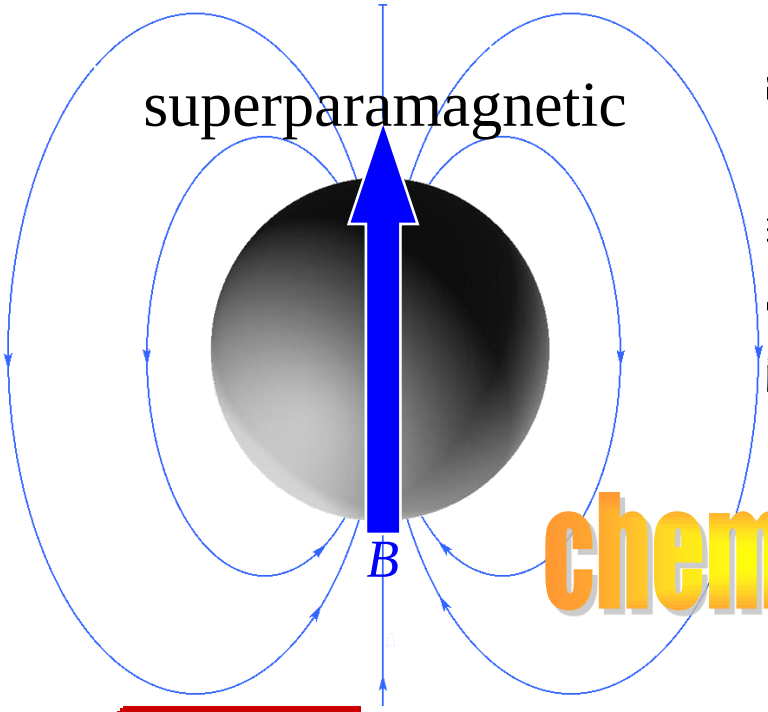
From magnetic nanoparticles to magnetoresistive biosensors

Andreas Hütten

XLVI Zakopane School of Physics 2011, Zakopane, May19th

What are the basic ideas?



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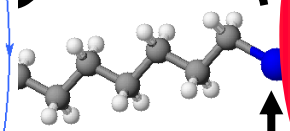
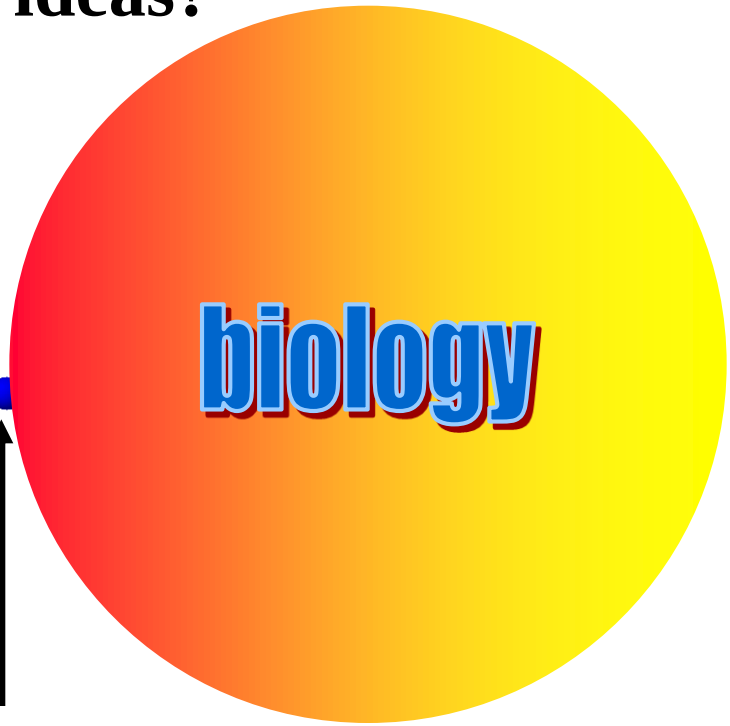
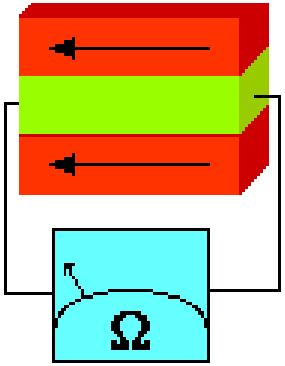




chemistry

tail group
can be
functionalized



physics

XMR – sensor: GMR or MTJ (TMR)

(1) Interparticular interaction in solution:
Magnetic nanoparticles
as reconfigurable matter

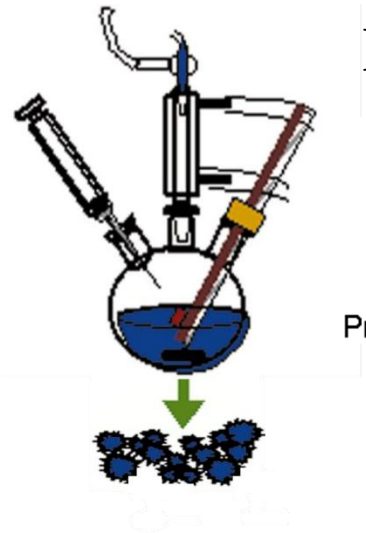
(2) Nanoparticular XMR-sensors ?

(3) A concept of detecting magnetic beads:
a magnetic ratchet

Snythesis and Characterization

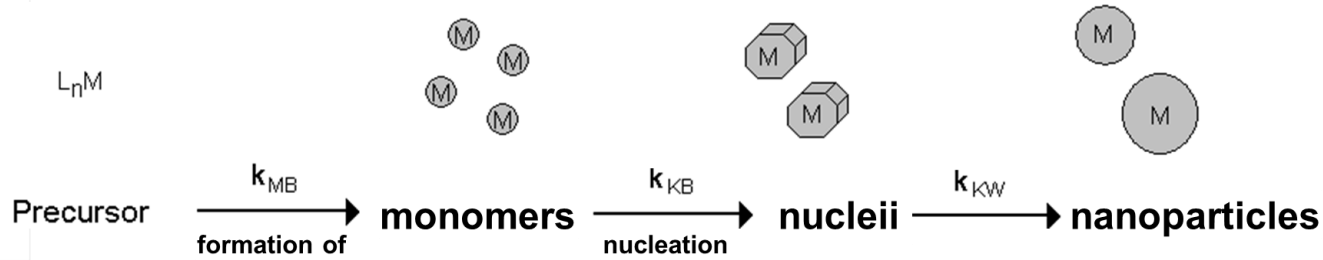
Synthesis of Co - Nanoparticle

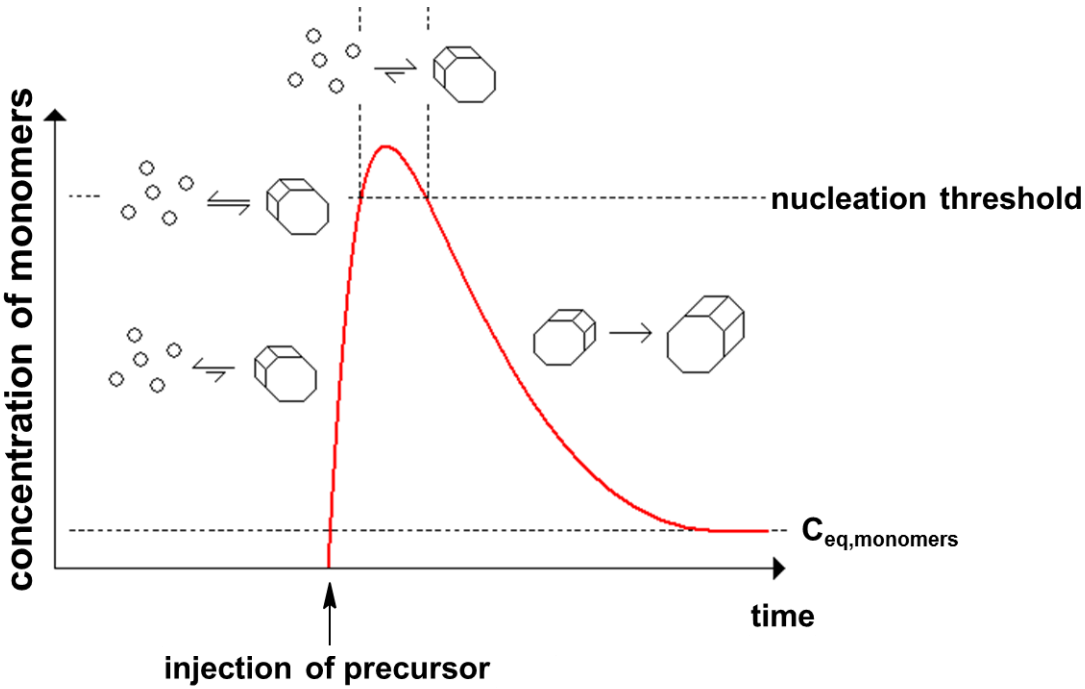
Thermolysis* of $Co_2(CO)_8$ with Oleic acid, TOPO in *o*-DCB



LaMer model:

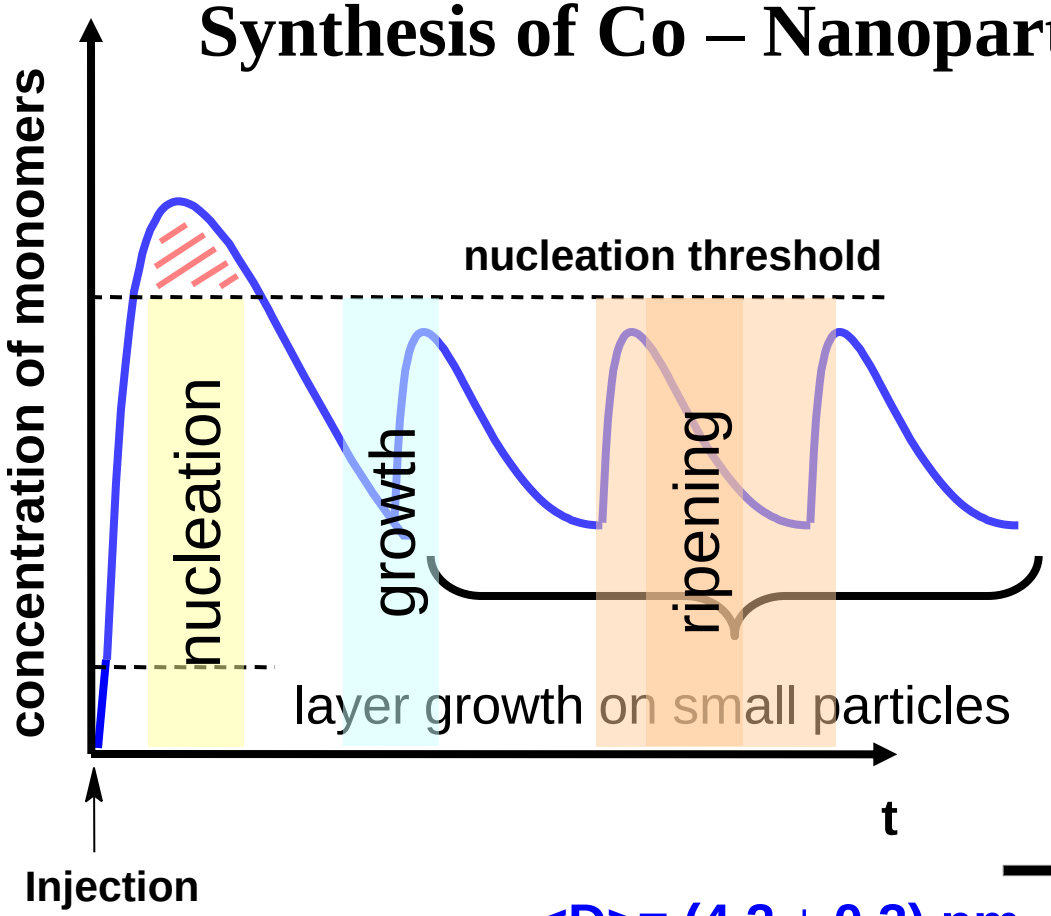
*V. K. La Mer, R. H. Dinegar, *J. Am. Chem. Soc.* 1950, 17(11), 4847-4854

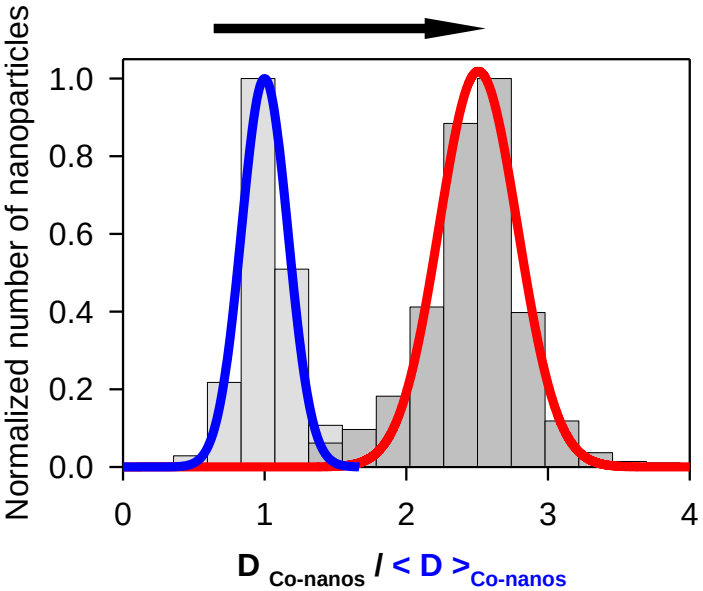




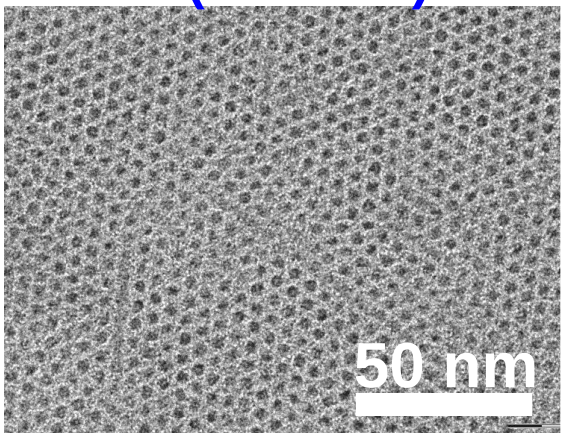
*C.B. Murray, S. Sun et al., IBM J. Res. & Dev. 45 (2001) 47
*V. F. Puntes, K.M. Krishnan, A.P. Alivisatos, SCIENCE 291 (2001) 2115

Synthesis of Co – Nanoparticle: size control

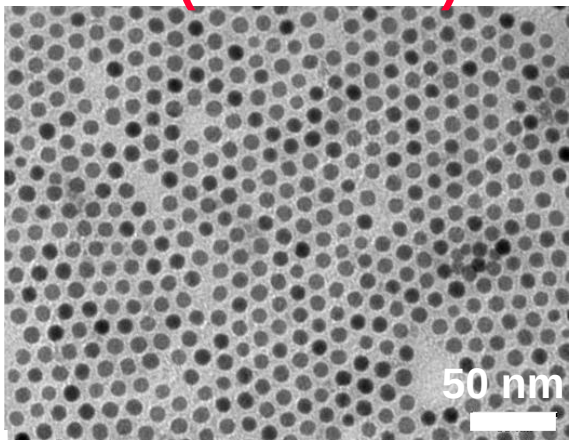




<D>= (4.2 ± 0.3) nm



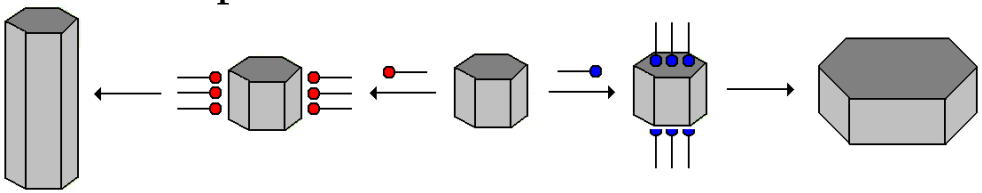
<D>= (10.1 ± 0.6) nm



Synthesis of Co – Nanoparticle:

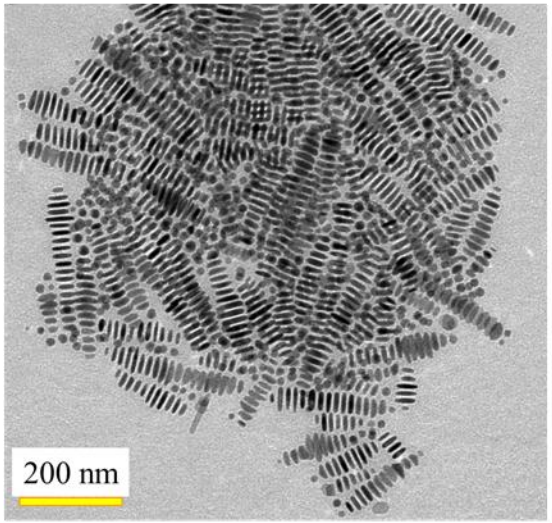
binding of ligand head groups to spezific nucleii surfaces

▶ **control of morphology:**

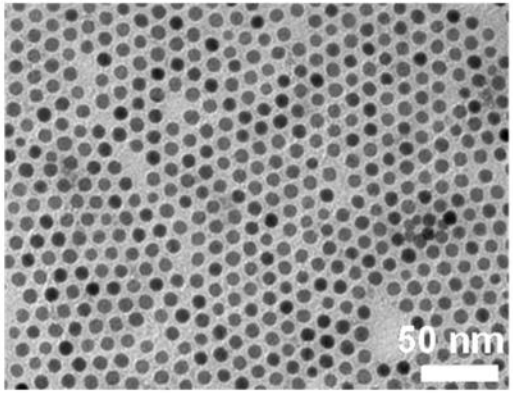


resulting Co – particle morphology:

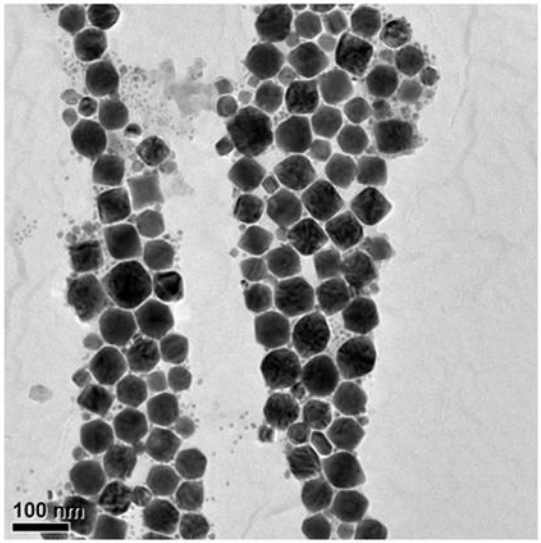
Co – discs



Co – spheres

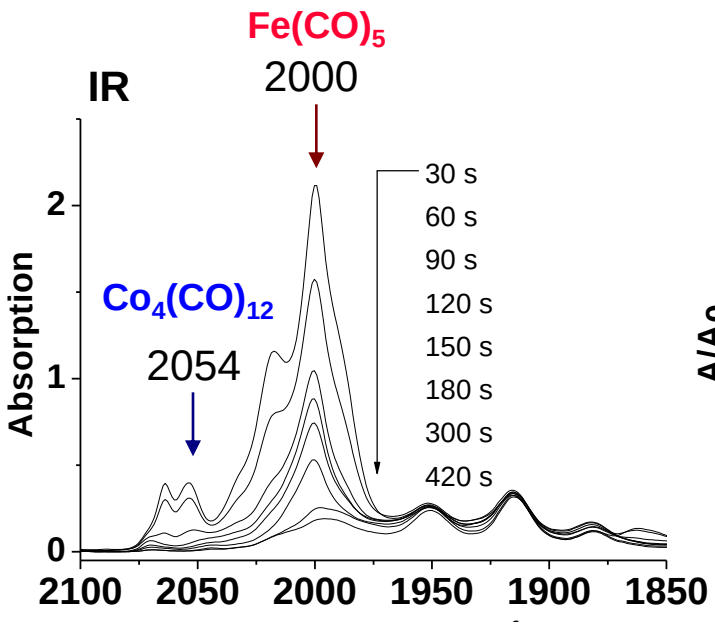


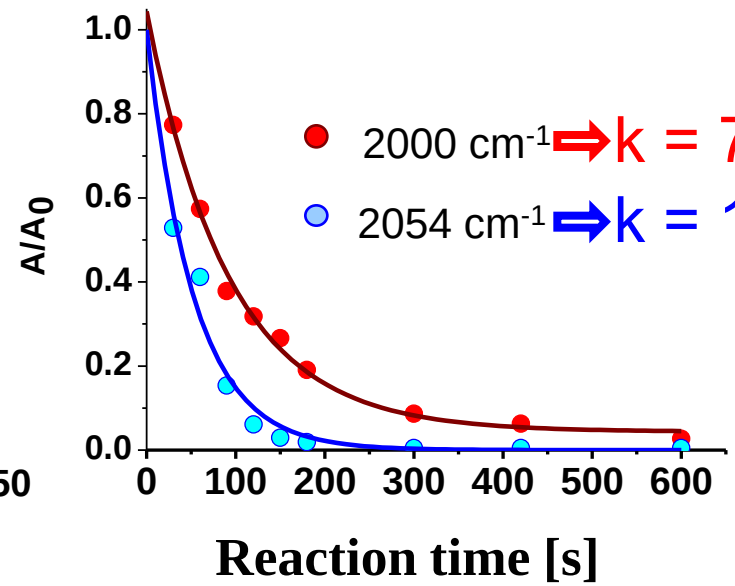
Co – cubes



Tailoring the magnetization employing alloyed nanoparticles: Kinetic of $Co_2(CO)_8$ - and $Fe(CO)_5$ - precursor decomposition

Evolution of the precursor decomposition employing IR - spectroscopy





2000 cm^{-1} ⇒ $k = 7{,}52 \cdot 10^{-3}\ s^{-1}$

2054 cm^{-1} ⇒ $k = 1{,}46 \cdot 10^{-2}\ s^{-1}$

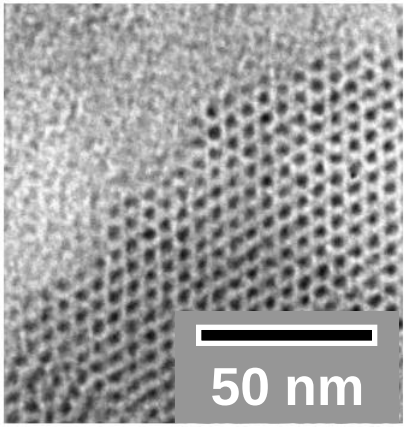
⇨ Fe-precursor decomposes much slower

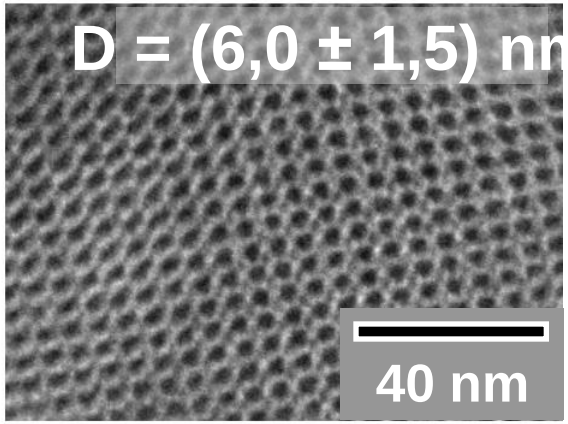
Tailoring the Magnetization employing alloyed nanoparticles

$Co_2(CO)_8$
+
$Fe(CO)_5$

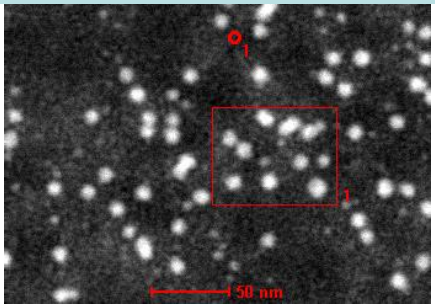
182°C,
fast injektion
Oleic acid
TOPO

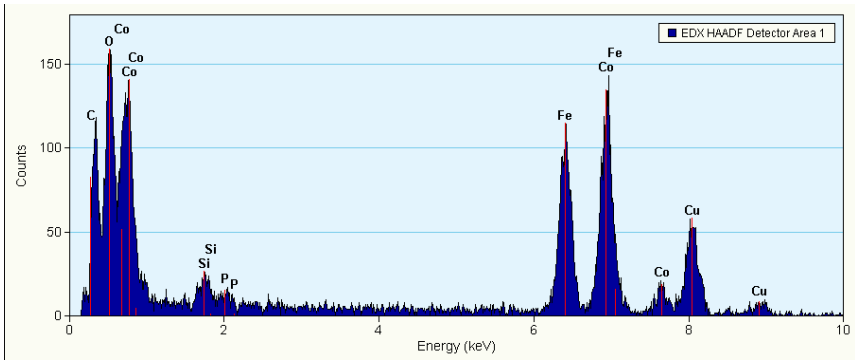
1,2-Dichlorbenzne

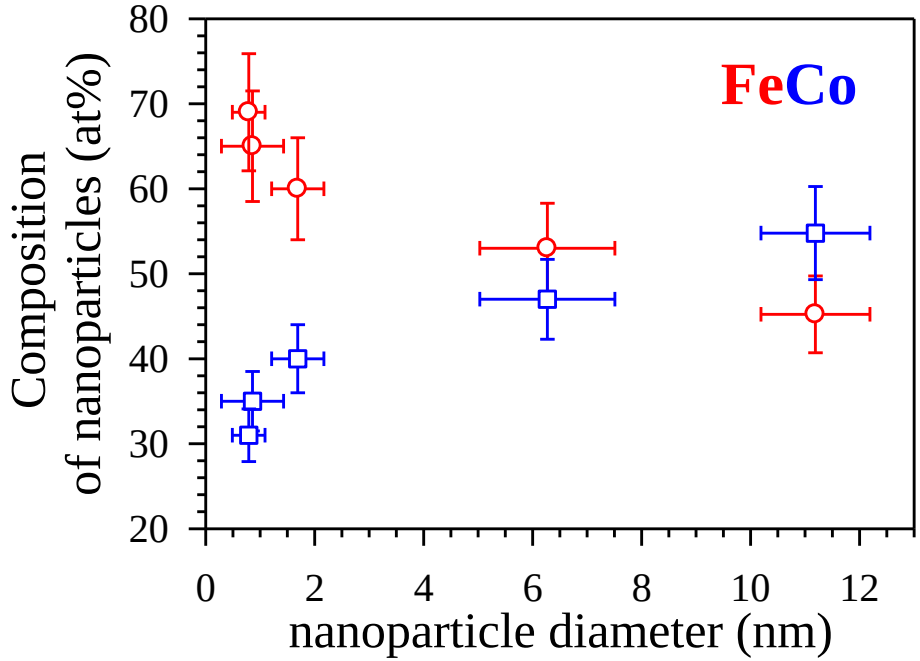




Fe(K) 46.8 at%
Co(K) 53.2 at%







La Mer model:

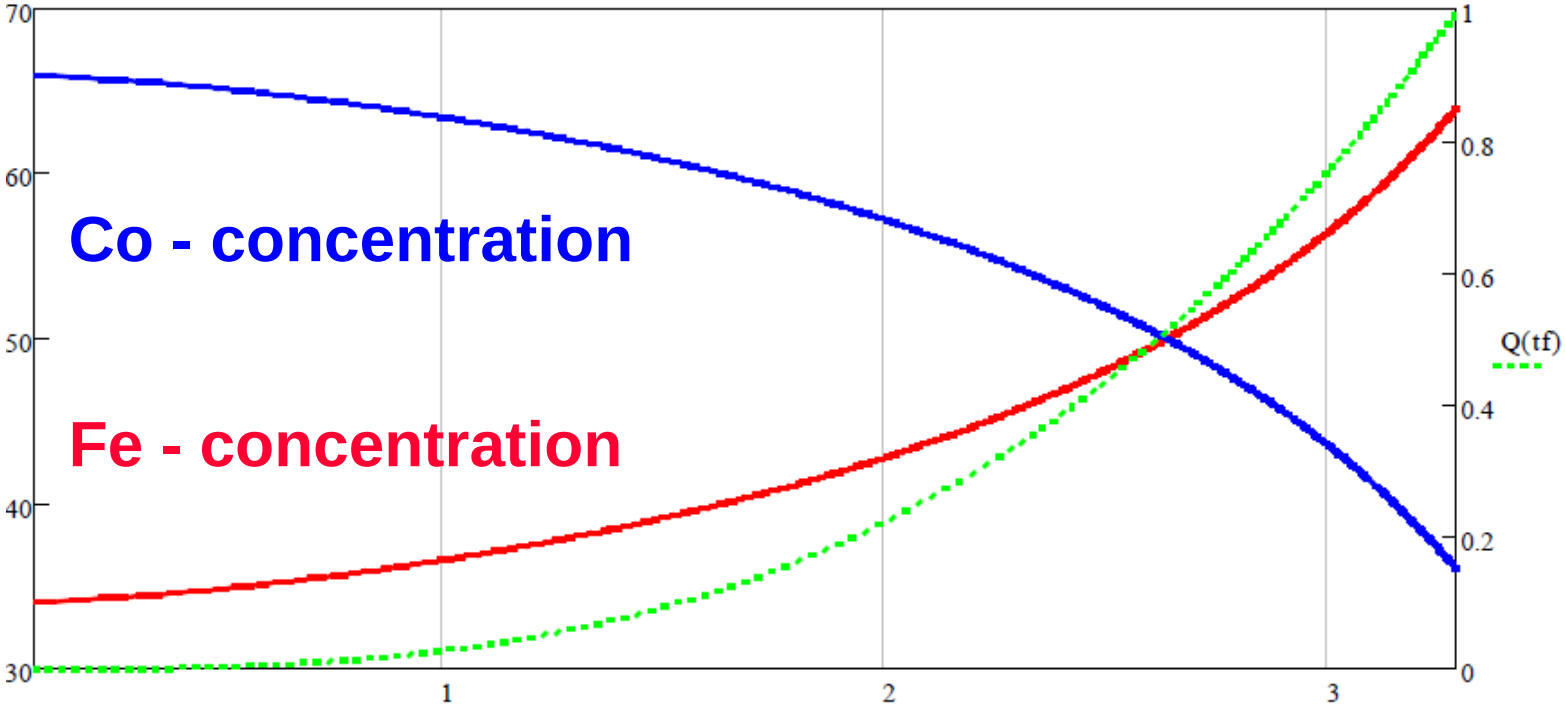
$Fe(CO)_5$ — Rate of decomposition

$k_{Fe} = 7{,}52 \cdot 10^{-3}\ s^{-1}$

$k_{Co} = 1{,}46 \cdot 10^{-2}\ s^{-1}$

$Co_4(CO)_{12}$ — Rate of decomposition

"*Monomers*" —Rate of formation→ FeCo



Radius of 6.6 nm FeCo nanoparticle

A. Hütten, D. Sudfeld, I. Ennen, G. Reiss, K. Wojczykowski, P. Jutzi, JMMM 293 (2005) 93

Alternative Iron – Precursor

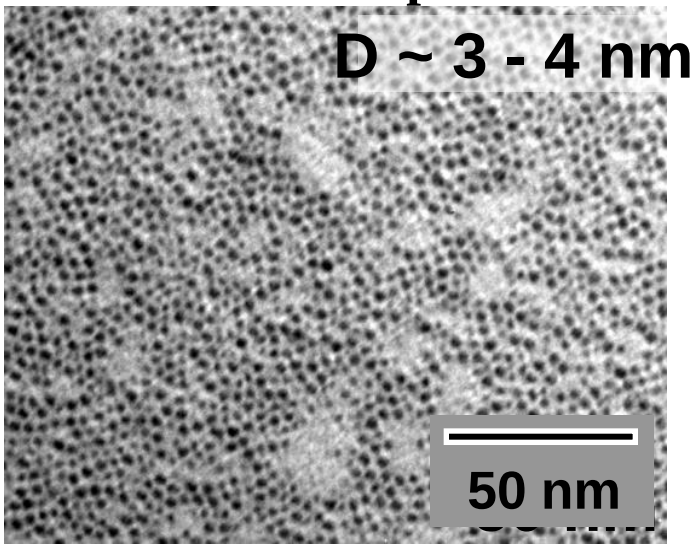
$$Fe_3(CO)_{12} + 3TOPO \rightarrow 3Fe(CO)_4TOPO$$

→ fast decomposition rate: $1{,}82 \cdot 10^{-2}\ s^{-1}$

→ allows to synthesize FeCo – nanoparticles

→ allows to synthesize pure Fe – nanoparticles without additional ligands („*single source*“)

Pure Fe – nanoparticles:



La Mer model:

$Fe(CO)_4TOPO$

$k_{Fe} = 1.82 \cdot 10^{-2}\ s^{-1}$

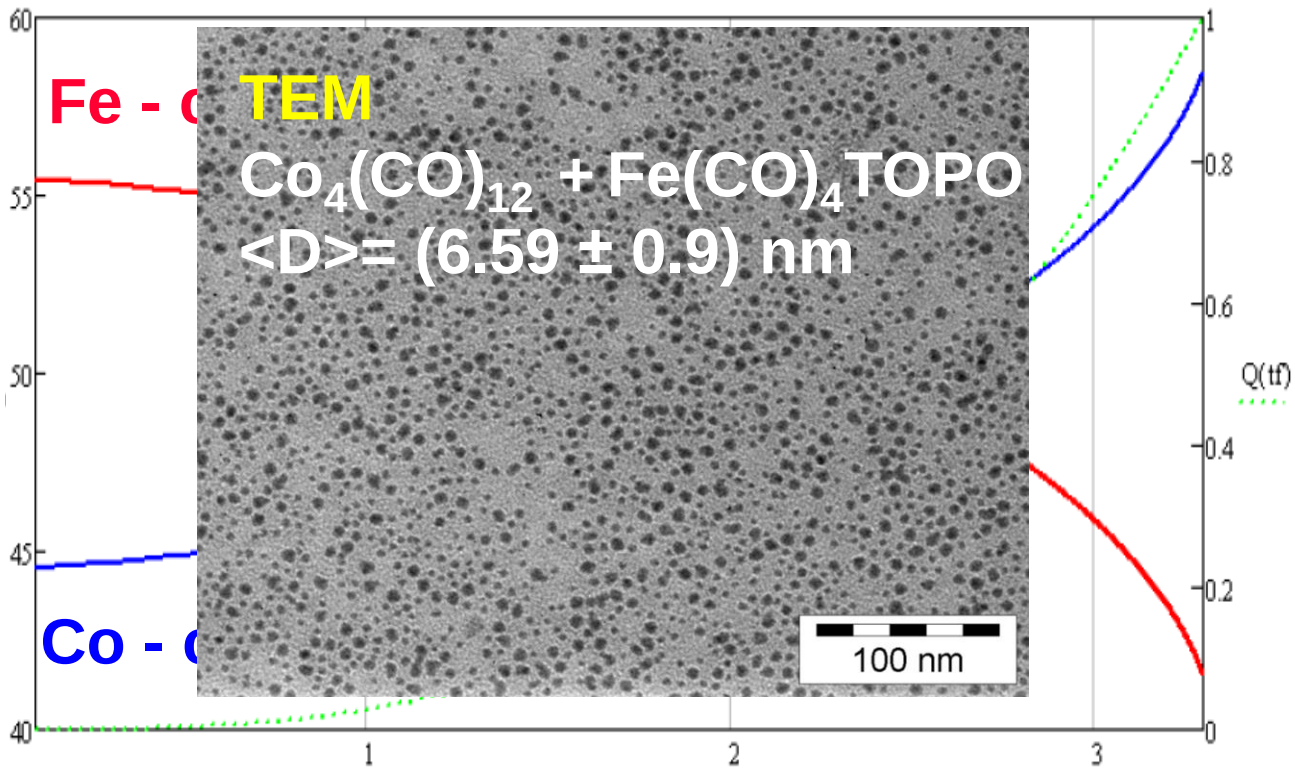
$k_{Co} = 1{,}46 \cdot 10^{-2}\ s^{-1}$

$Co_4(CO)_{12}$

Rate of decomposition

Rate of decomposition

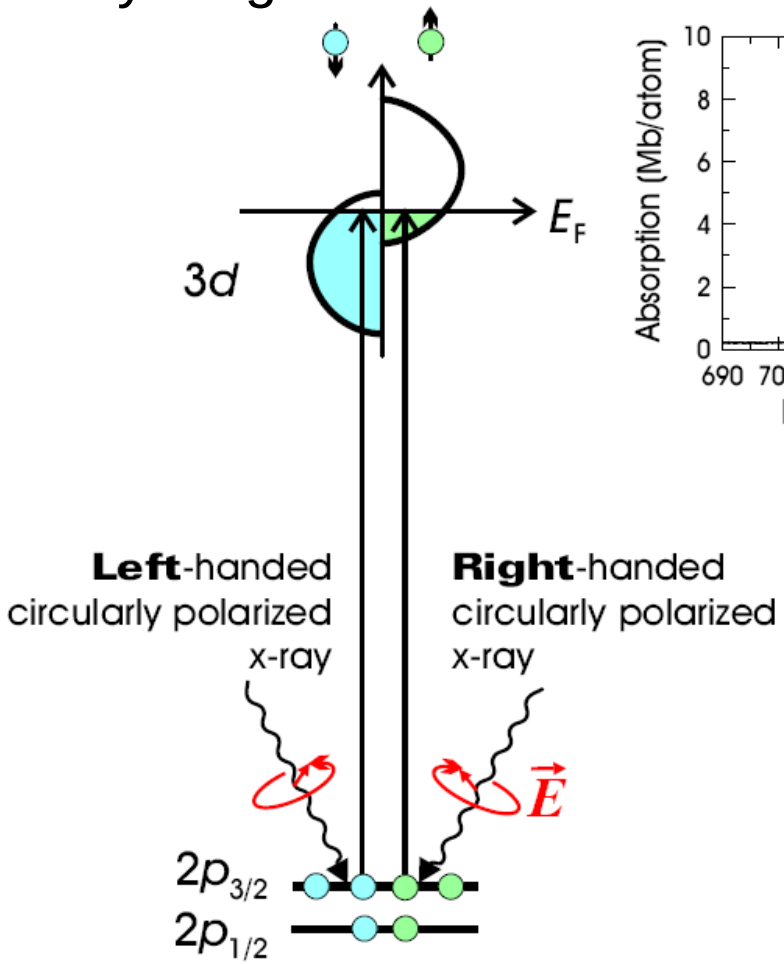
"*Monomers*" $\xrightarrow{\text{Rate of formation}}$ FeCo

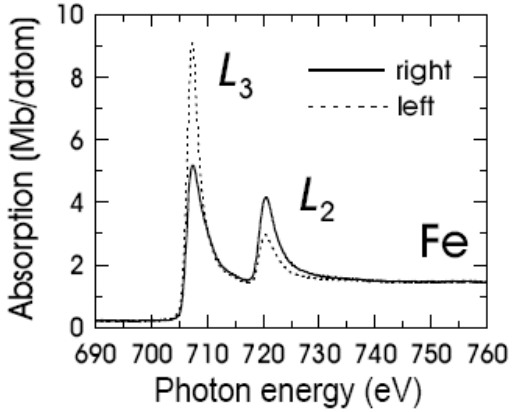


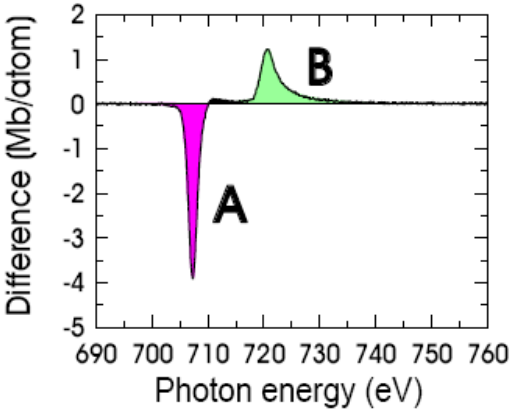
Radius of 6.6 nm FeCo nanoparticle

How to get information about the FeCo-particles composition? → The answer is XMCD:

X-ray magnetic circular dichroism







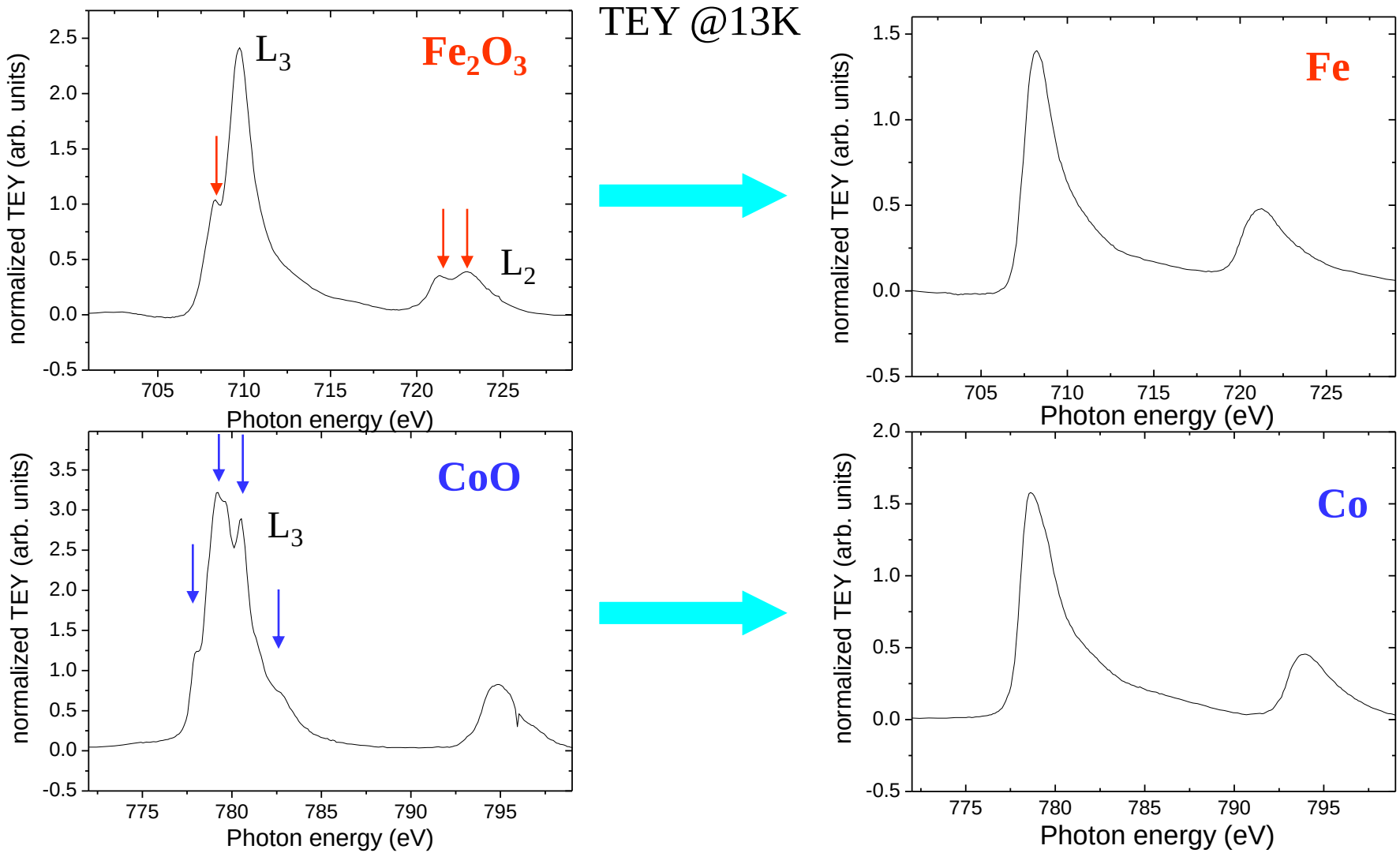
XAS ((right + left)/2):

- element specific due to different energy ranges
- chemical state due to fine structure

XMCD (right-left):

- information about spin and orbital magnetic moment

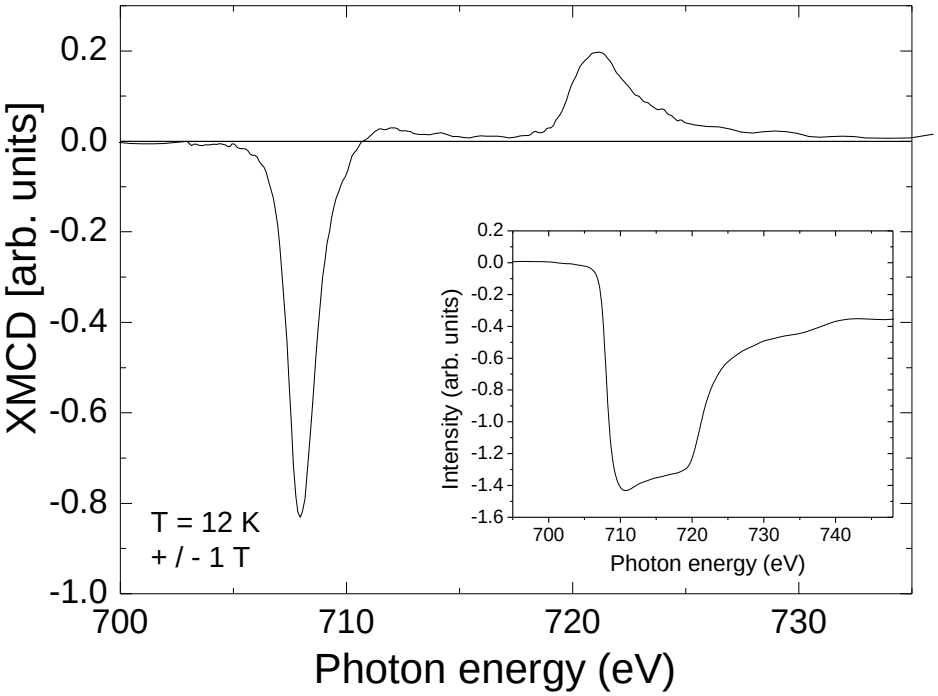
X-ray absorption spectroscopy of FeCo - nanoparticles



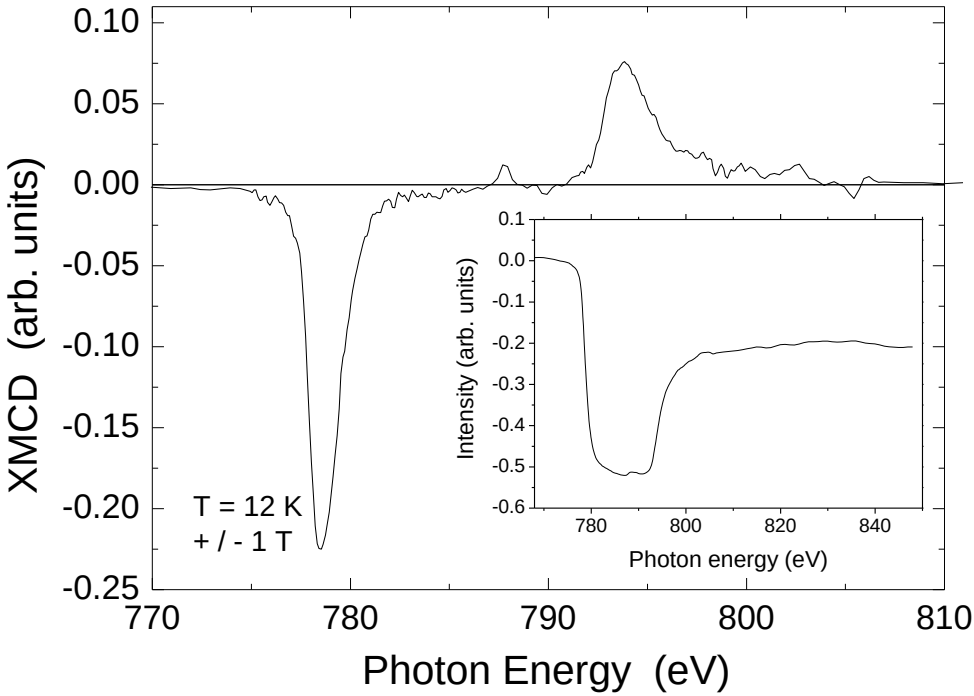
Dr. Ulf Wiedwald, Ulm University, Germany

XMCD of metallic FeCo particles

Fe edge



Co edge



→ Fe: $\mu_L/\mu_S \approx 0.066$

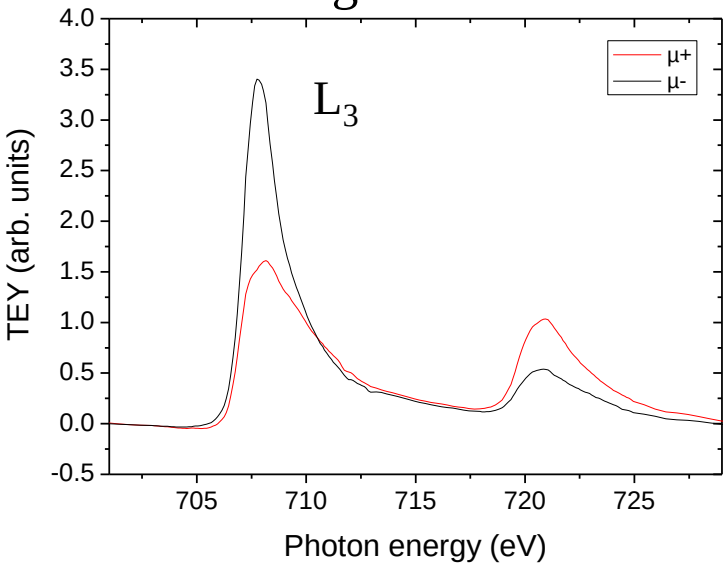
μ_L/μ_S (bulk): 0.043 bcc-Fe)

→ Co: $\mu_L/\mu_S \approx 0.112$

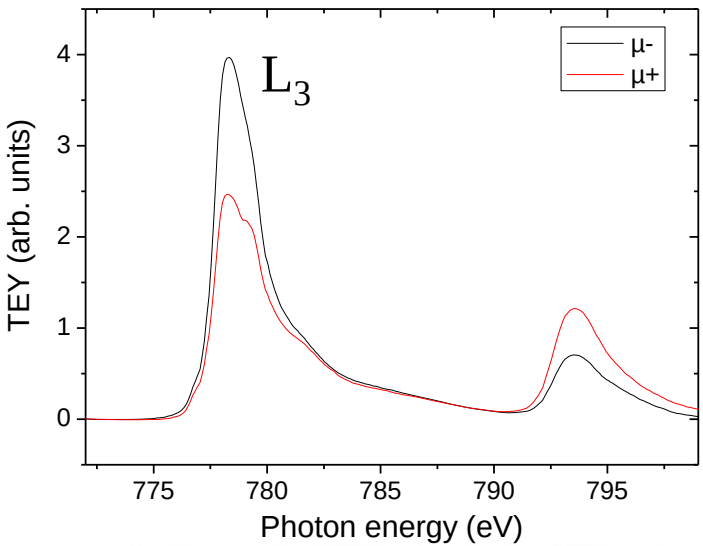
X-ray absorption spectroscopy of FeCo - nanoparticles

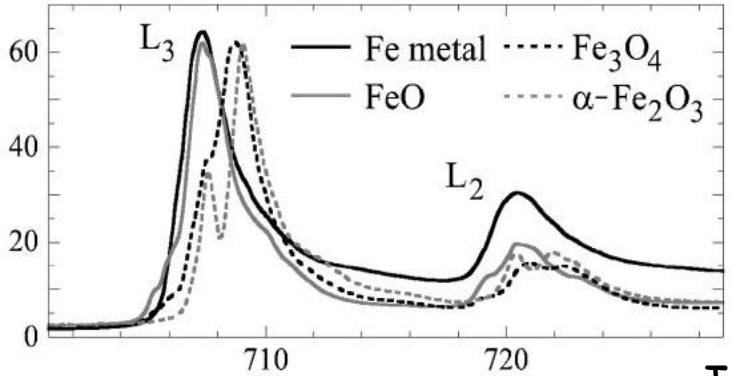
After 10 min in 1mbar O_2

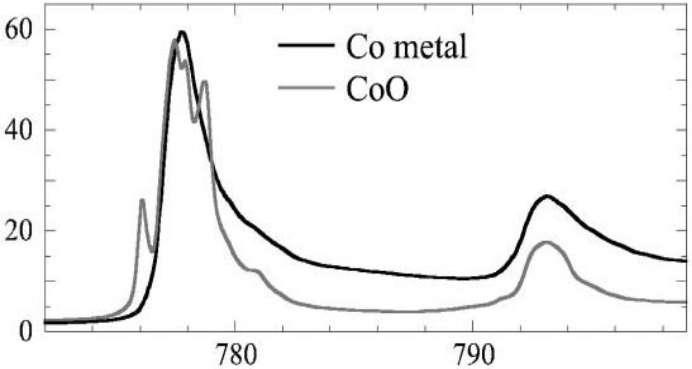
Fe edge



Co edge







T. J. Regan et al., Phys. Rev. B 64 (2001) p.214422

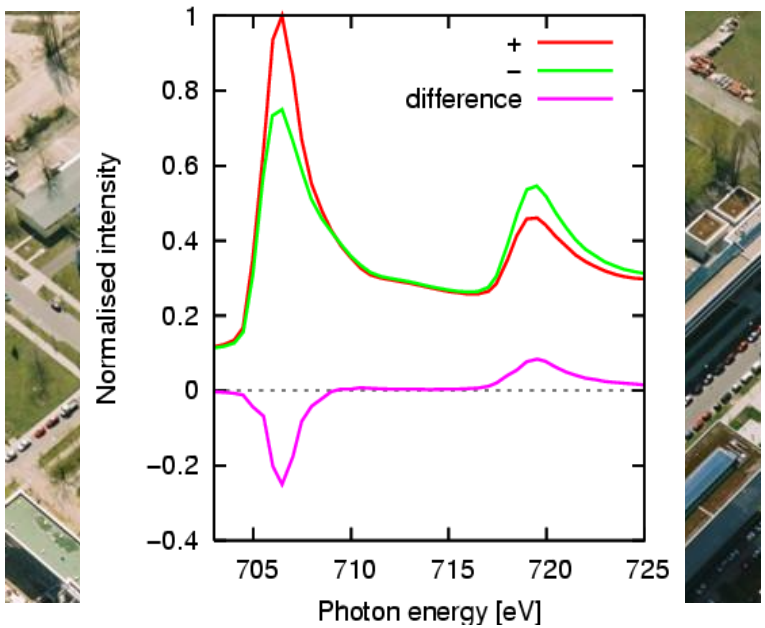
Dr. Ulf Wiedwald, Ulm University, Germany

Transition to single particle analysis?

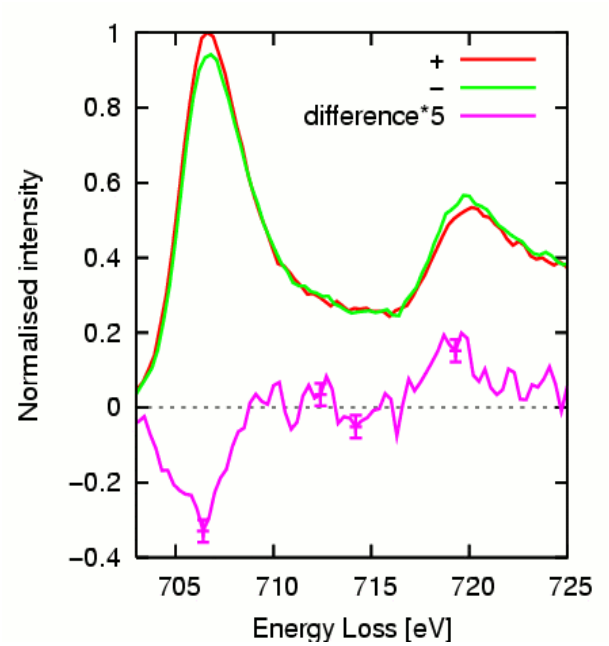
→ Inga Ennen & Peter Schattschneider (TU Wien)

Photon absorption ⟷ Inelastic electron scattering

XMCD



EMCD



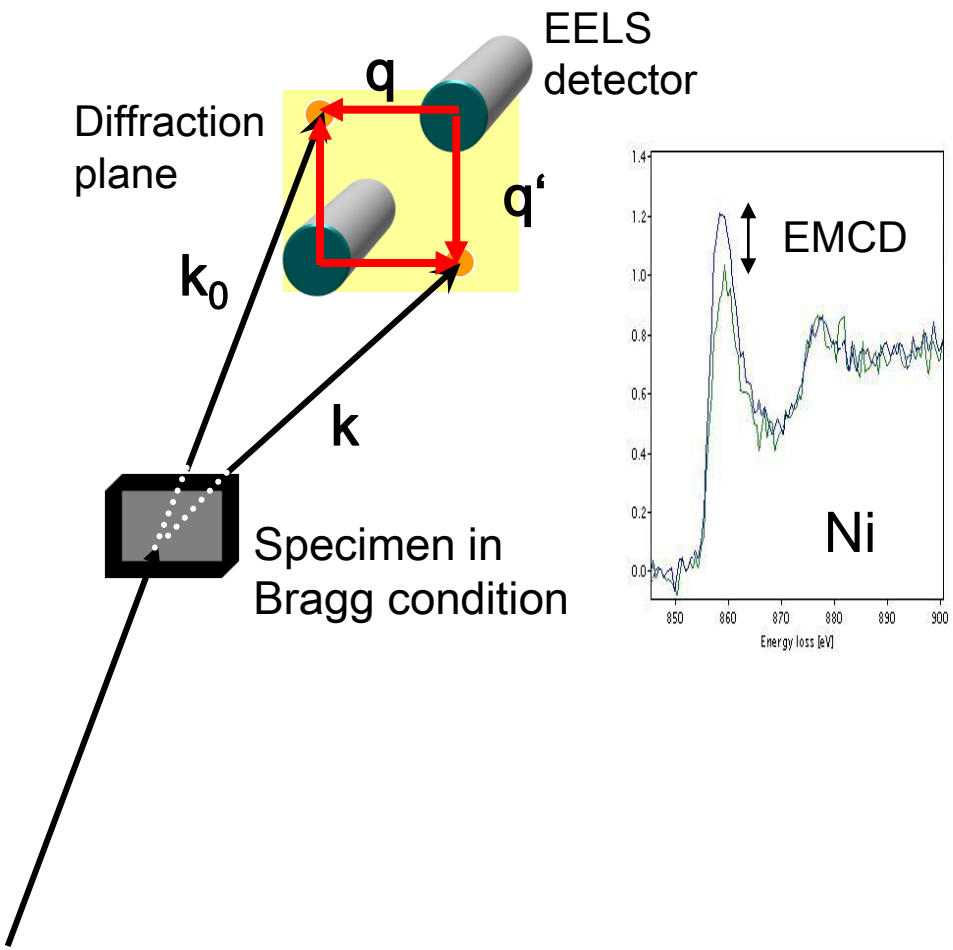
Energy Loss Magnetic Chiral Dichroism

P. Schattschneider et al., Nature 441 (2006) 486-488

Energy Loss Magnetic Chiral Dichroism

Requirements:

- $q \perp q'$
- $|q| = |q'|$
- phase shift

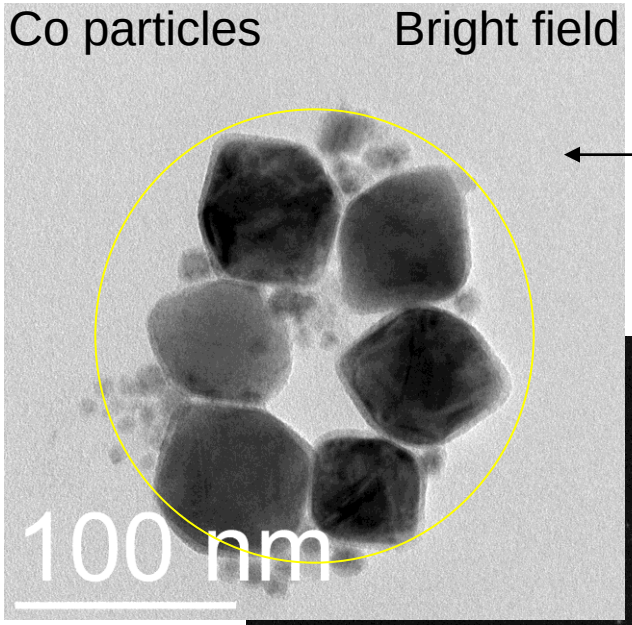


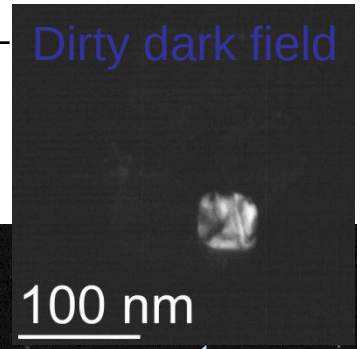
EMCD signal

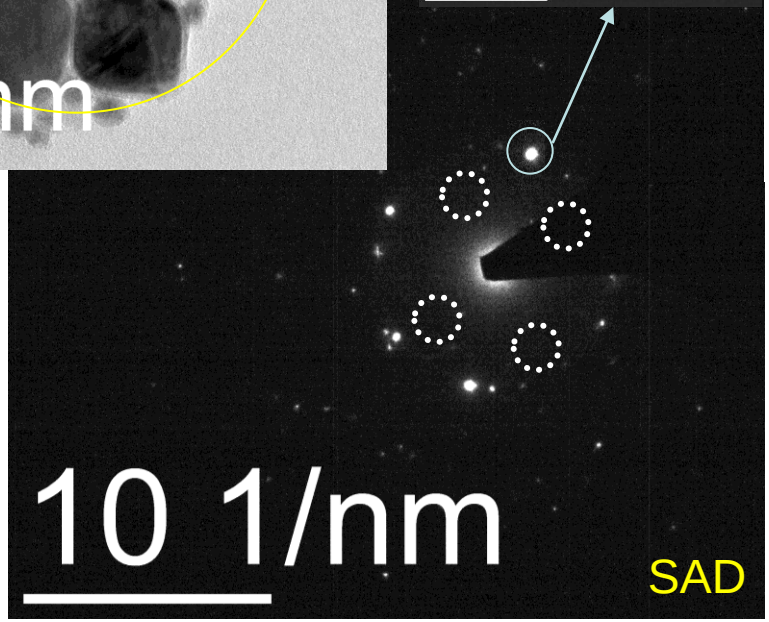
$$\propto (\mathbf{q} \times \mathbf{q}') \cdot \mathbf{M} \, sin\varphi$$

P. Schattschneider et al., Nature 441 (2006) 486-488

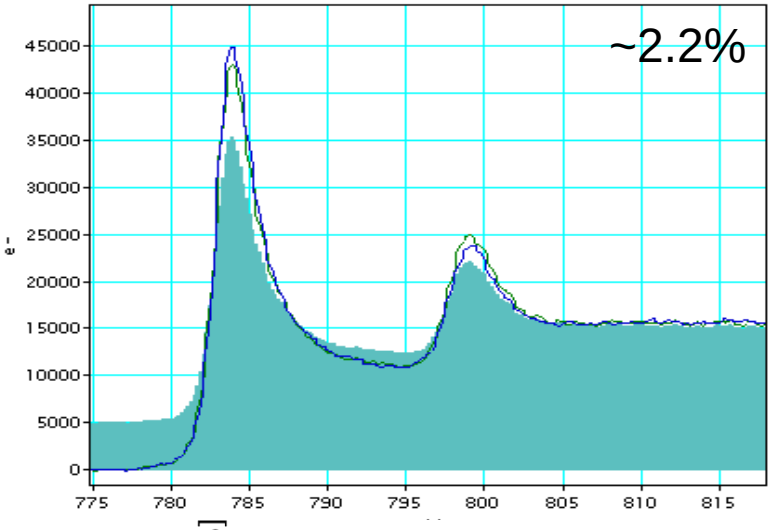
EMCD of Co Nanoparticles

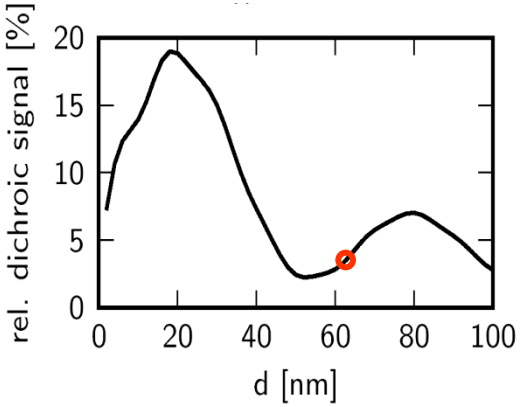






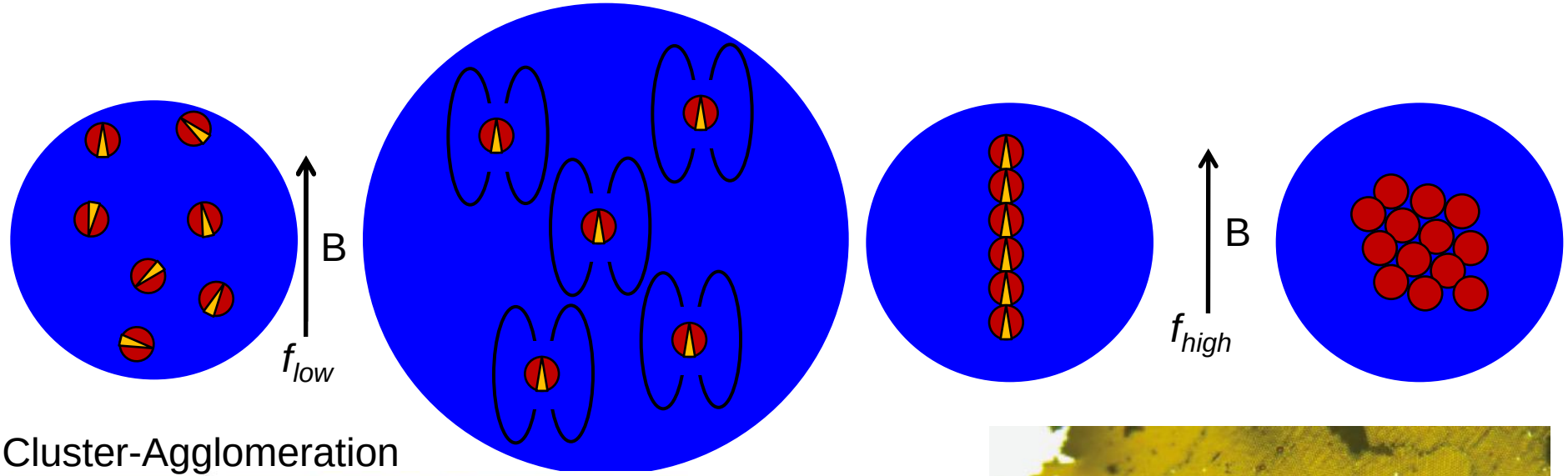
EELS spectra
acquisition: 10s



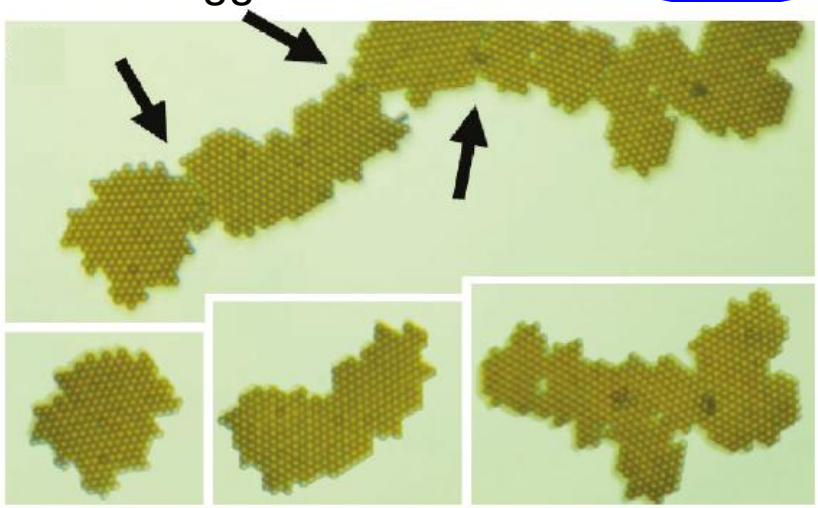


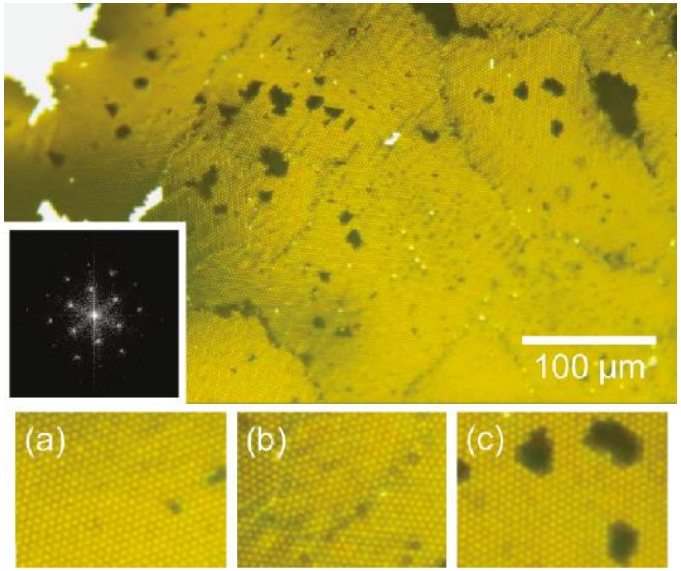
Interparticular interaction in solution: Magnetic nanoparticles as reconfigurable matter

Magnetic nanoparticles as reconfigurable matter:
M270 beads as model system wich can optically be monitored

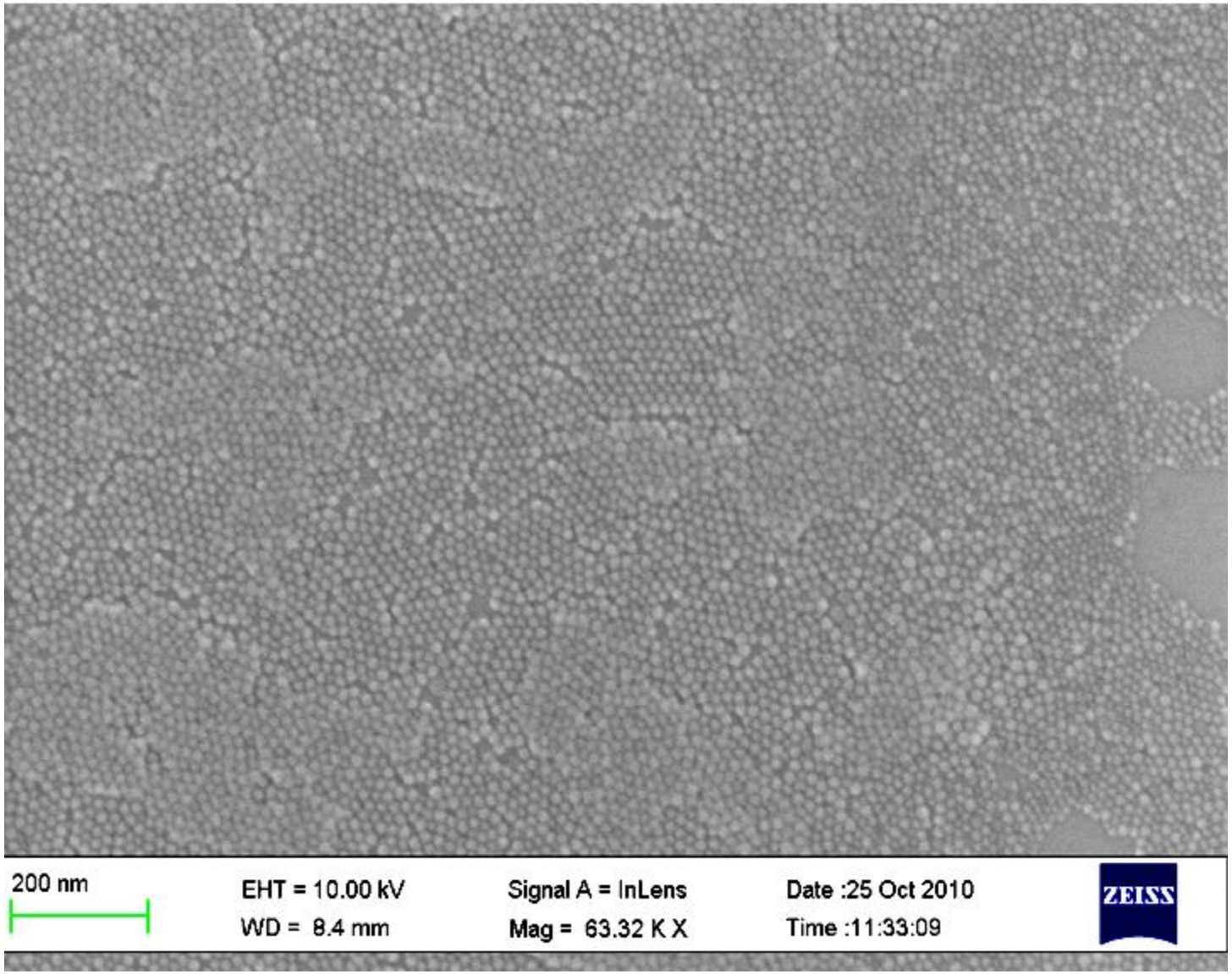


Cluster-Agglomeration



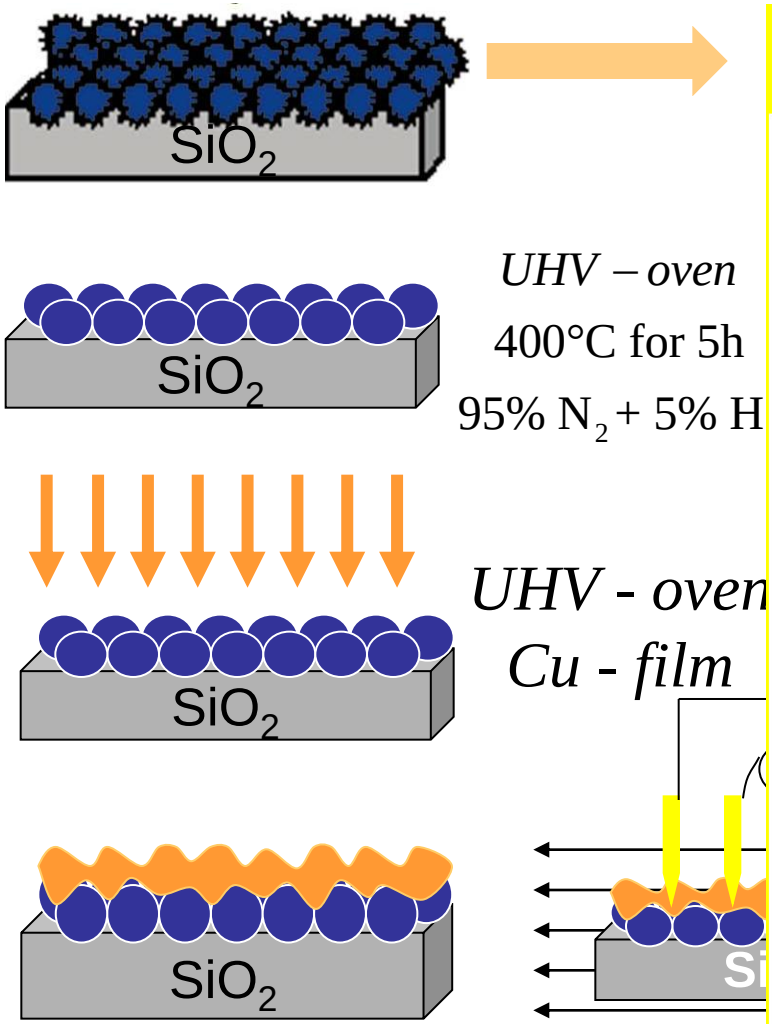


Transfer from beads to magnetic Co-nanoparticles



Nanoparticular GMR – Effect:

$\langle D \rangle_{\text{Co-nanoparticle}} = (8 \pm 0.2)$ nm

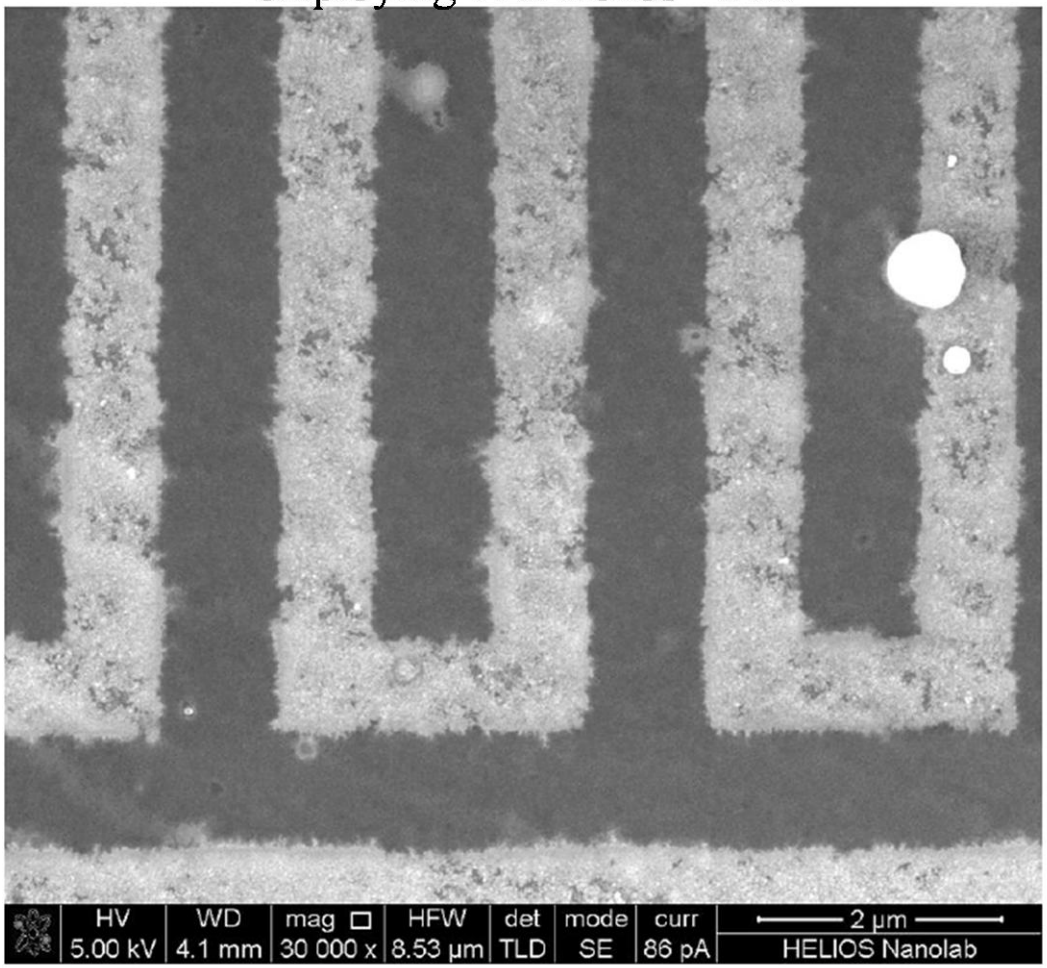


GMR effect at RT:

Magnetowidersland:

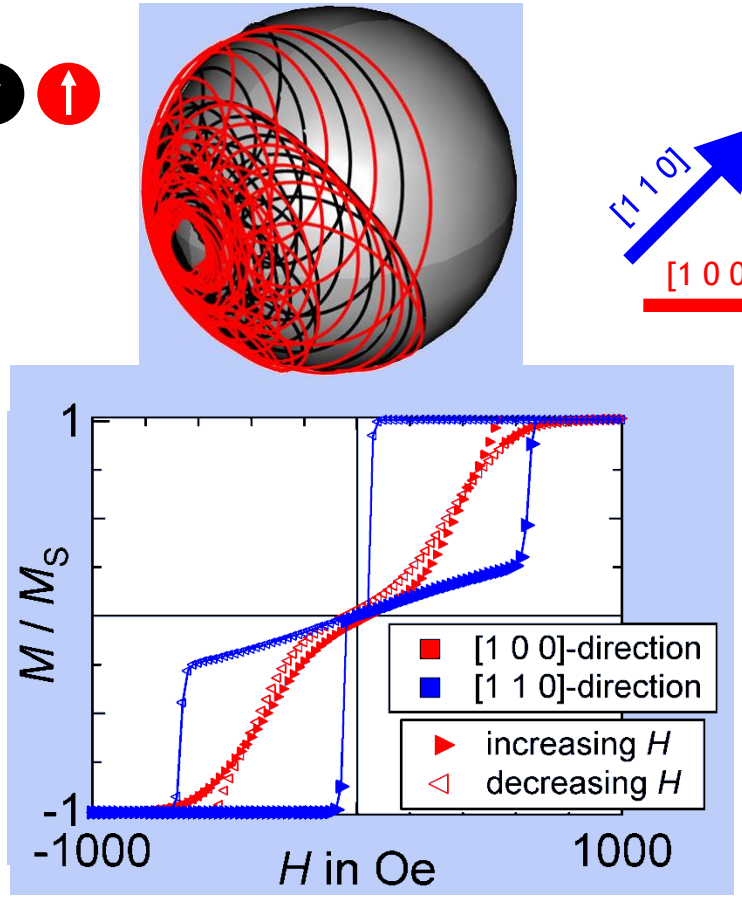
Magnetische Messungen:

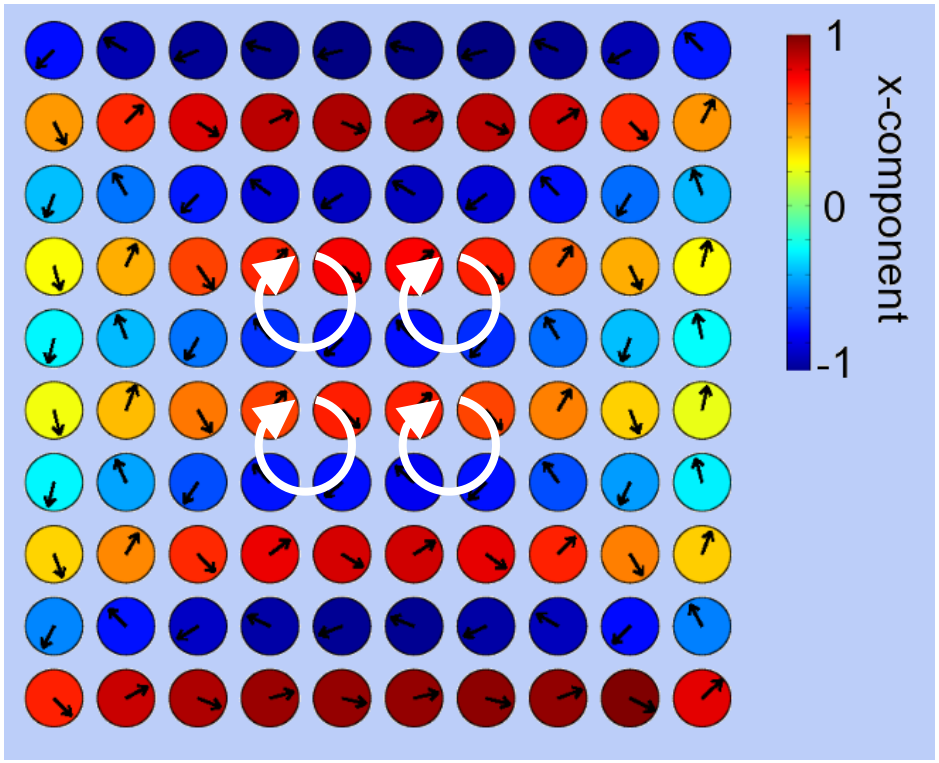
Mäander shaped GMR-sensor fabricated employing FEI Helios - FIB



PhD th

Interaction dynamics of two-dimensional particle assemblies: Lattice approach employing Landau-Lifshitz equation

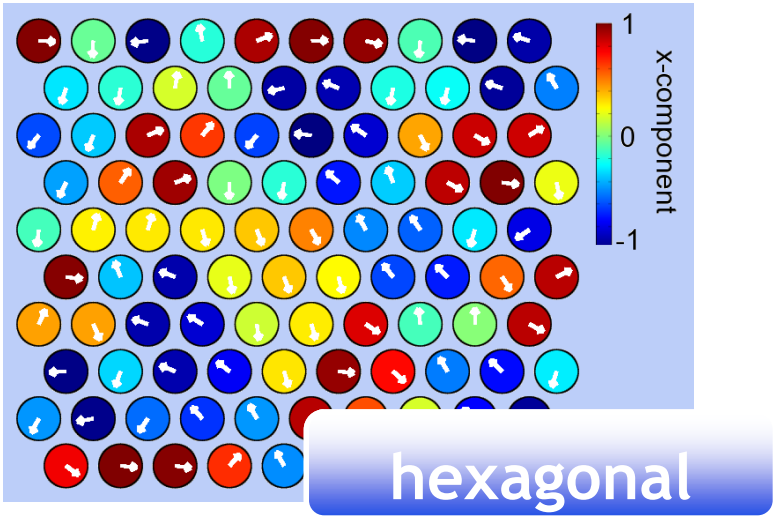


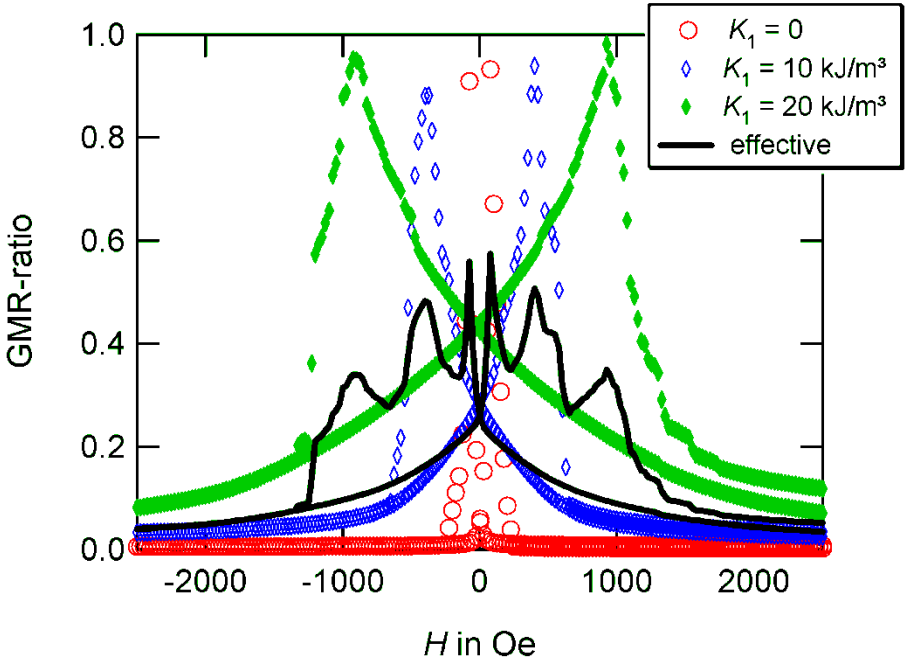


- antiferromagnetic vortex equilibrium state
- anisotropic hysteresis effects

A. Weddemann, A. Auge, F. Wittbracht, D. Kappe, A. Hütten, "Dynamic simulations of the dipolar driven demagnetization process of magnetic multi-core nanoparticles", J. Magn. Magn. Mat. 322 (2010) 643.

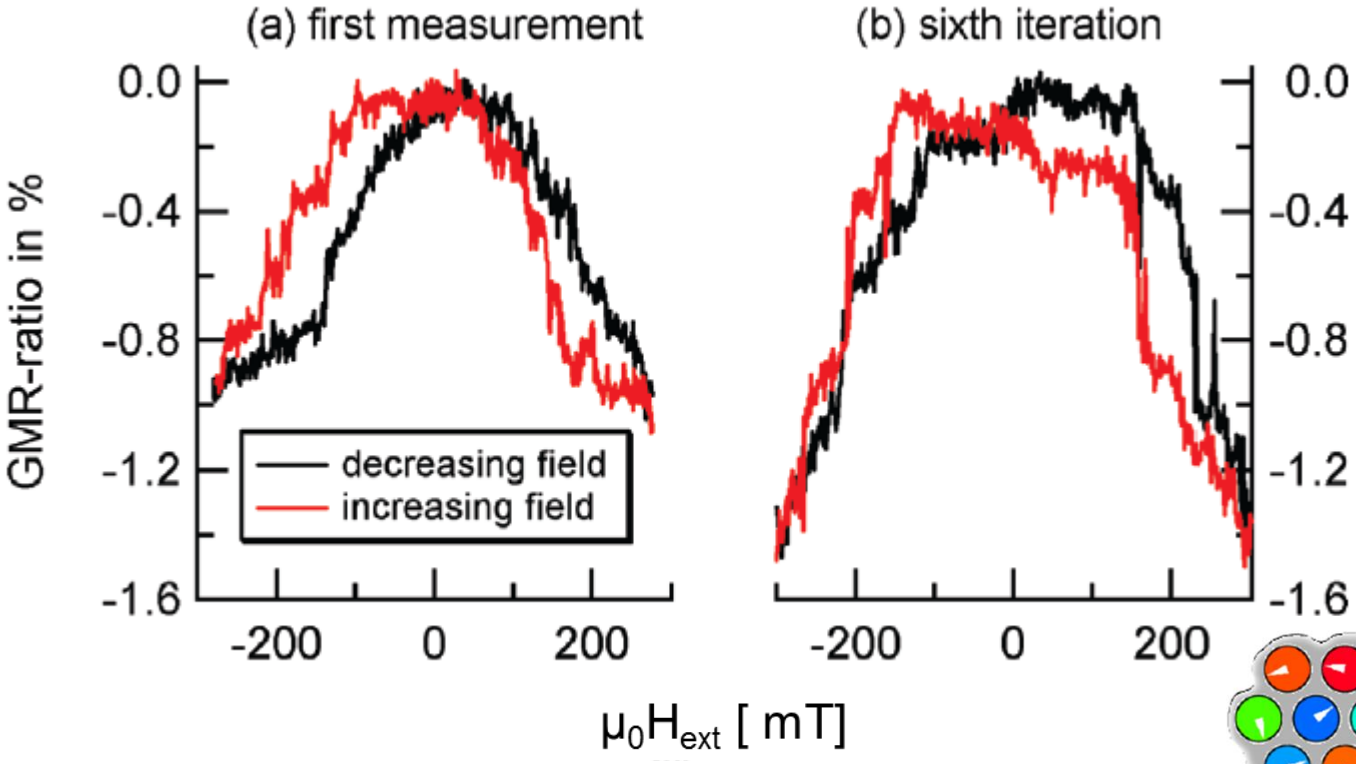
Nanoparticular GMR-ratio as a function of next neighbor coordination and distribution of magnetocrystalline anisotropy

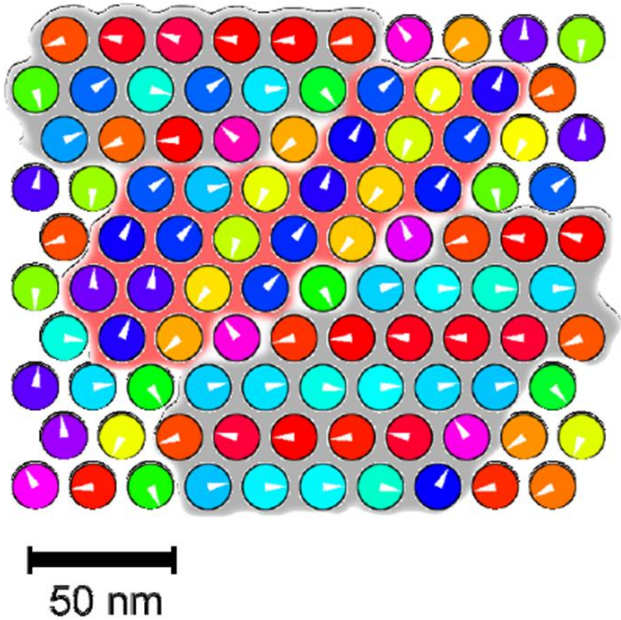




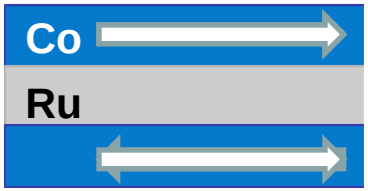
Reconfiguration of interparticular magnetic interactions

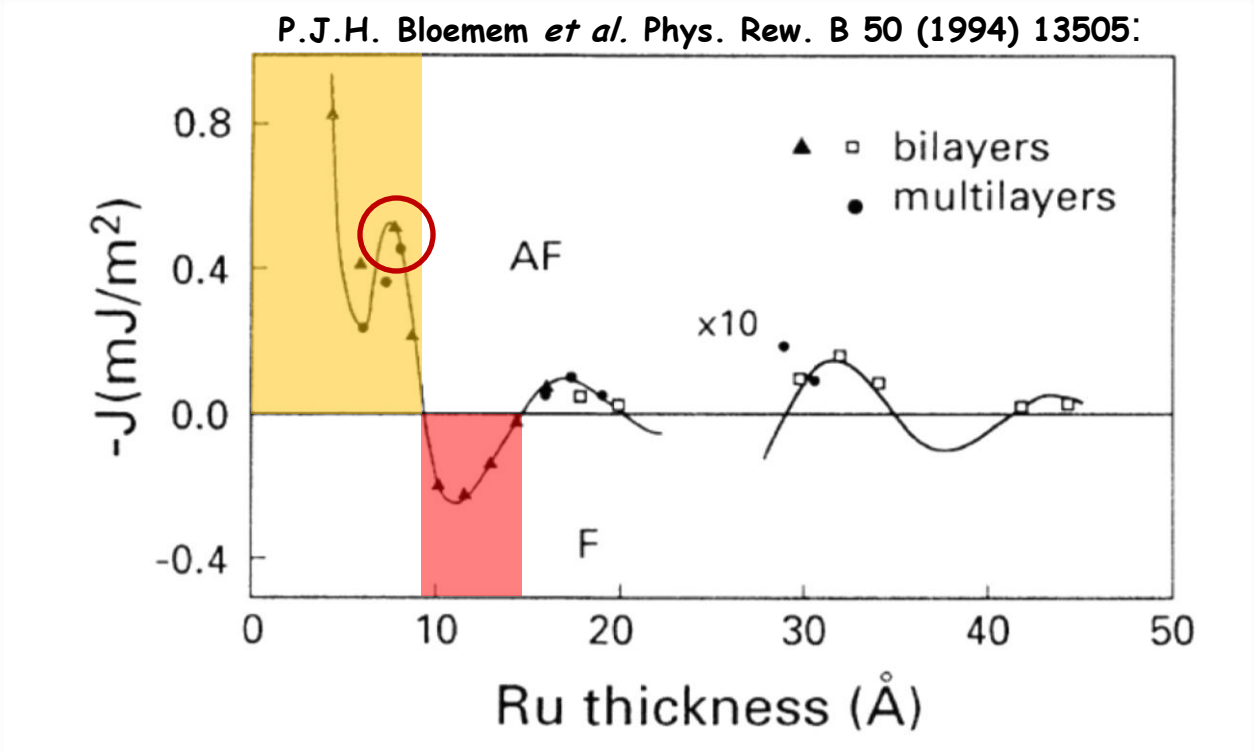
$< D_{Co} > = (14.9 \pm 0.4)$ nm

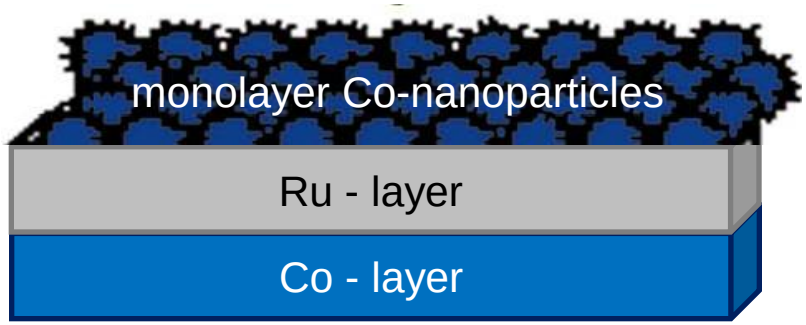




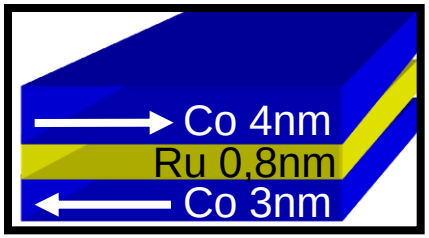
Transferring of spacer layer coupling onto Co nanoparticular monolayers



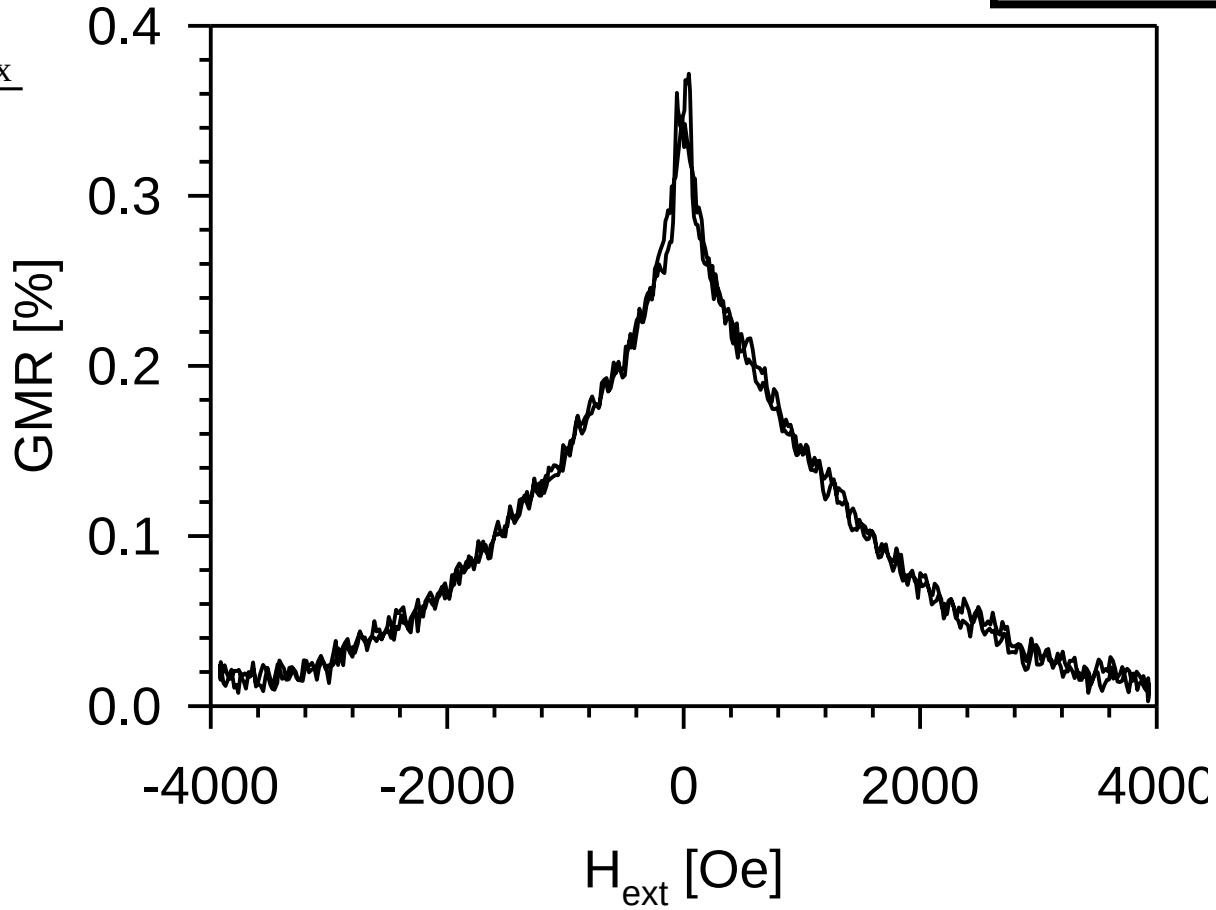




Co $_{3nm}$/Ru $_{0.8nm}$/Co $_{4nm}$ trilayers

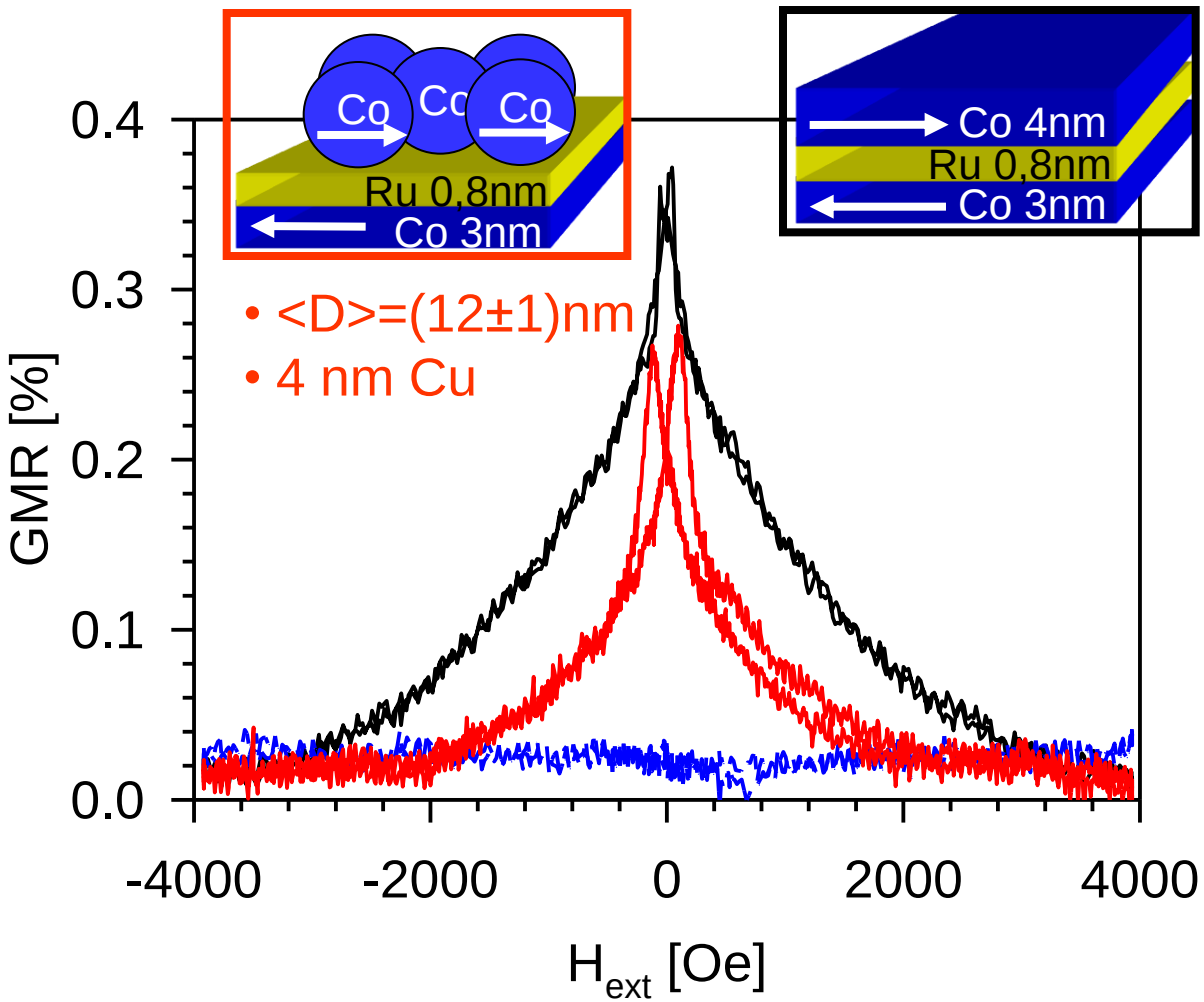


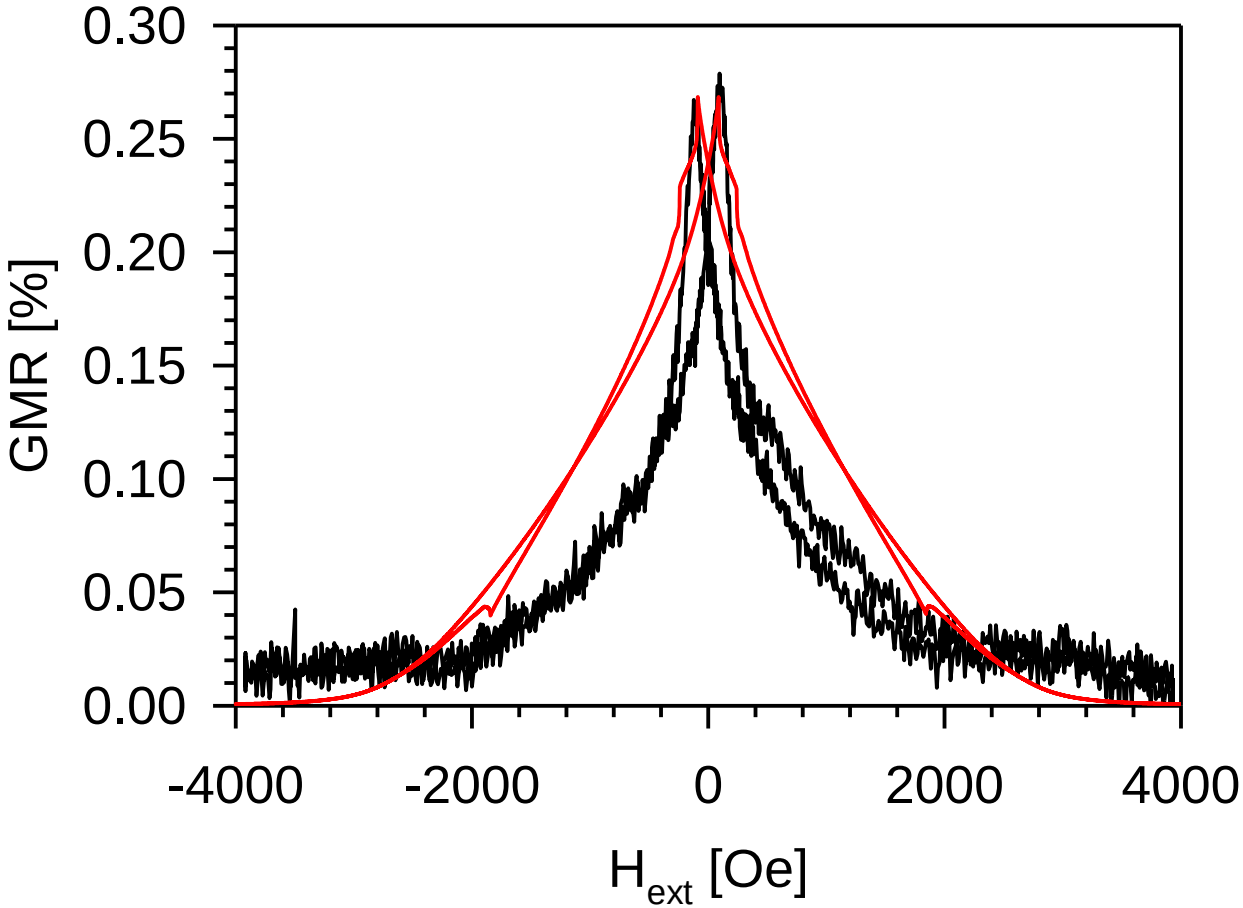
$$GMR = \frac{R_{min} - R_{\max}}{R_{\max}}$$



$$J_{AF} = \mu_0 H_{sat} \frac{M_1 d_1 M_2 d_2}{M_1 d_1 + M_2 d_2} = -0.23 \frac{mJ}{m^2}$$

$Co_{3\,nm}/Ru_{0.8\,nm}/Co_{12\,nm}$ - nanoparticles



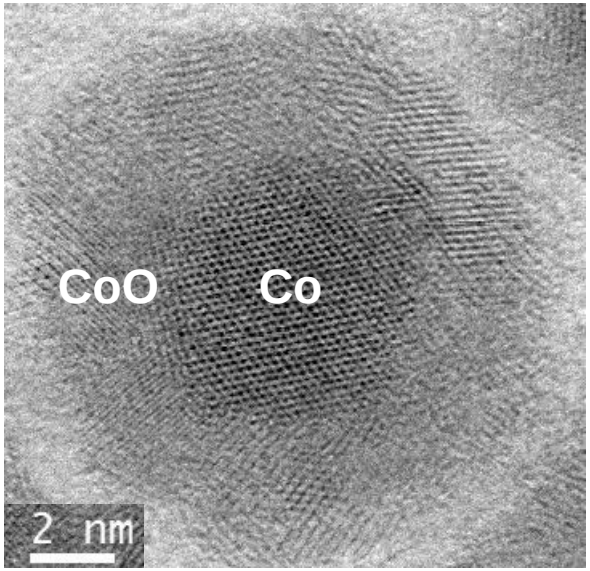


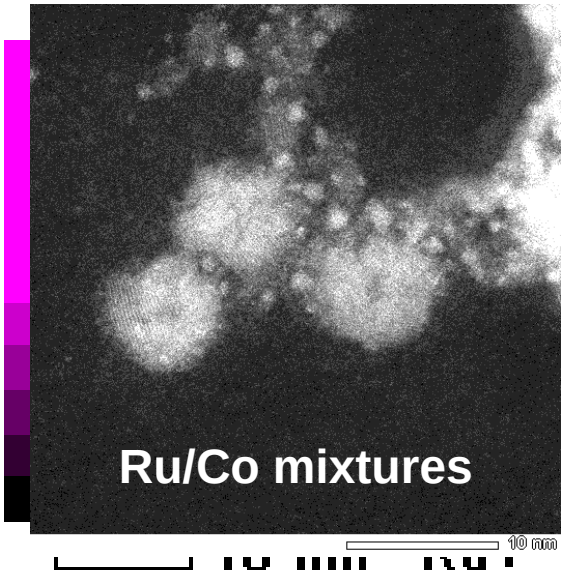
$$E(\alpha,\beta) = -M_{Co}t_{Co}H_{ext}\cos(\alpha) - M_{CoNP}D_{CoNP}H_{ext}\cos(\beta) - J_{AF}\cos(\alpha-\beta) - J_Q\cos^2(\alpha-\beta) + K_{eff,Co}t_{Co}\sin^2(\alpha-\gamma_i) + K_{eff,CoNP}t_{CoNP}\sin^2(\beta-\gamma_i)$$

► **Co nanoparticular monolayers behave like thin film layers**

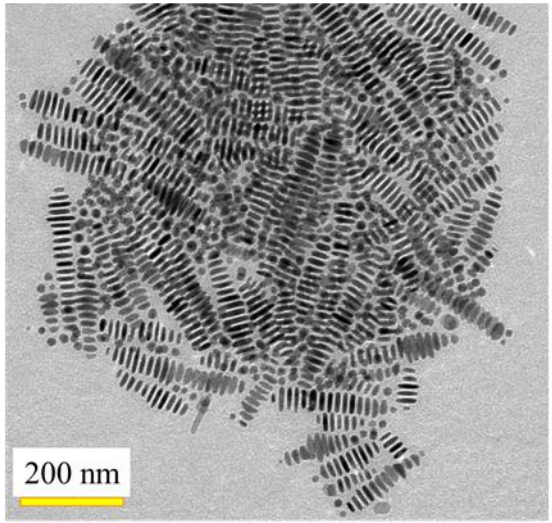
Printing of magnetic India ink

Potential magnetic India inks:

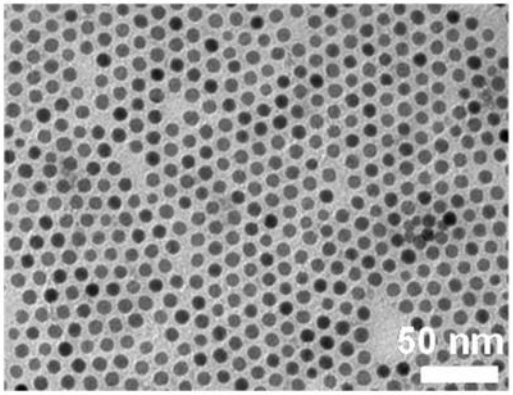




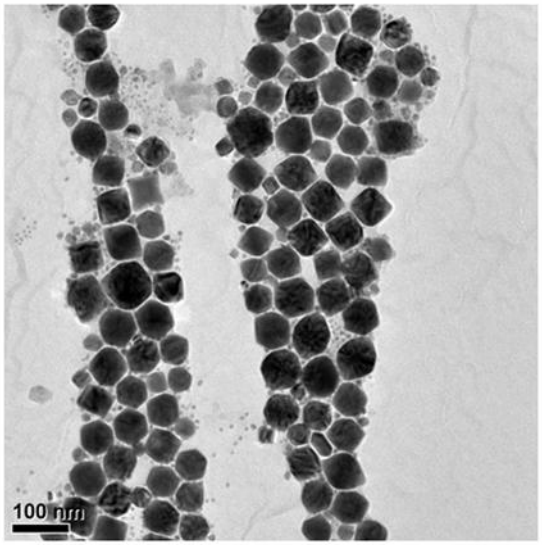
Co – discs



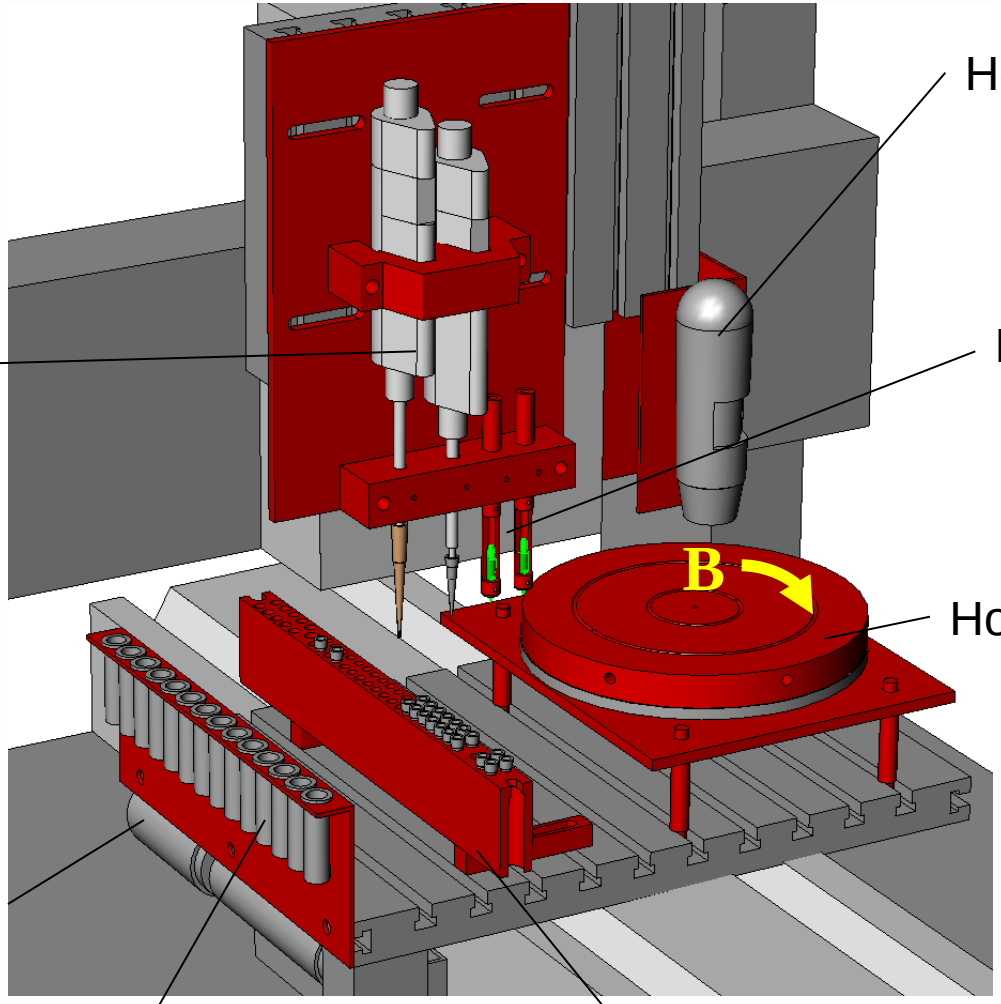
Co – spheres



Co – cubes



Printing nanoparticular GMR-sensors:



Horizontal view

Mixing and dipping pipettes

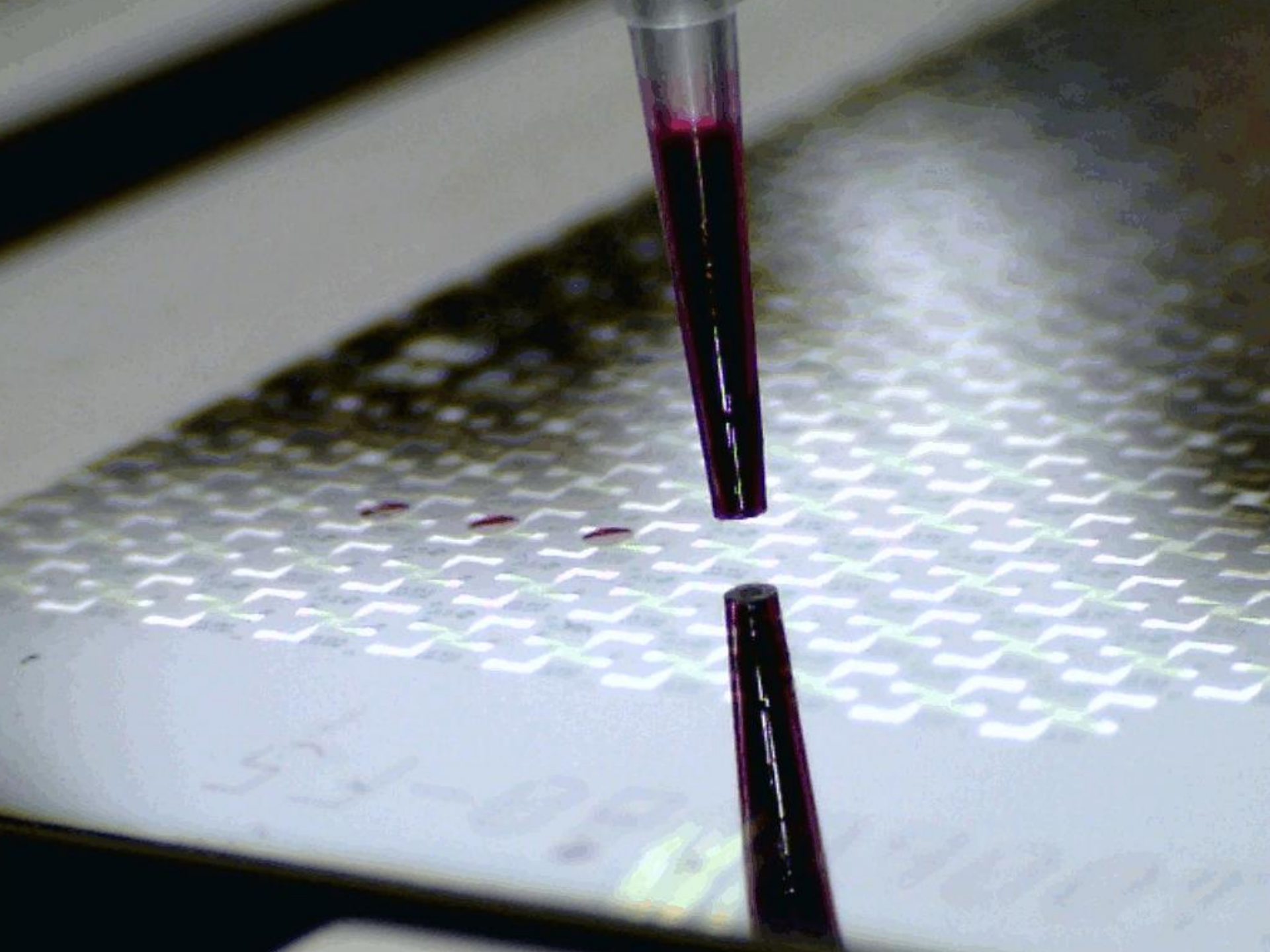
Print heads

Hot plate (400°C)

stroboscope

Tubes for mixture and cleaning

Pipette tip holder with dropper



Combining Magnetic nanoparticles with XMR-senors for the next generation of biosensors

Sensor design has three major drawbacks:

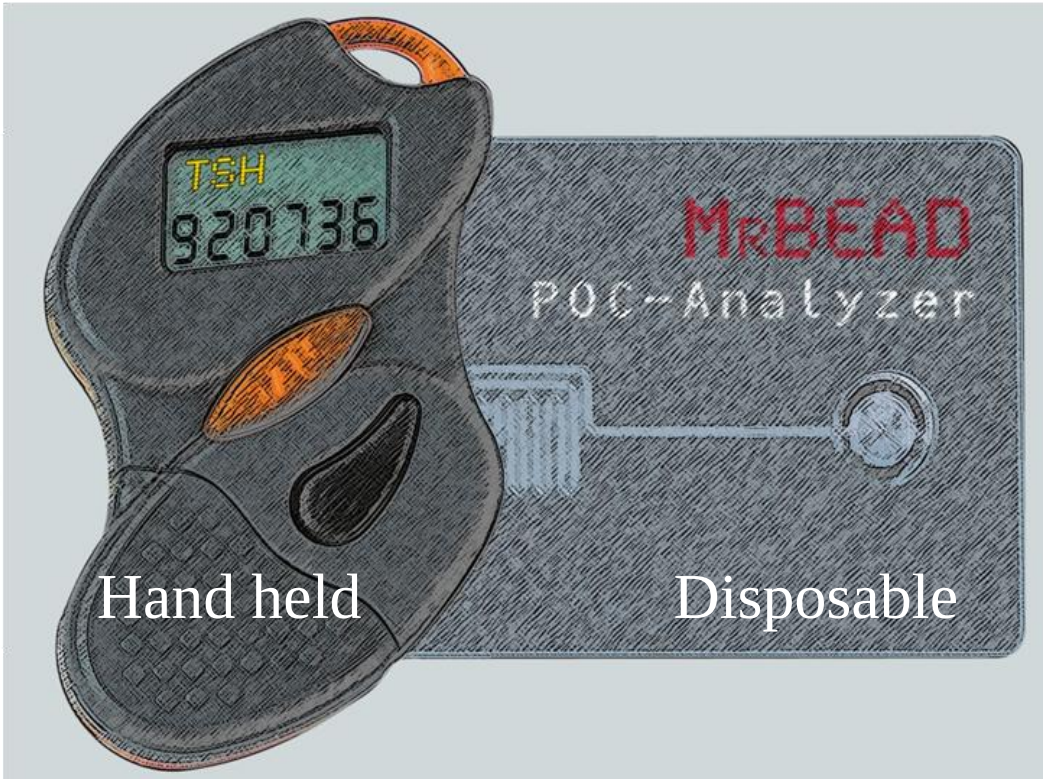
(1) Sensor surface has to functionalized

PROJEKTTRÄGER FÜR DAS

VDI|VDE|IT Bundesministerium für Bildung und Forschung mst|projektinfo

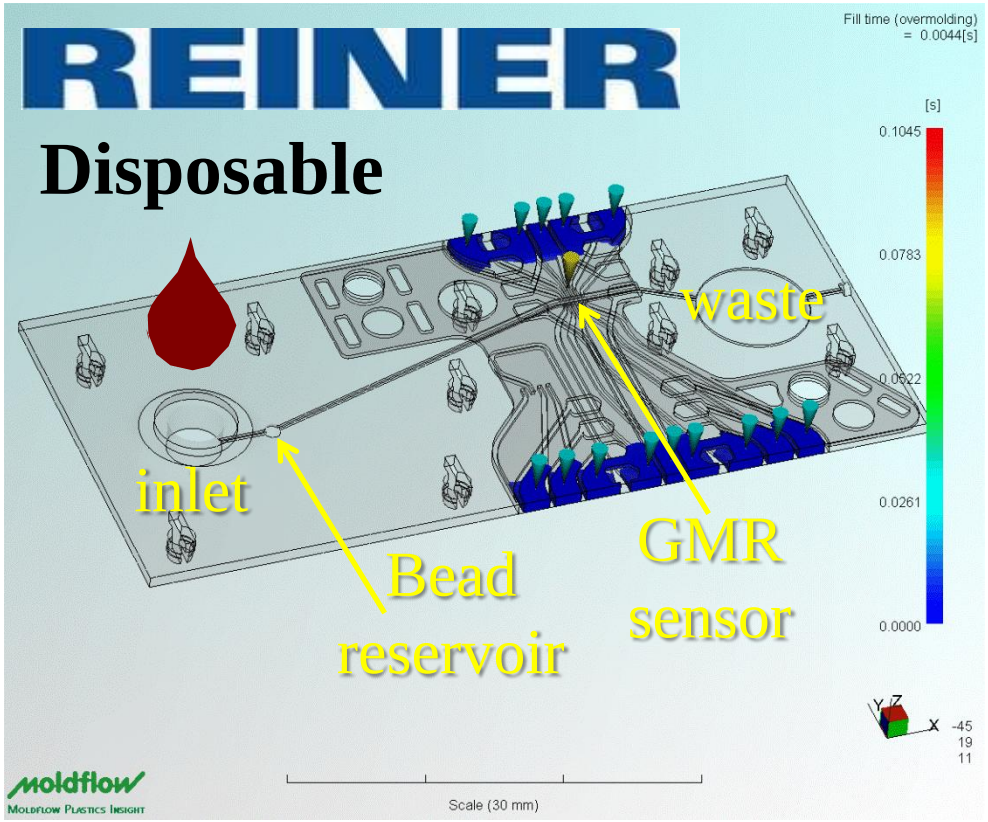
Bioanalytik auf der Basis biobeschichteter Magnetic Beads und MR-Sensoren - MrBead

- MicroCoat GmbH, Bernried
- IGEDI GbR, Karlsruhe
- Sensitec GmbH, Lahnau
- Reiner GmbH Co. KG, Furtwangen
- I-sys Autotec GmbH, Karlsruhe
- ACI ecoTec GmbH Co, St. Georgen
- BIT Analytical Instr, Schwalbach
- Uni Bielefeld, Bielefeld

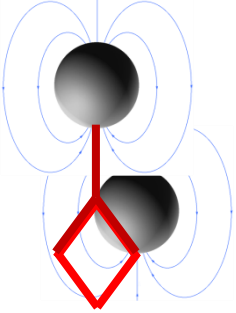


(2) Bead - GMR sensor interactions in microfluidic channel

bead height is very critical

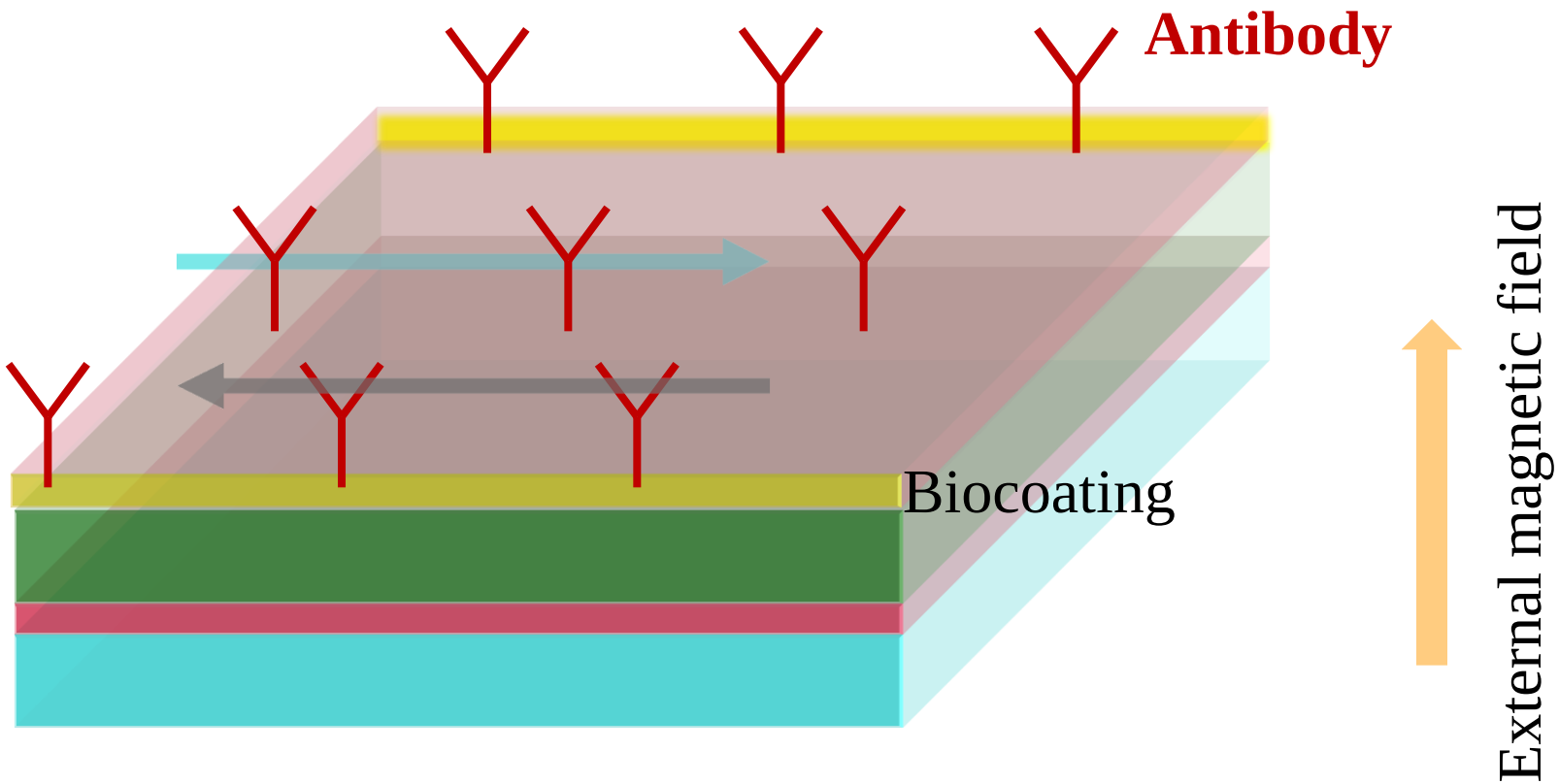


disposable_synfig_01_complete.avi



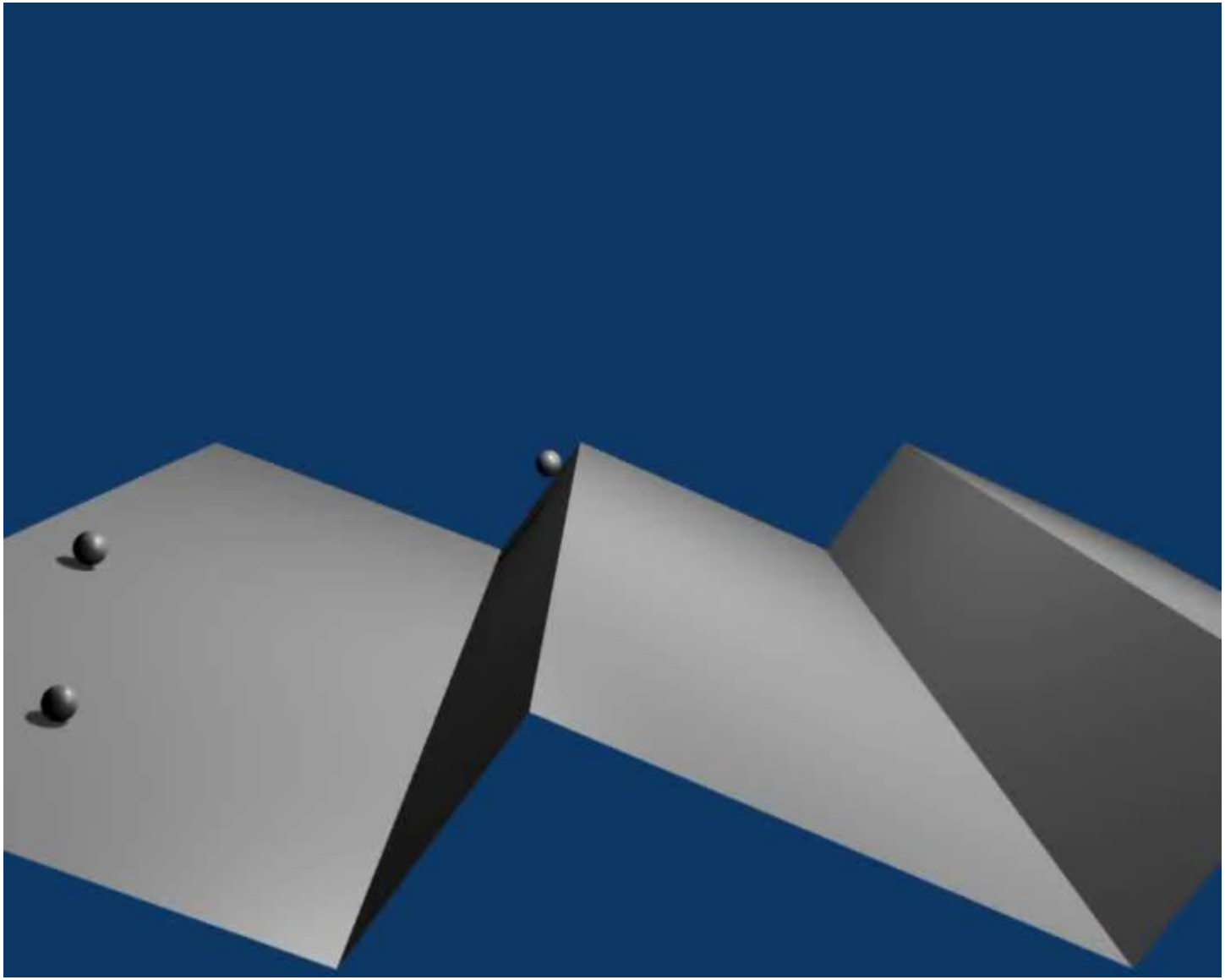
(3) Washing to remove unspecifically bound beads:

Antigen in blood plasma



Pumping is required !

Moving magnetic Beads in strayfield range to the sensors ⇒ Concept of magnetic on-off ratchet:



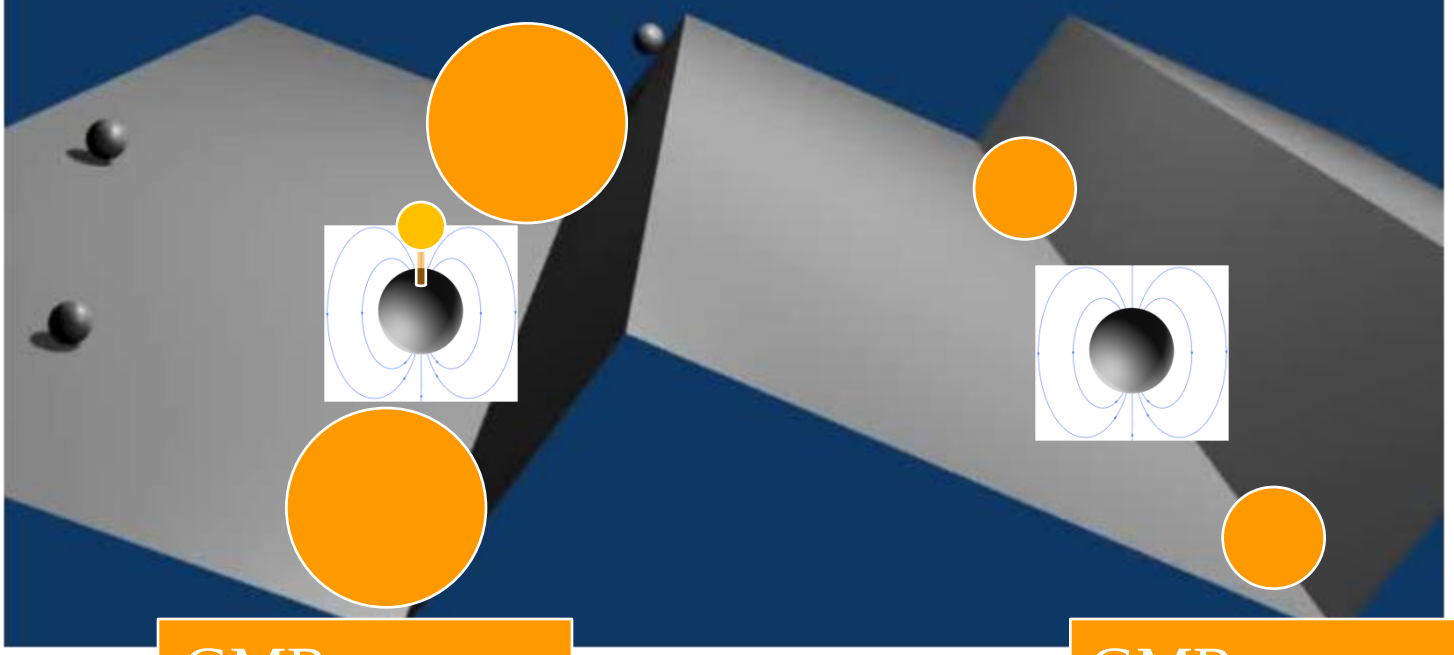
A. Auge, A. Weddemann, F. Wittbracht, A. Hütten, "Magnetic ratchet for biotechnological applications", APPLIED PHYSICS LETTERS 94 (2009) Article Number: 183507.

Combining Brownian motion and a magnetic potential allows for:

- fluidic system without pumps
- intrinsic separation of beads of different sizes
- intrinsic separation of beads carrying “Biomolecules”

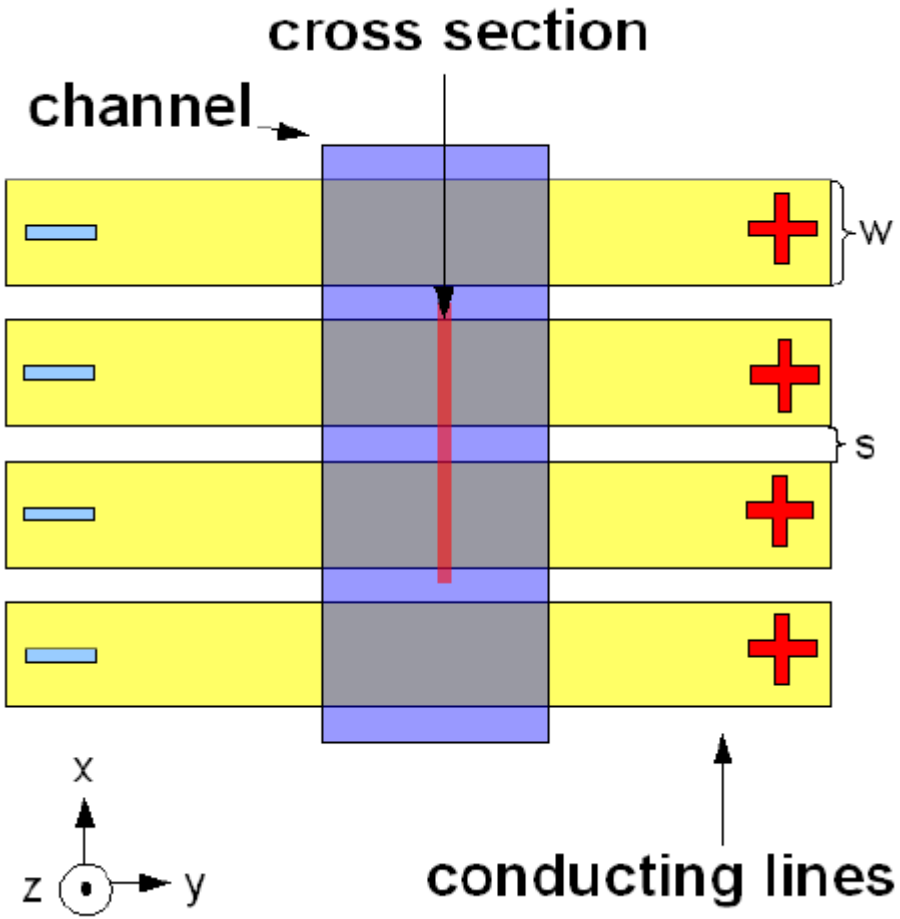
→ detection can be transferred to bead surface

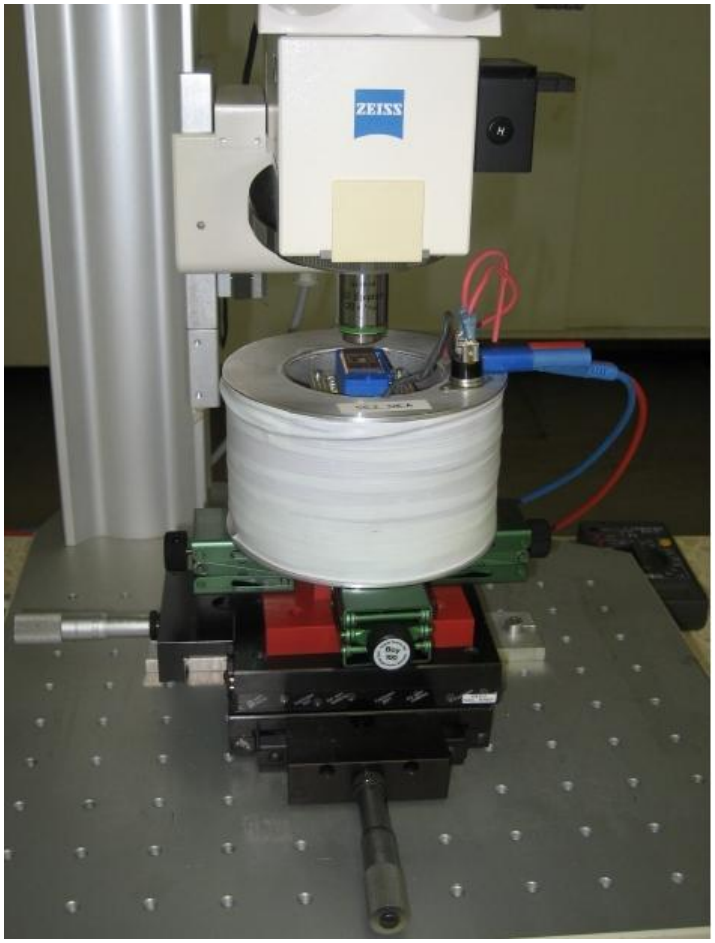
→ dynamic detection process required



Moving magnetic Beads without pumps
⇒ Concept of magnetic on-off ratchet:

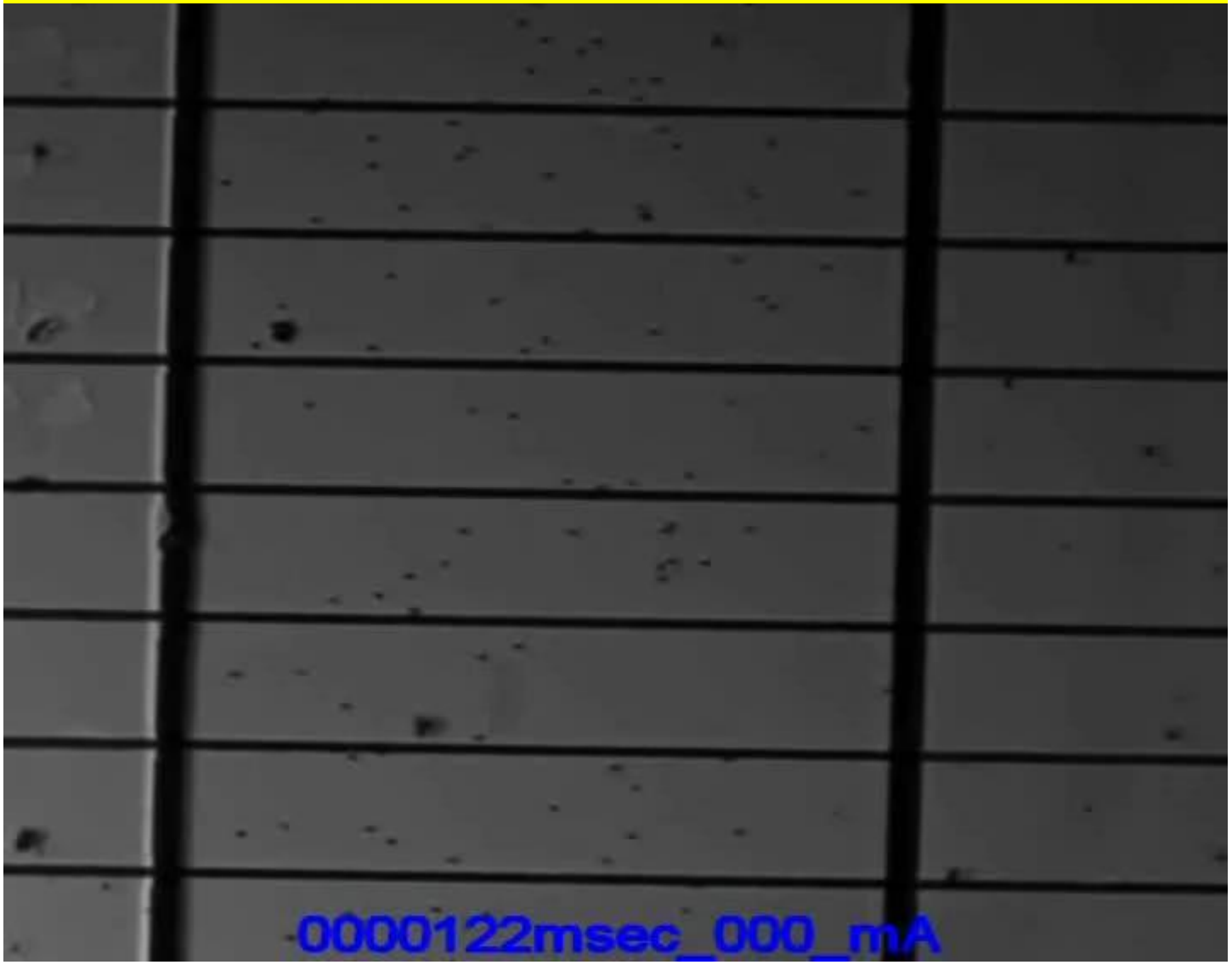
An magnetic on-off ratchet with a spatially asymmetric potential can be realized combining conduction lines in (x,y) – and a magnetic coil field in z – direction





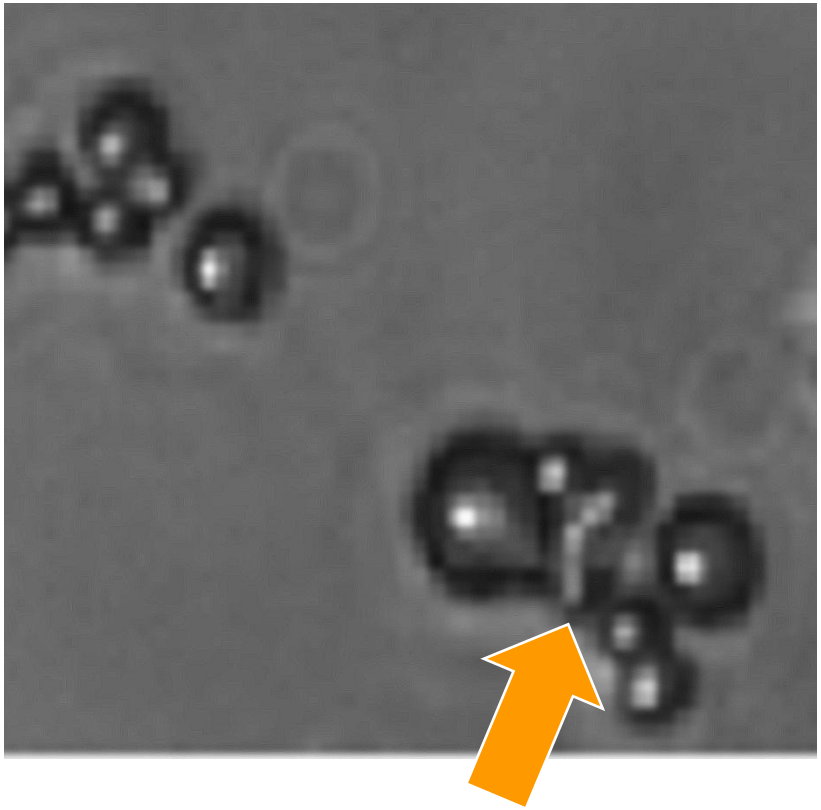
Moving magnetic Beads without pumps
⇒ Concept of magnetic on-off ratchet:

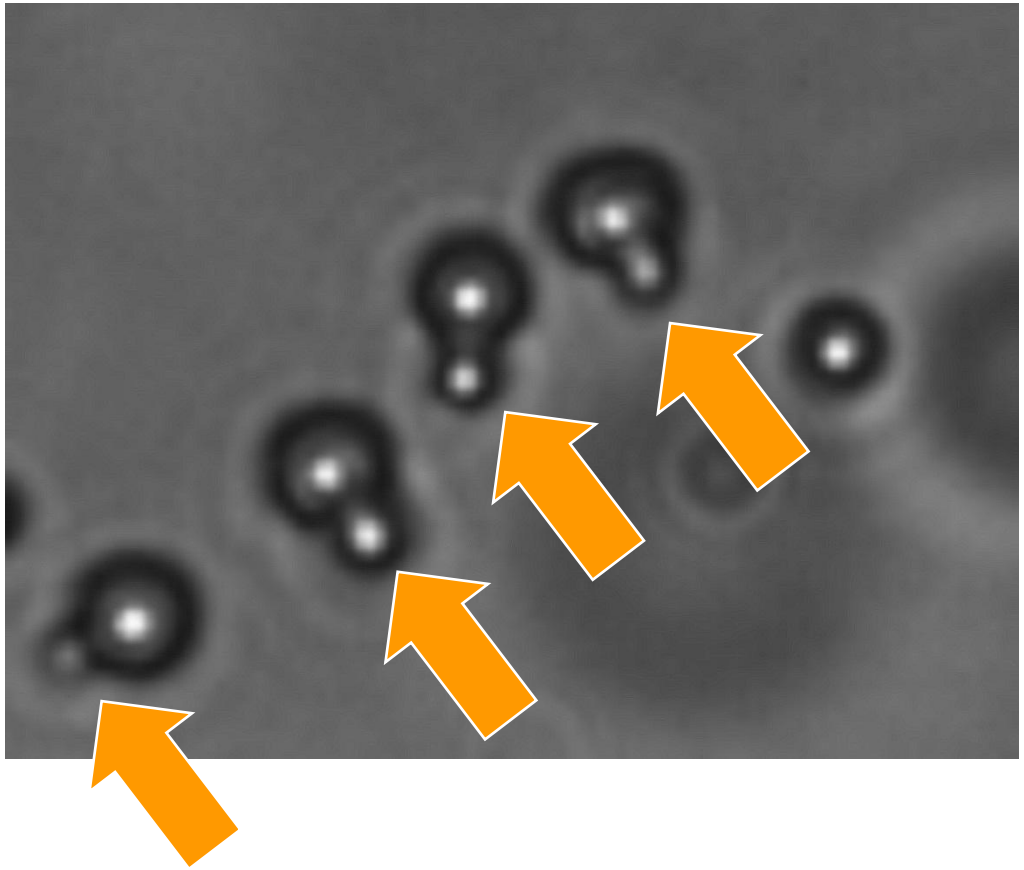
⇒ experimental realization



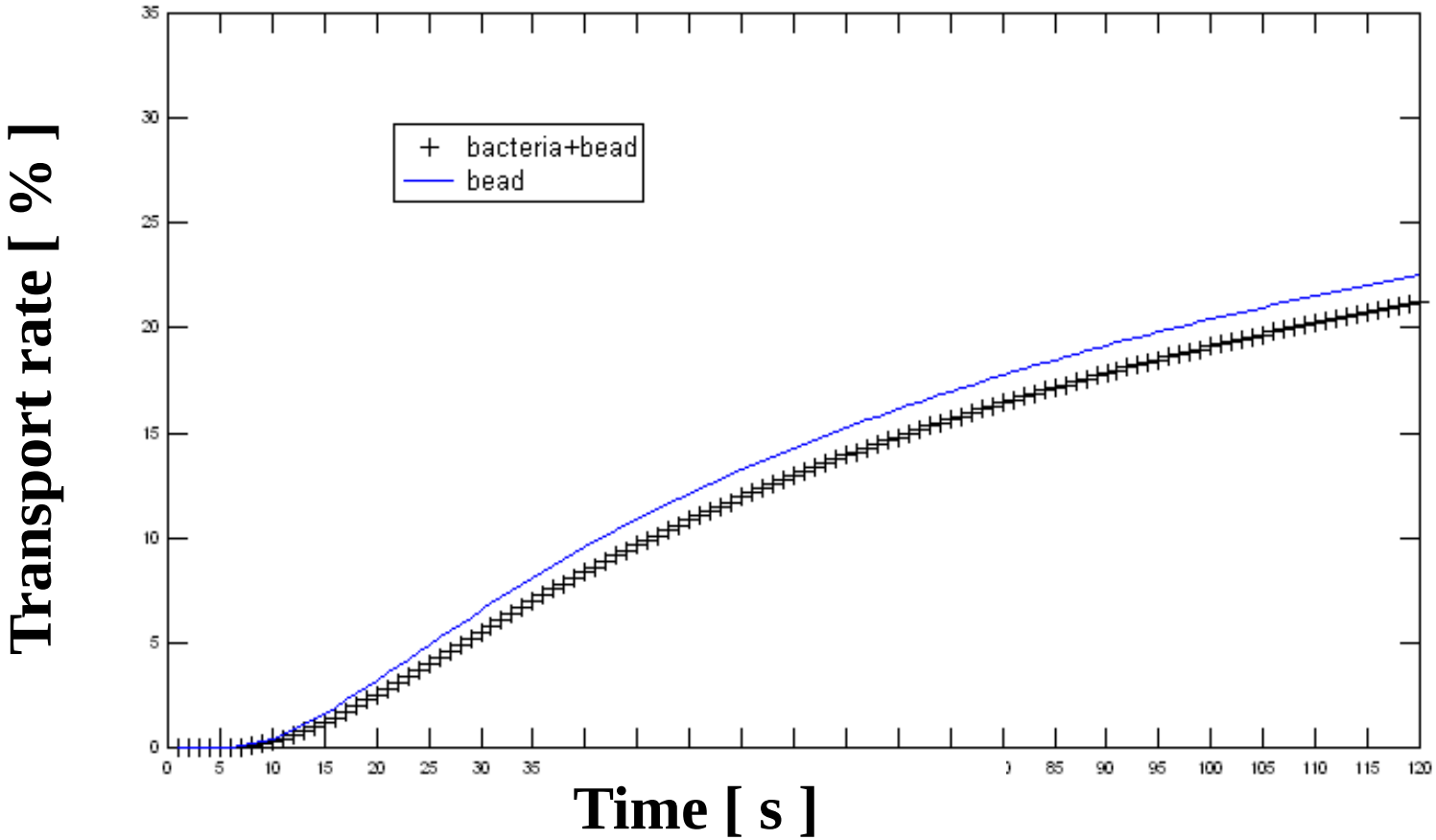
Proof of principle:

Diffusion of
Chemagen beads <D> = 1.5 μm with Lawsonia bacteria
Compared to “naked” beads





Chemagen beads <D> = 1.5 µm without Lawsonia bacteria

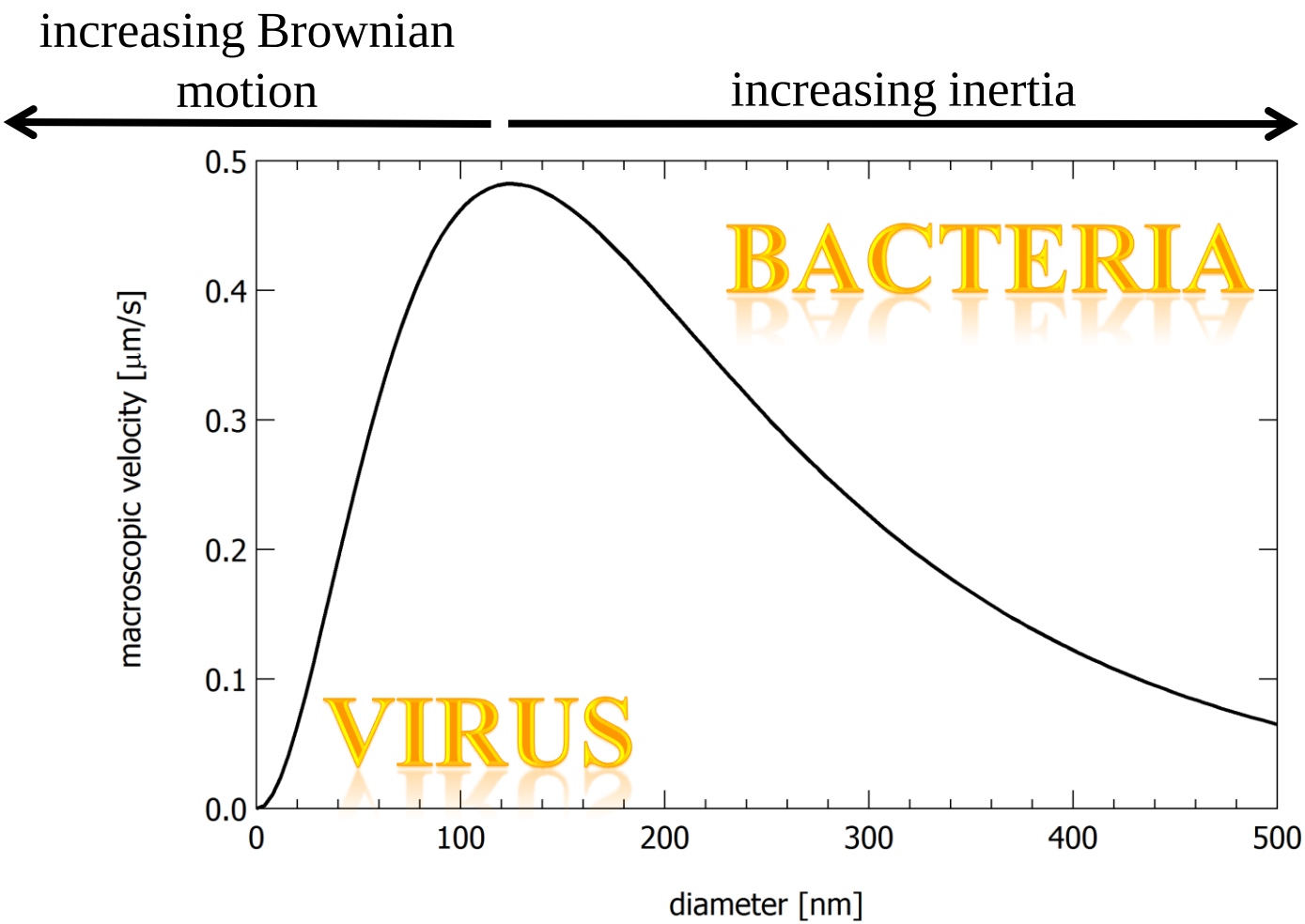


Chemagen beads <D> = 1.5 µm with Lawsonia bacteria

Transferring the detection on to the beads:

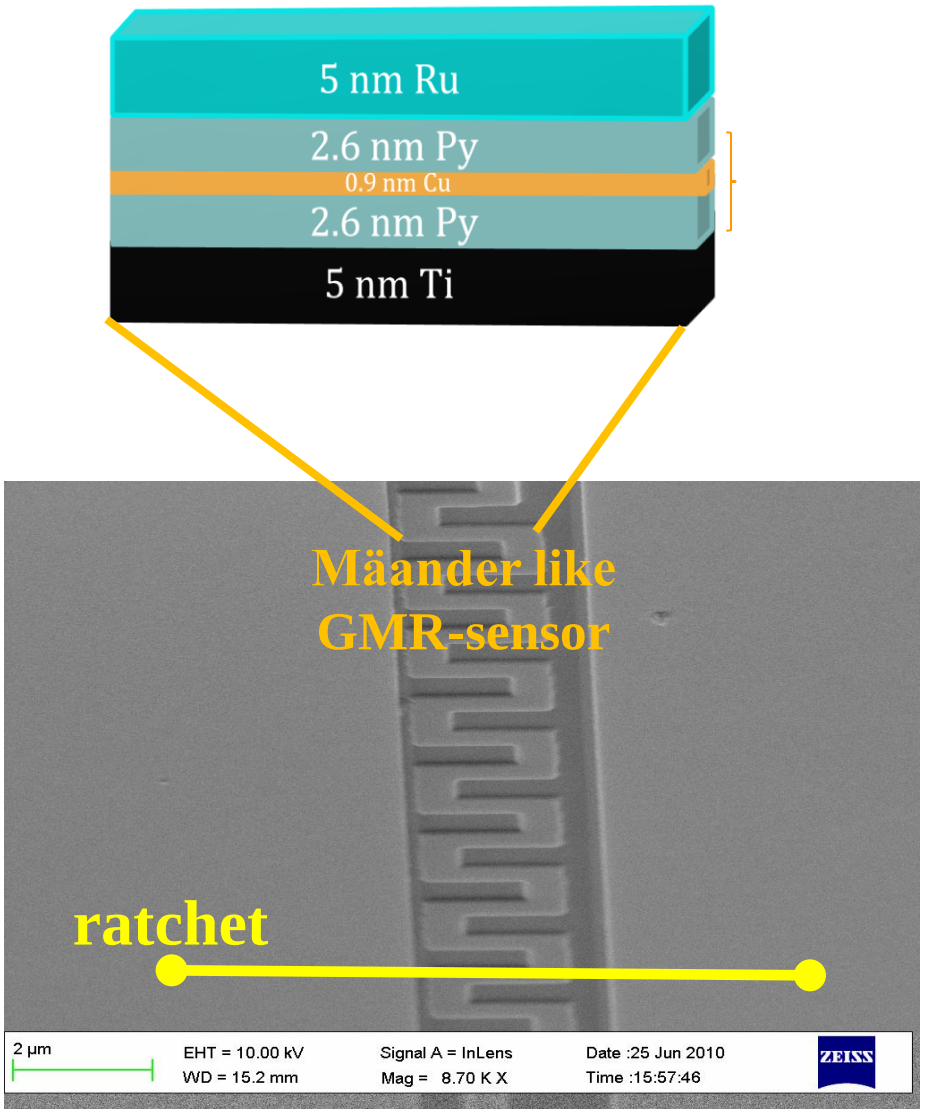
adjusting bead size to bimolecular size

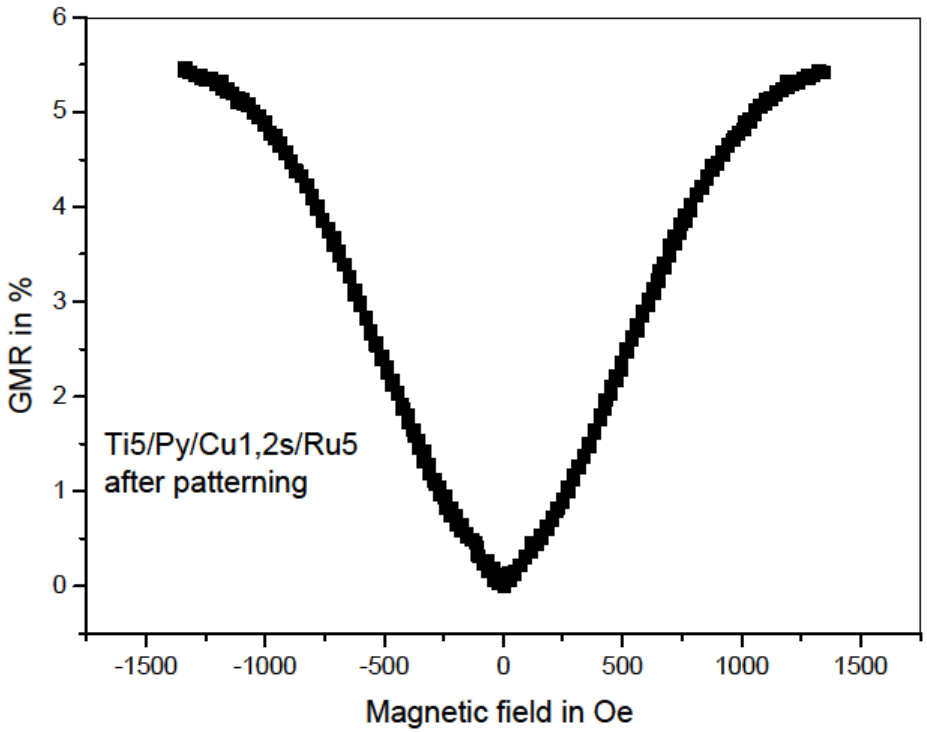
→ possible size range



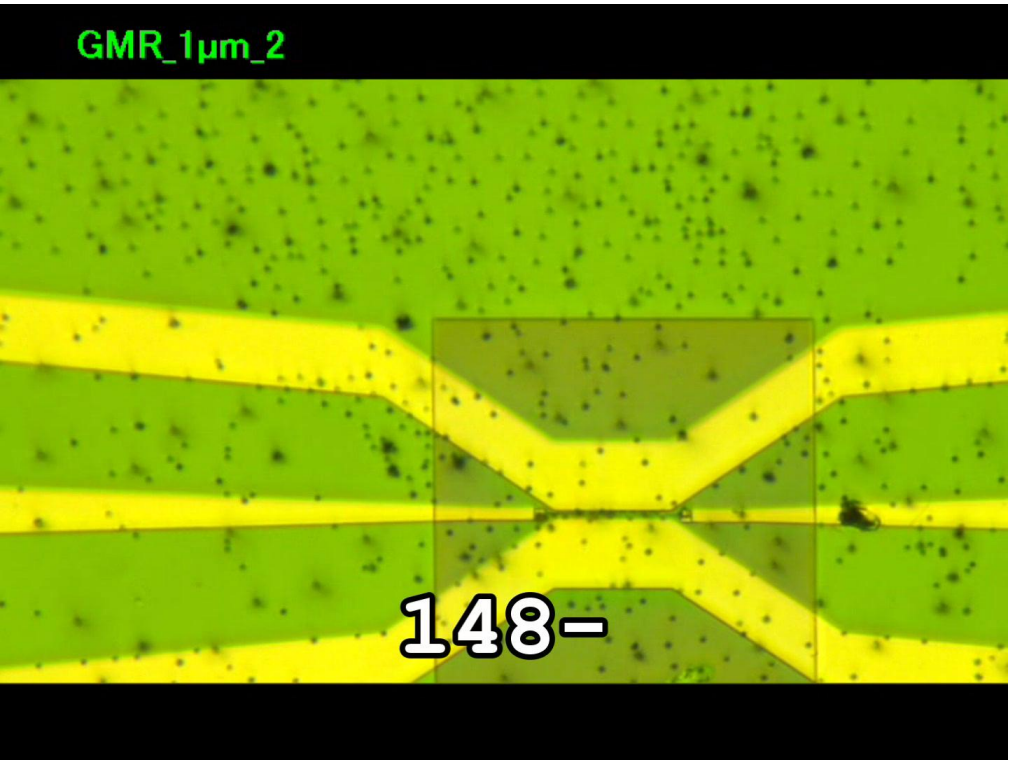
Challenge to measure dynamically:

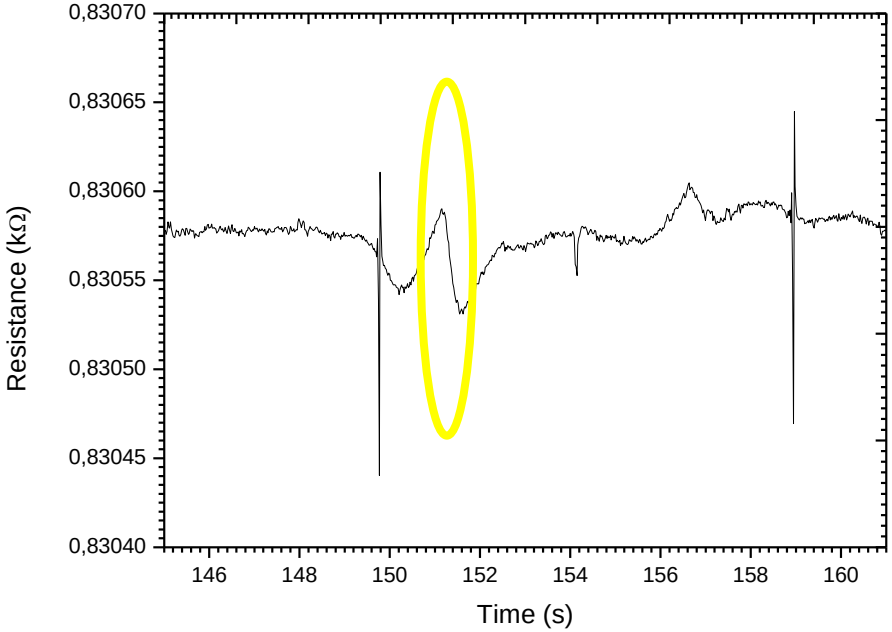
integration of GMR-sensors into the ratchet





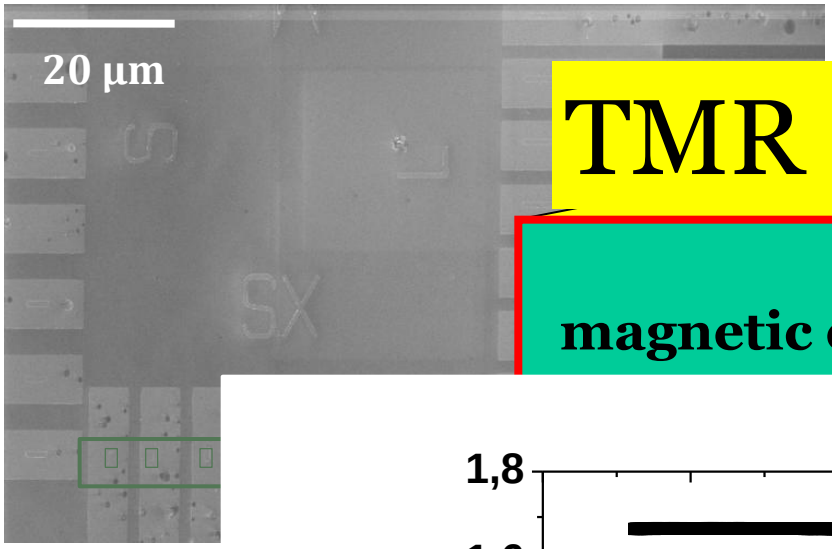
Dynamic detection with GMR-Sensors in the ratchet





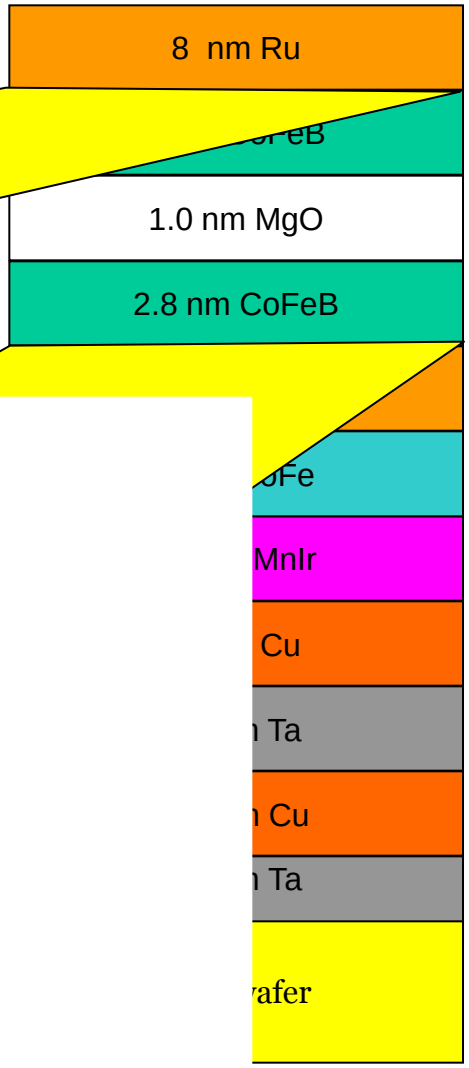
only 0.006% GMR-effect-amplitude

Transition GMR- → TMR-sensors

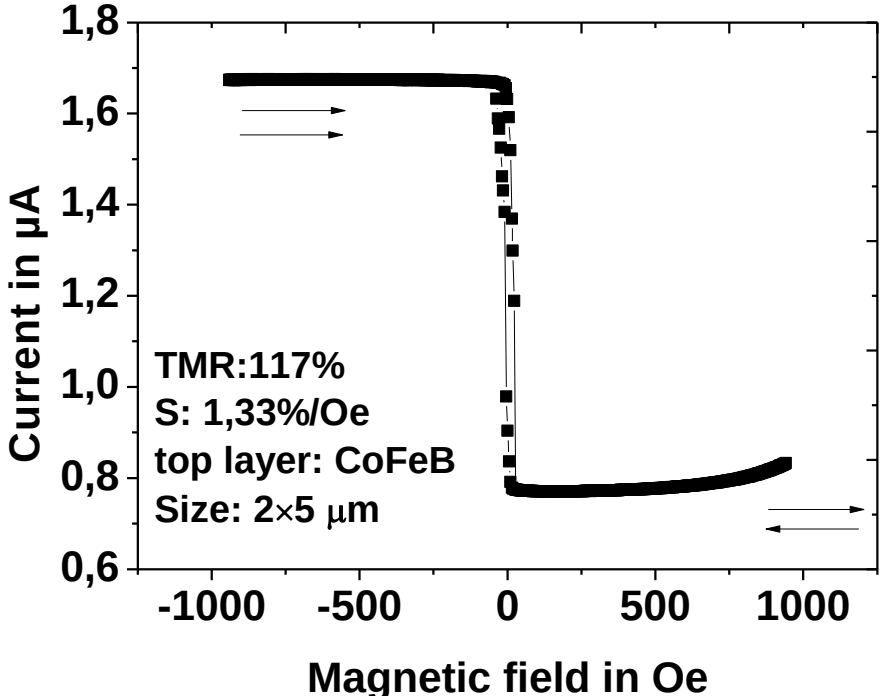


TMR - Cell

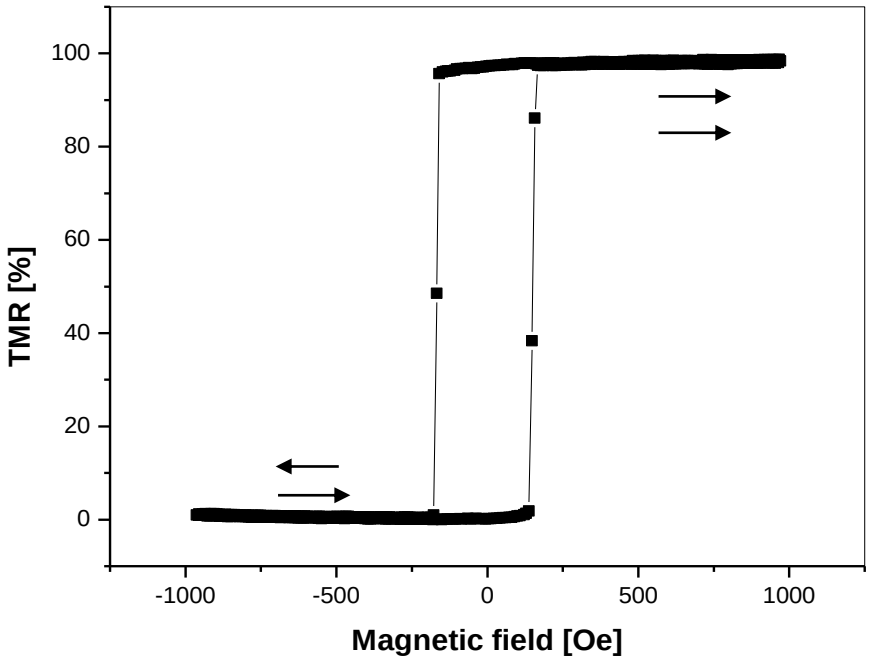
magnetic electrode

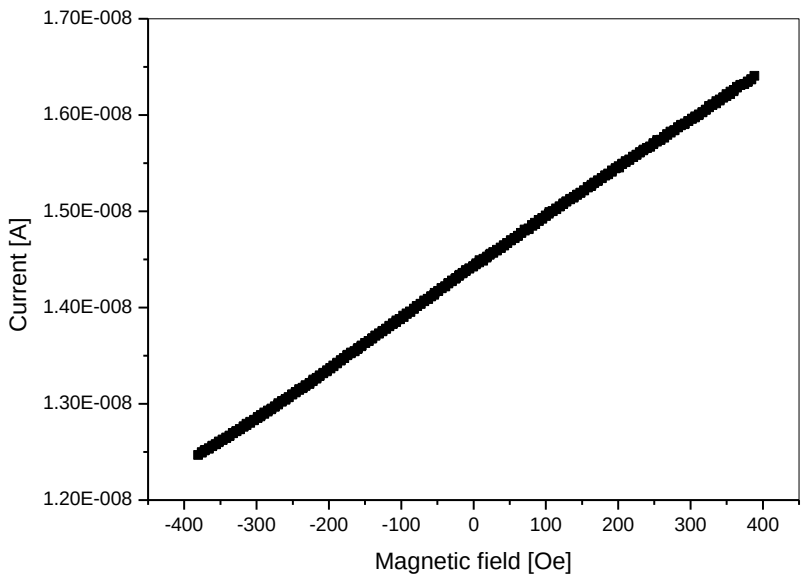


Total are
Dimensio
Distance

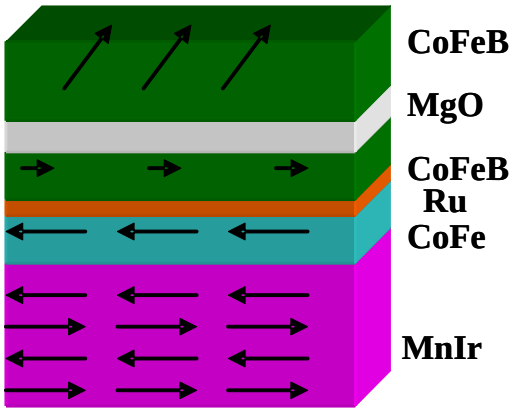


Linear TMR - output:

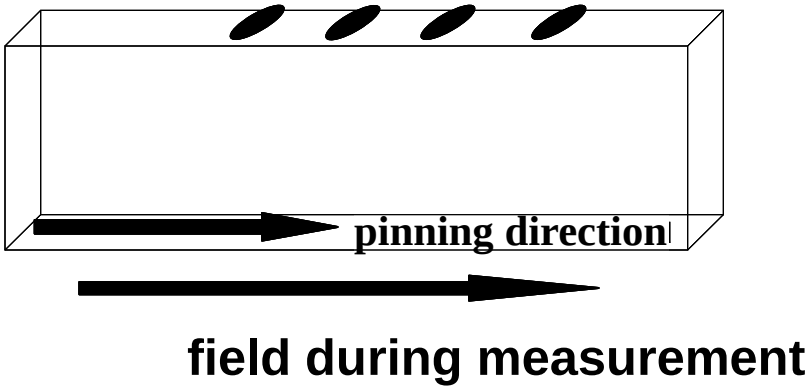




free sensor layer

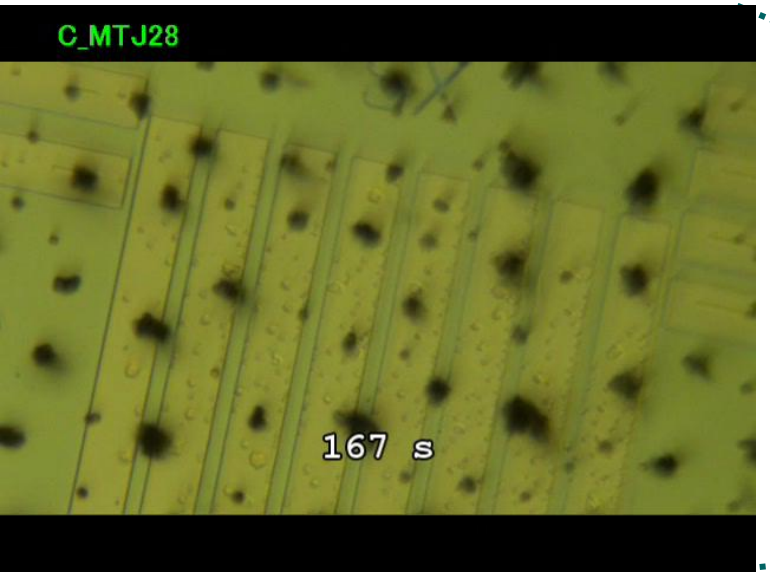


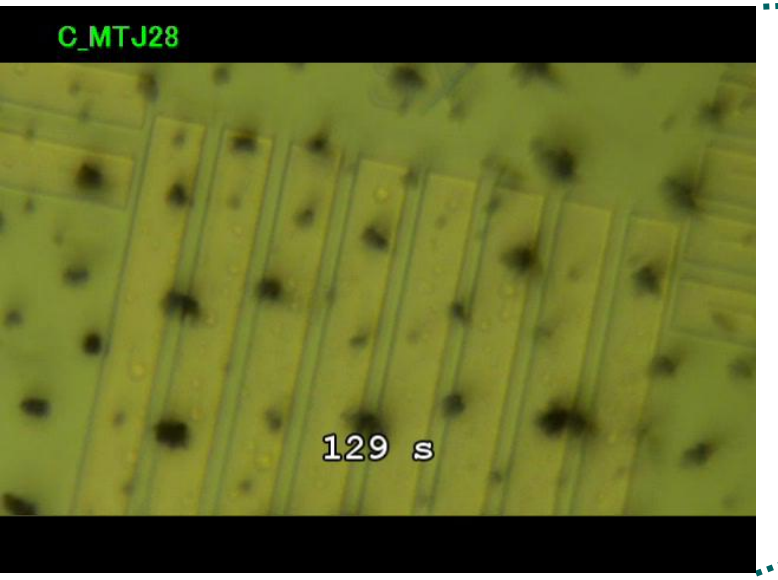
Microstructured TMR – sensors:

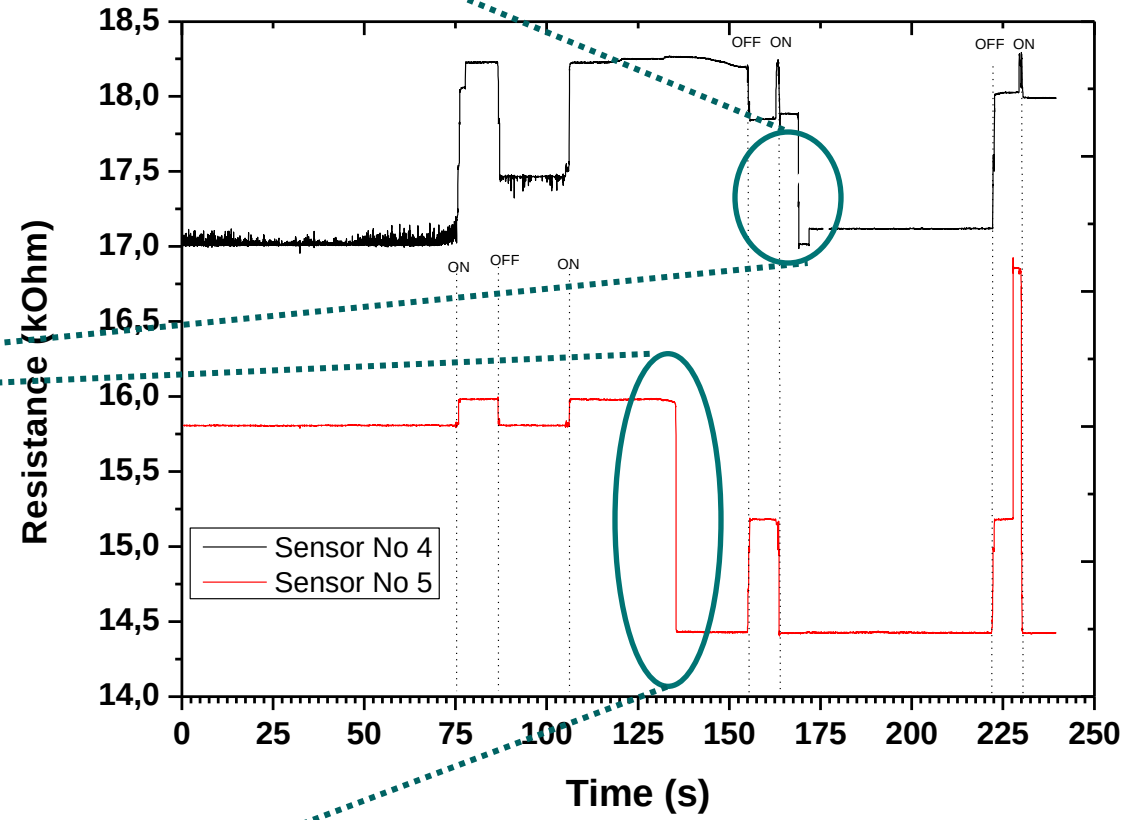


Magnetization of the free layer follows the shape anisotropy

Dynamic detection with MTJ-Sensors in the ratchet







9.6 % MTJ-signal-amplitude with only one bead

Many thanks to

my students at the University of Bielefeld:

Many thanks to