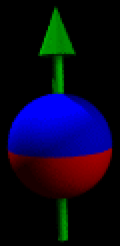
Fundamentals of spin-polarized tunneling

- an experimental approach -



Henk Swagten

Eindhoven University of Technology
The Netherlands

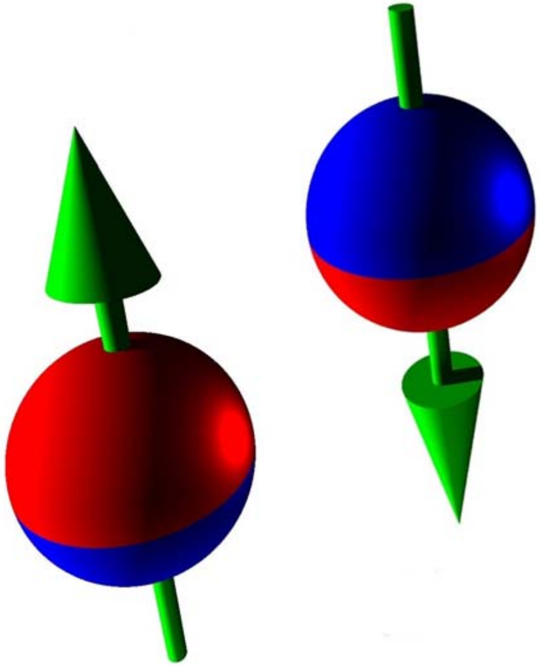
collaborations with MIT, PAN Warsaw, Philips

What we will discuss …

- From GMR towards spin-polarized tunneling
- Spin polarization
- Few words on preparation/oxidation
- Interface/barrier sensitivity
- MRAM's and application issues
- Spin filtering (if time allows me …)

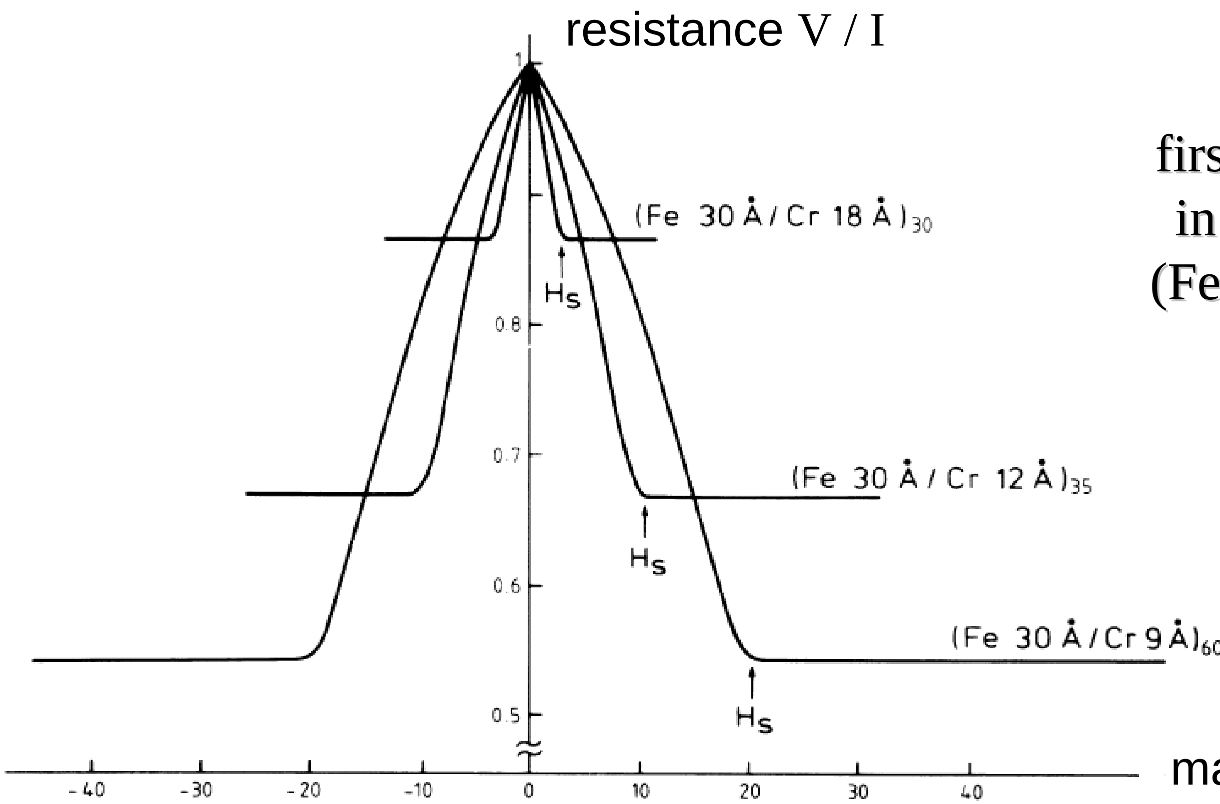
The "smell" of electrons: charge, but also spin

2 QM spin directions: magnetic moment up/down



Spin electronics:
combining spin transport & magnetization

Giant MagnetoResistance (GMR)

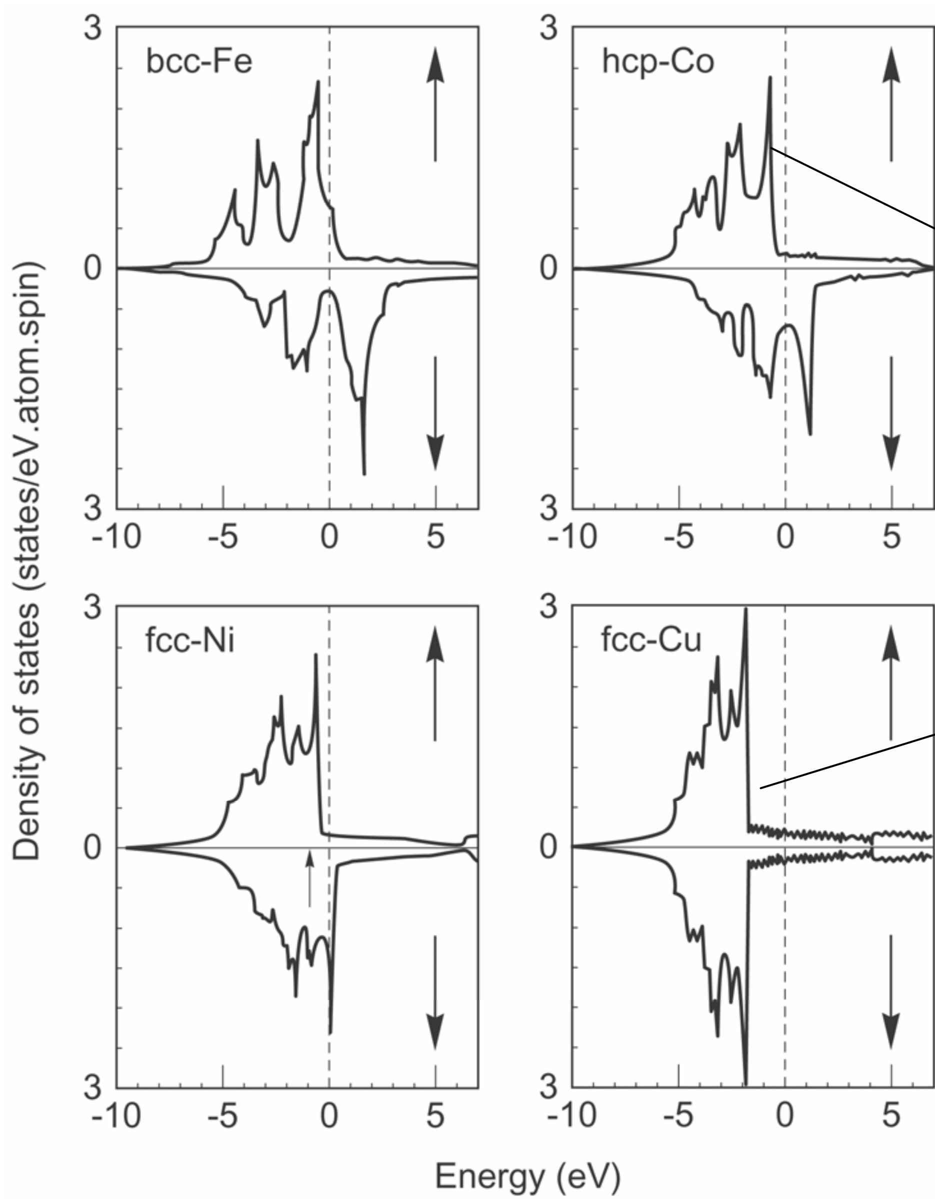


magnetic field

first observation
in Fe/Cr ML's
(Fert et al. 1988)

- **magnetic engineering**
- **spin-dependent scattering**
- **(nanometer) layer thickness**
- **matching electronic structure**

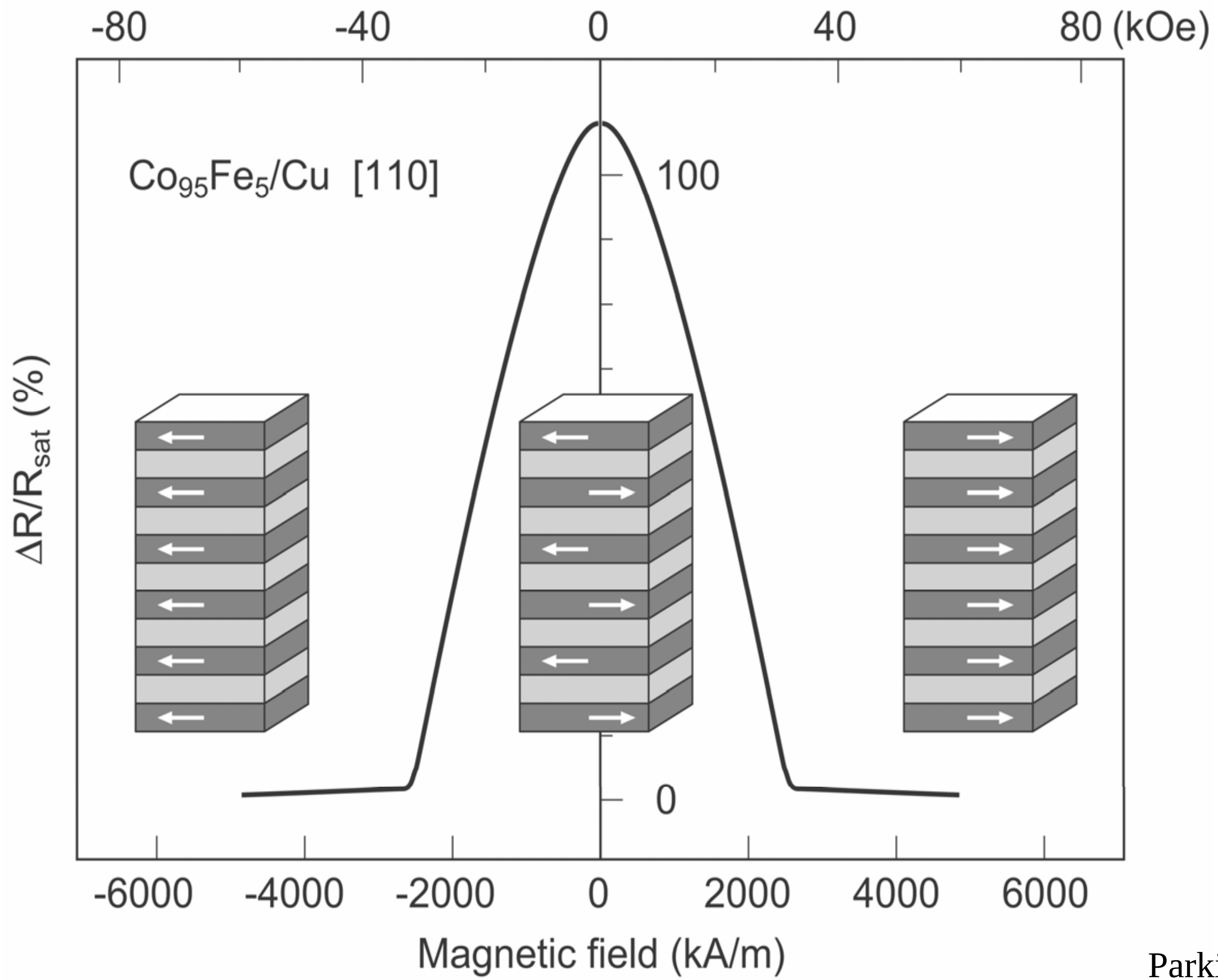
Example of matching: Co and Cu



strong similarity for majority bands

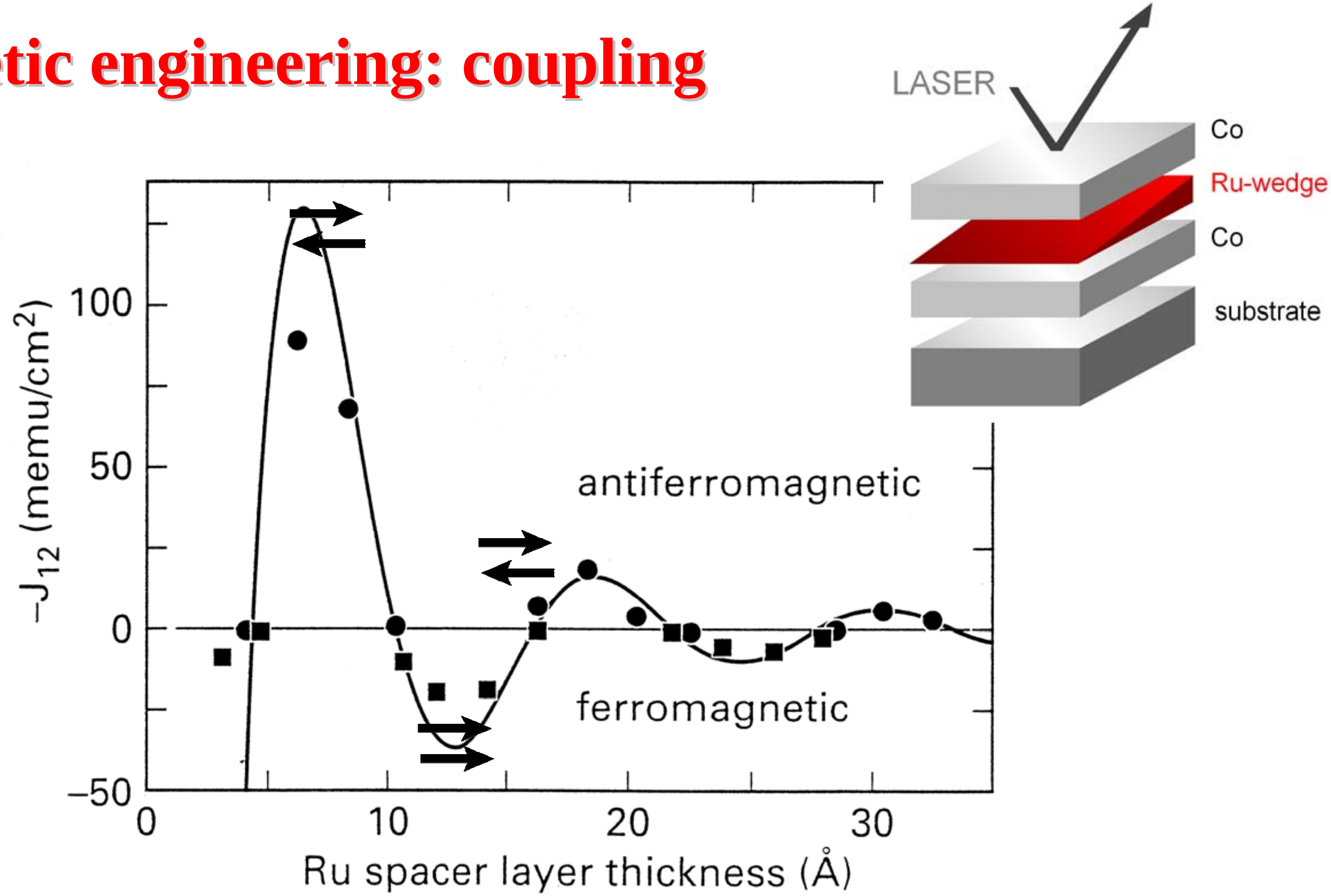
reality much more complicated though …

GMR is very large for magnetic multilayers
(world record 110%)



Parkin / IBM

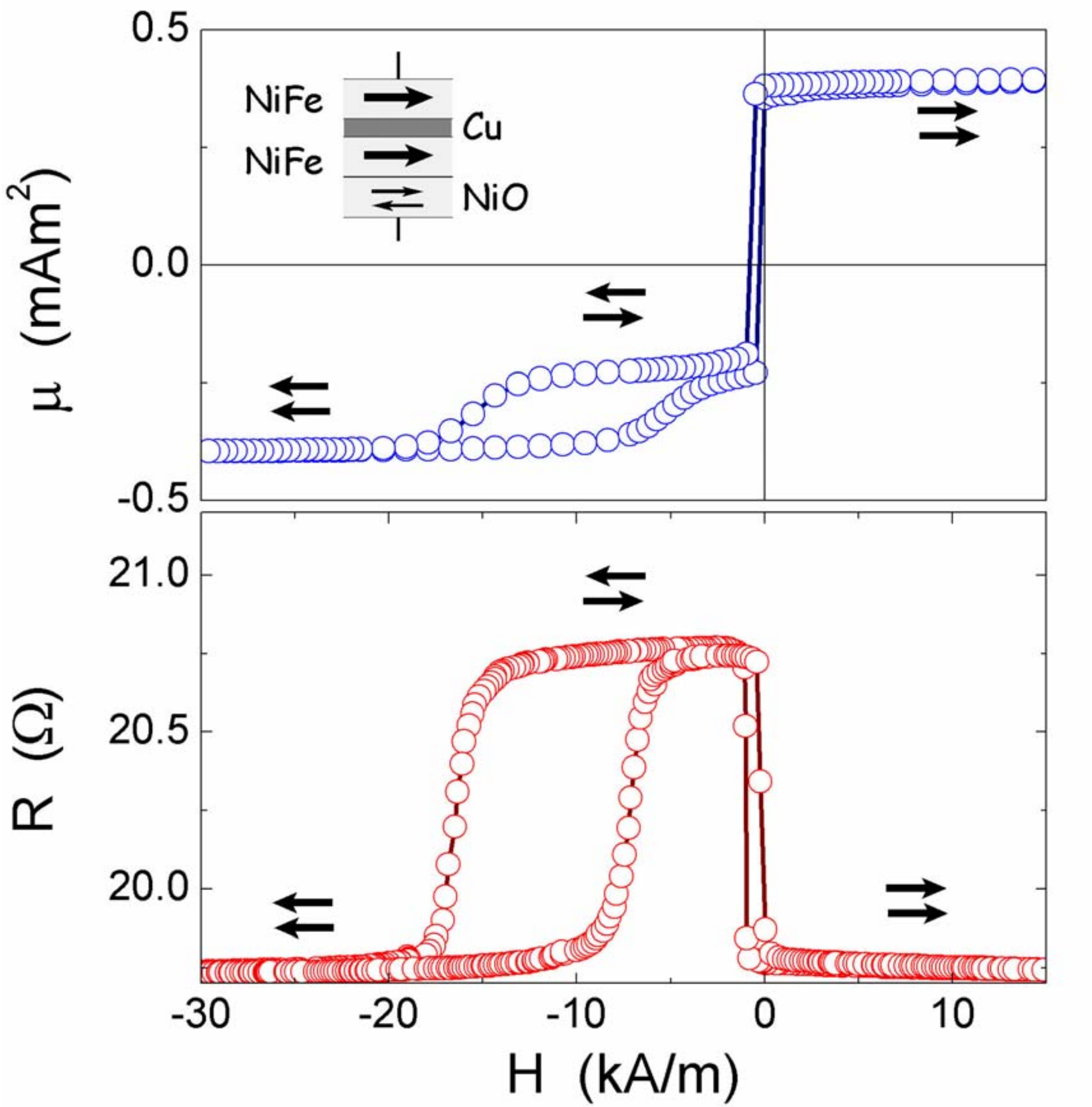
Magnetic engineering: coupling

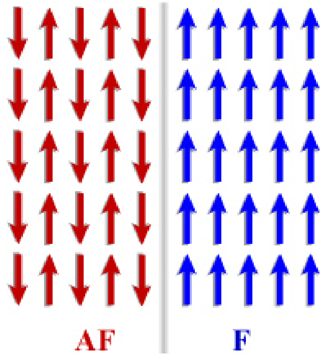


- **Oscillatory interaction observed by MOKE effect**
- **Due to spin-dependent interference effects at interfaces**
  (see e.g. models by Bruno and others)

Many routes to magnetic engineering

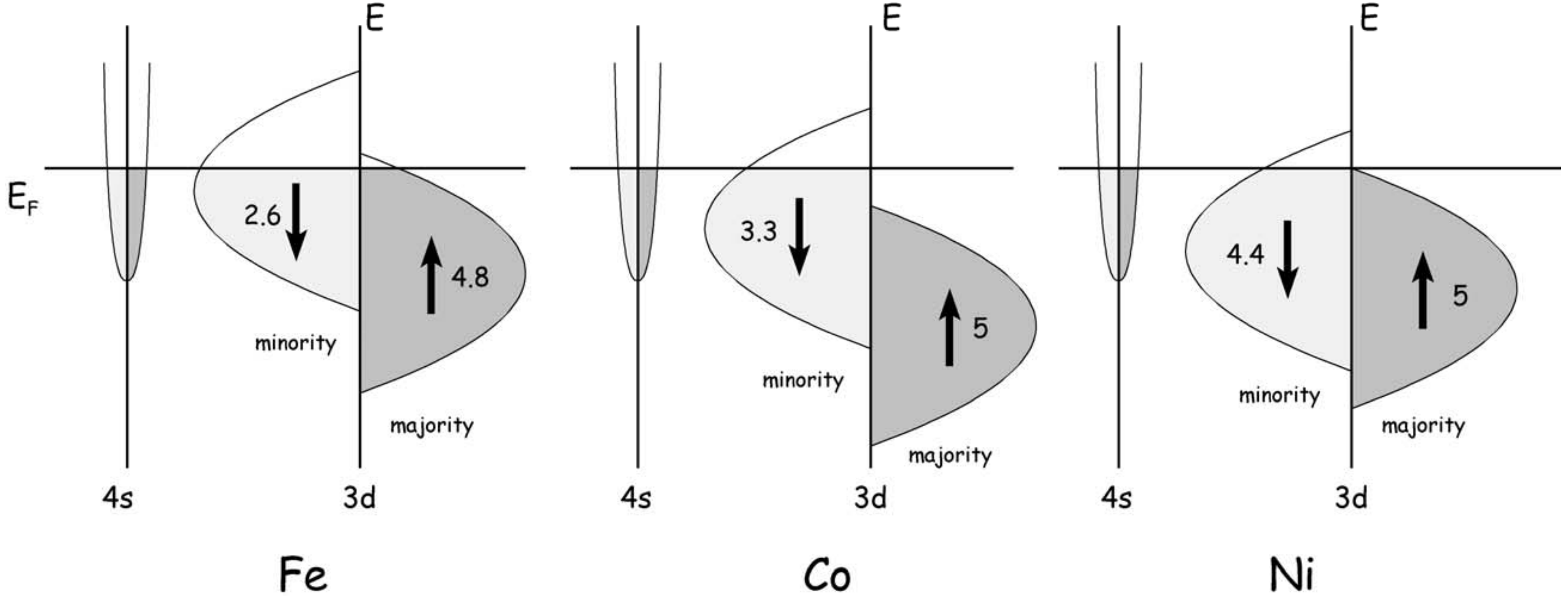
e.g.: exchange biasing to an antiferromagnetic layer





Spin-dependent scattering and GMR

Current carried mostly by s-electrons $$\sigma^{\uparrow(\downarrow)} = \frac{e^2\, n^{\uparrow(\downarrow)}\, \tau^{\uparrow(\downarrow)}}{m}$$



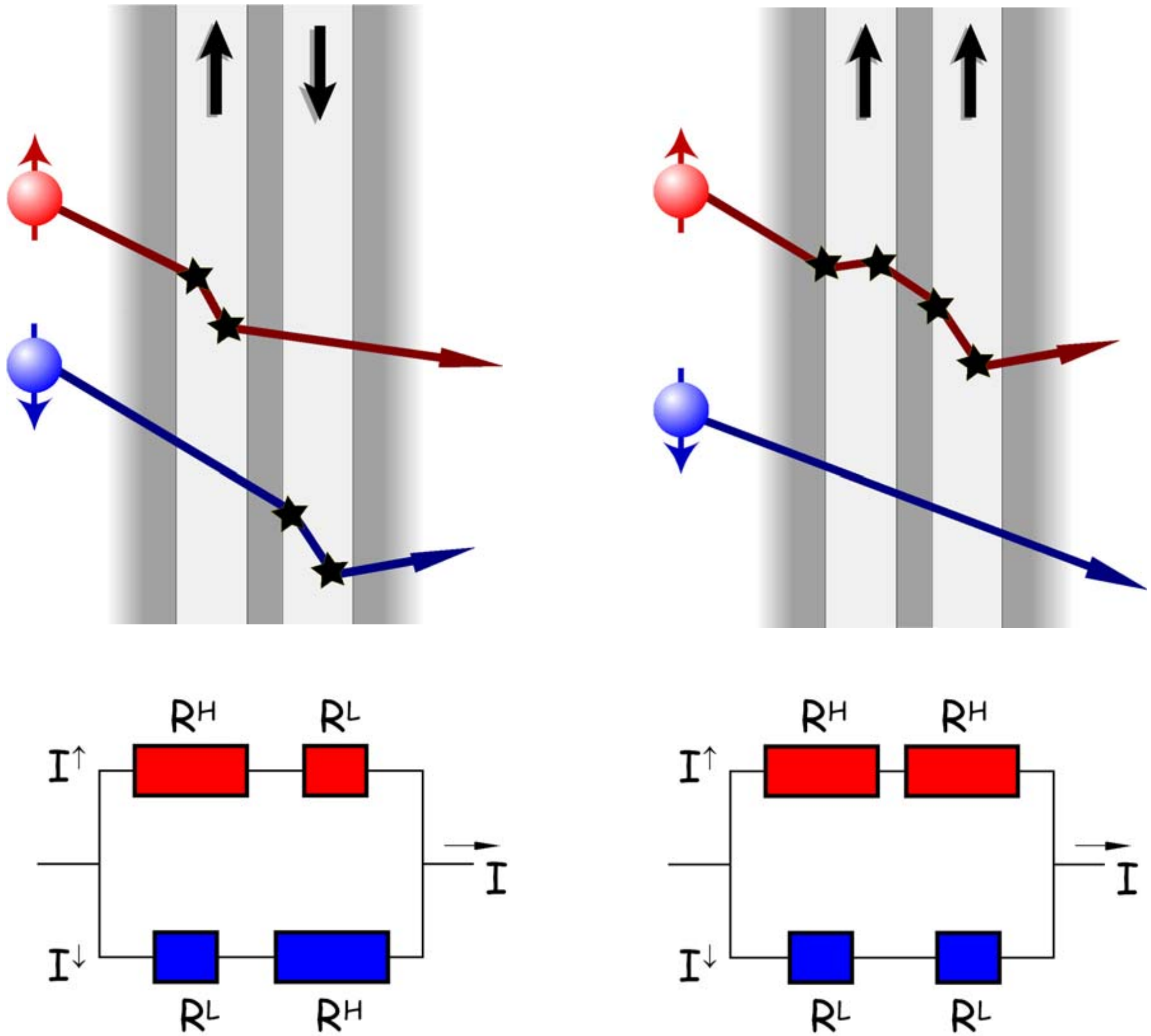
$$\tau^{\uparrow(\downarrow)} \propto \frac{1}{|V_{sc}^{\uparrow(\downarrow)}|\; N^{\uparrow(\downarrow)}(E_F)}$$

perturbations of lattice periodicity

large number of d states to scatter into

A simple two-current model to explain GMR

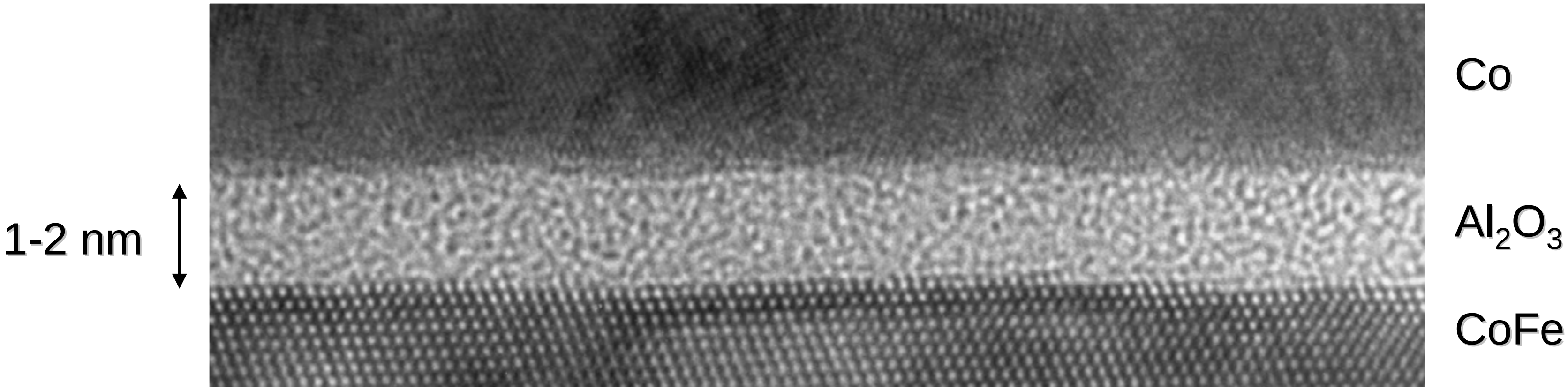
H small **H large**



R large **R small**

Since its discovery: ongoing research (physics & applications)

Mid-nineties: a new scientific breakthrough



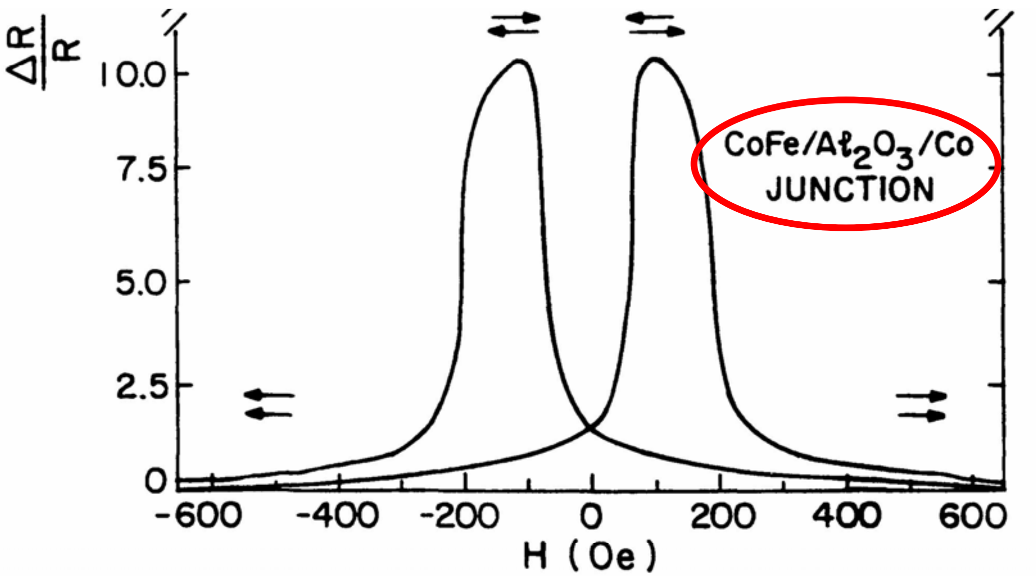
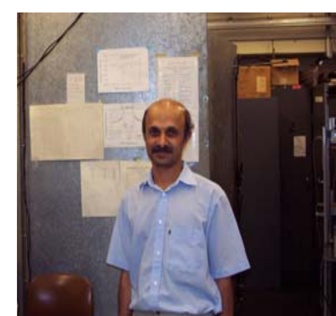
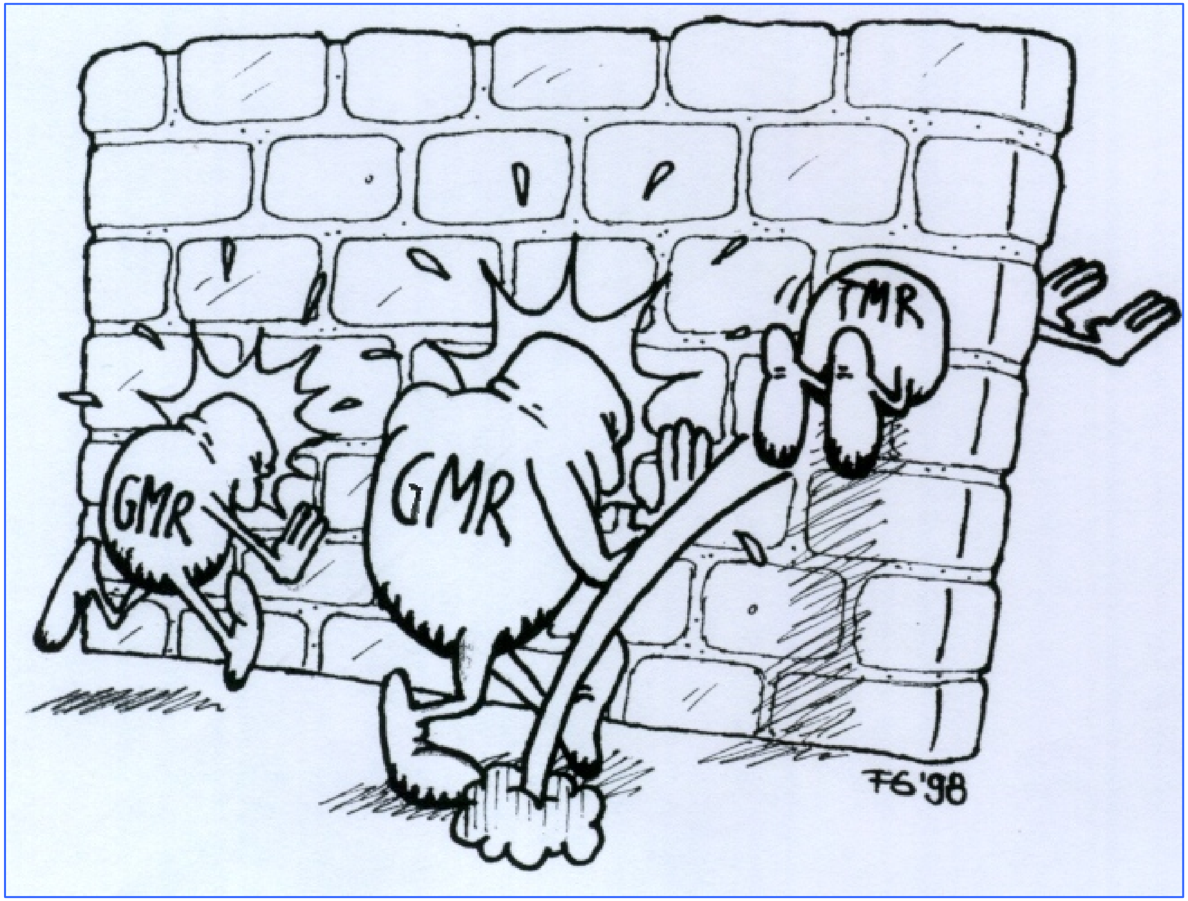


FIG. 2. Resistance of $CoFe/Al_2O_3/Co$ junction plotted as a function of H in the film plane, at 295 K. Also shown is the variation in the CoFe and Co film resistance. The arrows indicate the direction of M in the two films (see text).

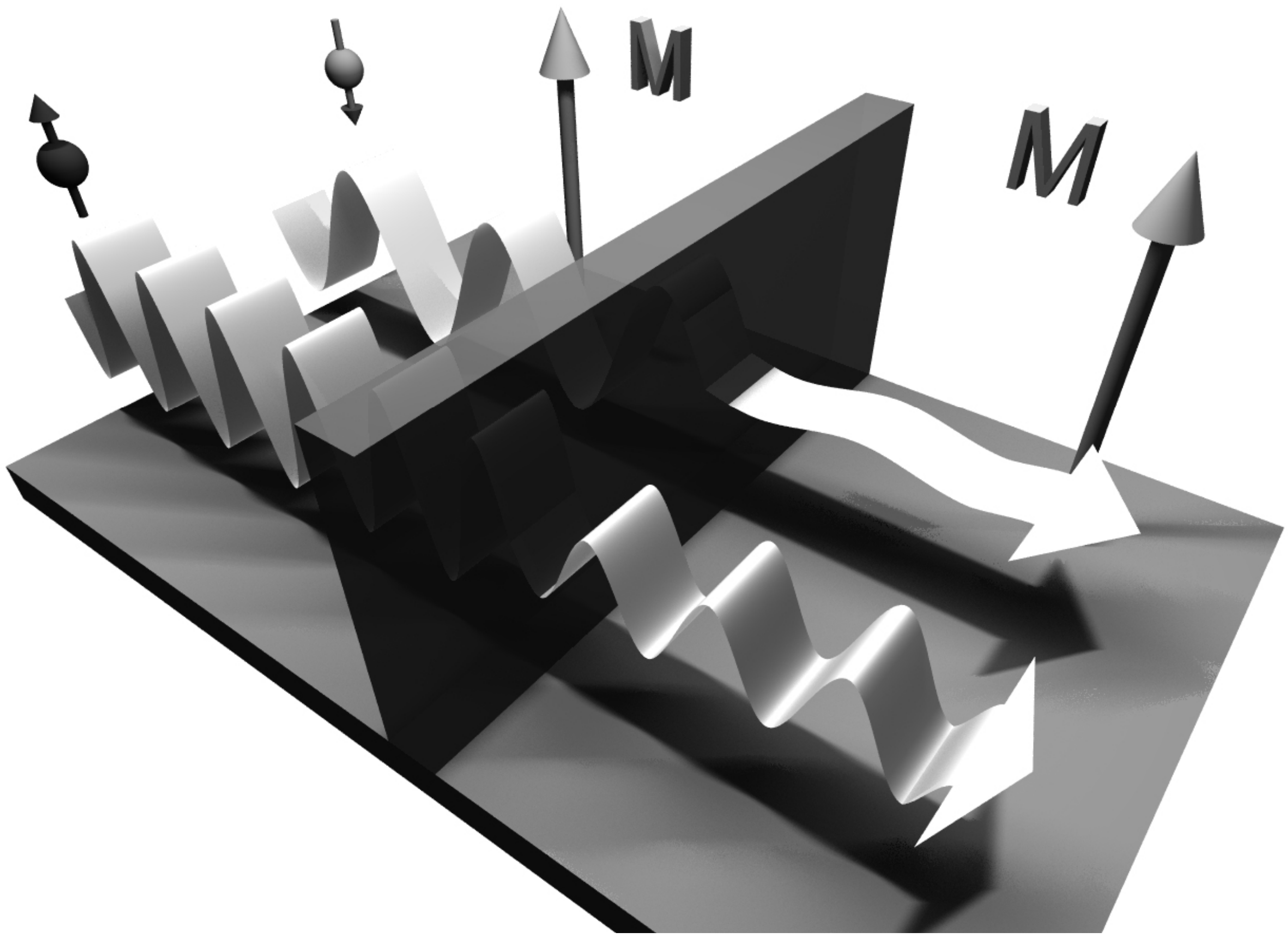


Moodera - MIT

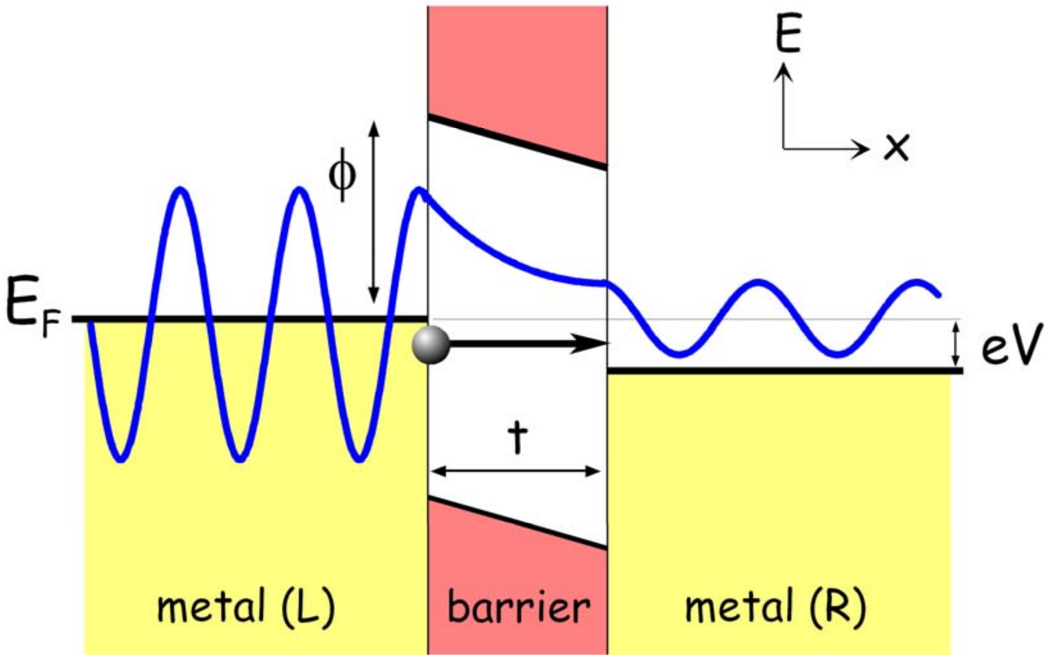
Beyond classical conduction ....



Tunneling current: (again) spin dependent



Tunneling current in (magnetic) junctions

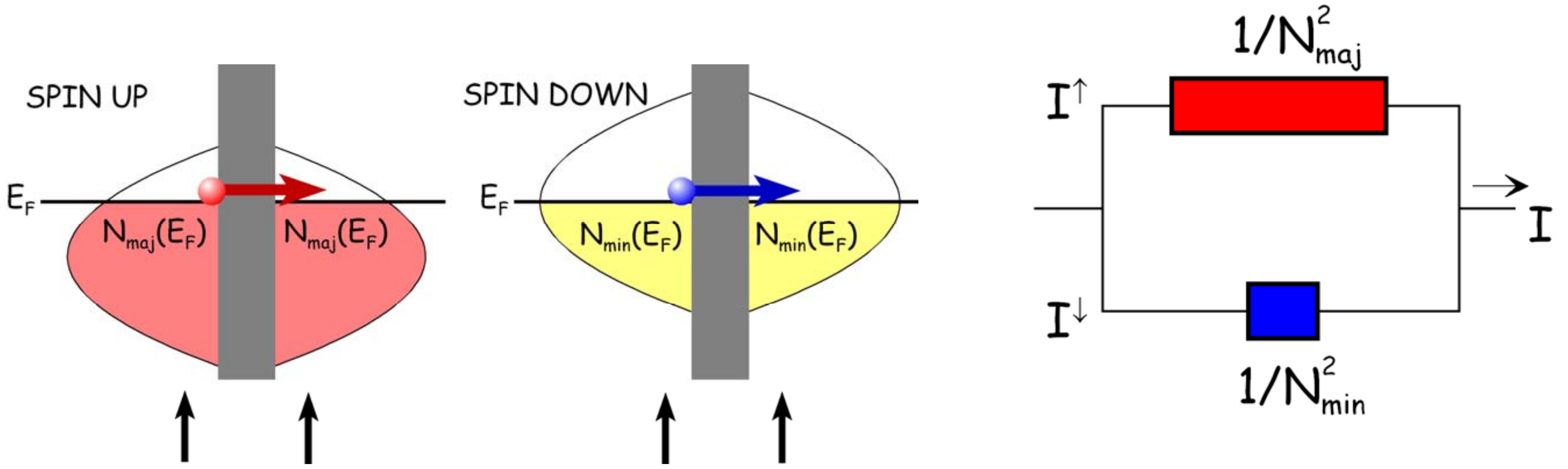


$$I \propto (\text{number electrons}) \times (\text{number empty states})$$

$$I_{tot} \propto \int_{-\infty}^{+\infty} N_l(E)\, N_r(E+eV)\, |M|^2 \times f(E) f[1-f(E+eV)]\, dE$$

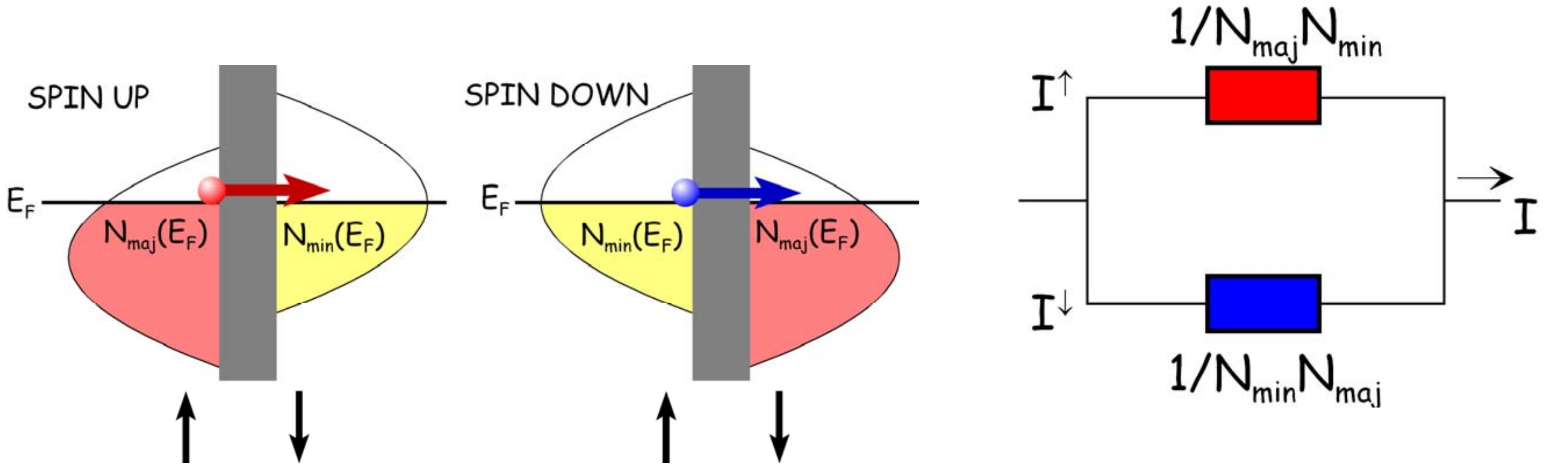
$$\boxed{I_{tot} \propto N_L(E_F) \times N_R(E_F)} \qquad eV \ll E_F \quad T \to 0$$

Simple (Jullière) model for tunnel magnetoresistance



parallel

antiparallel



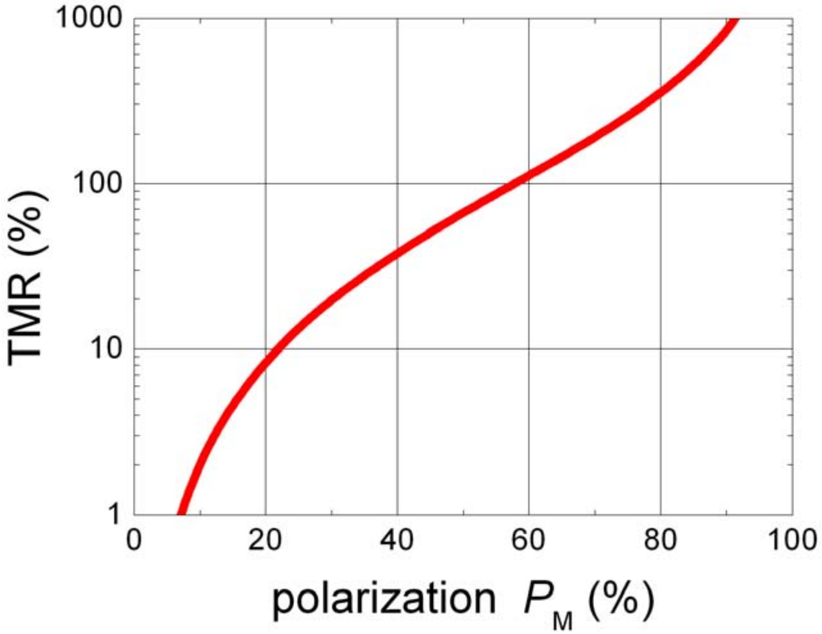
$$\mathrm{TMR} = \frac{\Delta R}{R} = \frac{R_{AP} - R_P}{R_P} = \frac{2 P_M^1 P_M^2}{1 - P_M^1 P_M^2}$$

$$P_M = \frac{N_{\mathrm{maj}}(E_F) - N_{\mathrm{min}}(E_F)}{N_{\mathrm{maj}}(E_F) + N_{\mathrm{min}}(E_F)}$$

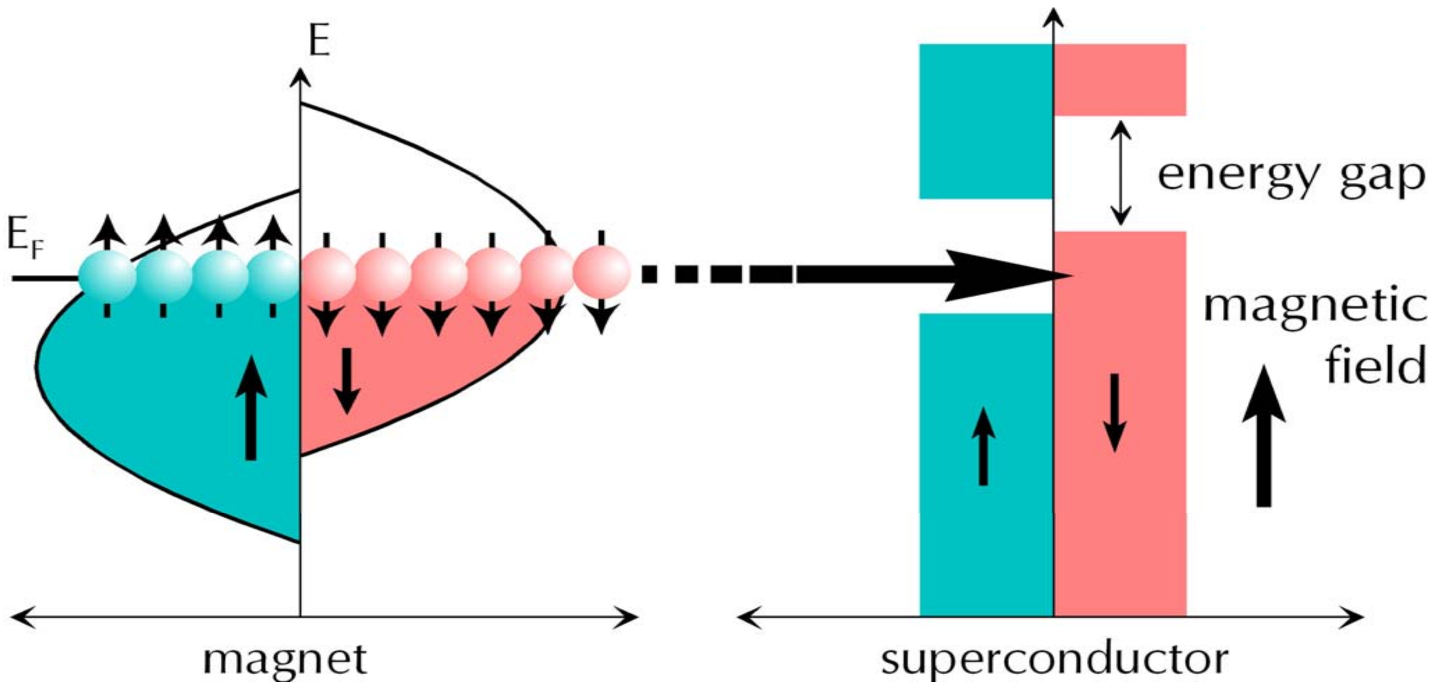
P_M : tunneling polarization magnetic metal

P_M = 50 % → TMR ≈ 67%

Note: GMR of spin-valve trilayers < 15%

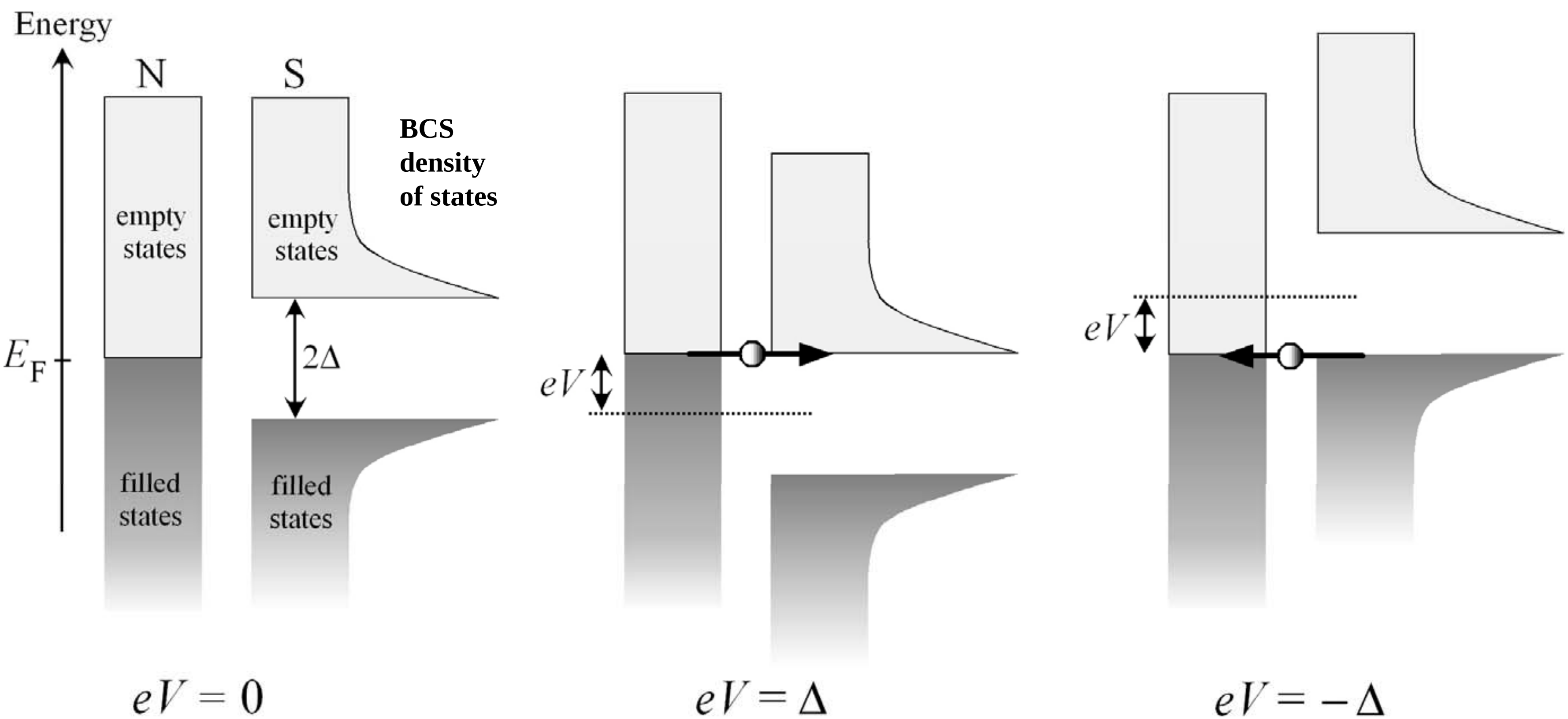


How to measure spin polarization?



Ultrathin superconducting Al can do the job ….

Energy diagrams metal / superconductor junction



Superconductor band gap Δ determines current onset

Current *I*

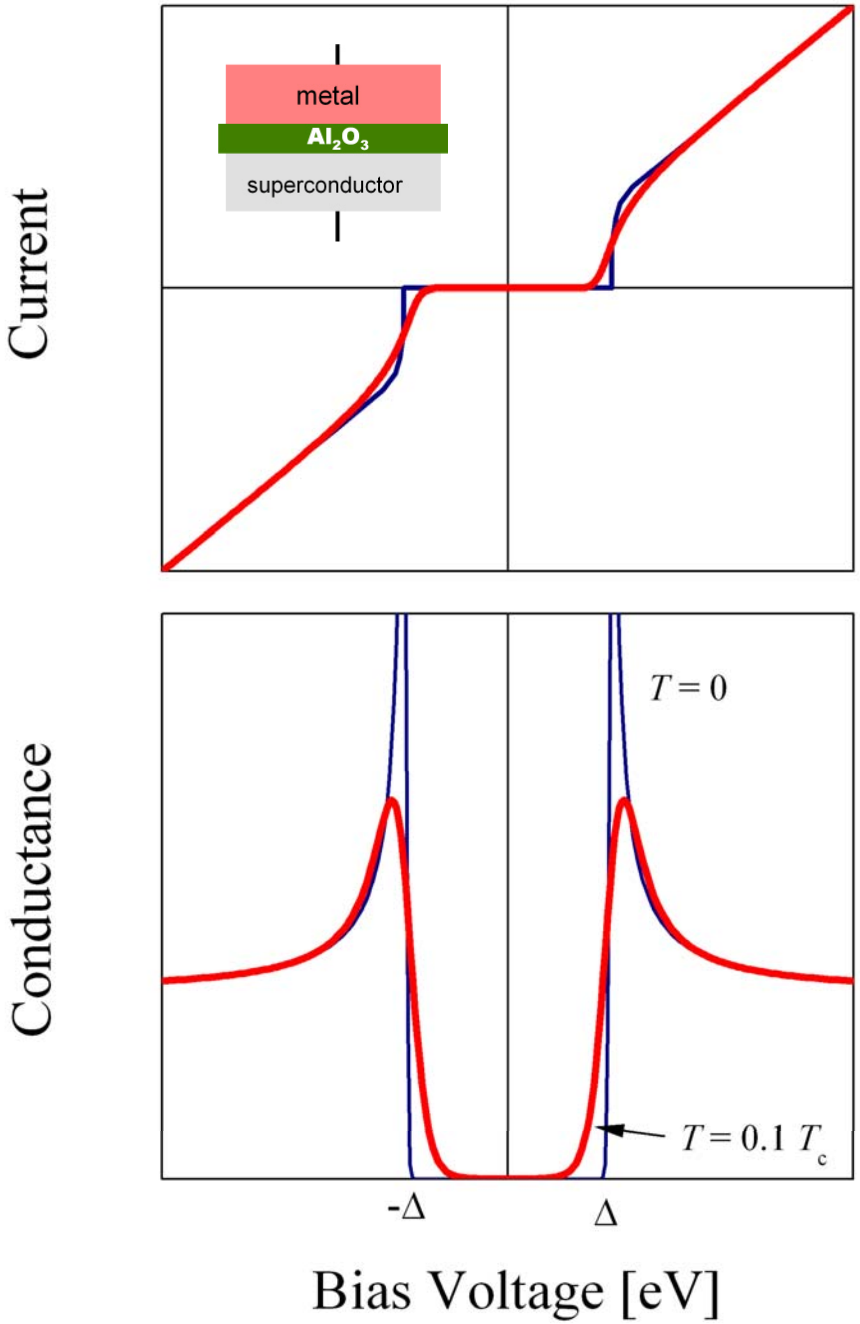
- Superconductor band gap probed in I/V curves

- Thermal broadening

Conductance $G = dI / dV$

- $G \propto N_{left} \times N_{right}$

  direct probe of superconductor DOS

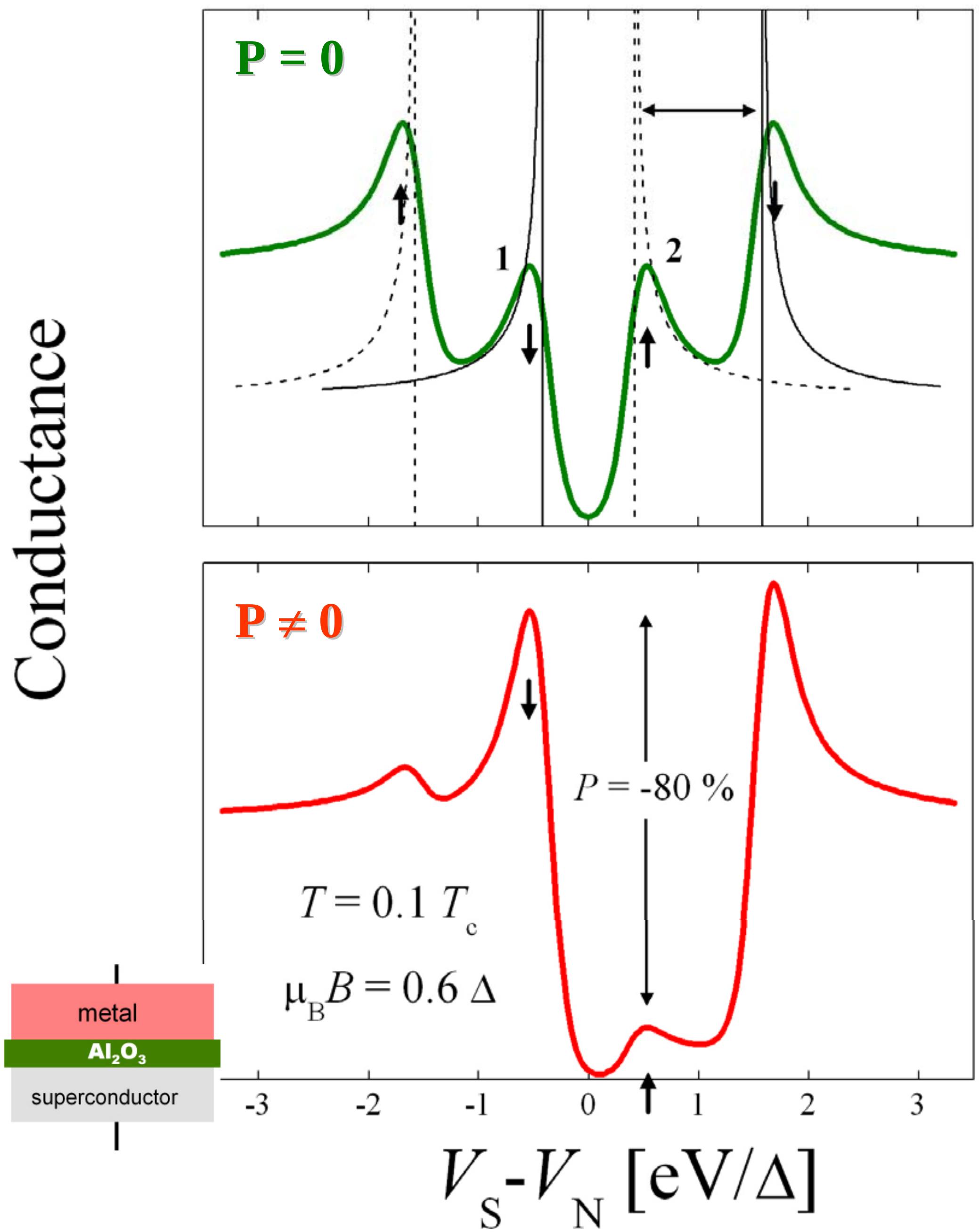


Effect of Magnetic field:

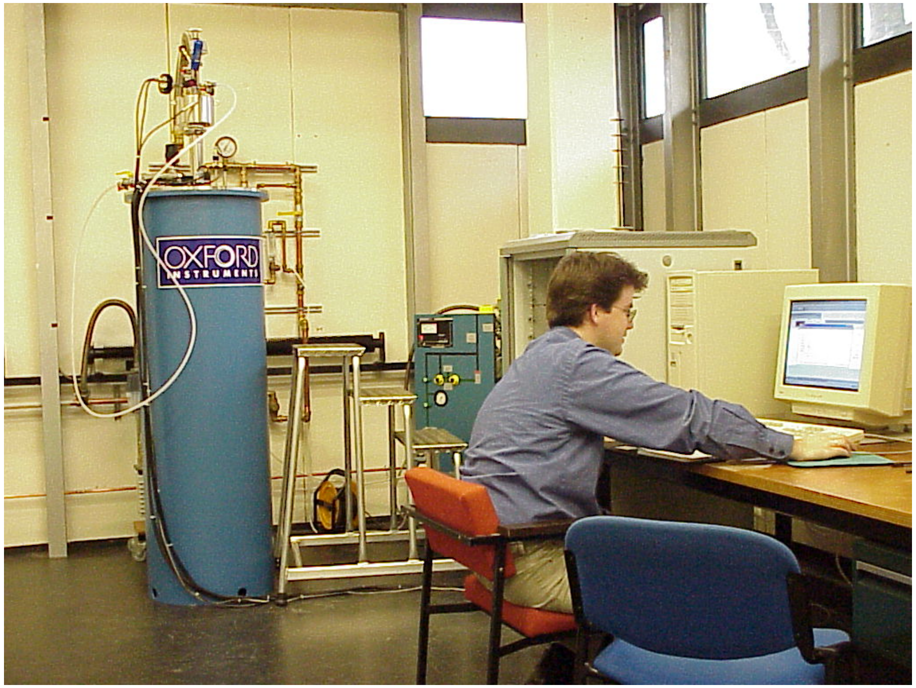
Conductance asymmetry measure for spin polarization

$$P = \frac{G^{\uparrow} - G^{\downarrow}}{G^{\uparrow} + G^{\downarrow}}$$

sign of P_M measured as well

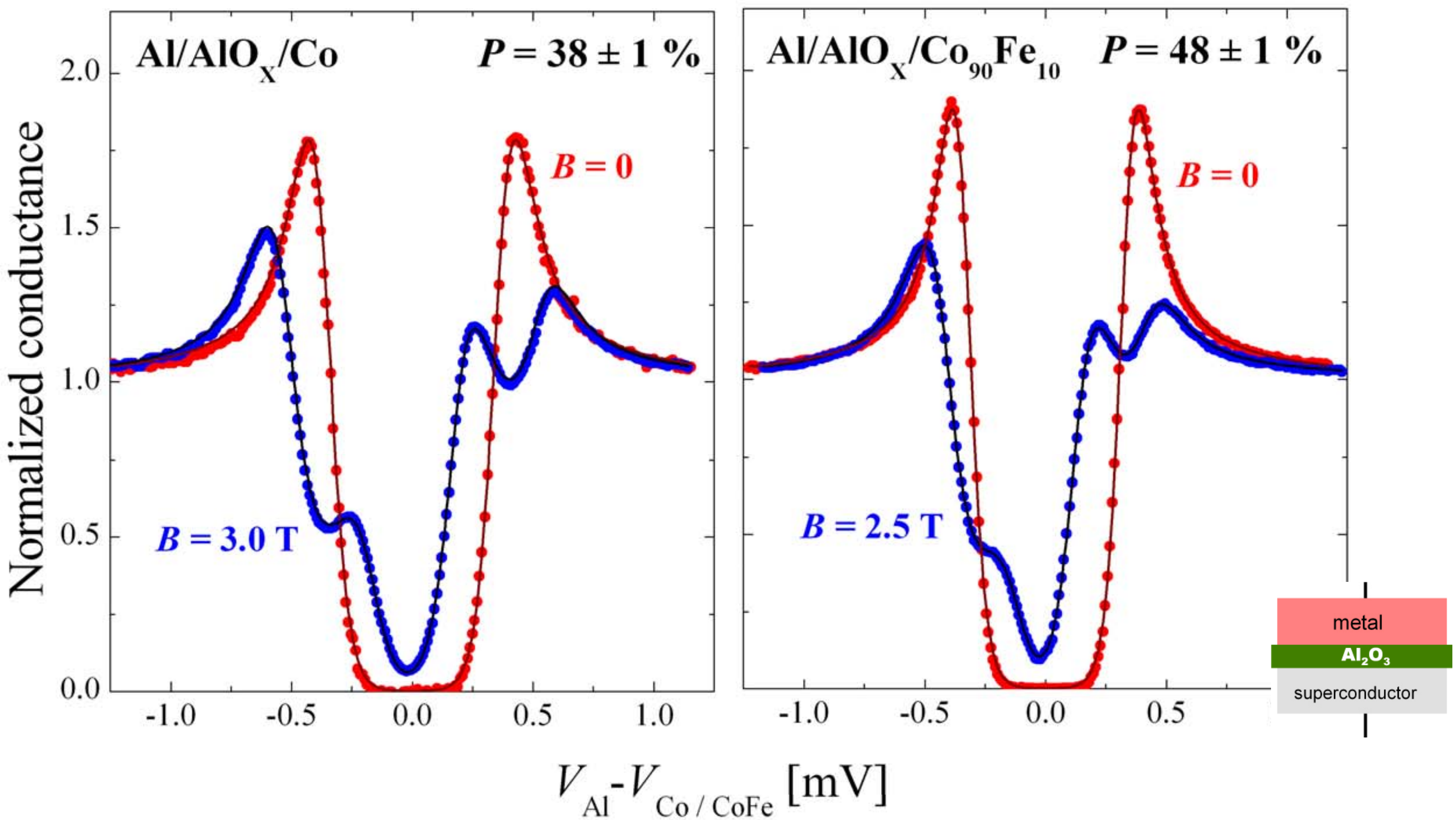


Superconducting junctions measured at T = 0.3 K



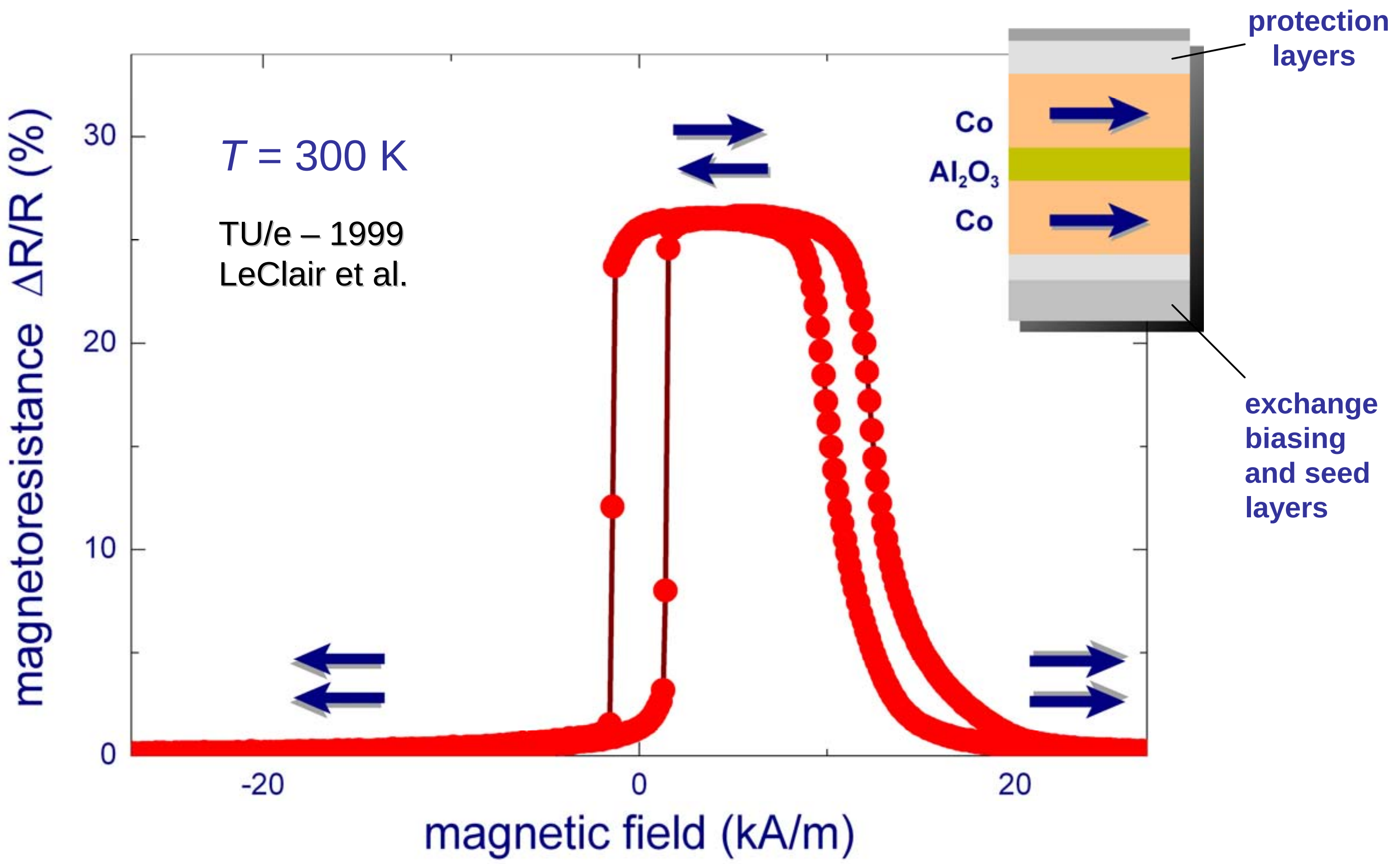
Issues: superconductor properties T_C , B_C , Δ
in relation to layer growth, field alignment

Example: polarization in Al / AlOx / Co (CoFe)



$$\Delta R/R = \frac{2P_M^1 P_M^2}{1 - P_M^1 P_M^2} \quad \rightarrow \quad \text{TMR} \approx 30\ \% \text{ for Co/Al}_2\text{O}_3\text{/Co !}$$

Tunnel magnetoresistance (TMR): follows Julliere!

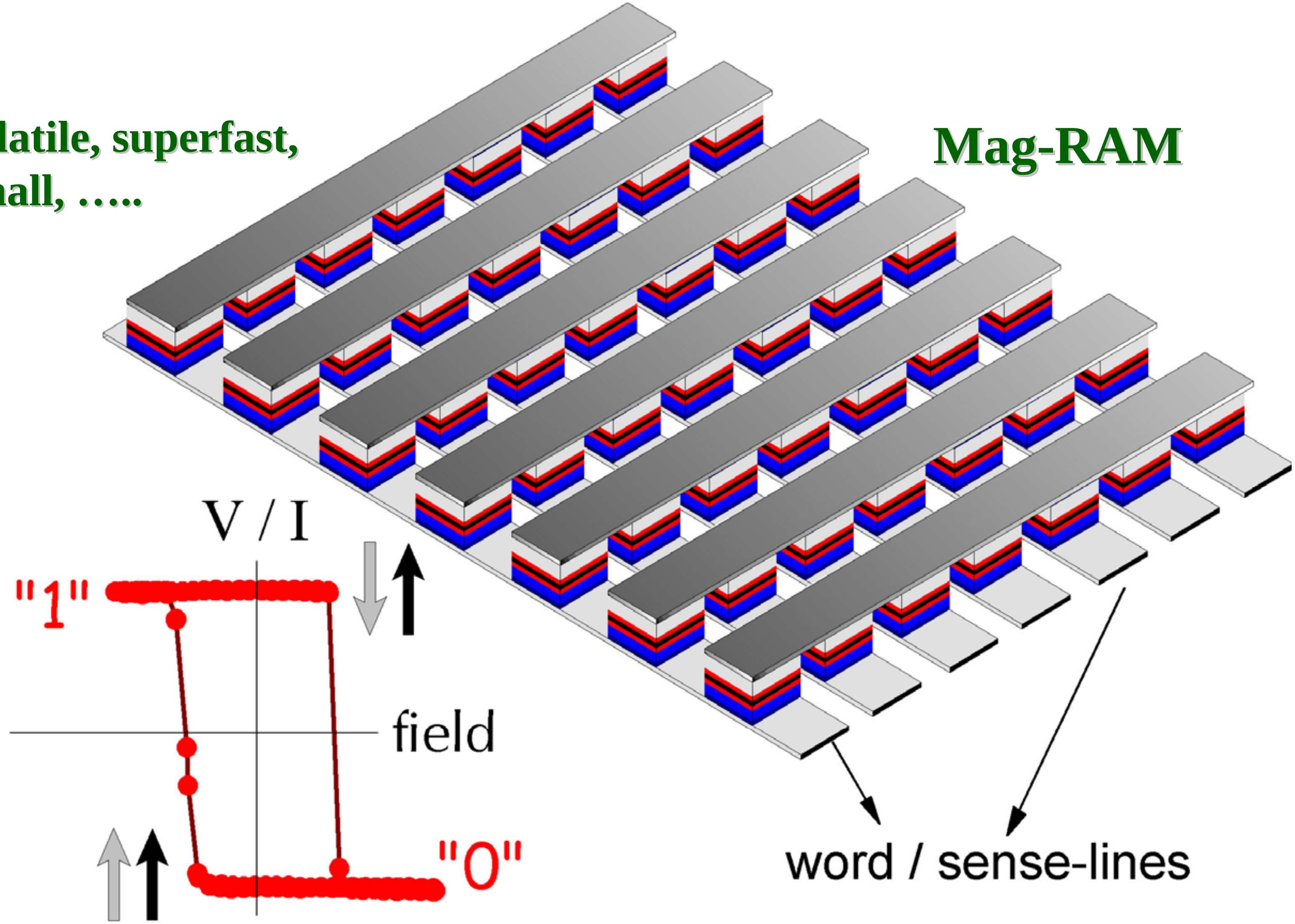


record January 2004: > 70% at RT → applications!

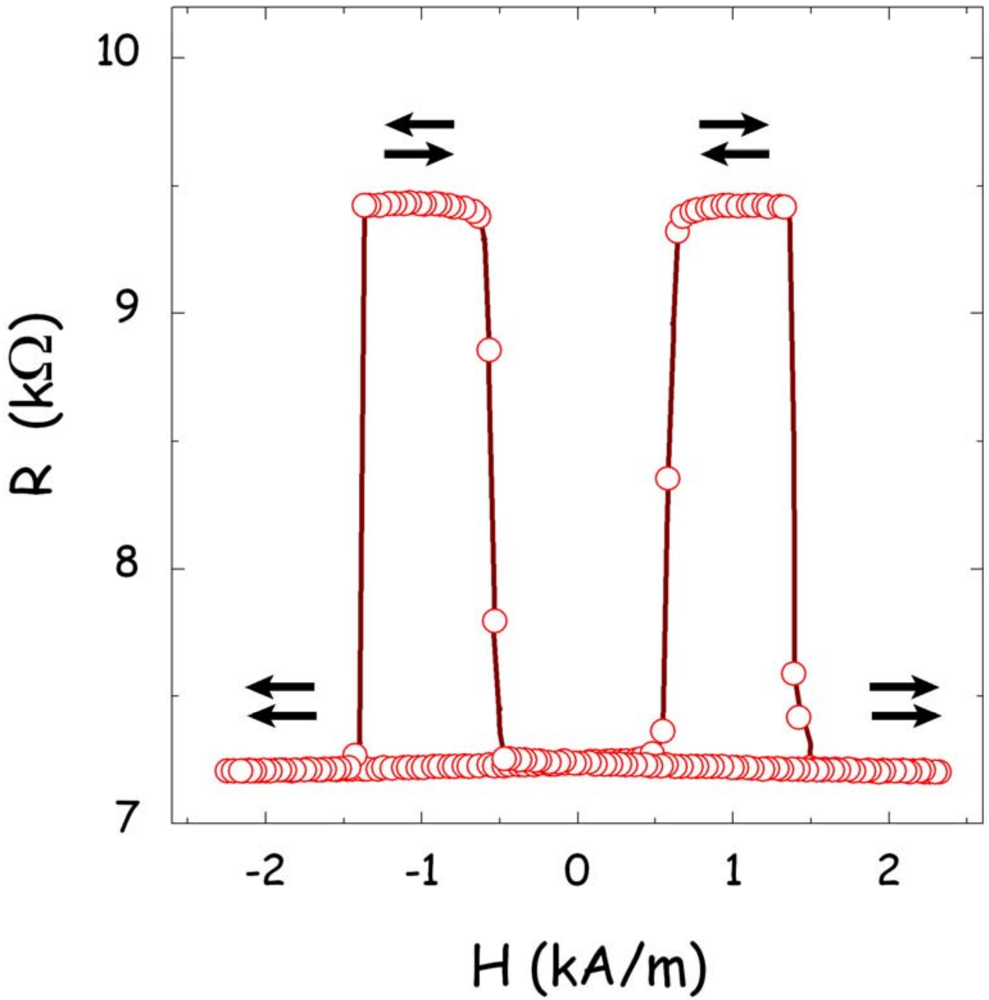
Most appealing application: memories ….

Non-volatile, superfast, very small, …..

Mag-RAM

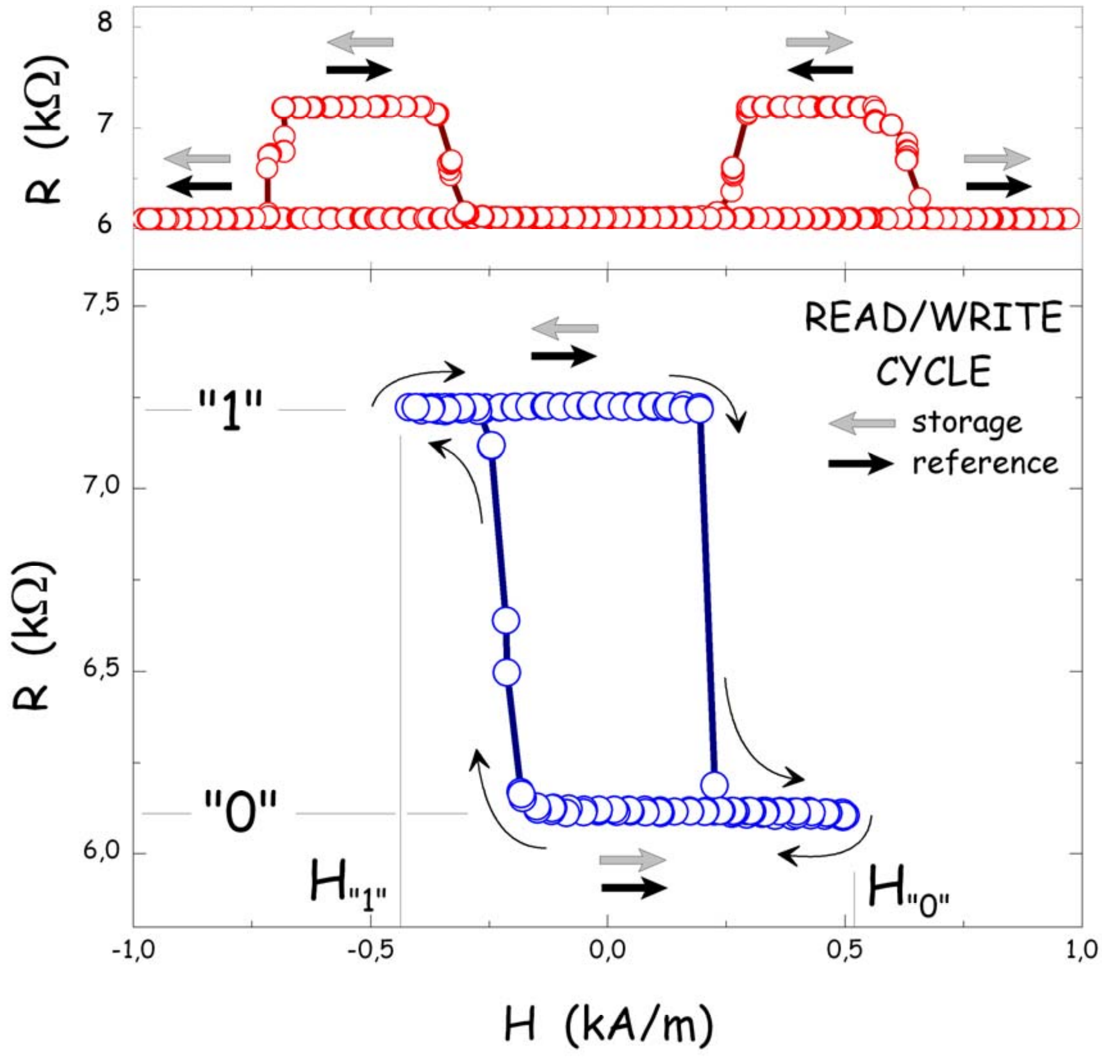


2 resistance states correspond to logical “0” and “1”

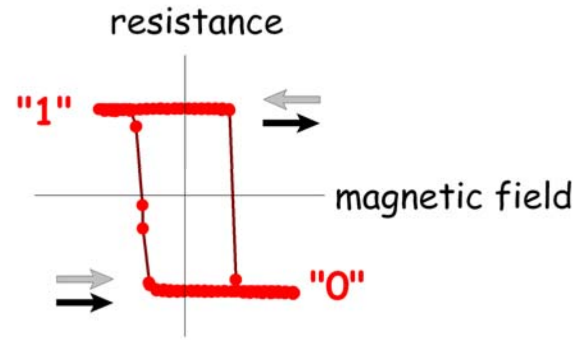


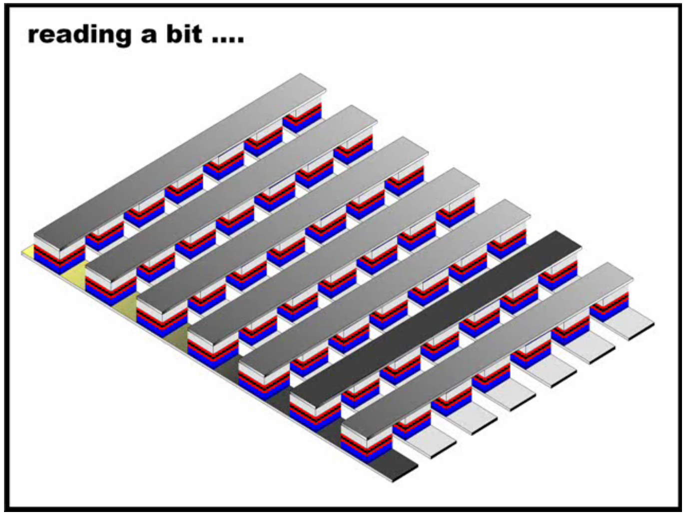
However: only one state at *H* = 0 ?

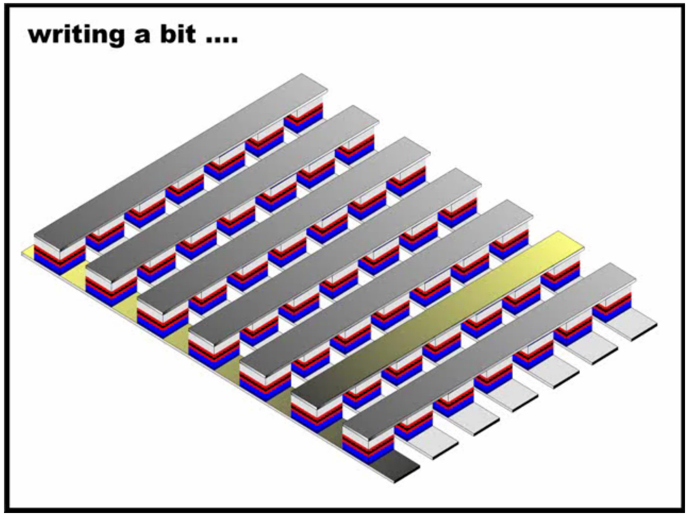
TMR for storage: read/write strategy



Mag-RAM







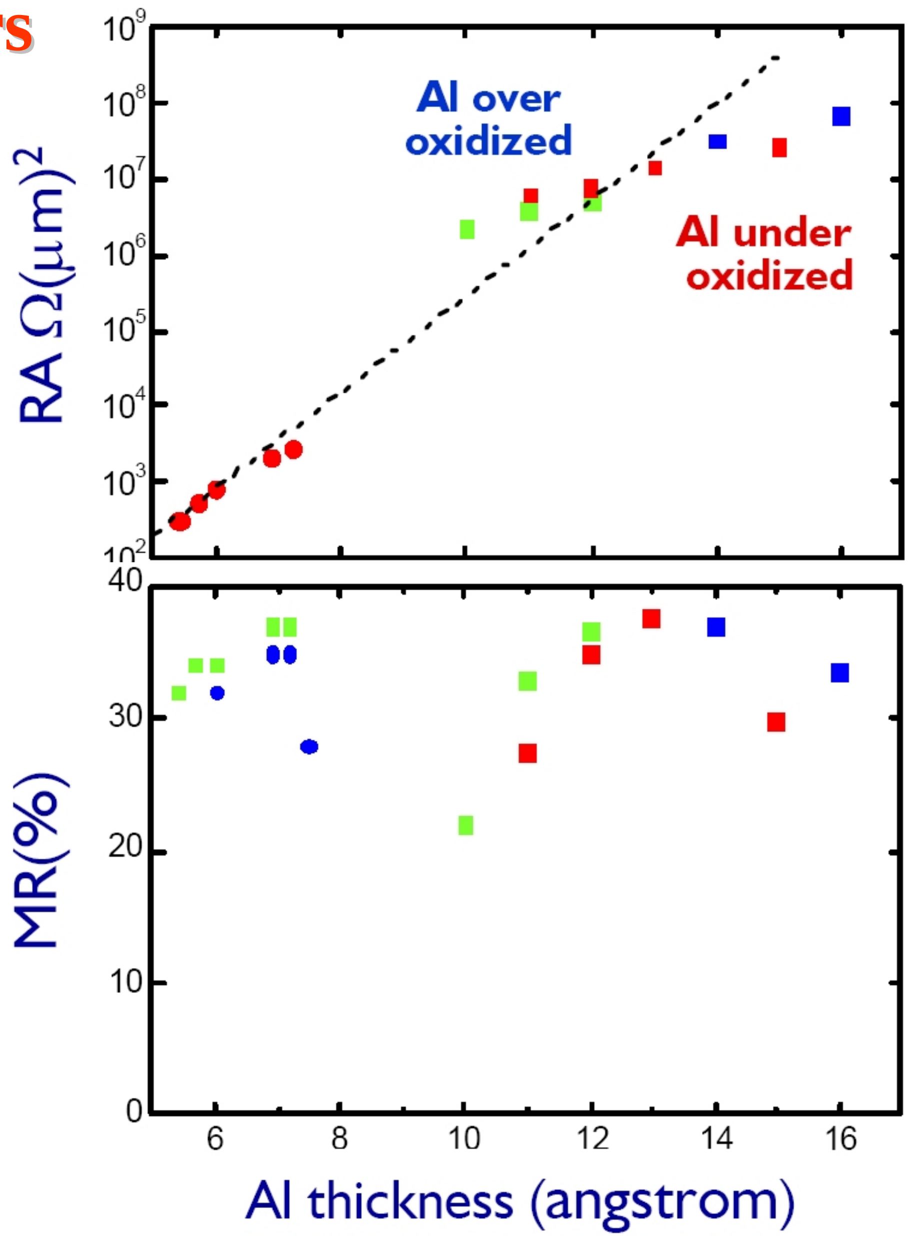
Issues:

- wafer uniformity
- reduction bit size → R increases
  → thinner barriers !

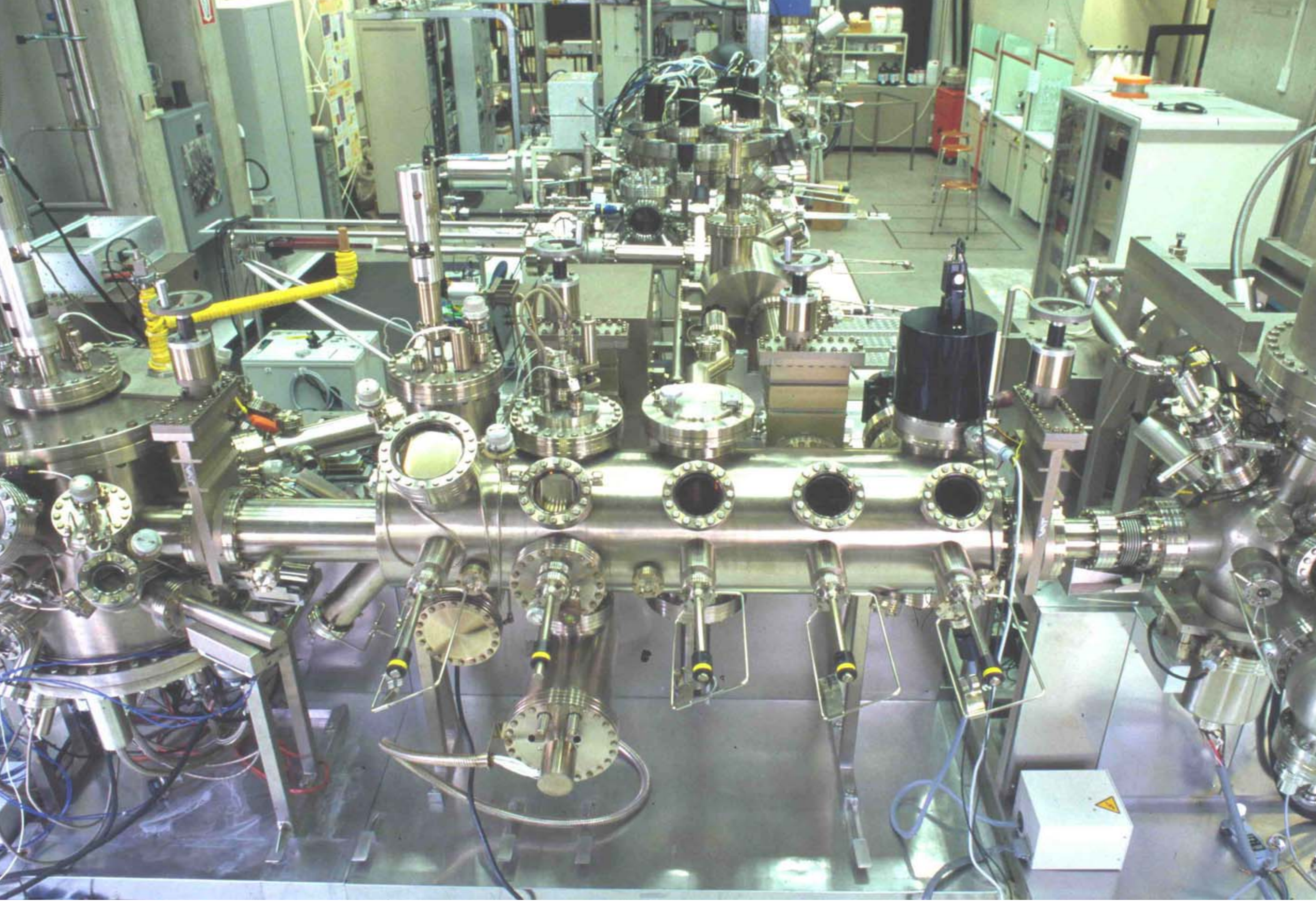
Towards ultrathin barriers

- uniformity
- pinholes
- voltage breakdown
- magnetic coupling
- …..

Fabrication crucial!



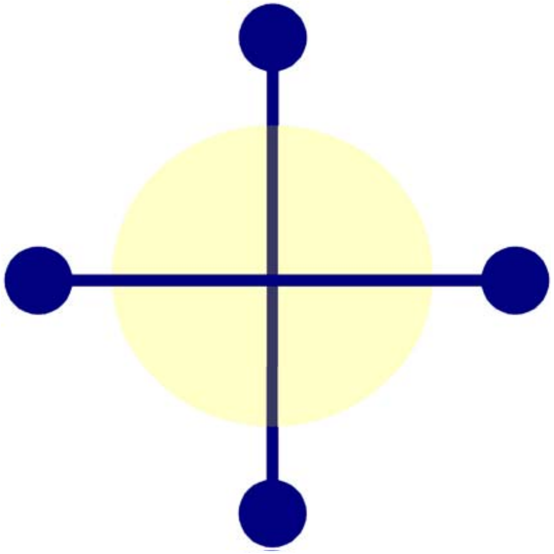
IBM 2003

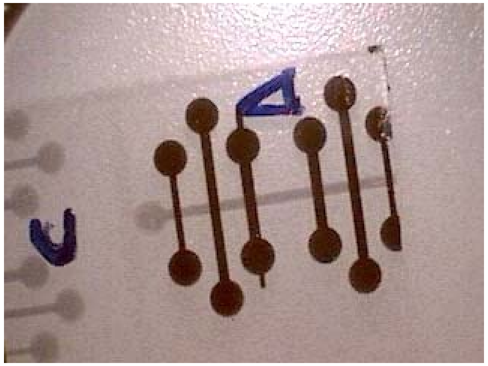


UHV lab “EUFORAC” at TU/e (atomic LEGO)

Shadow mask evaporation & UHV sputtering

Few words on preparation ....

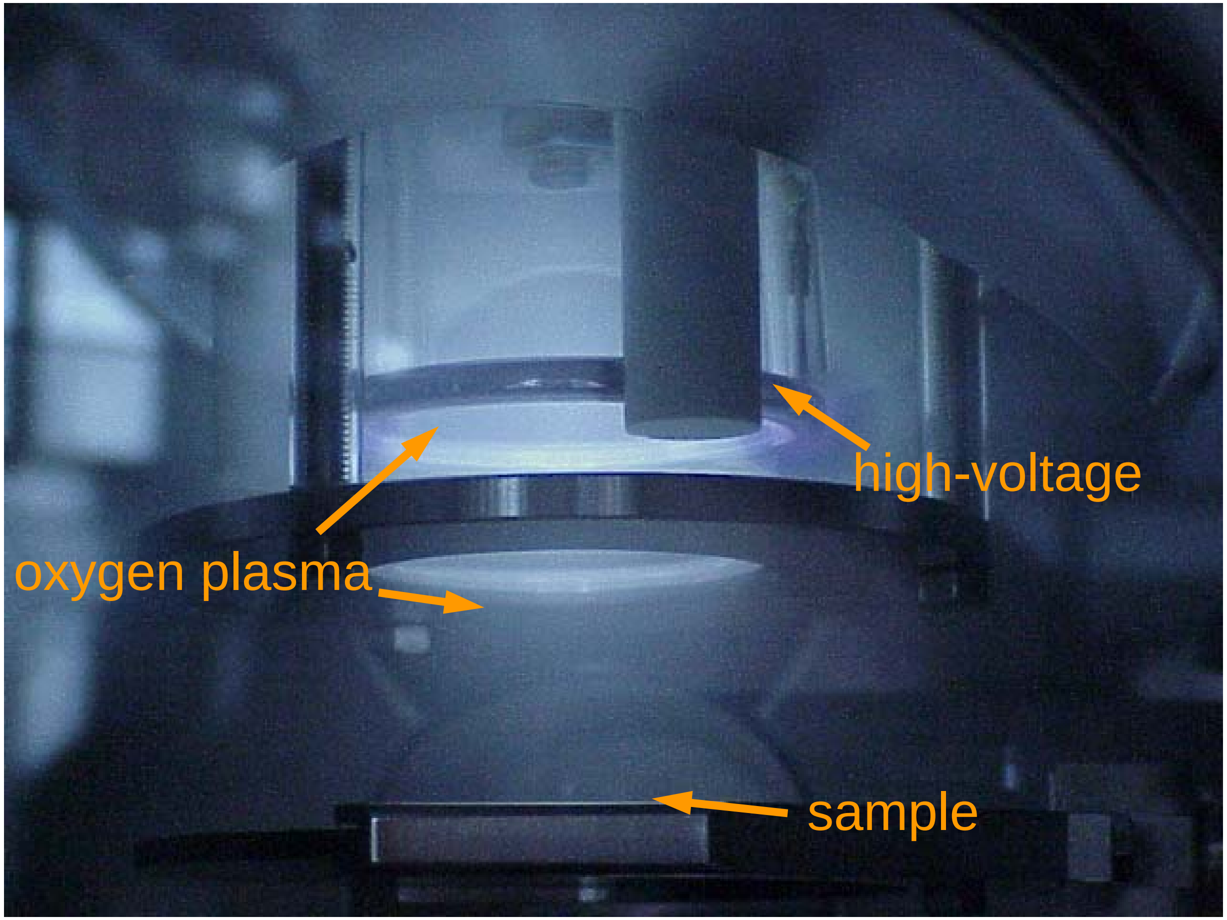




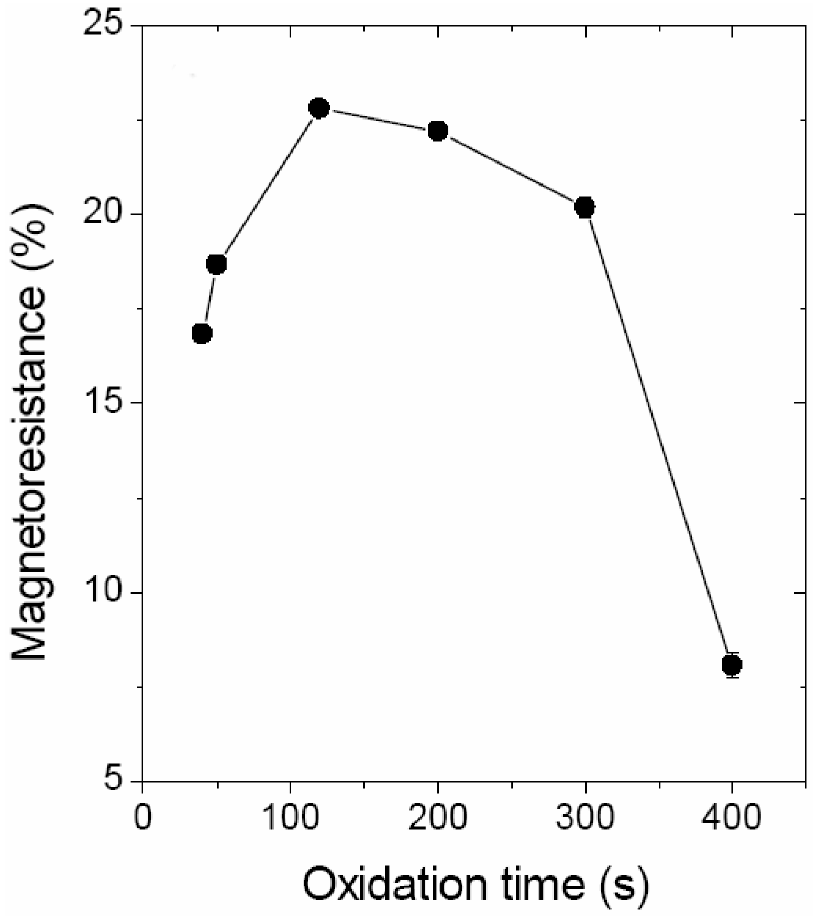
line widths: 0.2 – 0.5 mm

4. top electrode deposition & capping

Oxidation key to device performance

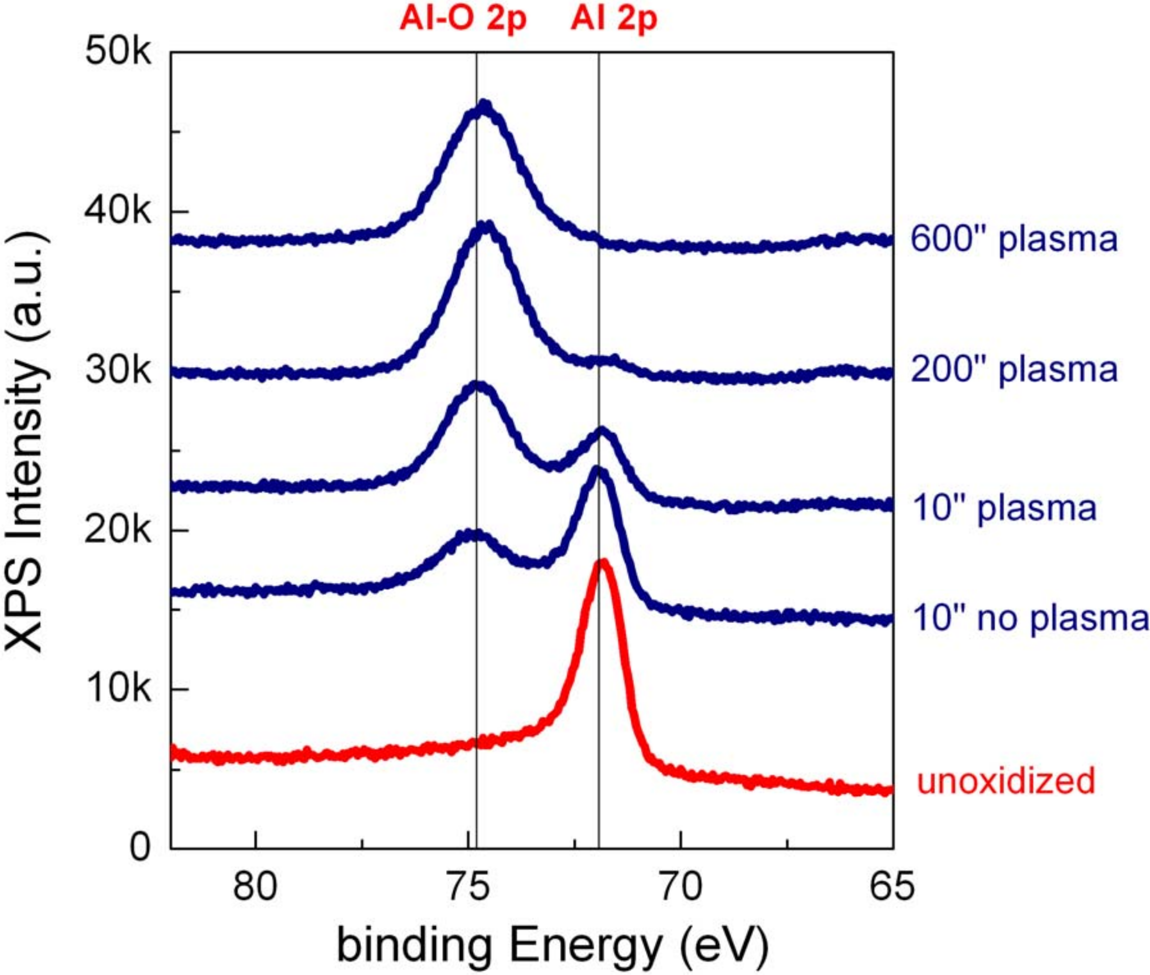


Oxidation key to performance:
no over- or under-oxidation



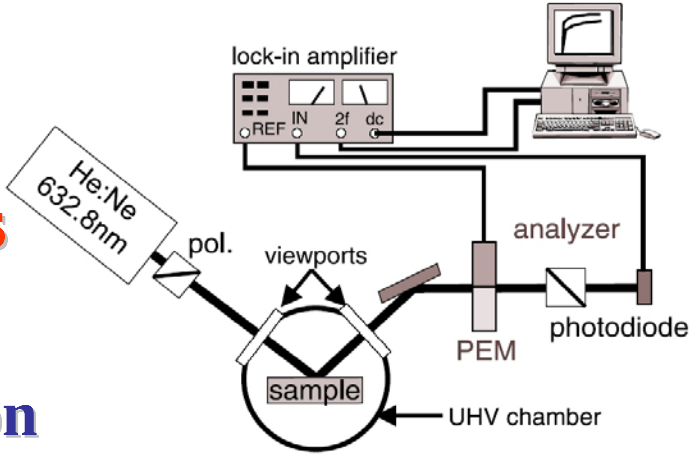
$Co_{90}Fe_{10}$ based MTJ's
(Koller TU/e)

In–situ X-ray Photoelectron Spectroscopy



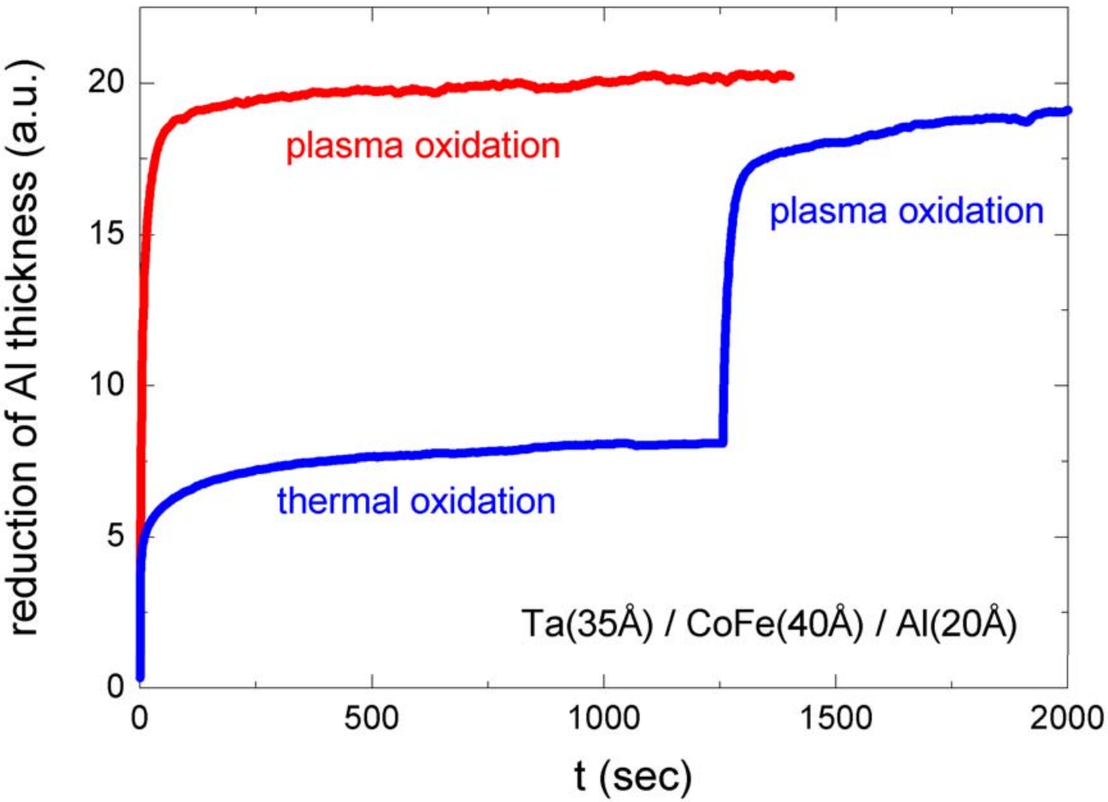
Sensitive probe (better than 1 ML) of oxidation stage

Differential ellipsometry, measuring polarization changes

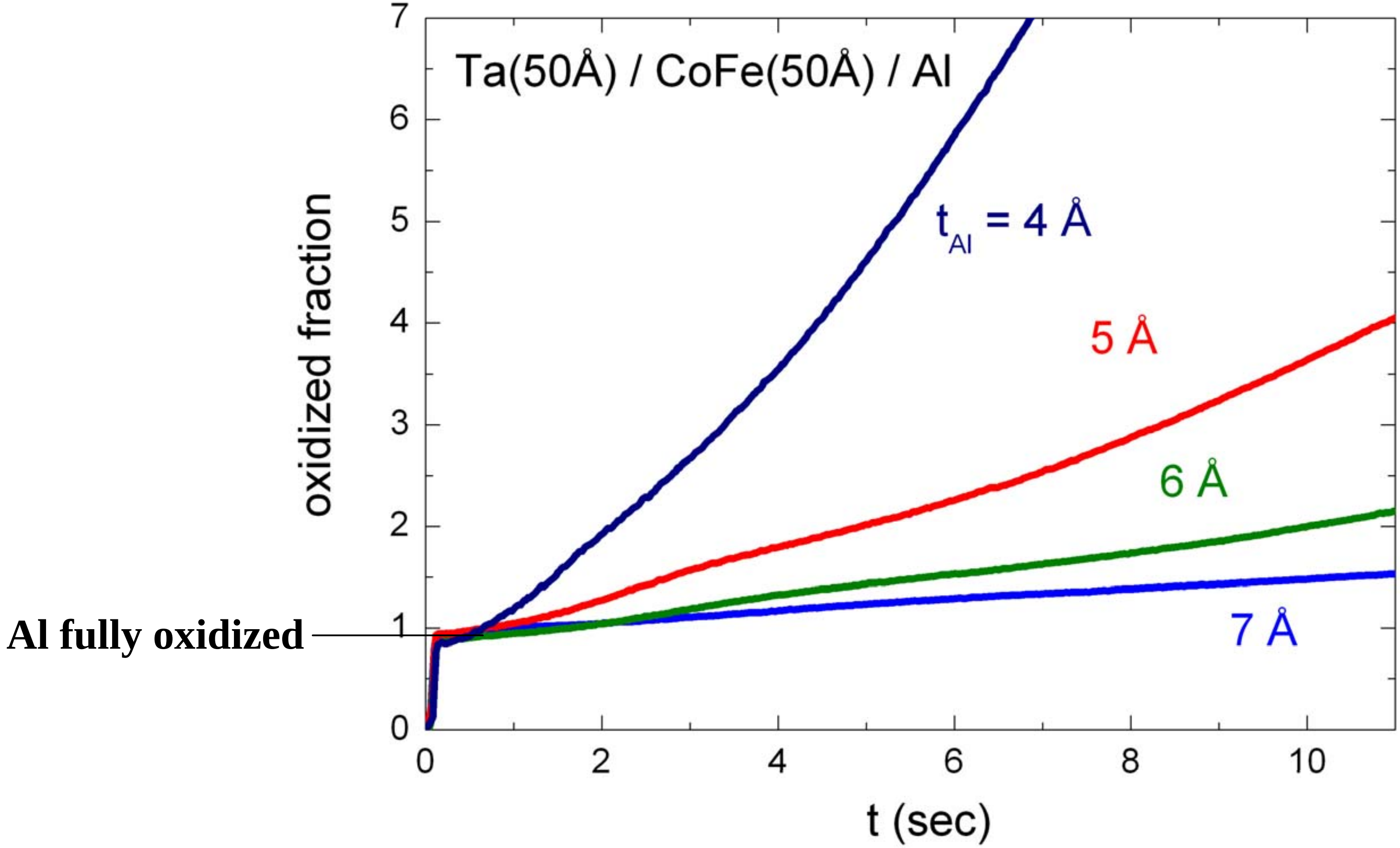


Optical determination of Al oxidation

- in-situ
- non-destructive
- oxidation dynamics can be probed

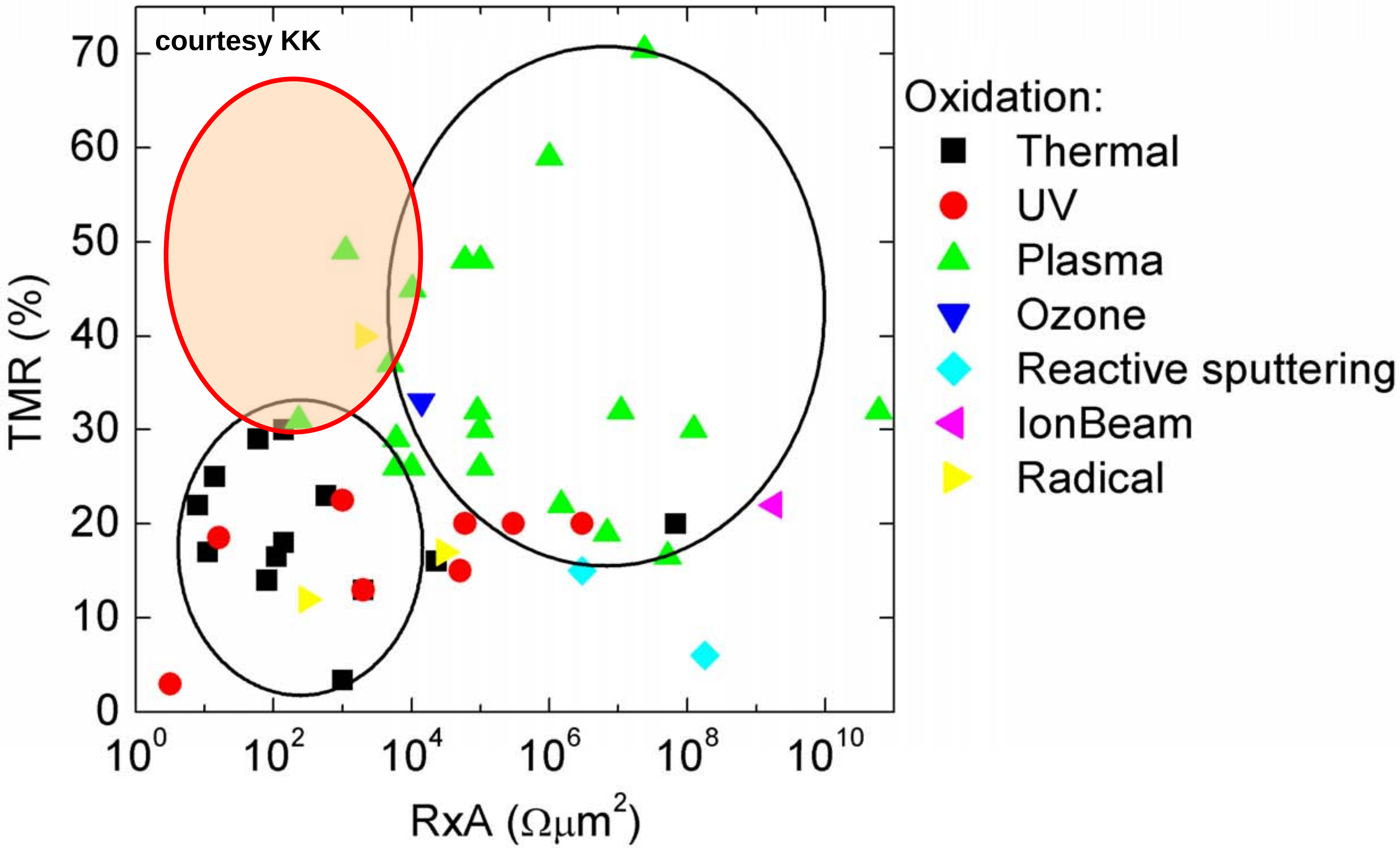


Ultrathin Al for applications (MRAM)



Over-oxidation can be directly probed!

AlOx based junctions: TMR vs. R×A product



- plasma oxidation gives highest TMR
- other oxidation processes yield lower R×A

Back to physics …

Julliere's formula $$\Delta R/R = \frac{2P_M^1 P_M^2}{1 - P_M^1 P_M^2}$$

$$P_M = \frac{N_{\mathrm{maj}}(E_F) - N_{\mathrm{min}}(E_F)}{N_{\mathrm{maj}}(E_F) + N_{\mathrm{min}}(E_F)}$$

P_M : tunneling polarization magnetic metal

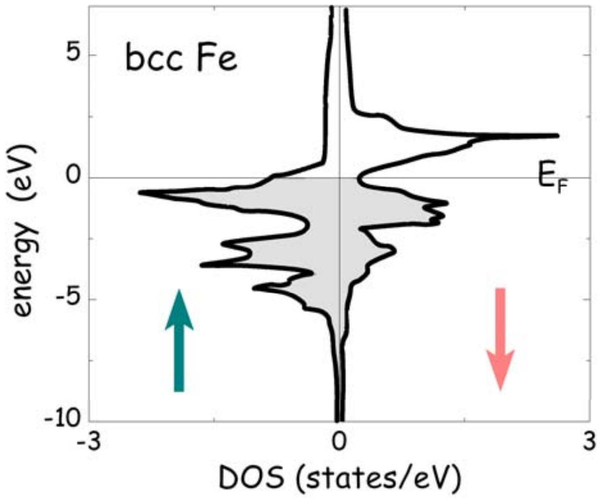
Is that all?

Spin tunneling, a closer inspection

$$I_{tot} \propto \int_{-\infty}^{+\infty} N_l(E)\, N_r(E+eV)\, |M|^2 \times f(E) f[1-f(E+eV)]\, dE$$

- DOS in reality not simple
- d electrons more localized:

$$|M|^2_{s-p} > |M|^2_d$$

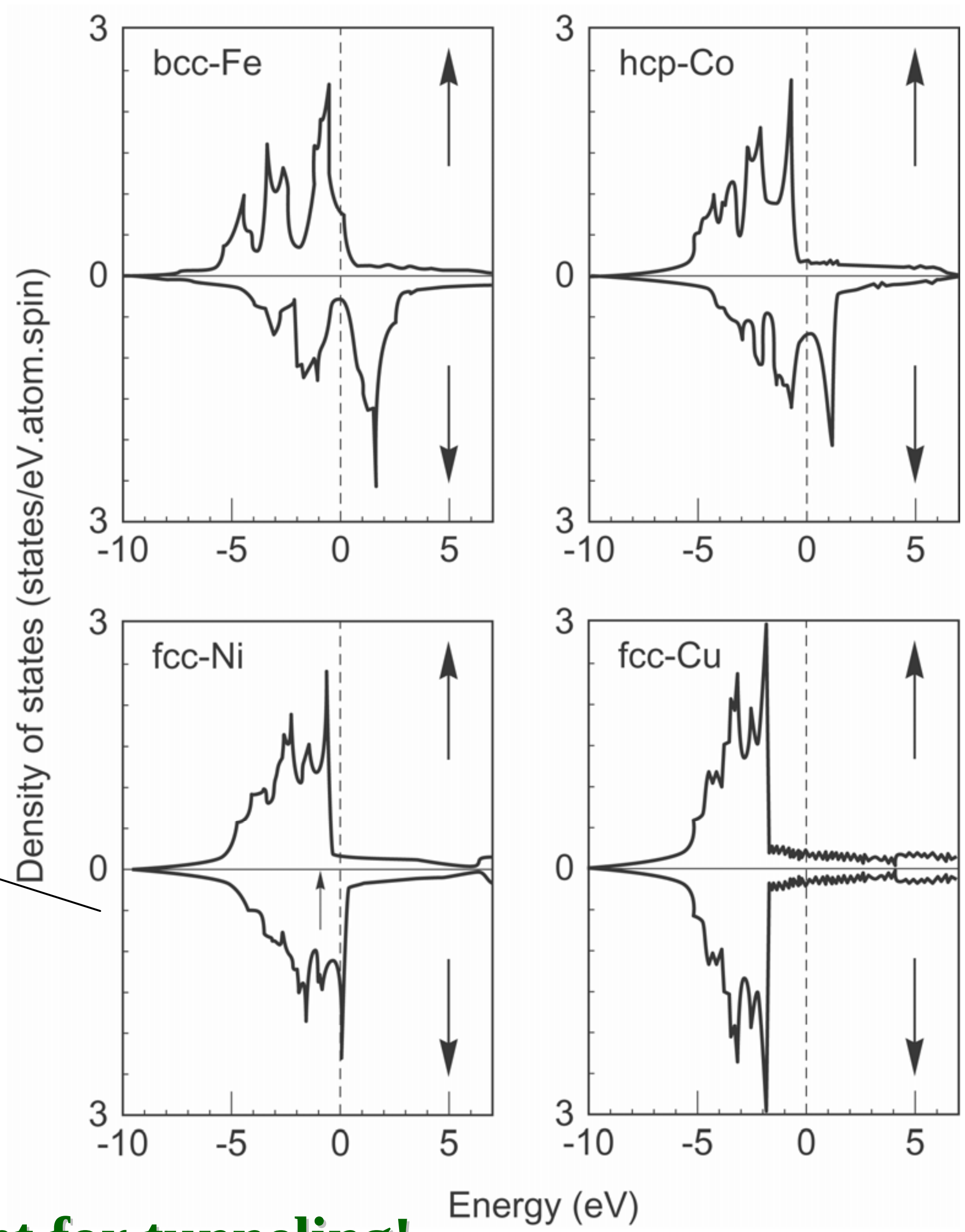


CONCLUSION:
tunneling spin polarization certainly not directly related to "static" DOS!!!

Nice example: fcc - Ni

$$P_M = \frac{N_{\text{maj}}(E_F) - N_{\text{min}}(E_F)}{N_{\text{maj}}(E_F) + N_{\text{min}}(E_F)}$$

$$P_M < 0$$



However: $P_{Ni} > 0$
in tunneling devices
with Al_2O_3 barriers;

s wave functions dominant for tunneling!

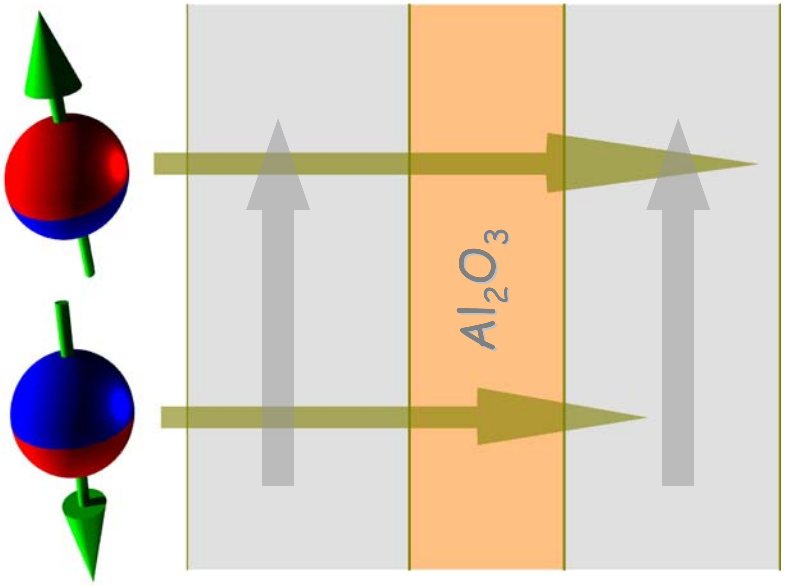
Tunneling Spin Polarization NOT intrinsic ….

$$P_M = \frac{N_{\mathrm{maj}}|M_{\mathrm{maj}}|^2 - N_{\mathrm{min}}|M_{\mathrm{min}}|^2}{N_{\mathrm{maj}}|M_{\mathrm{maj}}|^2 + N_{\mathrm{min}}|M_{\mathrm{min}}|^2} \quad \text{at } E_F$$

…. but weighted with transmission probabilities, and thus depends on:

- **barrier height/shape**
- **disorder in barrier**
- **bonding at FM – I interfaces**
- **electronic structure (s,d, …) of insulator**
- **……**

Role of barrier for *P* ?



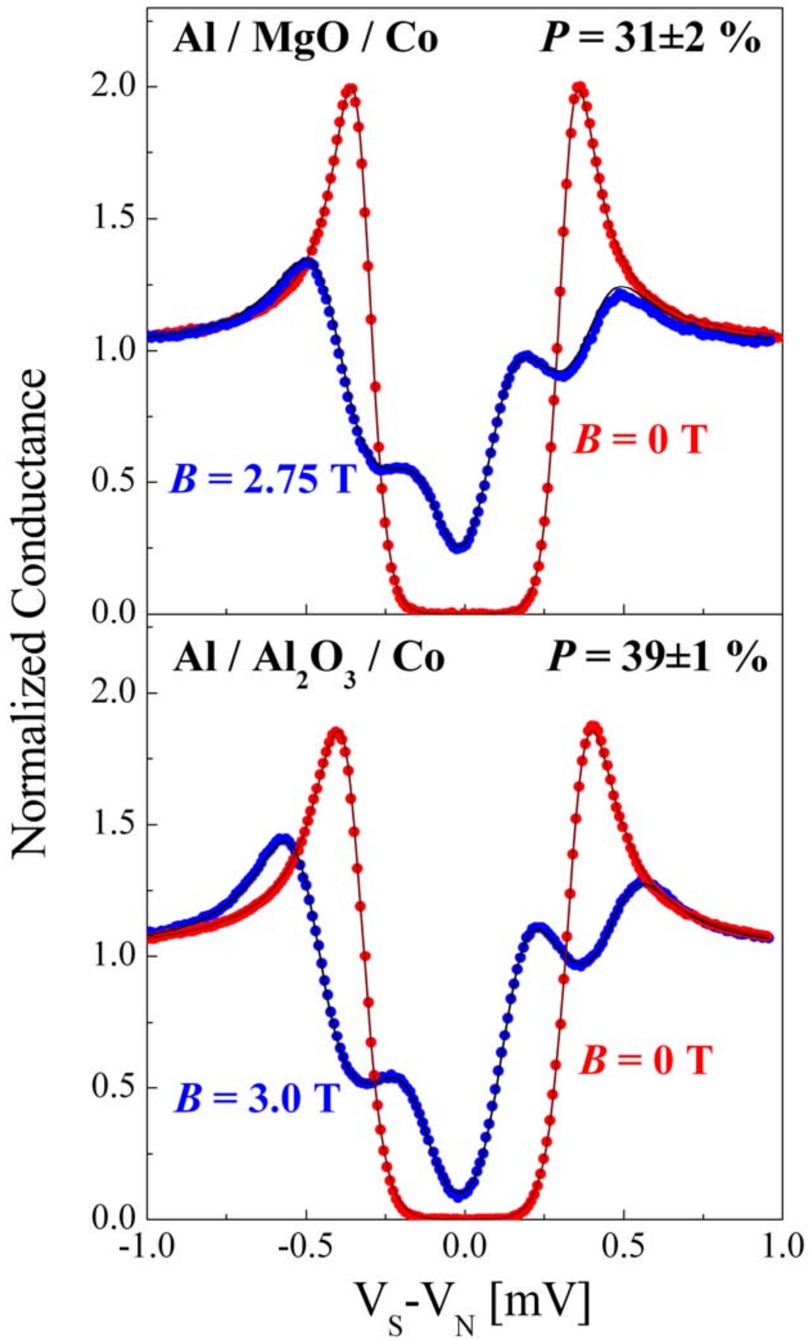
Other barriers than AlOx ?

Amorphous Al_2O_3, MgO

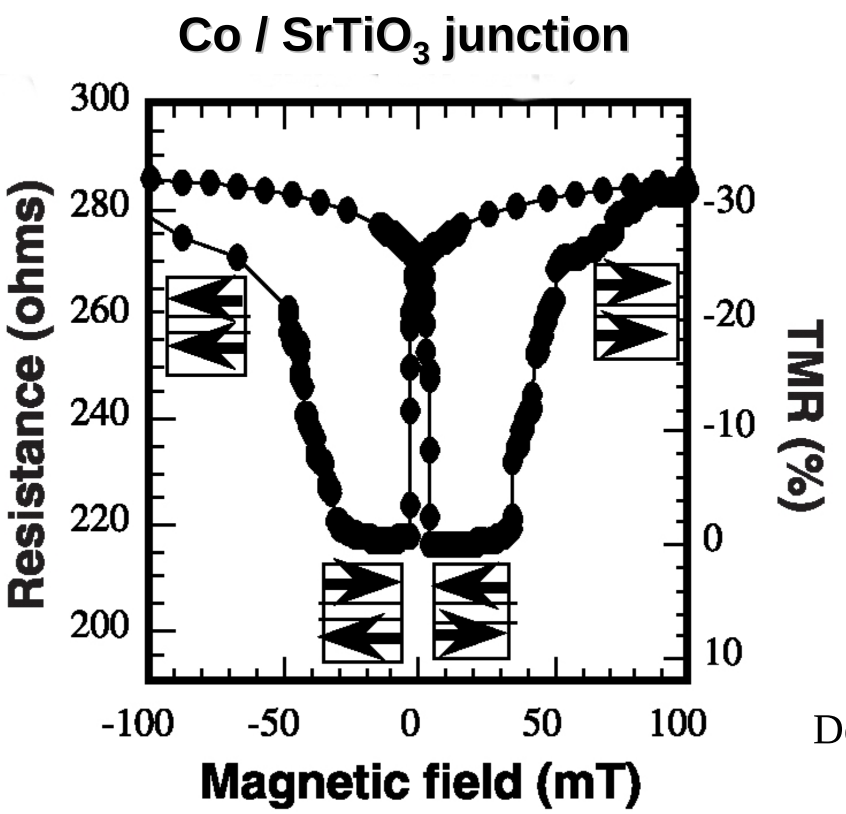
- MgO also yield positive *P* (above +30% for Co)

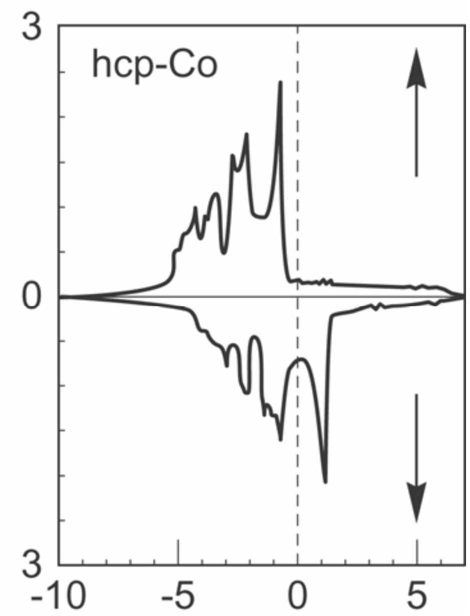
- for similar barriers (amorphous, no d orbitals) no great differences

- tunneling dominated by s wave functions



Barriers with d-orbitals: TMR may even reverse!



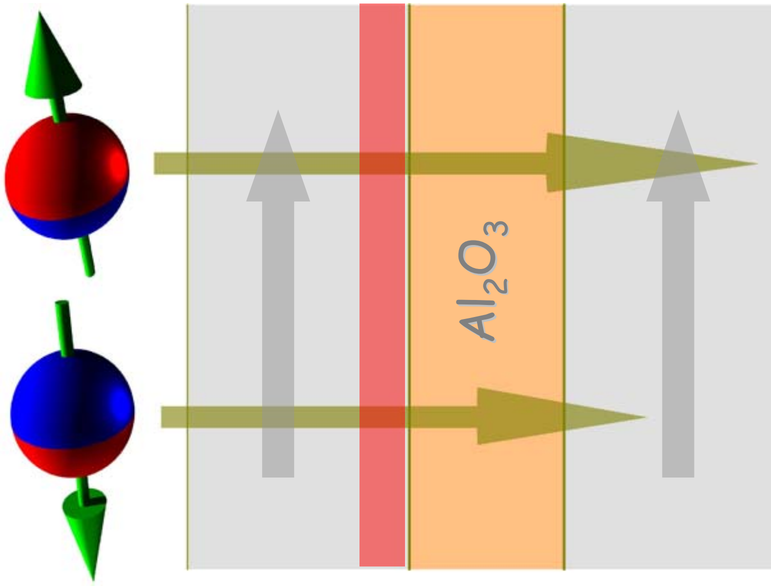


De Teresa et al.

Tunneling due to d-d nature of interfaces

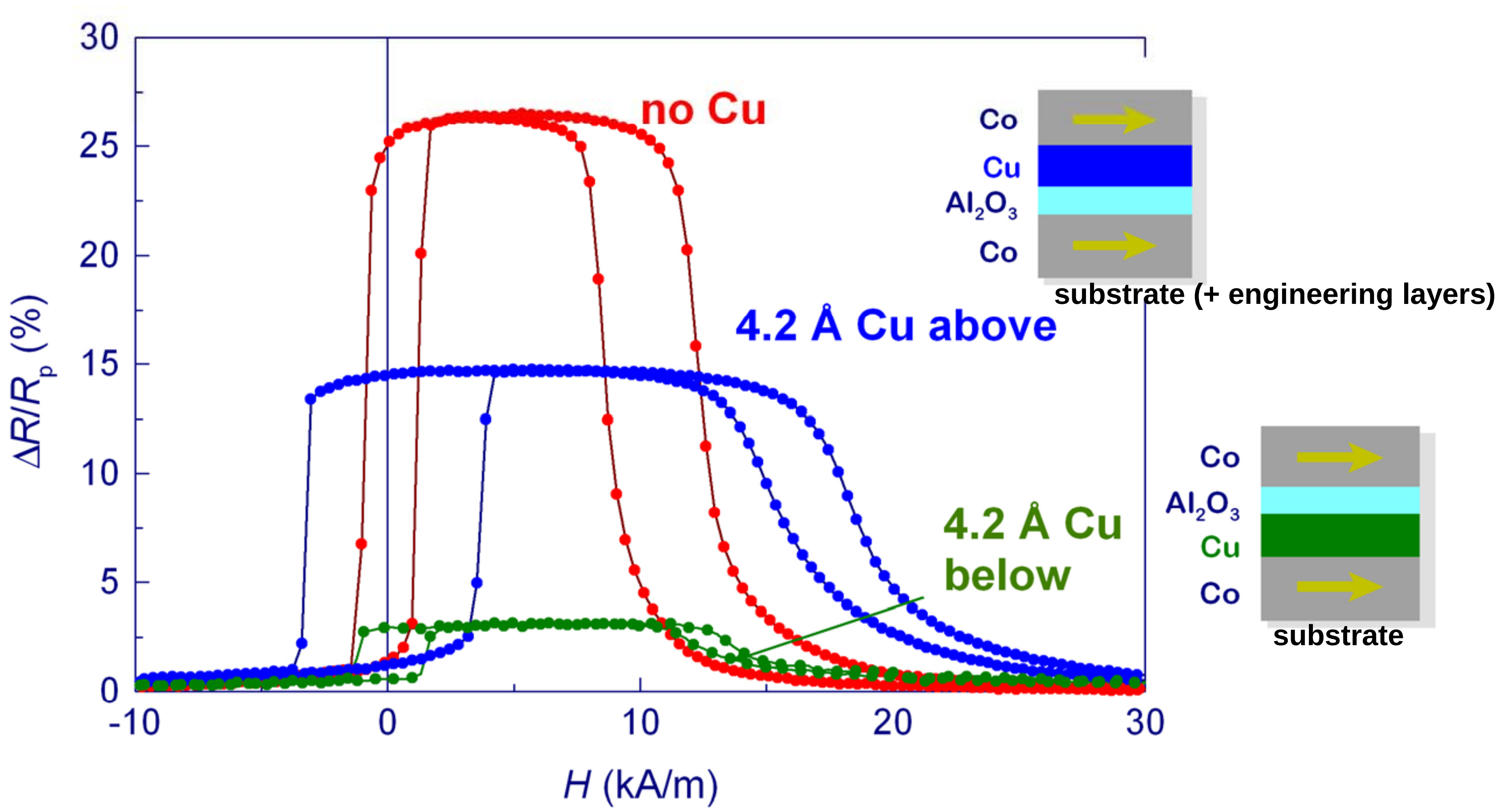
Therefore: negative d polarization of Co is probed

Role of the interfaces for *P* ?



“dusting” with nonmagnetic thin layers

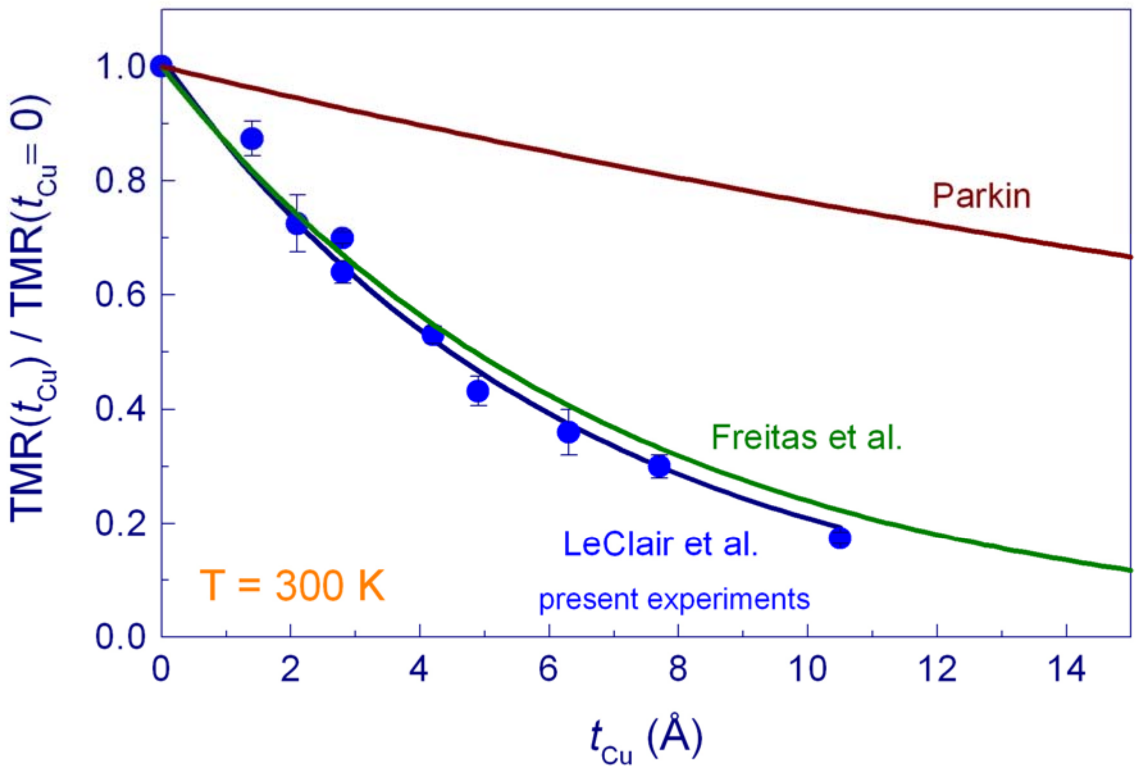
Interface dusting with Cu ….



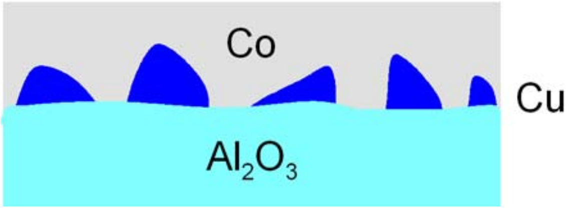
Only location of Cu differs: probably growth related!

Cu on top of Al_2O_3: no intrinsic polarization decay

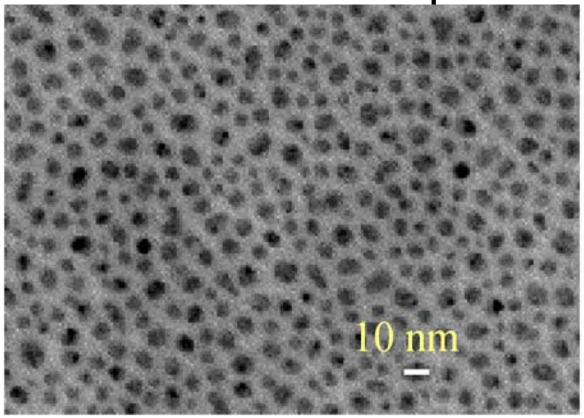
- cluster-like growth of Cu
- Co in direct contact with Al_2O_3
- decay of TMR artificially inflated: NOT intrinsic



side view



top view



15 Å of Cu on Al_2O_3

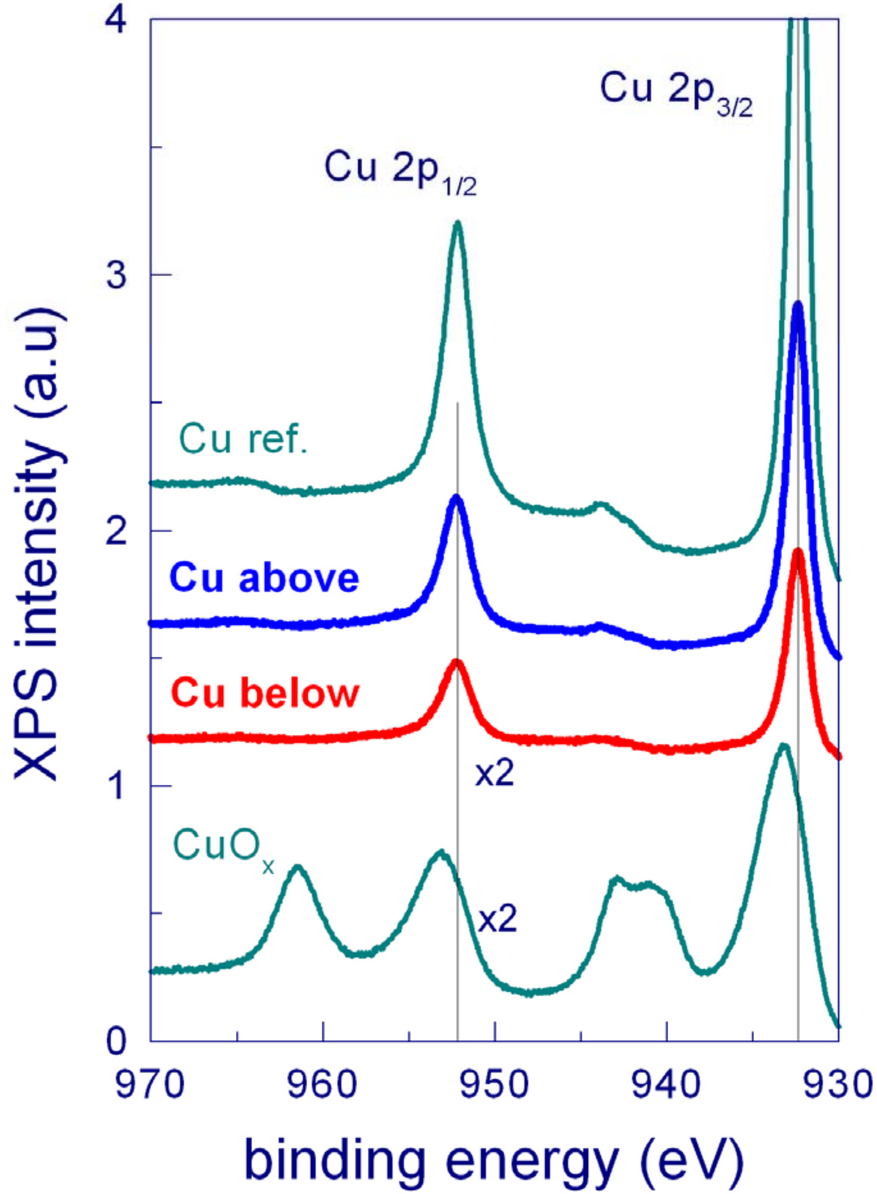
(courtesy Paris group)

XPS: any Cu oxides or alloys at barrier?

- **Formation of Cu oxides or Co-Cu alloys can be traced with XPS**

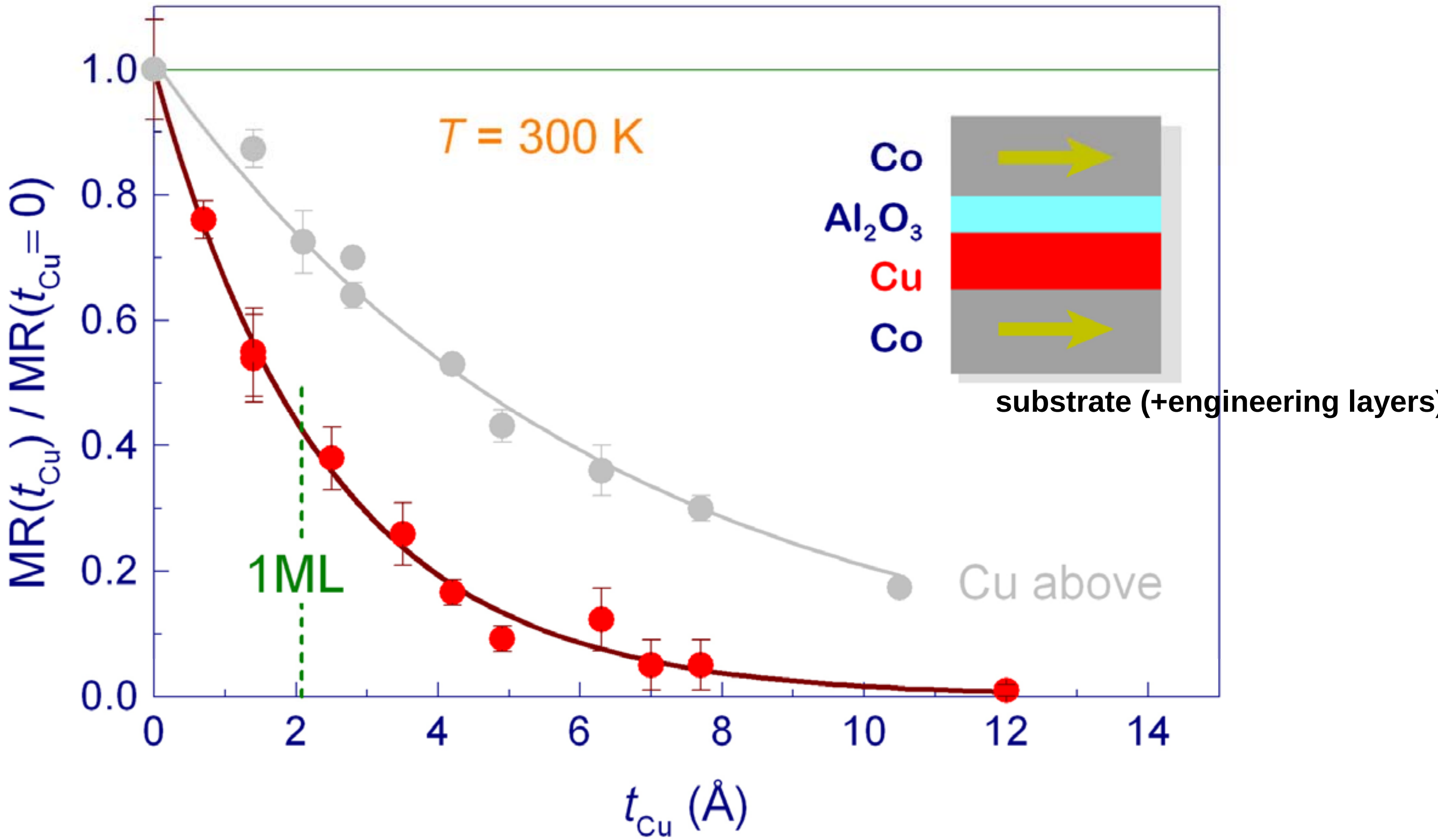
- **In-situ XPS:**
  - **- Cu above AlOx**
  - **- Cu below AlOx**
  - **- Ref. Cu, CuOx**

No Cu oxide, no alloys!



Cu on Co: extremely fast lost of polarization

1 ML of Cu reduces TMR by factor 2



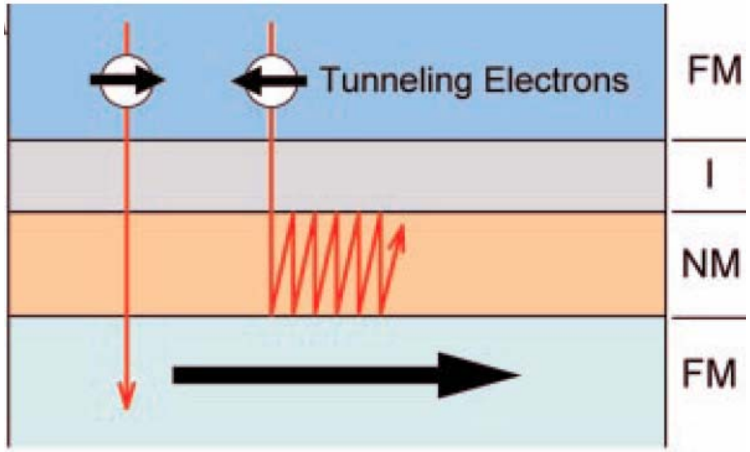
Why is decay length so fast?

- **loss of coherence (Zhang, Levy),**
  $k_{//}$ conservation violated (amorphous barriers)

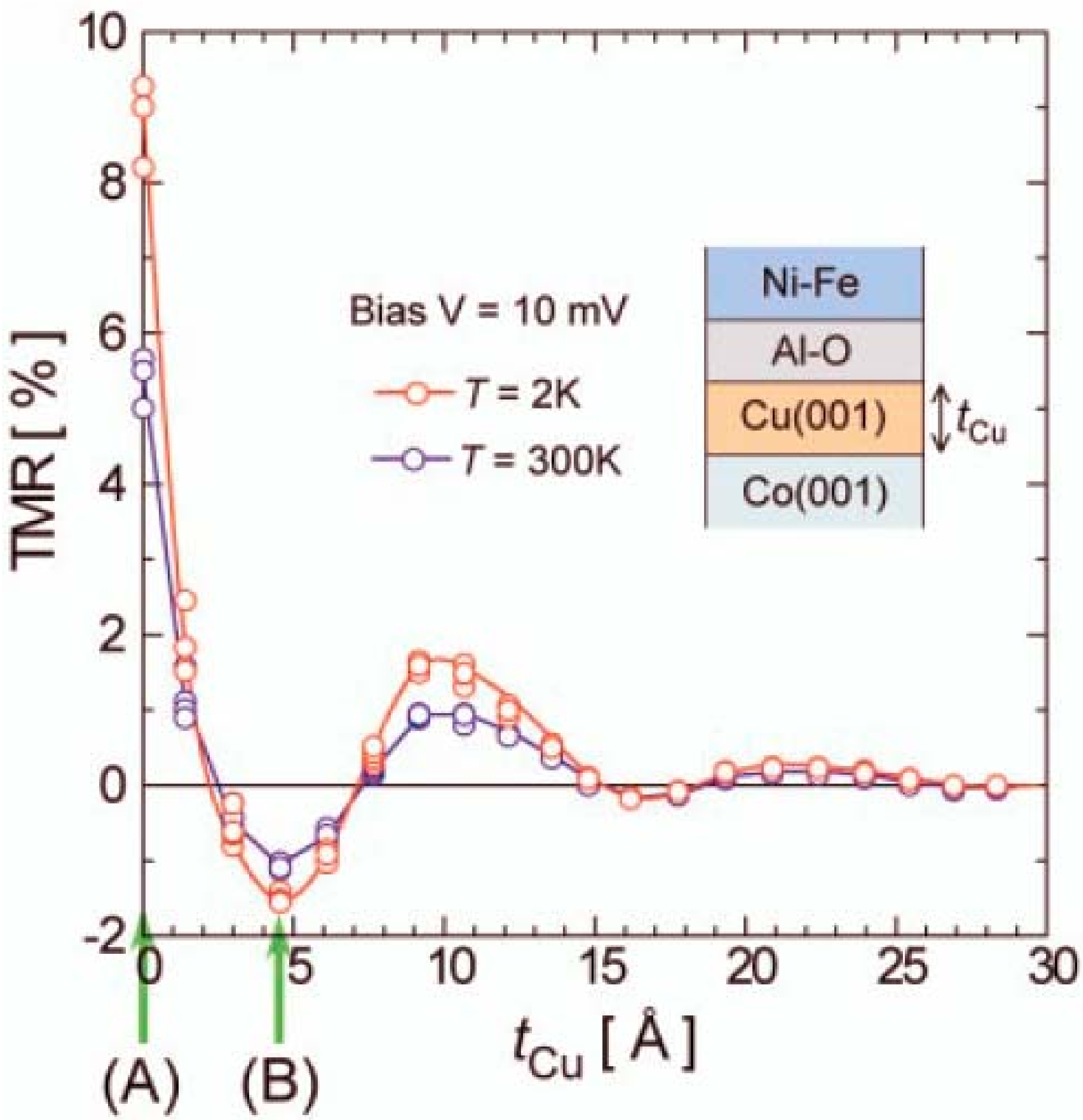
- **contradictory to free-electron calculations,**
  showing strong QW-oscillations

Quantum oscillations in TMR: resonant tunneling

Coherent reflection/ transmission at interfaces



… using epitaxial layers

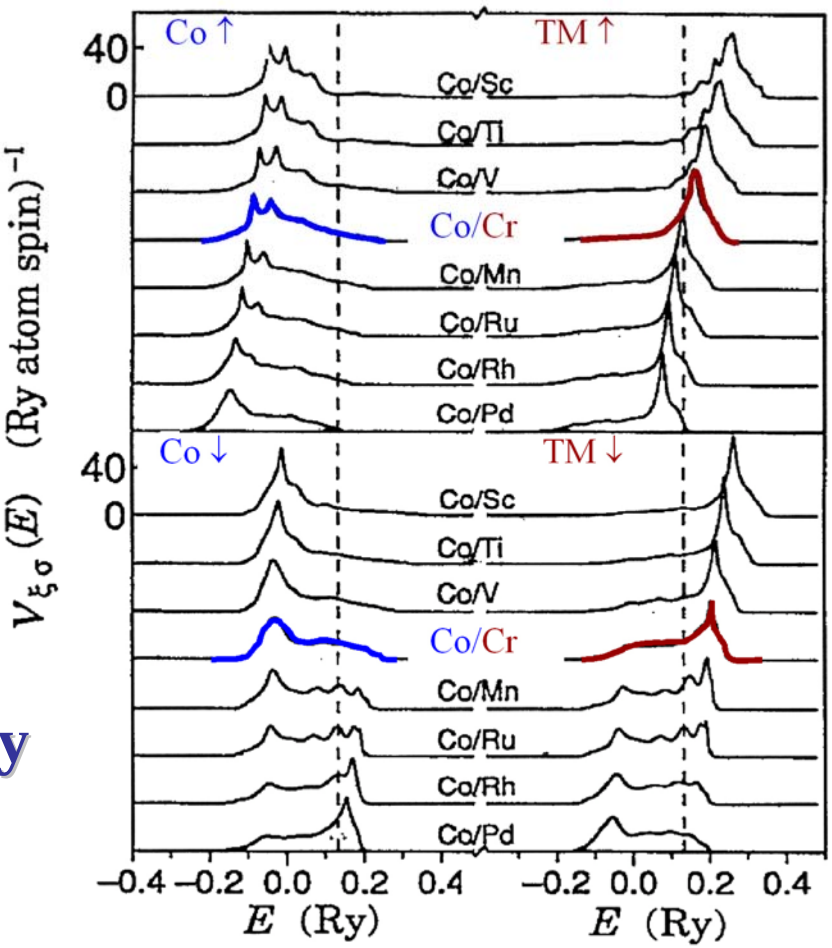


Yuasa et al.

What to do next?

- could we engineer interfacial electronic structure?
- Co/TM interfaces well-known;
  large band mismatch
  e.g. Cr and Ru: majority s-p LDOS suppressed

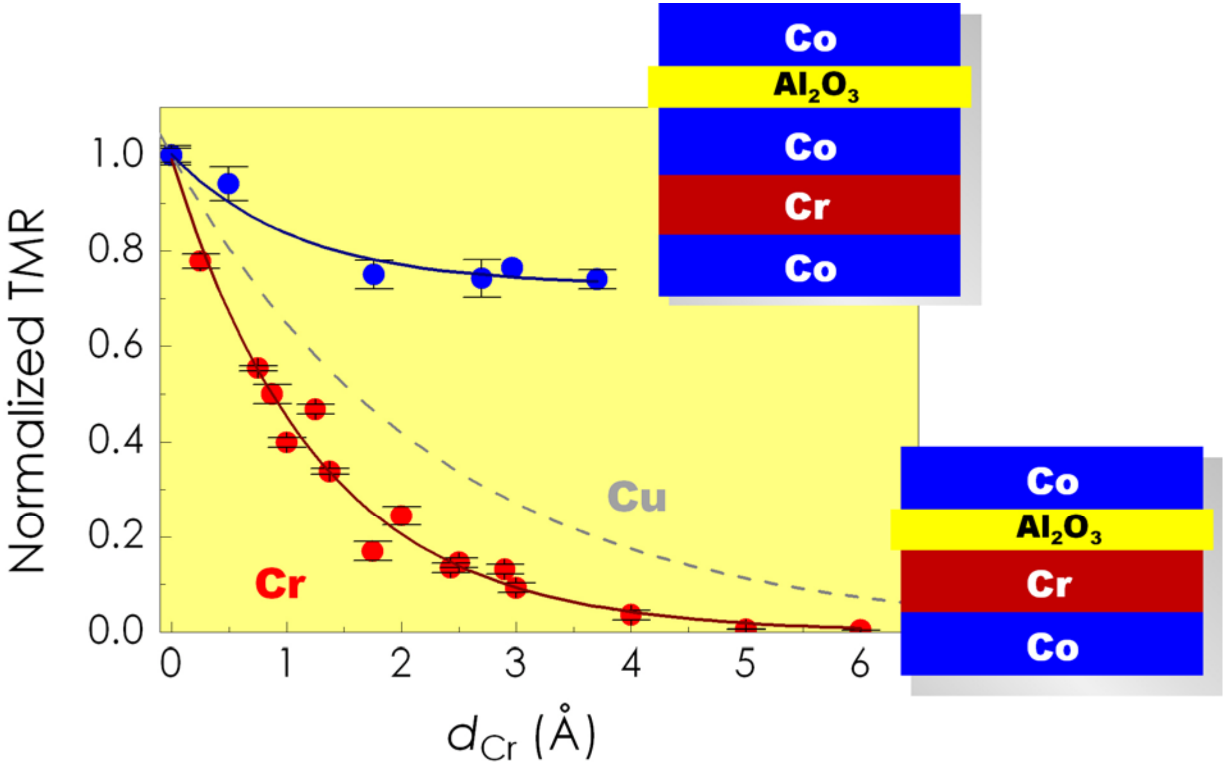
Maekawa et al. 1993



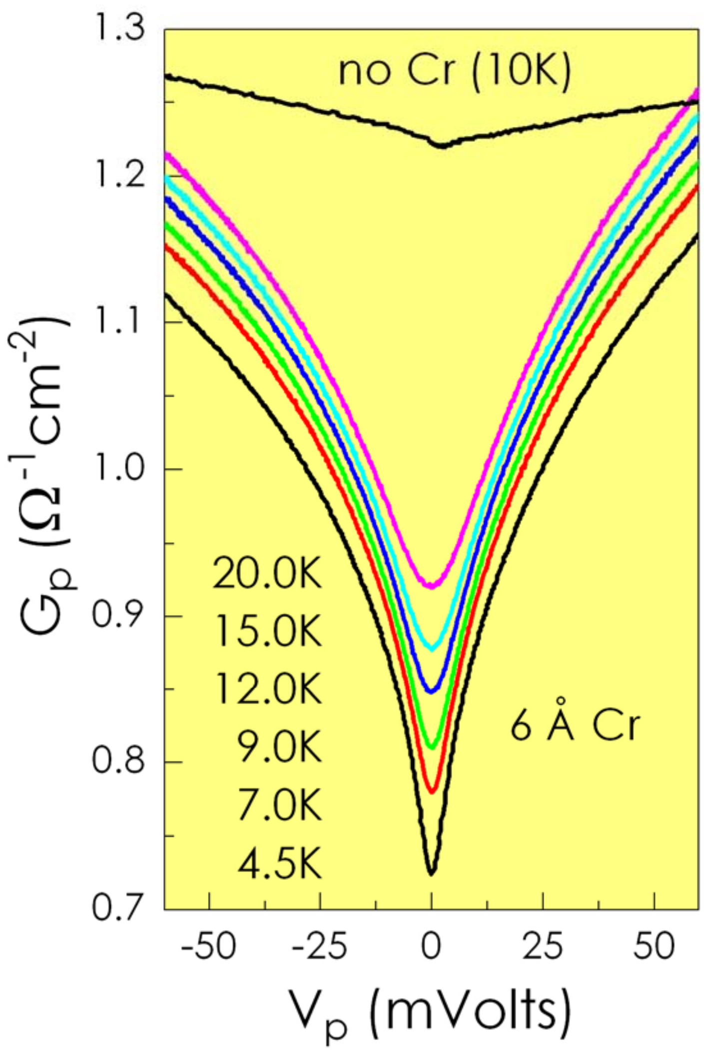
Collapse and recovery of polarization by Cr

- rapid decay for Cr interlayers (twice as fast as Cu); effective polarization nearly 0 for 1ML Cr due to preferential scattering of minority electrons

- TMR restored with only 10Å of Co: interface effect!



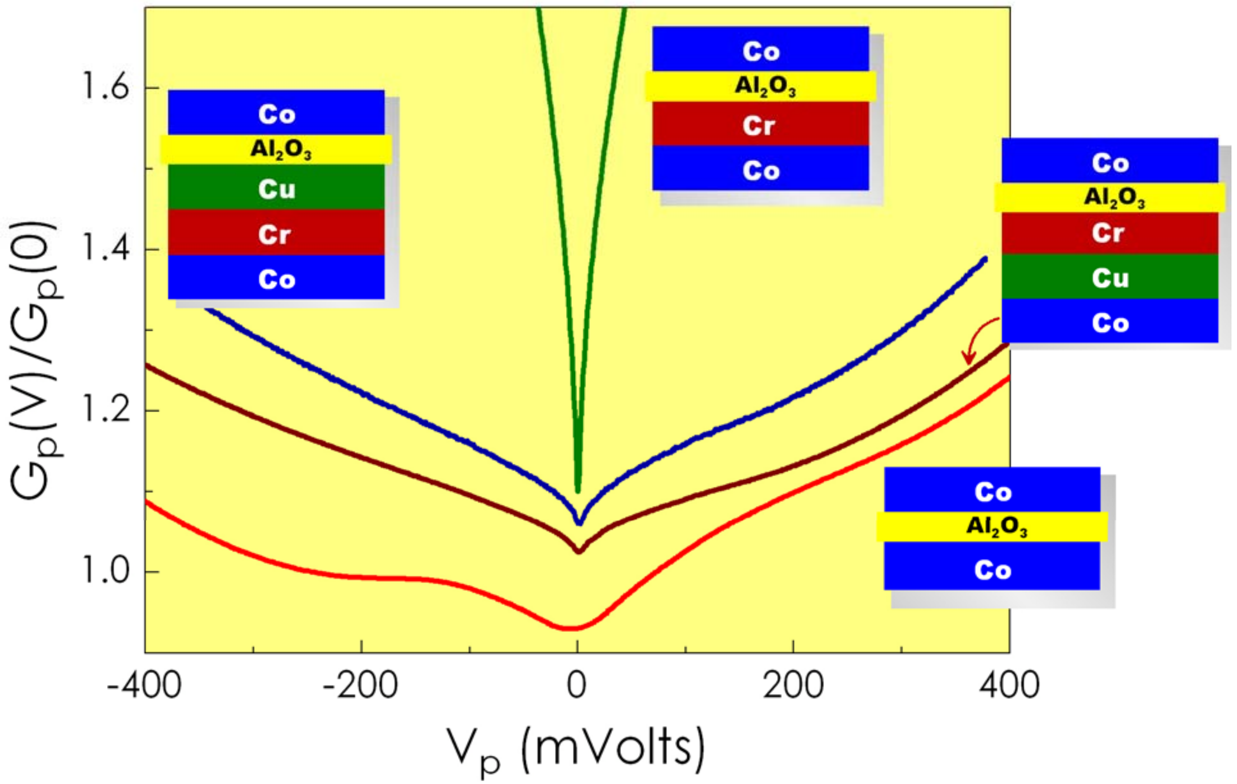
Evidence of altered electronic structure



- **large zero-bias anomalies only for junctions with Cr**
- **physical mechanism**
  - **altered interface DOS**
  - **scattering of conduction electrons by Cr d moments**

Is the interface responsible?
Which interface is responsible?

Evidence of altered electronic structure



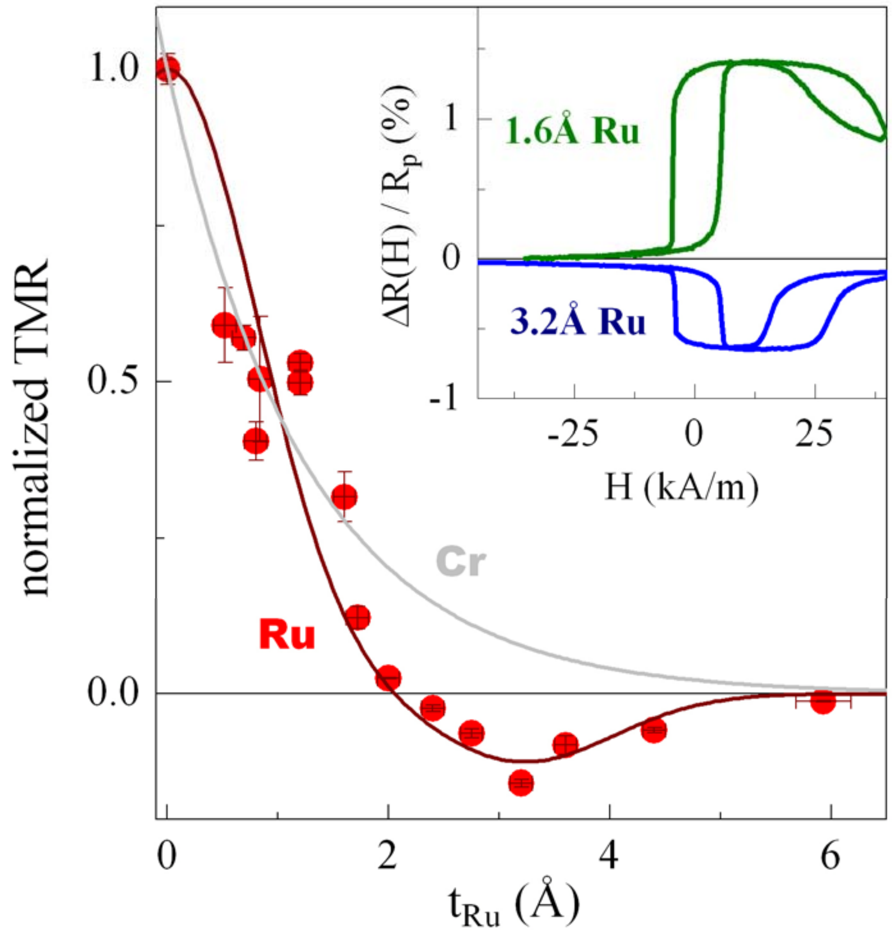
anomalies only when Cr is backed by Co and near barrier interface
"burying" Co/Cr or separating Co and Cr (by Cu) removes them

so: Co/Cr interface responsible, must be near barrier

Similar LDOS mismatch: Ru as interlayer

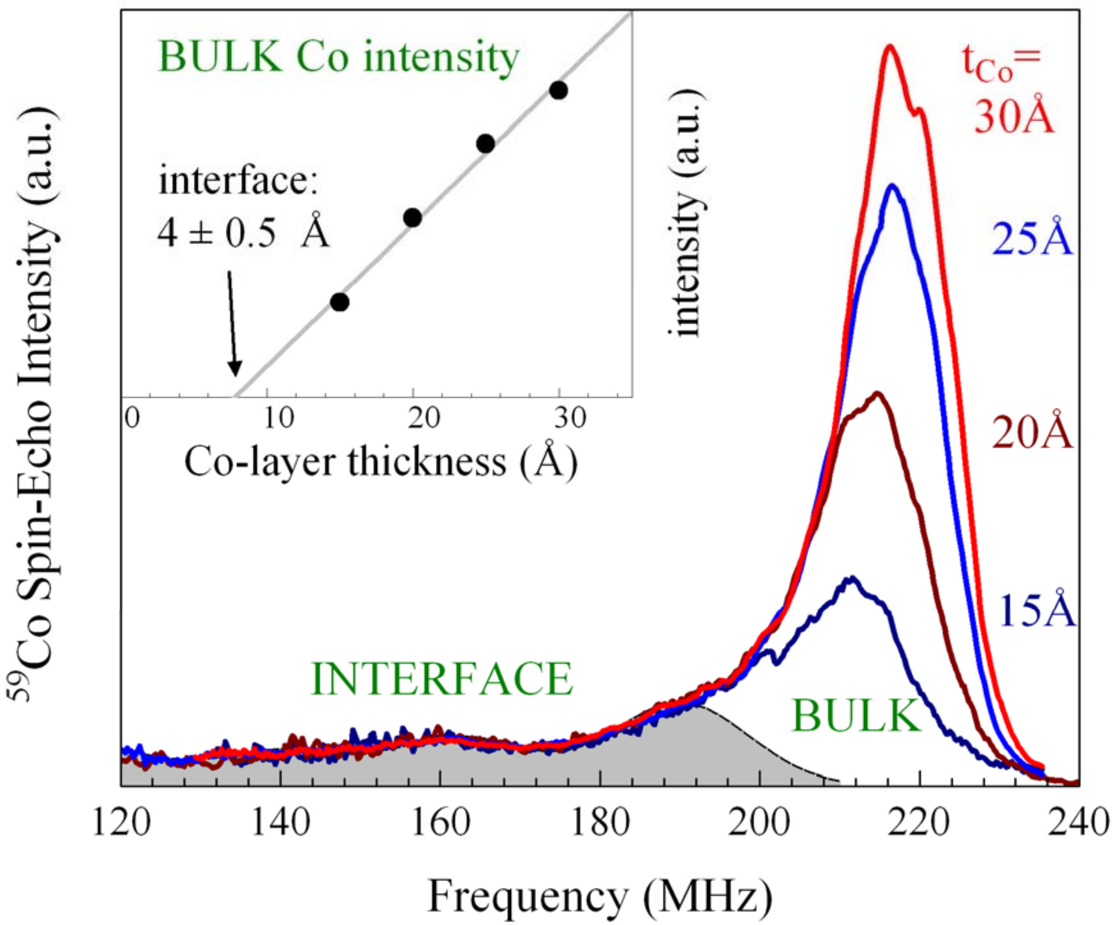
- fast decay: consistent with Cr (also zero bias anomalies seen)
- however: sign reversal at 1ML! magnetic behavior unchanged

What could make TMR negative in the Ru case?

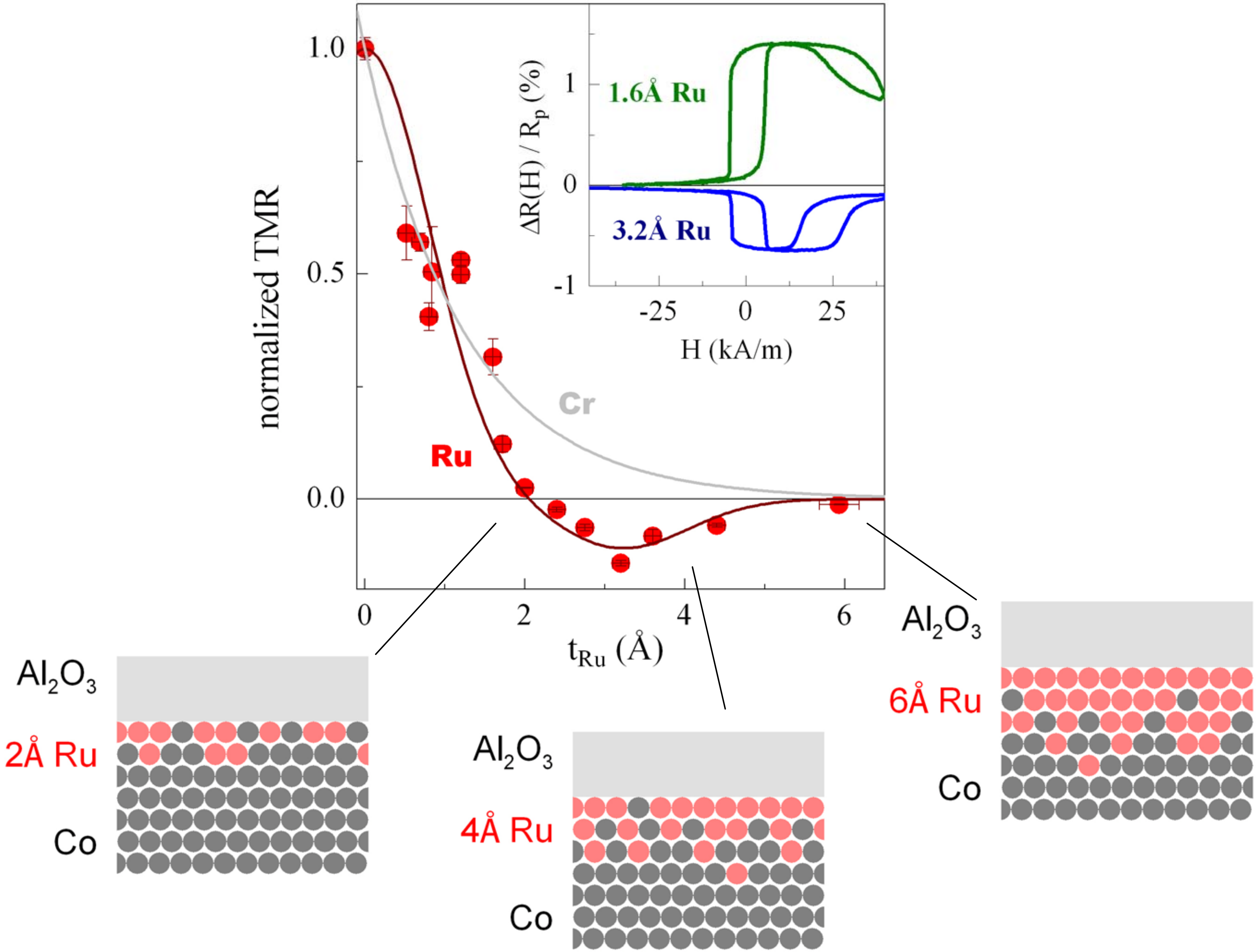


^{59}Co NMR: probing the interface alloy

NMR measures local field at Co nuclei
sensitive to local environment: bulk vs. interface

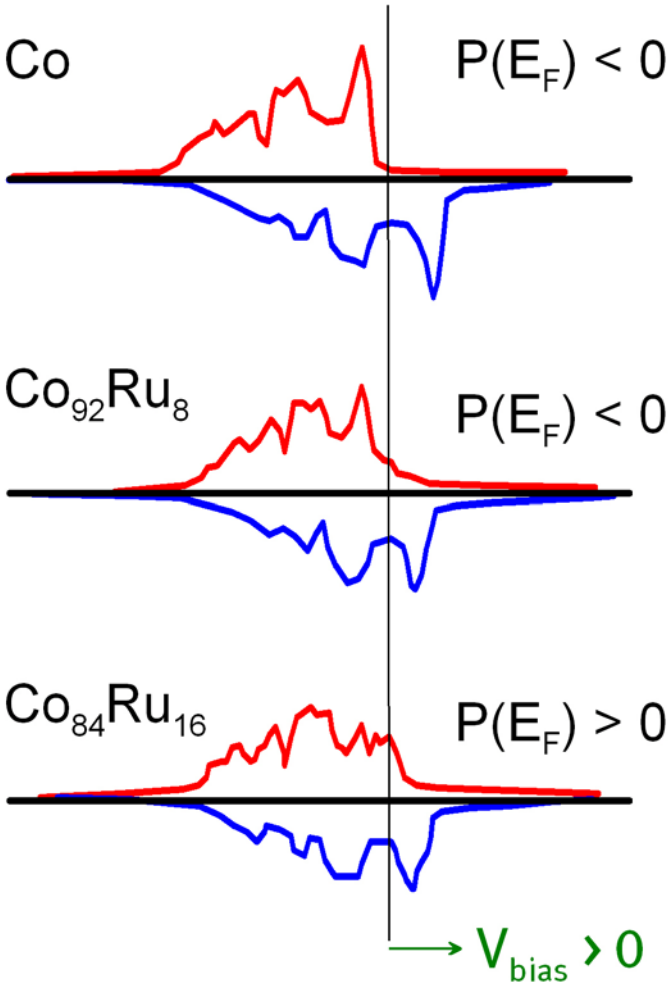


- **Co/Ru multilayers with variable t_{Co}**
- **for vanishing bulk signal: contribution only from interfaces**
- **result: 4-5 Å Co/Ru alloyed at interface**



normalized TMR
1.0
0.5
0.0
0
2
4
6
t_{Ru} (Å)
Cr
Ru
ΔR(H) / R_p (%)
1
0
-1
-25
0
25
H (kA/m)
1.6Å Ru
3.2Å Ru
Al_2O_3
2Å Ru
Co
Al_2O_3
4Å Ru
Co
Al_2O_3
6Å Ru
Co

Toy model based on LDOS calculation



- tunneling polarization tracks d-dominated P inversely
- majority DOS peak shifts through E_F by adding Ru

this explains negative TMR

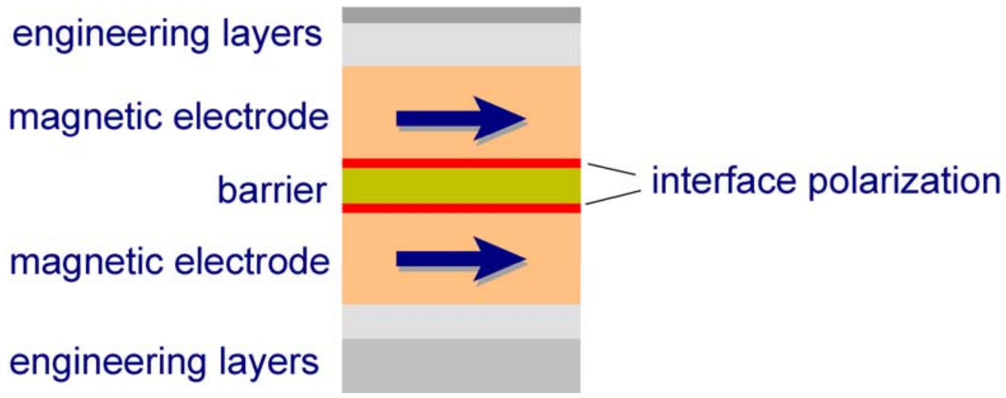
- with positive bias, DOS above E_F is scanned of Co-Ru alloy

explains sensitive bias dependence when P reverses sign (not shown)

Conclusions on interface/barrier engineering

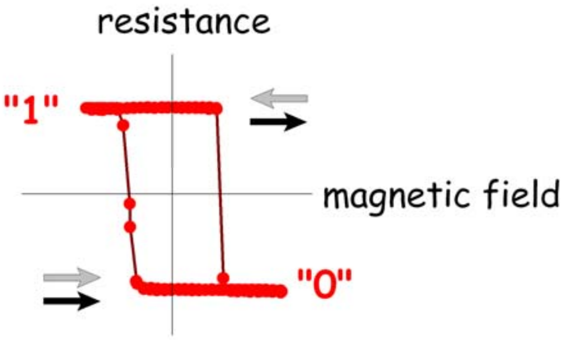
- **Spin tunneling determined by combined system of barrier & (magnetic) interfaces**

- **Engineering magnetic junctions for (large) TMR: interfaces at barrier are key!**



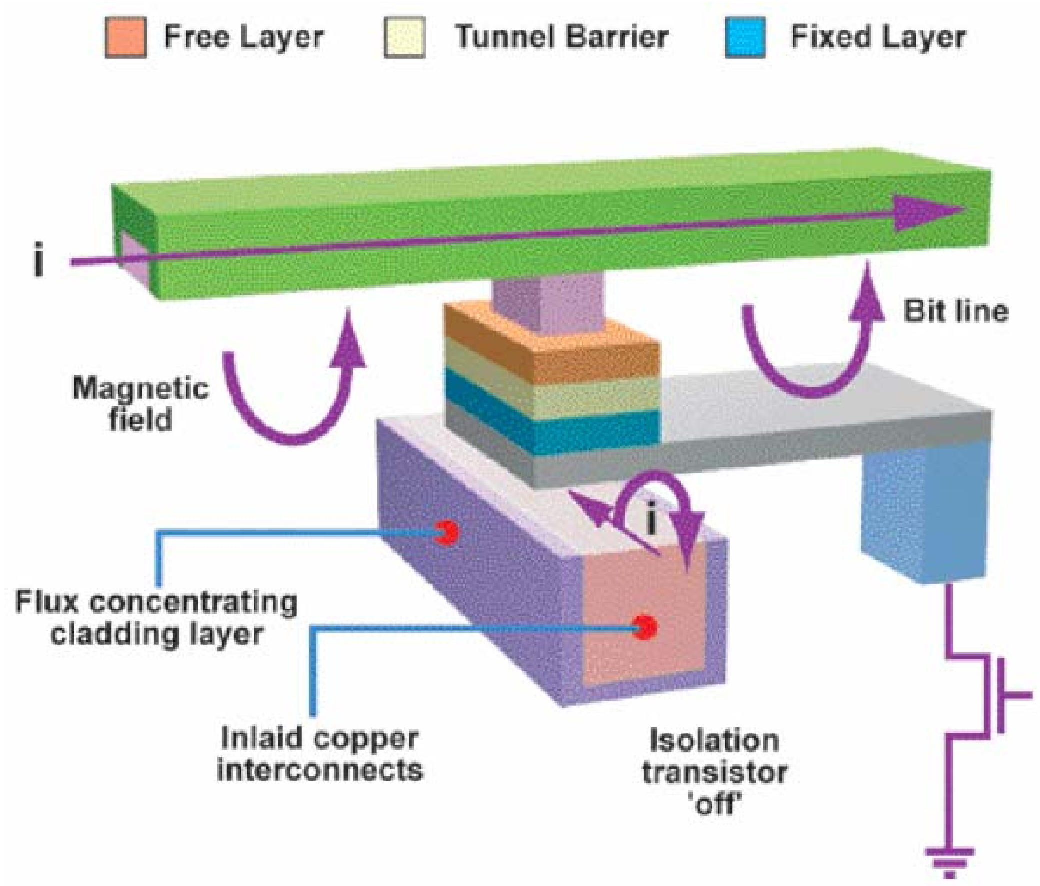
Back to MRAM application issues …..

- wafer uniformity
- dielectric breakdown
- barrier pinholes
- process temperature



Mag-RAM

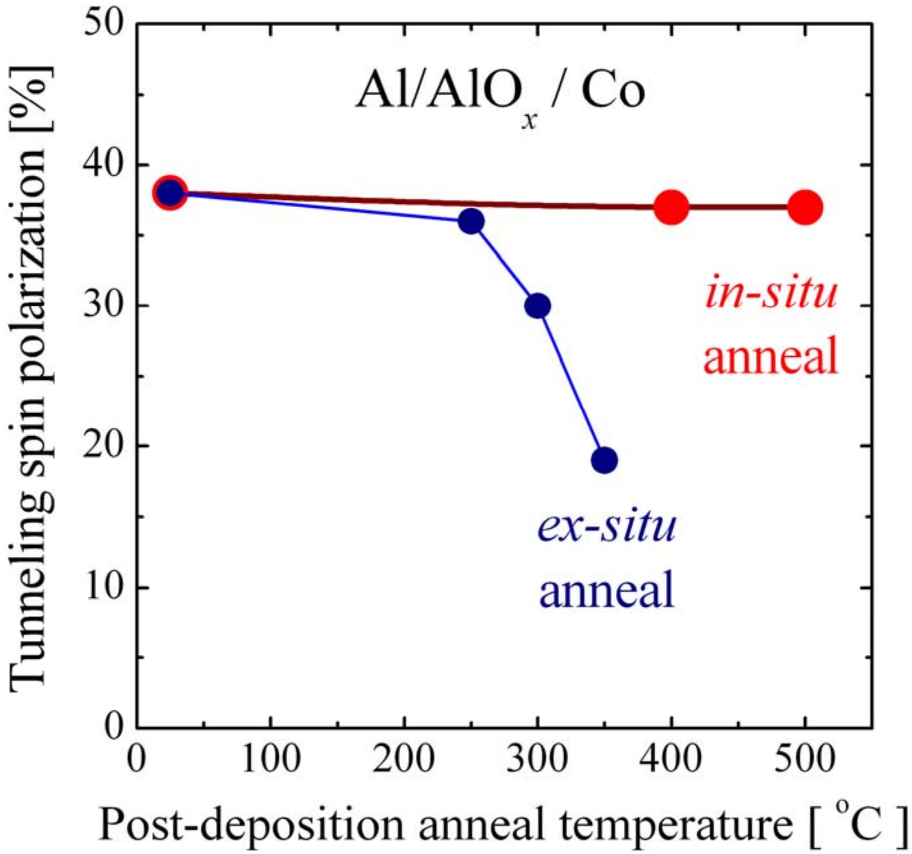
Implemtentation into CMOS: high-temperature steps



Motorola MRAM

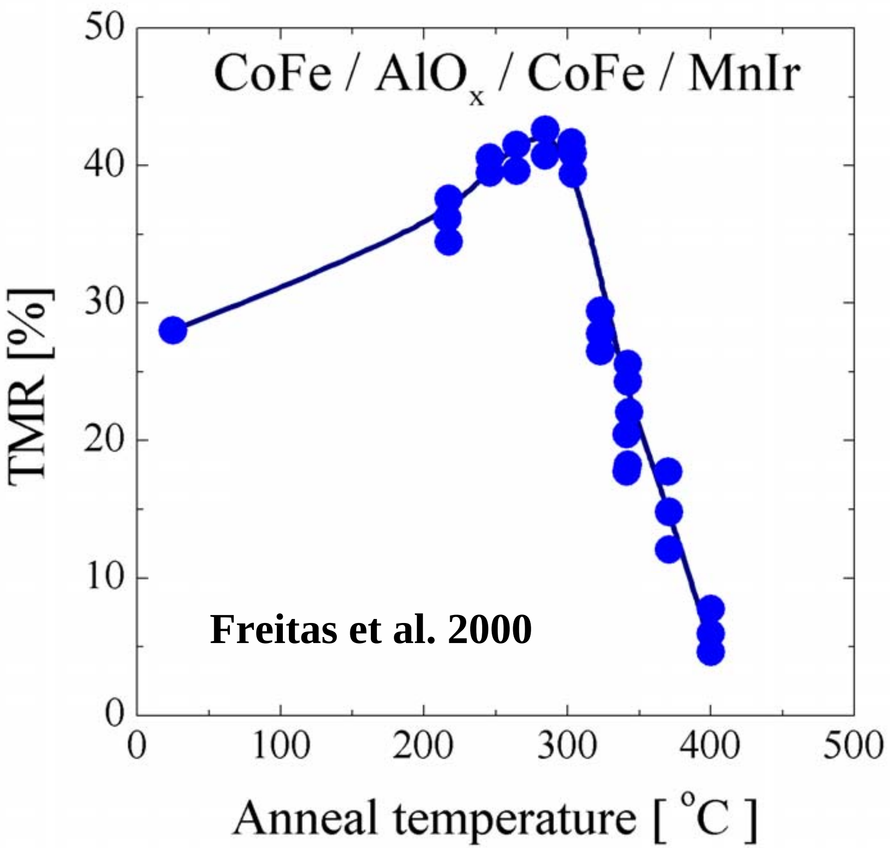
Does TMR survive high-temperature treatments?

First of all: *P* is extremely thermally stable (up to 500°C)



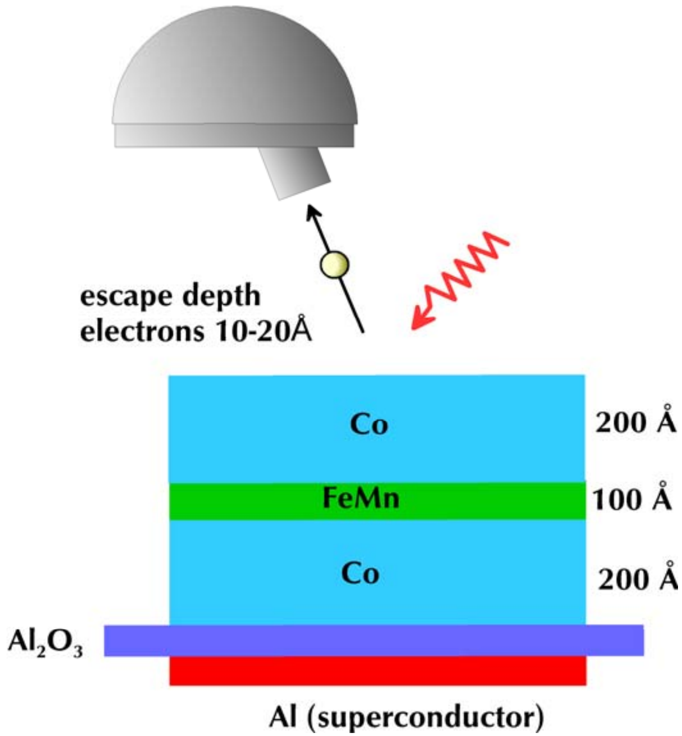
- **take good care of annealing conditions!**
- **note: *P* changes, but NO other junctions property**

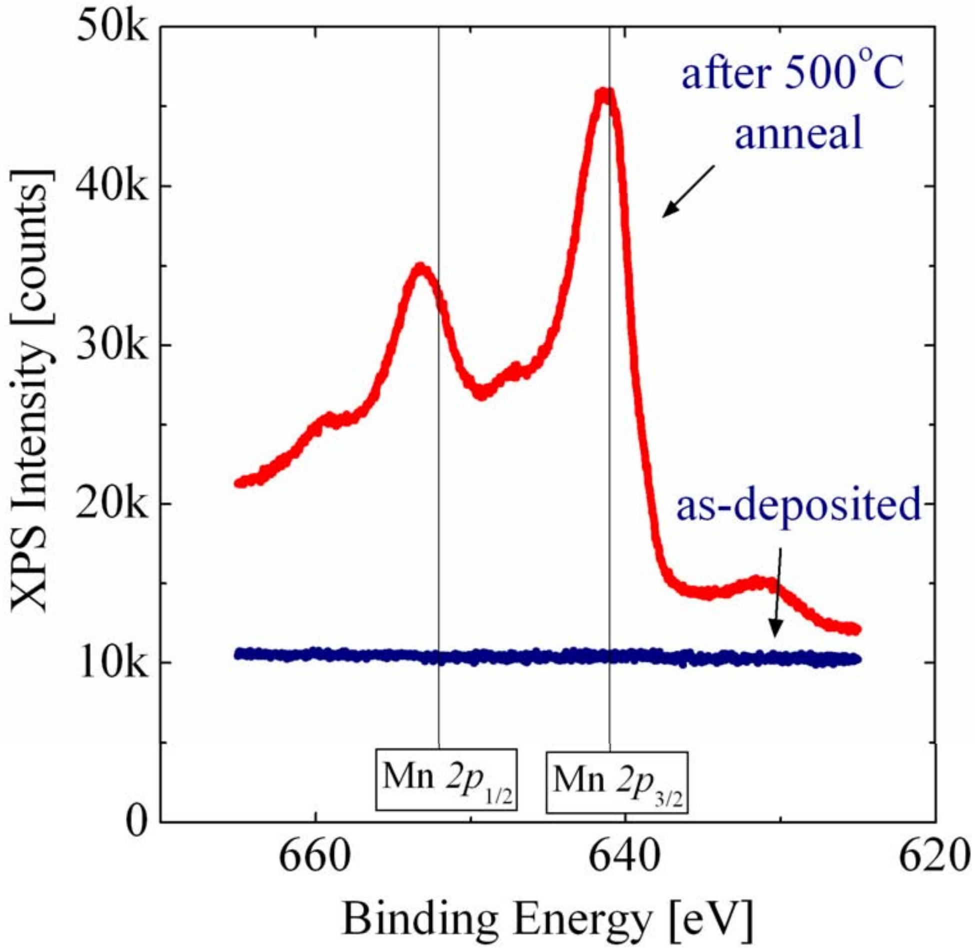
However: collapse of TMR beyond 300°C



- R×A product not affected: tunneling barrier OK
- Mn diffusion from exchange-bias layer involved! (see e.g. Freitas et al.)

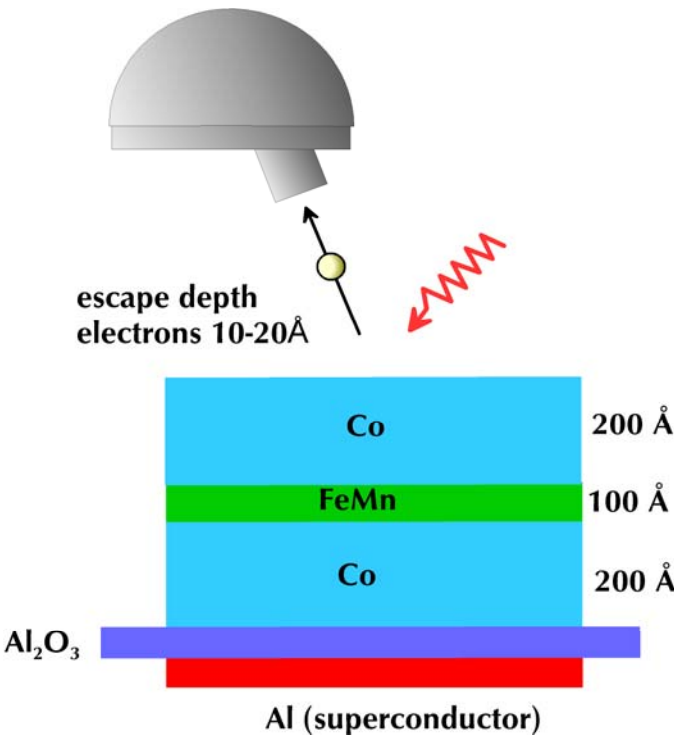
XPS on FeMn / Co(200Å) to probe surface composition

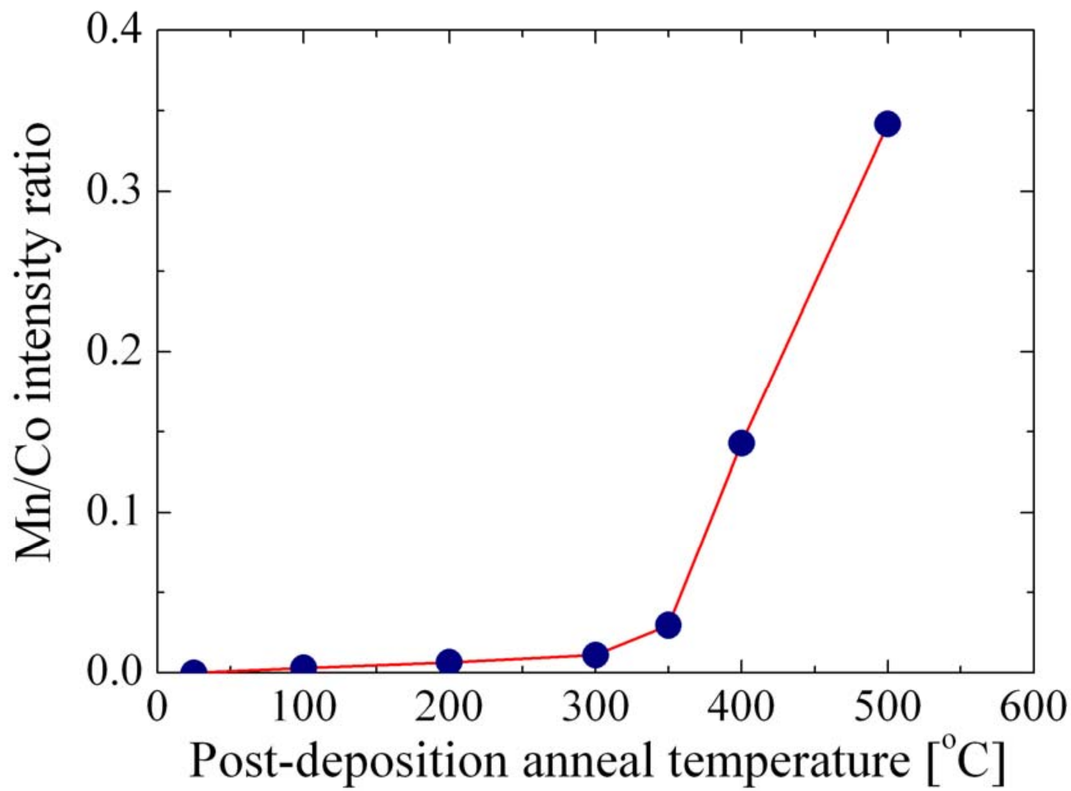




Mn signal emerges after anneal: it diffuses!

Mn/Co ratio from XPS as function of T_{anneal}

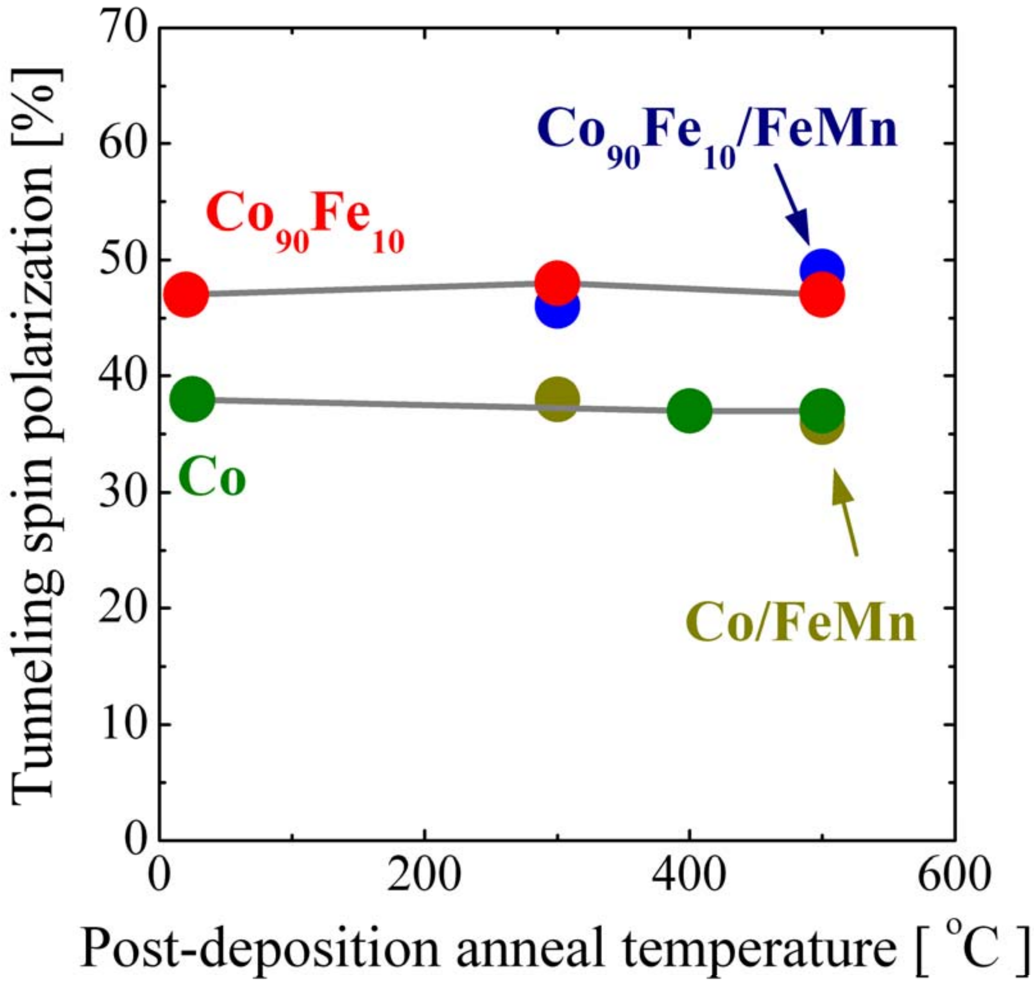




Mn clearly diffuses beyond T = 300°C ….

Related to TMR (polarization) collapse!?

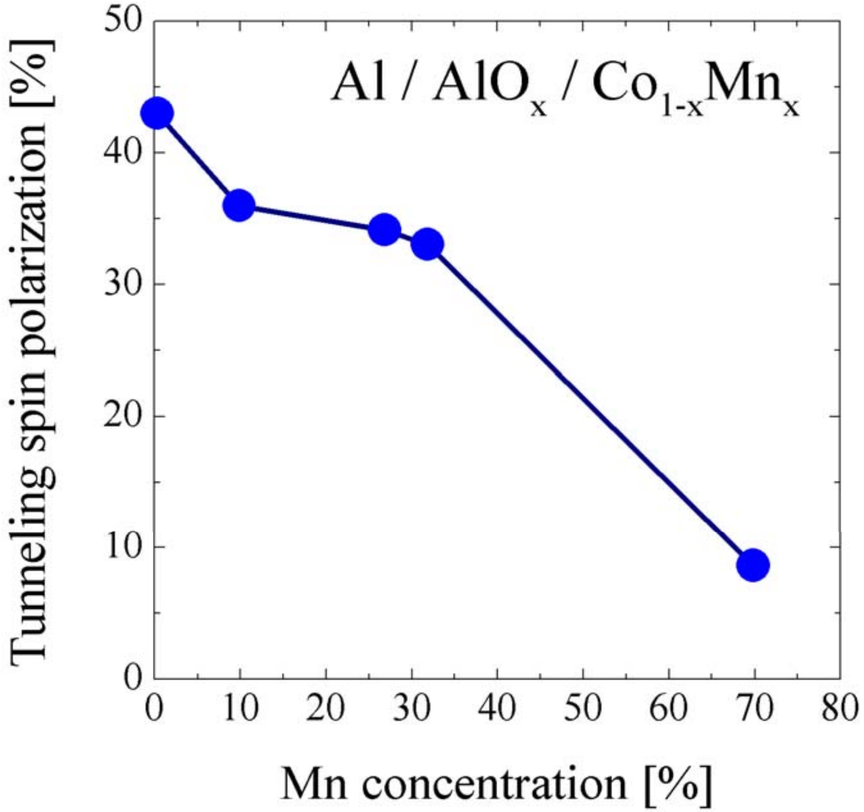
Surprise: Al / AlOx / Co(Fe) / FeMn junctions



Nó effect on *P* is visible!

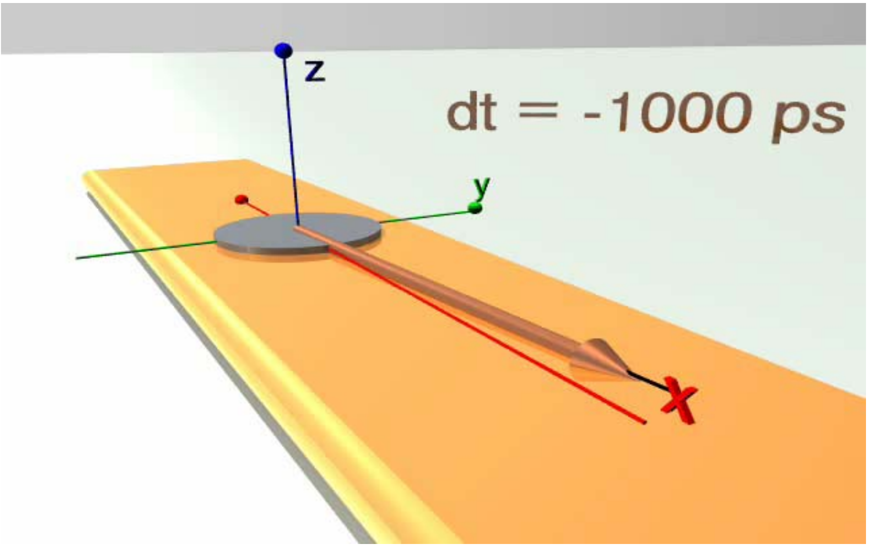
No conclusive answers yet why TMR collapses ….

- Mn at the Co(Fe) / AlOx interface is NOT decrimental to tunneling spin polarization
- In agreement with Moodera, Kim et al. (PRB 2002)



Current/future research directions: few examples

- switching dynamics (MRAM-cells)

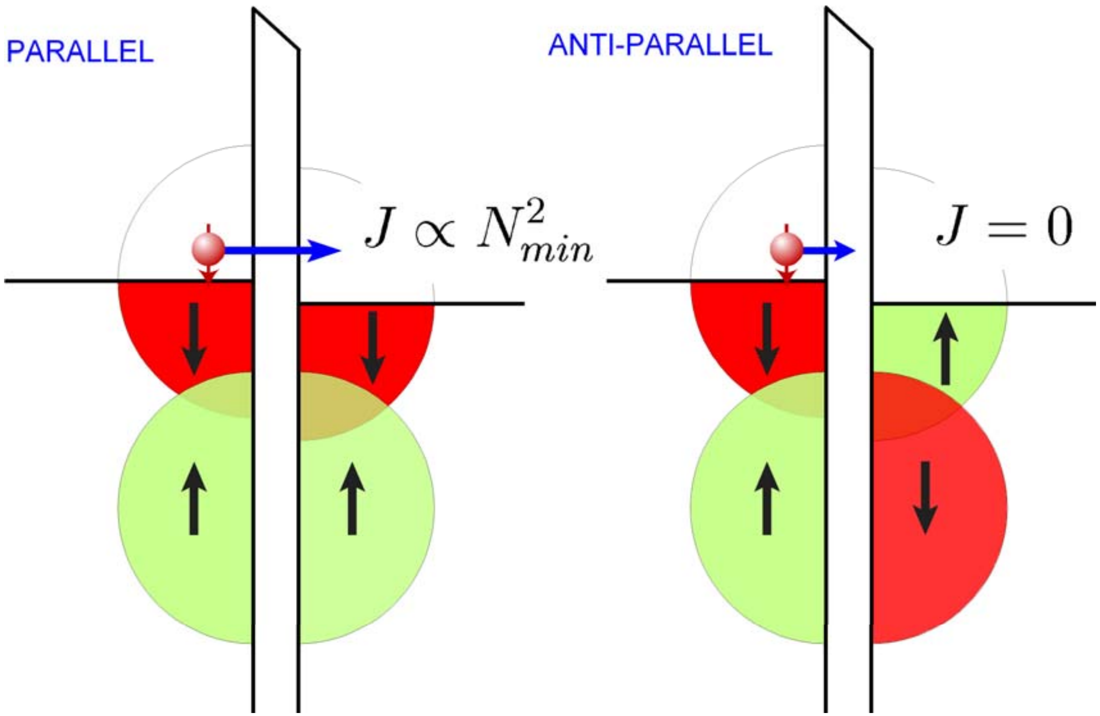


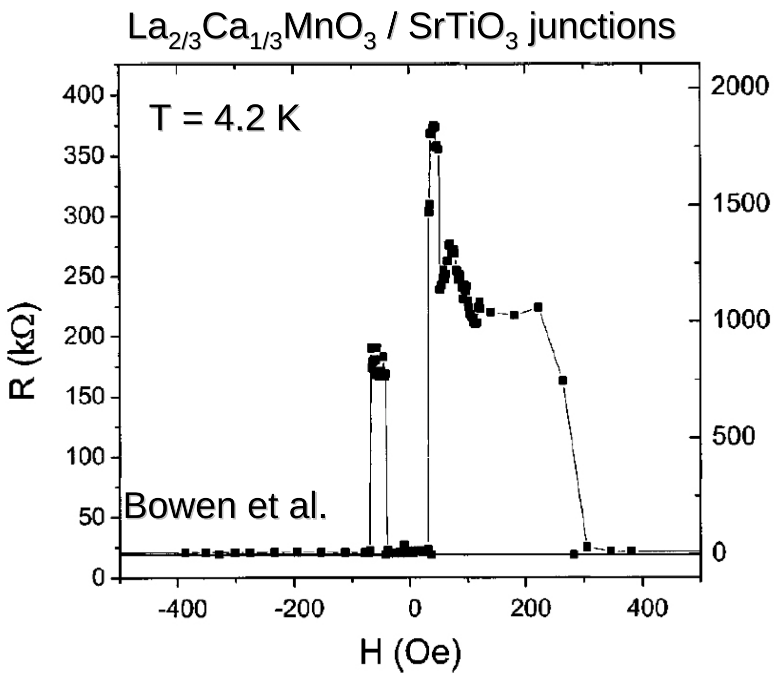
Real-time spin dynamics of NiFe dot by current pulse TU/e 2003

- epitaxial junctions (nice physics, high TMR !)
- half-metallic electrodes ($P_M \rightarrow$ 100%)
- organic (molecular) spintronics
- barriers for semiconductor spintronics

Challenge for TMR materials: $P \rightarrow 100\%$

$$\Delta R/R = \frac{2P_M^1 P_M^2}{1 - P_M^1 P_M^2}$$ approaches infinity!

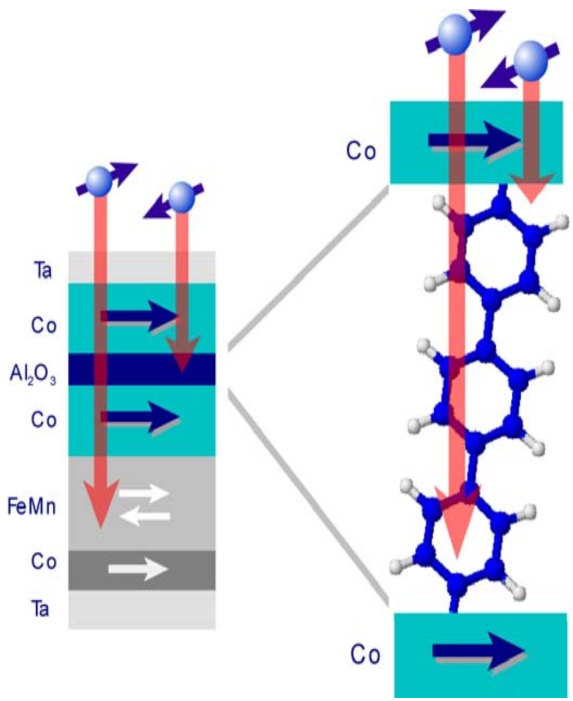




"half-metallic" candidates: LSMO, CrO_2, Fe_3O_4, …..

Current/future research directions: few examples

- switching dynamics (MRAM-cells)
- epitaxial junctions (nice physics, high TMR !)
- half-metallic electrodes ($P_M \rightarrow 100\%$)
- organic (molecular) spintronics

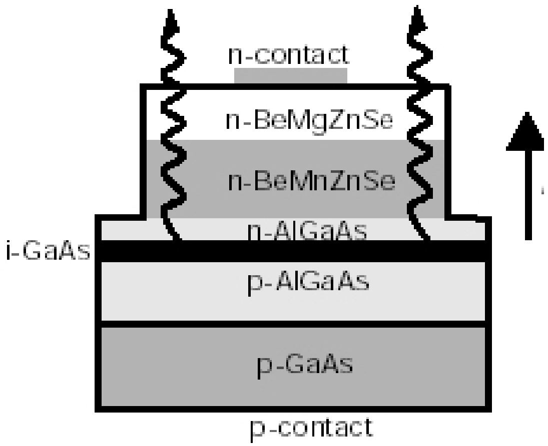


see recent
Nature paper (2004)

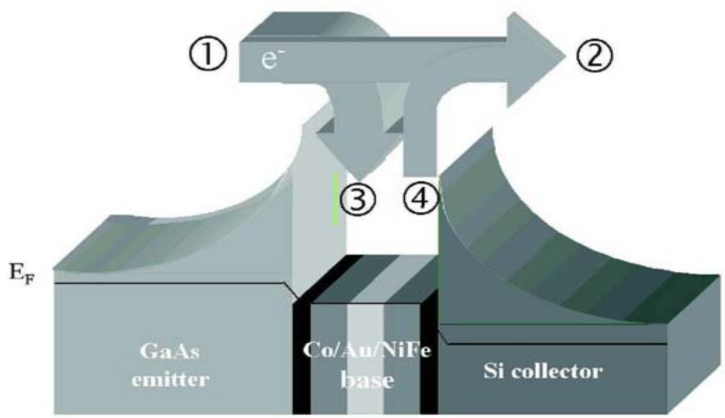
- barriers for semiconductor spintronics

Spin injection into semiconductors

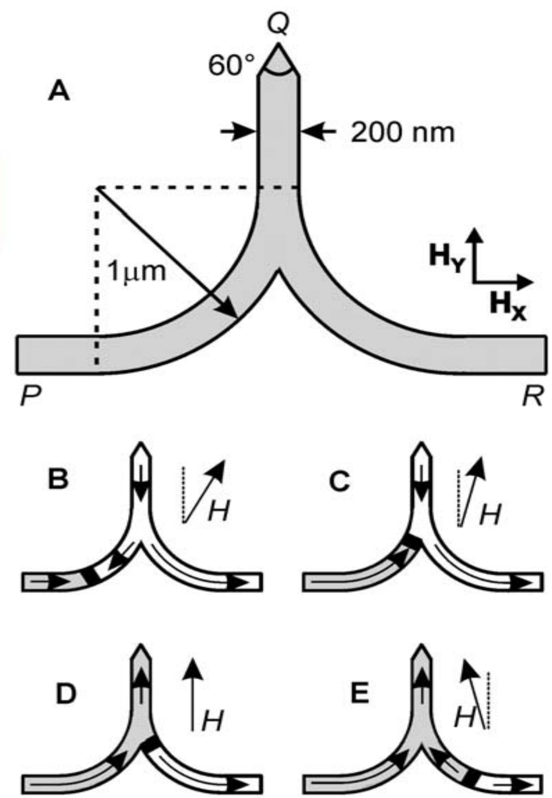
b
Spin LED (DMS)

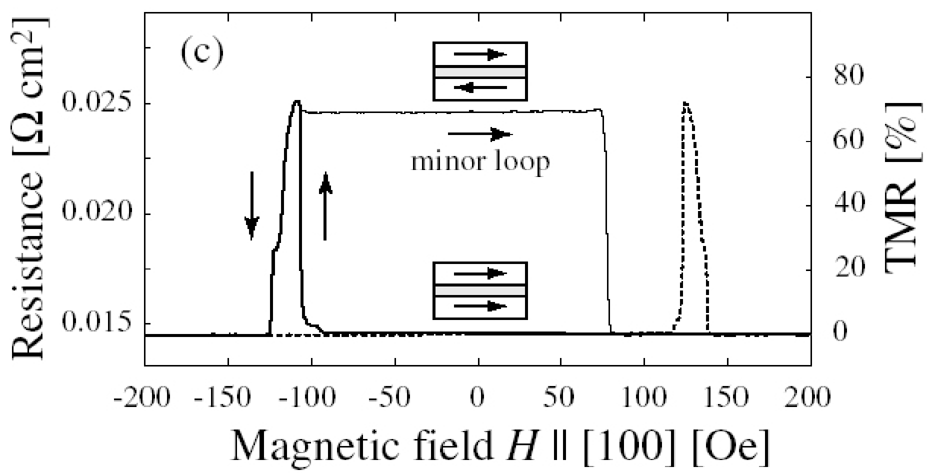


Spin transistor (Si, GaAs)



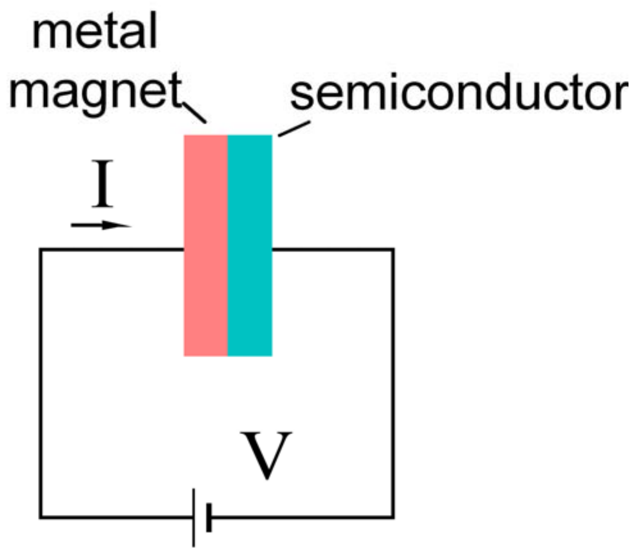
Spin logic



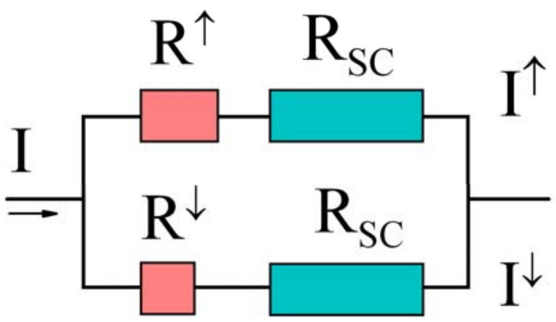


Semiconductor (GaMnAs) spin sources

Spin injection:
a fundamental obstacle ....

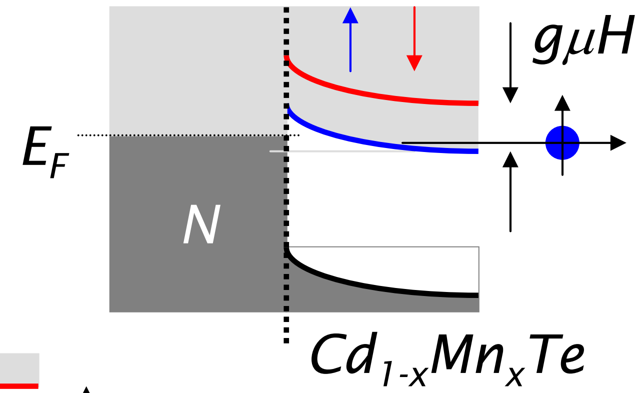


- semiconductor high R, conductivity mismatch
- effectively no injection, spin lost in semiconductor

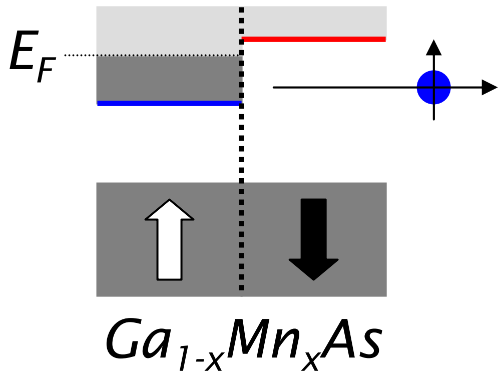


Some solutions ….

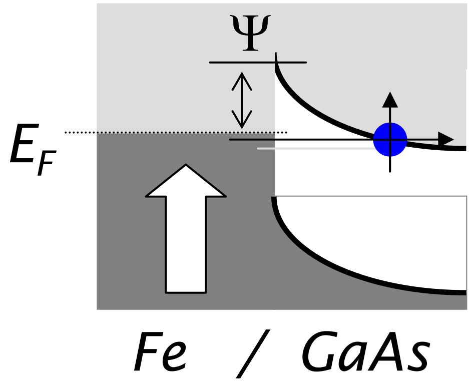
Spin filtering by DMS - Fiederling 1999



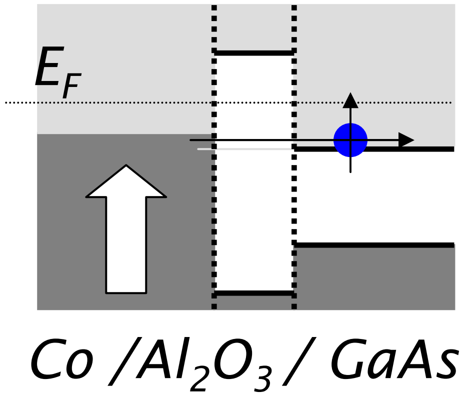
Ferromagnetic semiconductors
Ohno 1999



Injection over tunnel barriers,
Schottky barriers
Jonker 2000

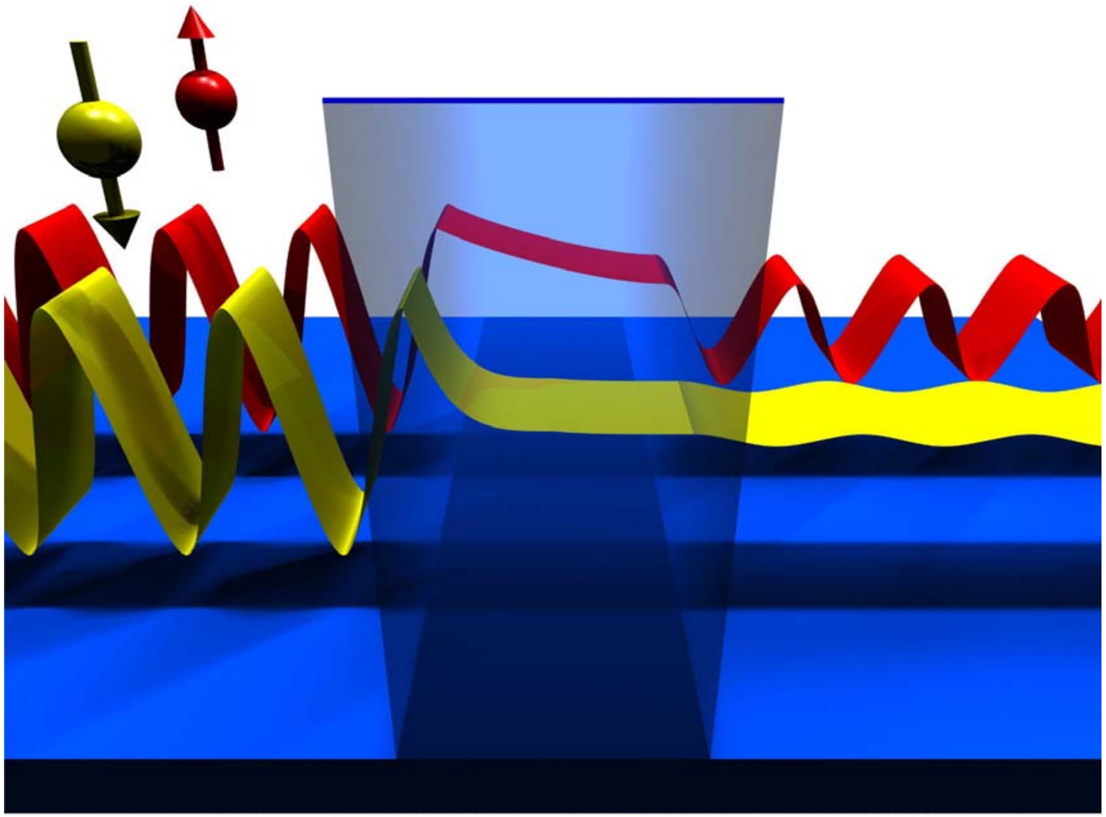


Injection over tunnel barriers,
Al_2O_3 barriers
De Boeck 2002



Present approach:

combining (near) 100% spin polarization and large resistance of magnetic semiconductors



- EuS: model magnetic semiconductor
- novel magnetoresistance effect
- possibility of spin injection

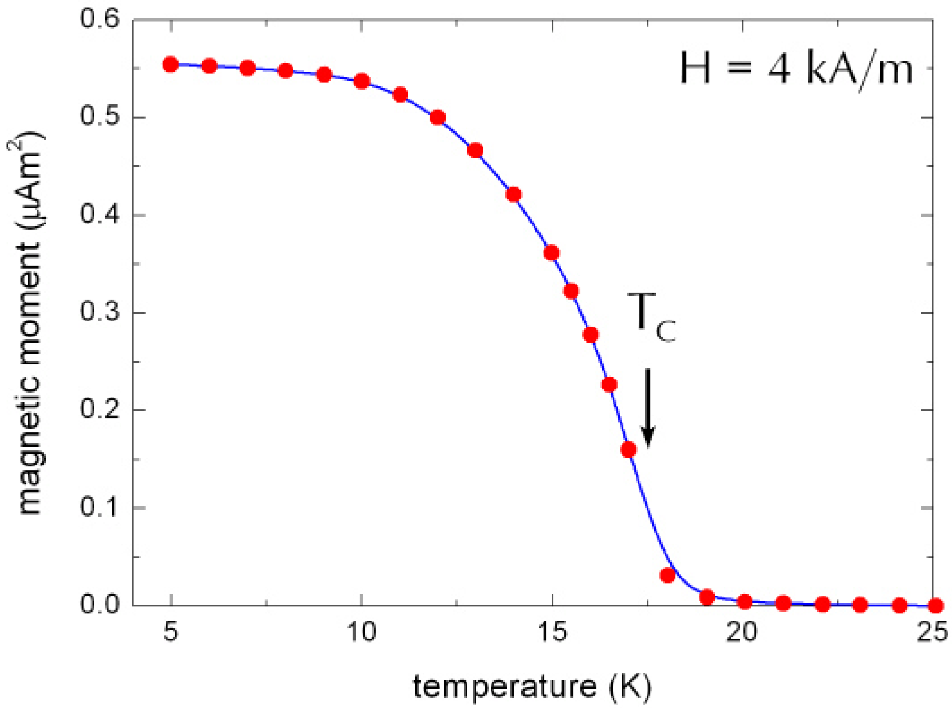
- **Why EuS, why 100% spin polarization?**

- **How to make a new spin-dependent device?**

- **Can we use EuS for spin injection?**

Magnetism of EuS: model Heisenberg ferromagnet

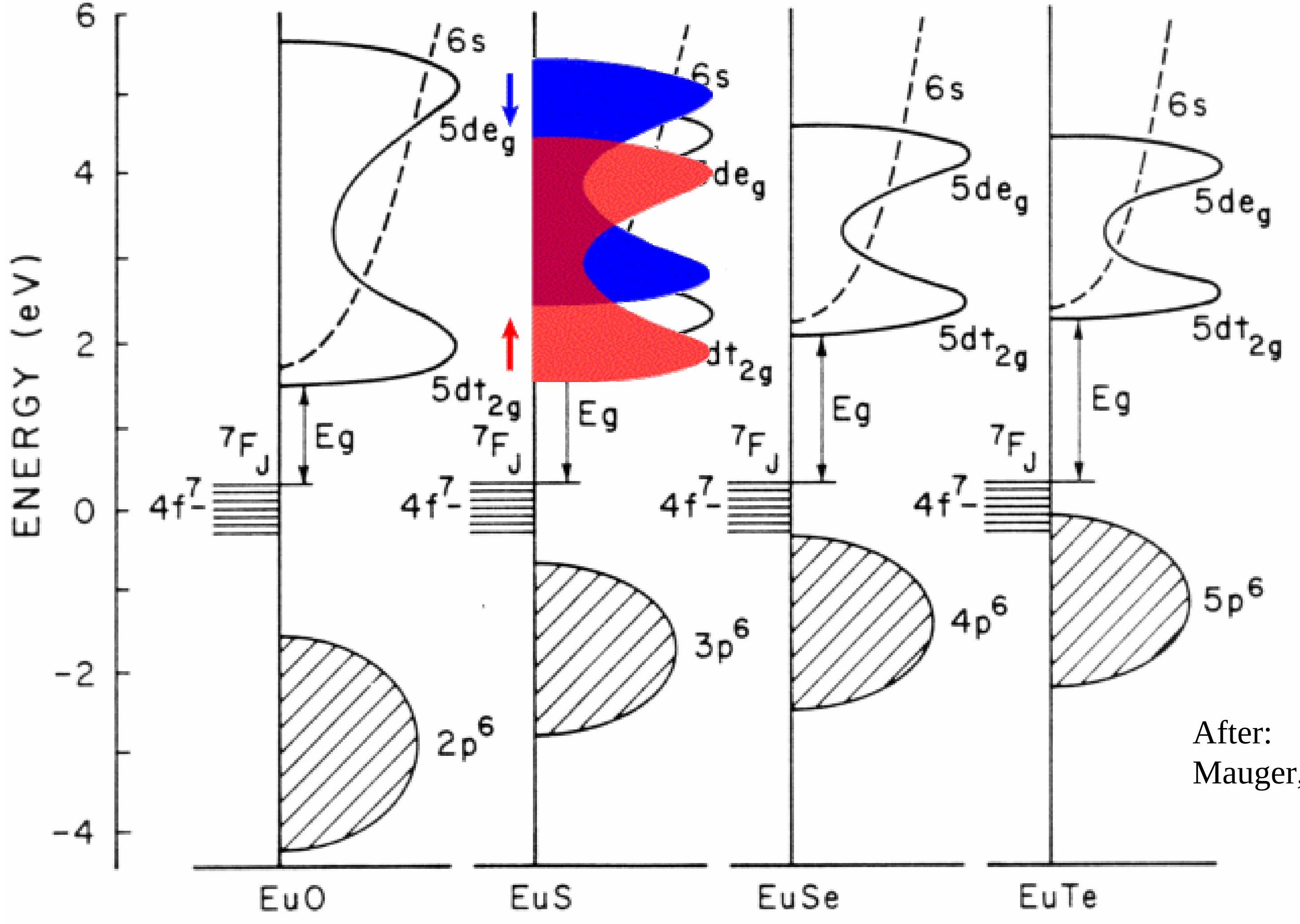
S = 7/2 ($4f^7$) J_{NN} ~ +0.22K, J_{NNN} ~ -0.1 K



- 30 nm EuS on PbS: bulk-like behavior, T_C ~ 17 K

- ferromagnetism down to very thin layers (Story et al., 2000)

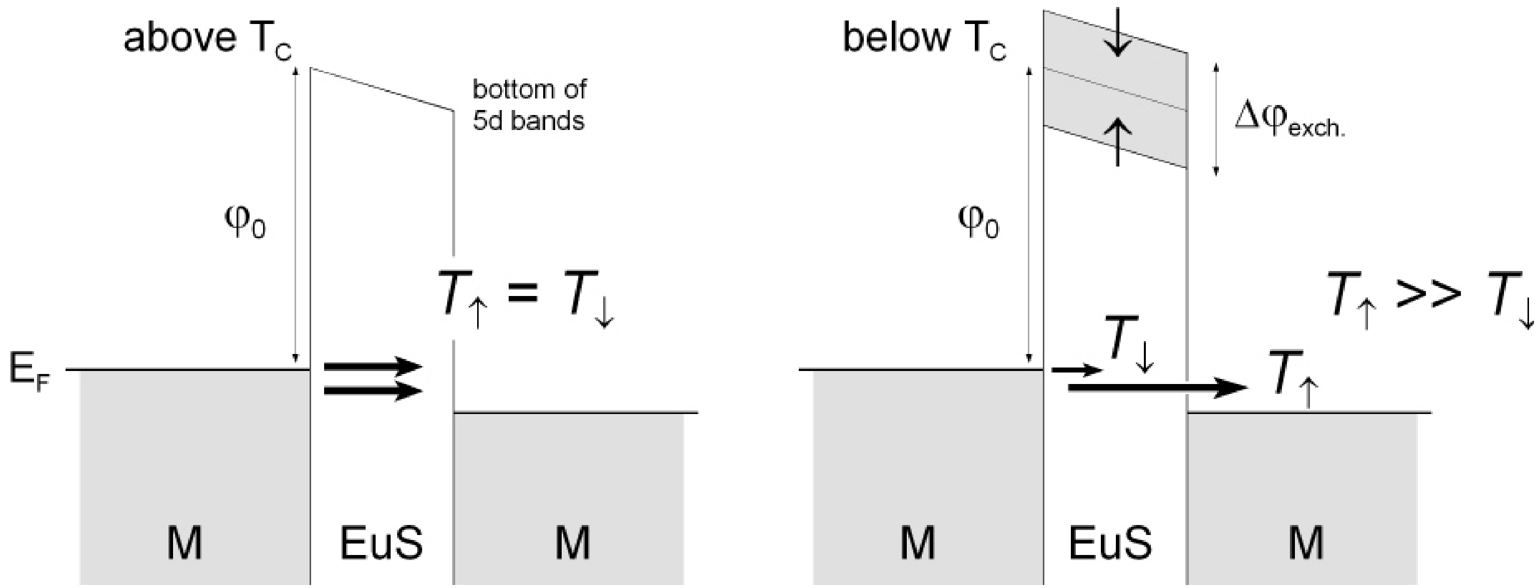
Band structure of Eu chalcogenides



After:
Mauger, Godart '86

Spin-splitted 5d conduction bands key!

Spin-dependent transmission: semiconductor spin polarization



$$P_S = \frac{T_\uparrow - T_\downarrow}{T_\uparrow + T_\downarrow} \quad \text{with} \quad T_{\uparrow\downarrow} \propto e^{-\alpha\sqrt{\varphi_{\uparrow\downarrow}}}$$

using realistic $\varphi_{\uparrow\downarrow}$ ⟹

$$P_S \approx 100\%$$

Au/EuS/Al: superconductor probes EuS spin splitting

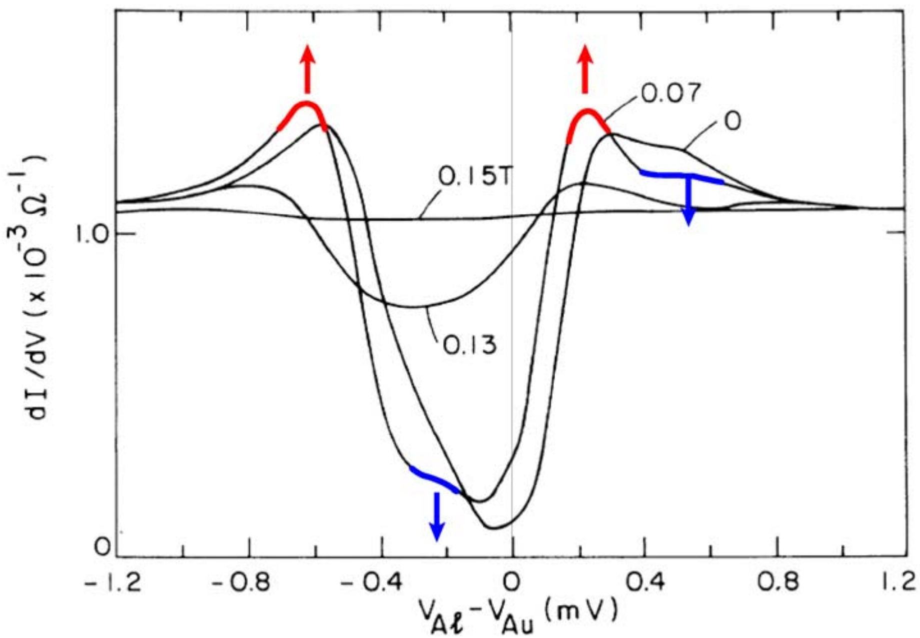
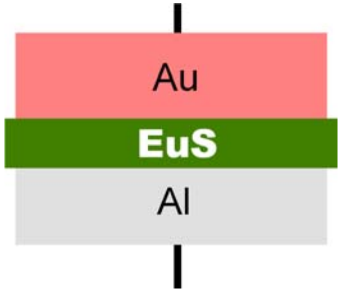
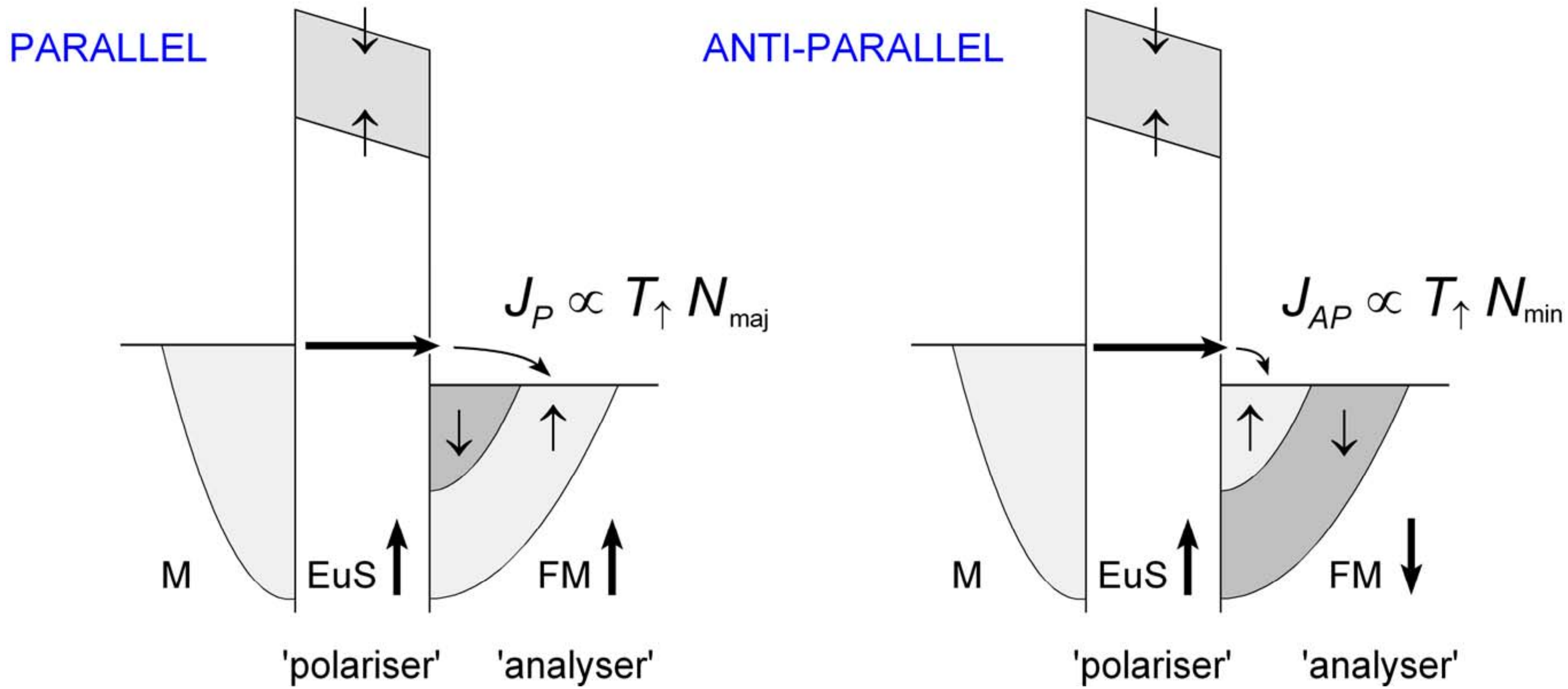


FIG. 2. Conductance vs voltage for a Au/EuS/Al junction from set 2 (Au and EuS deposited at 300 K) at T = 0.4 K for various values of H. A fit of theory to the curves gives P = 80% ± 5%. Curves were all taken in increasing field. Hysteresis was observed in decreasing H, but is not shown.



semiconductor spin polarization P_S more than 80% (Moodera '88)

Construction of a new magnetoresistance device

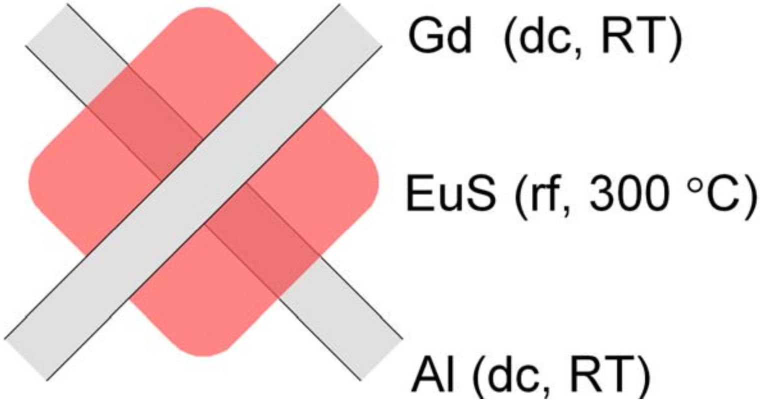


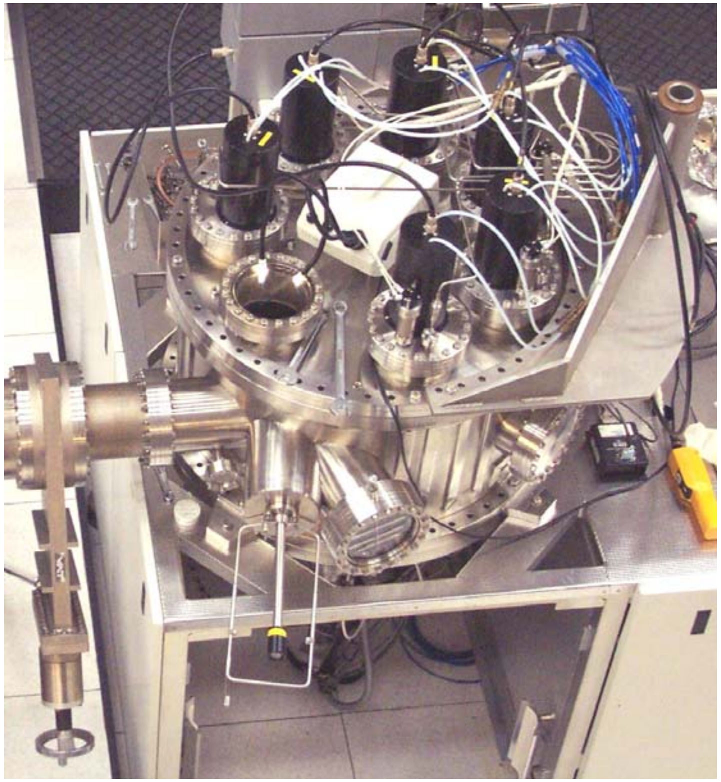
Magnetoresistance:

$$\frac{J_P - J_{AP}}{J_{AP}} = \frac{2P_S P_M}{1 - P_S P_M}$$

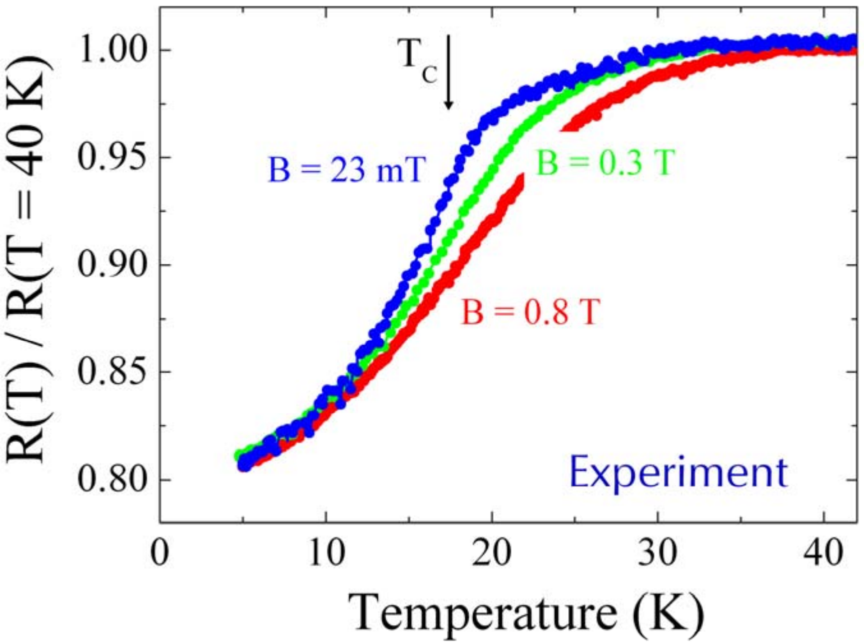
Device preparation: shadow masks & UHV sputtering

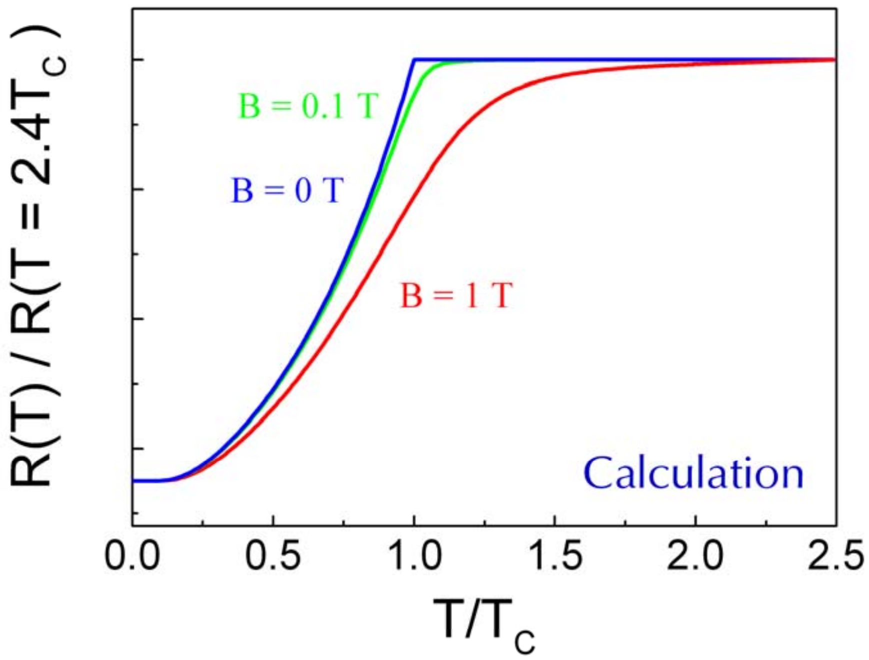
typical central part of device stack





Spin Filtering: T dependence of the junction resistance



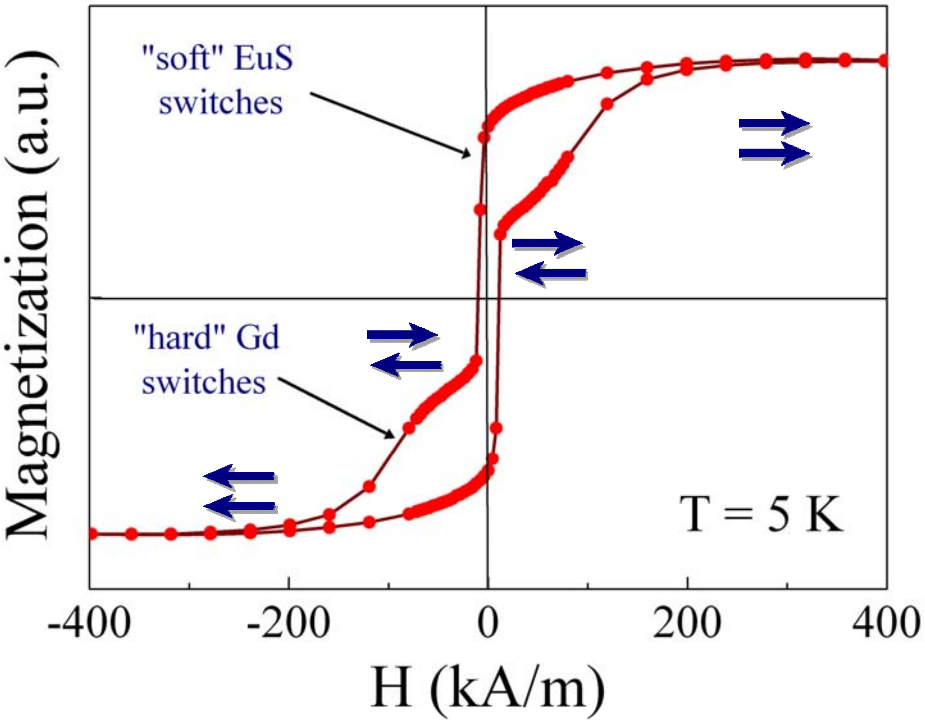


Exchange splitting: $\Delta\varphi_{ex} \propto M(T,B)$

Therefore: spin-up electrons tunnel preferentially below T_C

Independent switching of magnetic constituents?

GaAs(001) / 5 nm EuS / 5 nm Gd



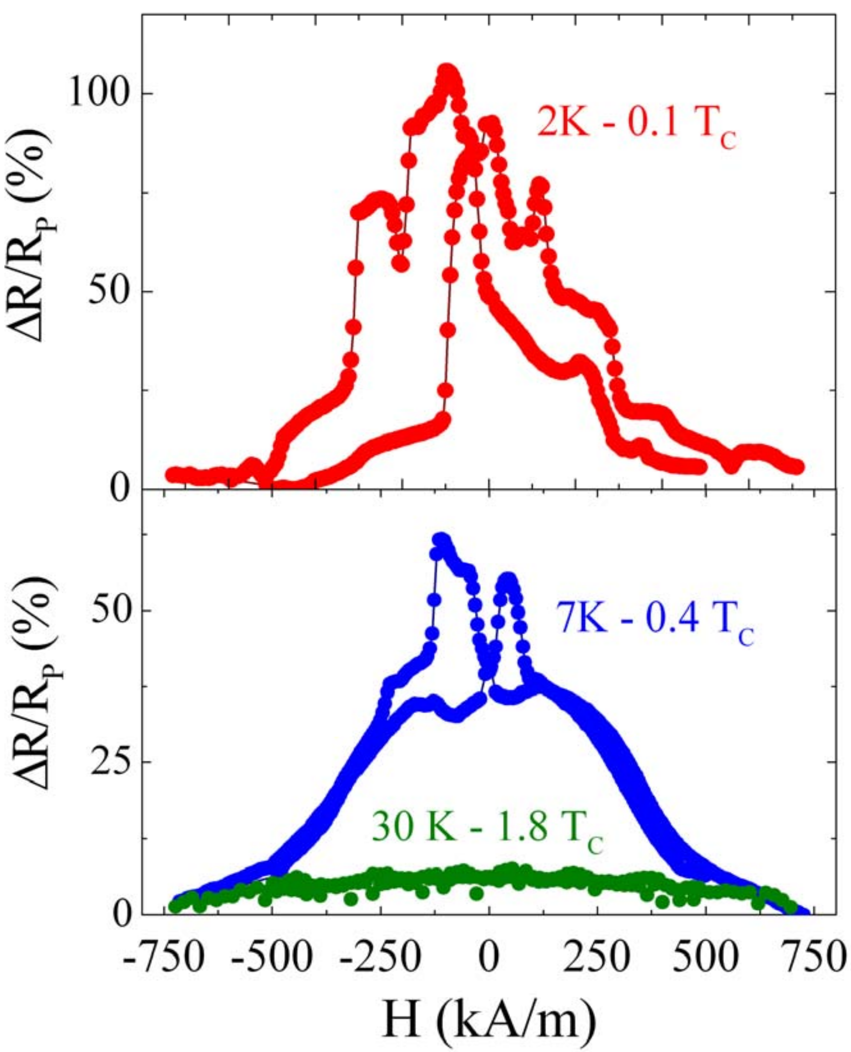
Coupling mechanism under investigation (may depend on growth)

EuS and Gd seem to be decoupled

However, ...

Spin filter magnetoresistance

50Å Ta / 30Å Al / 50Å EuS / 150Å Gd



Irregular switching: magnetism Gd (interface EuS) not well under control!

T **<** $\boldsymbol{T_C}$ **: MR > 100% observed decreases as *T* increases**

T **>** $\boldsymbol{T_C}$ **: no spin filtering, no MR**

$$\frac{\Delta R}{R_P} = \frac{2P_S P_M}{1 - P_S P_M}$$

Gd: P_M **~ 45% (Kant *et al.* 2002)** ➡ $P_S > 80\%$

agreement with Moodera et al.!

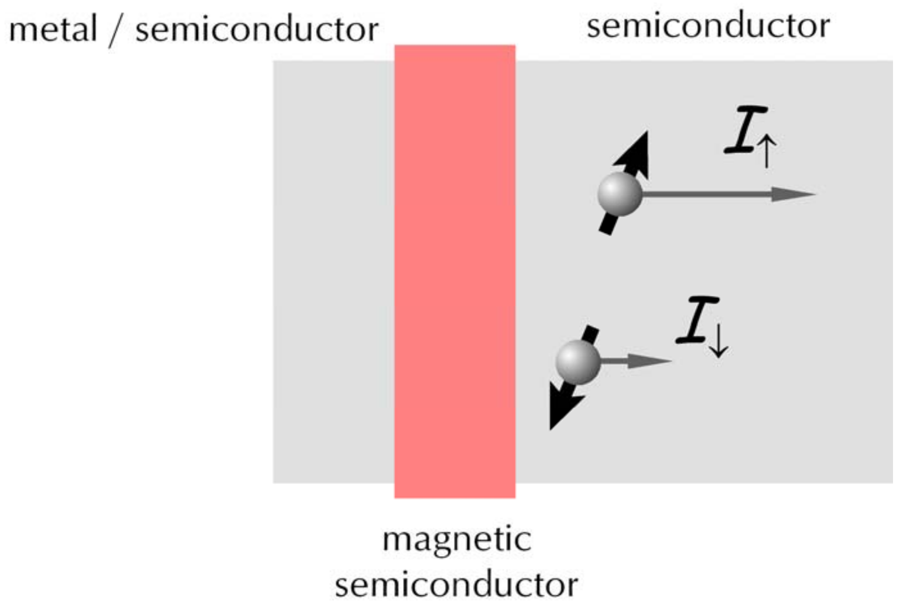
Conclusions so far ....

- Eu chalcogenides can be grown as tunnel junctions, compatibility with (some) metals

- tunneling barriers act as strong spin filters

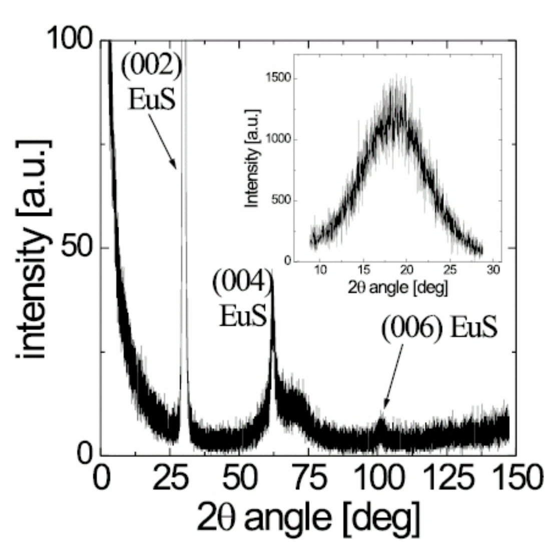
- can be used to create novel MR devices (see LeClair et al. APL 2002)

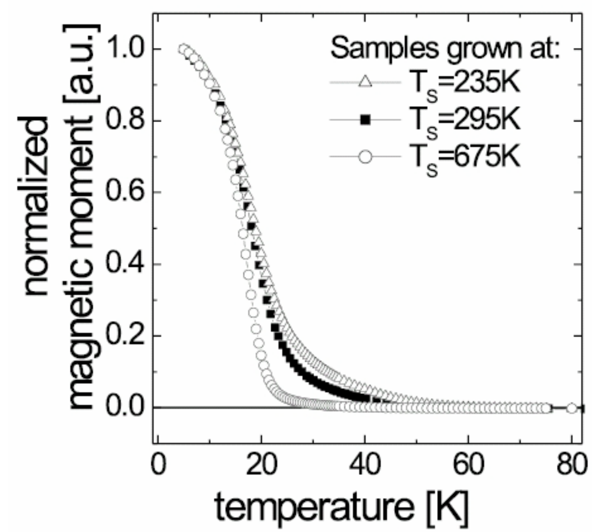
Next step: spin injection into semiconductor



Aim: all-semiconductor device structure!

What would be a first semiconductor choice?

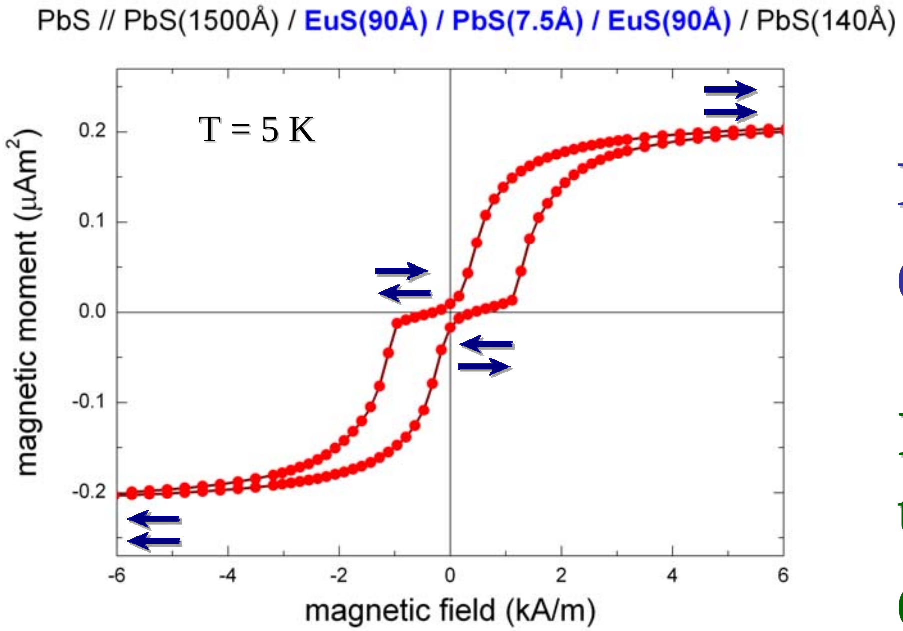




Keller, von Molnar et al. (Intermag 2002)

EuS on GaAs? Optical detection of spin-current …

Our start-up choice: diamagnetic narrow-gap PbS



Smits, Kowalczyk 2002

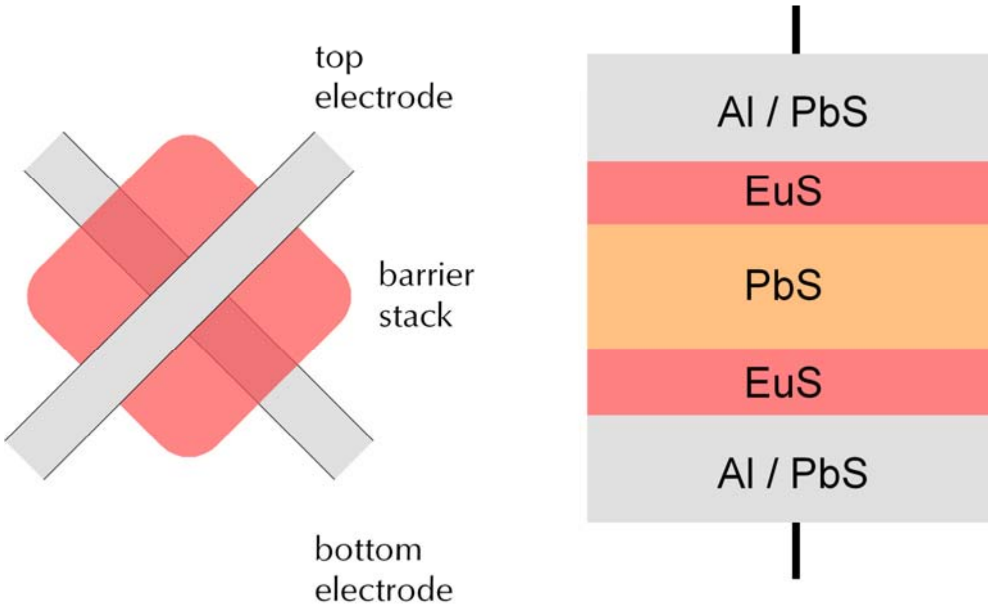
Epitaxial growth established

(Story, Sipatov et al. PRB 2000)

Interlayer coupling across thin PbS: sharp interfaces!

(Kepa et al. Europhys. Lett. 2001)

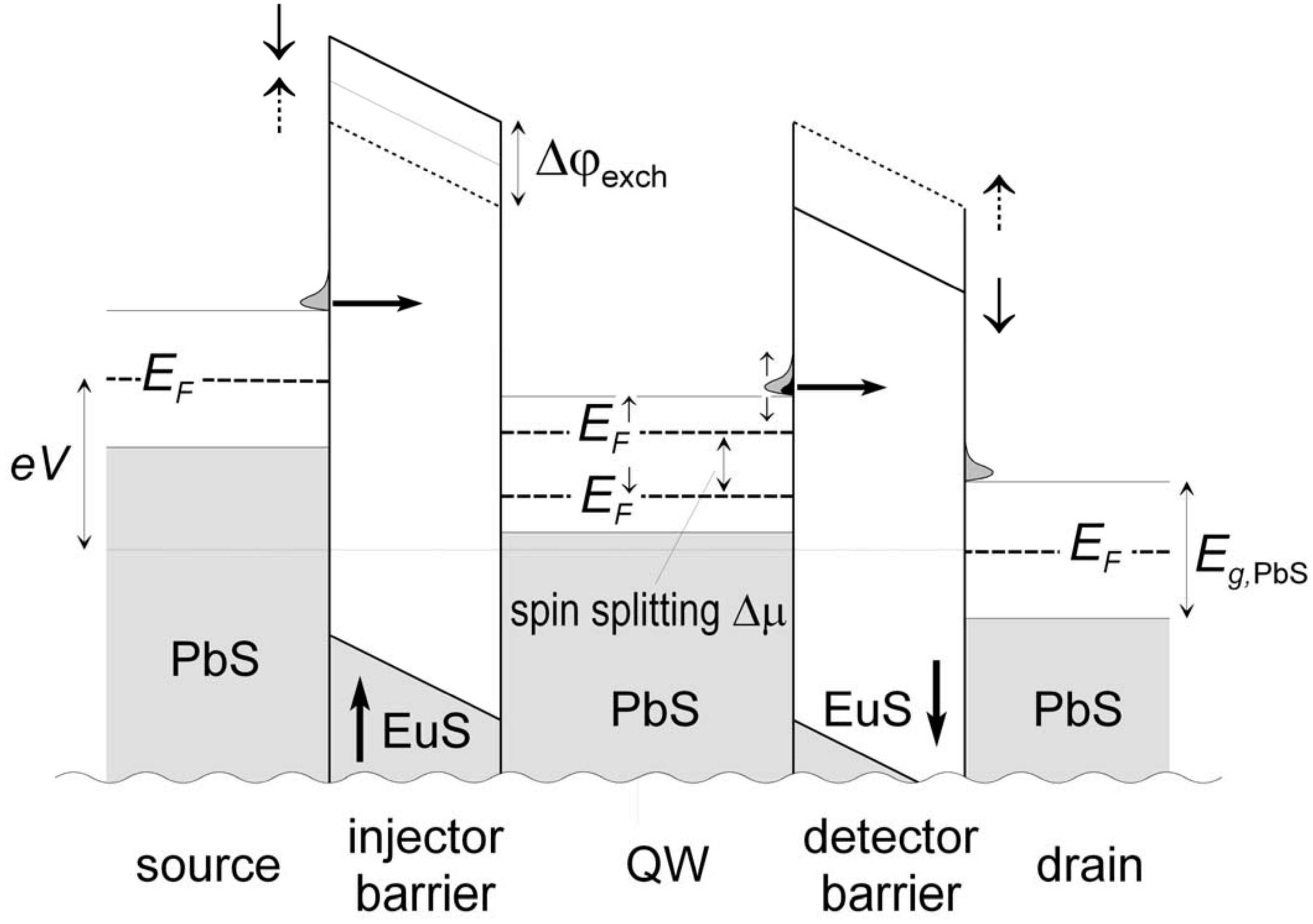
Proposed device, electrical detection scheme



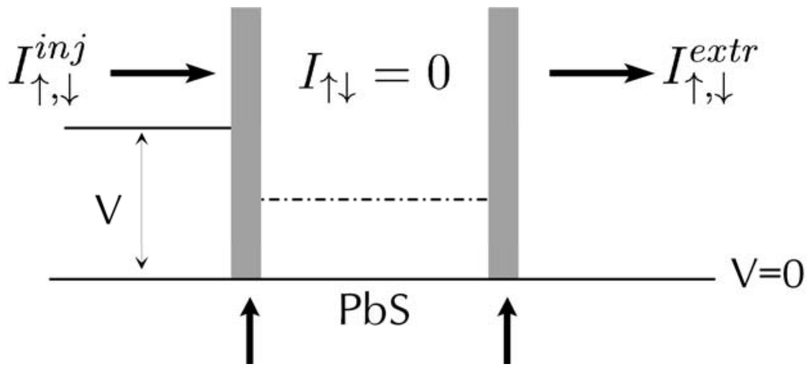
Materials issues: - poor growth of metals on EuS
- good lattice matching EuS / PbS

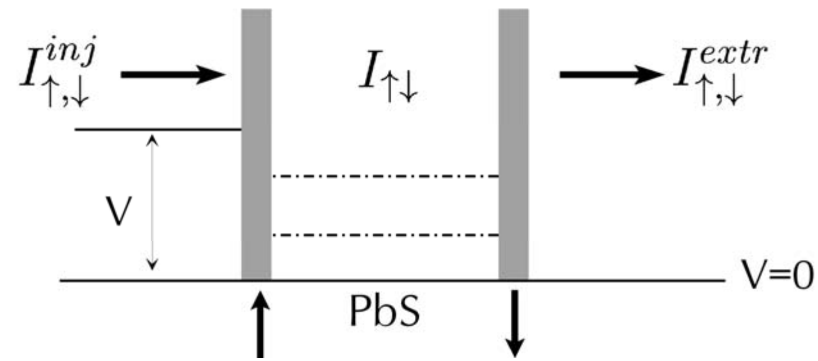
Device preparation still in progress ....

Anti-parallel magnetization: spin splitting in PbS



Modeling the system (following Valet & Fert)





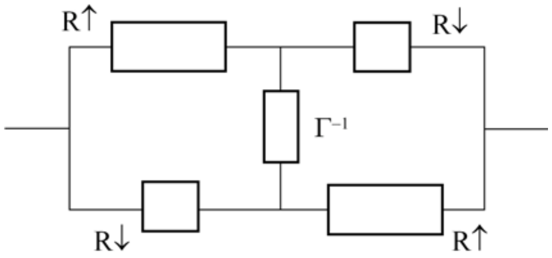
- spin relaxation current in PbS: $I_{\uparrow\downarrow} = \dfrac{e\,N(E_F)\,Vol}{\tau_{sf}}\,(\mu_\uparrow - \mu_\downarrow)$

- current conservation: $I^{inj}_{\downarrow} + I_{\uparrow\downarrow} = I^{extr}_{\downarrow}$ **and** $I^{inj}_{\uparrow} - I_{\uparrow\downarrow} = I^{extr}_{\uparrow}$

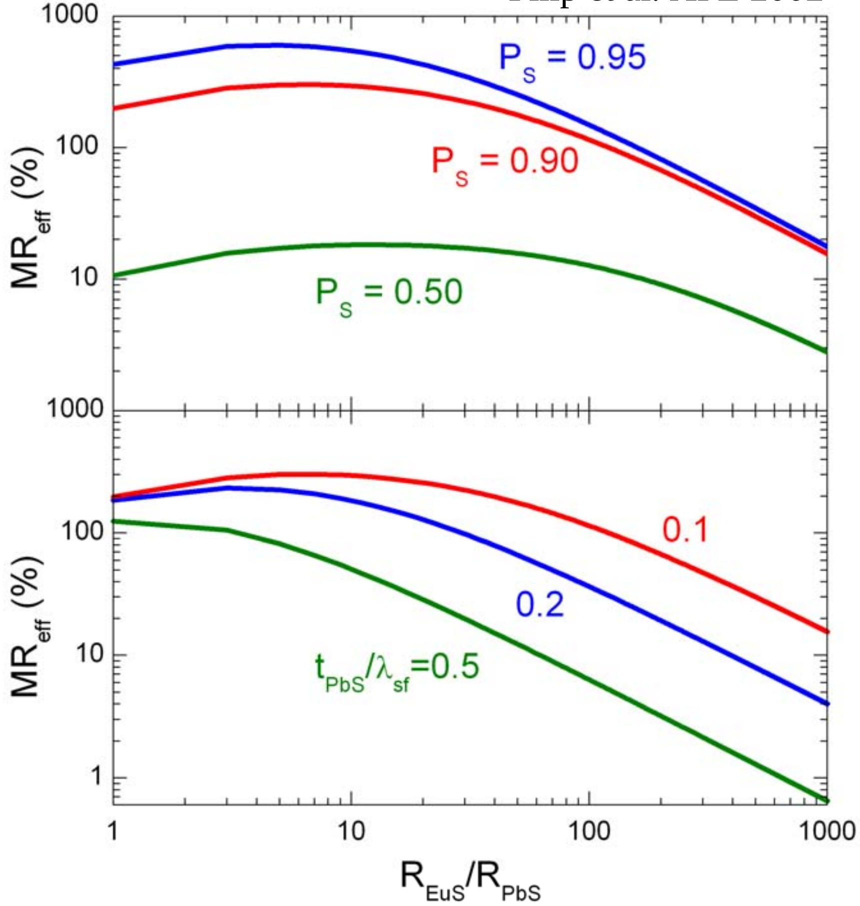
$$\Delta R/R = \frac{P_S^2}{1 - P_S^2 + \Gamma R_{EuS}} \qquad \Gamma = \frac{e\,N(E_F)\,Vol}{\tau_{sf}} = \frac{1}{R_{PbS}}\frac{t_{PbS}^2}{\lambda_{sf}^2}$$

Predicted magnetoresistance:

$$\Delta R/R = \frac{P_S^2}{1 - P_S^2 + \Gamma R_{EuS}}$$

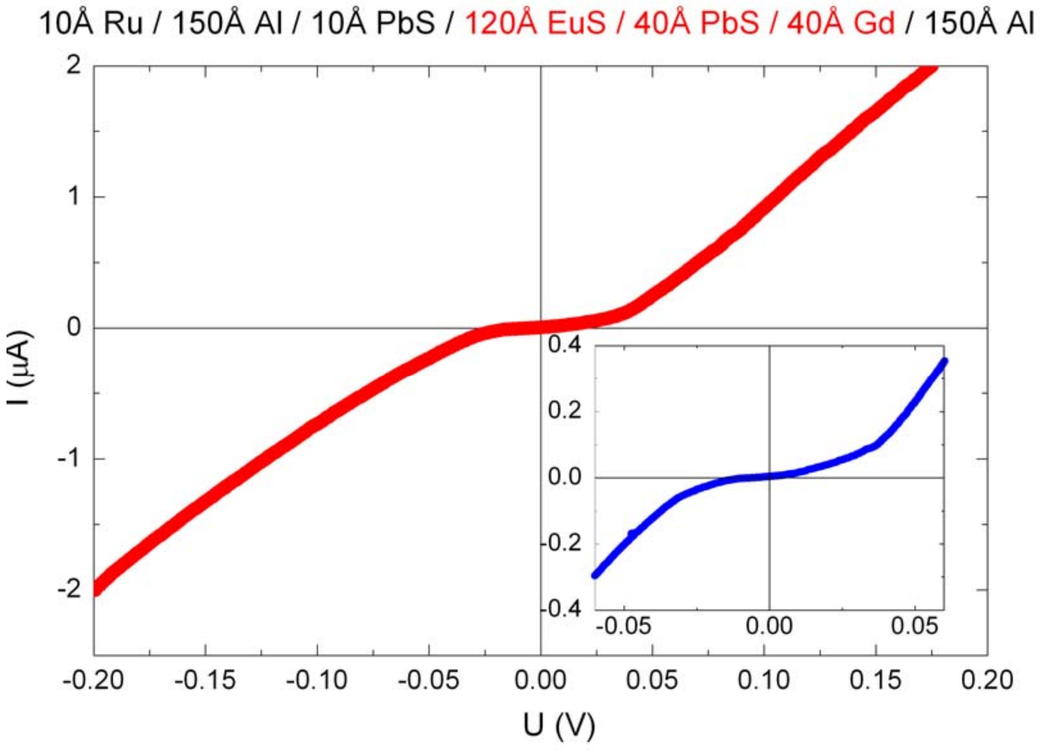


Filip et al. APL 2002



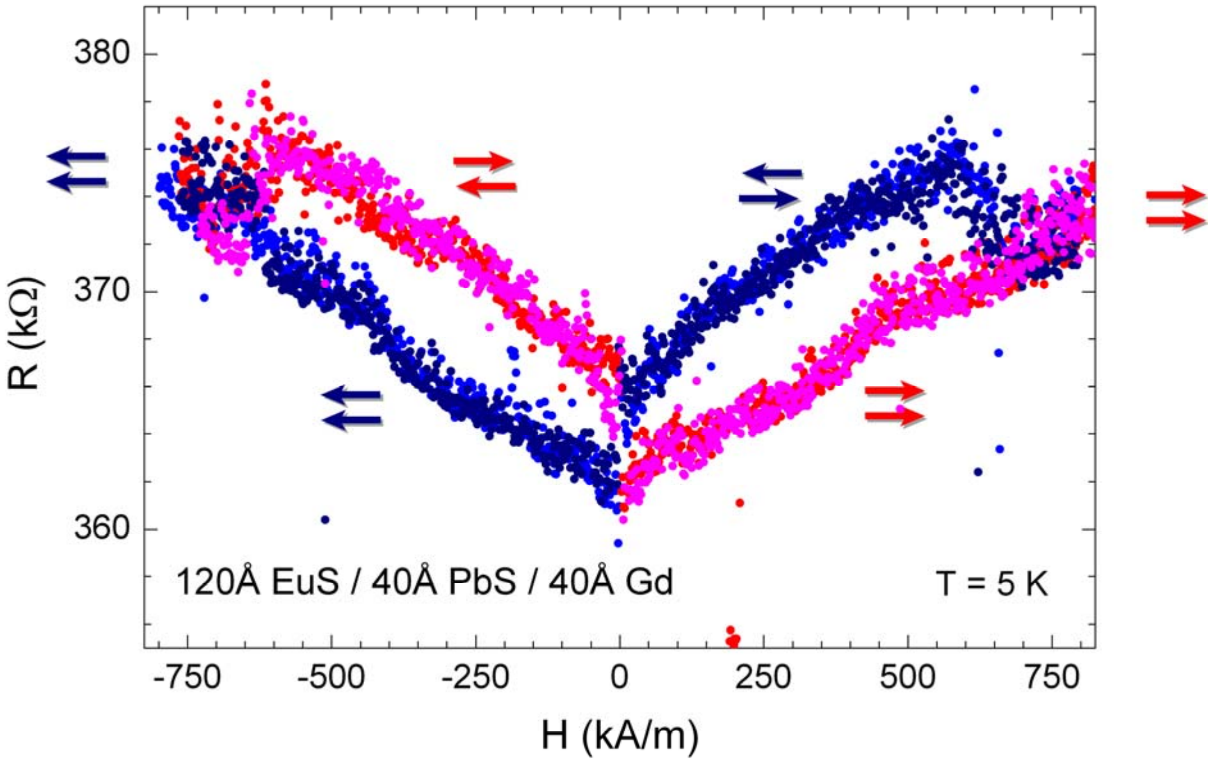
Including finite resistance PbS: $$(\Delta R/R)_{eff} = \Delta R/R \frac{R_{EuS}^2}{R_{EuS}^2 + R_{PbS}^2}$$

Back to reality: first results on EuS / PbS / Gd



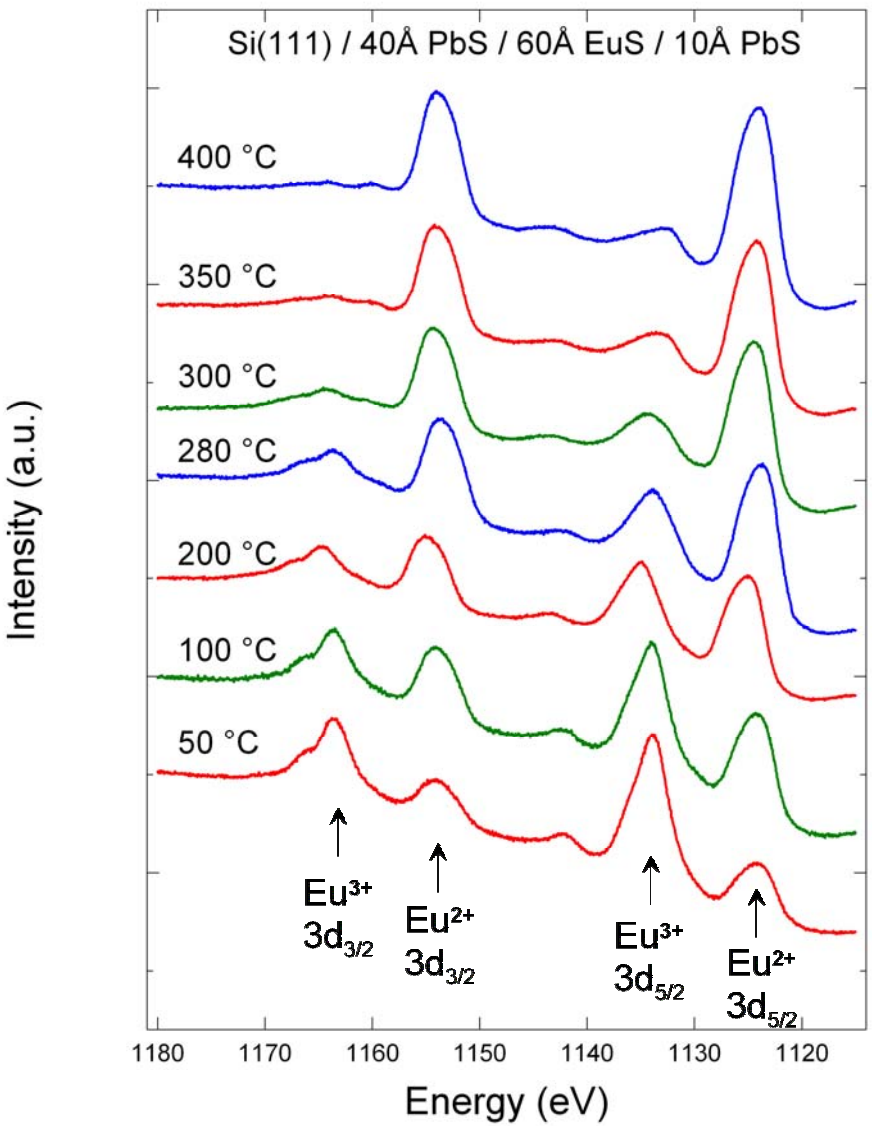
- tunneling is obvious from *IV* data
- however: gap seems rather small

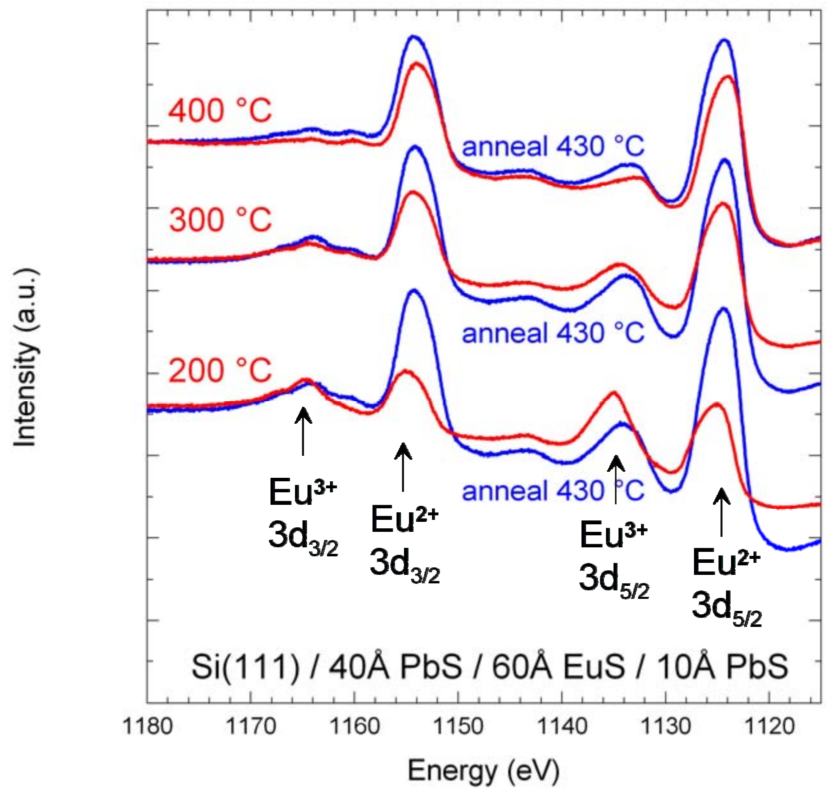
Magnetoresistance: clearly a magnetically related signal



Injection into PbS present, although MR effect very small !

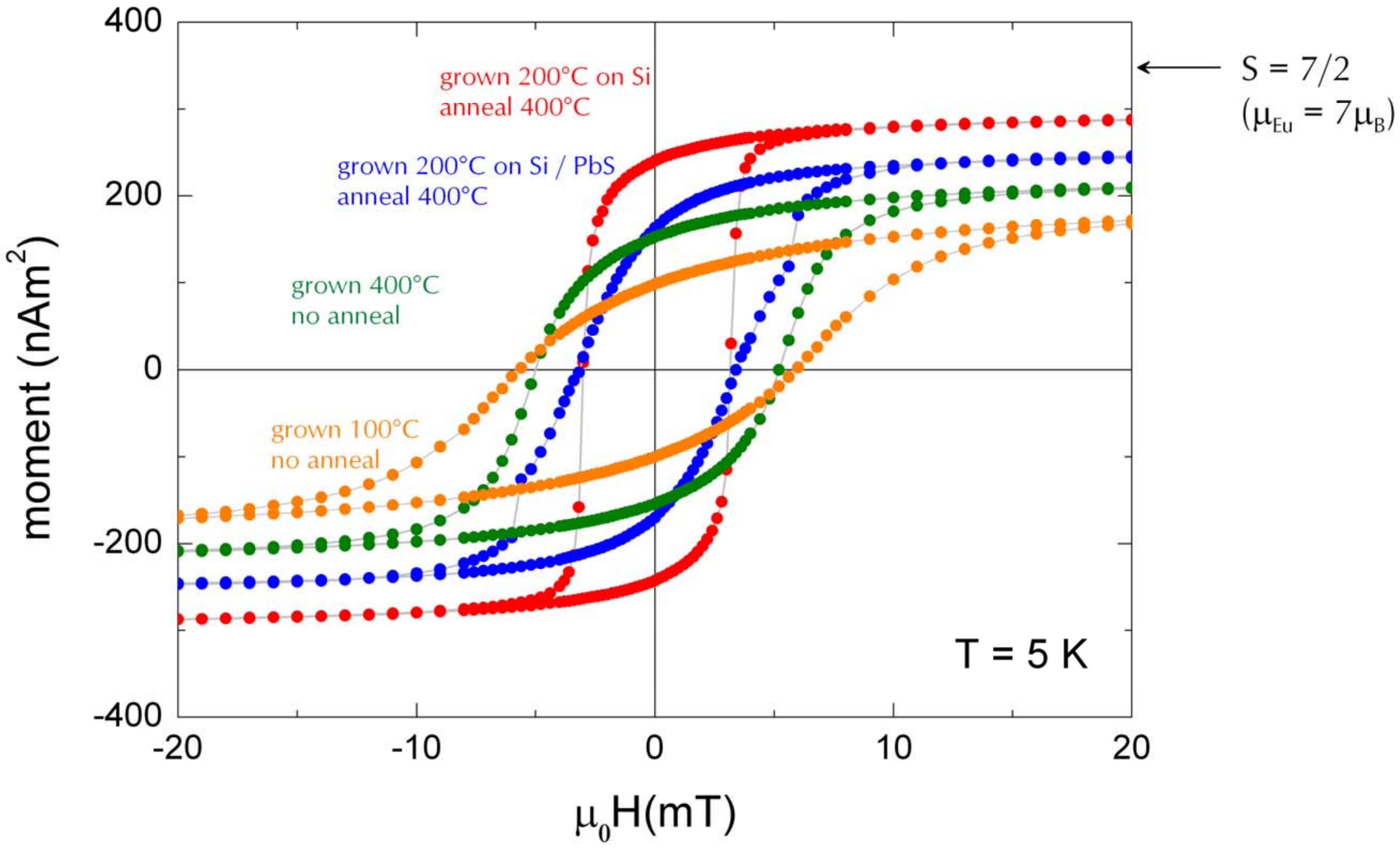
Improvements of EuS, PbS growth: in-situ XPS





- large Eu^{3+} signal; defects?
- larger growth temperature removes defects .... (though bad for roughness)
- annealing seems to help!

Did it help for our devices?



At least for the magnetism ..... (larger M_R, smaller H_C)

Conclusions

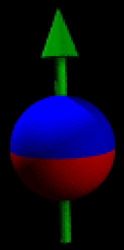
- spin injection may be feasible using EuS barriers
- first results are promising
- need for improved growth

Outlook

- realization spin injection in double barrier systems
- study spin relaxation in PbS
- alternative semiconductors

concluding:

Fundamentals of spin-polarized tunneling



- Rich physics has been observed, new phenomena are being explored

- Magnetic junctions suitable for novel applications (see next talk!)

Staff:

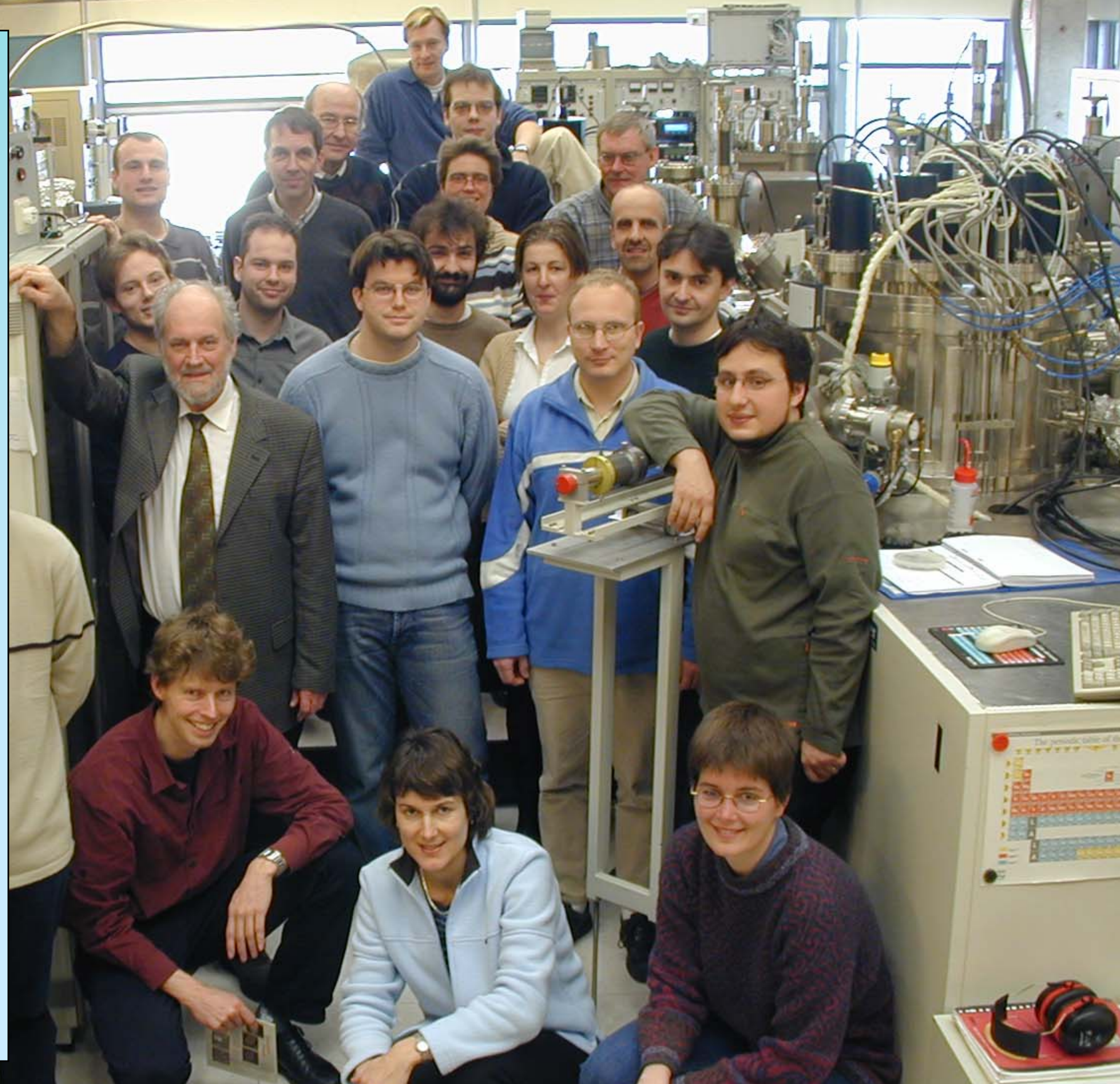
Wim de Jonge
Bert Koopmans
Jürgen Kohlhepp

PostDoc:

Andrei Filip

PhD’s:

Patrick LeClair
Corine Fabrie
Corné Kant
Karel Knechten
Paresh Paluskar
Jurgen Schoonus
Coen Smits



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