Single and Multilayered Magnetic Nanowires (for SPINTRONICS)
Preparation and Characterization

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OUTLINE

1. INTRODUCING THE PROBLEM(S)
   - ✓ methods of preparation
   - ✓ membranes (pores diameter, density and length)
   - ✓ compositions

   ⟷ **Possible applications**
2. NANOWIRES OR NANOWIRE ARRAYS for spinswitch devices, including spin-valves
3. CRYSTALLINE VERSUS AMORPHOUS MAGNETIC NANOWIRES
4. MAGNETIC INTERACTIONS between nanowires or/and between the different segments forming the multilayered structures (magnetic properties vs. applied field direction, magnetoresistance, magnetoimpedance, ferromagnetic resonance)
5. CONCLUDING REMARKS

Methods of Preparation

1) Nanopatterning using Focused Ion Beam
2) Nanopatterning using Electron-Beam Lithography

} Strictly limited to parallel configurations with the substrate

3) Electrodeposition into nanoporous templates

Advantages:

✓ more cost-effectively
✓ the arrays of nanowires can be easily fabricated over areas of several square centimeters

4) Fabrication of individual nanowires via step-edge decoration (Petrovykh, 1988; Tokuda, 2004)
5) Aqueous growth using electrical fields (Cheng, 2005)
6) Vapor-liquid-solid technique (Morales, 1998)
7) Laser ablation and chemical vapour deposition (CVD) to grow semiconductor nanowires

Membranes (1)

I. Ordered porous alumina arrays with sharply defined pore sizes and interpore spacings using two-step electrochemical anodization of aluminium

Masuda and Fukuda, **Science** 268 (1995) 1466
Li *et al.*, **J Appl Phys** 84 (1998) 6023
Nielsch *et al.*, **Nano Lett** 2 (2002) 677
Stadler *et al.*, **MRS Symp. Proc.** 853E (2005) I6.3.1

Advantages:

- ✓ The pores have excellent short-range ordered structure
- ✓ The pores diameter can be rigorously controlled (normally, ranging between 10 and 300 nm)
- ✓ The pores length can be also controlled (from a few μm to ~100-150 μm)

Disadvantages:

- ✓ The pores density can be somehow controlled (from 10^{11} to 10^{9})
- ✓ The parallelism of the nanopores – how good is that?

Membranes (2)

II. Monodomain alumina pore arrays obtained by electron-beam lithography and nanoimprint techniques

Li *et al.*, **Electrochem Solid State Lett** 3 (2000) 131

Masuda *et al.*, **Appl Phys Lett** 71 (1997) 2770

Stadler *et al.*, **MRS Symp. Proc.** 853E (2005) I6.3.1

Advantages:

✓ The pores density can be very well controlled
✓ The parallelism of the nanopores is much better

Membranes from I. and II. can be successfully used for applications in electronics, but there are not yet enough data about their biocompatibility for medical applications.

Membranes (3)

III. Etched ion-track membranes (mostly used are the polycarbonate membranes)

Whitney *et al.*, **Science** 261 (1993) 1316
Fearing and Legras, **Nuclear Instrum Methods Phys Res** B131 (1997) 97
Piraux *et al.*, **Nuclear Instrum Methods Phys Res** B131 (1997) 357

Advantages:

- ✓ The pores density is lower, even down to a single nanowire (Enculescu, 2003)
- ✓ The pores can be as small as 15 nm
- ✓ Potentially good for biomedical applications
- ✓ Offer the possibility of investigating the magnetic properties of almost magnetically isolated magnetic nanowires

Disadvantages:

- ✓ Too "soft" to be integrated directly into conventional devices (as an alternative should be considered the use of different supporting layers, like Si or patterned insulator layers)
- ✓ Too short (max. 20 μm long), depending on the energy of the irradiating heavy ions

Membranes (4)

IV. Diblock copolymer templates

Thurn-Albrecht *et al.*, **Science** 290 (2000) 2126
Xu *et al.*, **Polymer** 42 (2001) 9091
Gates *et al.*, **Adv Funct Mater** 12 (2002) 219
Amundson *et al.*, **Macromolecules** 27 (1997) 6559

Advantages:

- ✓ An alternative to anodic alumina templates
- ✓ The lack of the barrier layer
- ✓ The ease of dissolution of the template to expose the wires

Disadvantages:

- ✓ The possible diameters are limited (14-50 nm with the interpore spacings of 20-90 nm)
- ✓ Difficult to align the nanopores completely perpendicular to the substrate for subsequent electrodeposition of nanowires

Membranes (5)

V. Nuclear track etching of mica

Possin, **Rev Sci Instrum** 41 (1970) 772
Williams and Giordano, **Phys Rev B** 33 (1986) 8146

VI. Phase-separated Al-Si alloys templates from which the Al has been etched

Fukutani *et al.*, **Adv Mater** 16 (2004) 1456

VII. Titanium oxide nanopores

Prida *et al.*, **J Nanosci Nanotechnol** 7 (2007) 272

VIII. Silica mesoporous templates

Terasaki *et al.*, **Microsc Microanal** 8 (2002) 35

IX. Radial nanopore arrays (alumina)

Sanz *et al.*, **J Appl Phys** 101 (2007) 114325

Compositions

- **Noble metals:** Au, Ag, Pt, Pd – mainly for biomedical applications
- **Transition metals:** Fe, Ni, Co, Cu, …
- **Other elements:** Bi, Pb, Si, …
- **Crystalline alloys:** FeNi (including permalloy), FeCo, FeCoNi, CoFeB, CoNiFe, FePt, CdTe, FeGa, etc.
- **Amorphous alloys:** FeP, NiP, CoP, CoNiP, FeCoNiB, CoFeB
- **Polymers**
- **Oxides:** $CoFe_2O_4$, Fe_2O_3, Fe_3O_4, SiO_2, etc.
- **Multilayered structures:** Au/Ag, CdTe/Au, Pt/Au, Fe/Au, Co/Pt, Ni/Au, Co/Ni, Co/Cu, CoCu/Cu, NiFe/Cu, FeGa/NiFe, etc.

Magnetic nanowires for spinswitch devices

Why magnetic nanowires are suitable for spinswitch devices? (1)

1. their intrinsic properties are directly related to the low dimensionality
2. they can be manipulated through the extra degrees of freedom inherent to their nanostructures
3. by manipulating the layers thickness (in the case of multilayered structures), the properties of the superlattice can be drastically modified
4. in those multilayeres where antiferromagnetic alignment of the magnetic layers is realized, giant magnetoresistance can be achieved
5. by manipulating the structure of the constituent layers and the metal volume fraction, a wide-range of nanostructure-induced physical properties can be systematically varied and tailored

Magnetic nanowires for spinswitch devices

Why magnetic nanowires are suitable for spinswitch devices? (2)

1. in multilayer systems, GMR occurs as H_{ext} changes the relative directions of the magnetic layers – the effect of spin-dependent electron scattering and spin-dependent interface potentials are the fundamental mechanisms responsible for the observed GMR
2. in the CIP (current in the planes) geometry, the GMR effect vanishes when the layers thicknesses exceed the electron mean free path
3. on the contrary, in the CPP (current perpendicular to the planes) geometry, the spin-diffusion lengths are the relevant scaling lengths
4. as a consequence, GMR should be larger for current flowing in the perpendicular direction than in the CIP geometry when the layers thicknesses are between the electron mean free path (a few nm) and the spin-diffusion length (a few hundreds of nm)

Magnetic nanowires for spinswitch devices

Why magnetic nanowires are suitable for spinswitch devices? (3)

1. magnetic nanowires represent a new type of GMR nanostructure, with the special interest of measurements with the current perpendicular to the layers plane = CPP geometry

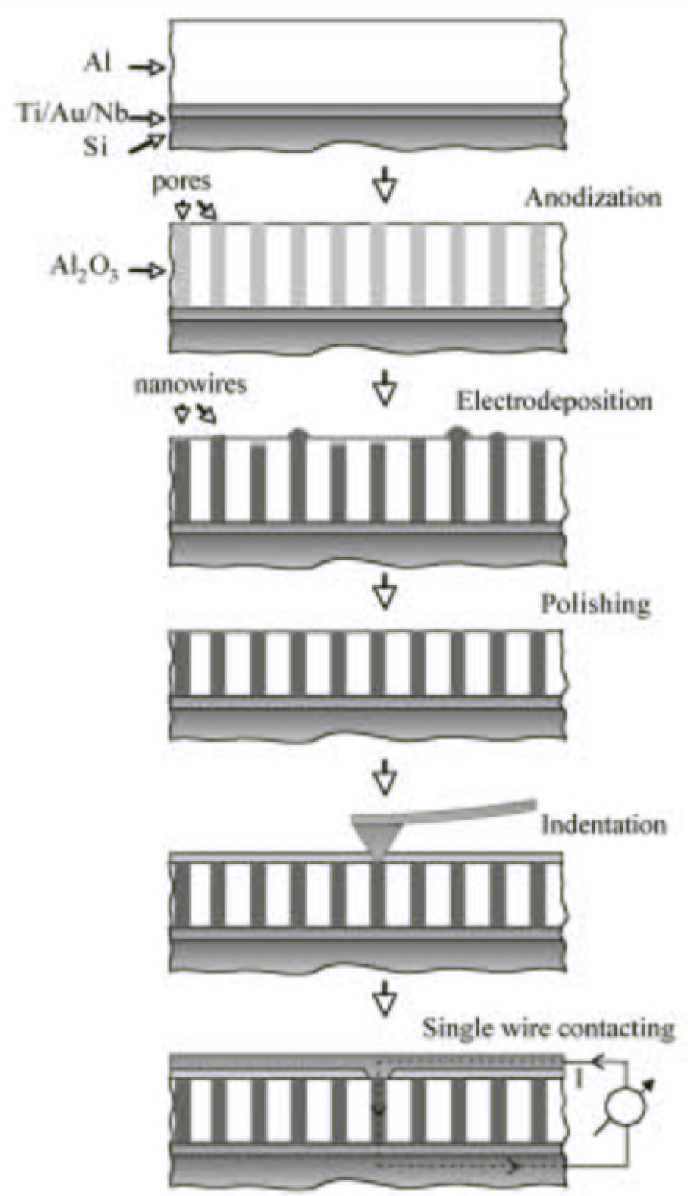
2. electrodeposition is a cheaper way to prepare multilayered materials

L. Piraux *et al.*, **Appl Phys Lett** 65 (1994) 2484
A. Blondel *et al.*, **Appl Phys Lett** 65 (1994) 3019

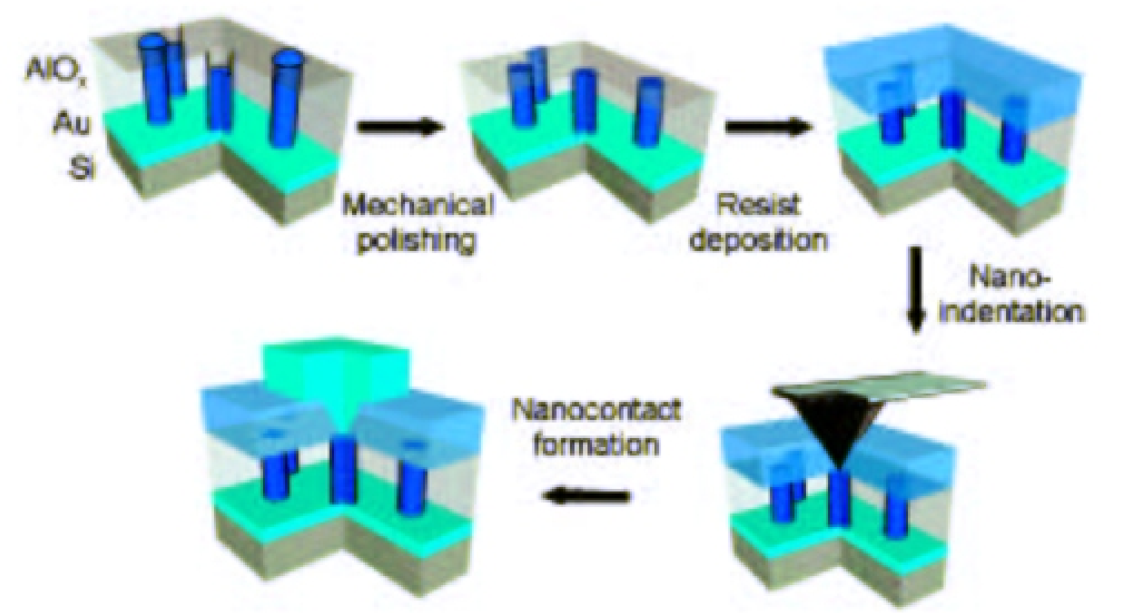
Studied multilayered nanowires for this purpose:
Co/Cu (Piraux, 1994; Blondel, 1994)
NiFe/Cu (Dubois, 1997)

Possible applications in: magnetic random access memory (MRAM) devices, advanced magnetic sensors such as automotive sensing applications, fast logic, high-density re-cording, and in high frequency devices for telecommunications.

Magnetic nanowires for spinswitch devices



Schematic illustration of the single-wire contacting process on an array of nanowires electrodeposited in a supported nanoporous alumina template.



S Fusil *et al.*, **Nanotechnology** 16 (2005) 2936
L Piraux *et al.*, **Nano Lett** 7 (2007) 2563

Our magnetic nanowires for spinswitch devices

✓ nanowires prepared by electrodeposition into Al_2O_3 commercial templates (Whatman® and Synkera® with pores diameters of 20-200 nm; pores length 40-60 μm)

✓ nanowires prepared by electrodeposition into "home-made" Al anodized templates (pore diameters 30-40 nm and pores length 50 to 100 μm)

✓ [NiFe/Cu], Co/[NiFe/Cu]/Co, [CoFeB/Cu], [CoNiP/Cu] multilayered nanowires - 100 to 300 consecutive sequences

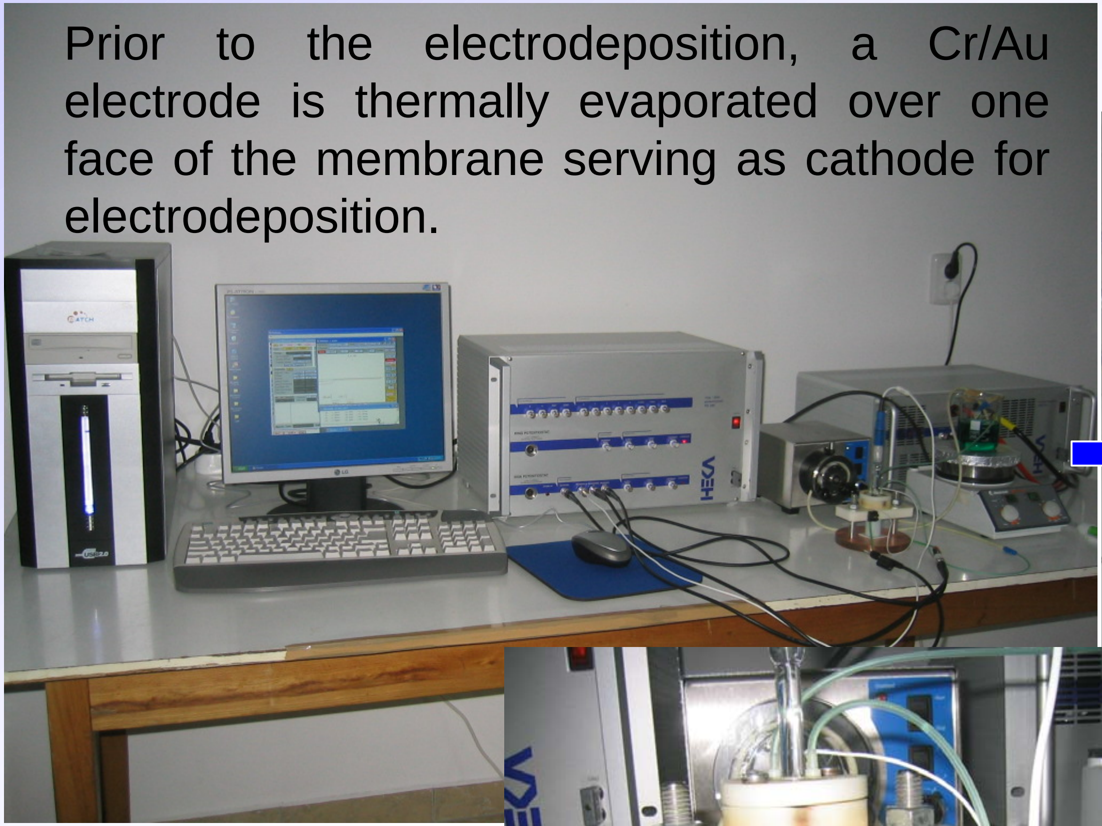
✓ the deposition bath consist in a single mixed solution of the corresponding salts

✓ $T_{deposition}$ = RT; $pH_{deposition\ bath}$ = 3; pH_{Co} = 3 and 6

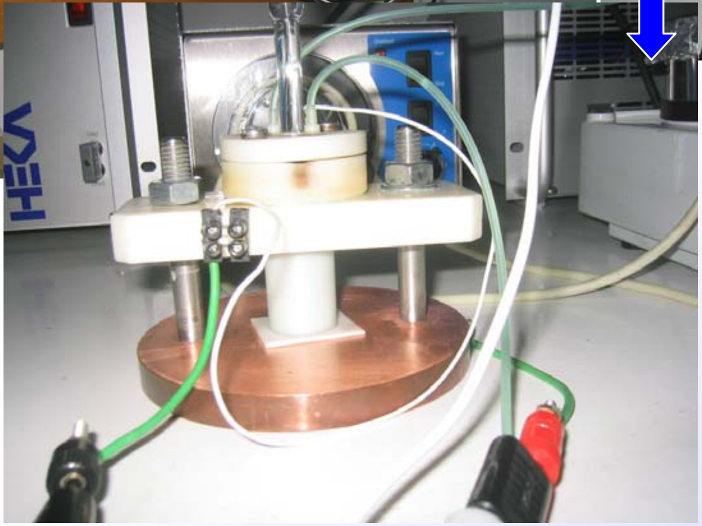
✓ the chosen layers have been deposited successively by changing the deposition potential

Preparation of magnetic nanowires – Experimental setup

Prior to the electrodeposition, a Cr/Au electrode is thermally evaporated over one face of the membrane serving as cathode for electrodeposition.



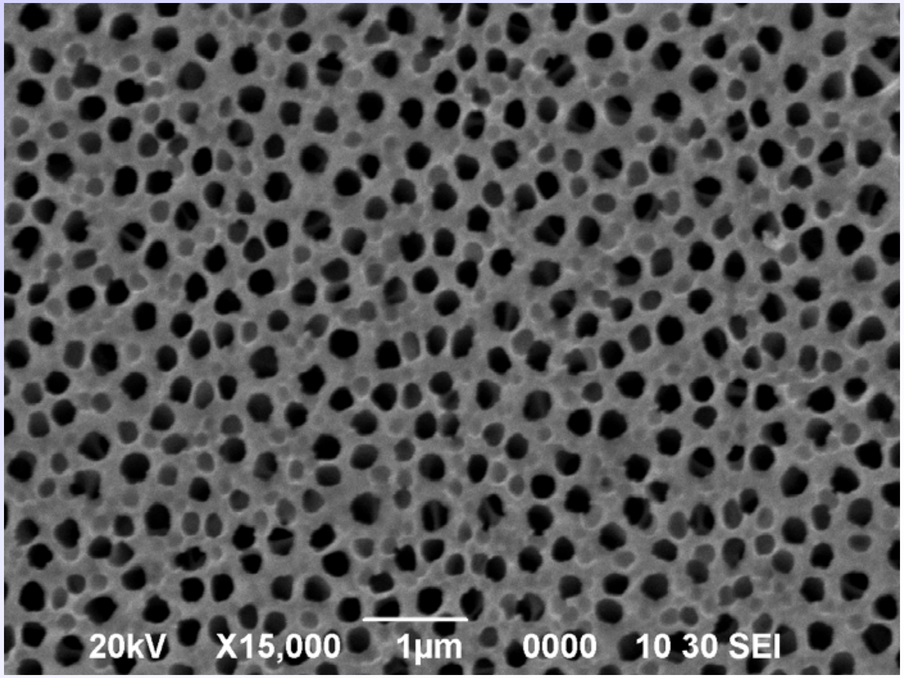
Electrochemical deposition



Reference electrode of Ag/AgCl.

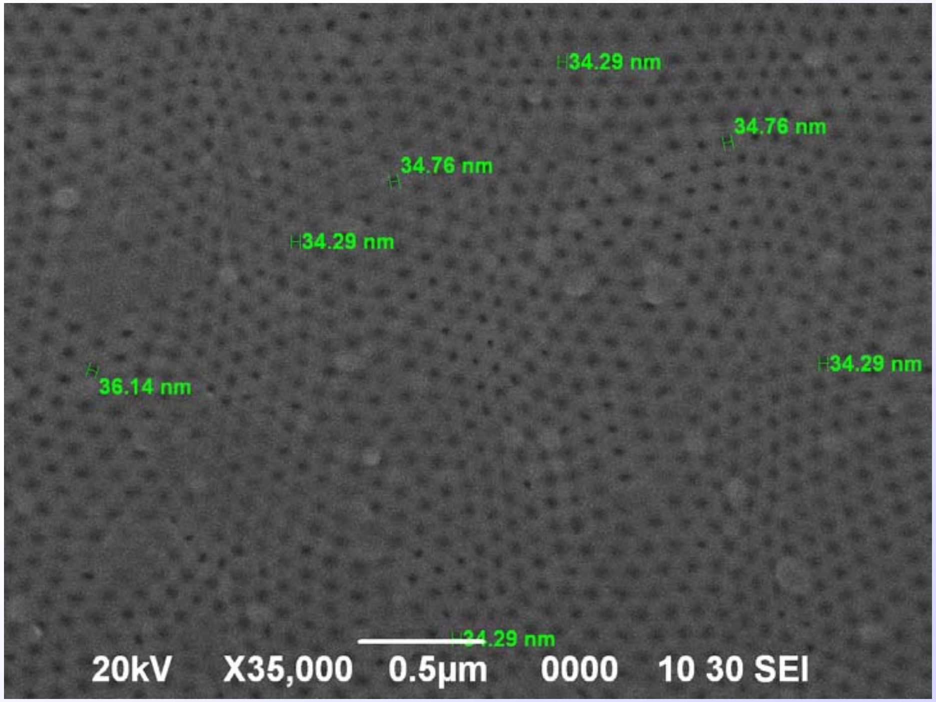
A platinum wire used as anod.

Our magnetic nanowires for spinswitch devices

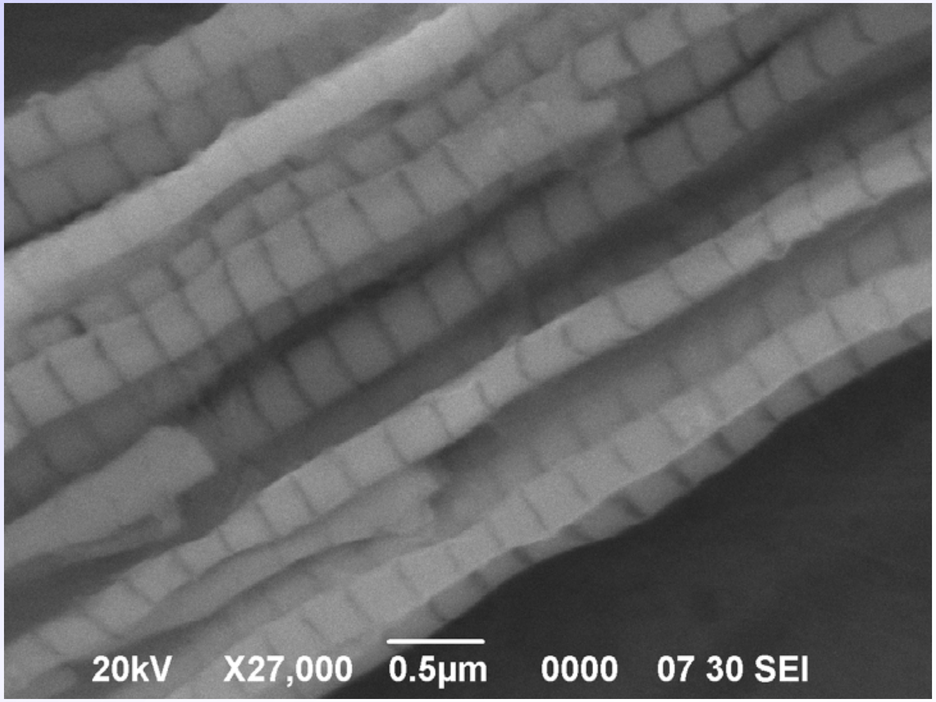


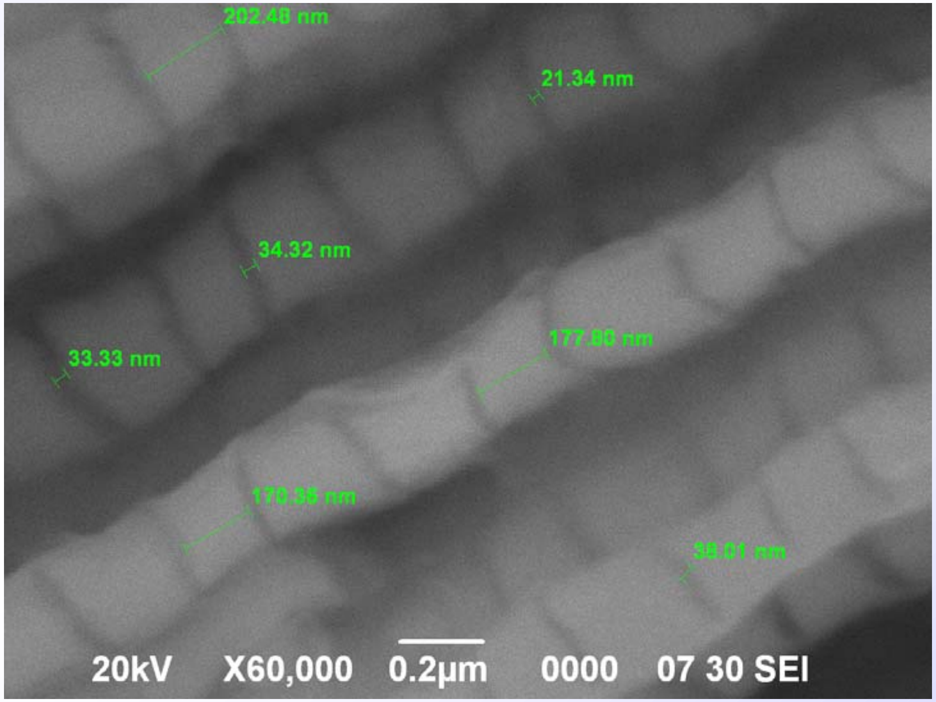
Whatman® membranes with the nominal pores diameter of 20 nm.

Synkera Technologies® membranes with the nominal pores diameter of 35 nm.



Our magnetic nanowires for spinswitch devices

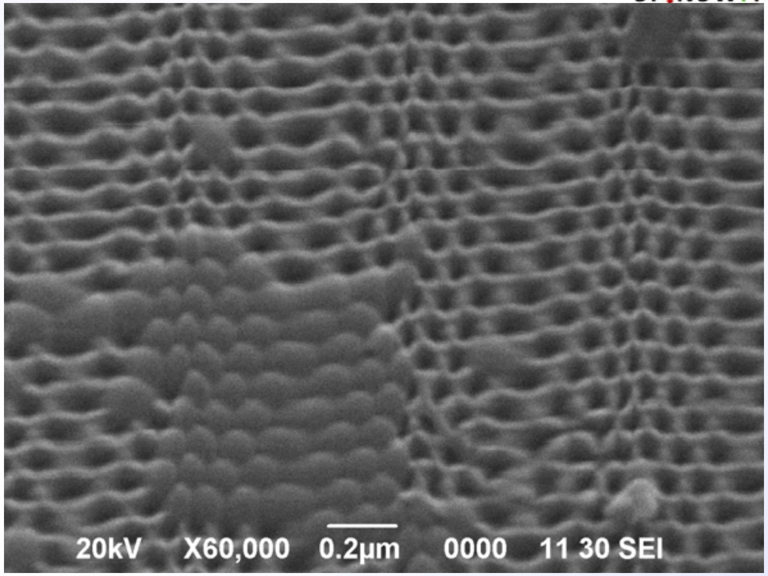


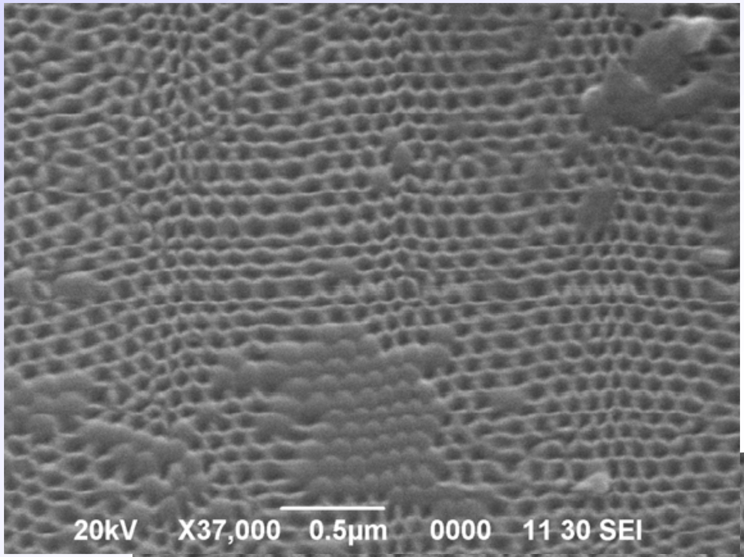


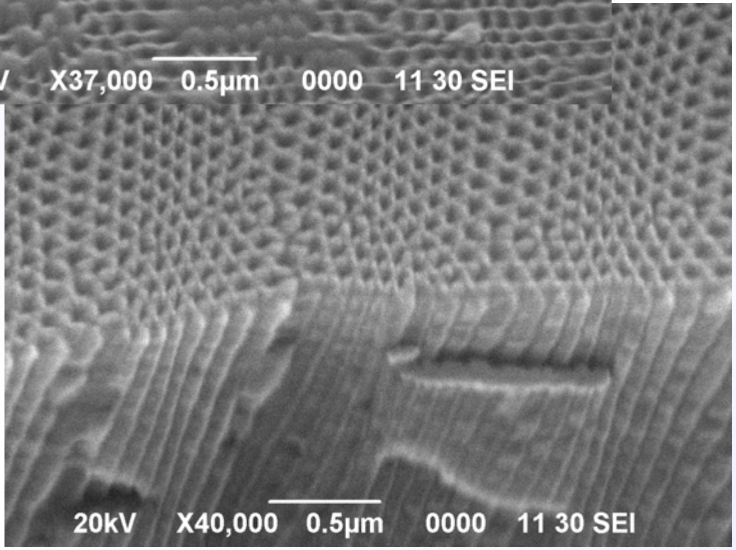
SEM images of electrodeposited [Py($Ni_{80}Fe_{20}$)/Cu] nanowires prepared in Whatman® membranes with the nominal diameter of 20 nm.

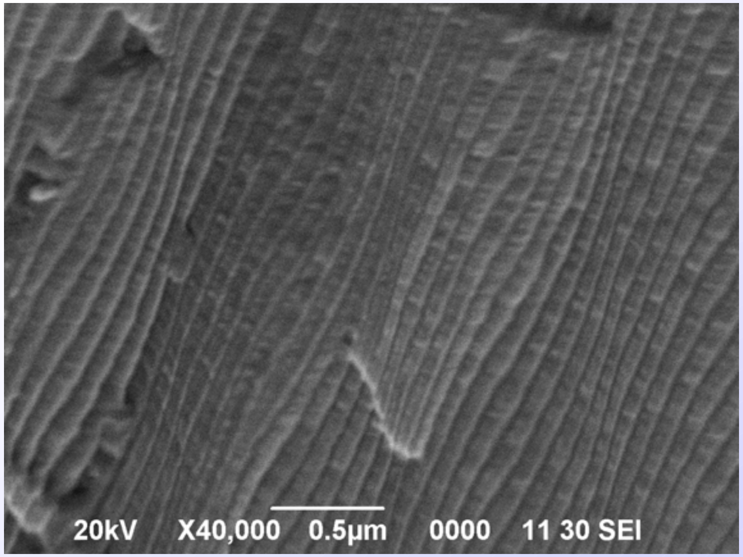
Our magnetic nanowires for spinswitch devices

SEM images of electrodeposited [Py/Cu] nanowires prepared in Synkera® membranes with the nominal diameter of 35 nm.





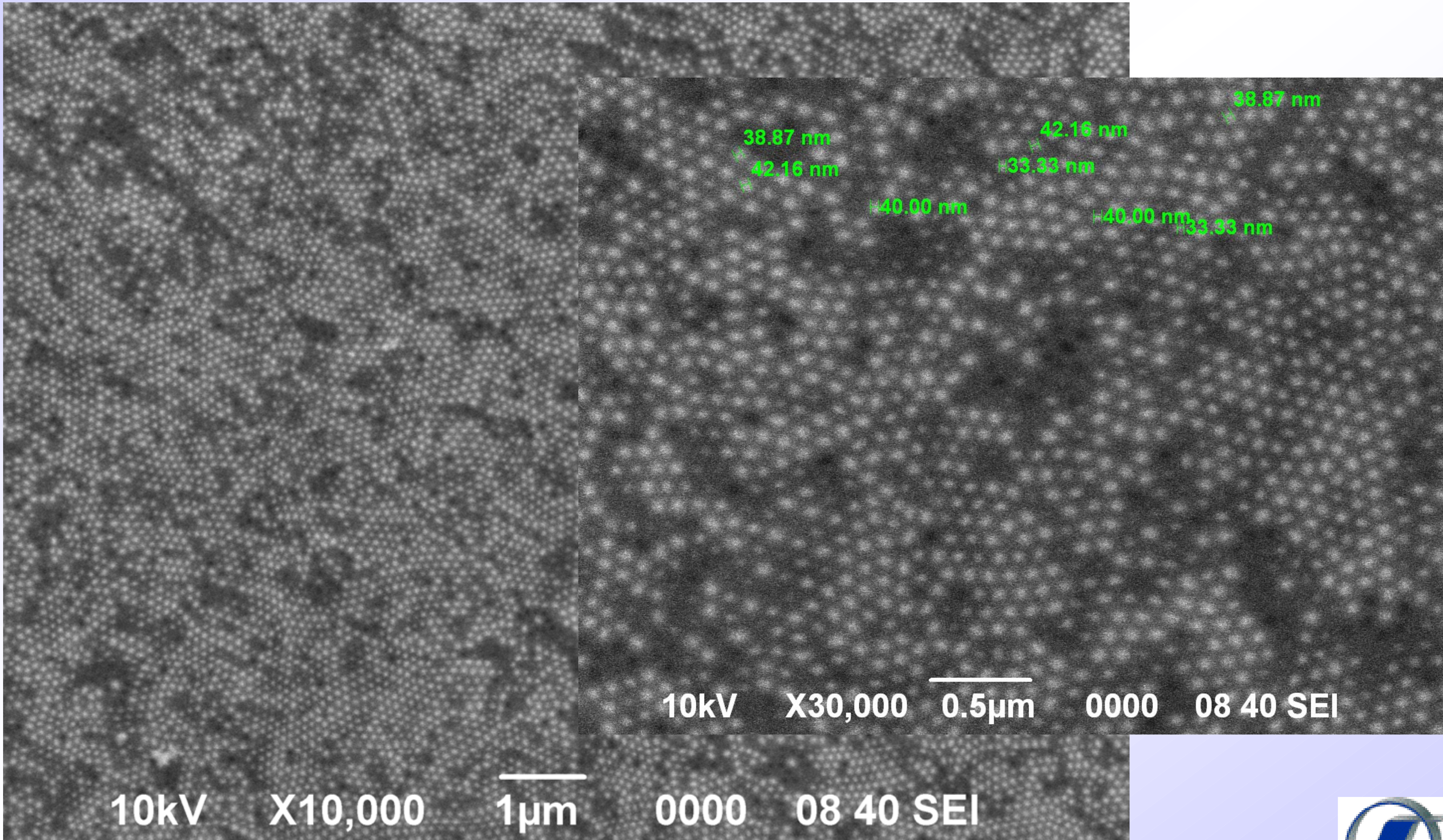




Our magnetic nanowires for spinswitch devices

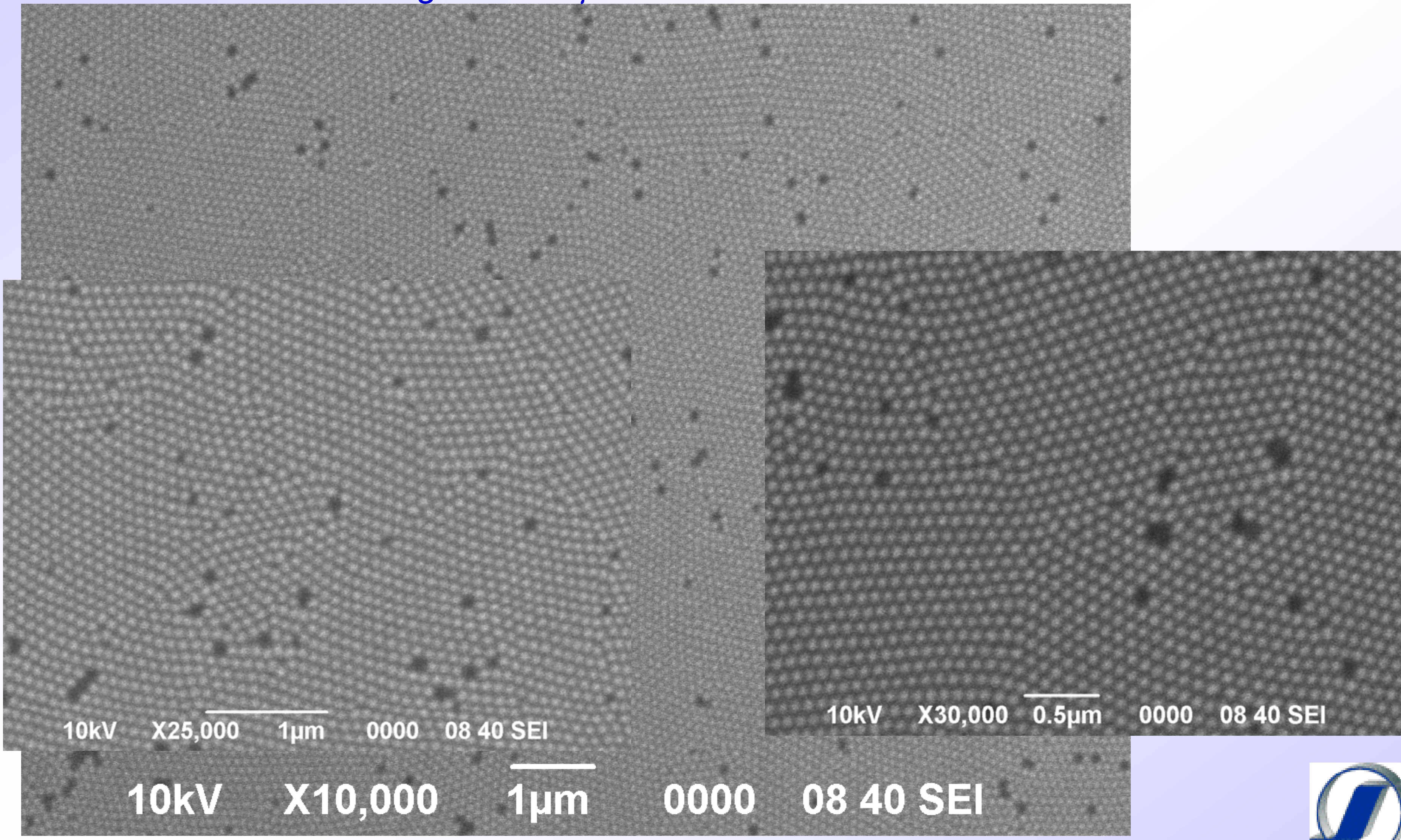
SP↓NSW↑TCH

Polished Synkera® membrane filled with [Py/Cu] nanowires of 35 nm



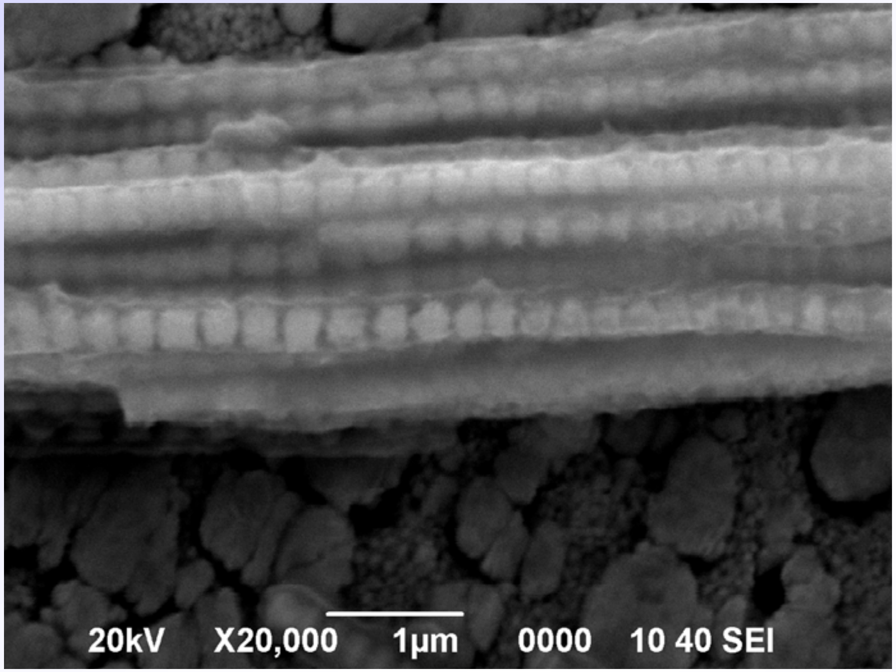
Our magnetic nanowires for spinswitch devices

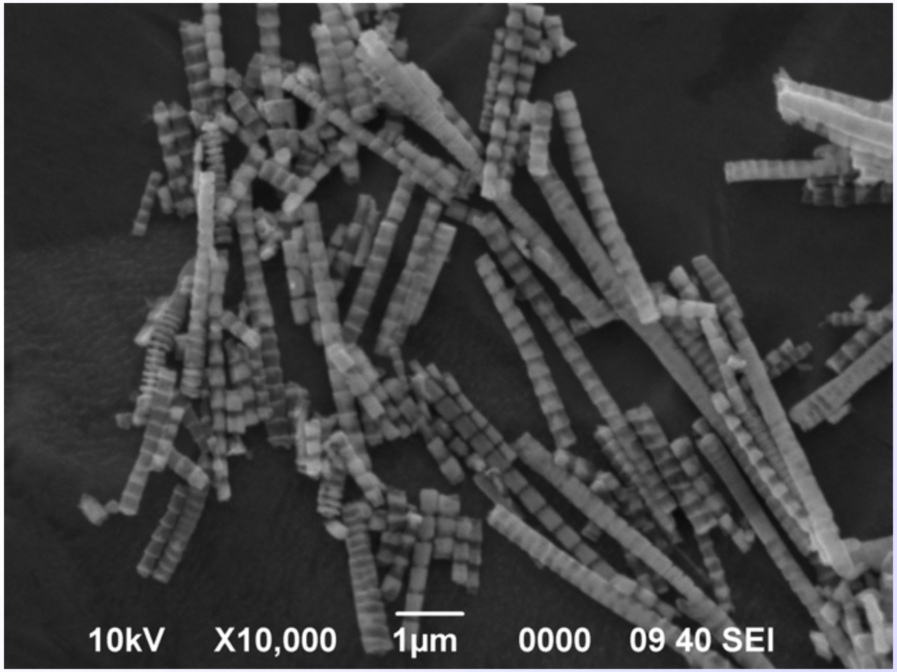
Polished "home-made" membrane filled with [Py/Cu] nanowires of 40 nm.
Nanowires length = 100 μm.



Our magnetic nanowires for spinswitch devices

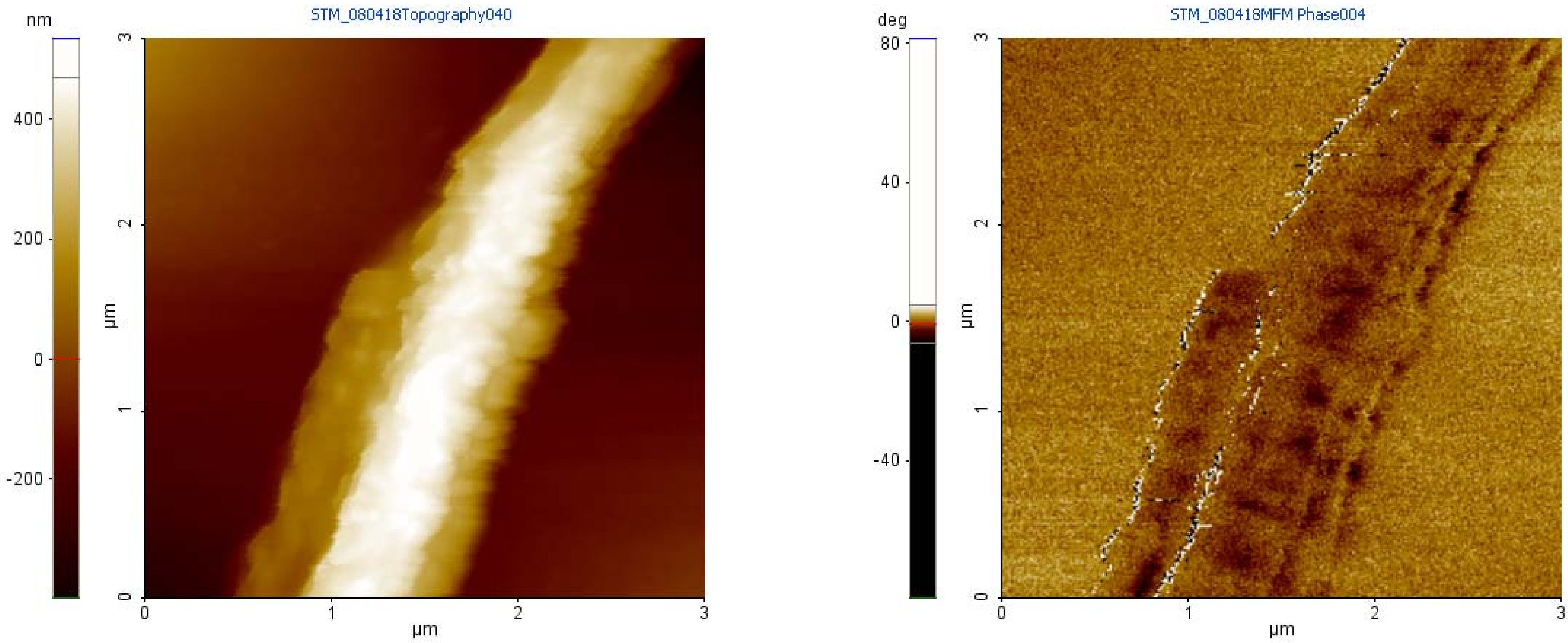
SEM image of electrodeposited [CoNiP/Cu] nanowires prepared in Whatman® membranes with the nominal diameter of 20 nm.





Our magnetic nanowires for spinswitch devices

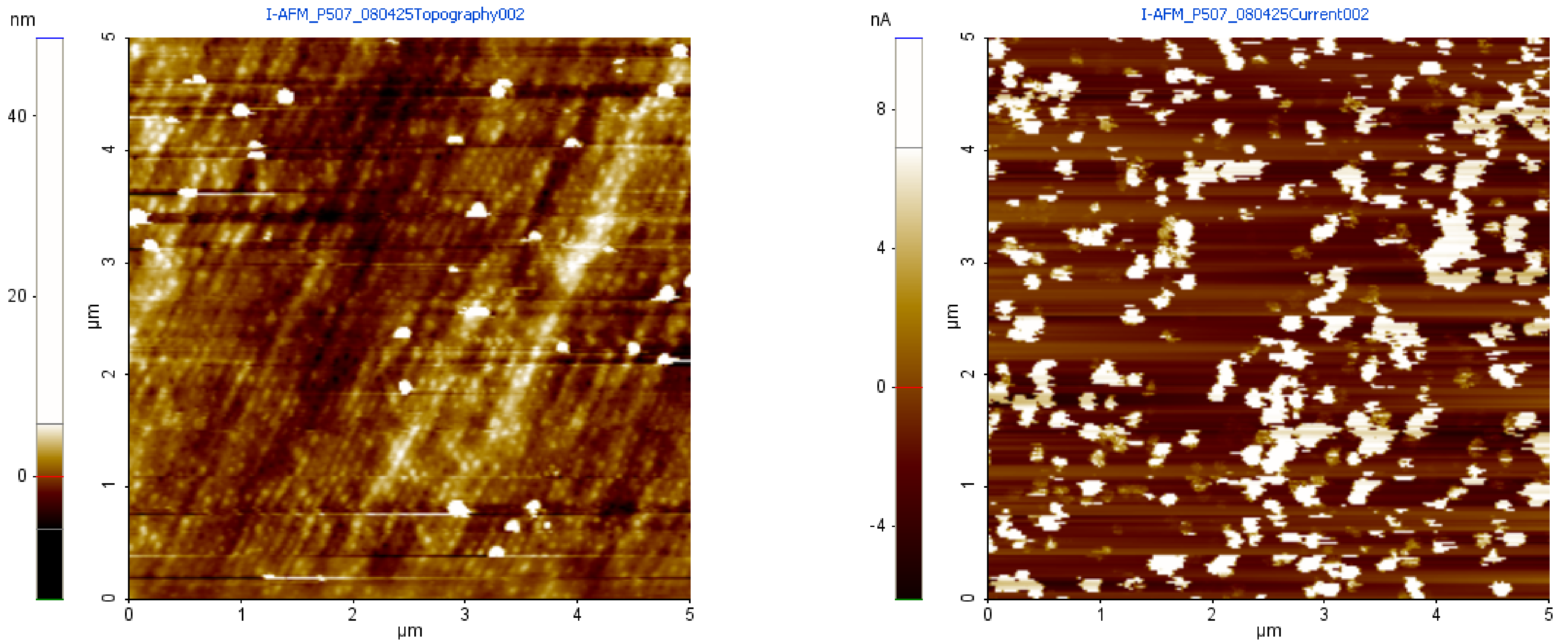
SPINSWITCH



AFM (left) and MFM (right) images of electrodeposited [Py($Ni_{80}Fe_{20}$)/Cu] nanowires prepared in Whatman® membranes with the nominal diameter of 20 nm.

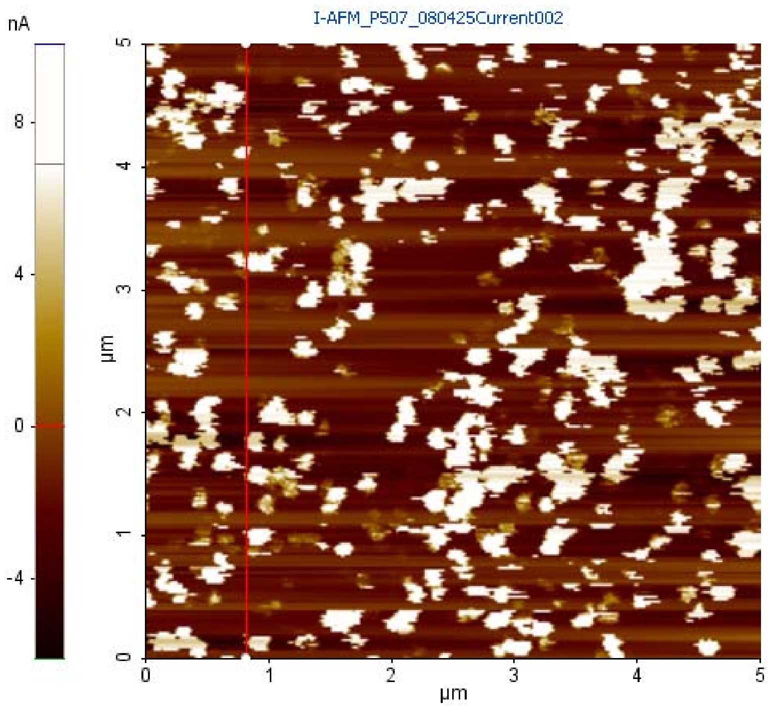
Our magnetic nanowires for spinswitch devices

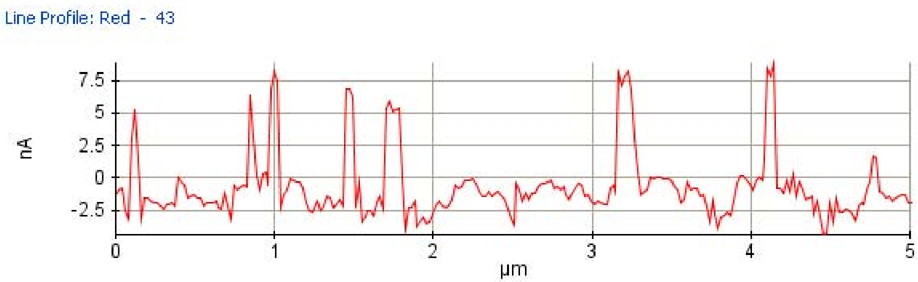
SPINSWITCH

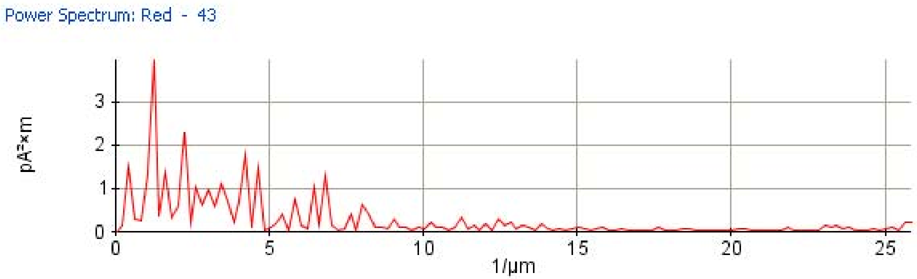


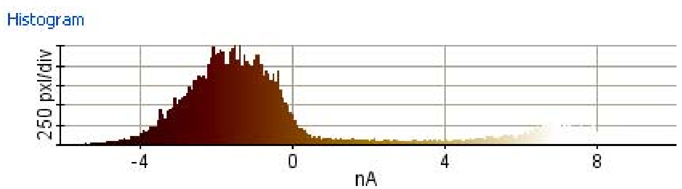
AFM (left) and Conductive-AFM (right) images of electrodeposited [Py($Ni_{80}Fe_{20}$)/Cu] nanowires prepared in Synkera® membranes with the nominal diameter of 35±5 nm.

Our magnetic nanowires for spinswitch devices







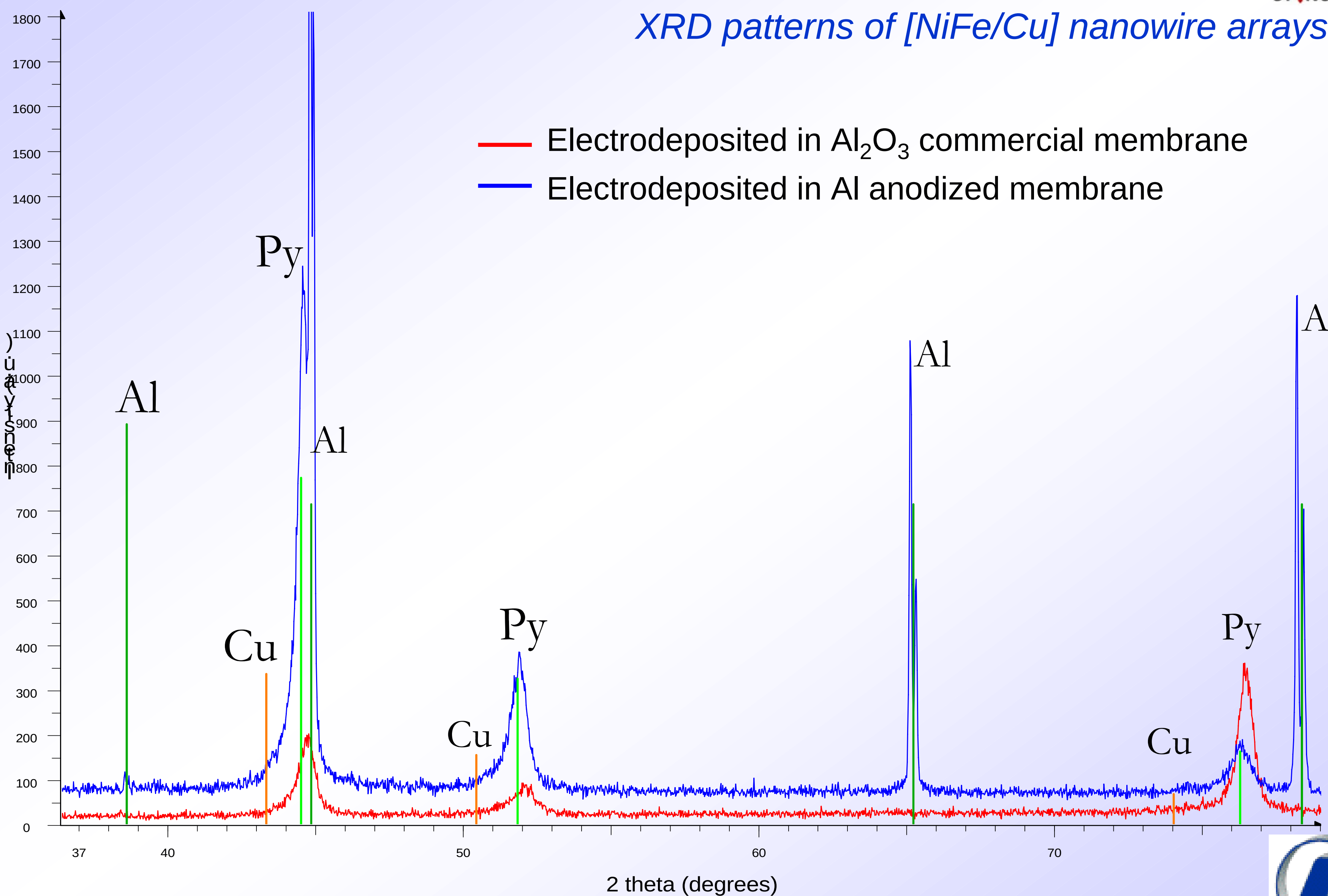


Conductive-AFM image of electrodeposited [Py($Ni_{80}Fe_{20}$)/Cu] nanowires prepared in Synkera® membranes with the nominal diameter of 35±5 nm.

Statistics

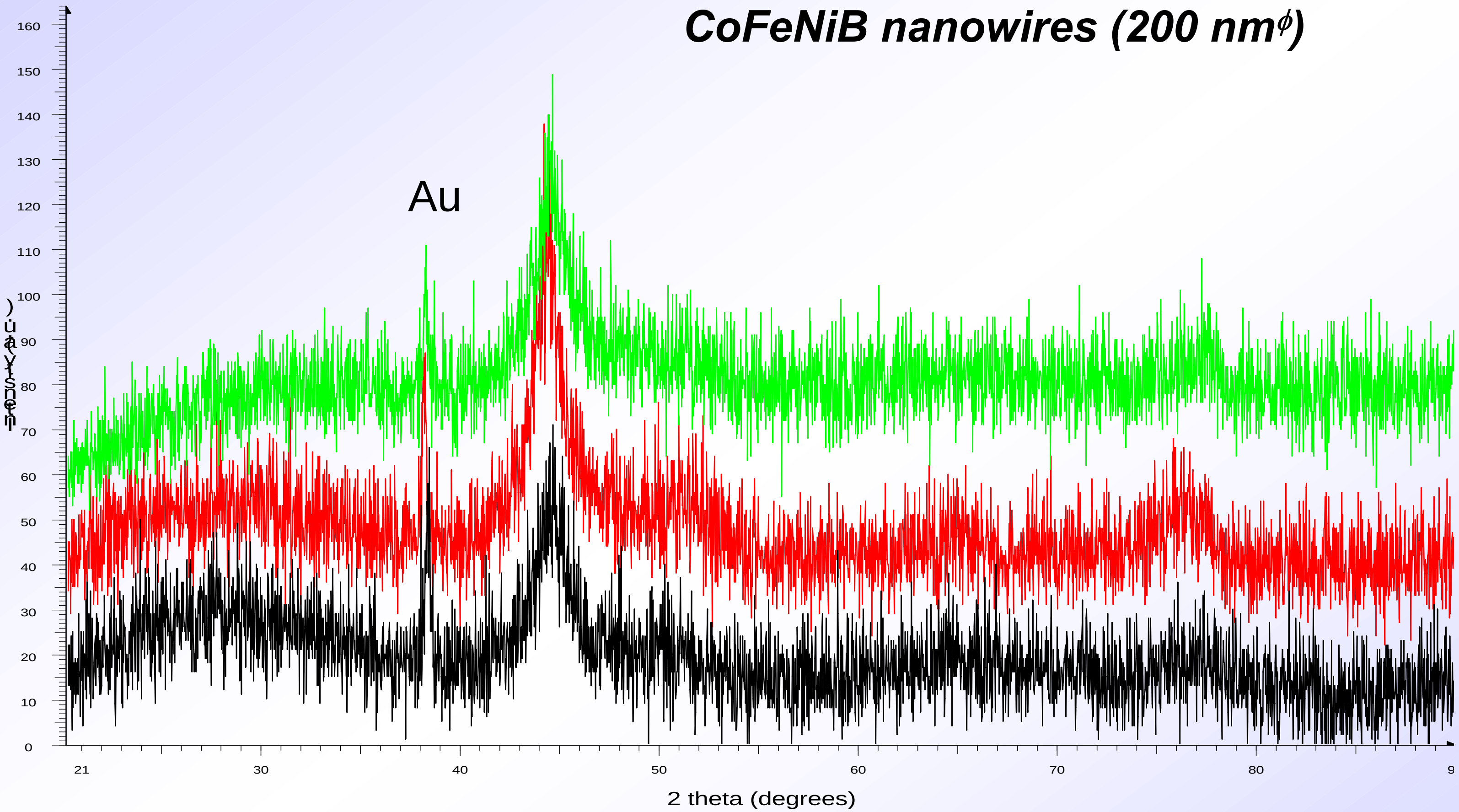
Line	Min(nA)	Max(nA)	Mid(nA)	Mean(nA)	Rpv(nA)	Rq(nA)	Ra(nA)	Rz(nA)	Rsk	Rku
Red	-4.393	8.800	2.203	-0.780	13.194	2.548	1.608	12.248	2.158	7.460

Crystalline versus amorphous magnetic nanowires



Crystalline versus amorphous magnetic nanowires

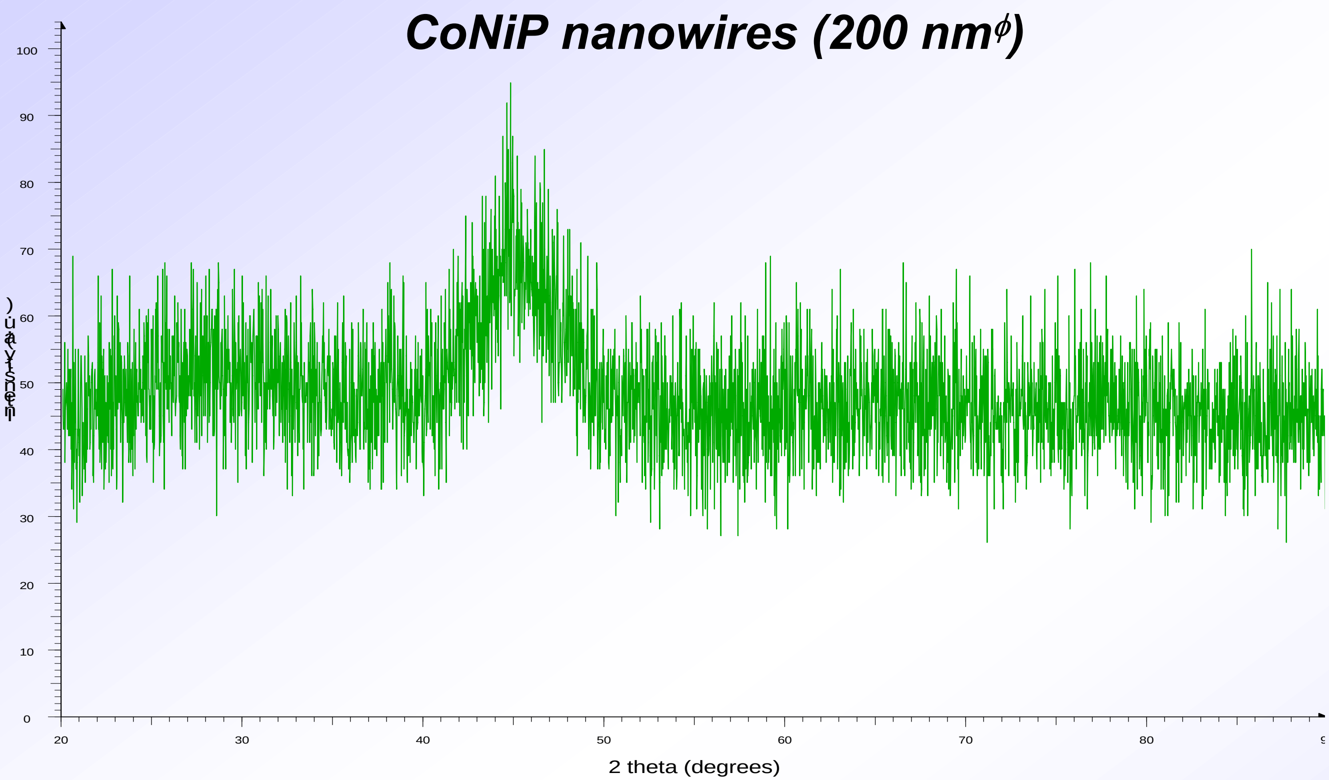
SPINSWITCH



The first amorphous nanowires have been reported by our group in NiP and CoP binary systems.

H. Chiriac *et al.*, **J Magn Magn Mater** 272 (2004) 1860

Crystalline versus amorphous magnetic nanowires

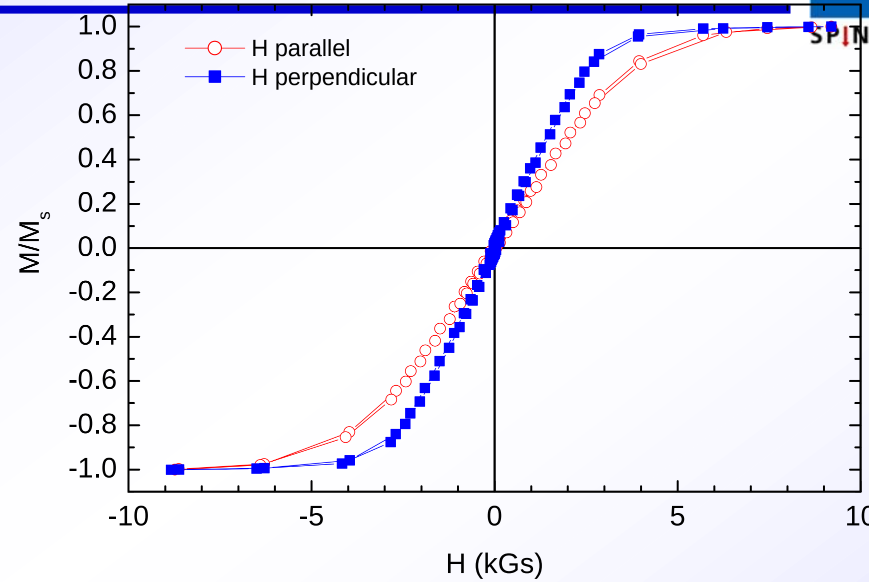


Why amorphous magnetic nanowires?

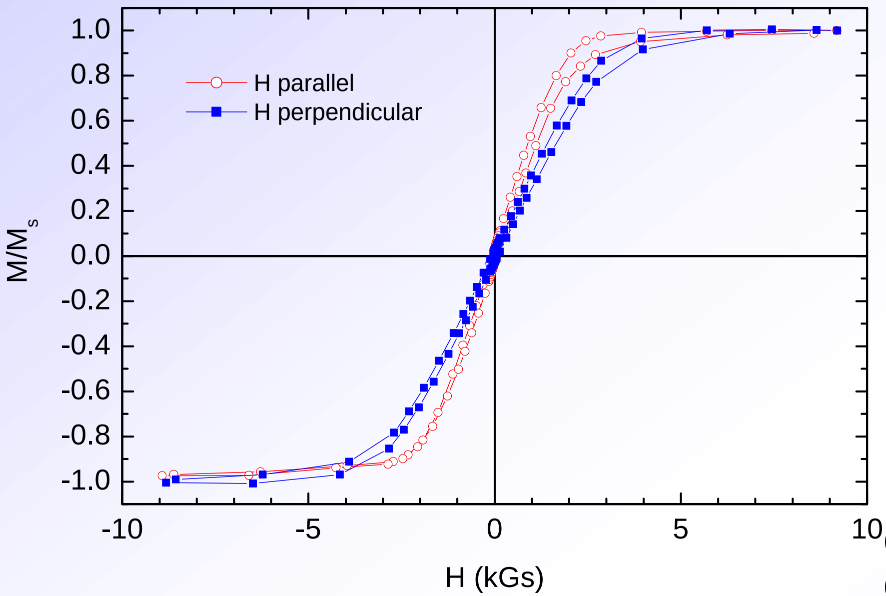
Because of the lack of magnetocrystalline anisotropy in amorphous materials.

Magnetic interactions – m-H loops

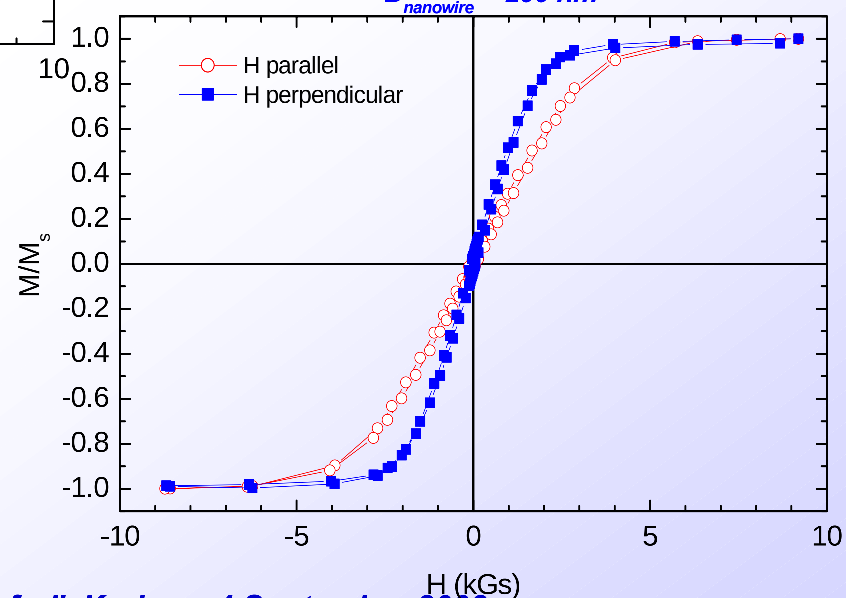
NiFe/Cu multilayered nanowires
$D_{nanowire}$ = 100 nm



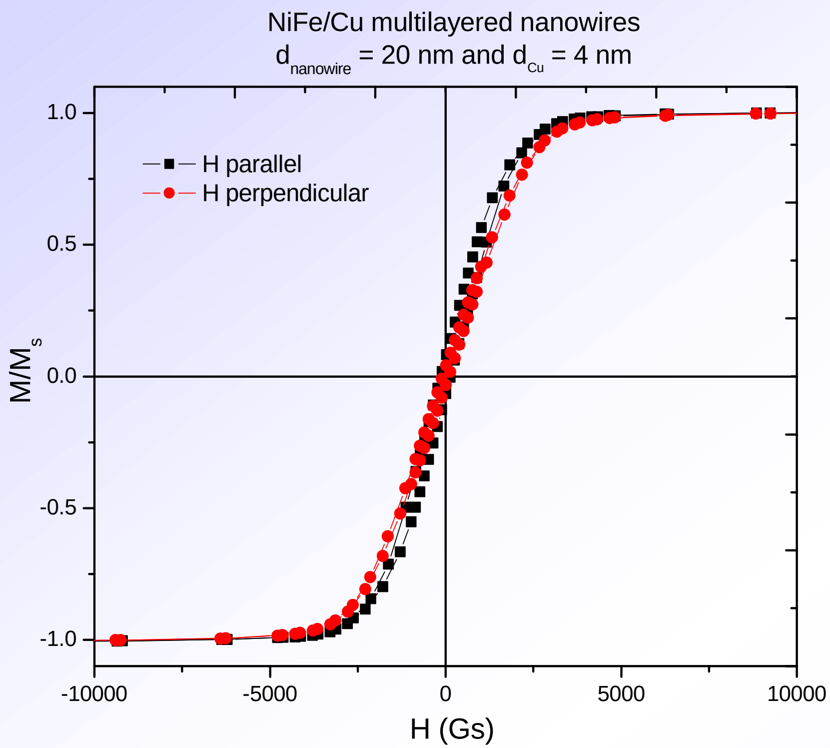
NiFe/Cu multilayered nanowires
$D_{nanowire}$ = 20 nm

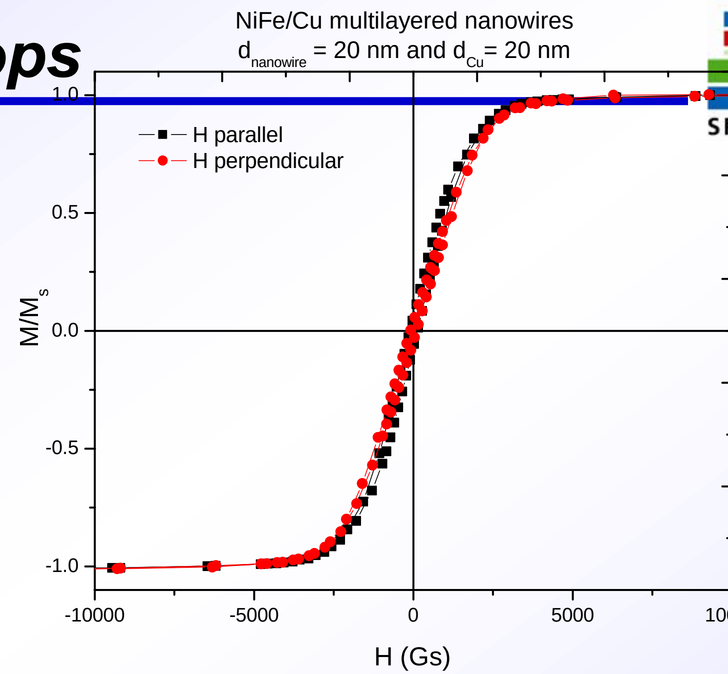


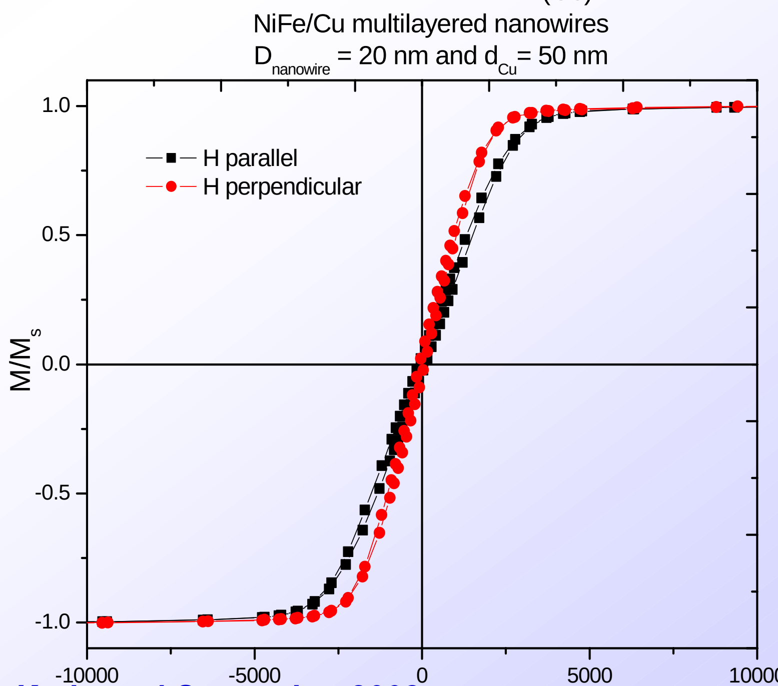
NiFe/Cu multilayered nanowires
$D_{nanowire}$ = 200 nm



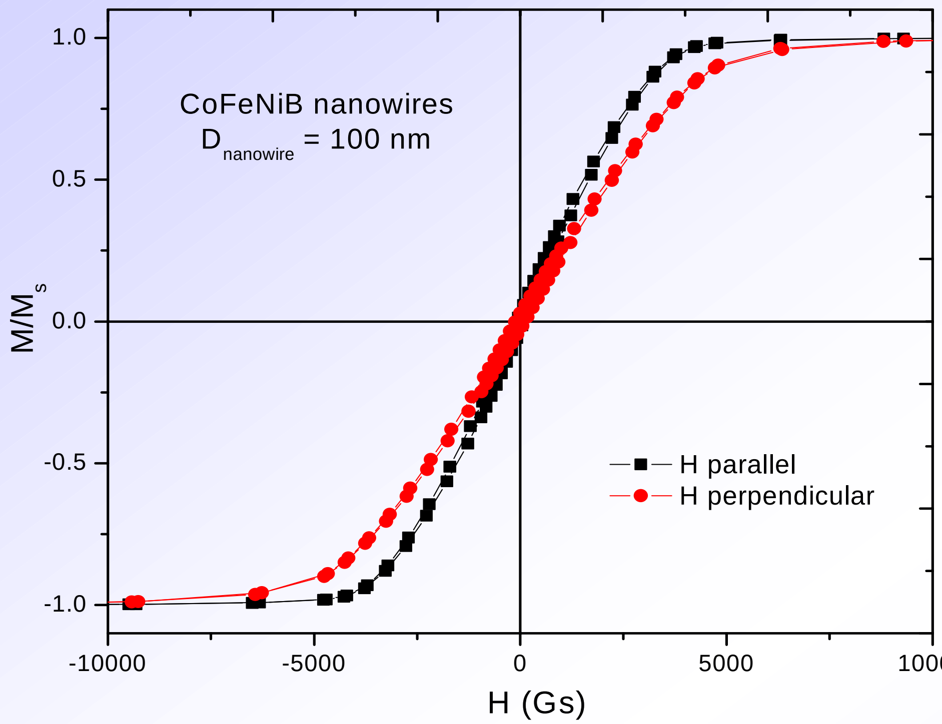
Magnetic interactions – m-H loops

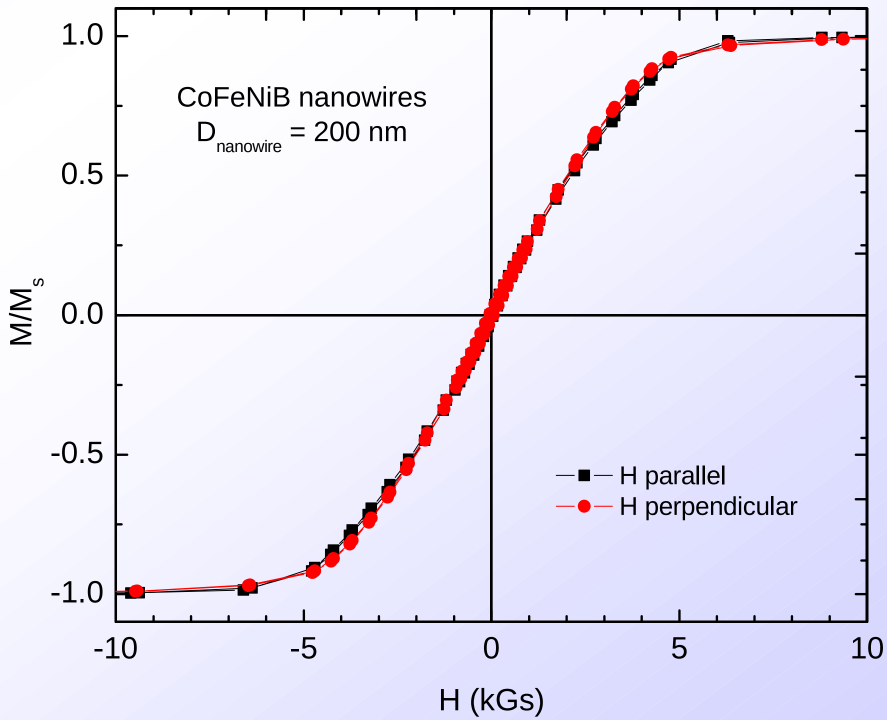






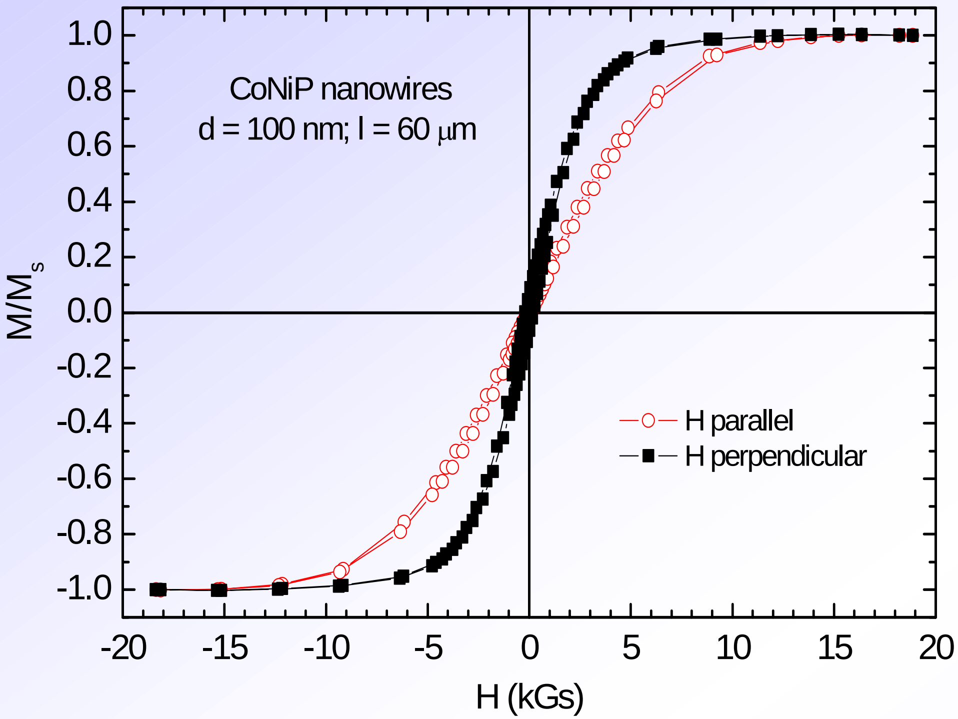
Magnetic interactions – m-H loops

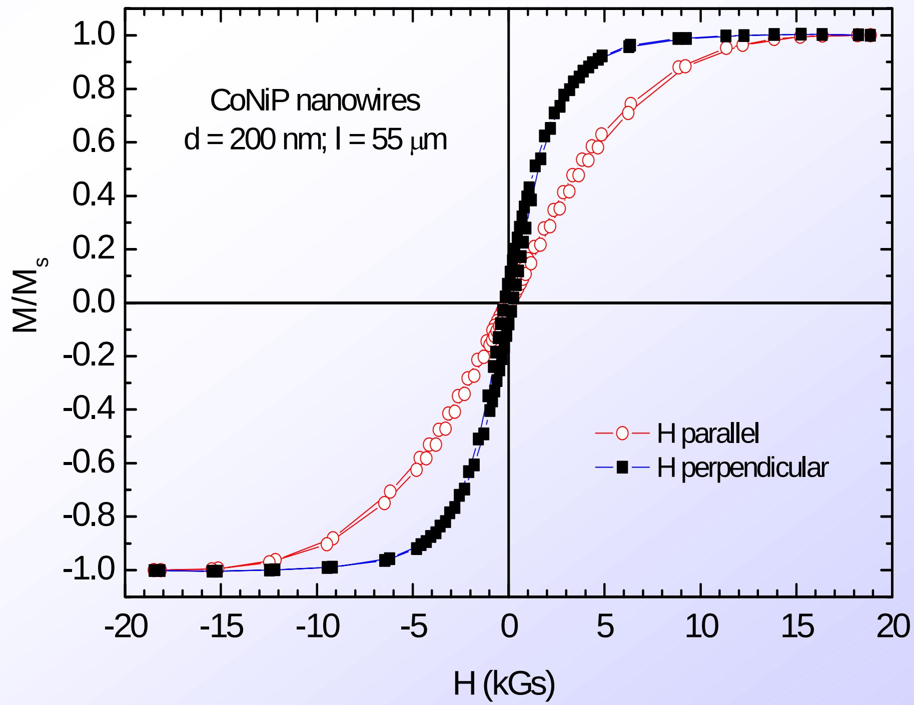




Amorphous nanowires

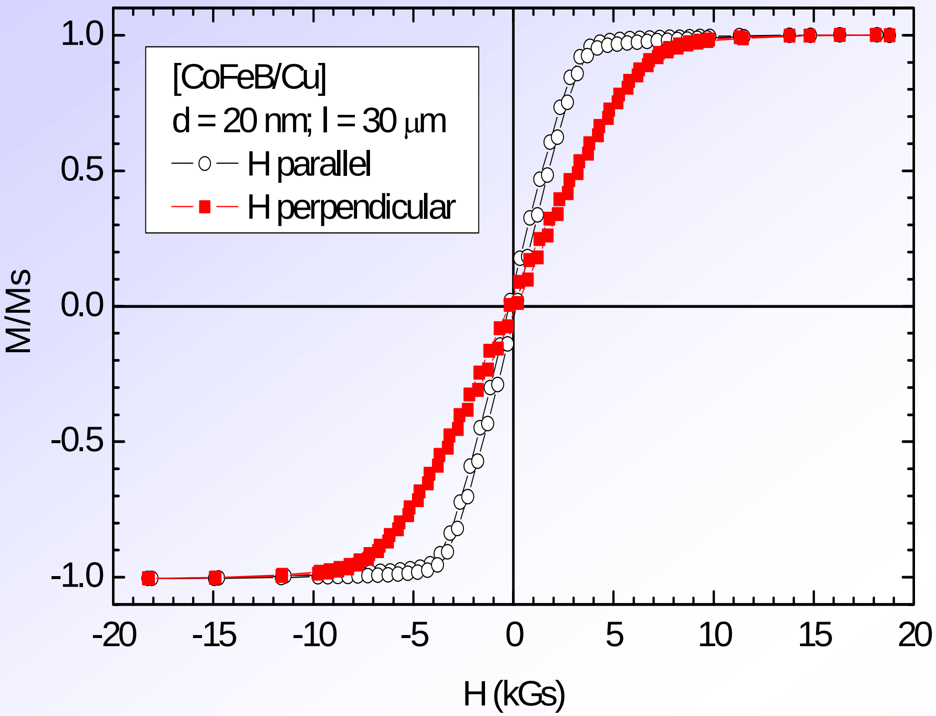
Magnetic interactions – m-H loops

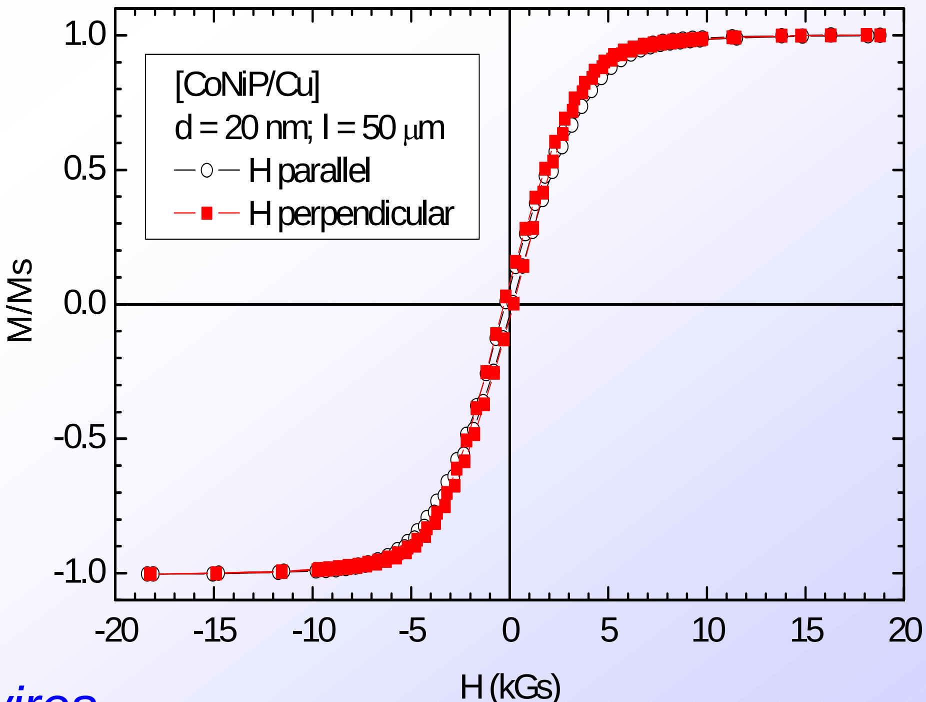




Amorphous nanowires

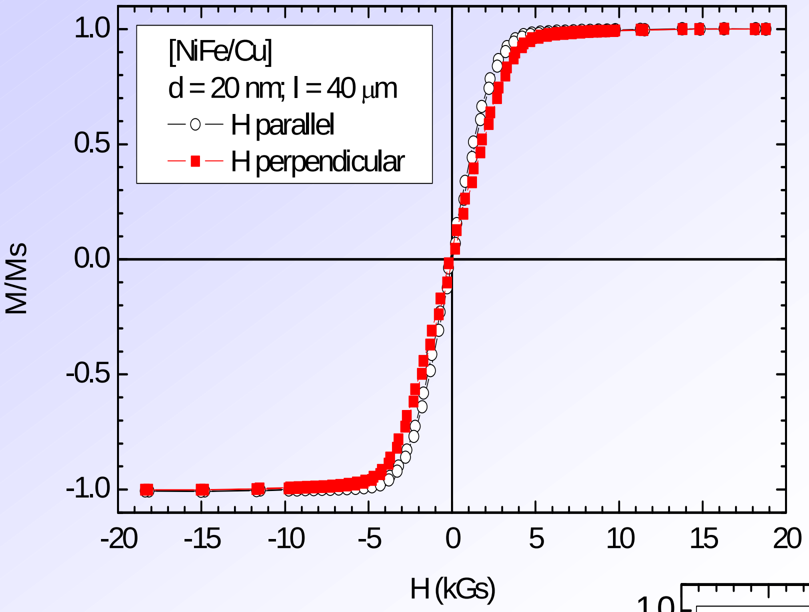
Magnetic interactions – m-H loops

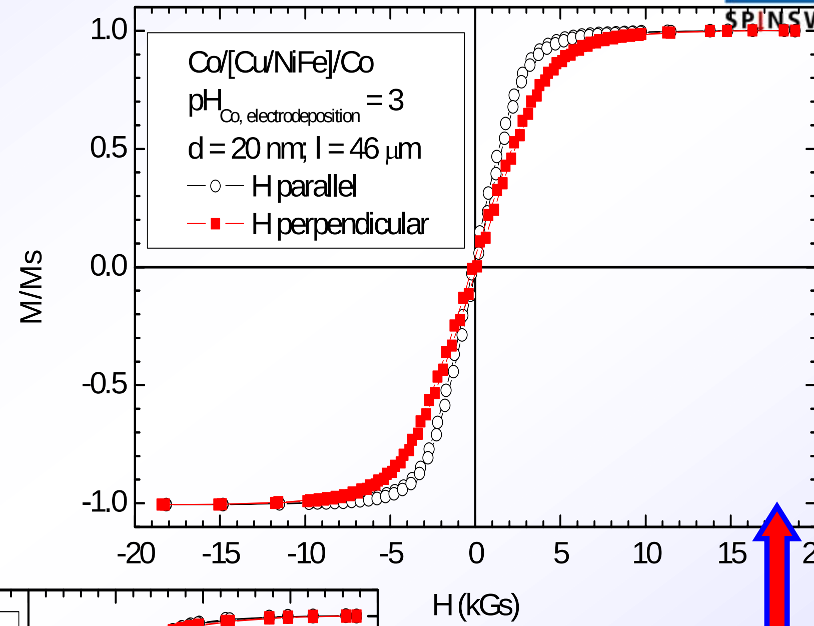




CoFeB and CoNiP - amorphous nanowires

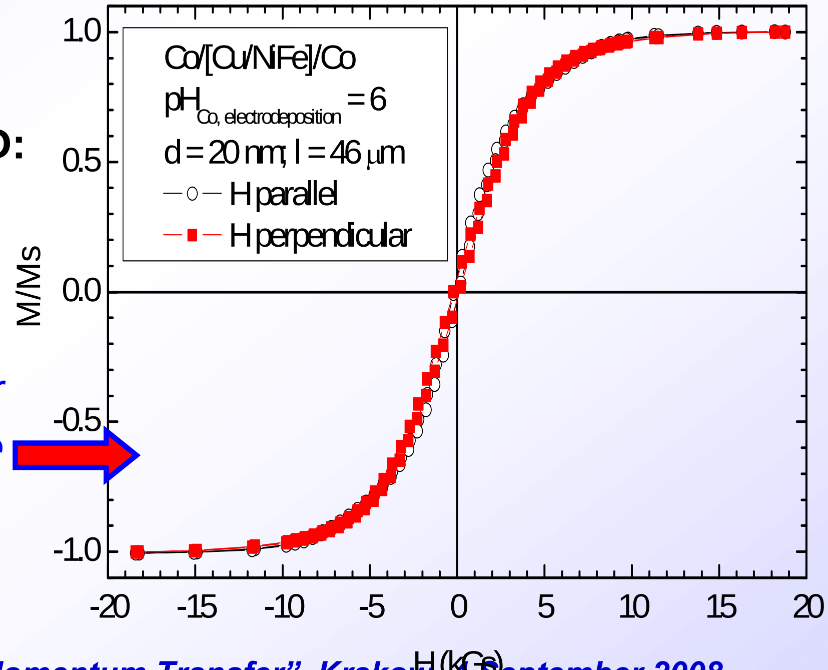
Magnetic interactions – m-H loops





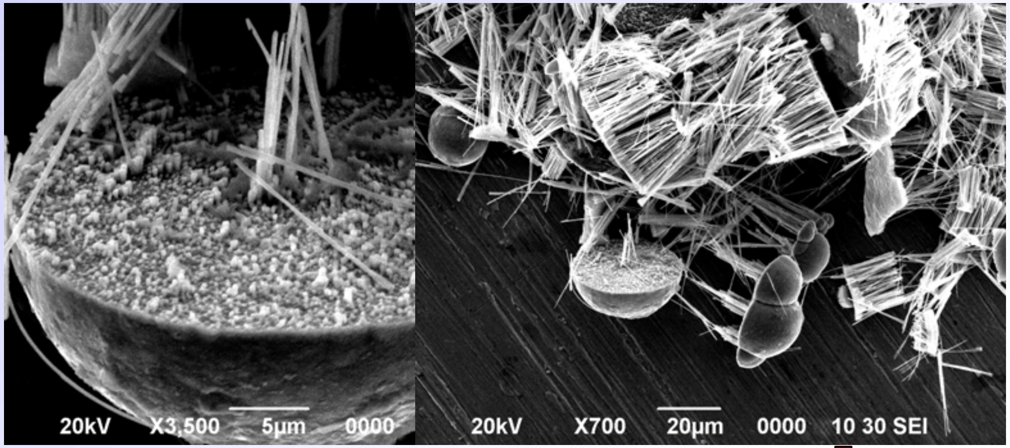
*c-axis of Co layer perpendicular to the nanowire**

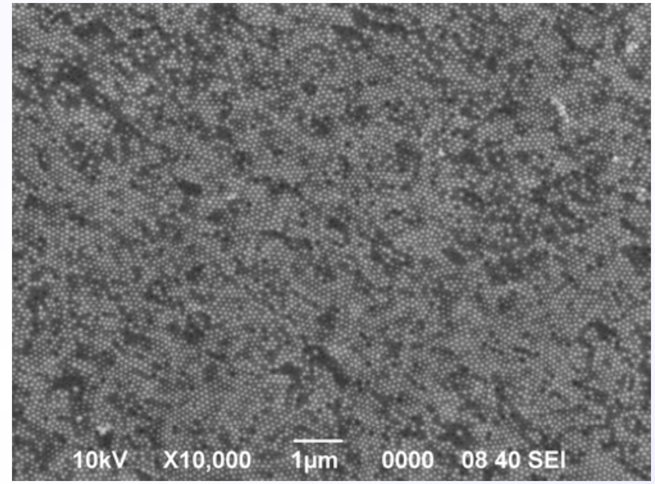
* M. Darques *et al.*, **J Phys D: Appl Phys** 37 (2004) 1411



*c-axis of Co layer parallel with the nanowire**

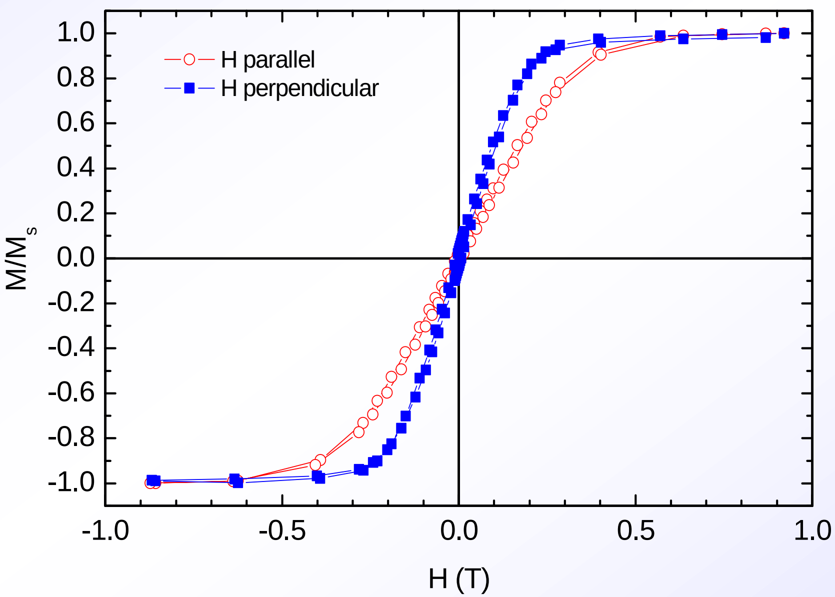
Magnetic interactions – m-H loops

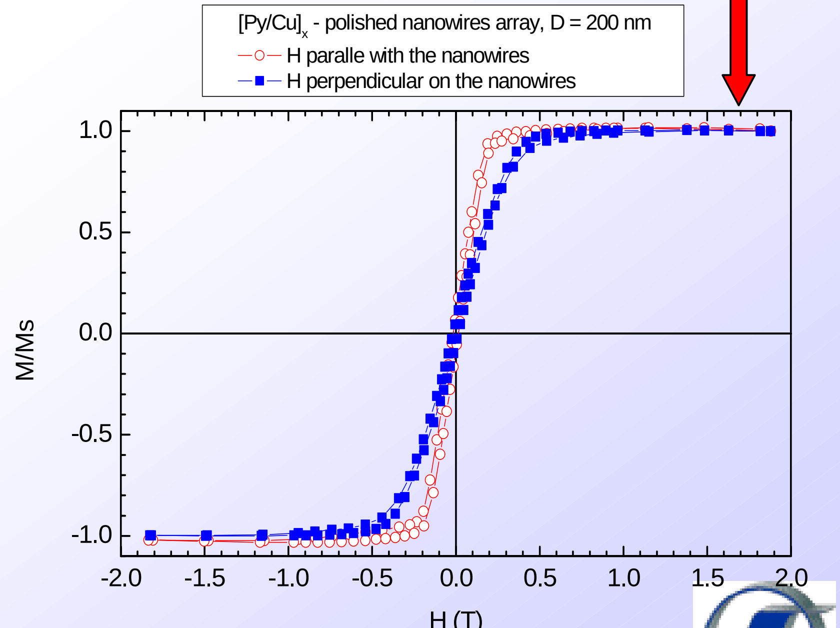




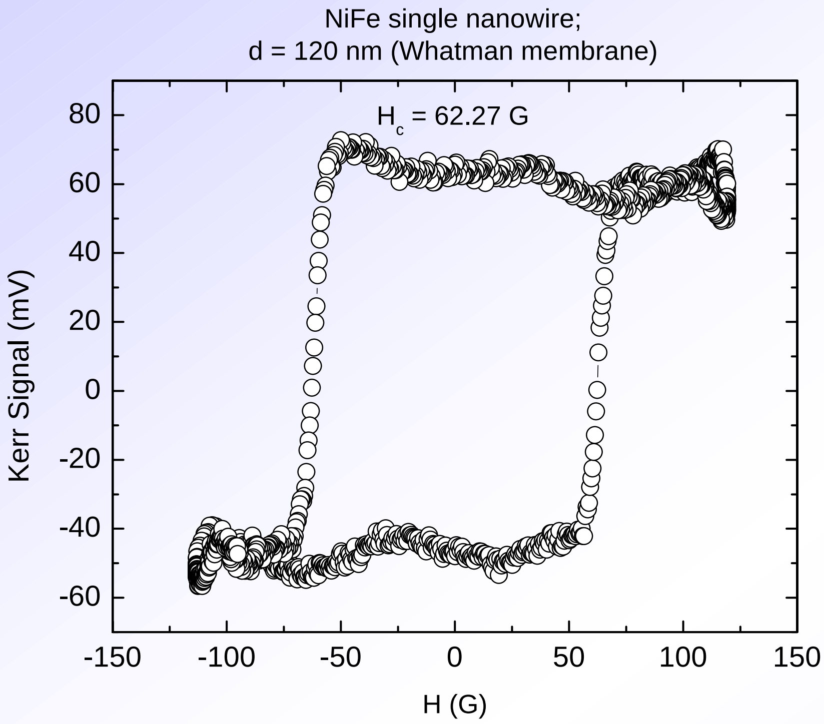
$[Py/Cu]_x$ multilayered nanowires

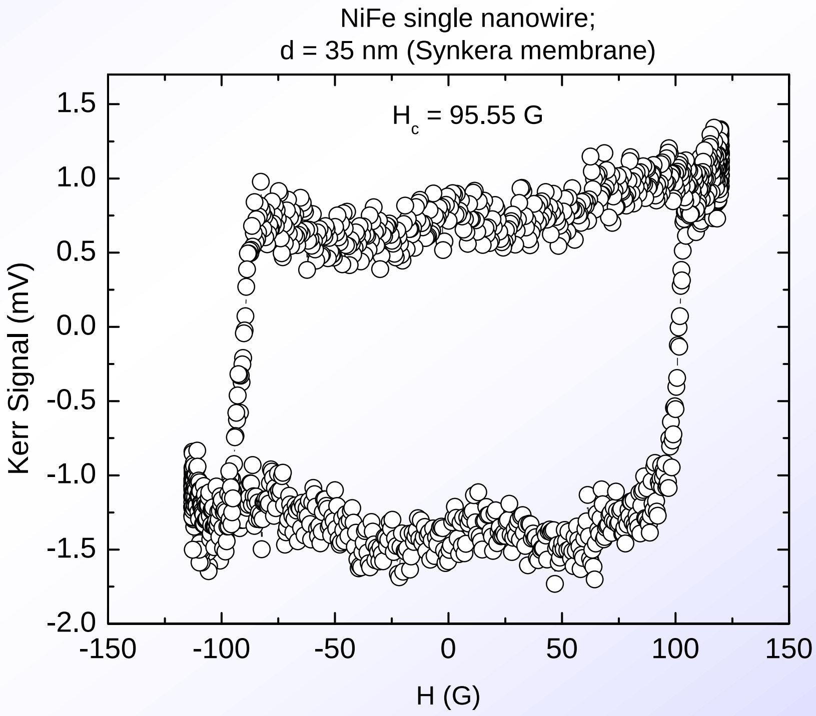
$D_{nanowire}$ = 20 nm



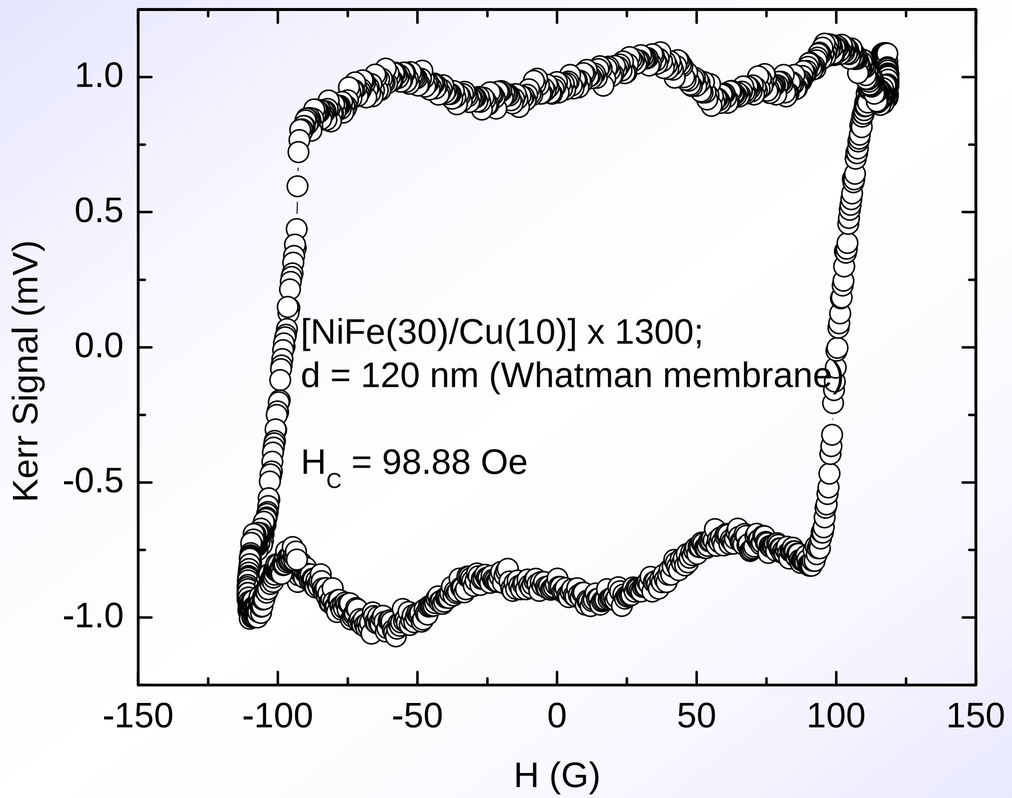


Magnetic interactions – NanoMOKE



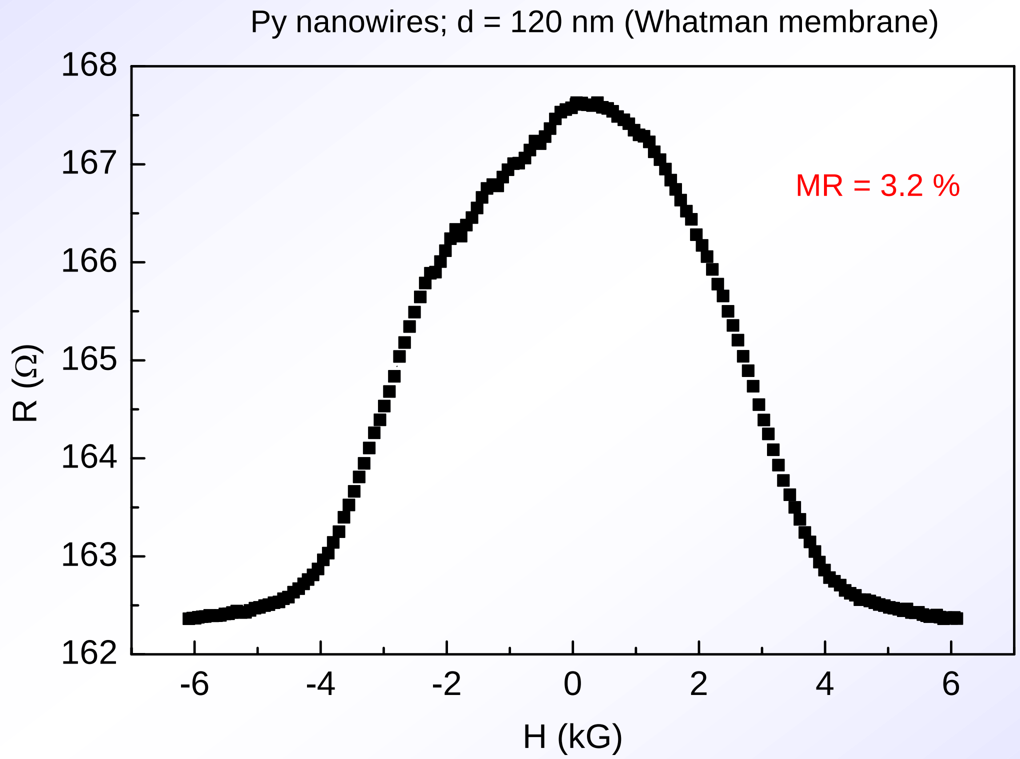


Magnetic interactions – NanoMOKE



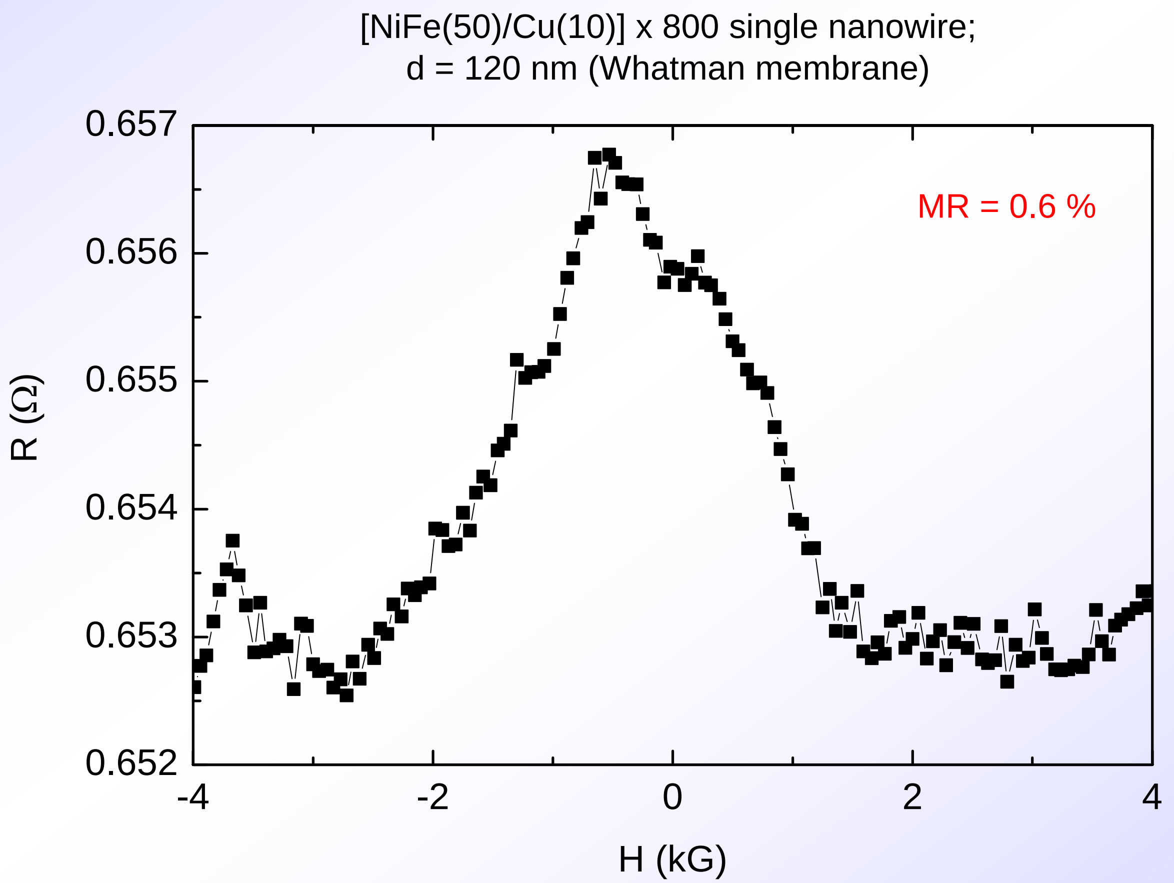
Magnetic interactions – magnetoresistance

- ***electrical contact on a number of nanowires – preliminary results***

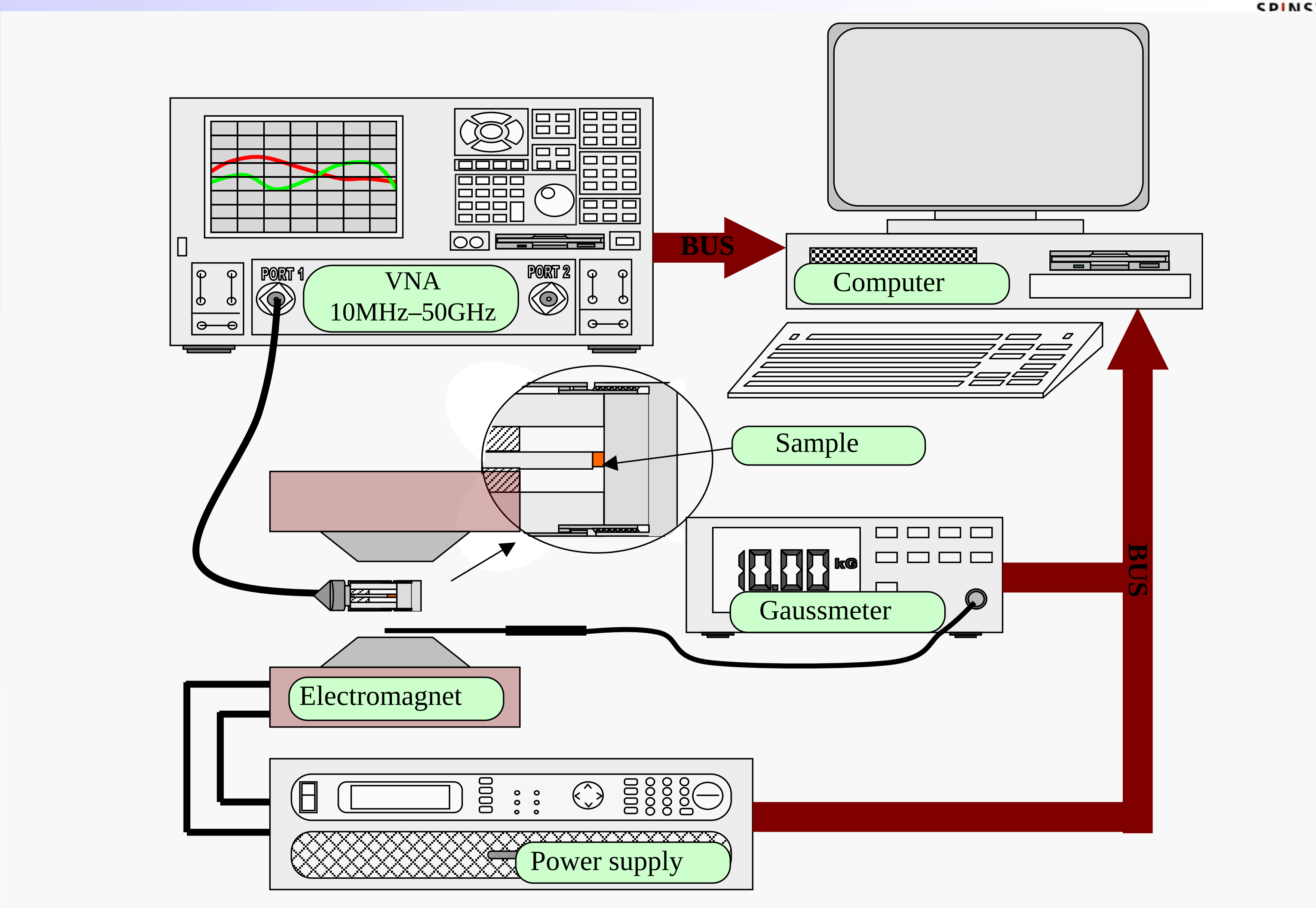


Magnetic interactions – magnetoresistance

➤ ***electrical contact on a single nanowire – preliminary results***

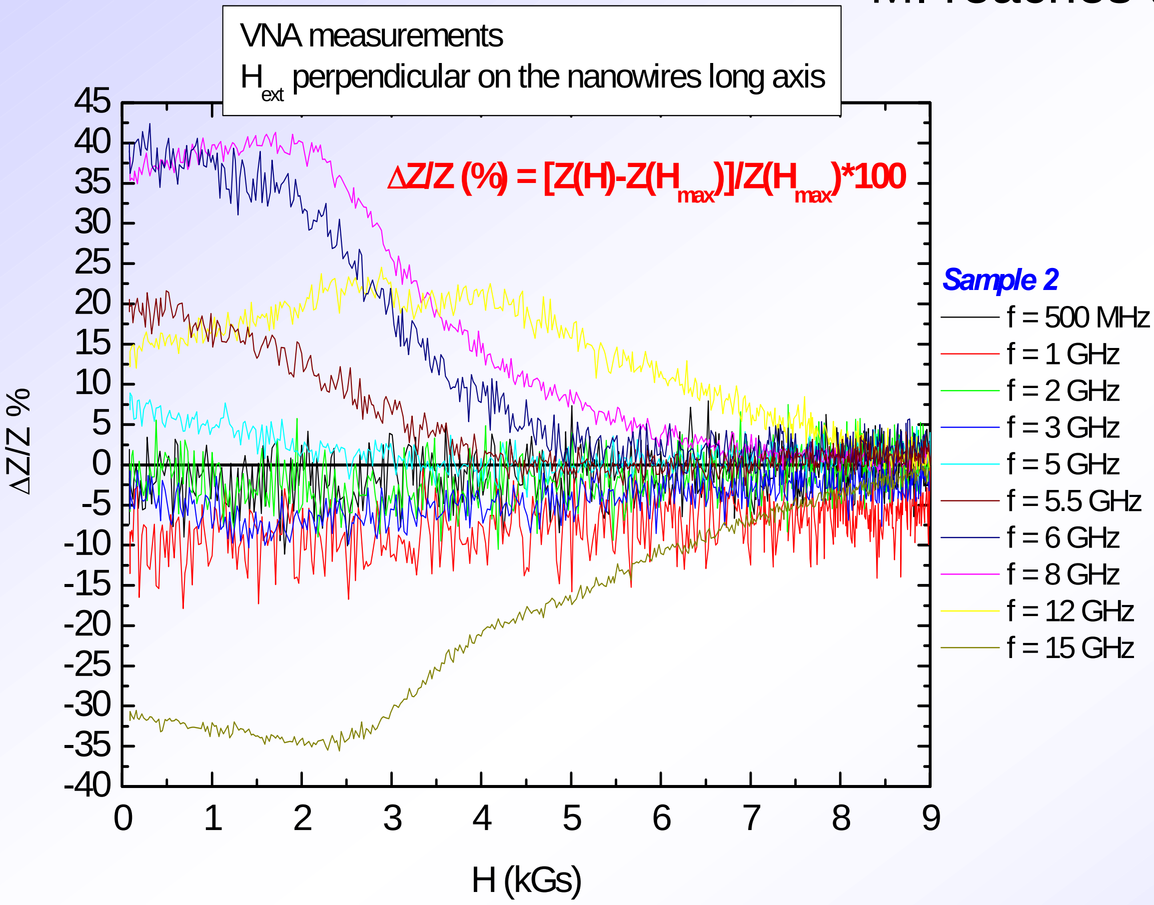


Magnetic interactions – magnetoimpedance



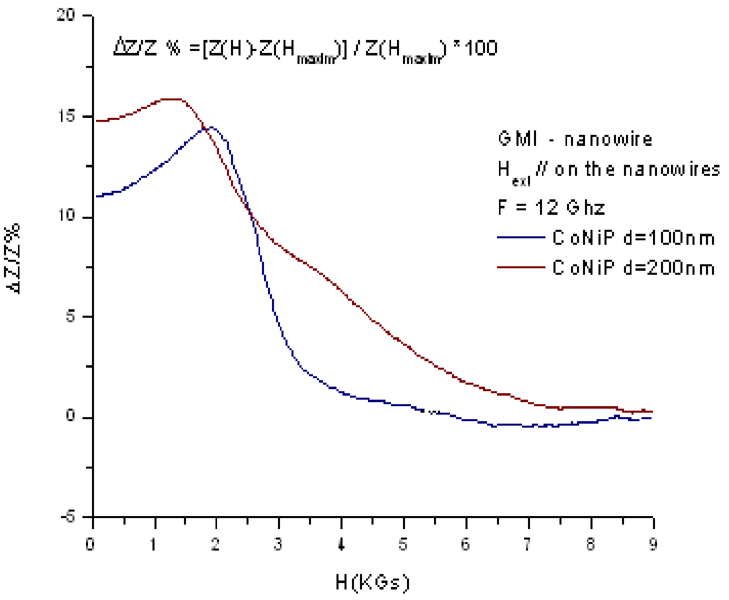
Magnetic interactions – magnetoimpedance

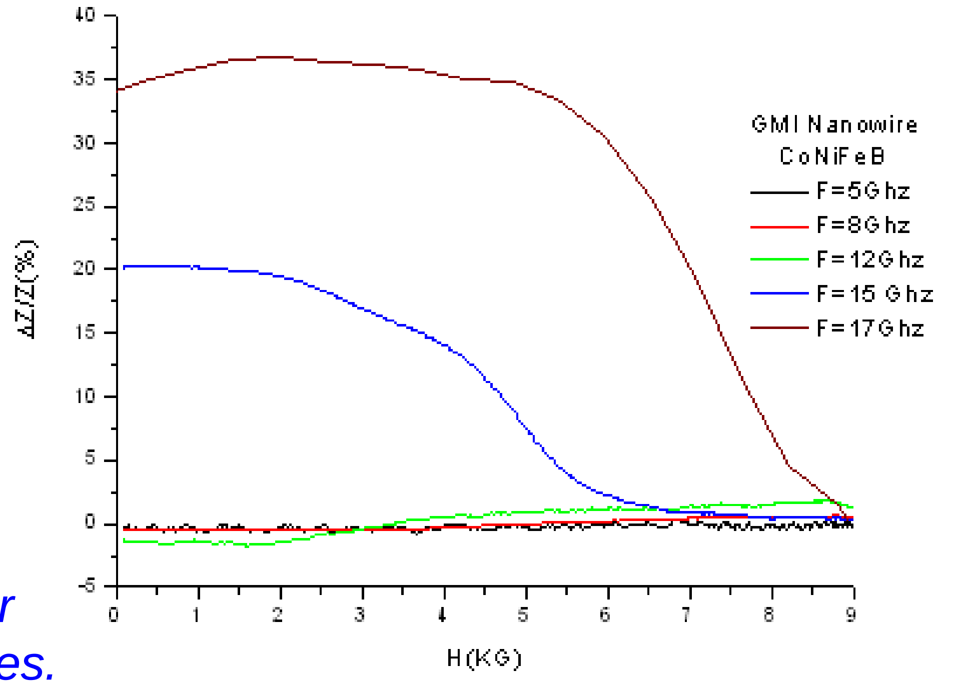
MI reaches the maximum value of 40%.



MI of [NiFe/Cu] nanowires;
$d_{nominal}$ = 20 nm

Magnetic interactions – magnetoimpedance

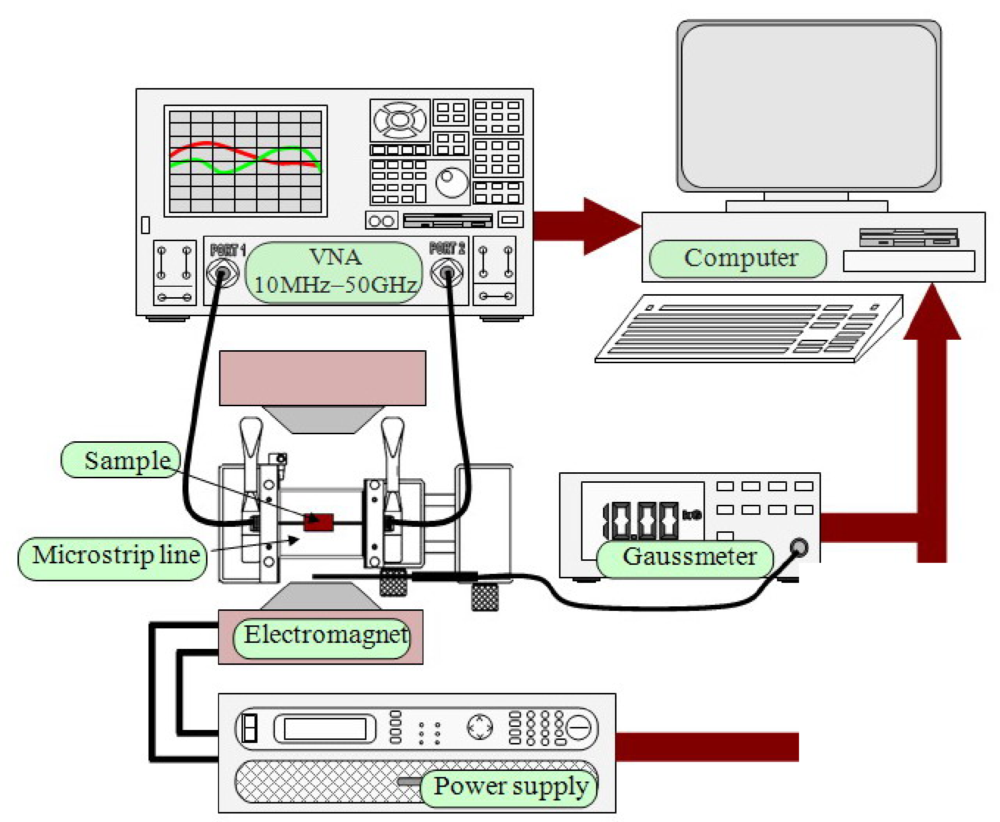




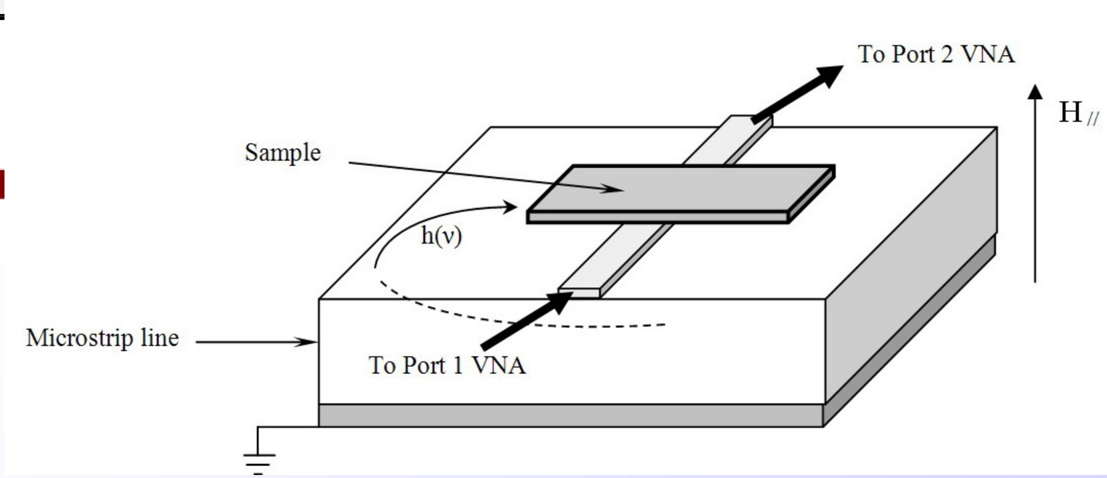
Magnetoimpedance vs. external field for CoNiP and CoFeNiB amorphous *nanowires.*
$d_{nominal}$ = 20 nm

MI reaches maximum 15% at 12 GHz for CoNiP nanowires and 37% at 17 GHz for CoFeNiB nanowires.

Magnetic interactions - FMR



FMR setup using a microstrip line



Position of the nanowire arrays relative to the microstrip line.

Magnetic interactions - FMR

✓ The electromagnetic losses in the microstrip line*, through which a microwave signal is transmitted, are measured.

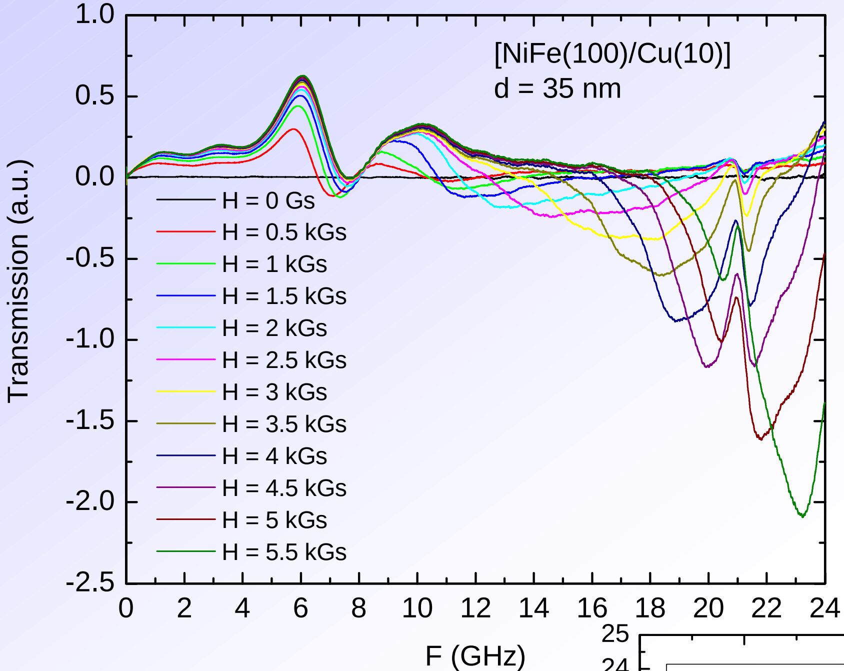
*S. Pignard *et al.*, **IEEE Trans Magn** 36 (2000) 3482

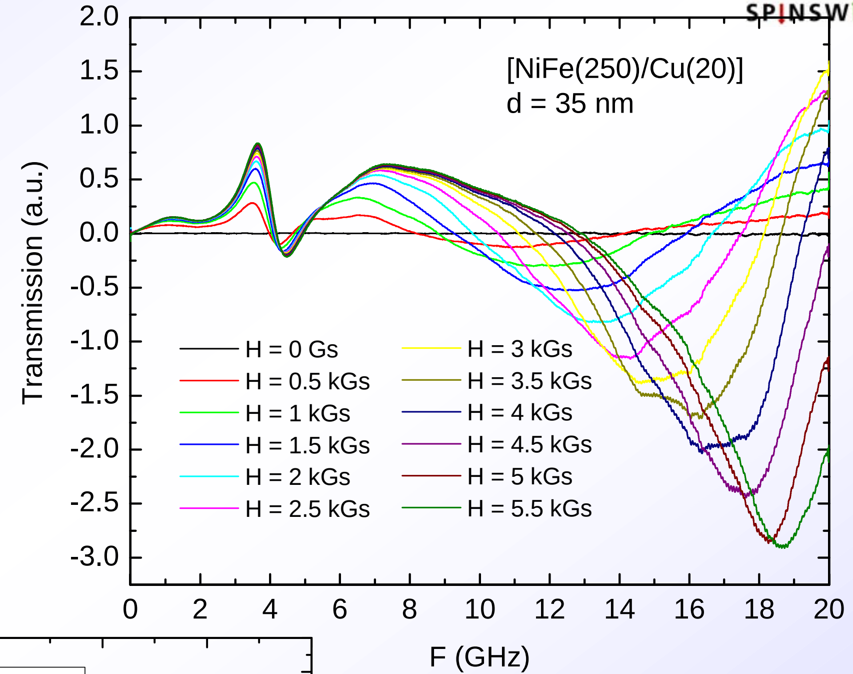
✓ The FMR spectra are obtained by varying the frequency of the microwave signal, for a given value of the external magnetic field.

✓ The FMR spectra are obtained by measuring the ratio $S_{21}(H)/S_{21}(H0)$, where $S_{21}(H)$ is the transmission signal for an external magnetic field H and $S_{21}(H0)$ is the transmission signal in the absence of the external magnetic field (the last term includes the noise and the peaks given by the impedance jumps caused by the contact between the microstrip line and the nanowires array).

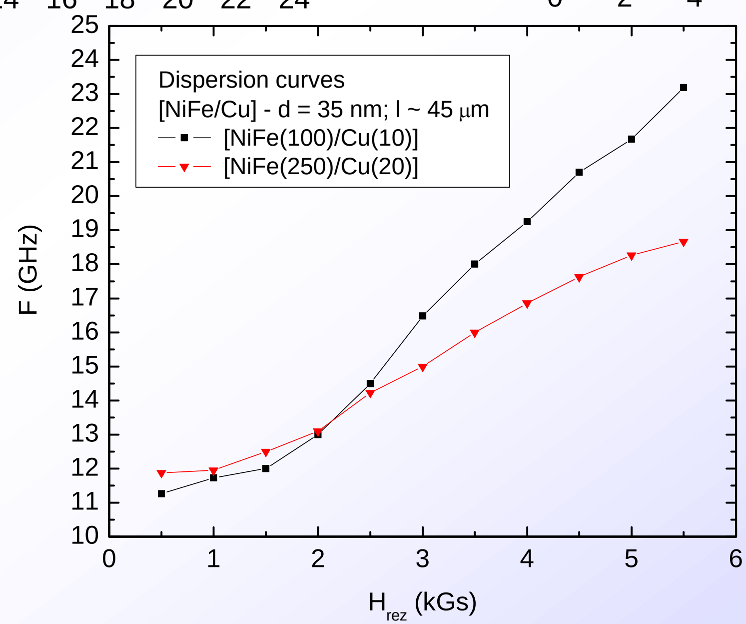
✓ The external d.c. magnetic field (max. 5.5 kOe) is parallel with the nanowires.

Magnetic interactions - FMR

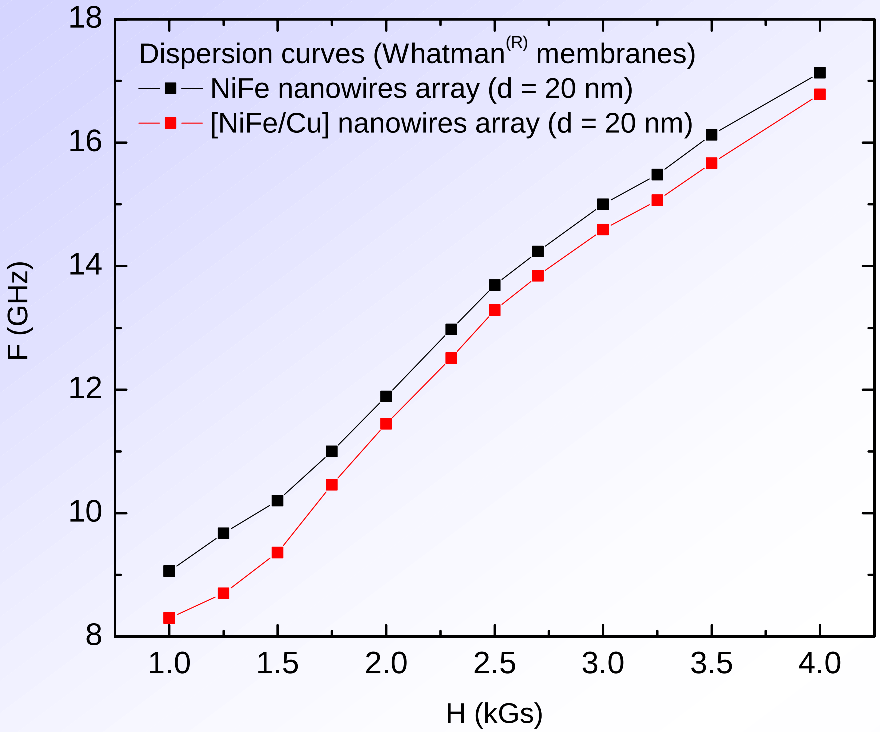


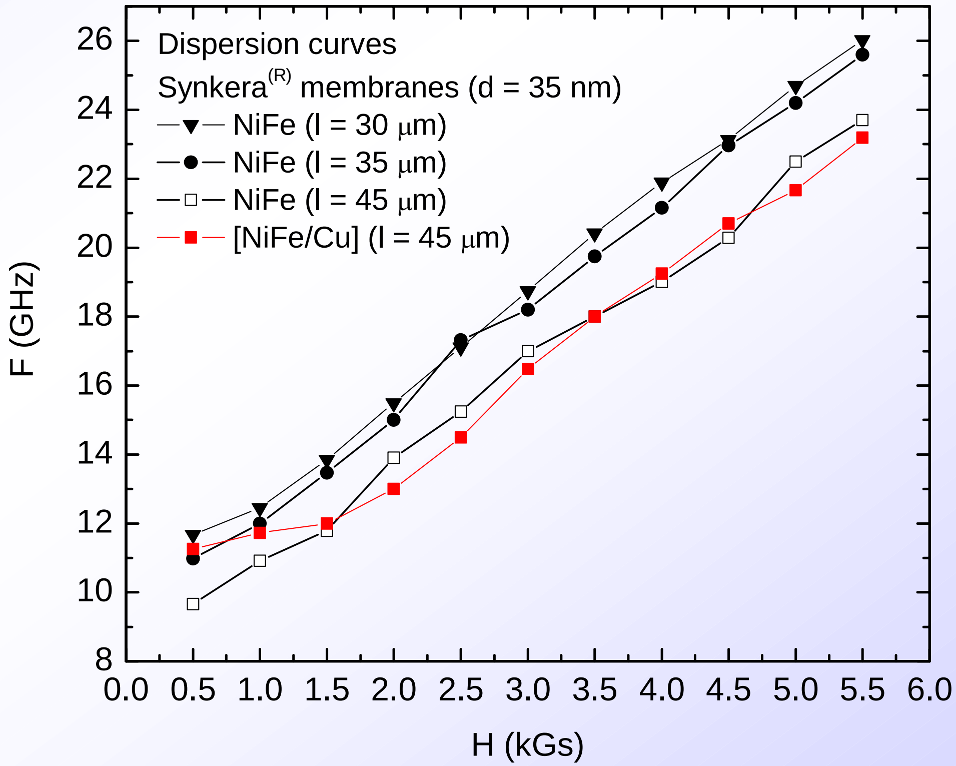


The dispersion curve shows a dependence of the resonance frequency on the aspect ratio of the nanowires, due to the shape anisotropy.



Magnetic interactions - FMR





The dispersion curve shows a dependence of the resonance frequency on the aspect ratio of the nanowires, due to the shape anisotropy.

Concluding Remarks

- Despite the progress done in what concerns the preparation and characterization of magnetic nanowires (and not only) by electrodeposition in the nanopores of different templates, there is still a lot to do in understanding the microscopic (nanoscopic?) behavior of such 1-dimensional structures.

  - The interactions between different layers constituting the multilayered nanowires is still far to be understood.

  - The periodicity and regularity of the membranes are still not completely solved.

  - The control of the alloys compositions, by controlling the deposition bath concentration and deposition parameters, is quite difficult, because the laws which apply for electrodeposited thin films are not always fulfilled for the nanowires.

- Despite all these problems, the nanowires could play a major role in many advanced applications.