REFREEPERMAG- FP7-EU Project

The first ever *Combinatorial Approach* for PM

RARE EARTH FREE PERMANENT MAGNETS

AN EU SUPPORTED PROJECT TO SEARCH FOR NON-RARE EATH CONTAINING PERMANENT MAGNETS

CALL: NMP.2011.2.2-4 Novel materials for replacement of critical materials (platinum group metals and rare earths)

GRANT AGREEMENT: 280670

START: 1ST MAY 2012- 30 APRIL 2015

COORDINATOR: Dr. D. NIARCHOS, NCSR Demokritos, Greece

http://.refreepermag-fp7.eu

REFREEPERMAG

Academic Partners

UPPSALA UNIVERSITET

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CSIC

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INSA TOULOUSE

UNIVERSITÄT DUISBURG ESSEN Open-Minded

Industrial Partners

WITTENSTEIN

magnetfabrik bonn

University of Delaware, USA

Industrial Technologies 2014

SMART GROWTH THROUGH RESEARCH AND INNOVATION

REFREEPERMAG- FP7-EU Project

1st AWARD (Oscar in magnetism!) for the best-performing-FP7 project

11 April 2014, Athens, GREECE

(INDUSTRIAL AND MATERIALS TECHNOLOGIES OF EU

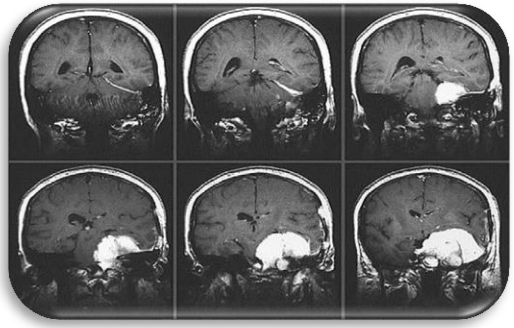
Permanent Magnets are Everywhere

Motors used in cars, airplanes and everywhere!!

Magnetic Cranes

Magnetic Levitation Train (v>250mph)

Roller Coaster in Six Flags in Southern CA (v>100mph)



MRI

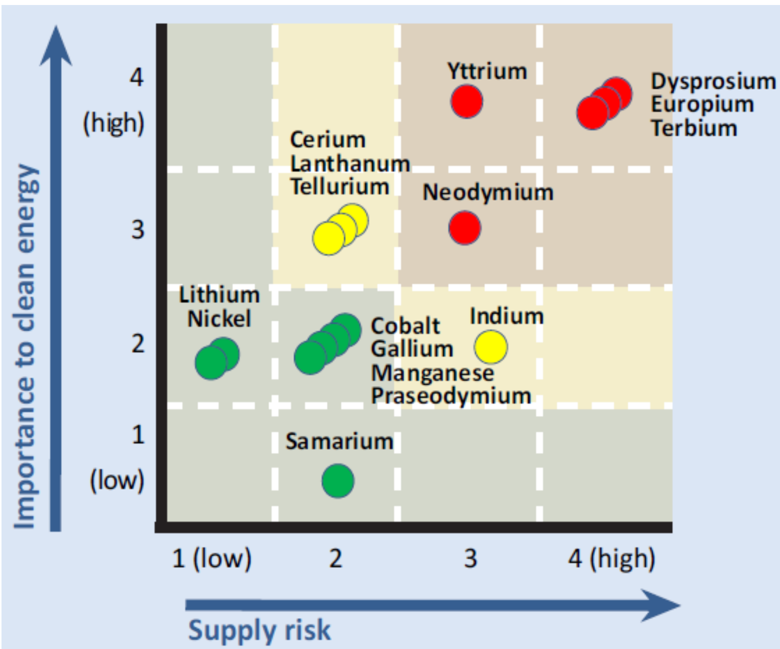
Computer Hard Drive

And many, many more……

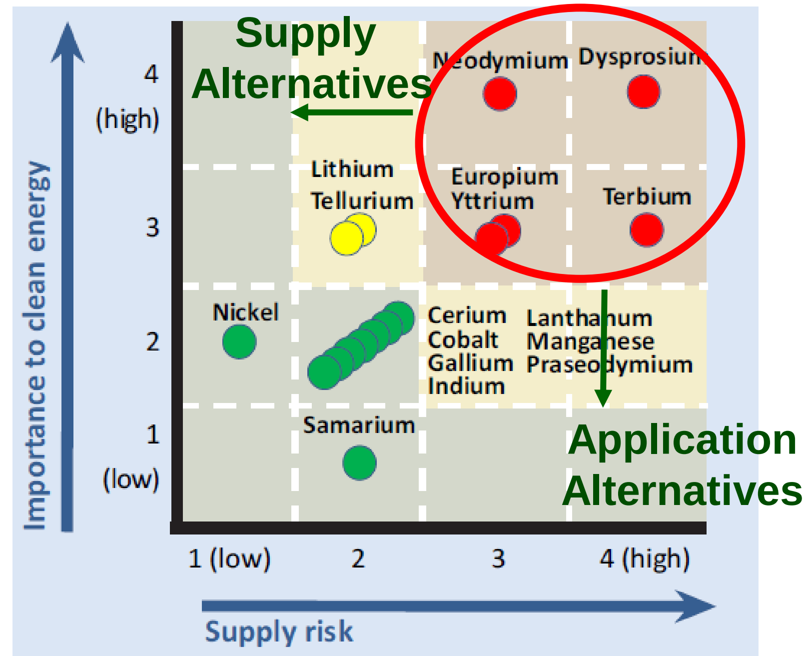
REFREEPERMAG

Rare Earth Criticality by Element

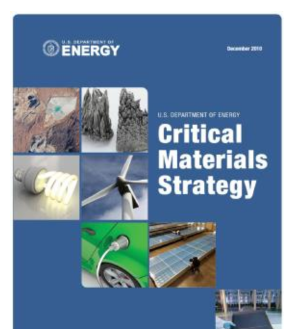
Short Term (0– 5 years)

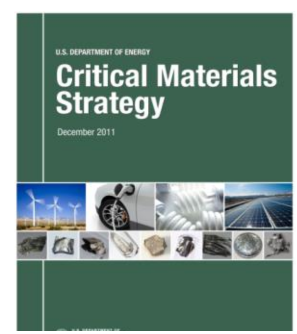


Medium Term (5– 15 years)



US DOE: Critical Materials Strategy (Dec 2010, 2011)





The challenges

The Problem

- Most of the well known PM are based on Rare-Earth Elements (Nd, Sm)
- Almost single source of supply is China

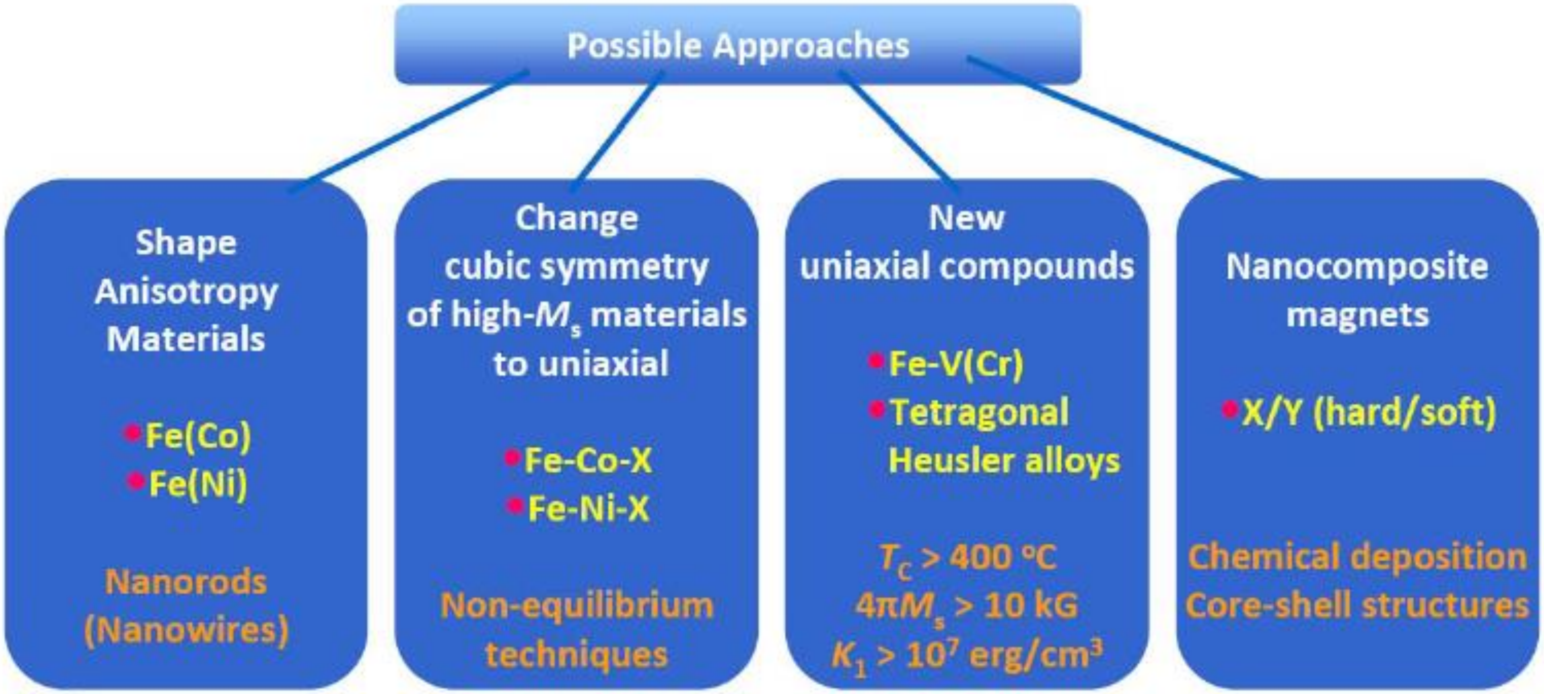
The Answer

- Replace as much as possible the rare-earths and maintain the PM properties

The Innovation

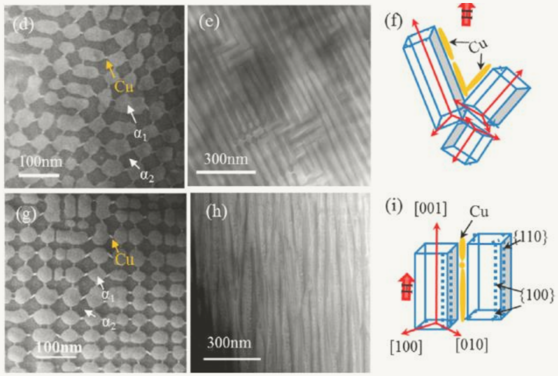
- Combinatorial Modelling of Fe-Co-X based alloys (Abundant and Inexpensive)
- Combinatorial Synthesis and Characterization
- Novel compaction techniques for sintered magnets

The Approach



The path towards Superior -Earth free high performance PMs is depicted in the Figure above.

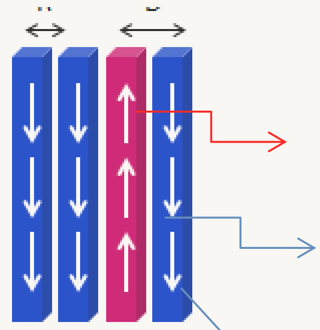
Such program needs to include scientists and engineers with a wide expertise fro m materials design (theory), phase diagrams, design of microstructures, applied m agnetic and fabrication techniques (combinatorial approach).



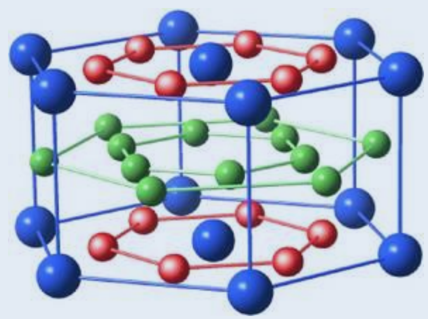
ALNICO

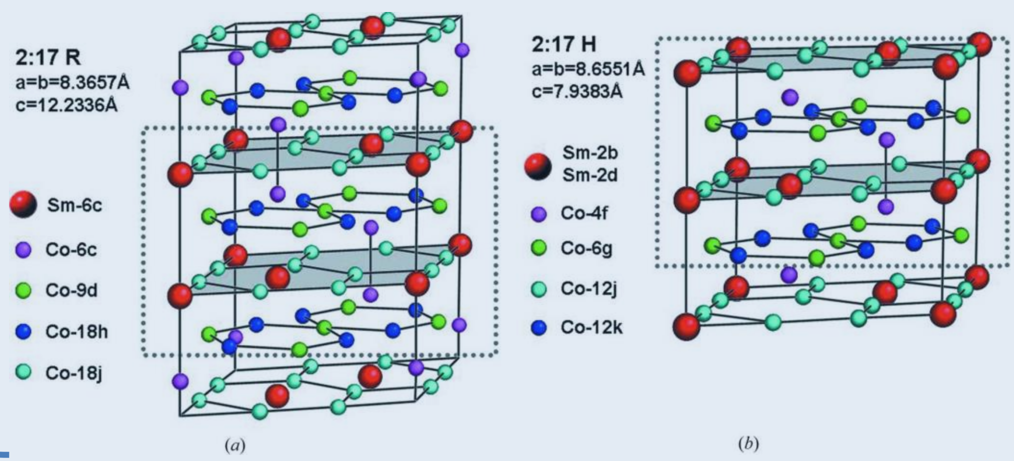
Hci can be increased by

- Reducing R ~ <15nm
- Increasing Fe:Co in bcc
- Increasing f to ~ 2/3
- Minimizing interaction
  - i.e. branching

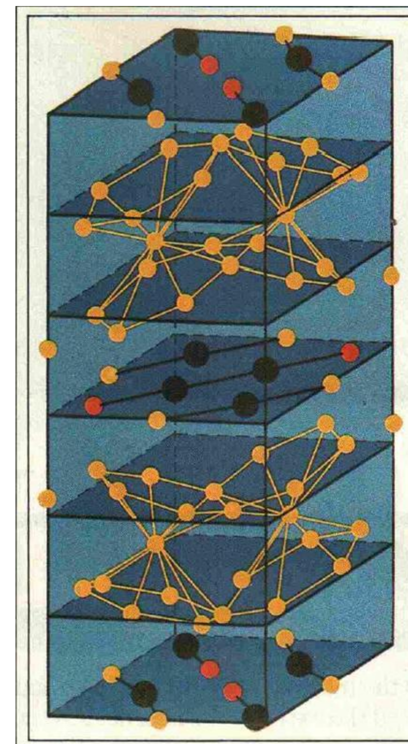


SmCo$_5$





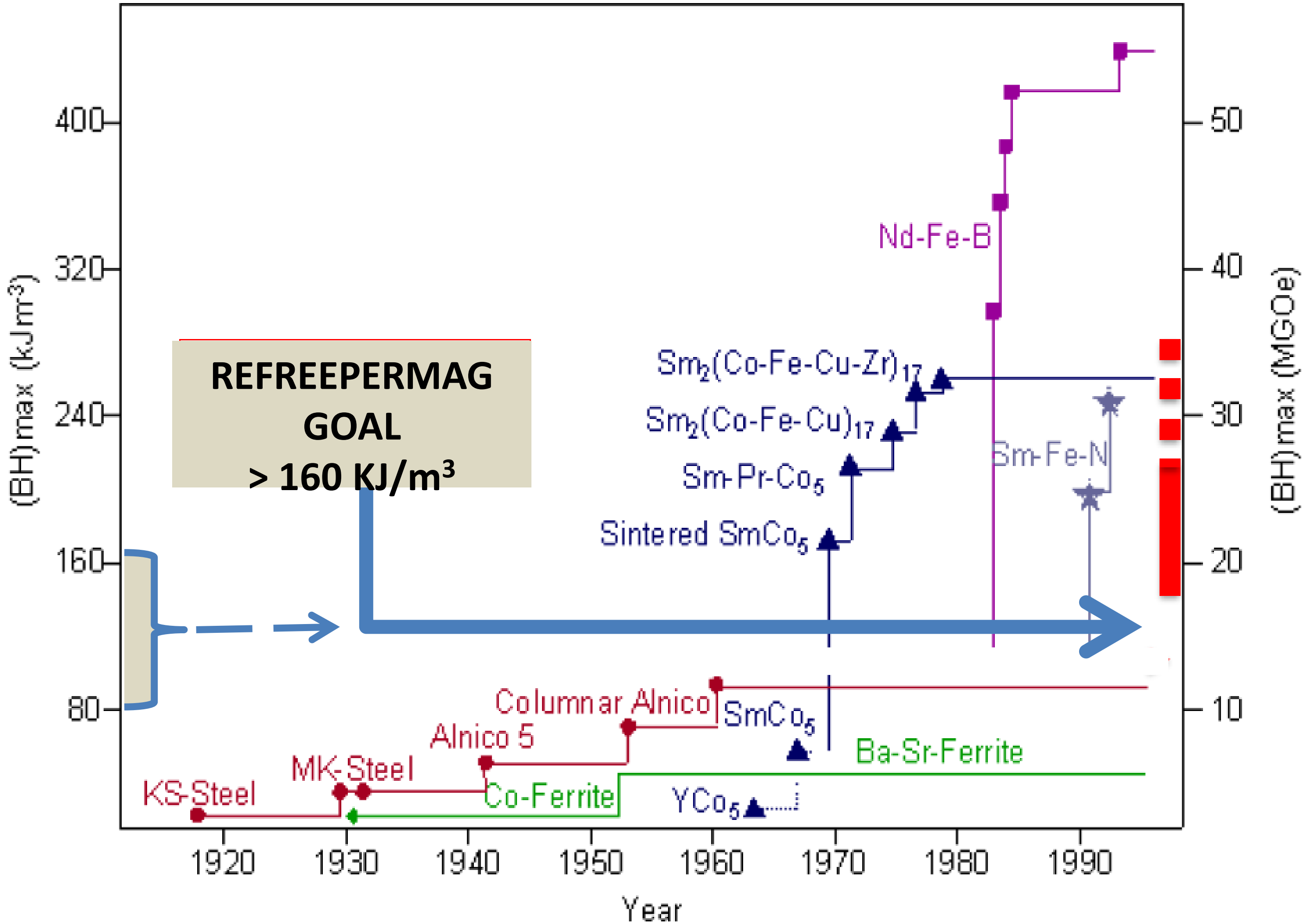
Sm_2Co_{17} type



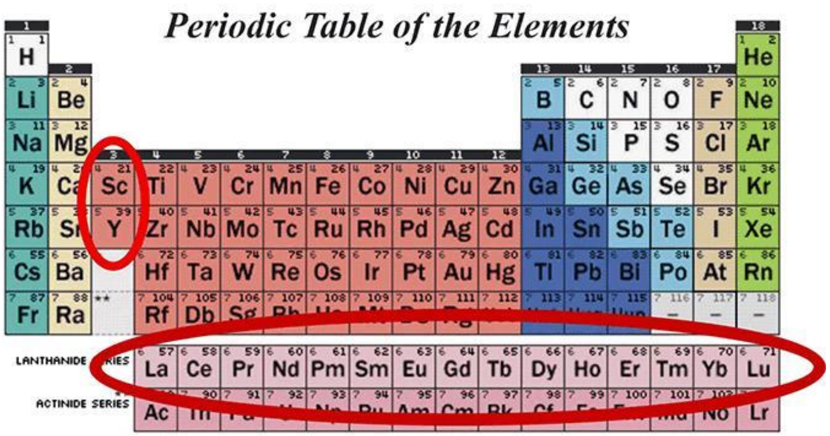
Repeating cells that contain 56 iron (yellow), 8 neodymium (black) and 4 boron atoms (red) make up MAGNEQUENCH.

$Nd_2Fe_{14}B$

GOAL of REFREEPERMAG



Our approach



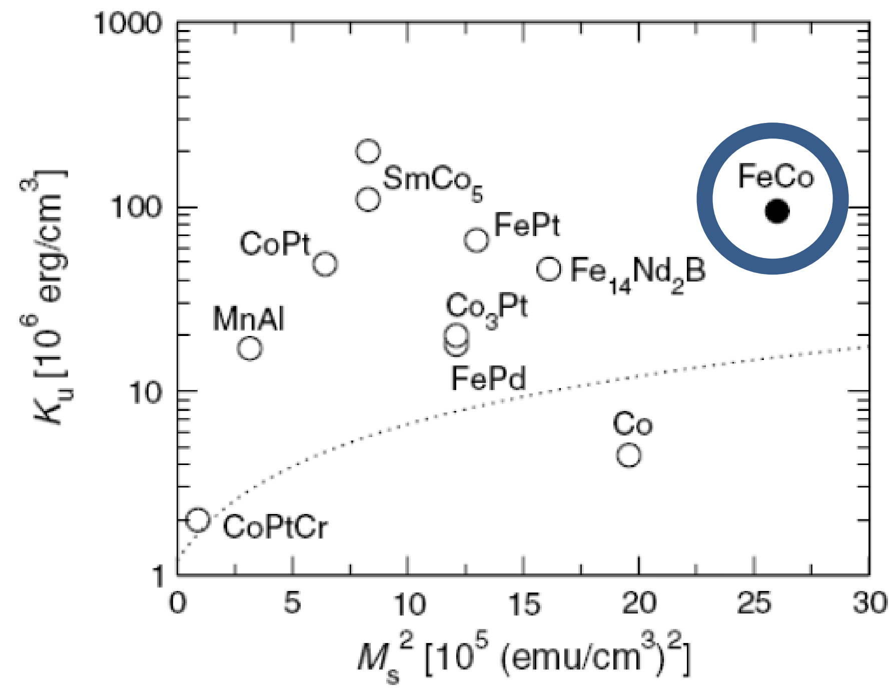


FIG. 2. Stability contour plot of high K_u materials, drawn after Fig. 1 of Ref. [3] (open circles). The present result for the tetragonal FeCo alloy with the maximum uniaxial MAE is included for comparison (closed circle). The dotted line is the 40 Gbits/in^2 stability boundary according to Charap *et al.* [23], assuming a write field of 5100 Oe and 12 nm grains.

Burkert et al. Phys. Rev. Let. 93 (2004) 027203

- **High performance permanent magnets with energy product 60 kJ/m3 <(BH)max < 160 kJ/m^3**
- **High coercivity (shape anisotropy)**
- **High Saturation Magnetization**
- **High curie temperature**

Modelling

Computational methods

- **DFT**
  - FP-LAPW method, implementation WIEN2k. Disorder via virtual crystal approximation (VCA)
  - Spin-Polarized relativistic KKR method, Munich SPR-KKR code
    Disorder via coherent potential approximation (CPA)

- Focus on tetragonal FeCo:
  - FeCo-C
  - FeCo-B
- Other systems which have been studied include:
  - $L1_0$ binary alloys (FeNi, CoNi, MnAl, MnGa). Paper submitted. Available at arXiv:1404.7097v1
  - $(Fe_{1-x}Co_x)_2B$.
    Finishing up this work in collaboration with Darmstadt group.

- **Micromagnetic Simulations**

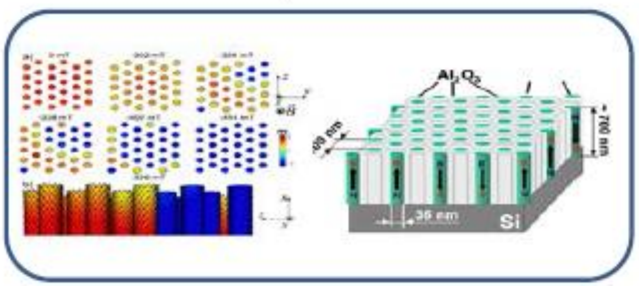
- Focus on
  - Co-nanowires
  - Fe-Co nanowires
  - Packing density
  - Caping of nanowires
  - etc

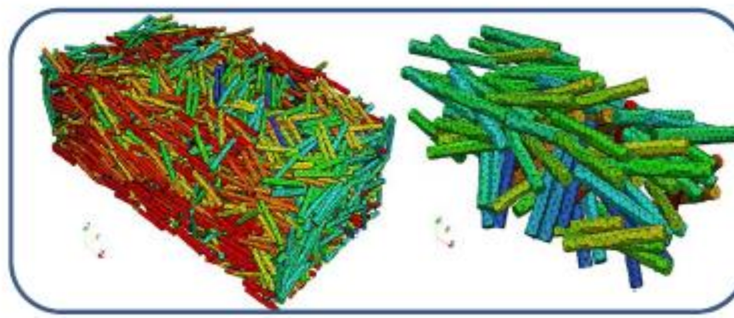
Modelling

- **Micromagnetic Simulations (J. FIDLER Presentation on Tuesday)**

REFREEPERMAG: Packed Co-, Fe- nanorods

- Design and fabrication of the next generation permanent magnets without critical materials based on nanotechnology strategies.
- Theoretical modelling including data mining concept (ab-initio and micromagnetic).
- Wide range of physical and chemical strategies like thin-film combinatorial synthesis and modified polyol-synthesis of nanowires, electrodeposition, etc.





magnetocrystalline shape anisotropy

$$H_c = H_n = \frac{2K_1}{J_s} + \left(N_\perp - N_\parallel\right)\frac{J_s}{\mu_0}$$

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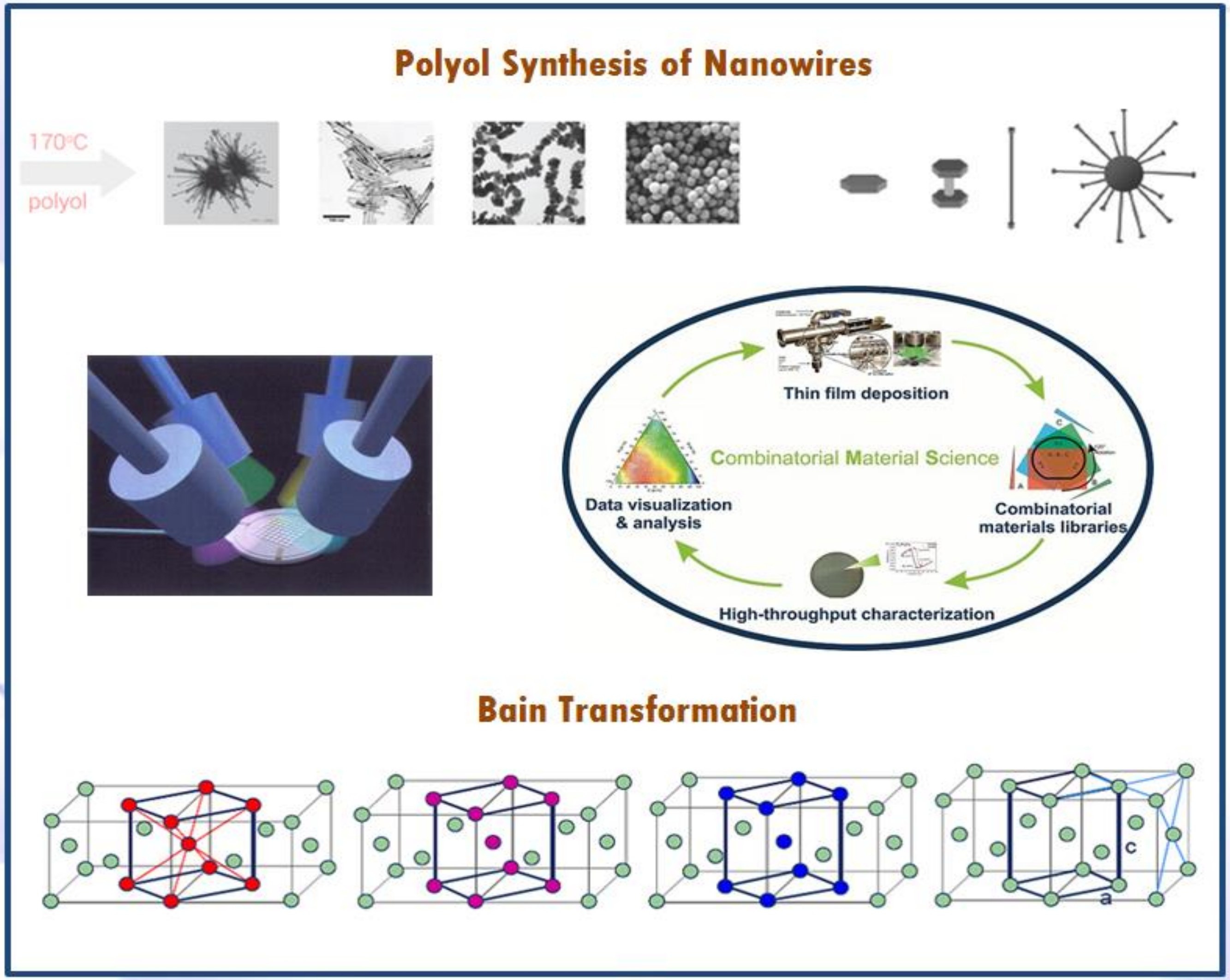
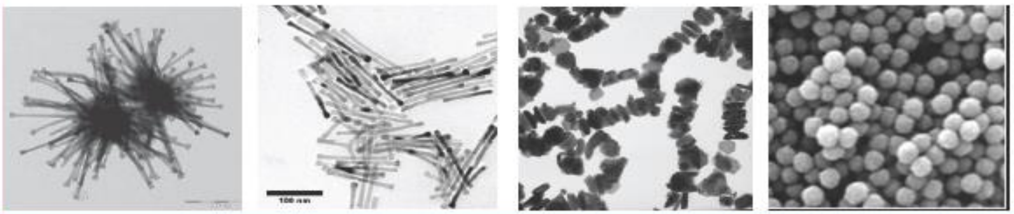
The Approach

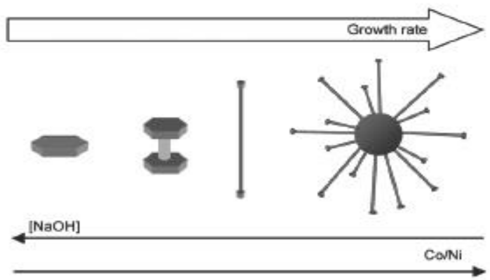
THE TECHNIQUES



The Polyol and Electrochemical Synthesis of Nanowires

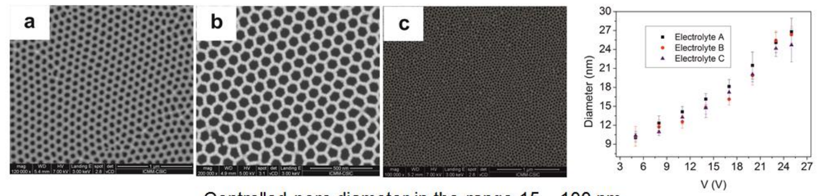
$M(C_nH_{2n+1}CO_2)_2$ (M = Co, Ni) —170°C, polyol→ **Cobalt and bimetallic Co_xNi_{1-x} particles**



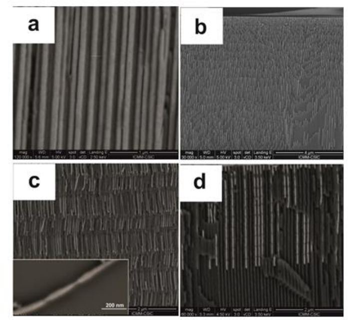


Electrochemical Synthesis

Home-made membranes



Controlled pore diameter in the range 15 – 100 nm



CoFe (High Ms)

CoFeCu (High Hc)

Regular or modulated diameter

Multilayer CoFe/Au

Devices

Chemical modification of the tips

Preparation of high-aspect ratio nanostructures

Task 2.1 Chemical synthesis

SubTask 2.1.1 Chemical Synthesis of {Fe-Co}-X-Y Nanostructures

SubTask 2.1.2 Electrochemical synthesis of CoFe rich nanowires

Task 2.2 Physical Methods-Nanoflakes

Task 2.3 Surface modification and recycling

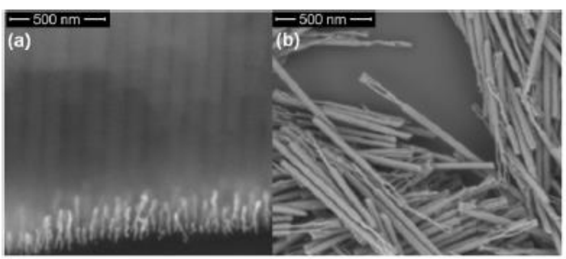
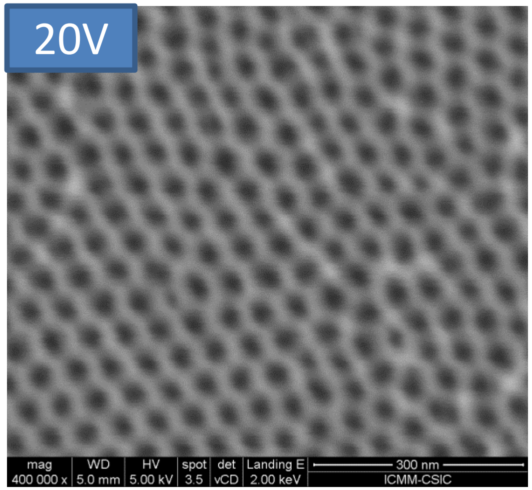
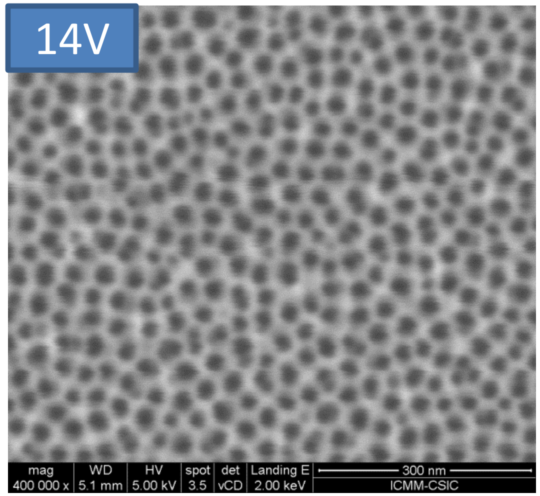


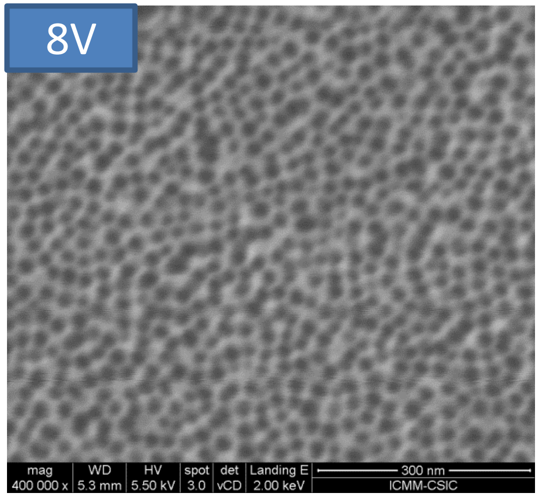
Fig. 10. Nanowires made by electrodeposition in AAO

Nanowires with reduced pore diameter : higher Hc

Top view images of different AAO templates with various diameters

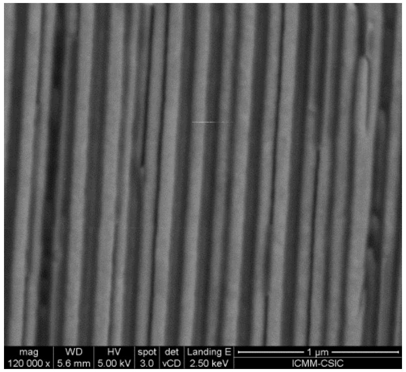




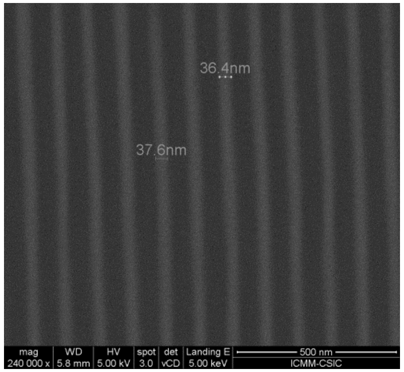


Reduce the pore diameter and keep the order ⟶ ALD

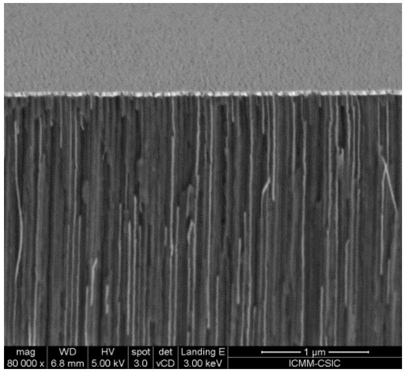
Cross-section images of different nanowires with various diameters



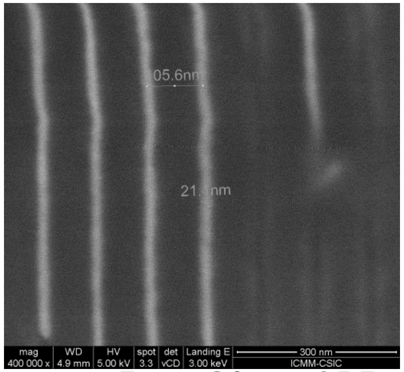
D_{NW}=80nm
D_{int}=100 nm



D_{NW}=35nm
D_{int}=100 nm



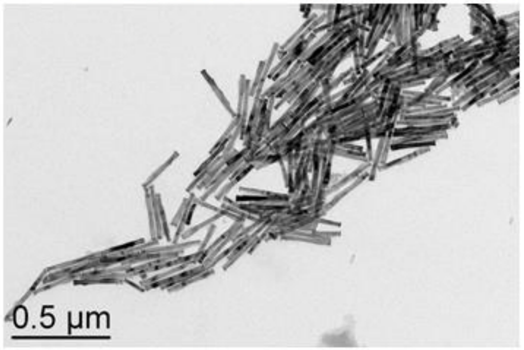
D_{NW}=20nm
D_{int}=50 nm



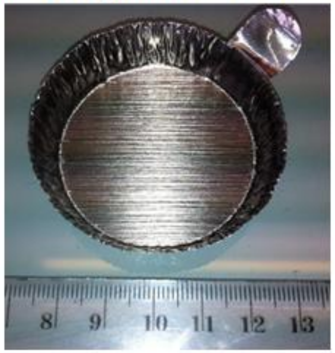
D_{NW}=20nm, ALD
D_{int}=105 nm

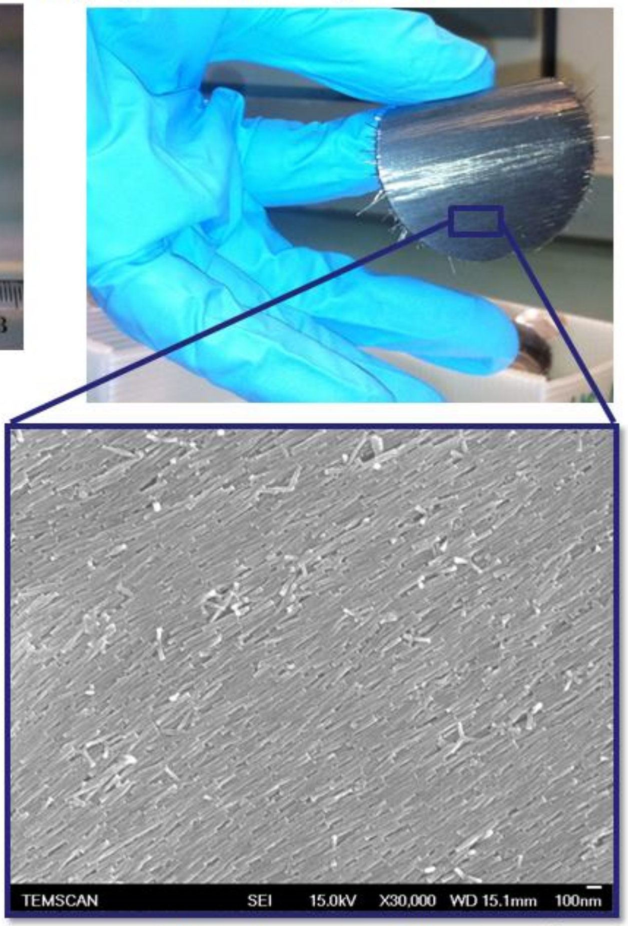
Chemical synthesis : Fabrication of macroscaled magnetic structures

1. Washing of NRs



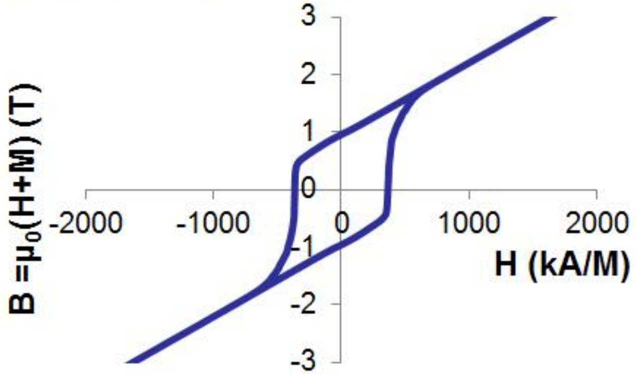
2. After alignment in the EM (1T)… *robust magnetic material*





Aligned array of NRs [3]

4. Hysteresis loop of a needle



✓Good alignment (M_r/M_s>95%)

→ BH_{max} = *100-165 kJ/m³*

May be we are the first Nanowire based PM!

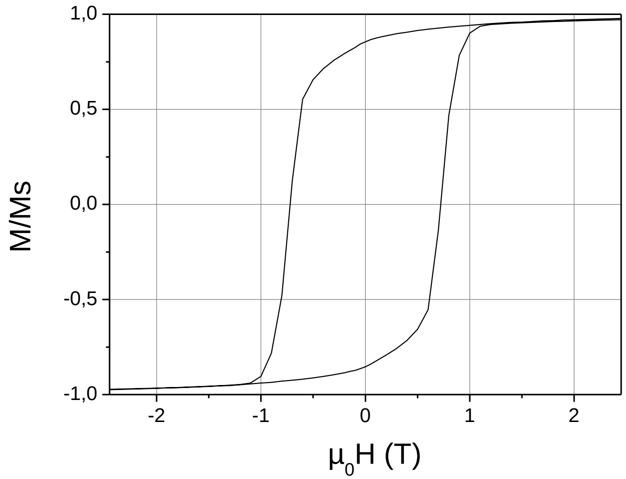
Nanowires with reduced pore diameter : higher Hc

Magnetic properties

Best values

$H_C \approx 5$ kOe (randomly oriented NRs)

$H_C > 7$ kOe (oriented NRs)



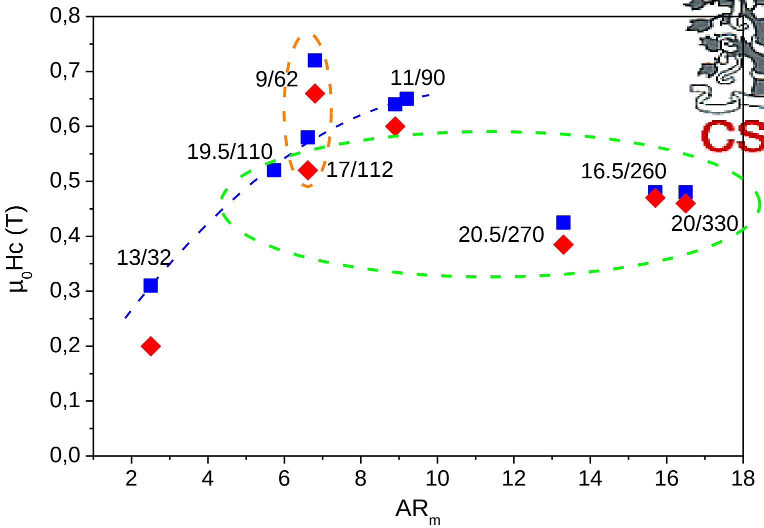
OUR TARGET

✓**Good alignment (M_r/M_s>95%)**

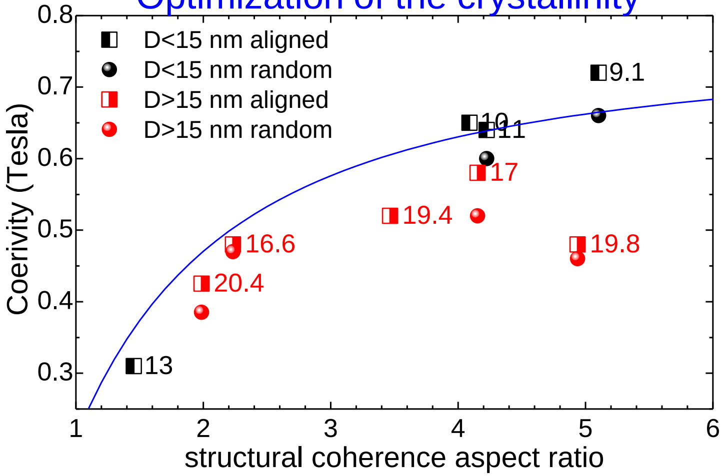
→ **BH_{max} = *100-165 kJ/m³***

Demonstrate the applicability of polyol –method for Fe-Co and Fe-Co-X alloys

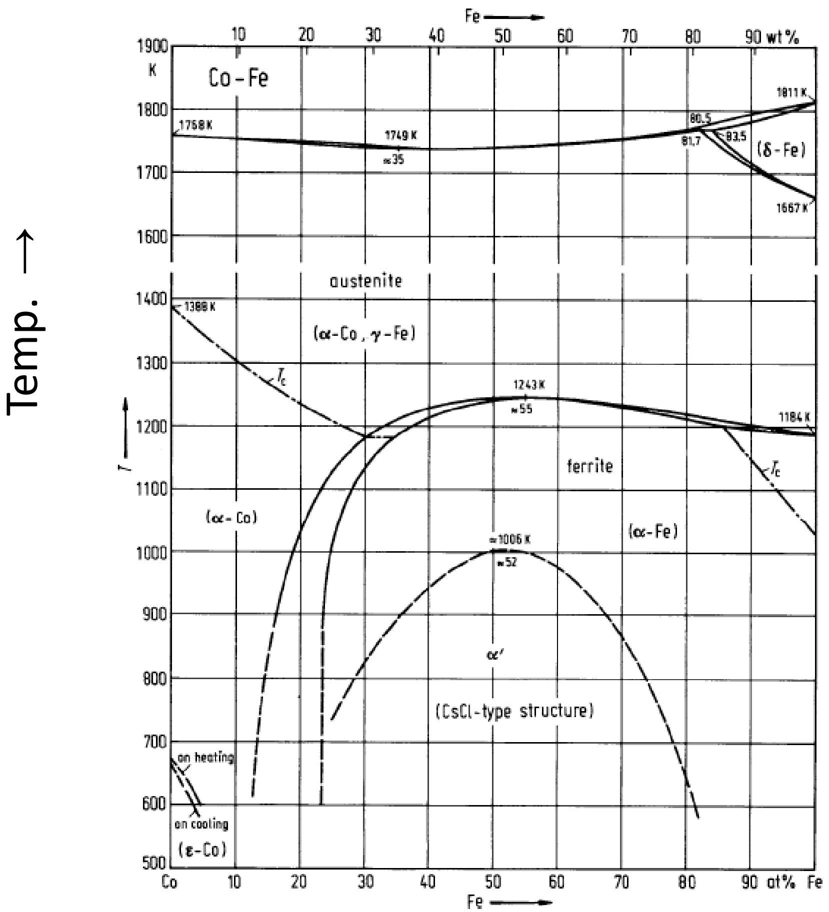
Optimization of the aspect ratio



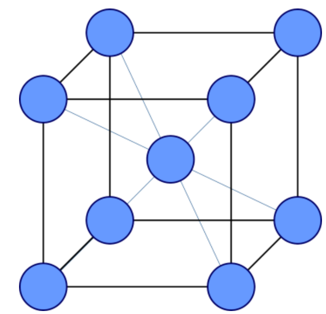
Optimization of the crystallinity



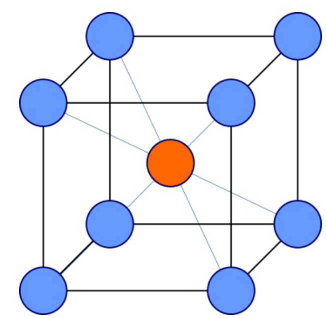
Chemical order in Fe-Co



bcc-disordered
736°C < T < 970°C



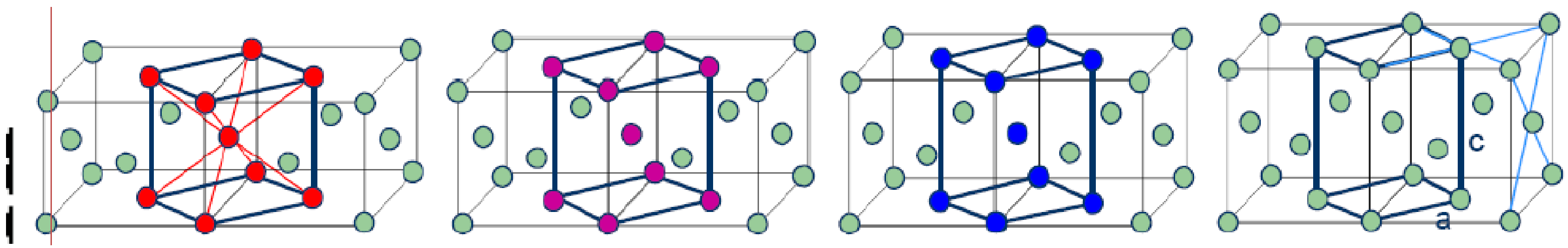
ordered CsCl-type (B2)
T < 736°C



The BAIN-PATH Combinatorial approach for PM

Inducing MCA in FeCo

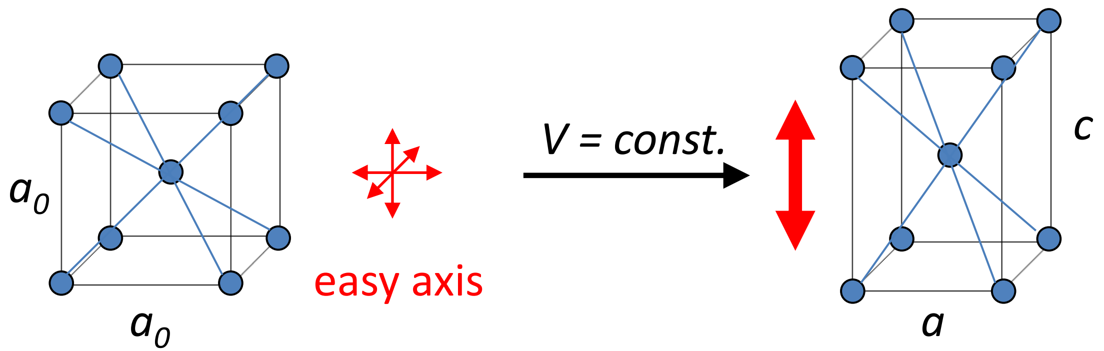
The bain path



bcc c/a~1 → stabilize metastable phases

c/a~1.41

Inducing magnetocrystalline anisotropy (MCA) in FeCo



$c > a$

$a_{Substrate} < a_0$

$c > a_0$

UPPSALA UNIVERSITET

Fe/Co alloys doped by B/C/N

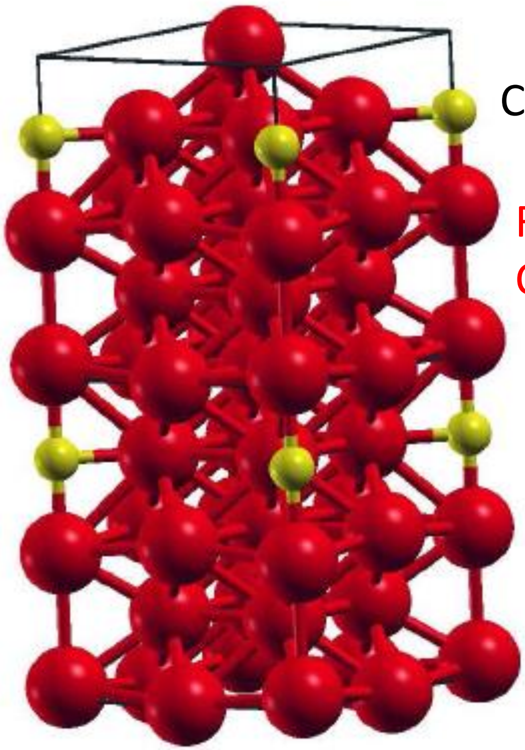
Carbon doping

Combinatorial approach- modelling

Composition	c/a	a (Å)	MAE (MJ/m³)	m (MA/m)
$(Fe_{0.7}Co_{0.3})_8C$	1.174	2.777	1.10	1.96
$(Fe_{0.4}Co_{0.6})_{16}C$	1.124	2.766	1.29	1.95
$(Fe_{0.39}Co_{0.61})_{16}C$	1.129	2.762	1.22	1.87
$(Fe_{0.35}Co_{0.65})_{16}C$	1.165	2.729	1.92	1.91
$(Fe_{0.4}Co_{0.6})_{24}C$	1.033	2.834	0.61	2.04
$(Fe_{0.35}Co_{0.65})_{24}C$	1.036	2.829	0.74	2.00

			No carbon	
Composition	MAE (μeV/atom)	m (μ_B/atom)	MAE (μeV/atom)	m (μ_B/atom)
$(Fe_{0.7}Co_{0.3})_8C$	76.5	1.88	54.0	2.42
$(Fe_{0.4}Co_{0.6})_{16}C$	90.2	1.87	222.0	2.16
$(Fe_{0.39}Co_{0.61})_{16}C$	85.3	1.87	236.3	2.15
$(Fe_{0.35}Co_{0.65})_{16}C$	133.5	1.82	353.9	2.10
$(Fe_{0.4}Co_{0.6})_{24}C$	42.8	1.98	46.7	2.17
$(Fe_{0.35}Co_{0.65})_{24}C$	52.0	1.94	48.2	2.12

Motivation: Stabilised strain in highly anisotropic Fe-Co-C



DFT data provided by Uppsala:

Composition	c/a	a (Å)	MAE (μeV/atom)	MAE (MJ/m³)
$(Fe_{0.7}Co_{0.3})_8C$	1.174	2.777	86.7	1.05
$(Fe_{0.4}Co_{0.6})_{16}C$	1.124	2.766	90.2	1.29
$(Fe_{0.39}Co_{0.61})_{16}C$	1.129	2.762	79.0	1.13
$(Fe_{0.35}Co_{0.65})_{16}C$	1.165	2.729	119.0	1.71
$(Fe_{0.4}Co_{0.6})_{24}C$	1.033	2.834	42.8	0.61
$(Fe_{0.35}Co_{0.65})_{24}C$	1.036	2.829	52.0	0.74

Suitable buffers:

Pd	a_{bcc} = 2.76 Å
Ir	a_{bcc} = 2.72 Å
Au_xCu_{1-x}	$0.3 \leq x \leq 0.5$

Aimed film composition: $(Fe_{0.4}Co_{0.6})_{16}C$

The first ever *Combinatorial Approach* for PM

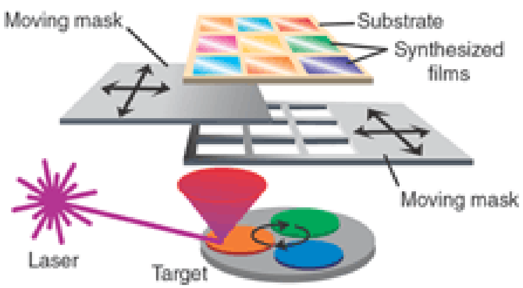
The old fashion approach for materials synthesis- SINGLE SPUTTERING

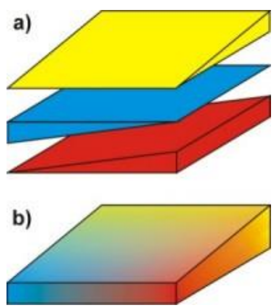
Sputtering

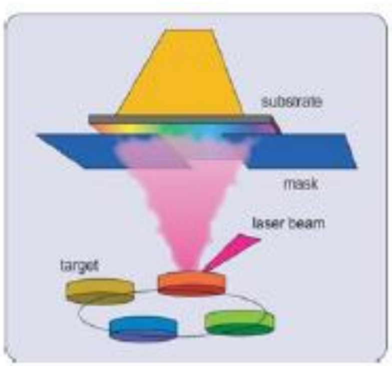
It takes one day per sample!!!

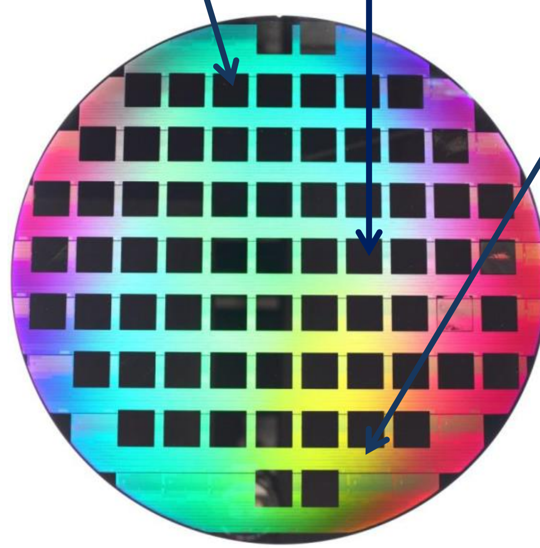
Sample 1 — Sample 2 . . . Sample X

The combinatorial approach for novel materials synthesis

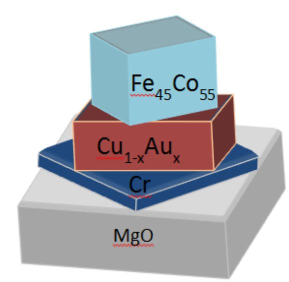






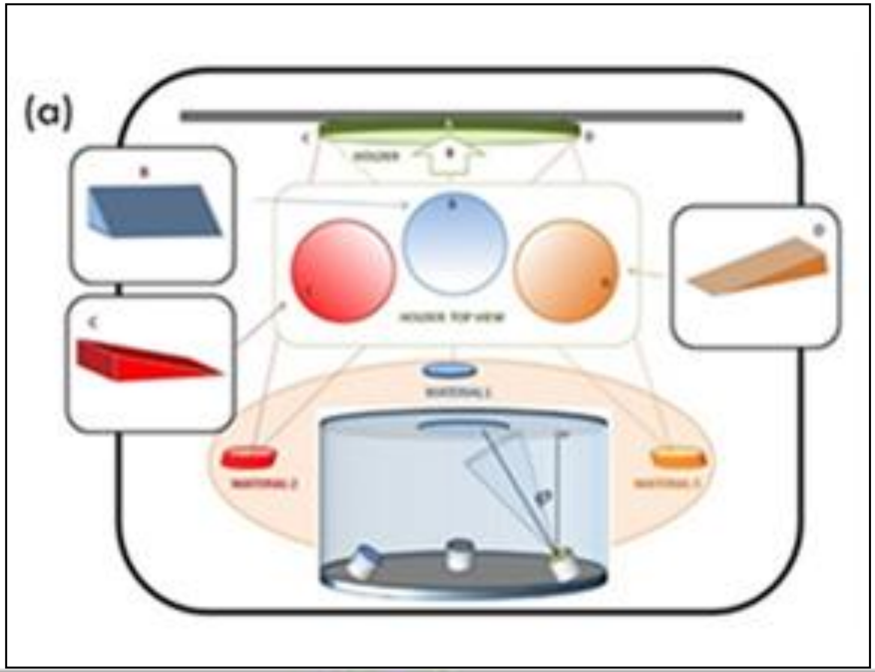


Epitaxial Growth of CoFe-X films

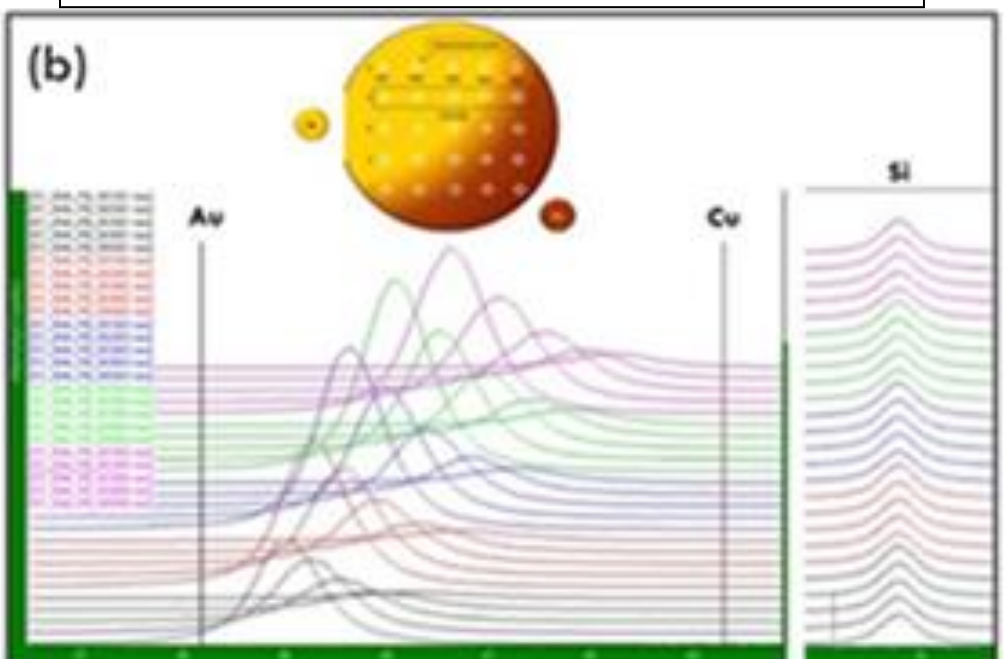


100 samples at once!!!!

EXAMPLE



COMBI-TRILAYER



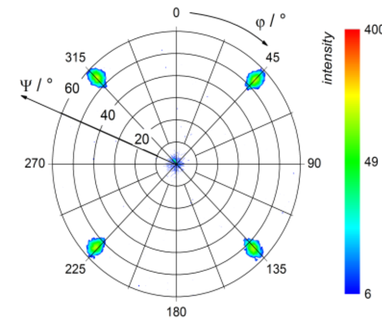
COMBI-XRD

Same with SEM, M-O Kerr, MAgScan, etc

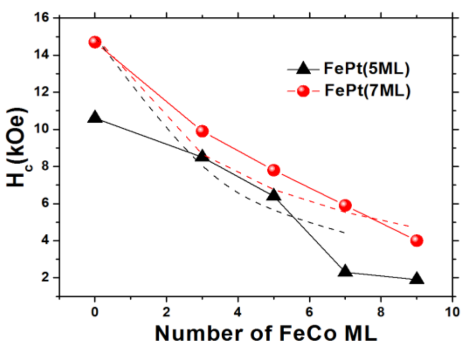
L1$_0$ FePt / FeCo bilayers

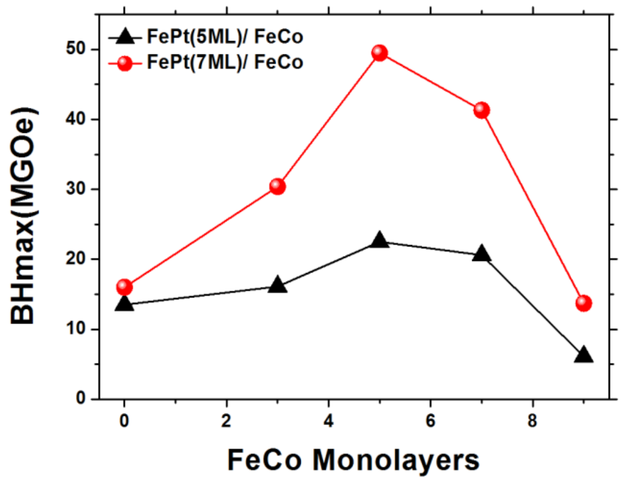
- Tailoring the coercivity through exchange coupling
- Ms value estimation

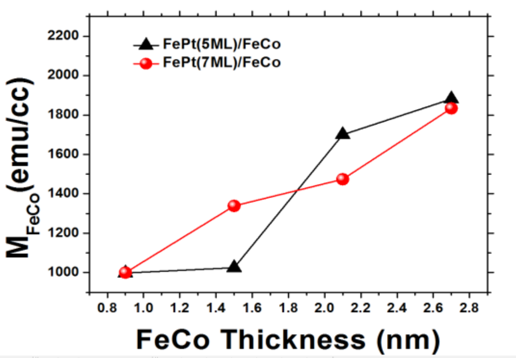
FeCo (0-9-ML)
L1$_0$ FePt (5 or 7-ML)
MgO Substrate



Perfect epitaxial growth







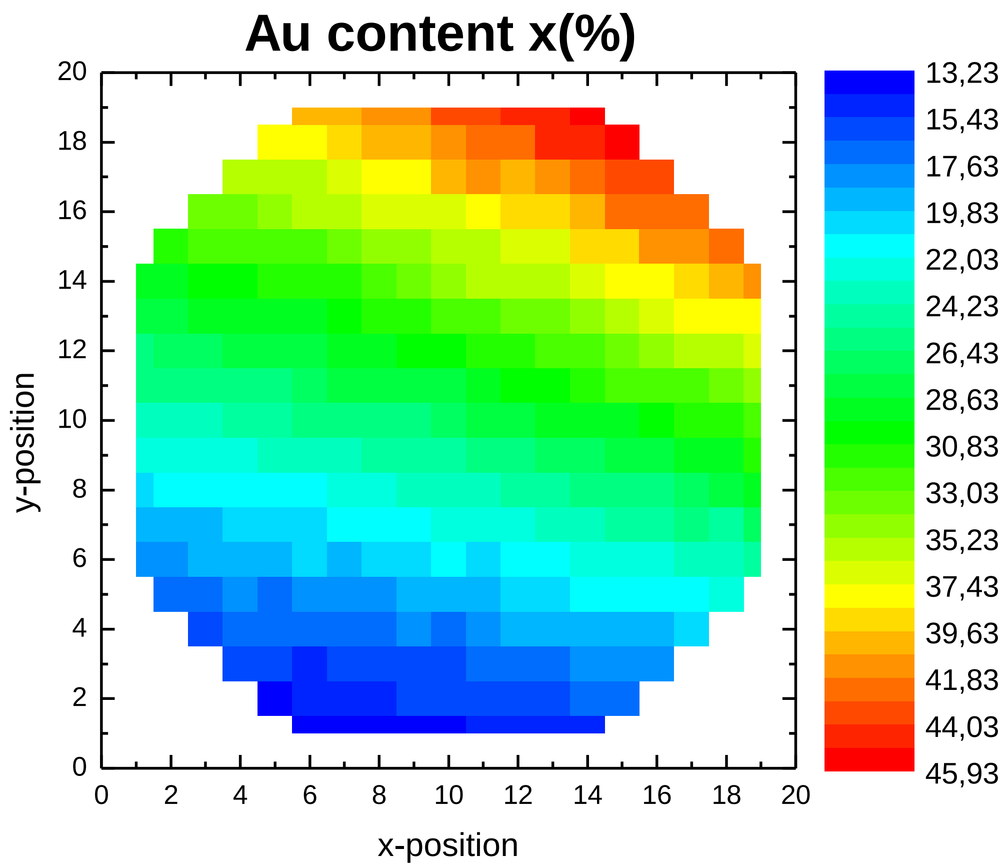
Maximum energy product
5ML FePt/5ML FeCo
~ **170-230 KJ/m^3**

& 7ML FePt/5 ML FeCo
~ **400 KJ/m^3**

FePt-20KJ/m^3

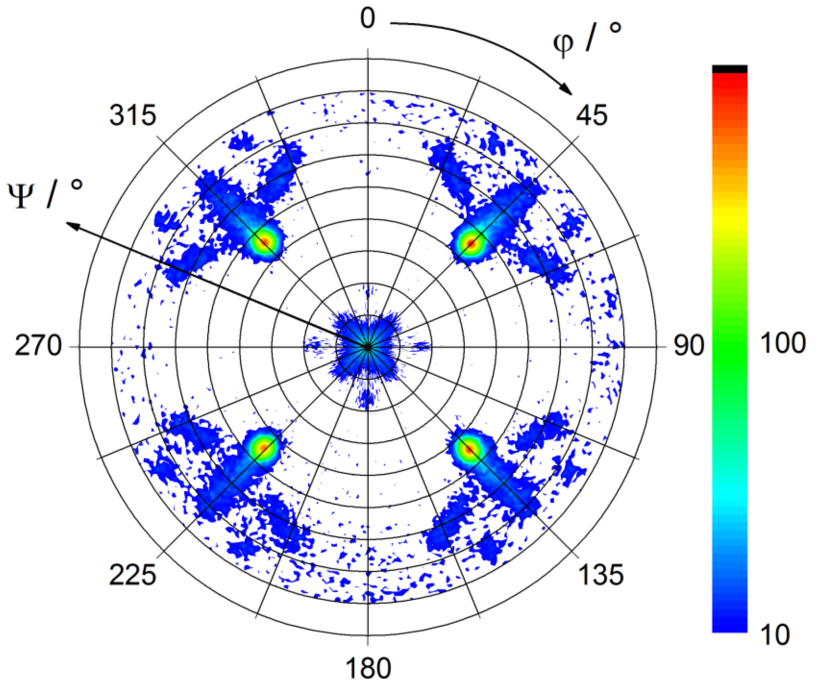
Compositional spread of Au content x(%) in Au_xCu_{1-x} buffer layer library.

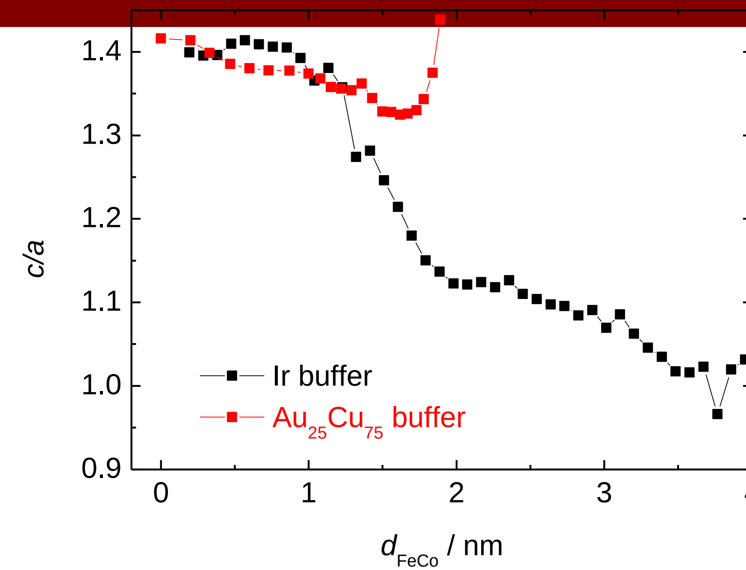
The main idea is that the in-plane lattice parameters of FeCo on AuCu will adopt those of AuCu and the out-of-plane lattice parameter c is expected to adapt accordingly, since the unit cell volume should remain constant.

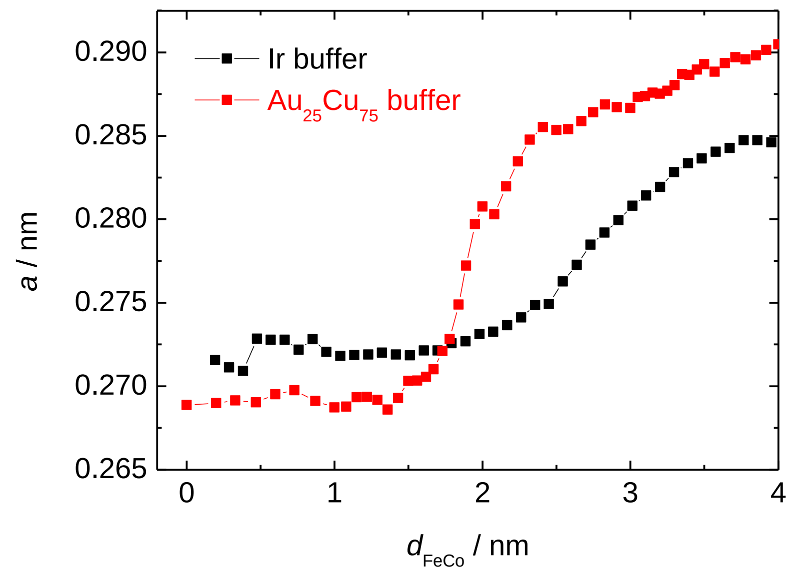


FeCo grown on Au-Cu buffer

FeCo(011) pole figure



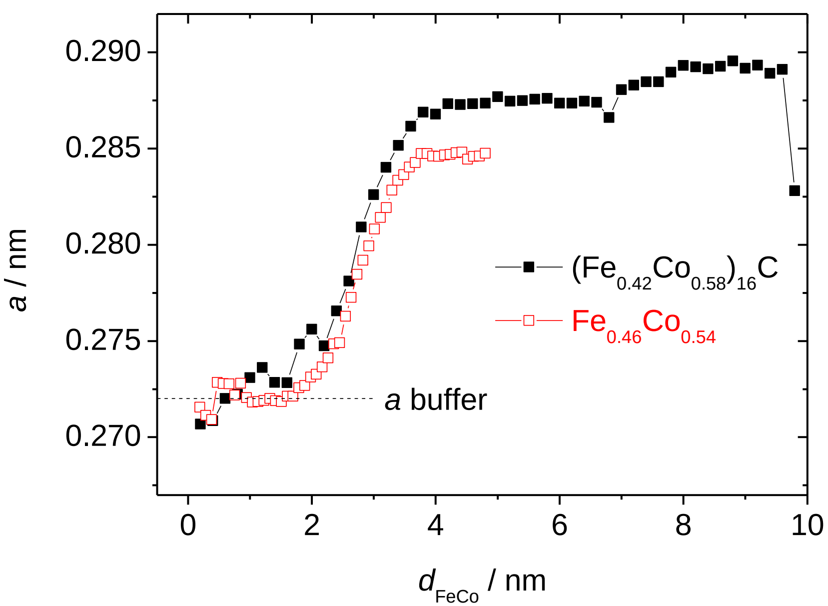


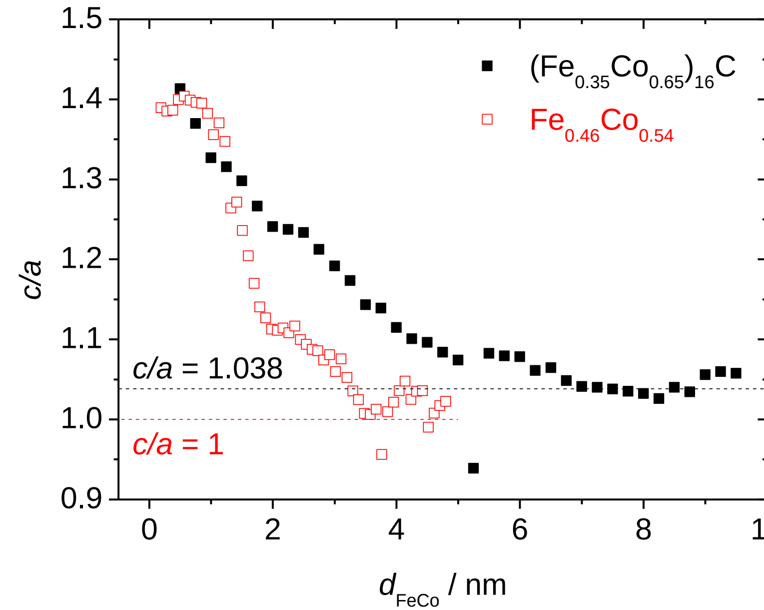


- Relaxation of FeCo promotes twinning and misorientation
- Critical thickness d_C is reduced on Au-Cu

RHEED verifies tetragonal distortion in Fe-Co-C

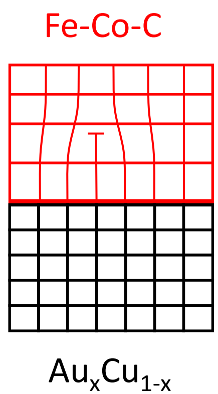
Calculated lattice parameters from in situ electron diffraction



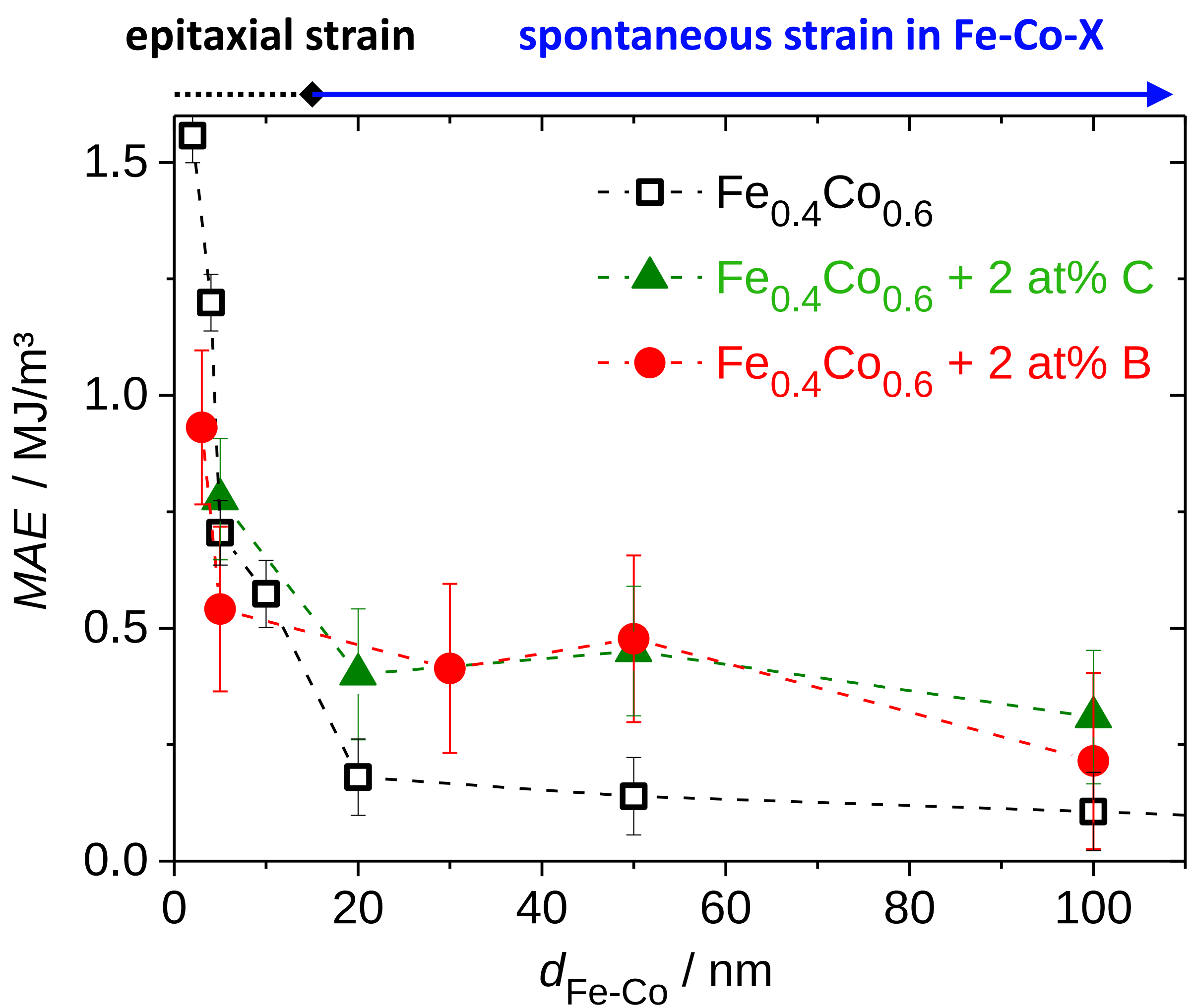


Relaxation in-plane starts already at d_{FeCoC} ~ 2 nm (as in Fe-Co)
⟶ no coherent growth of Fe-Co-C on buffer

Relaxation out-of-plane is retarded and stops at *c/a* > 1
⟶ Local strain energy minimum for tetragonal phase?



High MAE in binary Fe-Co only in ultrathin films
Alloying with C or B enhances MAE at higher film thicknesses



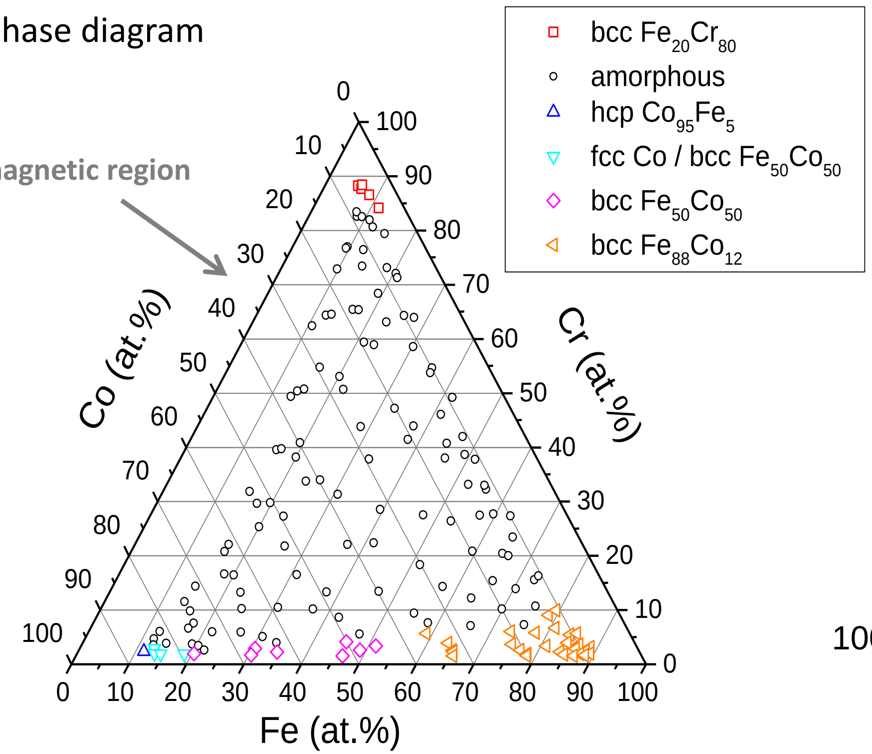
Challenge:
Experimental
C/B content
is limited
(no further tetragonal
distortion and/or
amorphisation)

Magnetic properties of Fe-Co-Cr
H_C is doubled when compared with the commercial Fe-Co-Cr-based magn

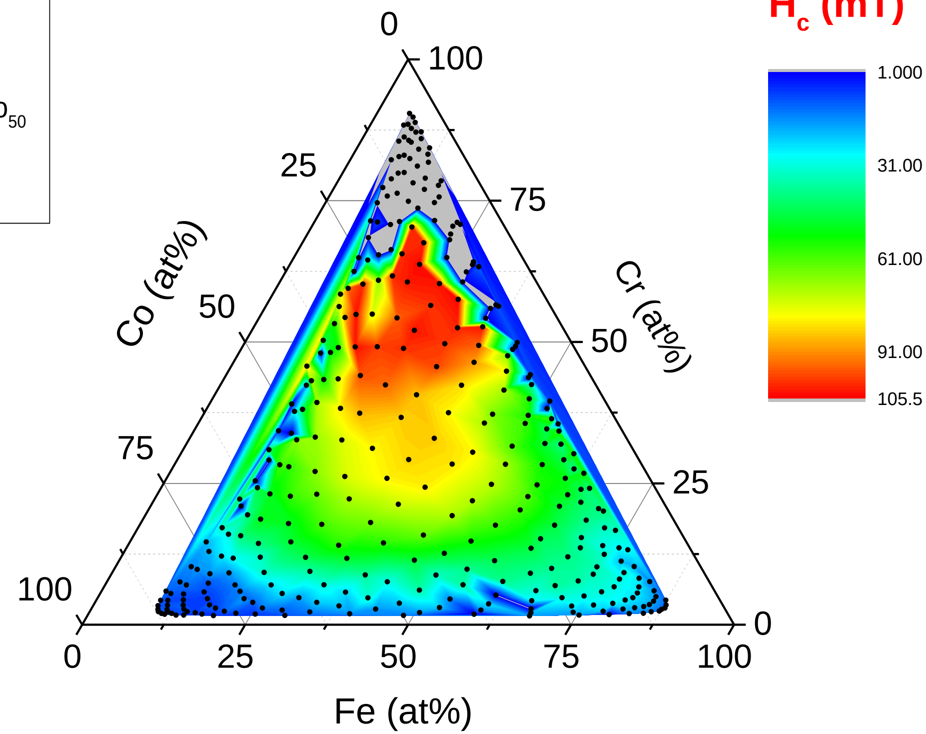
Co-deposition at RT, annealing at 550 °C

Phase diagram

Non magnetic region



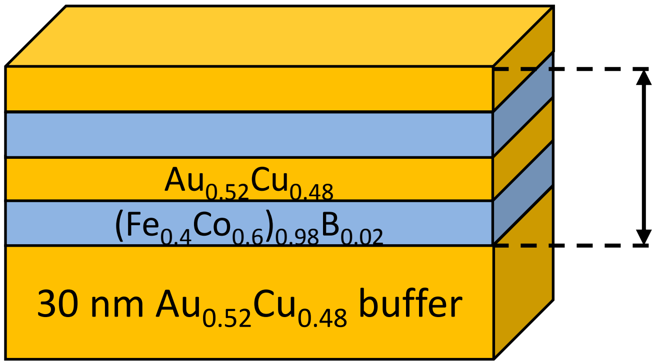
color-coded coercivity (H_c) diagram



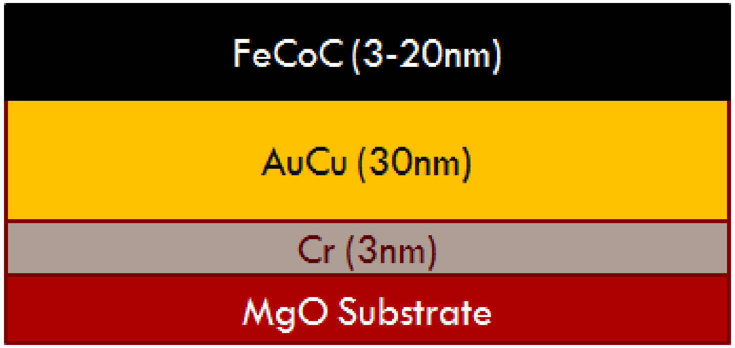
- Hc maximum (90mT) for Cr > 50%
- Magnetization (Mr) is 2 times lower than that of the commercial products; Mr/Ms ~ 0.5
- Energy product (HcMr) remains unaffected

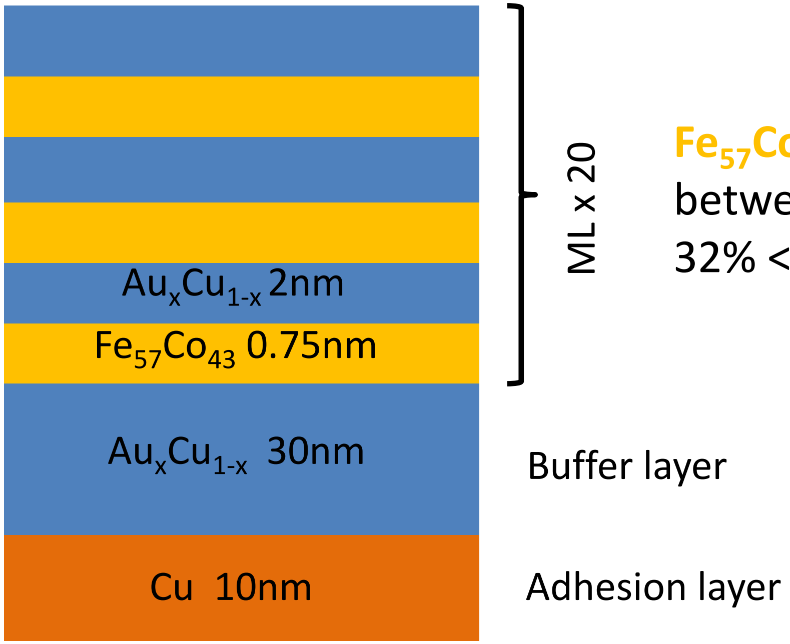
For **Fe-Co-Cr-Ni**:
the trend is the same!

Multilayers of type Fe-Co/ and Fe-Co-X/interlayer



$$100\text{ nm} = n \cdot (d_{Au\text{-}Cu} + d_{Fe\text{-}Co\text{-}B})$$

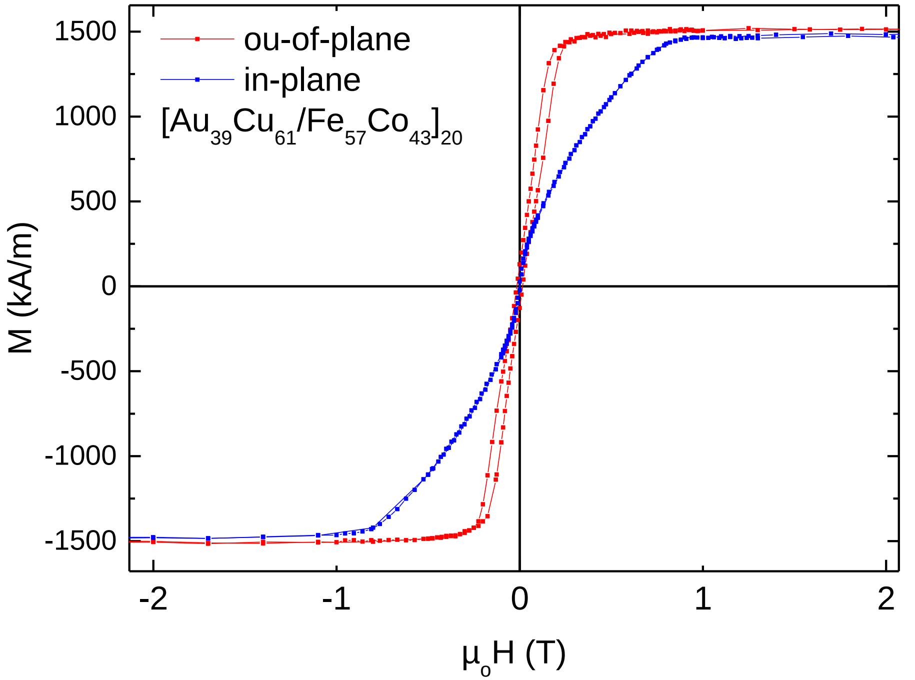


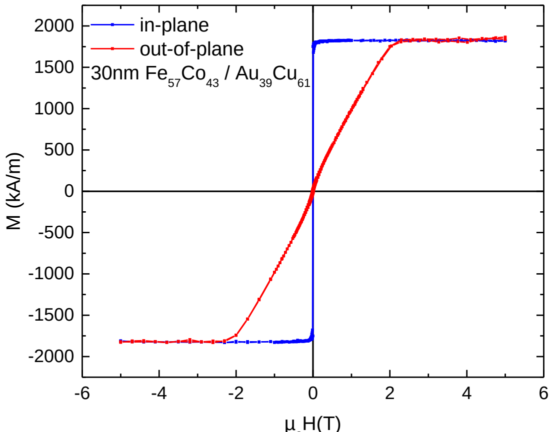


$Fe_{57}Co_{43}$ layer is clamped between two Au_xCu_{1-x} layers; 32% < Au < 67%

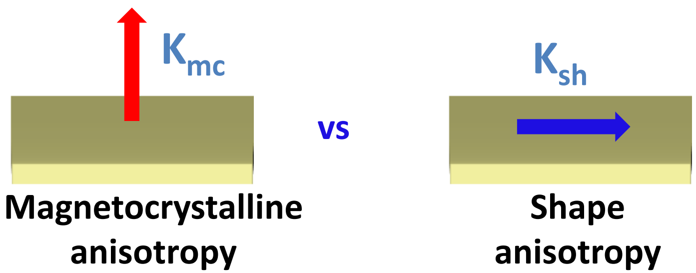
30nm single FeCo layer

[0.75nm $Fe_{57}Co_{43}$ / 2nm $Au_{35}Cu_{65}]_{20}$: easy axis is out-of-plane



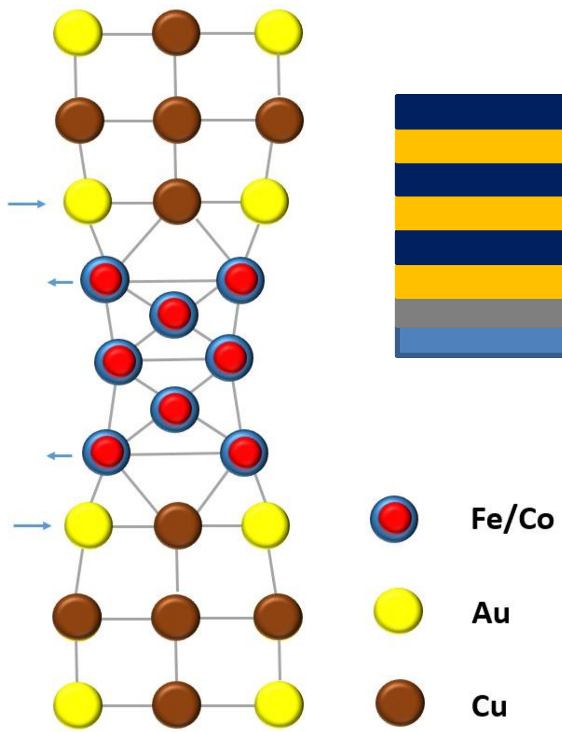


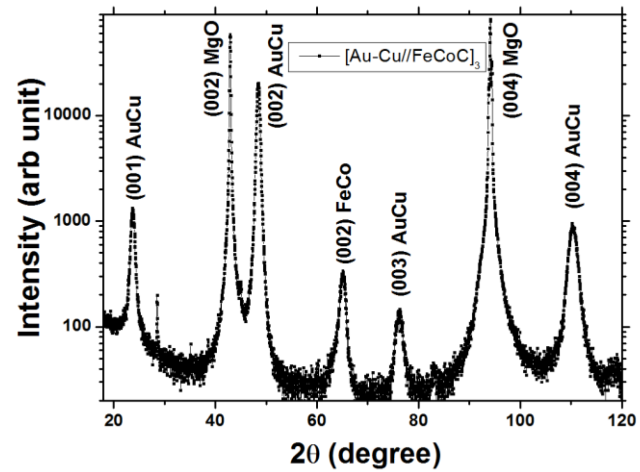
30nm single FeCo layer

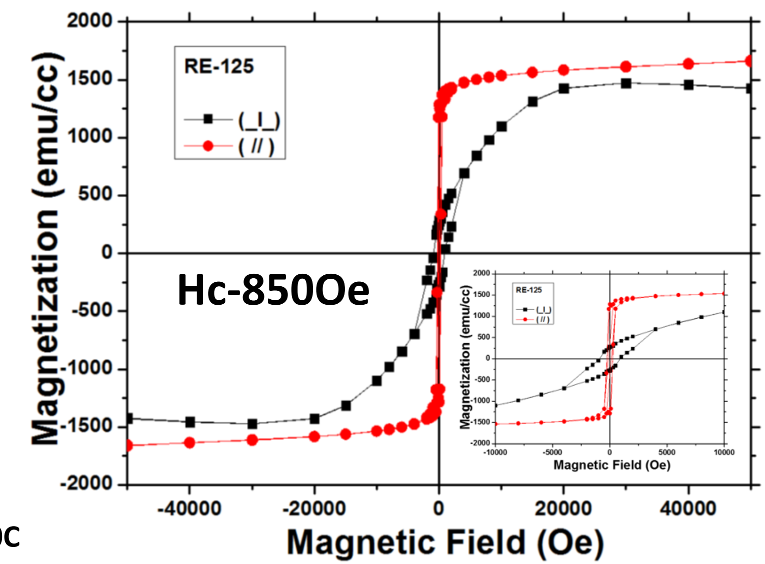


Transition of easy axis of magnetization

FeCoC-AuCu Multilayers







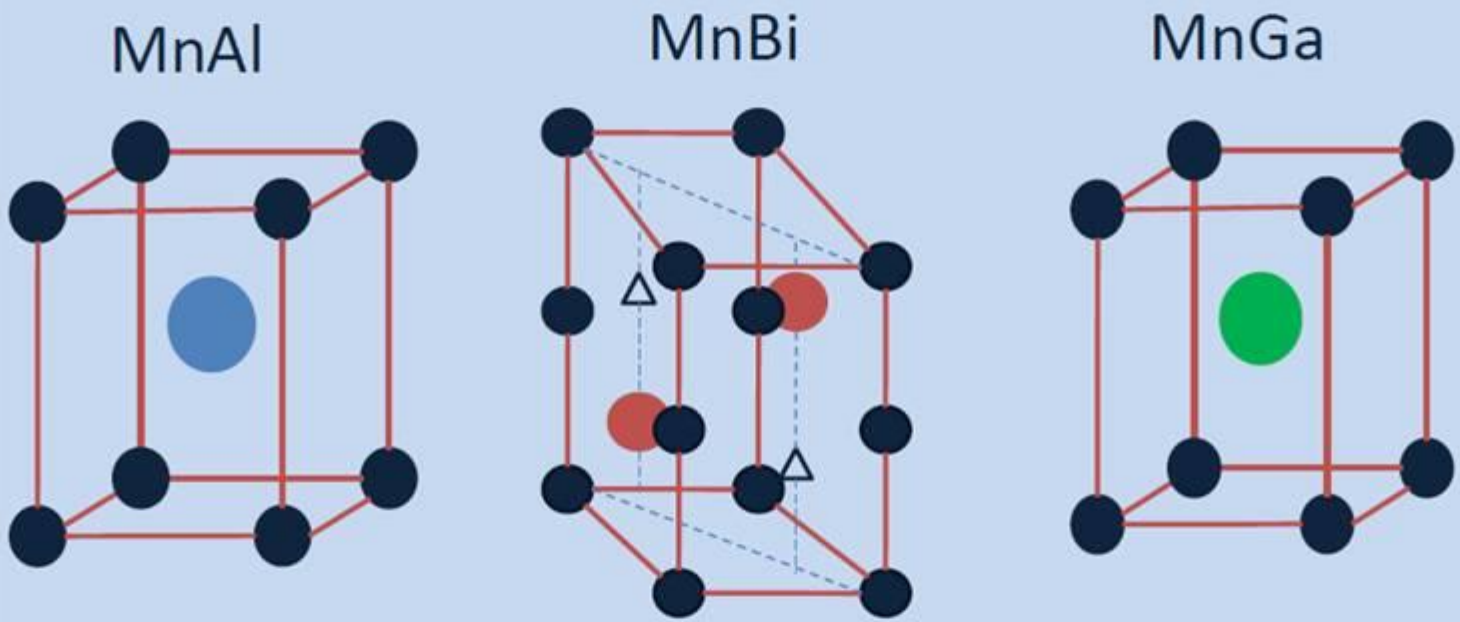
- Strain FeCoC both sides

- possibility for up scaling

Cr- (3nm) // $Au_{30}Cu_{70}$ - (10nm) // [$Fe_{45}Co_{55}$ (3nm) / $Au_{30}Cu_{70}$ (1nm)]$_{12}$ @300C

Synthesis and Study of Heusler alloys using conventional methods

Mn-Bi: a promising rare earth free material for permanent magnet applications



P4/mmm
(a= 2.77A, c=3.54A
c/a=1.23)
(CuAu, $L1_0$, $\tau-phase$)

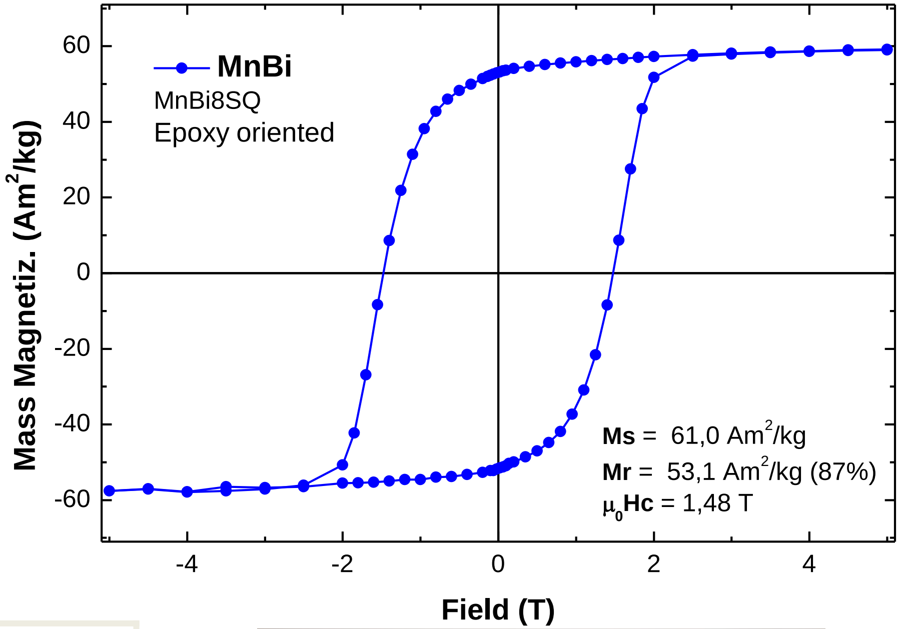
HTP & LTP : *$P6_3/mmc$*
(a=4.29A, c=6.12A   c/a=1.42)
QHTP: *$P222_1$* (distorted *$P6_3/mmc$*)
(a=4.34A, c=5.97A c/a=1.37

P4/mmm
(a=2.79A, c=3.08A
c/a=1.1)
(CuAu, $L1_0$, $\delta-phase$)

Synthesis and Study of Heusler alloys using conventional methods
Mn-Bi: a promising rare earth free material for permanent magnet applications

MnBi epoxy oriented:

Best results were found in samples with grain size of a few micrometers.



Property	Present Work	Ref 1	Ref 2
Ms (Am^2/kg)	61,0	60,0	74,0
Mr (%)	87%	91%	86%
μ_0Hc (T)	1,48	1,17	1,31

1. N.V. Rama Rao et al. J. Phys. D: Appl. Phys. **46** (2013)
2. J. Cui et al. J. Phys. Condens. Matter **26** (2014)

REFREEPERMAG

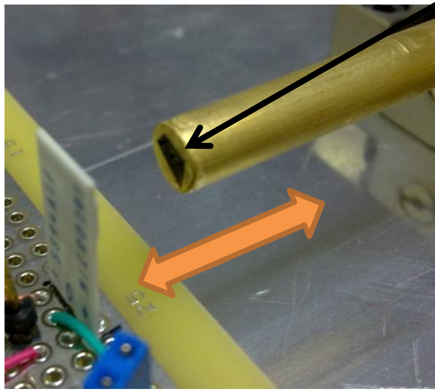
Towards applications

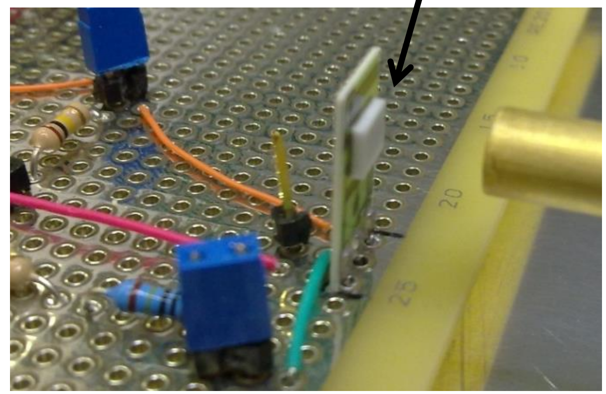
Sensors

Position

FeCo NWs Sample

Hall Effect Sensor

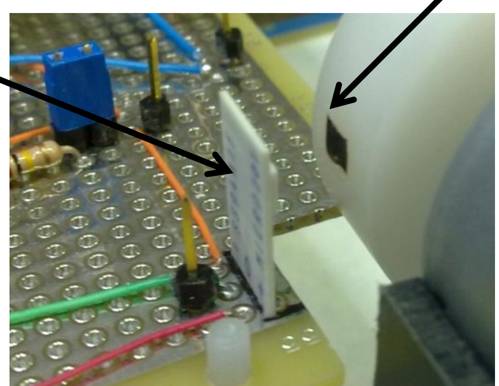


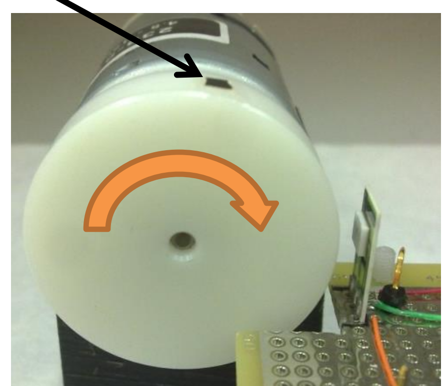


Tachometer

Hall Effect Sensor

FeCo NWs Sample





The VISION PLANS

GIVEN THAT

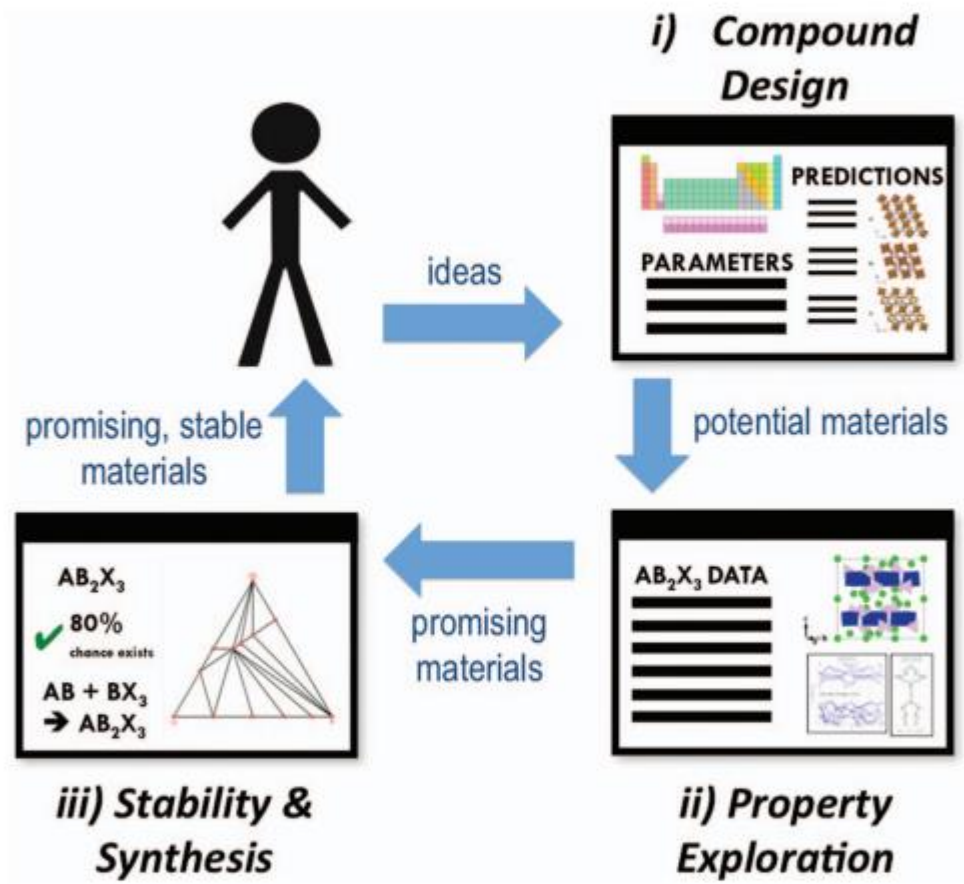
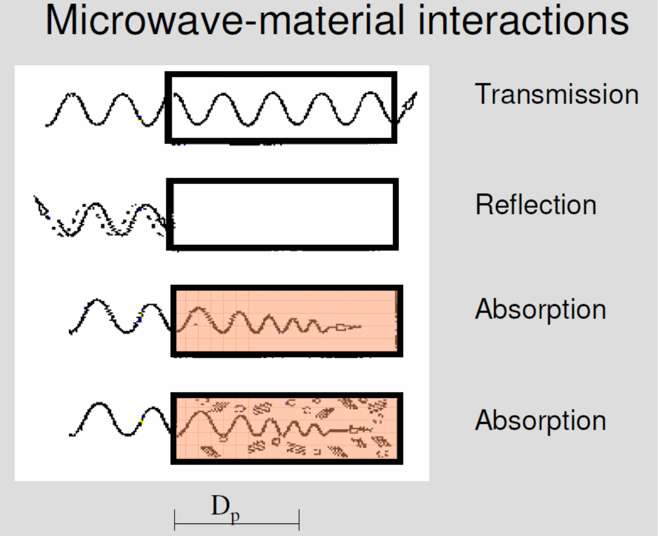


FIG. 7. Rapid prototyping and iterative materials design steps that might be performed *in silico*.

The VISION PLAN #3 Use microwave-synthesis Sintering



✓Complex dielectric permitivitty $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$

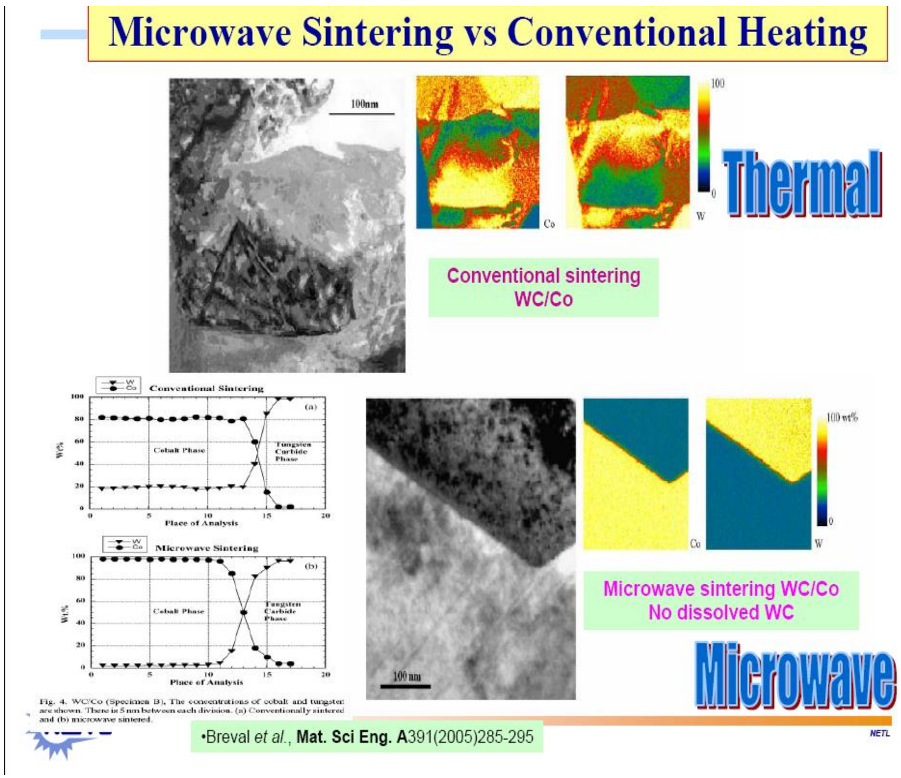
✓Complex magnetic permeability $\mu(\omega) = \mu'(\omega) + \iota \mu''(\omega)$

Proposal

Explore and commerialize "microwave synthesis and sintering" in magnetic materials . Our first results are very promising

Future Work-Suggestions- VISION PLAN #3

Based on the fact that "sharp" edges



Towards re-engineering of the grain Boundaries **– Less Dy NdFeB**

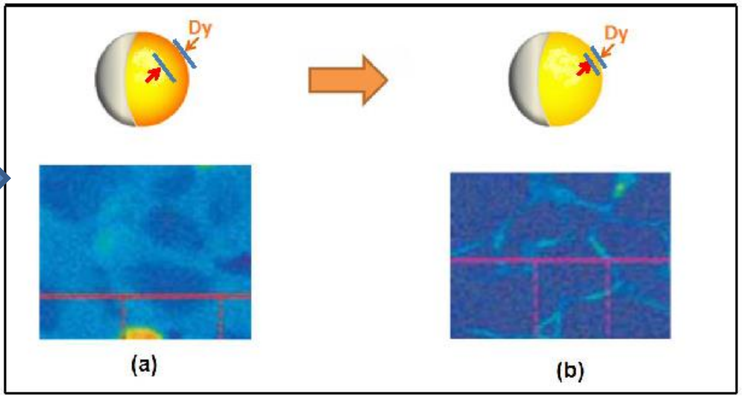


Fig. 4 Dy distribution using back-scattered electrons for (a) conventional and (b) improved (MS) –expected thinner grain boundary approach (less Dy or replace with a non RE-alloy)

In minutes rather hours!!!

MQ-2010

REFREEPERMAG- FP7-EU Project

Our Vision

- The REFREEPERMAG is expected to result in a **sustainable, long-lasting substitution of supply-critical materials** needed for innovations in the high-technology sectors of European industries.

- Substituting the increasing amounts of rare earths required in permanent magnets by other materials will release the pressure on the rare earths segment of commodity markets and **freeing RE resources for devices in display and microsensor technologies** where rare earths elements cannot be substituted.

- This will **drive down the cost of RE raw materials**, and on the long run will prevent legal or political disputes on trade restrictions, customs and import tax issues.

We do hope that this proposal will strengthen the effort towards the

“Materials Genome Global Effort”