Magnetic cluster deposition: from individual nano-objects to complex systems

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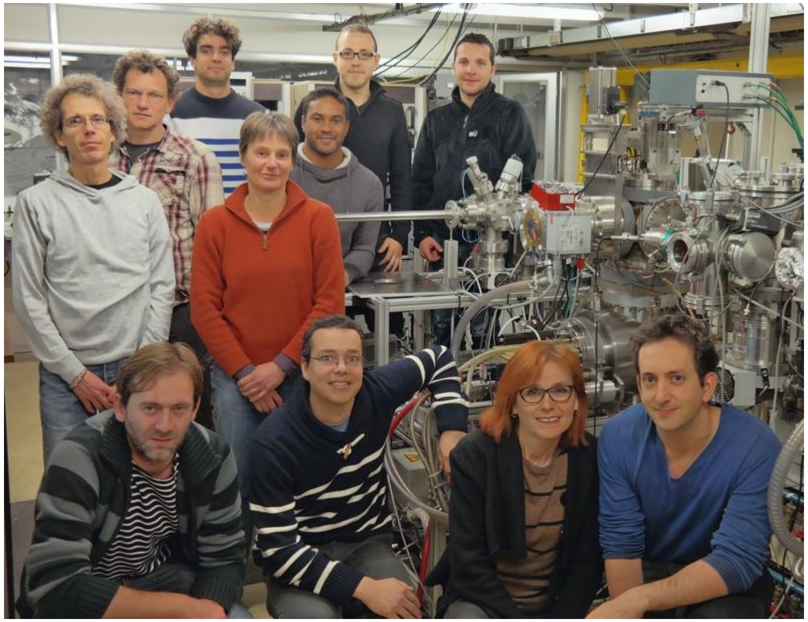
"Magnetic nanostructures" group



Small team (5 permanent researchers), leaded by Véronique Dupuis

- ✓ Cluster deposition
- ✓ Magnetic nanoparticles
- ✓ SQUID magnetometry and modelling
- ✓ Microscopy (STM, TEM) and many other techniques (x-rays…)

Model systems

⇒ Characterization of the intrinsic properties of nanomagnets

Nanomagnets as building blocks (bottom up approach)

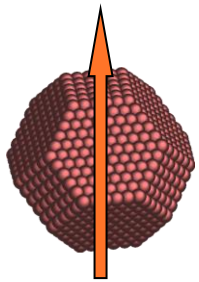
⇒ More complex systems (clusters on surfaces, nano-composites)

Outline

- Motivation and experimental approach of cluster deposition
- Specific behavior of bimetallic nanoparticles
- Analysis of magnetic measurements: intrinsic properties with diluted nanomagnet assemblies and beyond…
- Interface effects with nanomagnets on cristaline surfaces: FePt/graphene/Ir(111) and FeRh/$BaTiO_3$
- Nano-composites: Co clusters in a FePt matrix

Motivation

Our interest: small nanoparticles, between 1 nm and 10 nm diameter



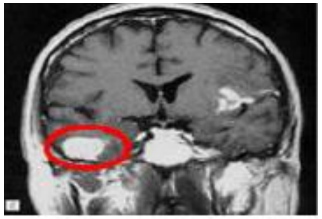
Monodomain particle (macrospin)

- ✓ Size reduction effects (importance of surface/interface)
- ✓ Miniaturization and new properties (multi-functional, exotic objects…)

General question: link between structure (at the atomic and nanometer scale) and magnetism?

⇨ How can the magnetic properties of nanostructures be controlled and tailored?

Fundamental research …and interesting for **potential applications**…

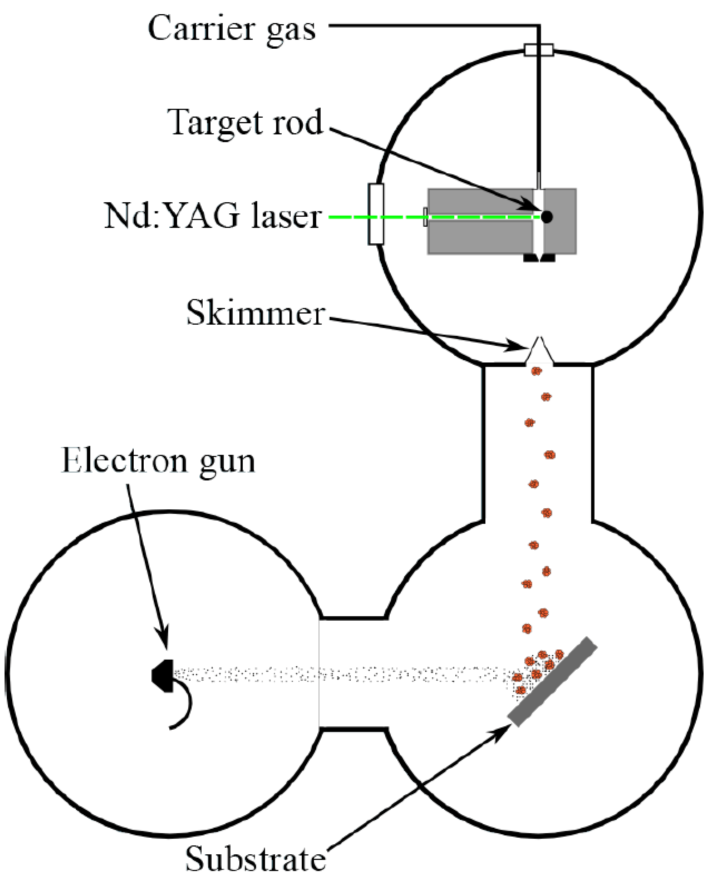


- Biological/medical applications
- Catalysis (transition metals and alloys)
- Magnetic storage applications
- Spintronic devices?

Synthesis challenge ⇨ Well-defined nanoparticle samples

Nanoparticle synthesis

Deposition of preformed clusters (physical route)



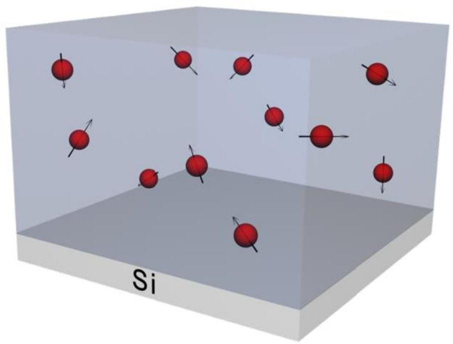
A. Perez *et al.*, Int. J. Nanotechnol. **7**, 523 (2010)

Low energy cluster beam deposition, based on a laser vaporization source

- ✓ Deposition under ultra-high vacuum
- ✓ Pure elements or alloys
  - ➡ Adjustable composition (target)
- ✓ Capping or co-deposition in a matrix
  - ➡ • Protect the particles
    • Avoid coalescence
- ✓ Random deposition
  - ➡ Interparticle distances distribution directly fixed by the dilution

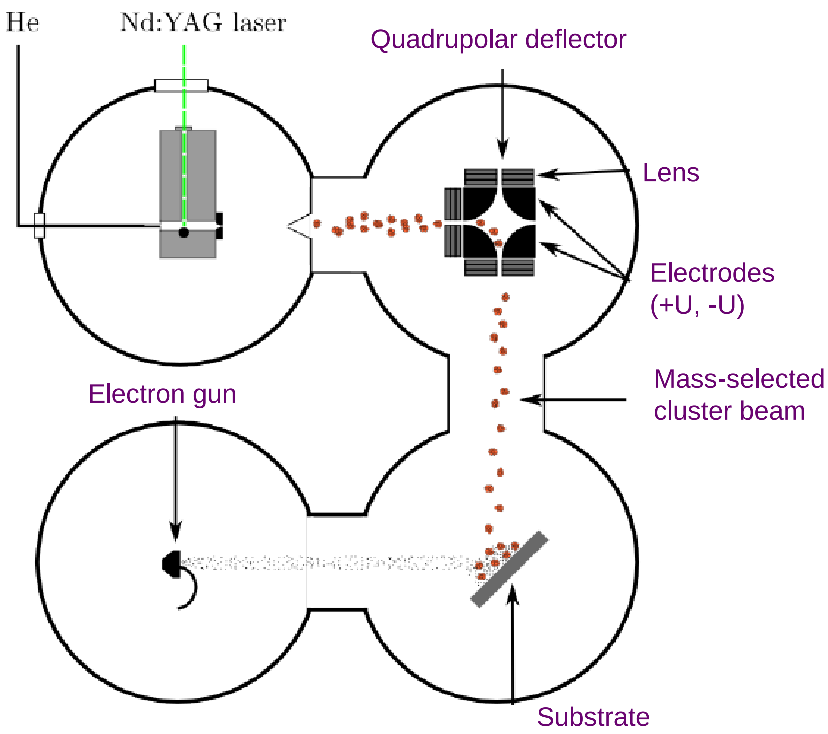
Typical nanoparticle diameter ~ 3 nm

Nanoparticle synthesis



- ✓ Deposition on any substrate
- ✓ 2D, multilayers or 3D samples
  (thin films of particles in a matrix)

This approach allows ex-situ characterization by many techniques (EXAFS, XRD, XMCD, TEM, SQUID…)



- ✓ Possibility of size selection
  (quadrupolar electrostatic deflector)

All the particles have the same velocity

➡ Selection of kinetic energy = mass selection

Nanoparticle synthesis

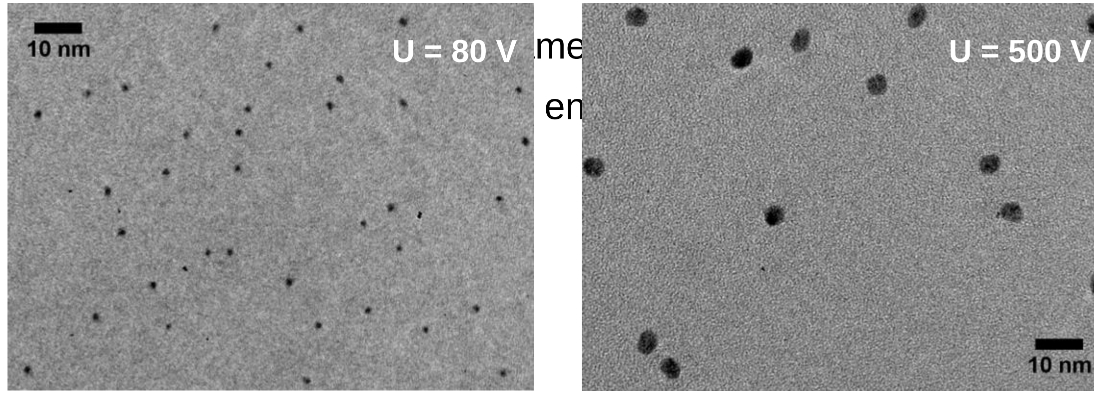
- Adjustable particle size, independently from the surface density.

⇩

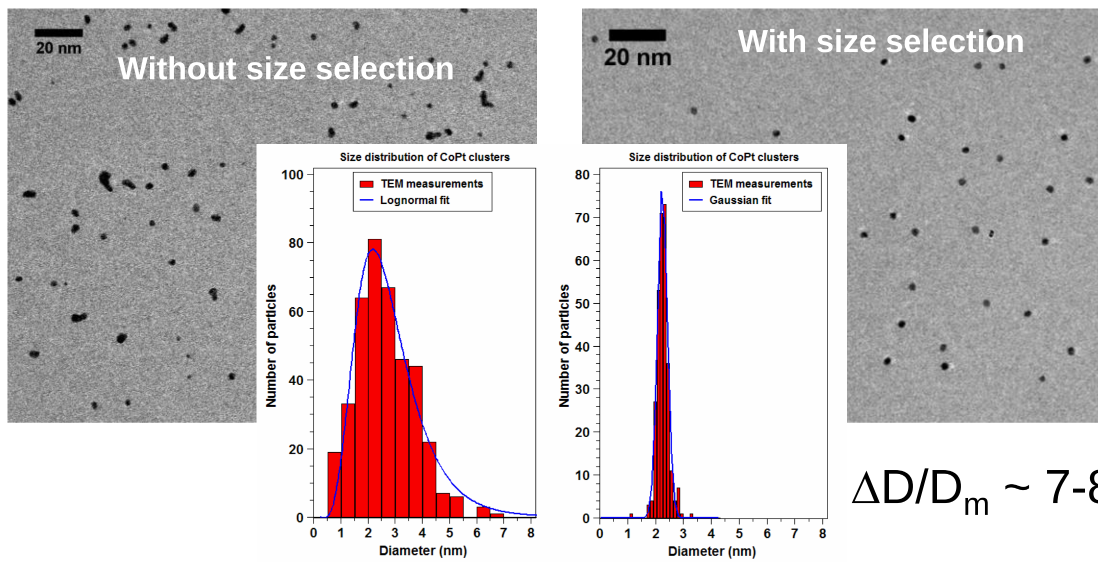
Diluted assemblies (avoid interactions)

✓ Typical concentration for 3D samples ~1% in volume

- Relative diameter dispersion lower than 10 % with size selection.

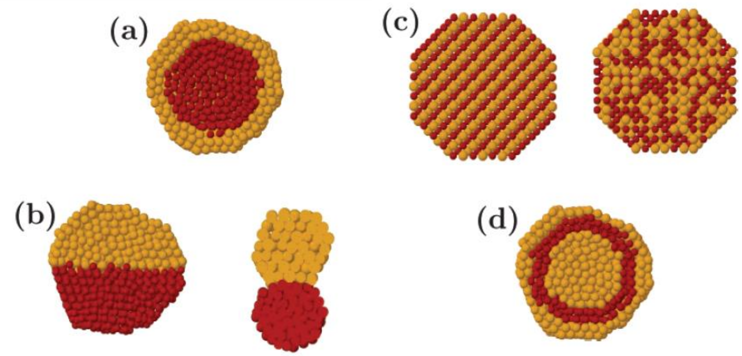


CoPt nanoparticles



$\Delta D/D_m \sim 7\text{-}8\ \%$

Bimetallic nanoparticles



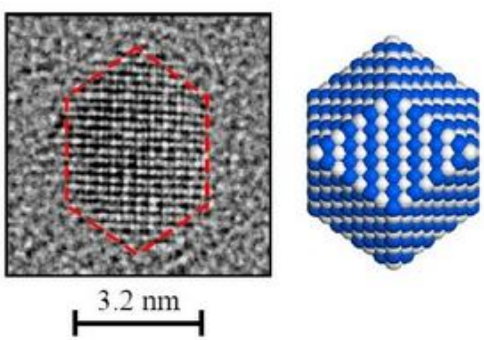
- Two types of atoms: additional degree of freedom
- Nanoalloys, bimetallic particles: different types of structures

New properties, combination of properties, at the nanoscale

Many bi-metallic systems can be produced by LECBD

V. Dupuis *et al*., Phys. Chem. Chem. Phys. **17**, 27996 (2015).

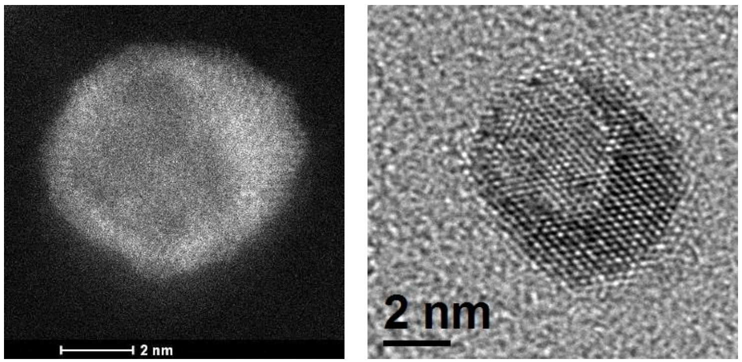
Ex. FeRh



A. Hillion *et al*., Phys. Rev. Lett. **110**, 087207 (2013)

Ferromagnetic order stable at low T (instead of anti-ferromagnetic)

Ex. CoAu

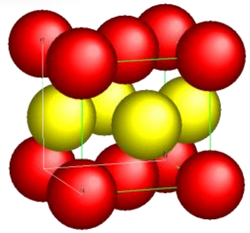


Original structures, magneto-plasmonic interest

Bimetallic nanoparticles

The case of CoPt and FePt nanoparticles

$L1_0$ phase



- Chemically ordered
- tetragonal cell (c/a < 1)

The $L1_0$ phase is stable at room temperature, but A1 is metastable

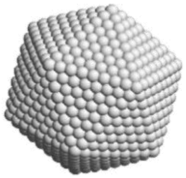
The $L1_0$ phase has a huge **magnetic anisotropy** constant (K_{eff}~ 5 MJ/m^3 for bulk CoPt)

→ Interesting for magnetic storage applications

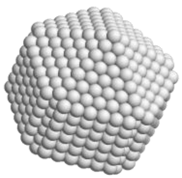
Open questions about the structure and magnetic properties of small nanoparticles:

Chemical order vs. size, finite size effects on the structure (defects, relaxation…), nanoalloy effects…

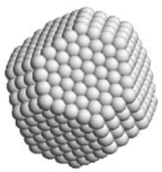
→ It is a challenge to determine the intrinsic magnetic properties of chemically ordered particles



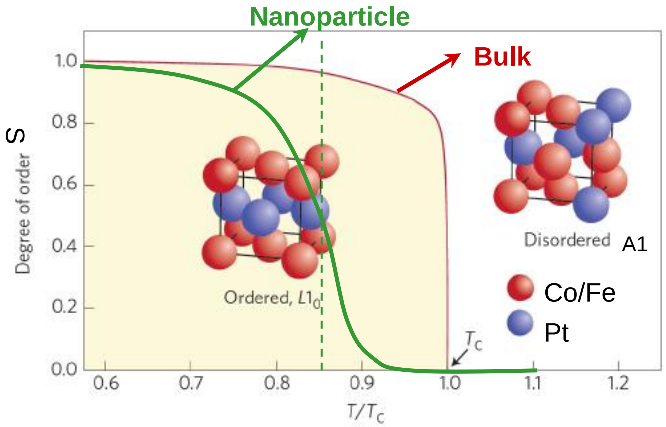
Icosahedron



Decahedron

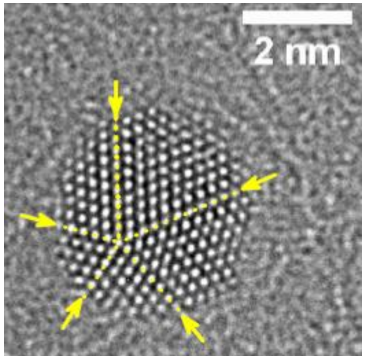


Truncated-octahedron



Bimetallic nanoparticles (CoPt / FePt)

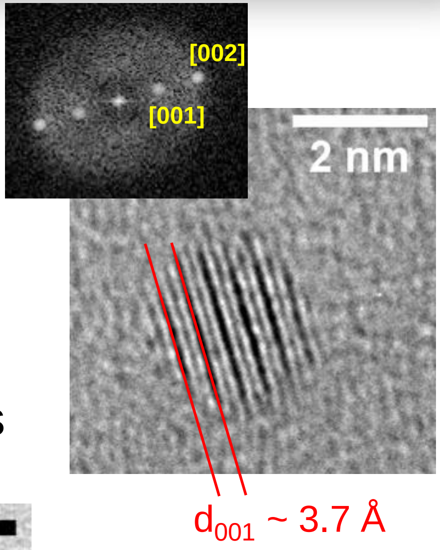
N. Blanc *et al.*, Phys. Rev. B **83**, 092403 (2011)
F. Tournus *et al.*, Phys. Rev. Lett. **110**, 055501 (2013)



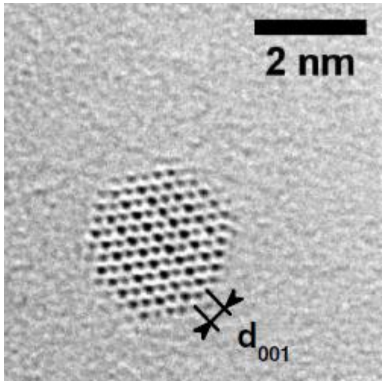
✓ Coexistence of fcc and multiply-twinned particles

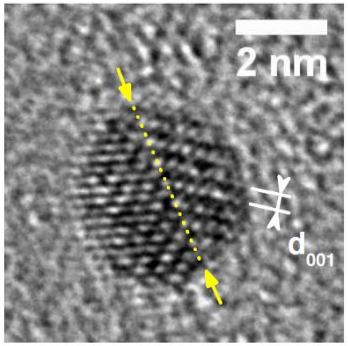
✓ No chemical order before annealing

✓ $L1_0$ contrast ([001] peak) after annealing, even for the smallest particles



✓ Single $L1_0$ domain or several domains (twins, variants)



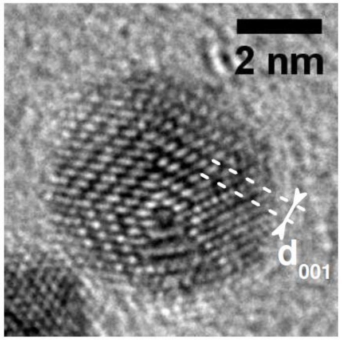


Decahedral particles with a chemical order

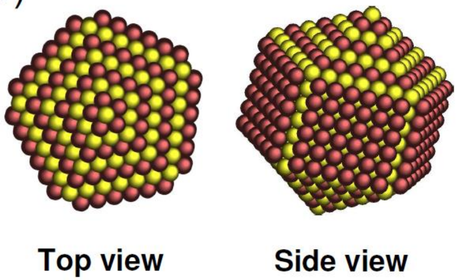
➡ Five $L1_0$ domains with c axes in different directions

Theoretically predicted structure!

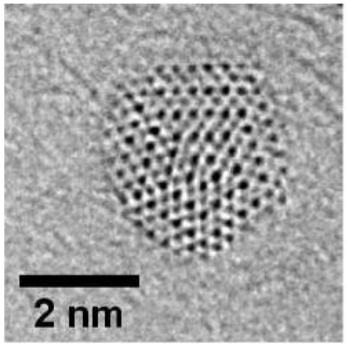
a)

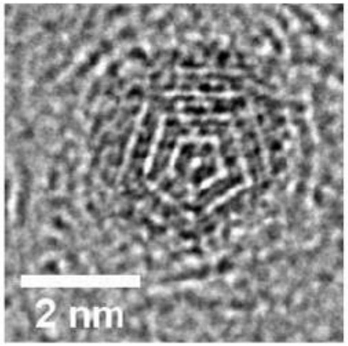


b)



FePt



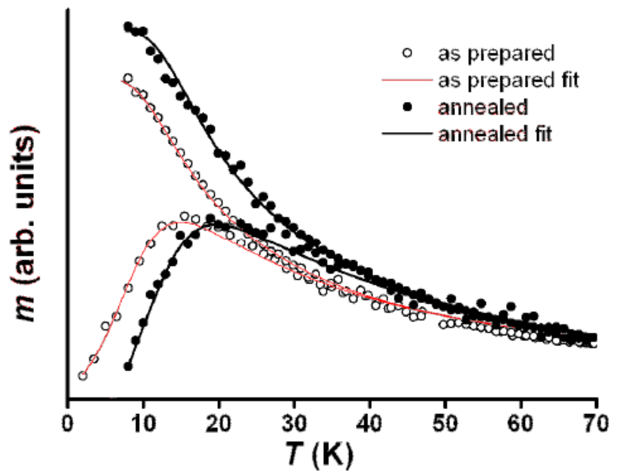


Bimetallic nanoparticles (CoPt / FePt)

Evolution of the magnetic properties (SQUID, XMCD measurements) upon chemical ordering but…

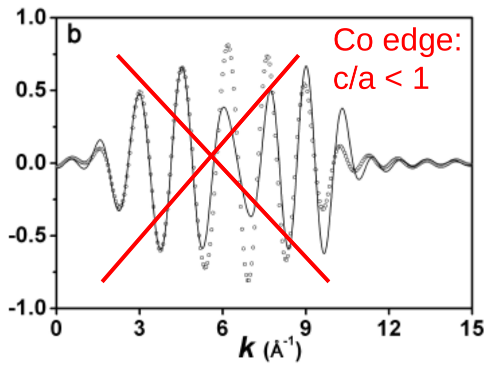
The magnetic anisotropy of CoPt nanoparticles remains much smaller than the bulk (of the order of 300 kJ/m^3 instead of 5 MJ/m^3)

F. Tournus *et al.*, Phys. Rev. B **77**, 144411 (2008)
F. Tournus *et al.*, Phys. Rev. B **81**, 220405(R) (2010)



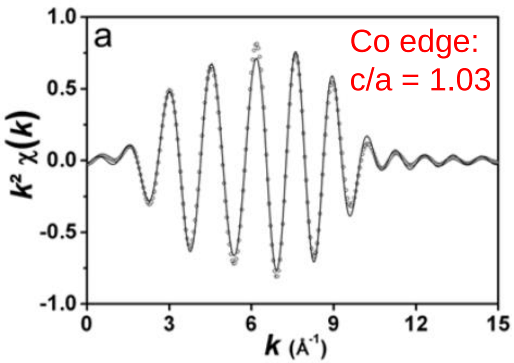
Possible explanations:

- ✓ Particles with several $L1_0$ domains
  ⇒ **Lowering of the anisotropy!**
- ✓ Coexistence of various structures
  ⇒ Anisotropy constant dispersion
- ✓ Relaxation of interatomic distances due to finite size: $d_{Pt\text{-}Pt} \neq d_{Co\text{-}Co}$



EXAFS measurements, DFT calculations
⇓
Tetragonalization different from the bulk

N. Blanc *et al.*, Phys. Rev. B **87**, 155412 (2013)
V. Dupuis *et al.*, Eur. Phys. J. B **86**, 1 (2013)



Analysis of magnetic measurements

Quantitative analysis of experimental curves

⟹ **Best fit procedure**

✓ Complementary measurements, analyzed with a combined fit (shared parameters)

- Low field susceptibility (ZFC/FC)
- Superparamagnetic magnetization loop
- Low temperature hysteresis loop
- Isothermal remanent magnetization (IRM)

✓ Efficient modelling for realistic assemblies of particles (**dispersion of size and anisotropy**, temperature…)

⟹ Ingredients: Stoner-Wohlfarth (macrospin), Néel relaxation

Negligible inter-particle interactions?

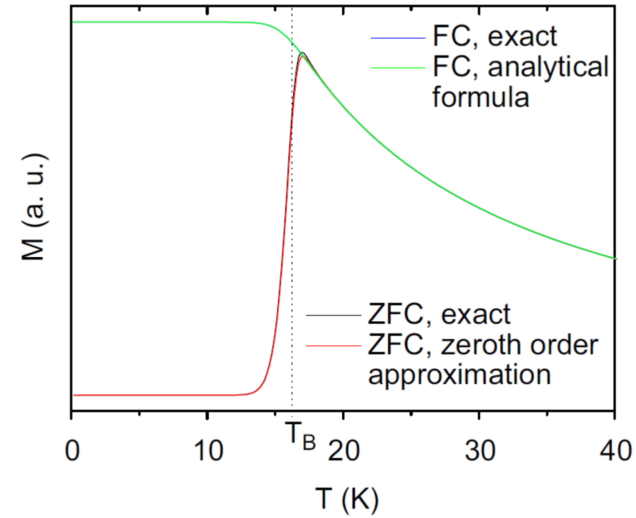
⟹ Intrinsic magnetic properties, signature of the individual nanomagnets

➢ Test of the theoretical models (macrospin, uniaxial anisotropy etc.)

➢ **Accurate determination of magnetic parameters (size and anisotropy…)**

Analysis of magnetic measurements

F. Tournus, E. Bonet, J. Magn. Magn. Mater. **323**, 1109 (2011).

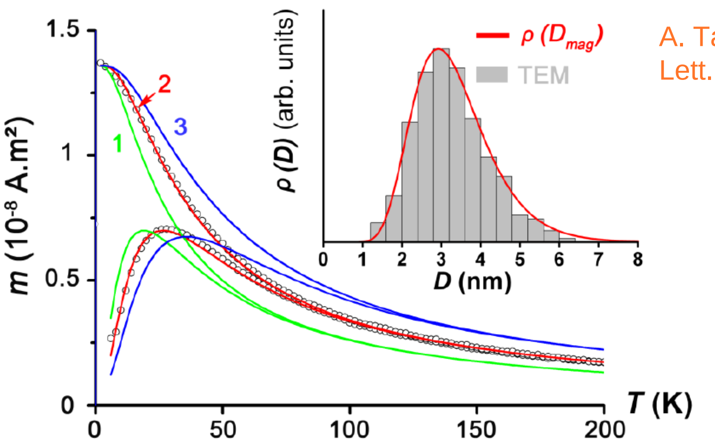


Efficient simulation of the entire ZFC/FC curves for an assembly with a particle size distribution

- ✓ "Progressive crossover model"
- ✓ Semi-analytical calculations

ZFC/FC curves sensitive to the magnetic size distribution

➡ A combined fit is more discriminating



A. Tamion et al., Appl. Phys. Lett. **95**, 062503 (2009)

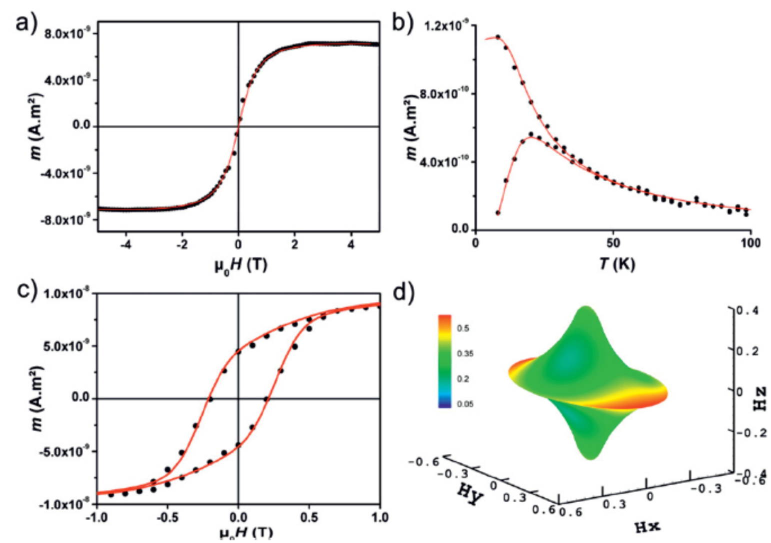
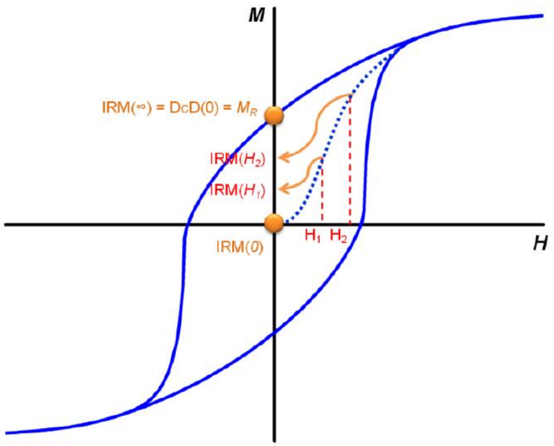


Fig. 4. (Color online) Hysteresis loops at 300 K (a), at 2 K (c) and ZFC/FC (b) for annealed CoPt nanoparticles embedded in C matrix. The solid lines correspond to the fit. Mean astroids associated to the biaxial fit (d).

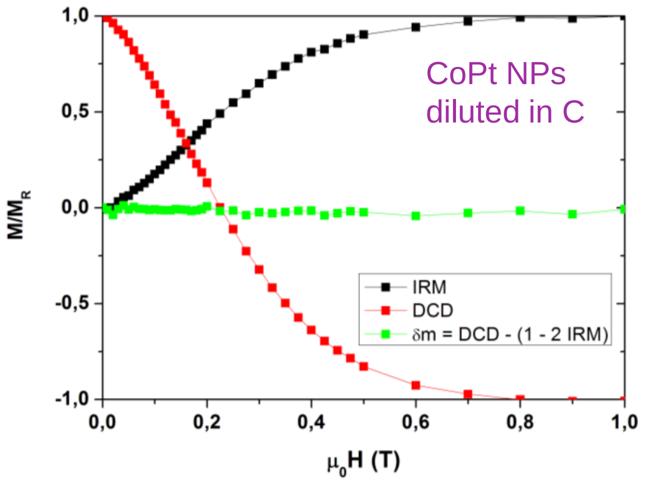
Beyond the uniaxial anisotropy approximation

➡ Bi-axial contribution
+ anisotropy constant dispersion

Analysis of magnetic measurements



Isothermal remanent magnetization → Signature of **irreversible** magnetization switching

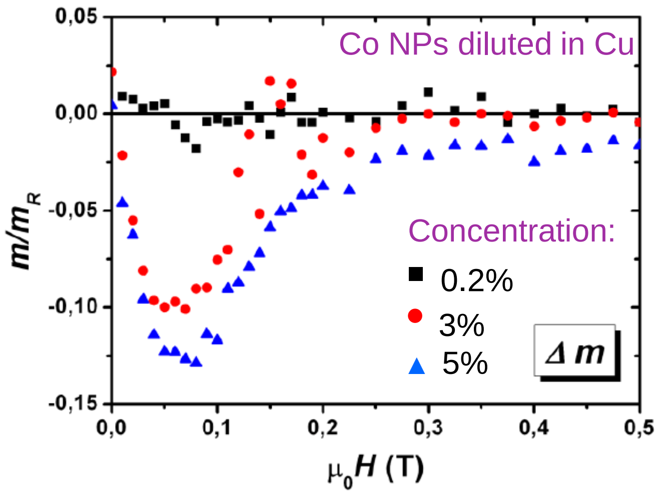


Δm parameter:

$\Delta m = DcD/m_R - (1 - 2\ IRM/m_R)$

If no interaction:

Δm = 0 verified



Δm is very sensitive to interactions!

✓ Modelling of IRM curves, without interactions

→ Fit of experimental measurements possible!

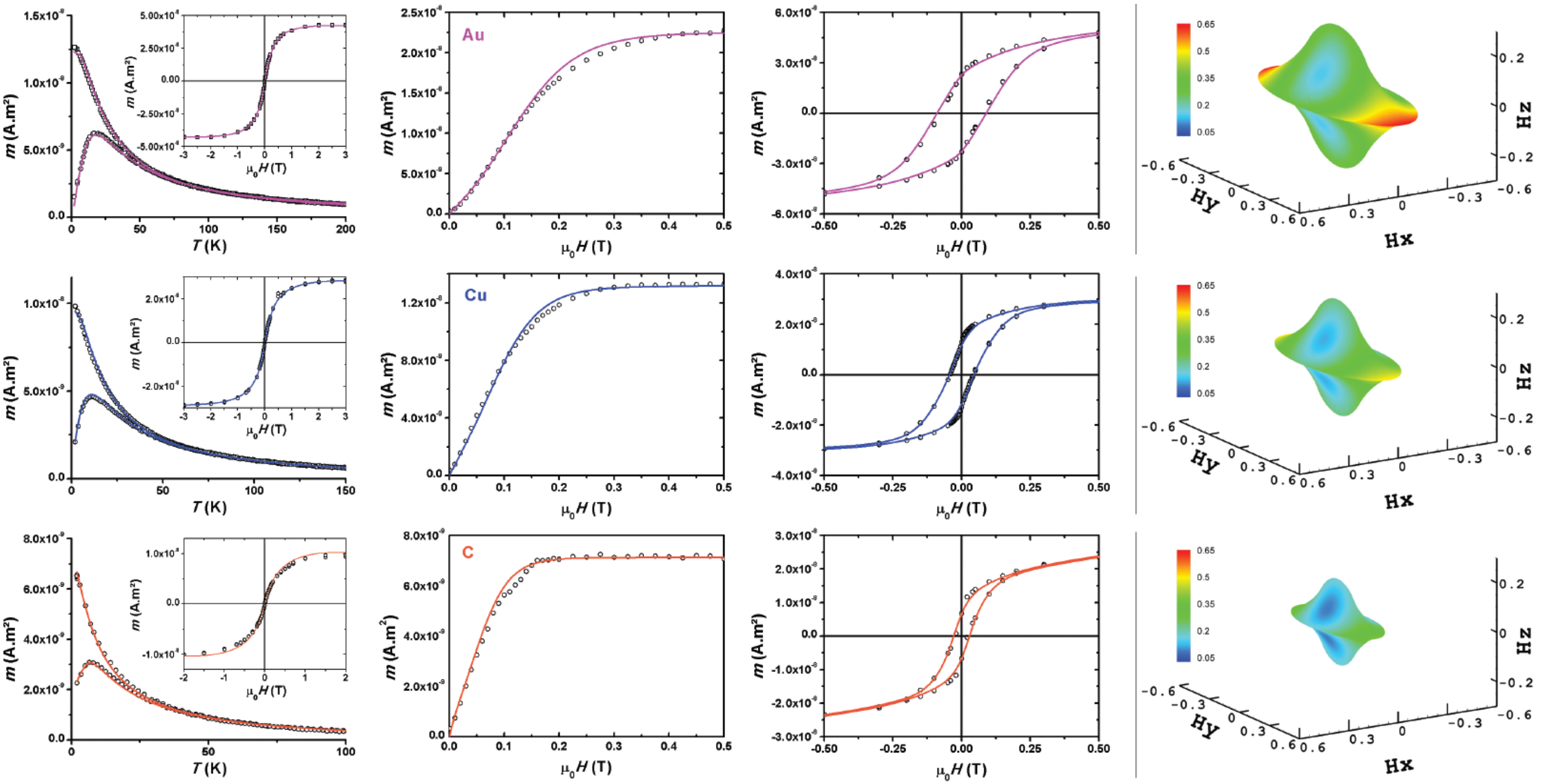
F. Tournus, J. Magn. Magn. Mater. **375**, 194 (2015).

Different physical processes → **IRM and ZFC/FC curves are complementary**

Analysis of magnetic measurements

Global fit

- Accurate determination of the “intrinsic” magnetic properties
- Original results with conventional magnetometry on nanoparticles



Diluted Co nanoparticles in different matrices

A. Hillion et al., Phys. Rev. B **95**, 134446 (2017)

First signature of interactions

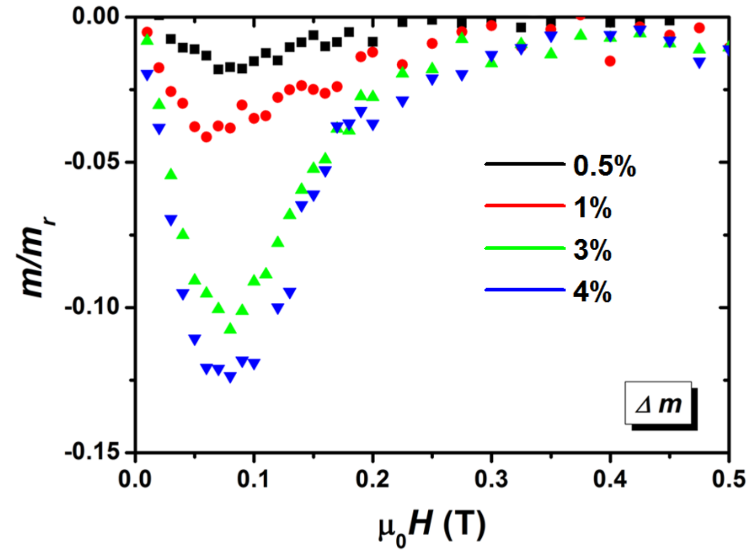
Co nanoparticles in gold, for increasing concentration

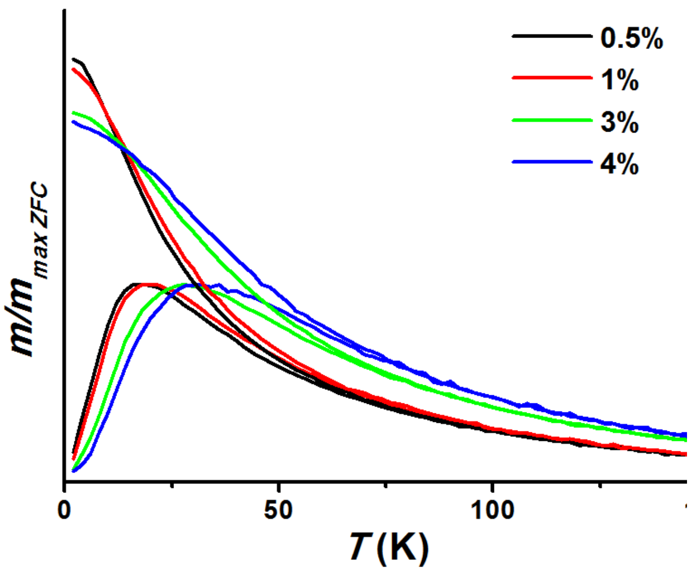
(low interaction regime, only a few percent of volume concentration)

A. Hillion et al., Phys. Rev. B **95**, 134446 (2017)

- Modification of the IRM/DCD curves

➡ Significant peak (<0) for the Δm parameter





- Impact on ZFC/FC

➡ Increase of the ZFC peak temperature!

✓ We know the properties of the deposited particles

✓ We know the nearest-neighbor (NN) distance distribution

➡ Particles can interact if they are close enough from each other, which can <u>modify the effective particle size distribution</u>

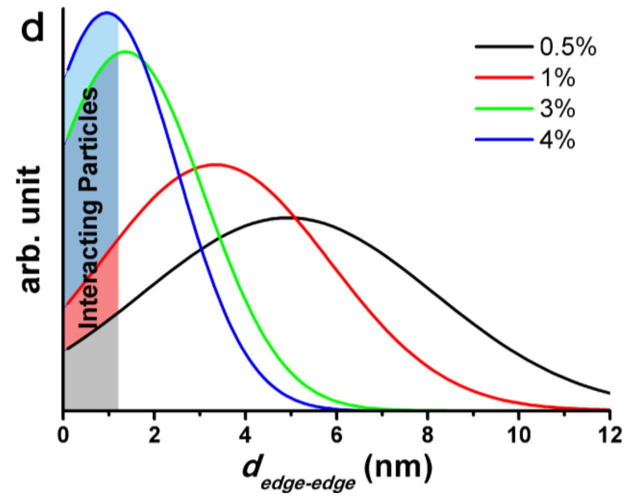
Magnetic dimerization

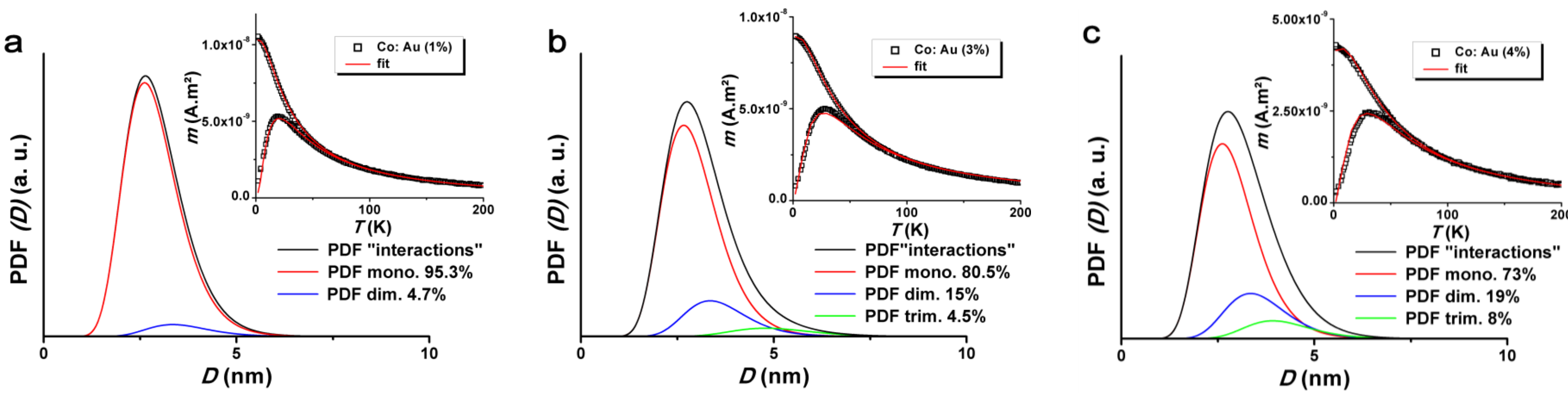
✓ Under a given **interaction length** ℓ^* particles form dimers (or trimers)

➡ The proportions of magnetic multimers directly depend on the concentration

Sample concentration	T_{max} (K)	$\mu_0 H_c$ (mT)	m_r/m_s	x_{dim} (%)	x_{trim} (%)
0.5 %	17	85	0.38	2	0
1 %	19	75	0.38	4.7	0.03
3 %	28	75	0.38	15	4.5
4 %	32	70	0.31	19	8

Statistical distribution of NN distances





✓ Interaction length ℓ^* **= 1.2 nm** for Co nanoparticles in Au: account for ZFC/FC evolution

➡ **"Super-ferromagnetic" dimerization**

(Exchange-like, RKKY…)

Magnetic interactions in other matrices

✓ In Cu, similar to Au

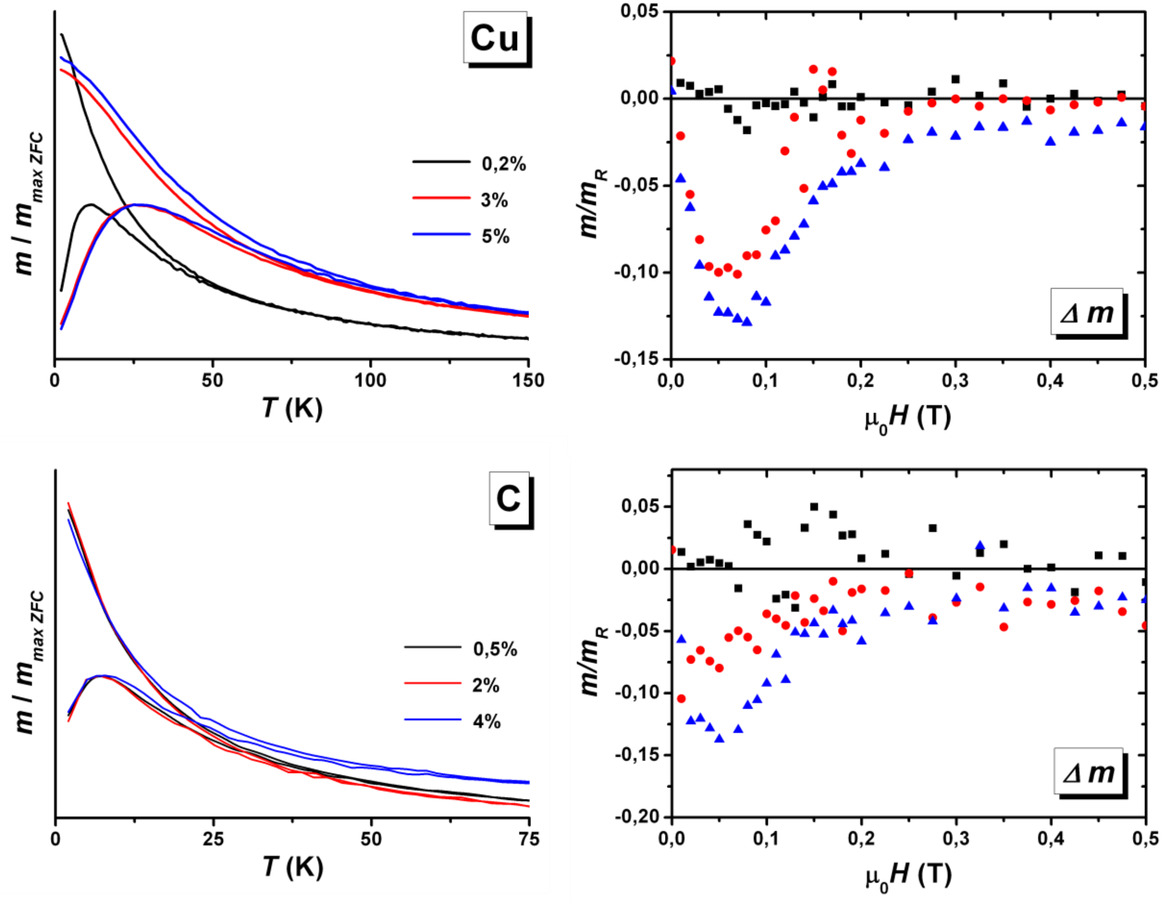
➡ Shift of the ZFC peak

✓ In C, almost no change of the ZFC/FC

➡ But similar Δm evolution!

Very different behavior in metallic matrices and C

- Co NP @ Cu: $\ell^* = 1.3$ nm
- Co NP @ C: $\ell^* = 0.3$ nm



- ZFC/FC sensitive to slight magnetic size changes
- Δm highly sensitive to dipolar interactions

For higher concentration, the model is not valid anymore ➡ collective effects…

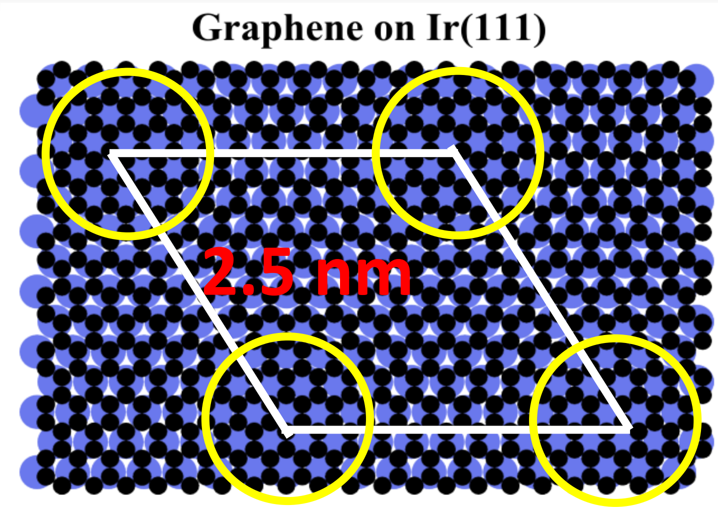
Outline

- Motivation and experimental approach of cluster deposition
- Specific behavior of bimetallic nanoparticles
- Analysis of magnetic measurements: intrinsic properties with diluted nanomagnet assemblies and beyond…
- Interface effects with nanomagnets on cristaline surfaces: FePt/graphene/Ir(111) and $FeRh/BaTiO_3$
- Nano-composites: Co clusters in a FePt matrix

Interface effects: NP/graphene/Ir

- Moiré pattern with graphene on Ir(111) (hexagonal lattice, a=2.5 nm)

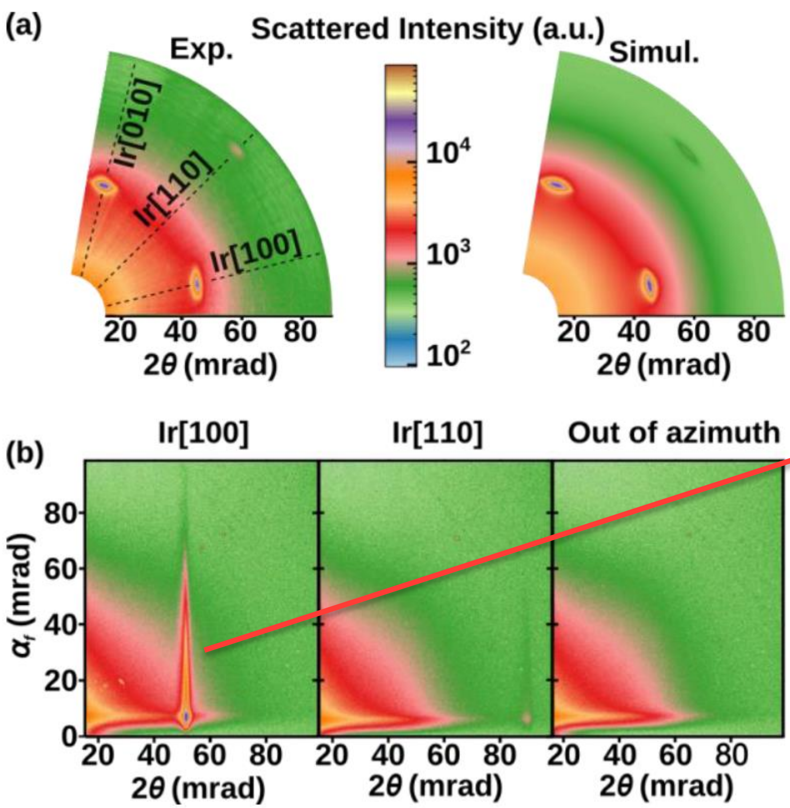
➡ Use as a **template** for NP organization: preferential pining sites



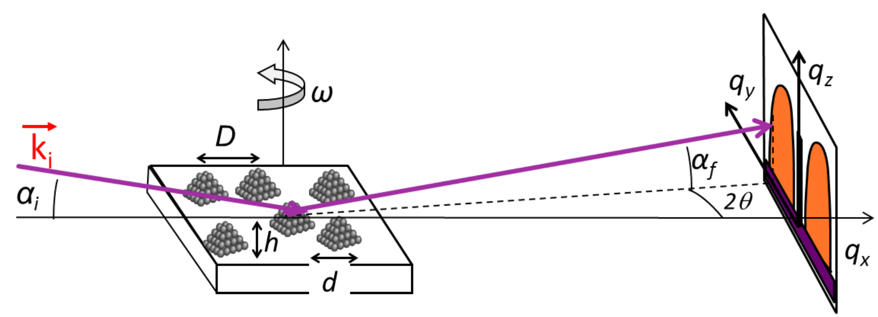
- Successful self-organization of small Pt nanoparticles deposited by LECBD

➡ Organization probed by GISAXS

Correlation peak (in Moiré directions), signature of coherent organization

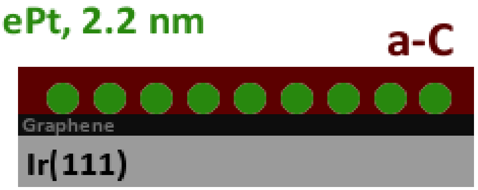


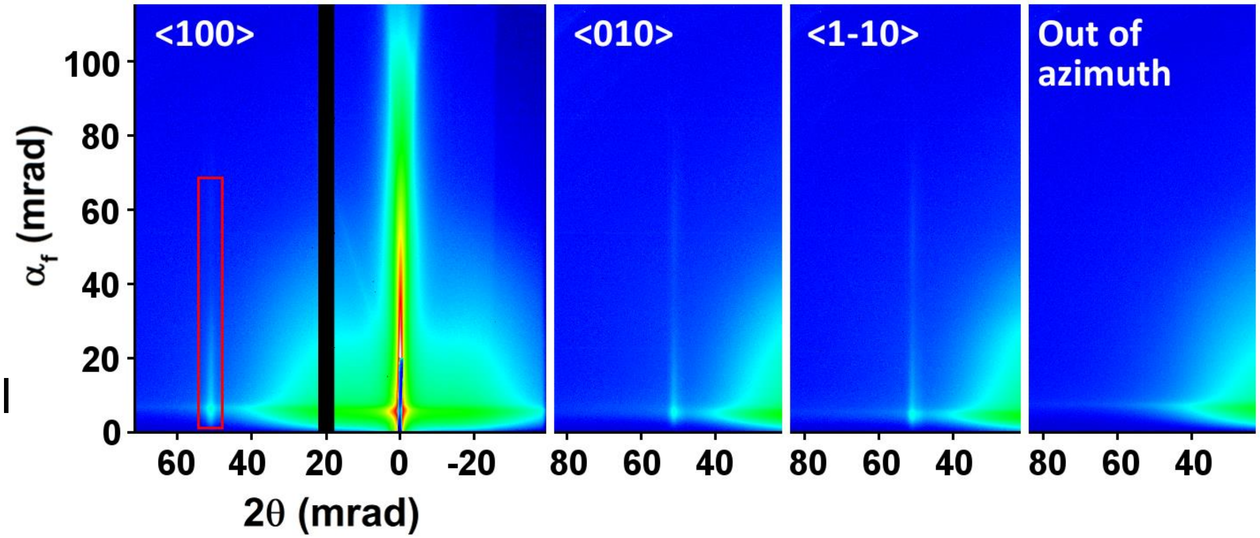
S. Linas et al., Scientific Reports **5**, 13053 (2015)



Grazing Incidence Small Angle X-ray Scattering

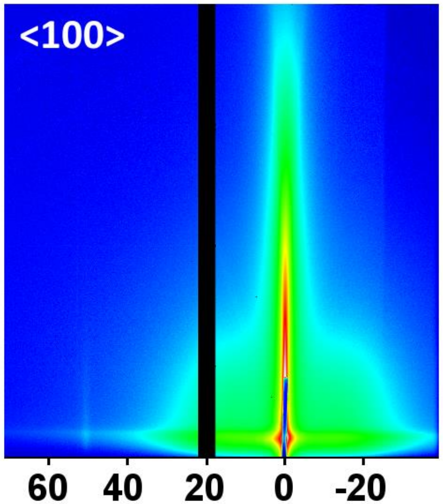
Interface effects: NP/graphene/Ir





- ✓ Same approach successful for size-selected **FePt** nanoparticles
  - ➡ (Partial) organization on the Moiré sites

Rk.: Organization was not possible using atomic deposition



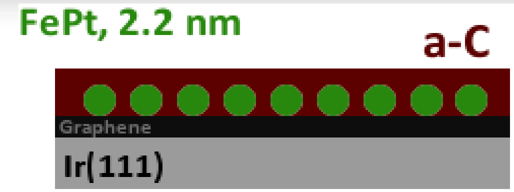
- ✓ A signature of spatial organization is preserved up to 600°C
  - ➡ Annealing compatible with $L1_0$ chemical ordering

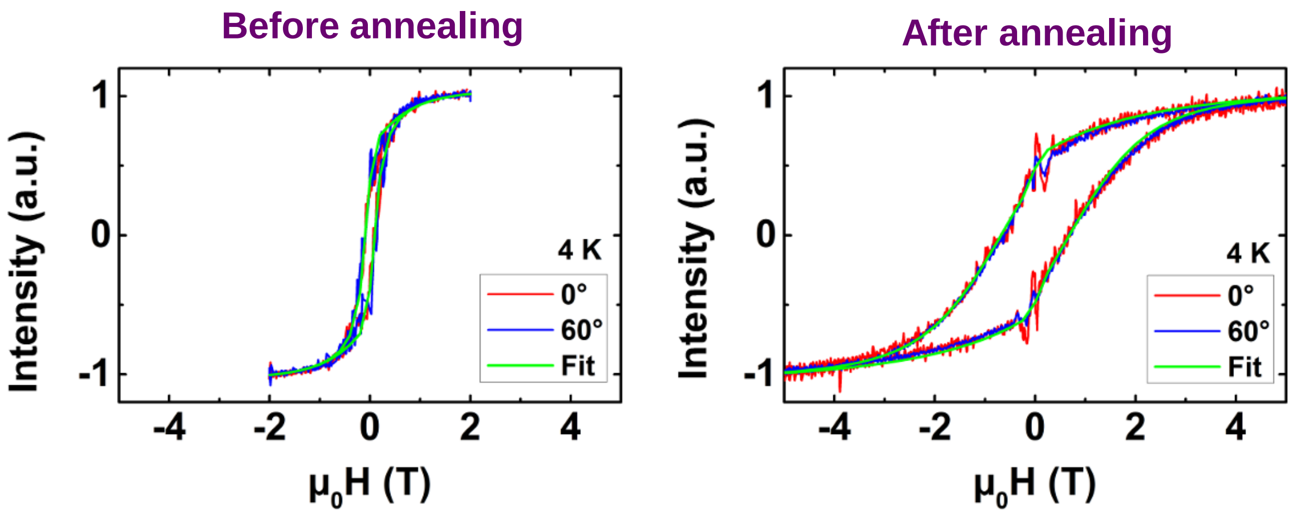
Quantitative analysis is still in progress…

- ✓ Sample also characterized by XMCD
  - ➡ Magnetic properties

Interface effects: NP/graphene/Ir

XMCD (Fe L edges)





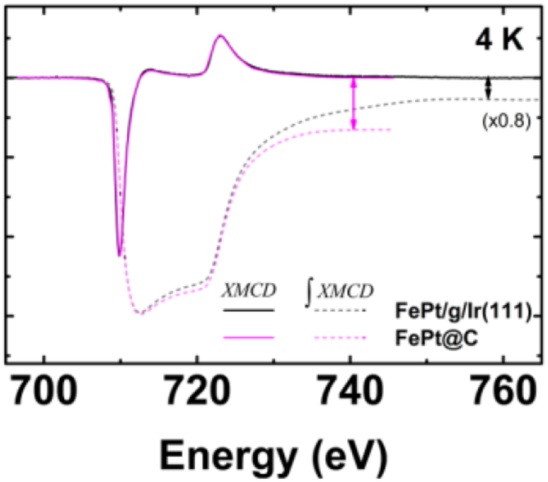
- ✓ No effect of incidence angle: isotropic behavior

- ✓ Huge increase of coercivity: particles with a magnetic anisotropy larger than 1 MJ/m^3 (and large dispersion)

  ➡ Must reflect L1$_0$ chemical ordering of FePt NPs

- ✓ In addition, evolution of Fe atomic moments
  - Large value of m_S before annealing (as for the bulk)
  - Lower m_L value than for particles in carbon matrix

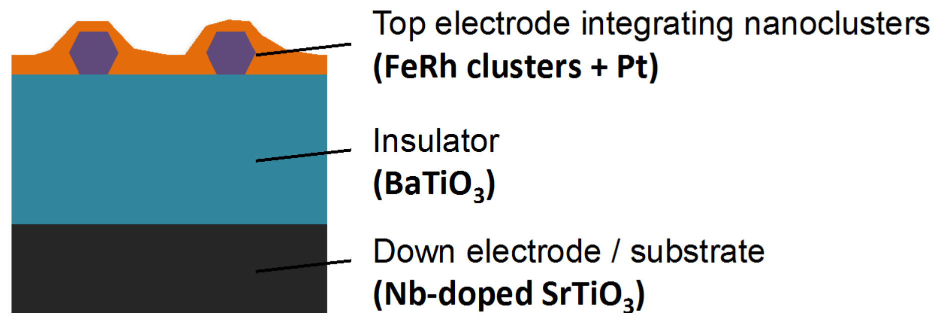
  ➡ Interface effect?



Interface effects: FeRh NP/$BaTiO_3$

Starting project

FeRh nanoparticles deposited on crystalline $BaTiO_3$ surface (ferro + piezoelectricity)



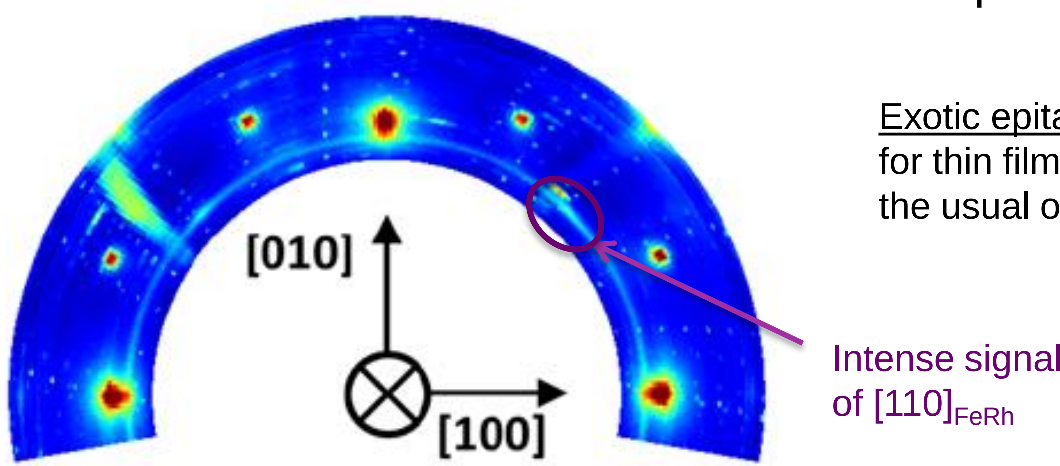
Electric field control of NP magnetic properties

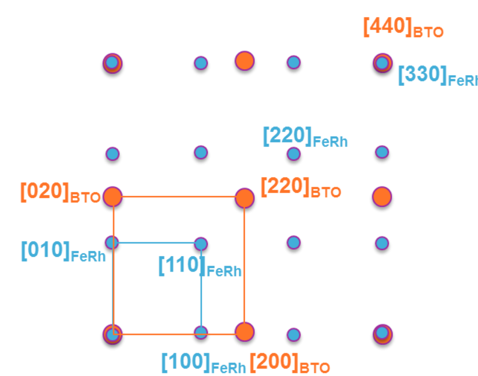
FeRh sensitive to charge effects and distortions

✓ First results on the structure (GIXRD):

- Chemically ordered B2 phase after annealing
- Epitaxial relationships

Exotic epitaxy (not observed for thin films) in addition to the usual one!

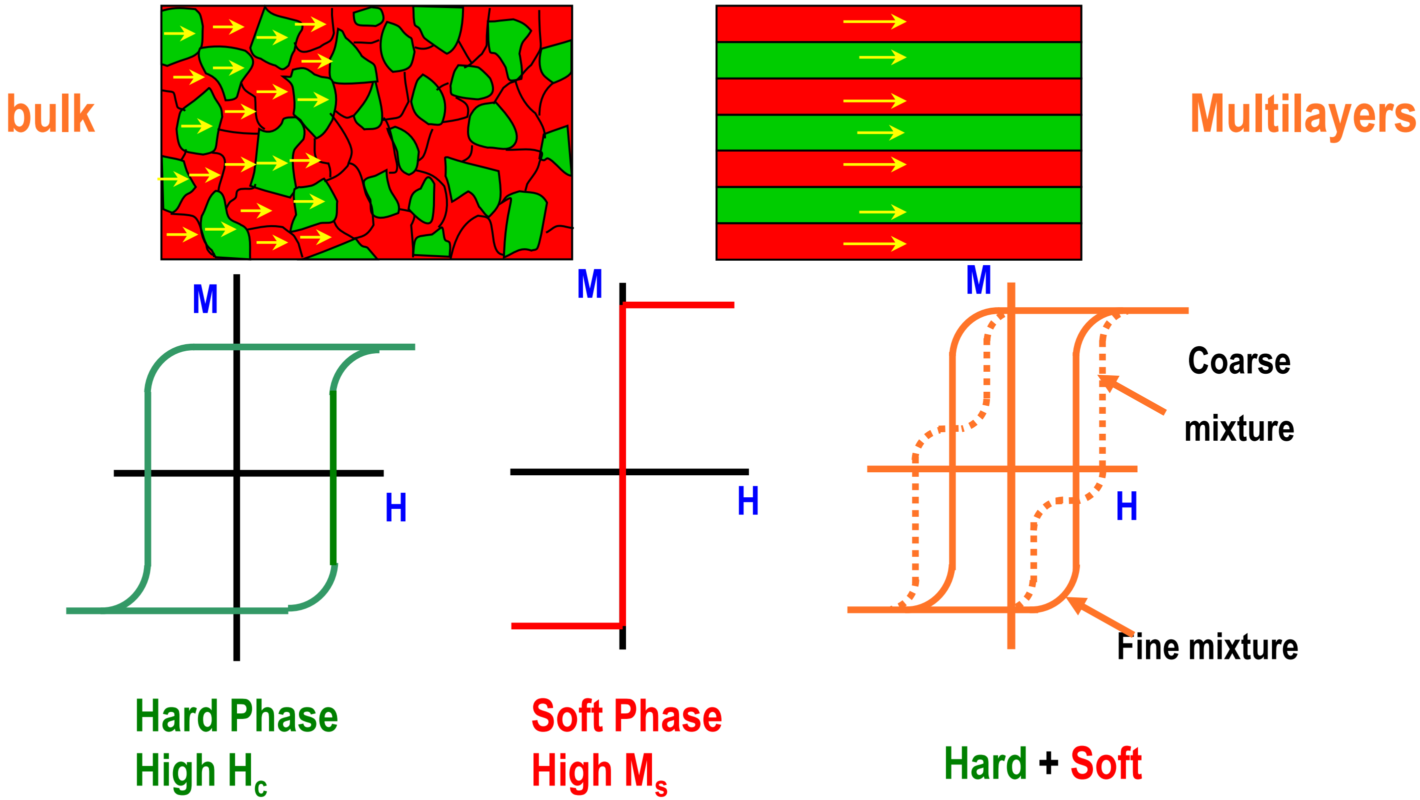




Commensurability: $2\,[220]_{BTO} = 3\,[110]_{FeRh}$

Nanocomposite magnets: Co@FePt

- **Principle:** Fine mixture of soft (high M_S) and hard (high K_u) phases for enhanced remanence and energy product
- **Requirement:** Nanosized and isolated soft grains (typical sizes < 10 nm)



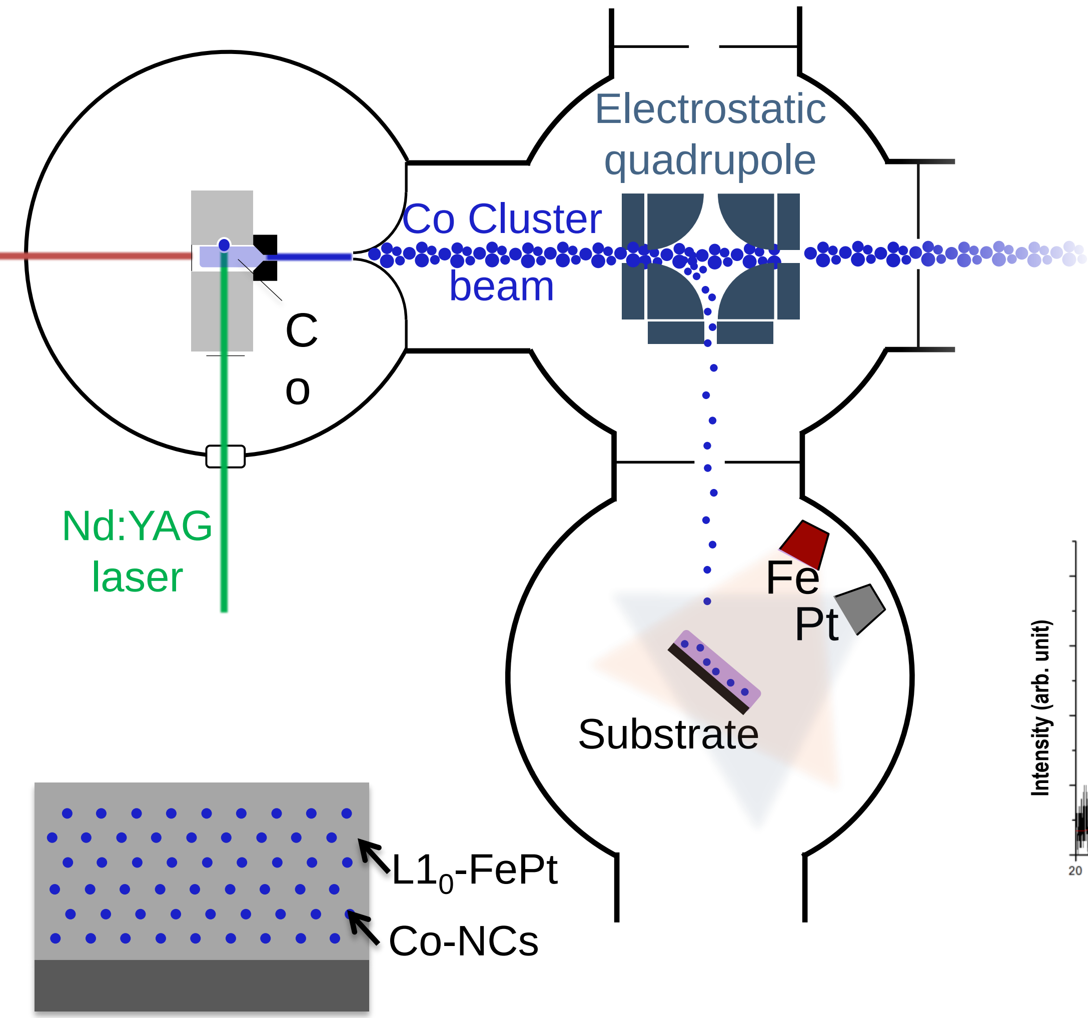
- **Our approach (by cluster deposition):**

Nanocomposite films made of $L1_0$-FePt with embedded Co nanoclusters

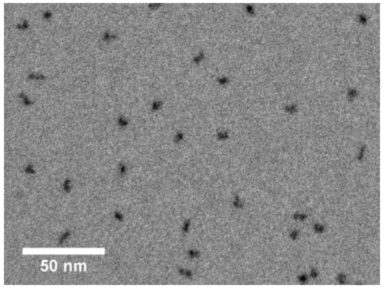
ANR « SHAMAN », Partners: I. NEEL (Grenoble), ESRF, ID12 (Grenoble), SPCTS (Limoges)

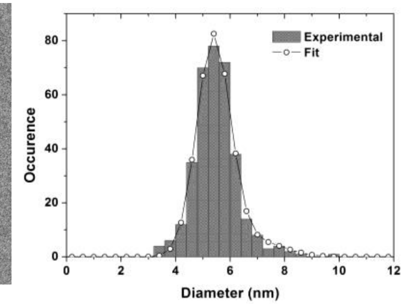
Nanocomposite magnets: Co@FePt

- **LECBD + e beam evaporators:** Sequential deposition of Co-NCs, Fe and Pt



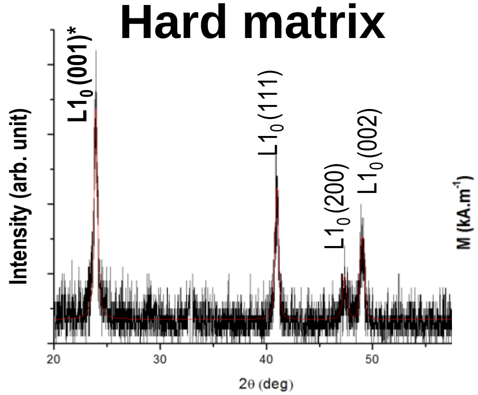
Soft nanosized grains

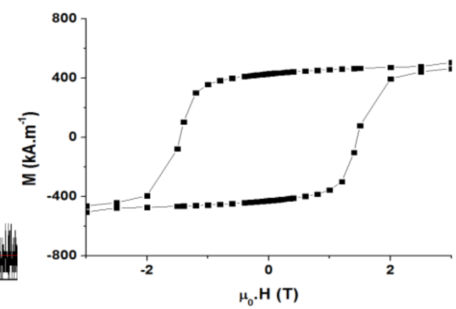




6nm Co nanoclusters (fcc)

Hard matrix

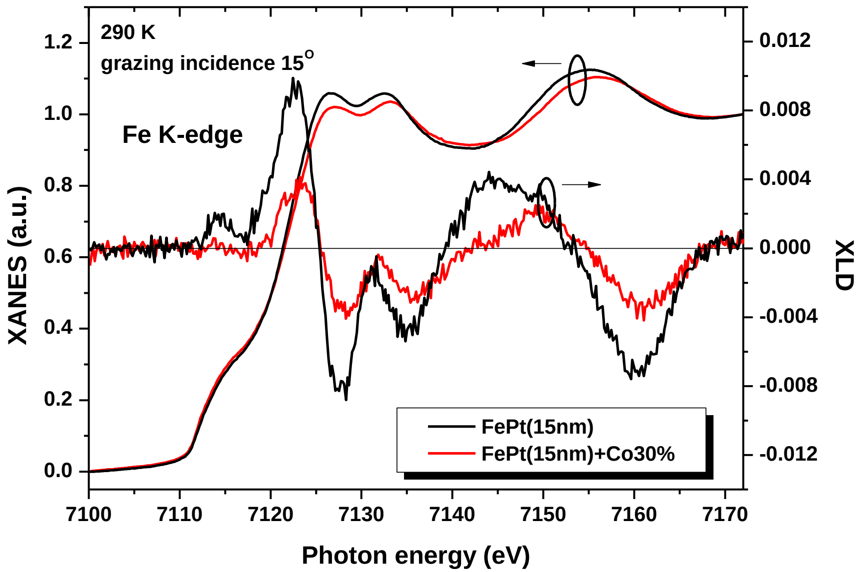


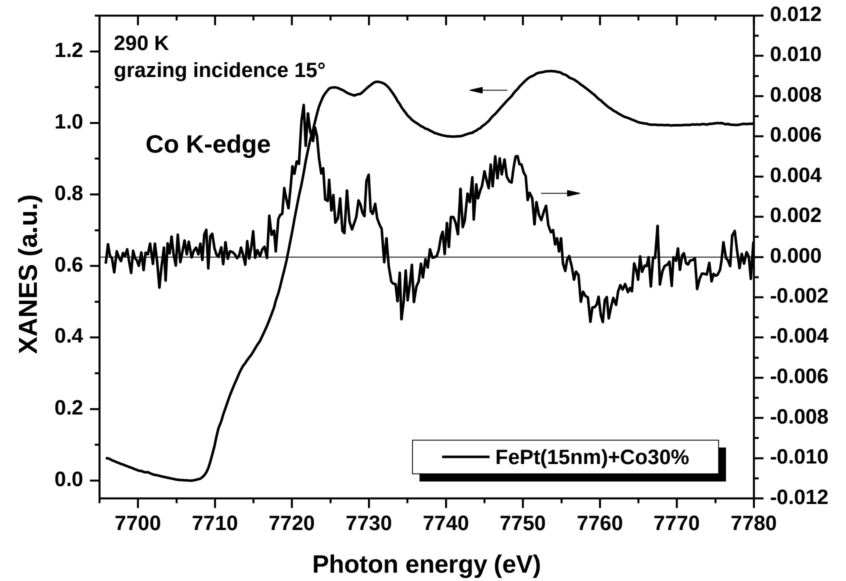


$L1_0$-FePt films obtained from {Fe/Pt} multilayer growth

Nanocomposite magnets: Co@FePt

✓ **First results with XAS at Fe and Co K-edges**





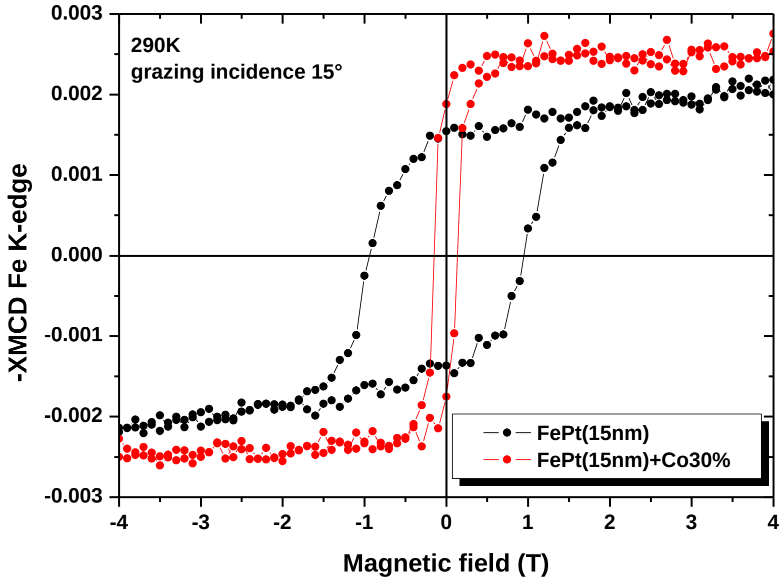
Effect of Co-NCs:
- (XANES) reduced lattice parameter on Fe environment
- (XLD) lower degree of texture

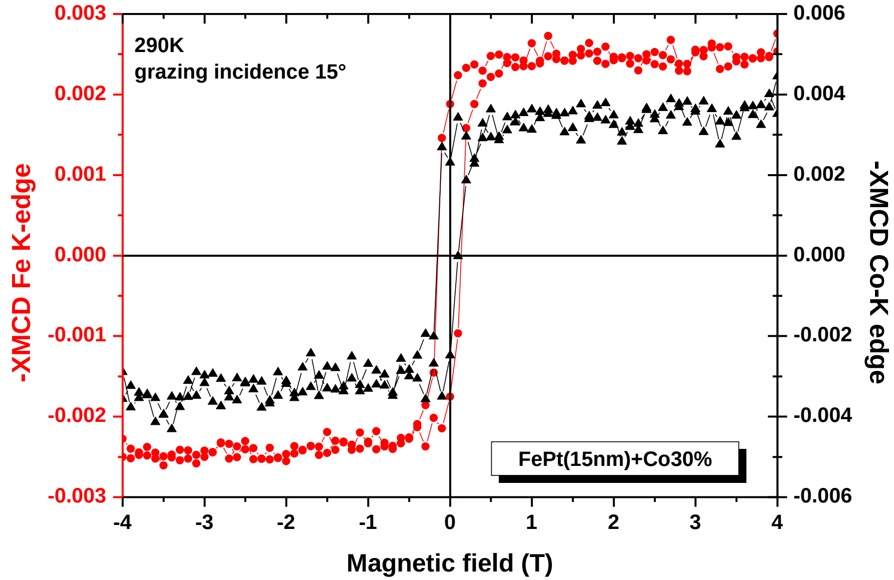
Tetragonal environment for Co atoms: from fcc to fct

Co atoms enter in the textured FePt phase

Nanocomposite magnets: Co@FePt

✓ **First magnetic results with XMCD (K-edges)**





Effect of Co-NCs:
H_C decreases ($\mu_0 H_C$ from 1.0 T to 0.2 T)
m_{Fe} increases

Same reversal for Co and Fe moments

Co and Fe moments are coupled
Single phase behaviour

Take-home message

Our motivation: How can the magnetic properties of nanostructures be controlled and tailored?

➡ Exotic effects with magnetic nanoparticles

Our approach: Well-defined and original samples by cluster deposition

➡ UHV deposition, size-selection, diluted assemblies, clusters on surfaces…

Our expertise: Investigation of small nanomagnets, from individual objects to complex systems!

➡ Magnetometry measurements and modelling, structural characterizations, synchrotron experiments…

Thank you!