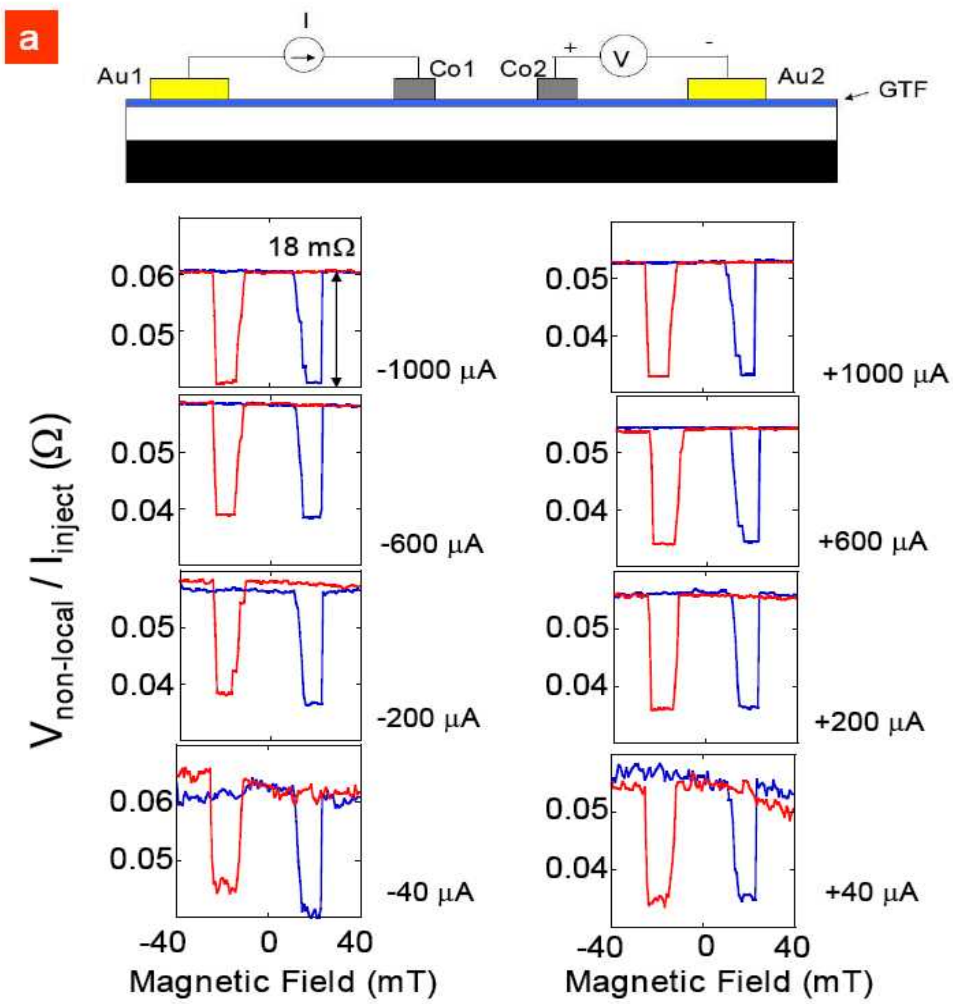


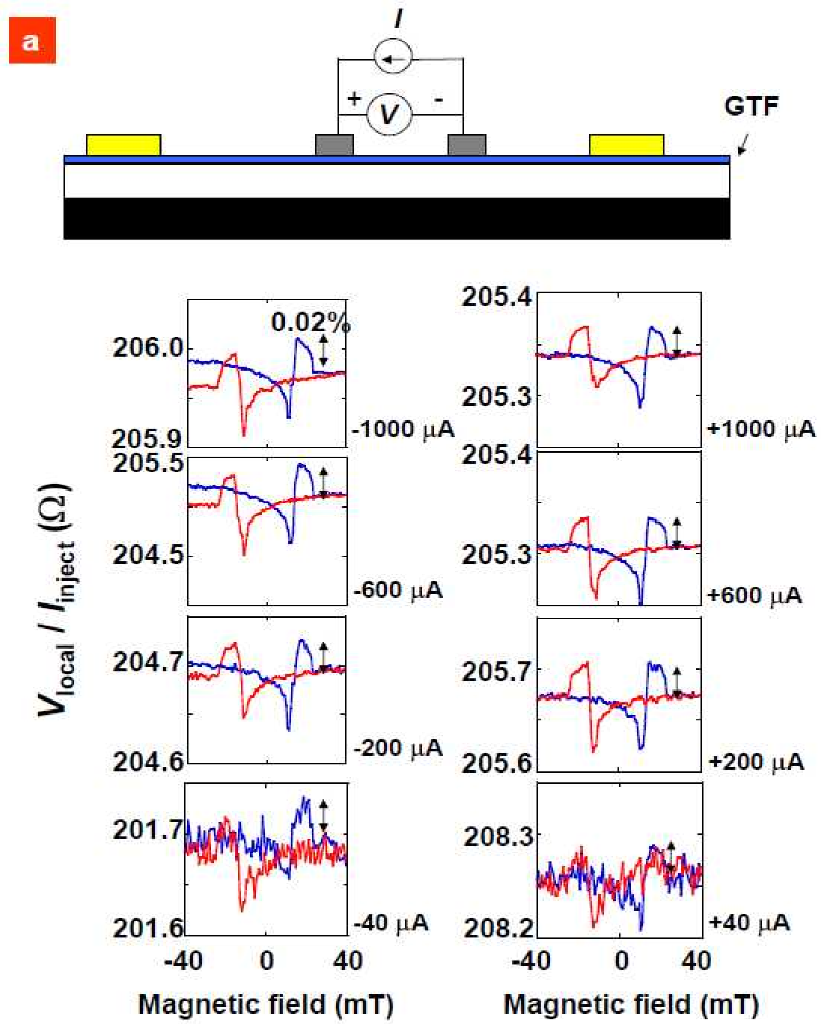
The previous report from our group (2)

Comparison

	Our study (GTF)		Tombros et al. (Single layer)
	120 K	RT	RT (Dirac point)
Diffusion constant, D ($10^{-2}m^2/s$)	0.8	2.1	1.3(P)~2.1(AP)
Spin flip length, λ (μm)	1.1	1.6	1.3(P)~1.5(AP)
Spin coherent time, τ (ps)	150	120	125(P)~100(AP)
Spin polarization, P	0.16	0.09	0.1

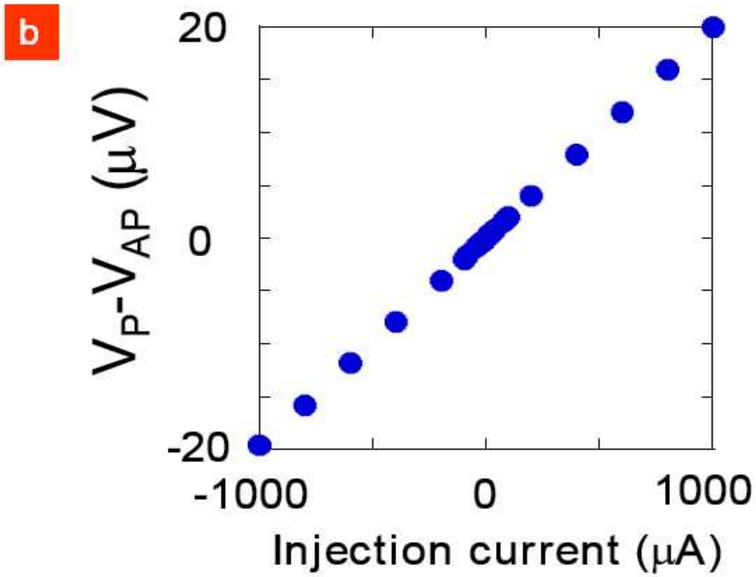
Injection current dependence of output signals



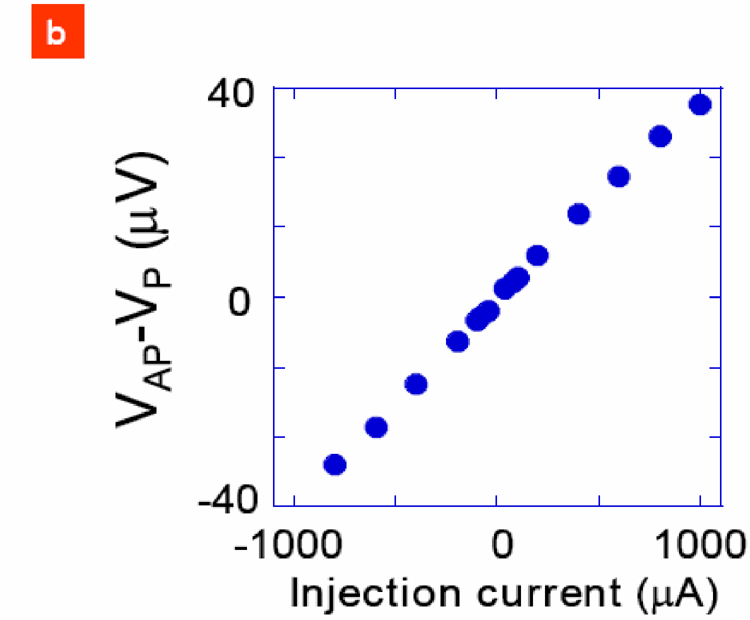


Robustness of spin polarization (1)

Injected current dependence of output voltages is linear.



"Non-local"

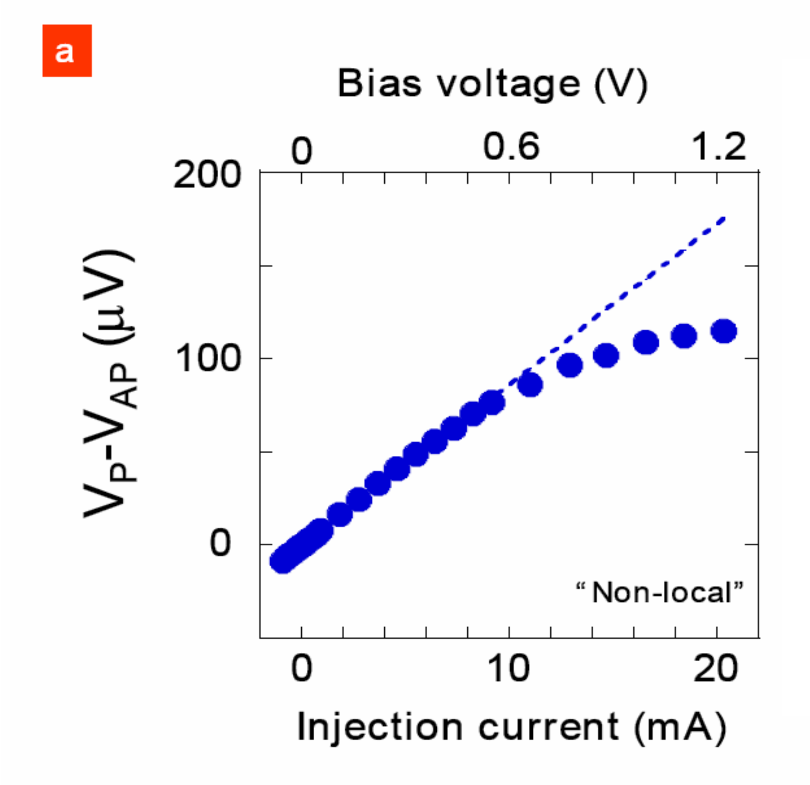


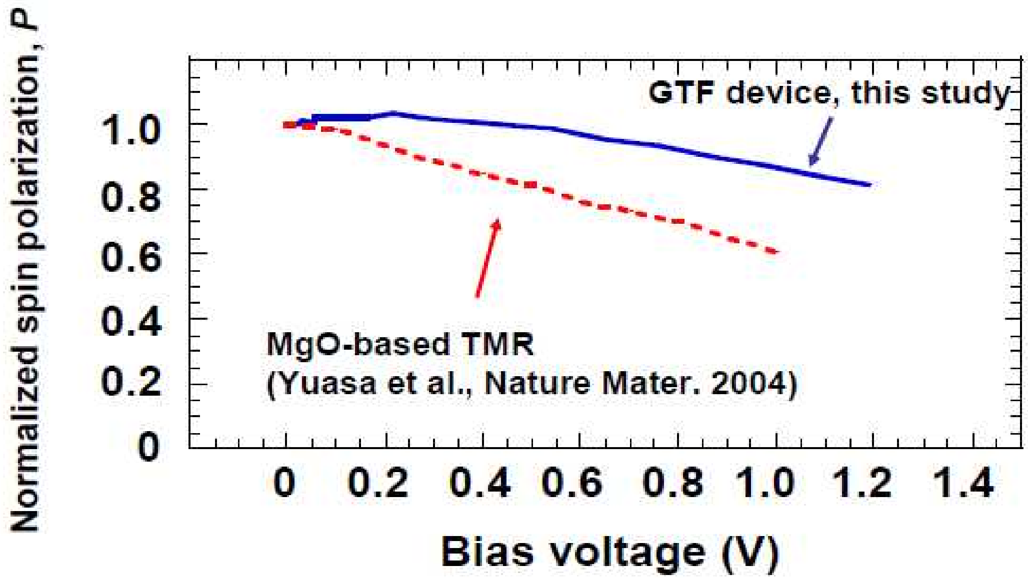
"Local"

$$\Delta V_{non-local} = \frac{P^2 \lambda_{sf}}{2\sigma_{GTF} A} \cdot I_{inject} \exp(-\frac{L}{\lambda_{sf}}),$$

***P* is constant !! = Robustness of spin polarization !!**

Robustness of spin polarization (2)





P was constant up to 0.5 V, and was still 81% at 1.2 V

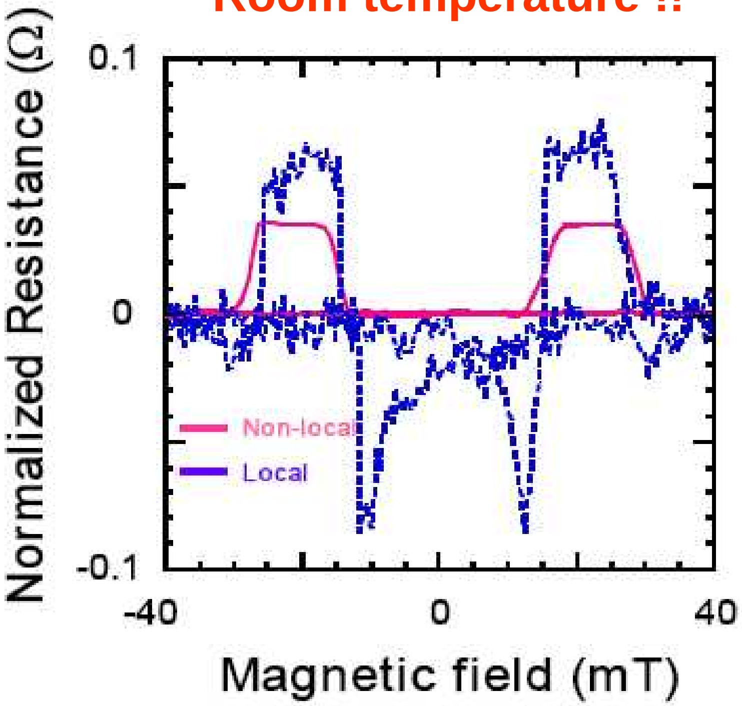
Comparison with that in MgO-TMR

M. Shiraishi et al., cond-mat 0810.4592.

Robustness of spin polarization (3)

Unprecedented robustness…?
Suppression of Magnon/Phonon excitation?

Room temperature !!



$2 \times$ (Non-local ΔR)
$=$(Local ΔR)

Ideal interface formation

More important message is….
"Theory and experiment firstly exhibit the good accordance in molecular spintronics."

We have succeeded in constructing a steadfast basis of molecular spintronics.

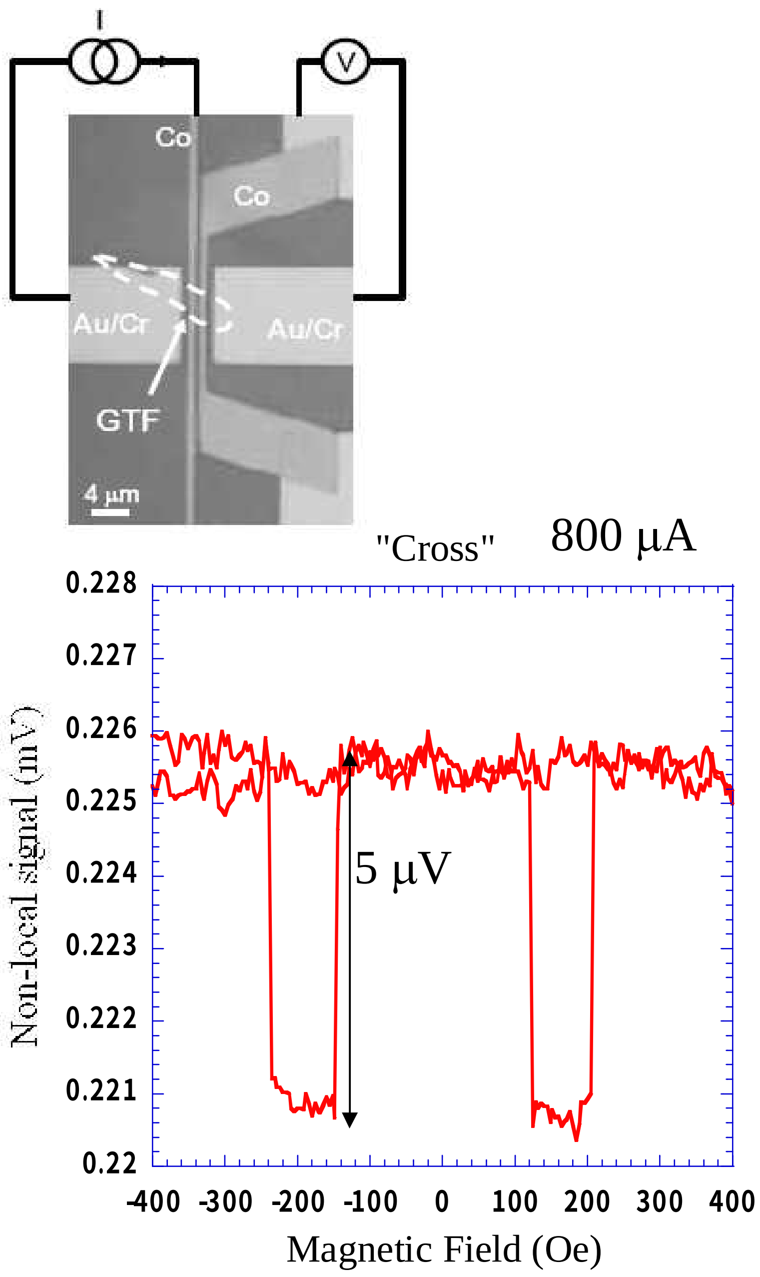
Conclusive remarks in Part II (graphene spintronics)

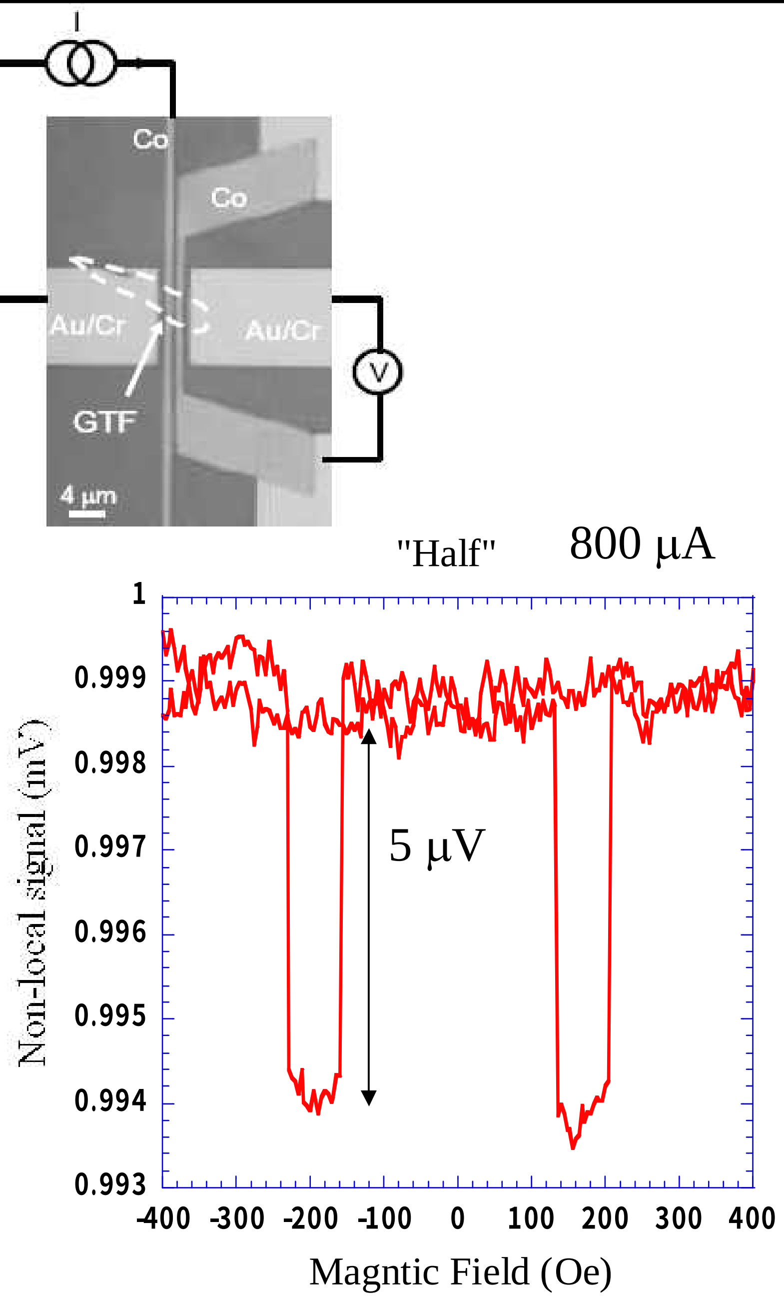
1. Spin injection and spin current detection in graphene
   (by non-local measurements)
2. Magnetoresistance effect at room temperature
   (by non-local & local measurements)
3. Estimation of spin transport properties
   (by Hanle-type spin precession)

1. Reliable results are provided.
2. Unprecedented robustness of spin polarization is found.
3. A theory and an experiment coordinate well
   in molecular spintronics.

Thank you very much
for your kind attention !!

Spin injection signals in graphene spin valves (1)

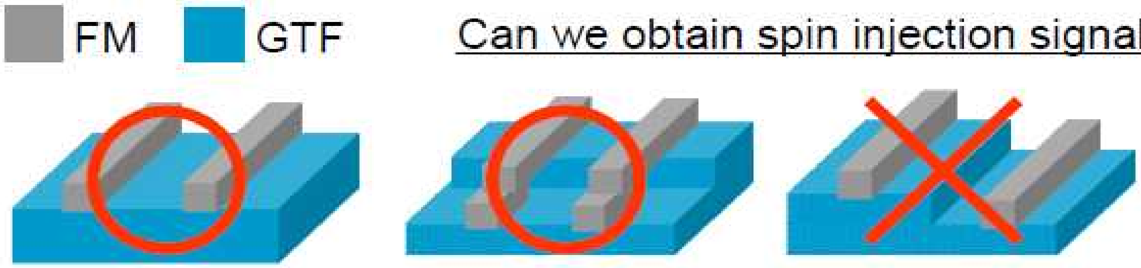




Structure of Graphene Thin Films

GTF has an additional degree of freedom: **Thickness**

<u>Can we obtain spin injection signals?</u>



<u>Interlayer hopping can cause spin flips.</u>

Spin injection signals in graphene spin valves (2)

Non-local signals in “cross” and “half” alignments.

If both are different…. Ohmic contact

If both coincide…. Schottky contact
(T. Kimura et al., JMMM 286, 88 (2005).)

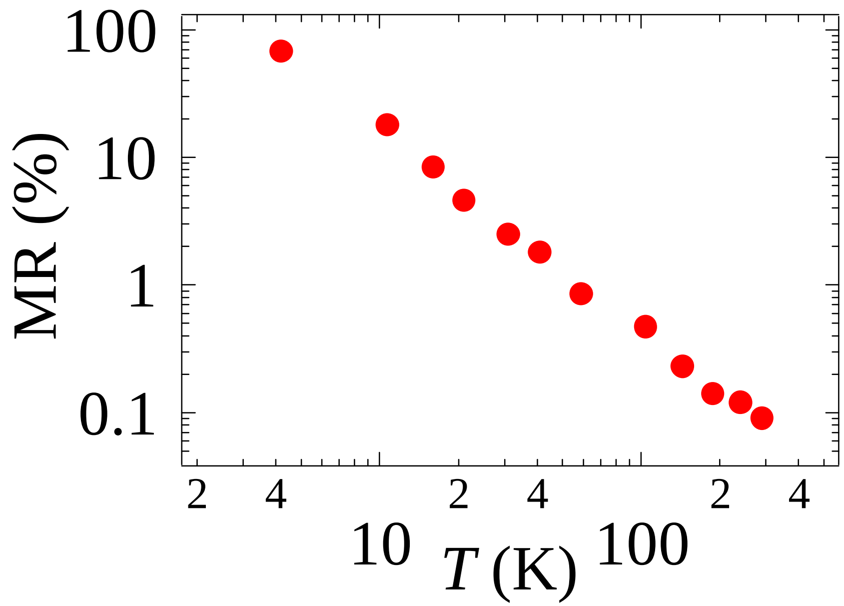
Schottky ? Conductance mismatch ?

Wire resistance : 100 Ω
Graphene resistance : 5 Ω
Device resistance :200-300 Ω

⇨ Contact resistance ? : 100 Ω

Unintentional contact resistance exists ?
Is it NECESSARY or NUISANCE ?

Temperature dependence of the MR ratio

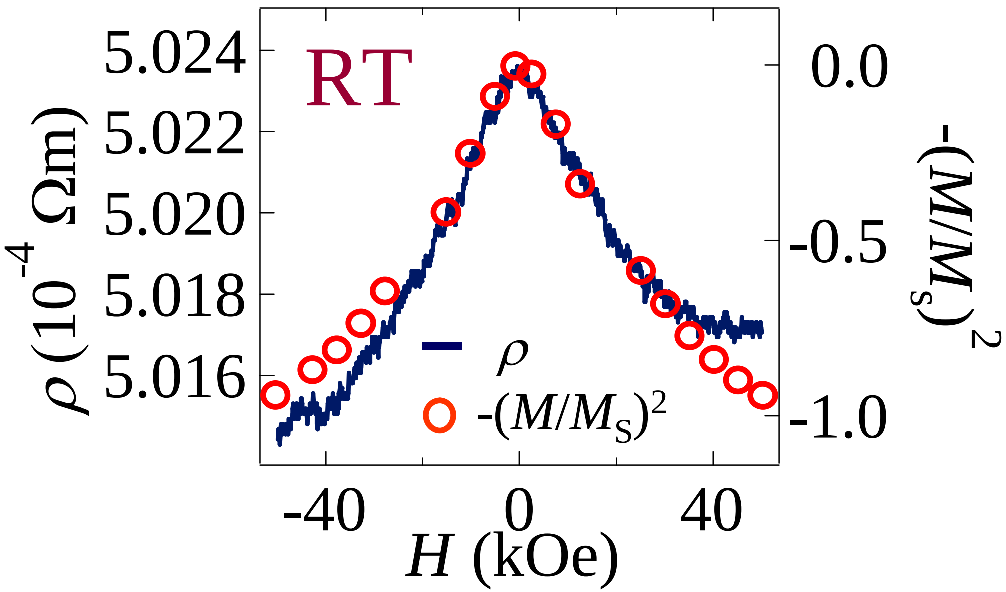


Drastic decrease of the MR ratio

4.2 K → RT

Sat. mag. decreased only 30%

Sat. mag. does not induce the decrease.

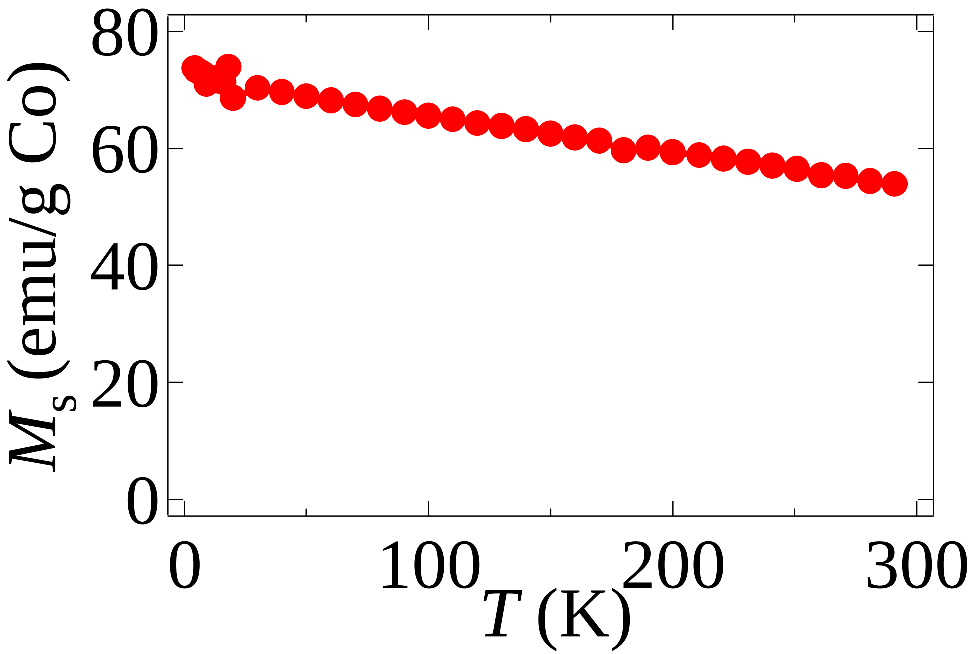


V = 100 mV

MR比 = ~ 0.1%

Observation of the MR effect at RT.

Temperature dependence of the saturation magnetization



MR ratio

4.2 K (68%) → RT (0.1%)

Sat. mag.

4.2 K (74 emu/g Co)

→ RT (54 emu/g Co)