UNIVERSITAT DE BARCELONA

150 ANYS EDIFICI HISTÒRIC

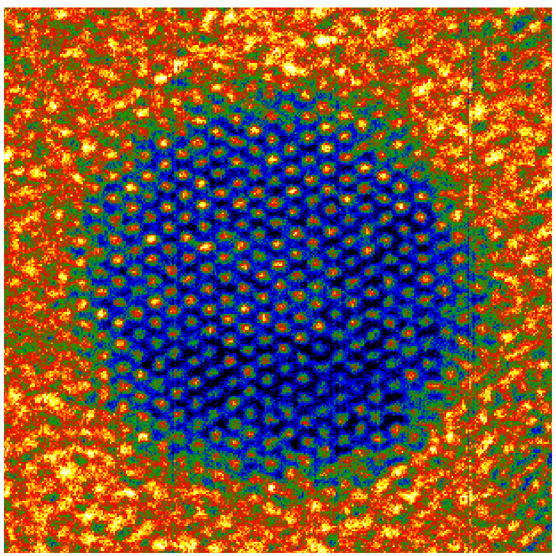
Institut de Nanociència i Nanotecnologia

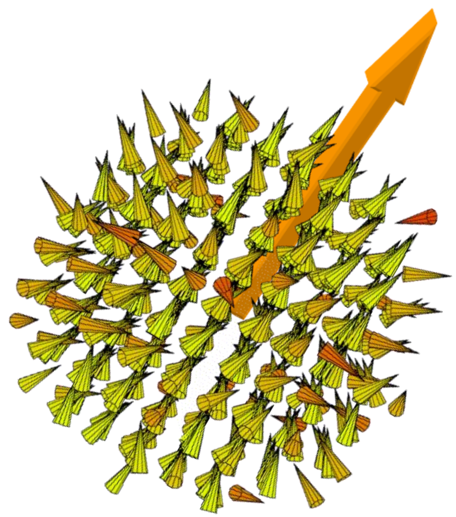
The Magnetic Nanoparticle Iceberg

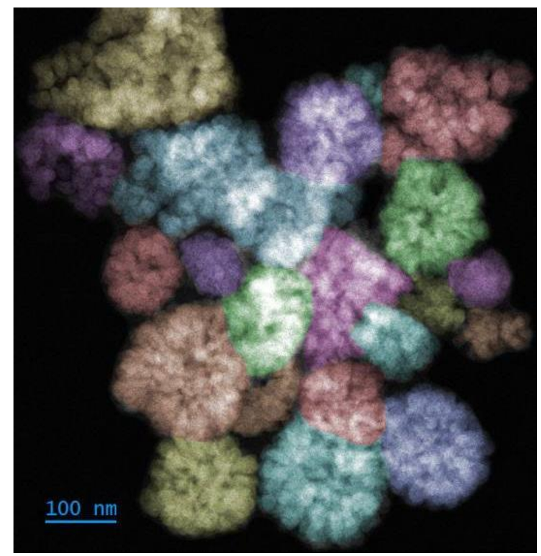
Xavier Batlle

Dept. Condensed Matter Physics and Institute of Nanoscience and Nanotechnology

University of Barcelona







GROUP OF MAGNETIC NANOMATERIALS

DEPARTMENT OF CONDENSED MATTER PHYSICS. INSTITUTE OF NANOSCIENCE AND NANOTECHNOLOGY (IN2UB).UNIVERSITY OF BARCELONA

Visit our website!

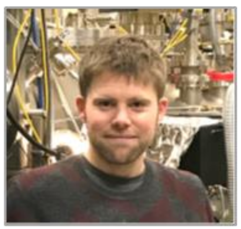

X. Batlle


A. Labarta


O. Iglesias


M. García del Muro


A. Fraile Rodríguez


E. Langenberg


A. I. Figueroa


C. Moya

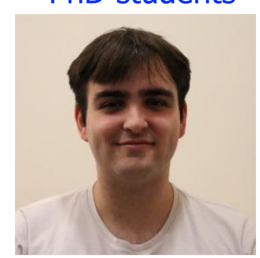

J. Rodríguez Álvarez

Ph.D. 2025
(A. Labarta/A. Fraile)


J. Ruiz Torres


J. Ara

PhD students


Beñat Albizbeaskoetxea

https://magneticnanomaterialsub.wordpress.co icmm CSIC

M. Puerto Morales

ICN2 Institut Català de Nanociència i Nanotecnologia

V. F. Puntes

HZB Helmholtz Zentrum Berlin

S. Valencia

PSI

A. Kleibert

ALBA

M. A. Niño

M. Foerster

Universidad de Oviedo

A. Hierro-Rodríguez

CNM Centro Nacional de Microelectrónica IMB

F. Pérez-Murano

X. Borrisé

PSI

J. Vila-Comamala

IMN micro nano Instituto de Micro y Nanotecnología

A. García-Martín

W UNIVERSITY of WASHINGTON

J.C. Idrobo

MINISTERIO DE CIENCIA E INNOVACIÓN

UNIÓN EUROPEA FONDO EUROPEO DE DESARROLLO REGIONAL "Una manera de hacer Europa"

AGENCIA ESTATAL DE INVESTIGACIÓN

For Women in Science unesco FONDATION L'ORÉAL

Generalitat de Catalunya

AGAUR Agència de Gestió d'Ajuts Universitaris i de Recerca

beatriu de pinós bp

UNIVERSITAT DE BARCELONA

IN2 Institut de Nanociència i Nanotecnologia UNIVERSITAT DE BARCELONA

ELECMI

CSUC

SH SERRA HÚNTER PROGRAMME

The driving force during the last 30 years:
from microns to nanometers

Why nanoscience and nanotechnology?

- Nanostructured (magnetic) materials

– Basic entities, nanometer in size (e.g., magnetic nanoparticles)

- Why interesting? – New phenomena:

– Feature size $\leq$ length scale

Magnetism: Exchange length, domain wall width and single domain

- Why useful? – New applications:

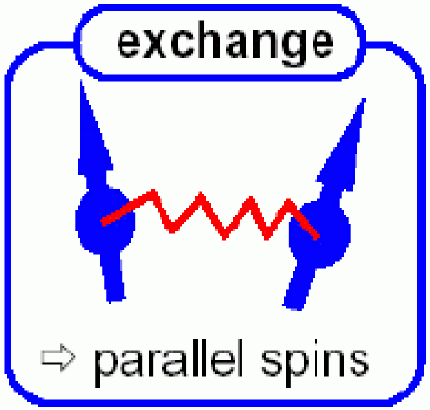
– Magnetic recording (1-10 Terabit/in^2) and sensors

– Bioapplications

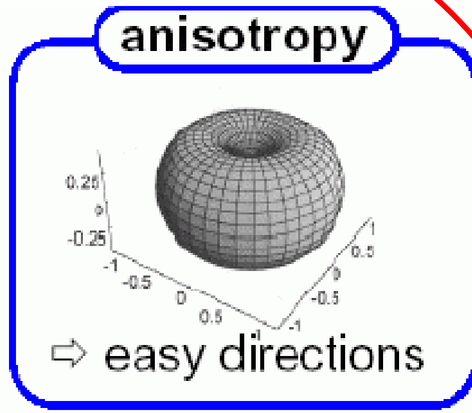
–

FIELD	PROPERTY	LENGTH SCALE
Electronics	Electronic Wavelength Inelastic mean free path Tunneling	1 - 10 nm 1 - 100 nm 1 - 10 nm
Magnetism	Domain wall Spin-flip scattering	10 - 100 nm 1 - 100 nm
Optics	Quantum well Evanescent wave decay length Metallic skin depth	1 - 100 nm 10 - 100 nm 10 - 100 nm
Superconductivity	Cooper pair coherence length Meissener penetration depth	0.1 - 100 nm 1 - 100 nm
Mechanics	Dislocation interactions Grain Boundaries Crack tip radi Nucleation/growth defect Surface corrugation	1 - 1000 nm 1 - 10 nm 1 - 100 nm 0.1 - 10 nm 1 - 10 nm
Catalysis	Surface topology	1 - 10 nm
Supramolecules	Kuhn length Secondary structure Tertiary structure	1 - 100 nm 1 - 10 nm 10 - 1000 nm
Inmunology	Molecular recognition	1 - 10 nm

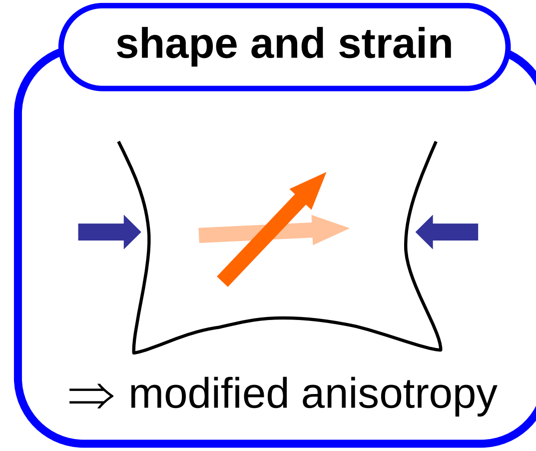
Main energy terms in magnetism

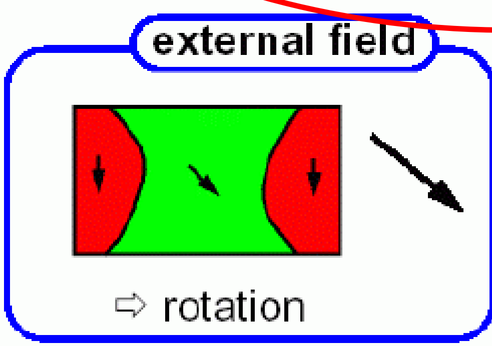


$$E = -\sum_{i,j} J_{ij}\, \vec{S}_i \cdot \vec{S}_j$$

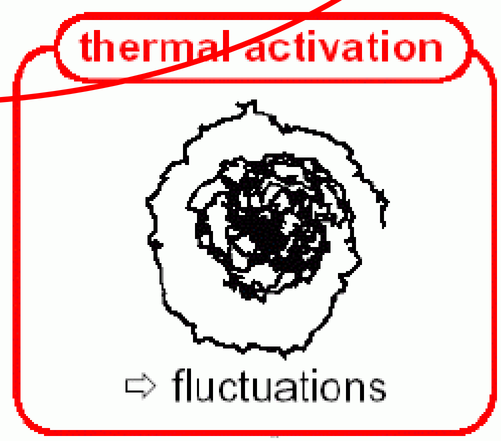


$$F = \frac{E_a}{V} = f(\theta, \varphi)$$

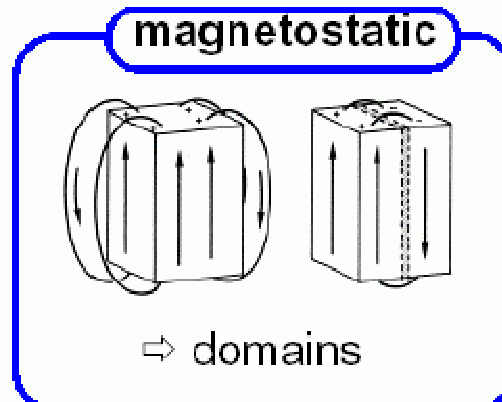




$$F = -\mu_0 \vec{M} \cdot \vec{H}$$



$$E = k_B T$$



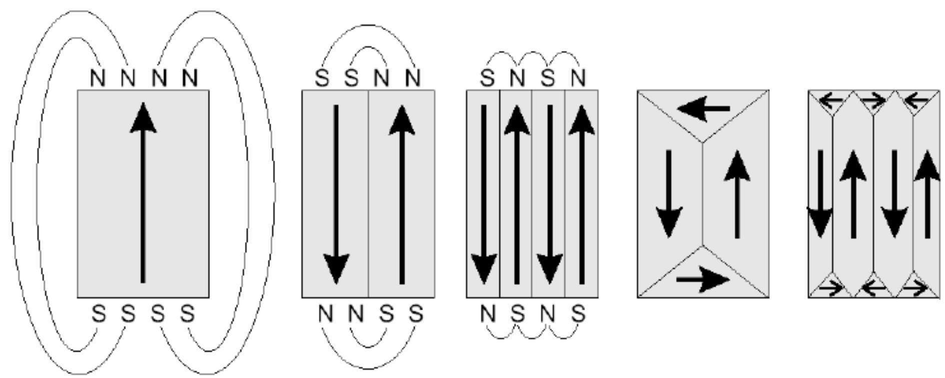
$$F = -\frac{\mu_0}{2} \vec{M} \cdot \vec{H}_d$$

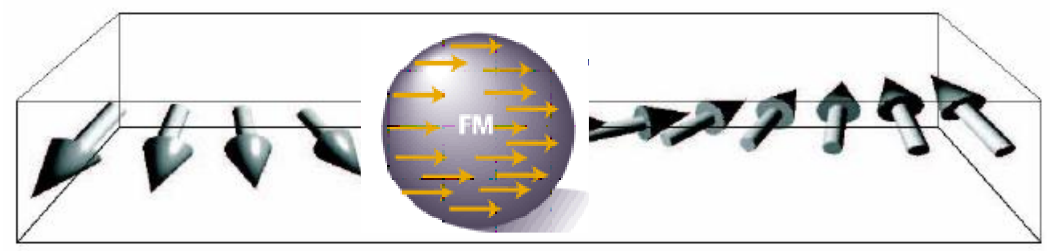
$$\vec{H}_d = -N_d \vec{M}$$

Characteristic length scales in magnetism

$$\delta_{DW} \propto \sqrt{J/K}$$

Domain wall width



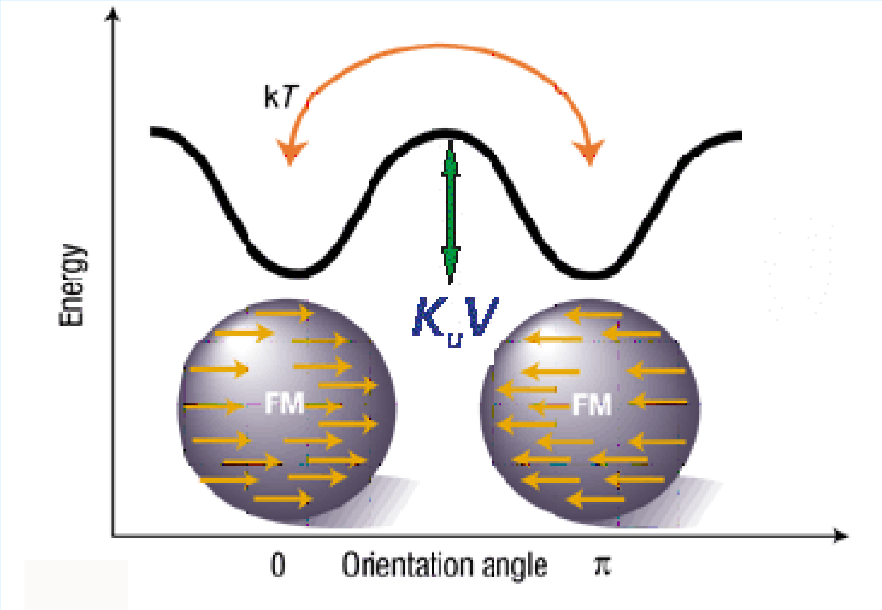


Magnetic recording *vs* biomedical applications

The superparamagnetic limit:

thermal fluctuations overcome the magnetic anisotropy barrier

$$t = t_0 e^{K_u V / kT}$$



Magnetic recording (t ≈ 10 years)

With the increase in recording density (reduction in volume), we need to keep the magnetic stability (patterned media, high anisotropy materials, exchange bias…)

Requirements for bio-applications (typically)

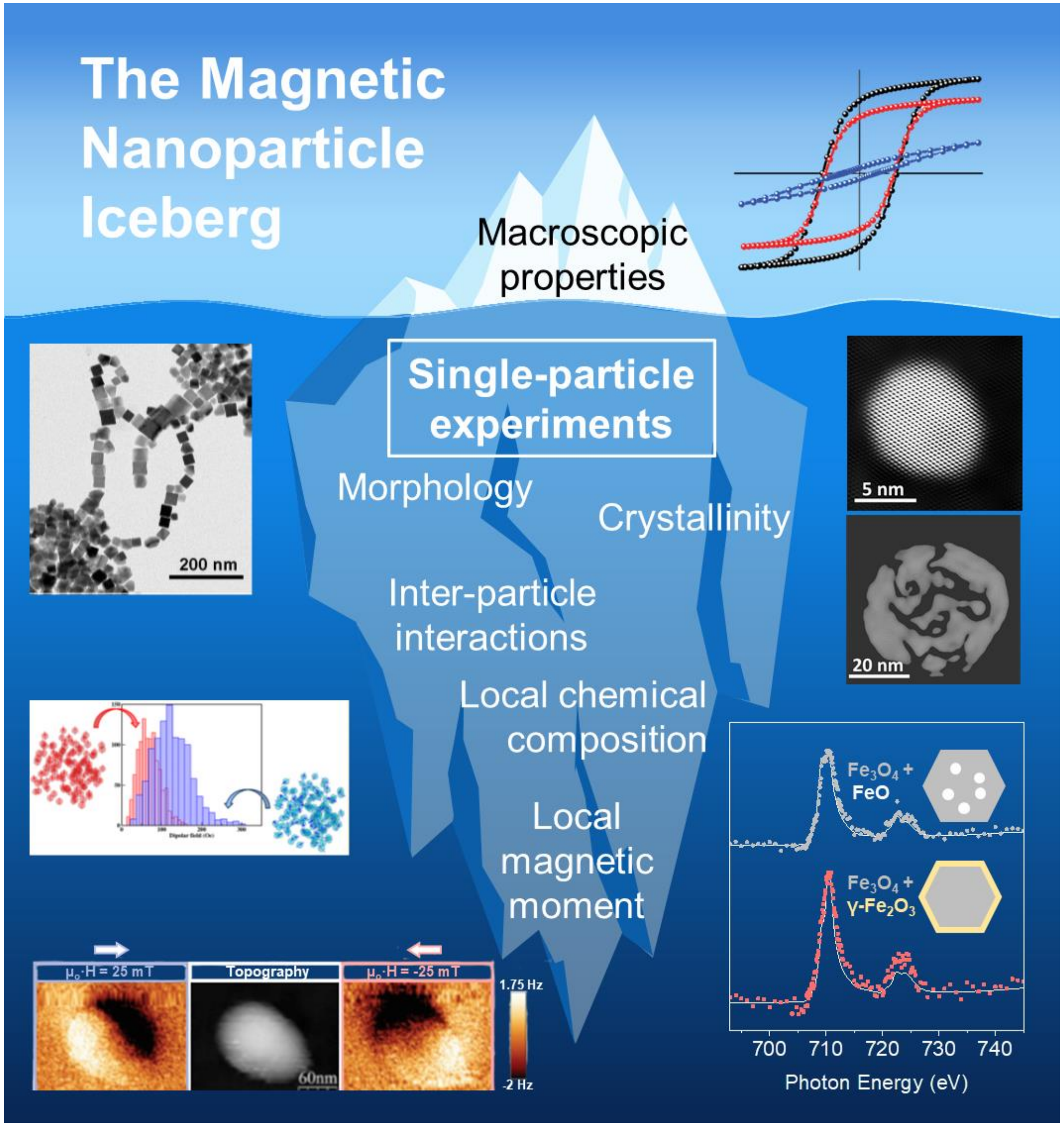
Superparamagnetic behavior

High magnetization

Limiting size *(in vivo)*

Biocompatibility and functionality

Main motto:
(nano)structure sets the function



X. Batlle et al. JMMM **543** 168594 (2022)

Fishing

Scuba diving

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS

J. Phys. D: Appl. Phys. 35 (2002) R15–R42 PII: S0022-3727(02)16015-3

TOPICAL REVIEW

Finite-size effects in fine particles: magnetic and transport properties

Xavier Batlle and Amílcar Labarta

Fishing (2000s)

Journal of Magnetism and Magnetic Materials 543 (2022) 168594

ELSEVIER

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Research articles

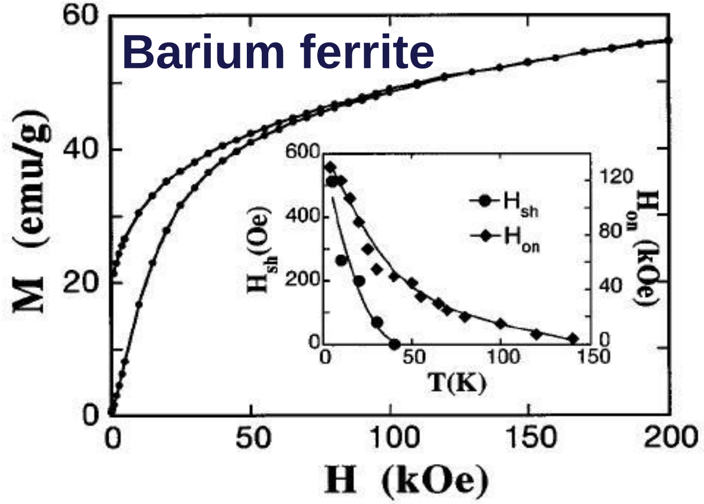
Magnetic nanoparticles: From the nanostructure to the physical properties

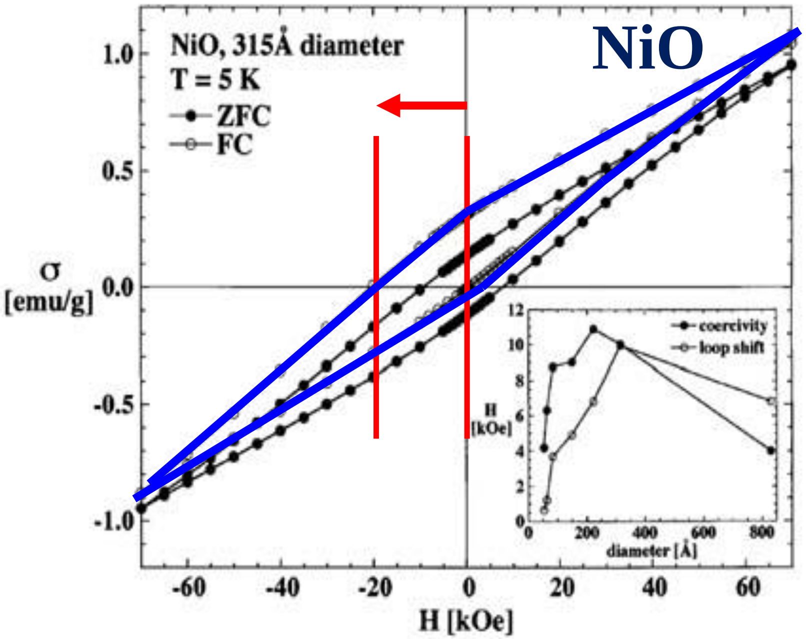
Xavier Batlle [a,b,*], Carlos Moya [b,c], Mariona Escoda-Torroella [a,b], Òscar Iglesias [a,b], Arantxa Fraile Rodríguez [a,b], Amílcar Labarta [a,b,*]

Scuba diving (2020s)

Particle-like behavior (2000s)

- Interplay among finite-size, surface and interface effects, and interparticle interactions
- New phenomena with respect to their bulk counterparts.





Low saturation magnetization,
high field irreversibility,
(broken symmetry at the surface)

Shifted hysteresis loops after FC:

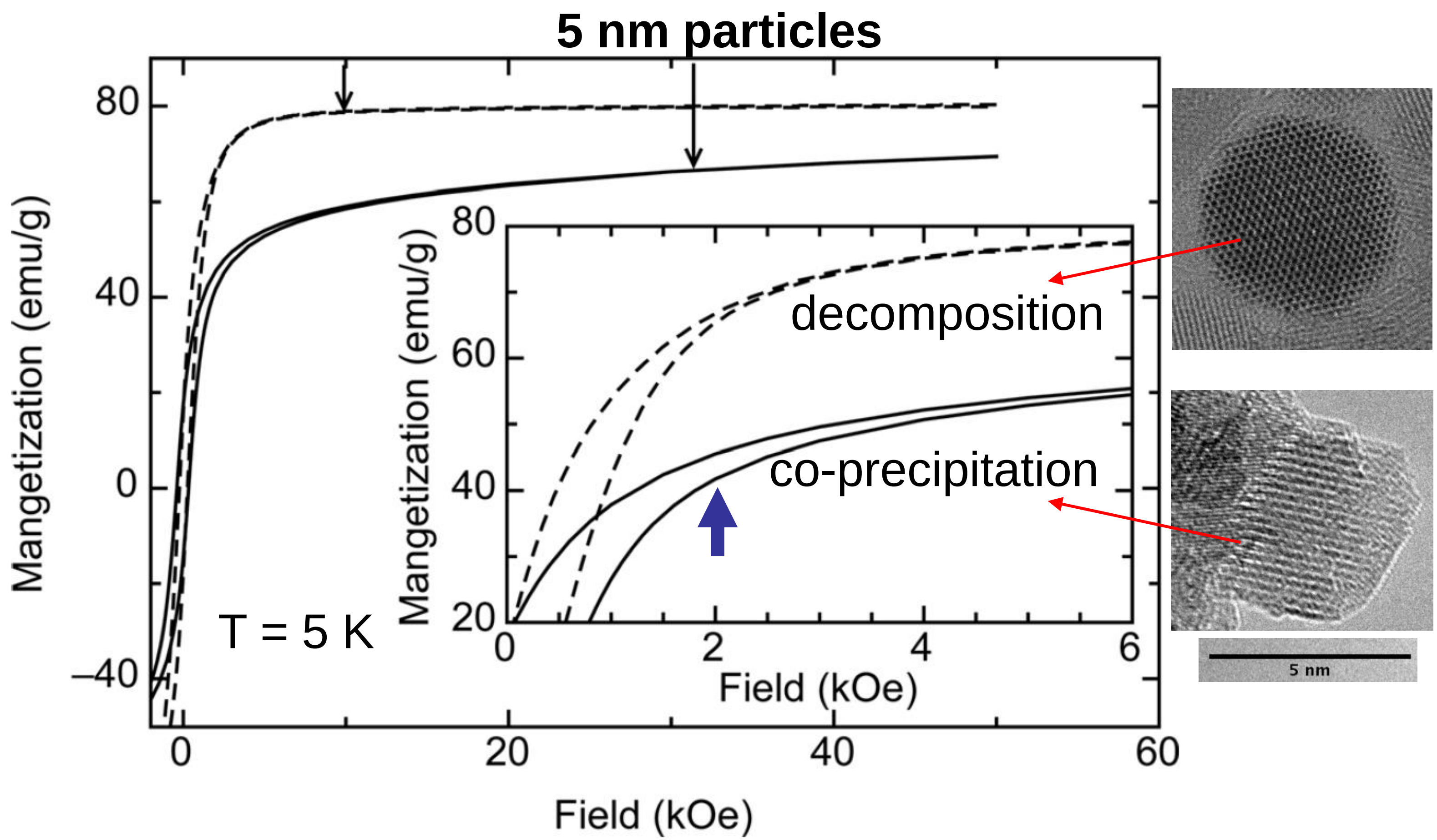
Disordered surface spin structure?
Glassy behavior?

Minor loop due to frozen disorder?

M. García et al., PRB **59**, 13594 (1999)

R. H. Kodama et al., PRL **79**, 1393 (1997)

Particle-like behavior vs. structural quality 5 nm $Fe_{3-x}O_4$



- **Low crystal quality** (co-precipitation): **particle-like M(H)** high saturation field, high closure fields and high differential susceptibility.
- **High crystal quality** (thermal decomposition): **bulk-like M(H)** curves.

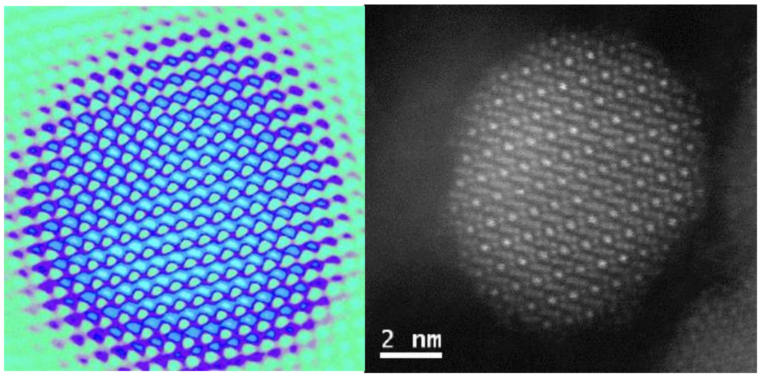
J. Appl. Phys. **109** (2011) 07B524 (invited)

From particle-like to bulk-like properties (2000s to 2020s)

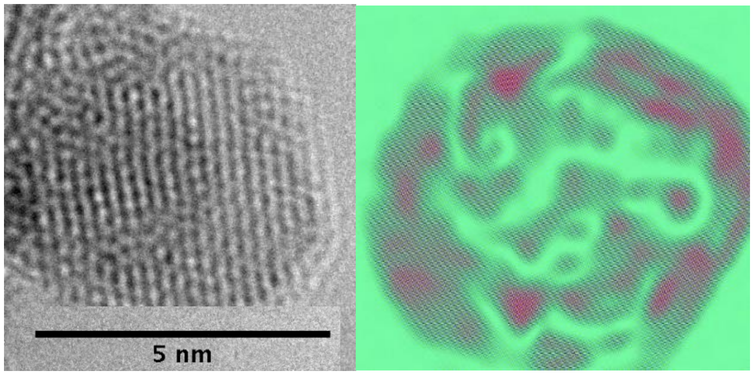
The leap forward in this interdisciplinary field has been three-fold:

1. Model samples:

✓ New synthesis methods enabling nanometer, monodisperse, single crystalline particles



High temperature methods
(e.g., thermal decomposition)

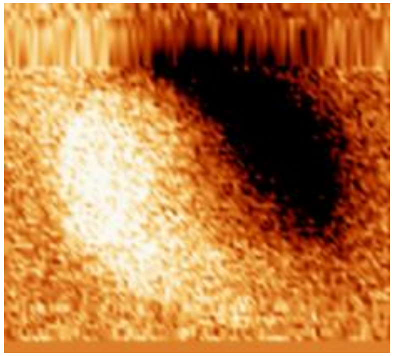


Low temperature methods
(e.g., coprecipitation)

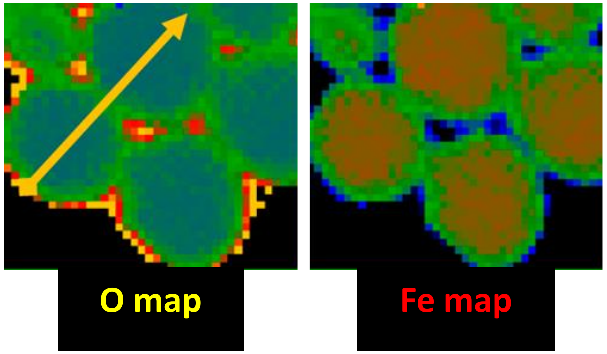
2. Single particle techniques and <u>3. Advanced theoretical models and simulations!!!</u>

✓ Element, valence and magnetic selectivity, with sub-nm resolution (in some cases)

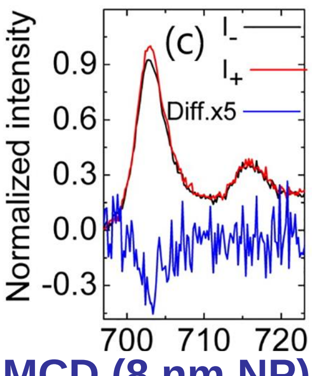
✓ Correlation between nanostructure (crystalline, chemical, magnetic…) and physical properties



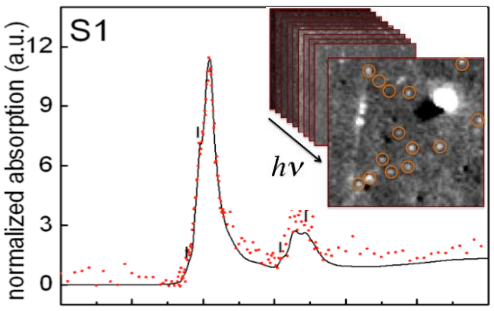
MFM (25 nm NP)



EELS (8 nm NP)



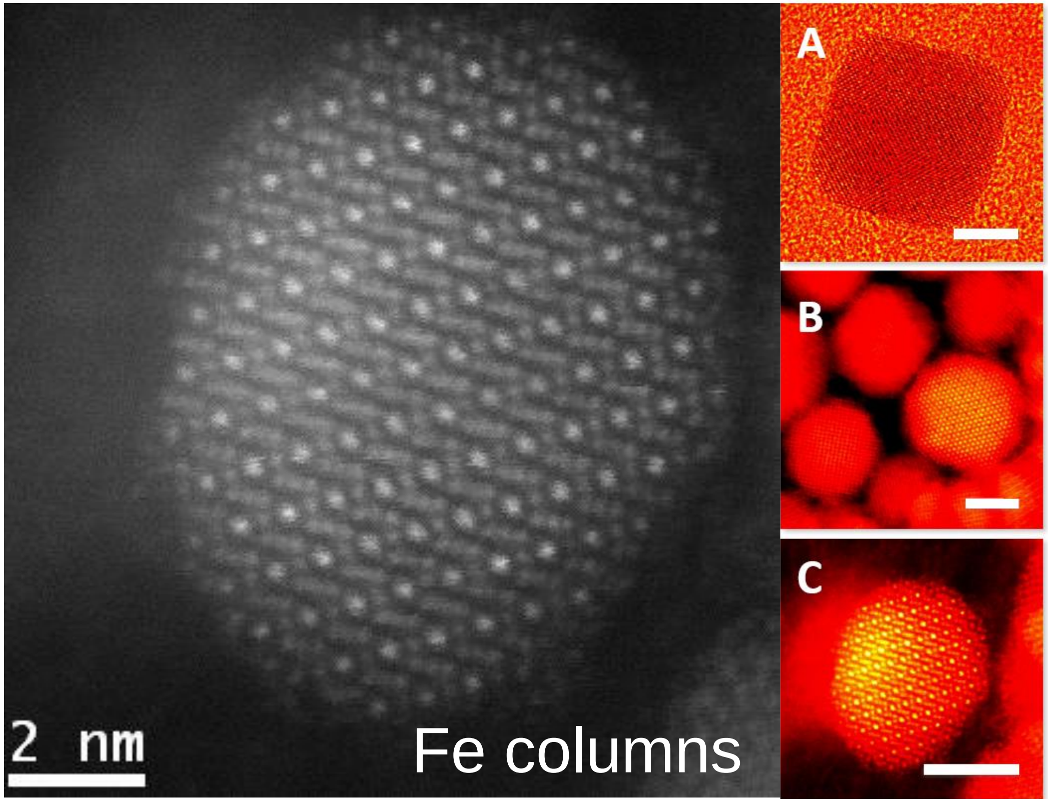
EMCD (8 nm NP)



XAS/XMCD/PEEM (15 nm)

First example: highly crystalline $Fe_{3-x}O_4$ NP

- Bulk magnetic and electronic properties
- Surface magnetization



M.P. Morales
ICMM-CSIC, Spain

M. Varela,
S.J. Pennycook,
J. Salafanca and
J. Gázquez,
Oak Ridge
National
Laboratory, US

S.T. Pantelides,
Vanderbilt Univ., US

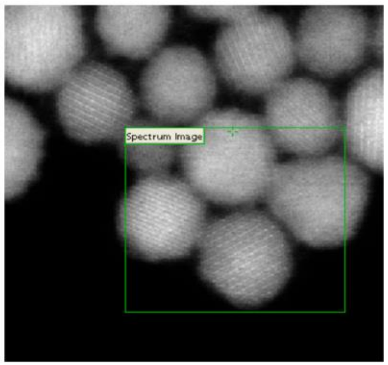
Aberration-corrected STEM (ADF image, Z-contrast)

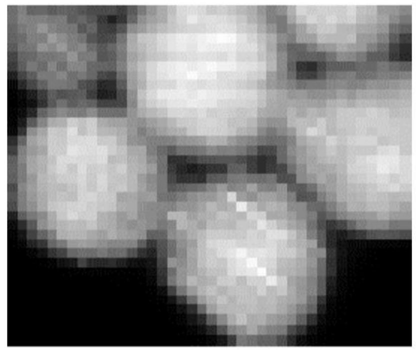
Nano Letters **12** (2012) 2499

Single particle measurements

Aberration-corrected STEM

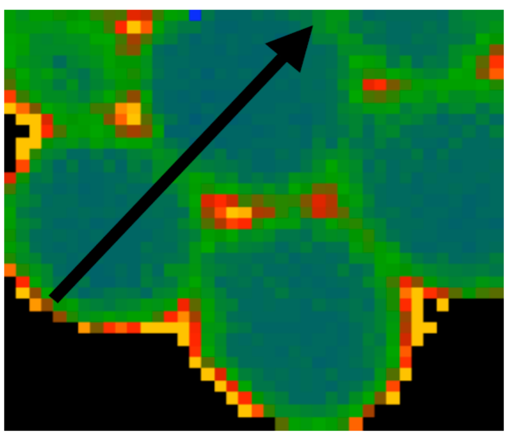
Sub-nanometer EELS analysis: chemical quantification



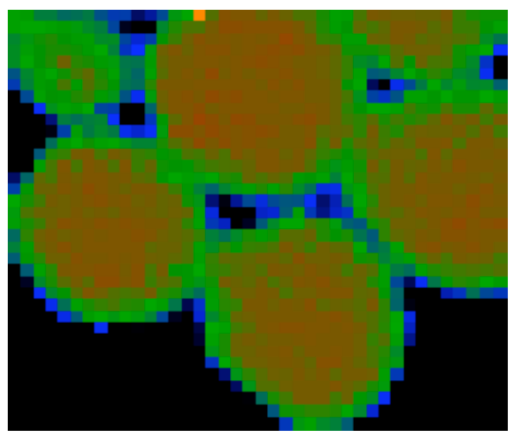


O relative concentration increases significantly at the surface, due to the carboxyl functional group in the oleic acid.

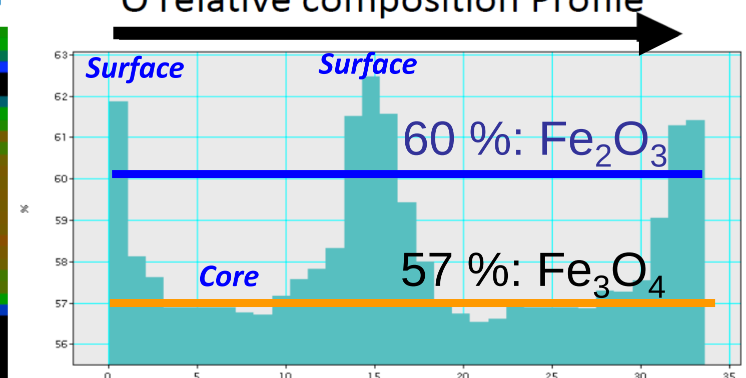
O relative composition map



Fe relative composition map



O relative composition Profile

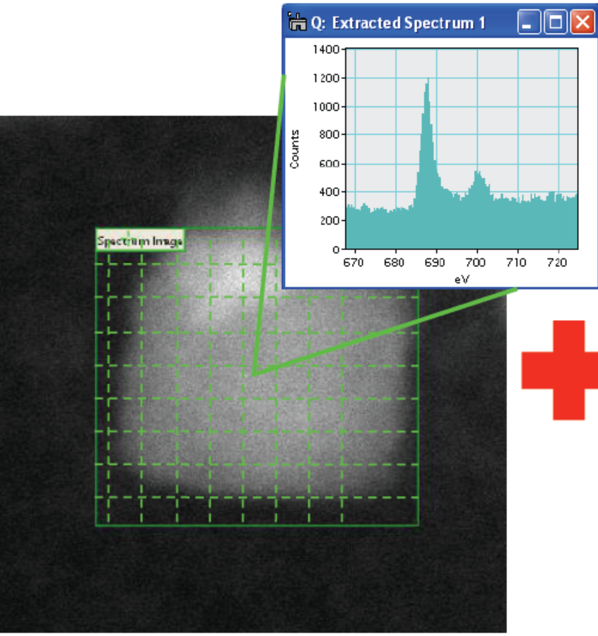


Average in the center 57%, which is consistent with Fe3O4 composition

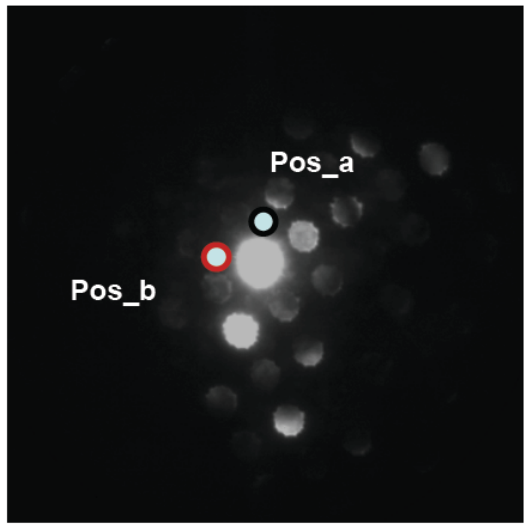
Nano Letters **12** (2012) 2499

Energy-loss magnetic chiral dichroism (EMCD) with nanometer resolution

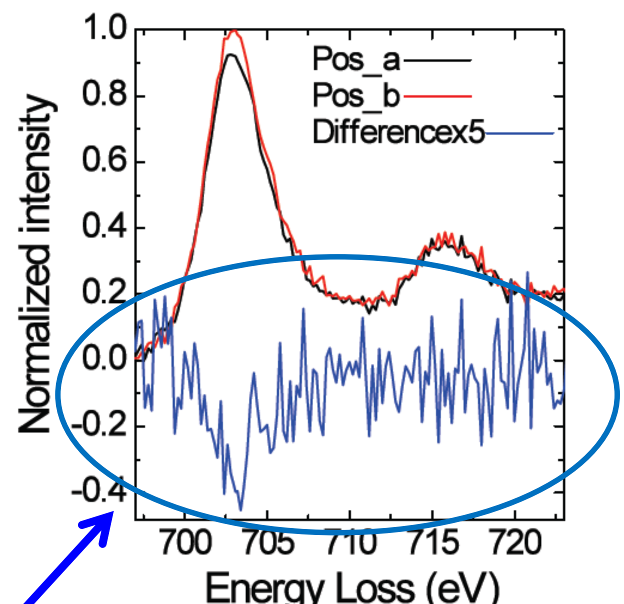
Averaged EELS spectra for a single nanoparticle



Spectrum imaging



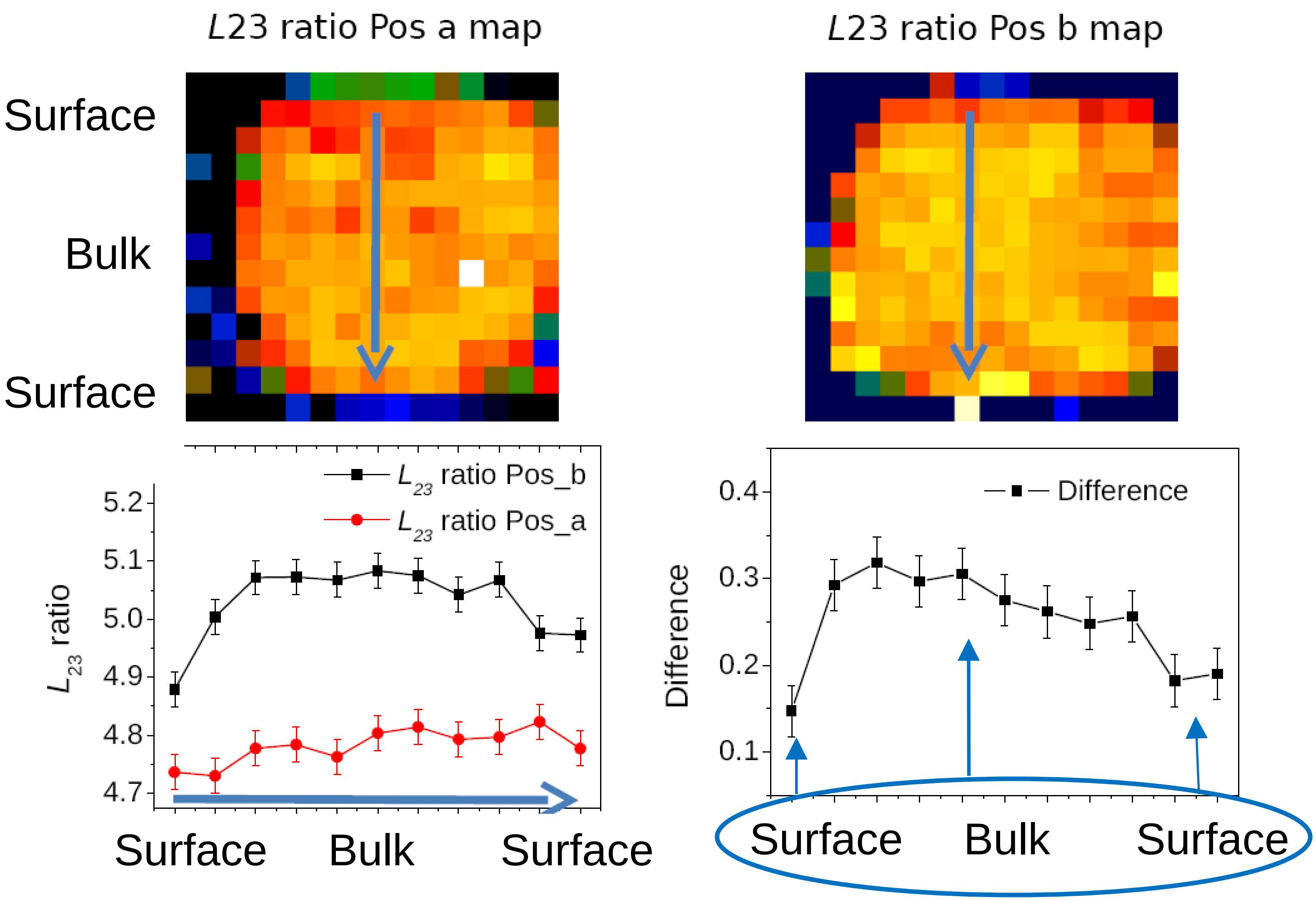
EMCD can be detected acquiring spectra at the two positions (black and red circles) and taking their difference



Energy-loss magnetic chiral dichroism: Fe $L_{2,3}$ edges for Fe_3O_4 nanoparticle for two conjugate configurations

ΔI (blue): *Proportional to Local Magnetic Moment*

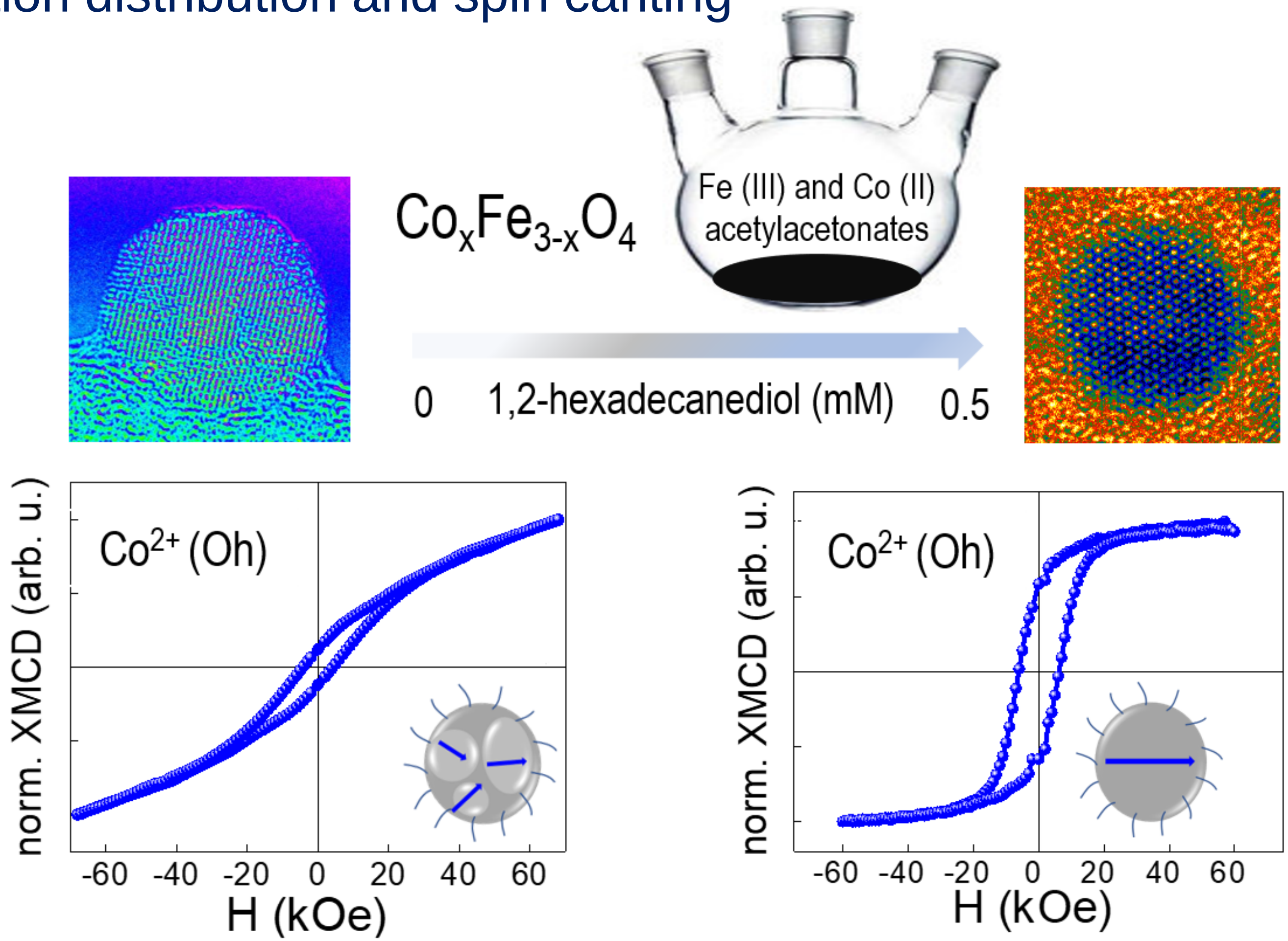
Spatially resolved EMCD signal: lower magnetization at the surface, but non-zero!



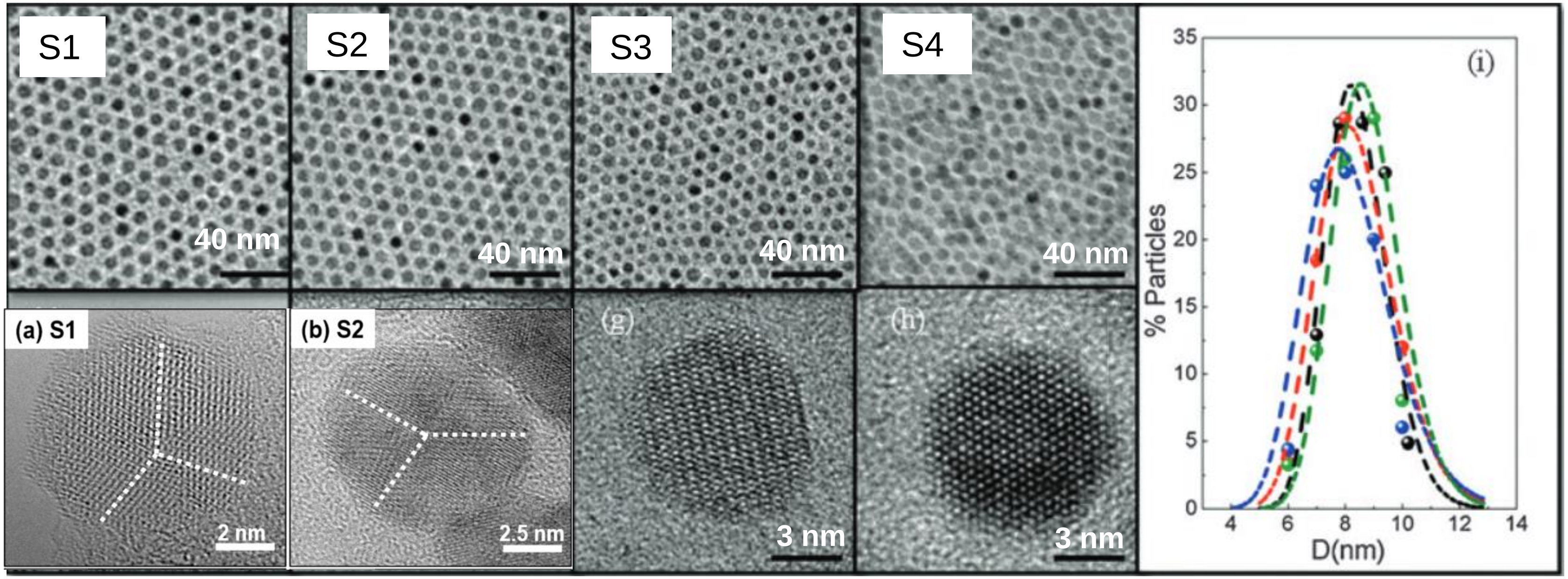
Nano Letters **12** (2012) 2499

Second example: Cobalt ferrite $Co_xFe_{3-x}O_4$ NP

- Quantifying the role of defects
- **Element- and site-sensitive** hysteresis loops (XMCD): probing cation distribution and spin canting

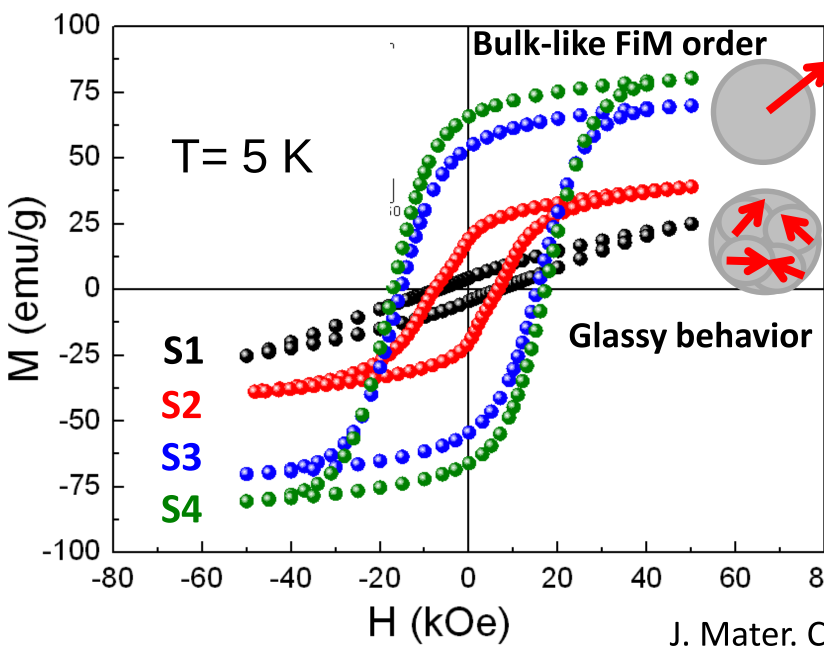


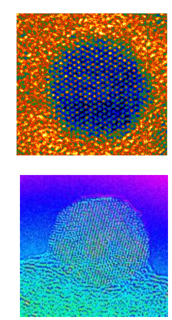
C. Moya, et al. : J. Phys. Chem. C **125**, 691 (2021)



\- → +

Crystalline quality





Inducing glassy magnetism in Co-ferrite NPs through crystalline nanostructure.

- Strong decrease of M_s and high irreversibility.
- Reduced value of the coercive field.
- Shift of the hysteresis loop after FC: minor loops

✓ Small crystalline domains cause highly frustrated FiM-like cores that become frozen in a glassy state at low T

J. Mater. Chem. C (2015) 3, 4522

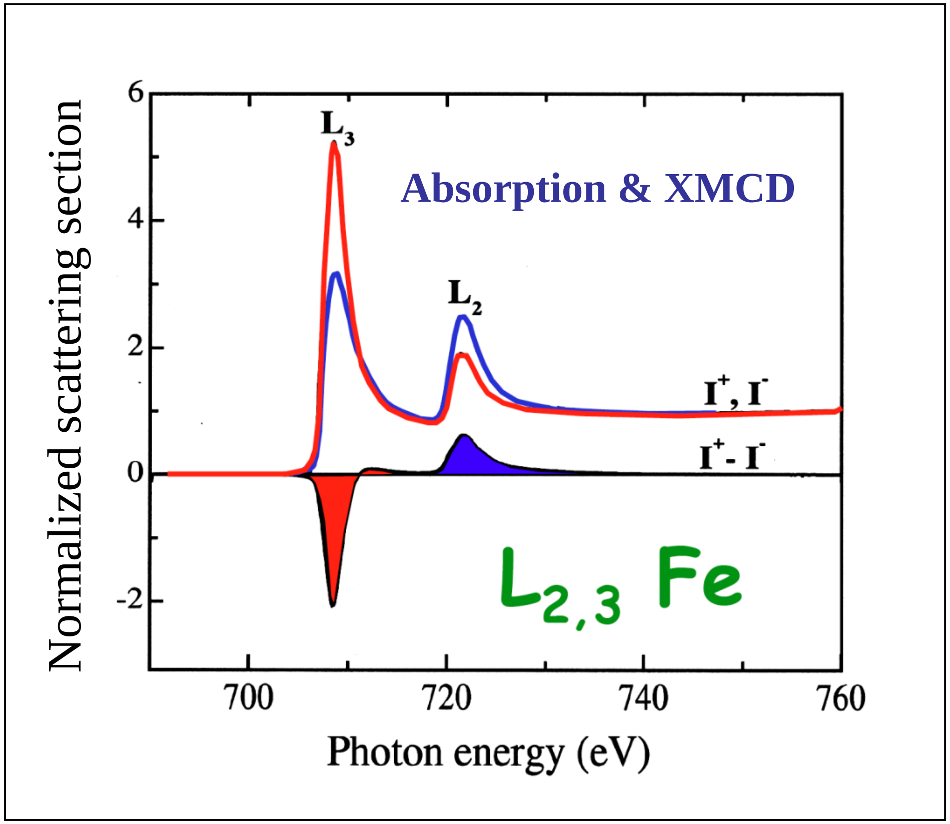
Phys. Chem. Chem. Phys. (2015) 17, 13143

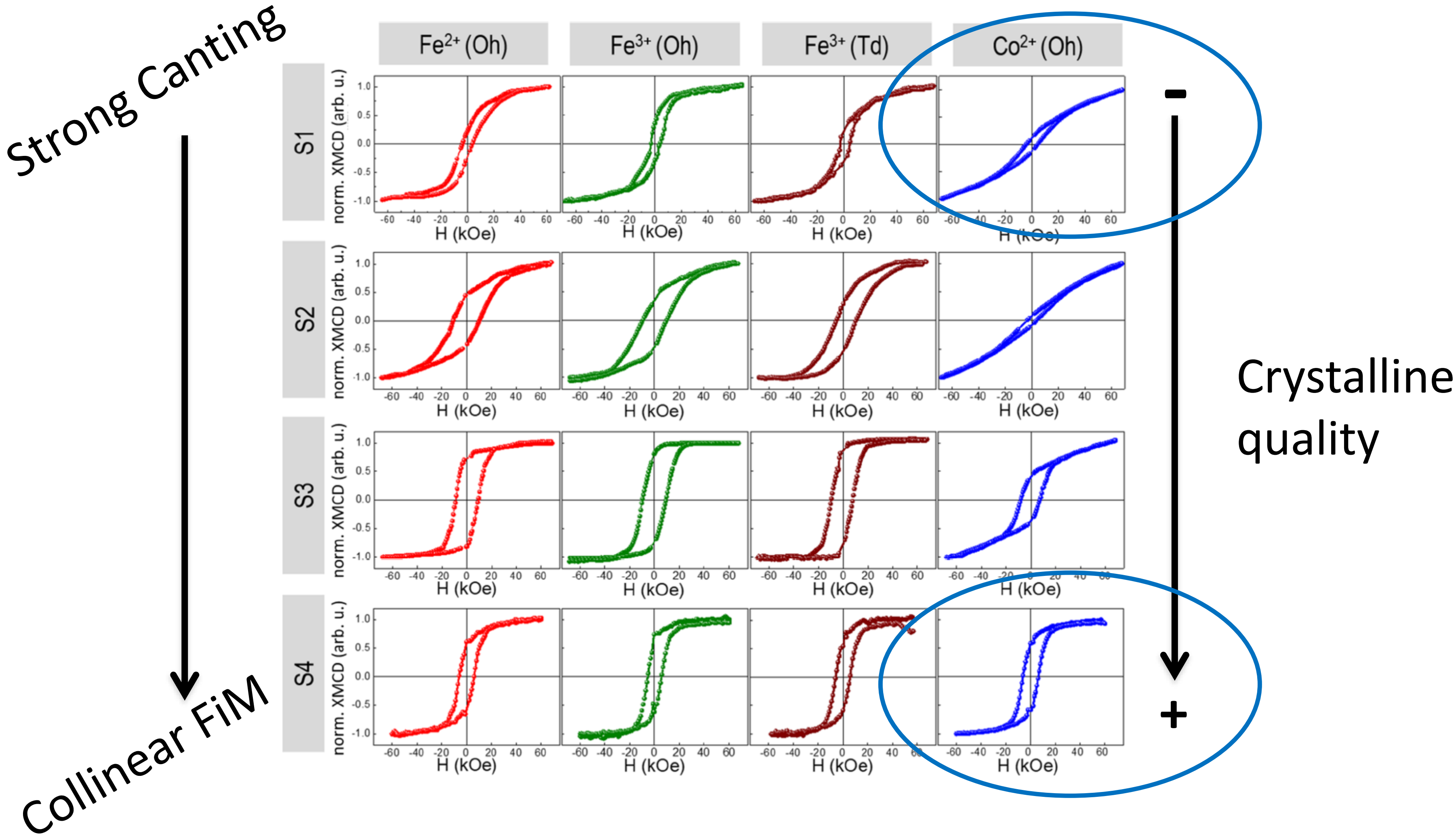
XAS & XMCD measurements

XAS and XMCD at the Fe $L_{2,3}$ edges (2p-3d transitions)

XMCD spectra: Difference between two absorption spectra (XAS) obtained with opposite circular polarizations (helicity).

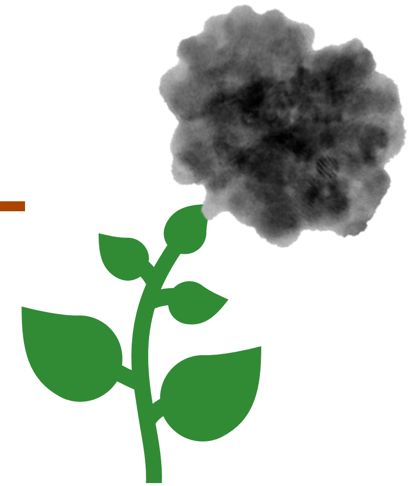
XMCD signal: proportional to the projection of the net magnetization of the absorbing atoms onto the beam propagation direction.



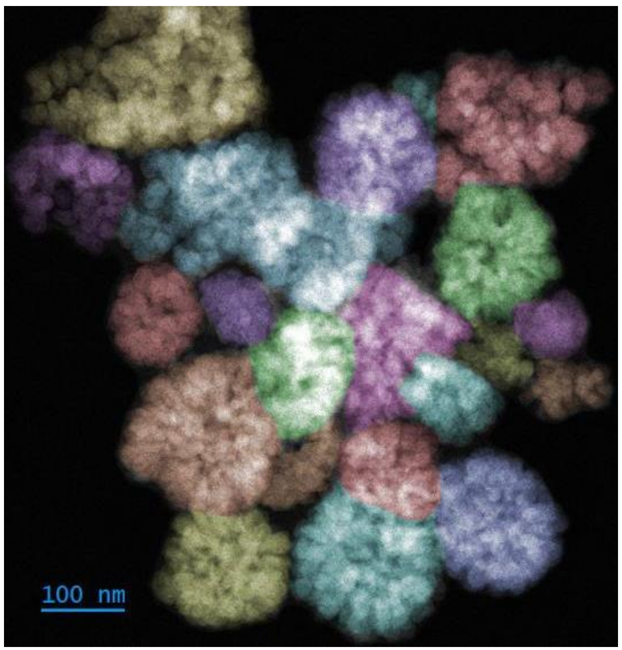


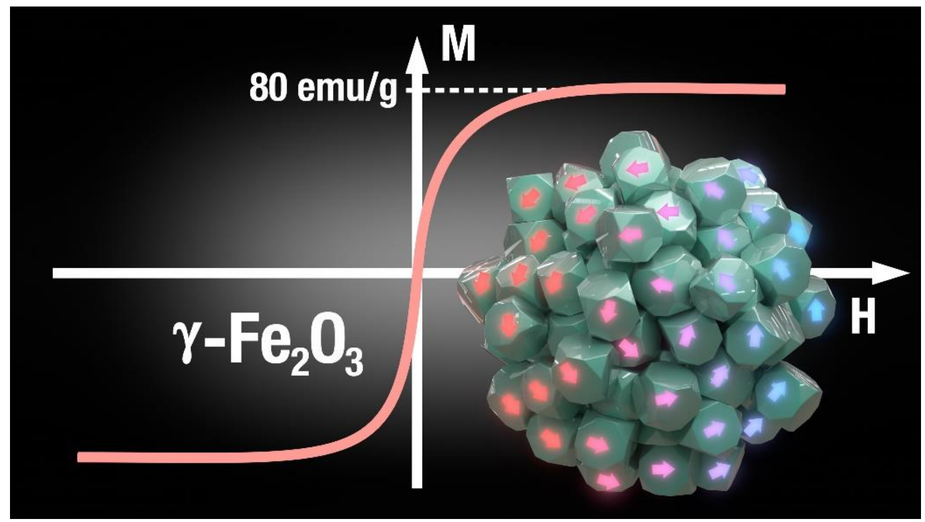
Strong Canting
Collinear FiM
Fe2+ (Oh)
Fe3+ (Oh)
Fe3+ (Td)
Co2+ (Oh)
S1
S2
S3
S4
norm. XMCD (arb. u.)
H (kOe)
-
+
Crystalline quality

Third example: Iron oxide nanoflowers (IONF)



- 3D crystal and spin texture in multicore γ-Fe_2O_3 NP



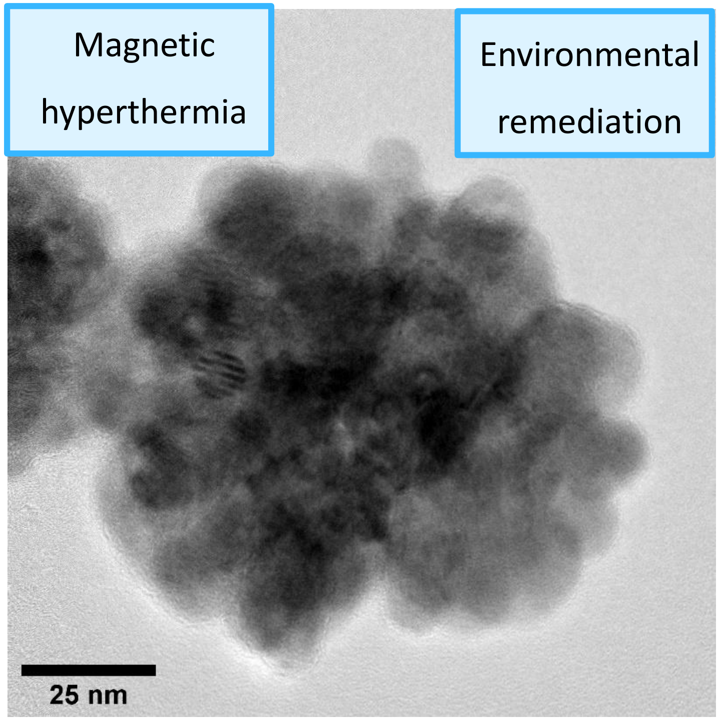


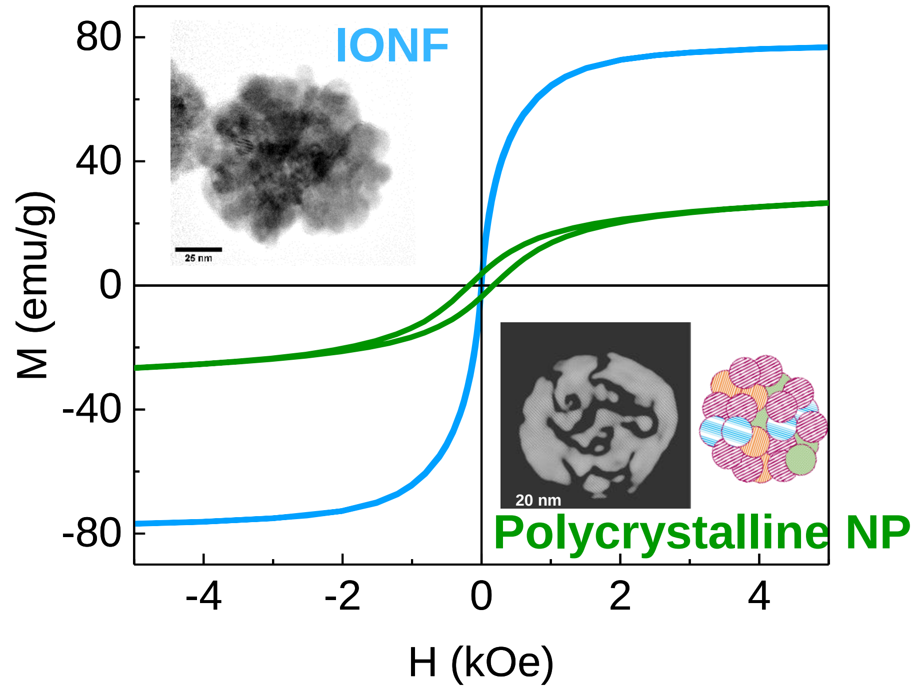
Materials for Medicine and Biotechnology Group (MaMBIO)

Gallo-Cordova, A. *et al. J. Clean. Prod.* **308**, 127385 (2021).

C. Moya *et al.,* Nanoscale 16, 1942 (2024)

Iron oxide nanoflowers: 3D texture in multicore γ-Fe_2O_3 NP



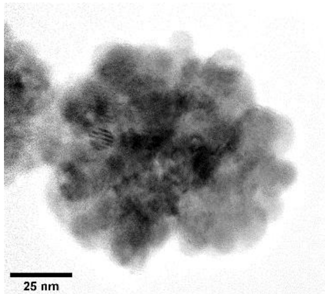


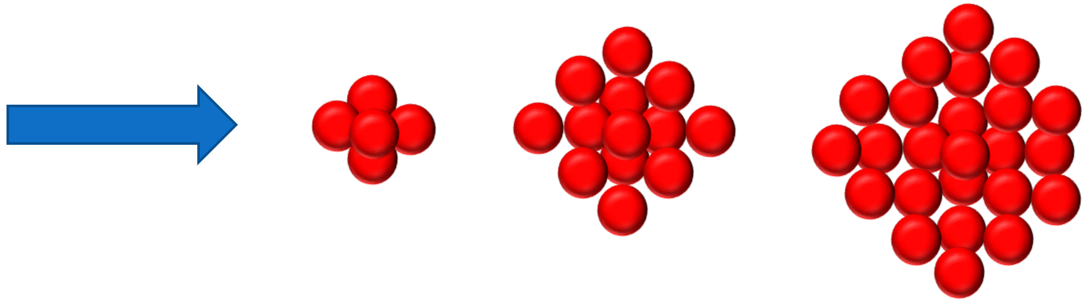
Origin of the 3D spin texture:

- 3D crystallographic correlations expanding beyond the core
- Leading to exchange coupling among the cores
- Resulting in *effective* superparamagnetic behaviour of the whole aggregate (*supra-ferromagnetism*)

C. Moya *et al.*, Nanoscale 16, 1942 (2024)

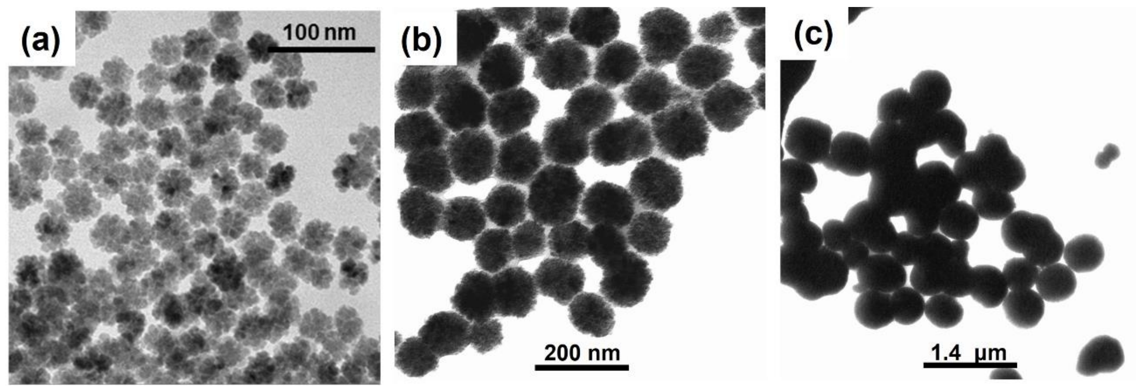
Synthesis method: From 40nm to 400 nm nanoflowers

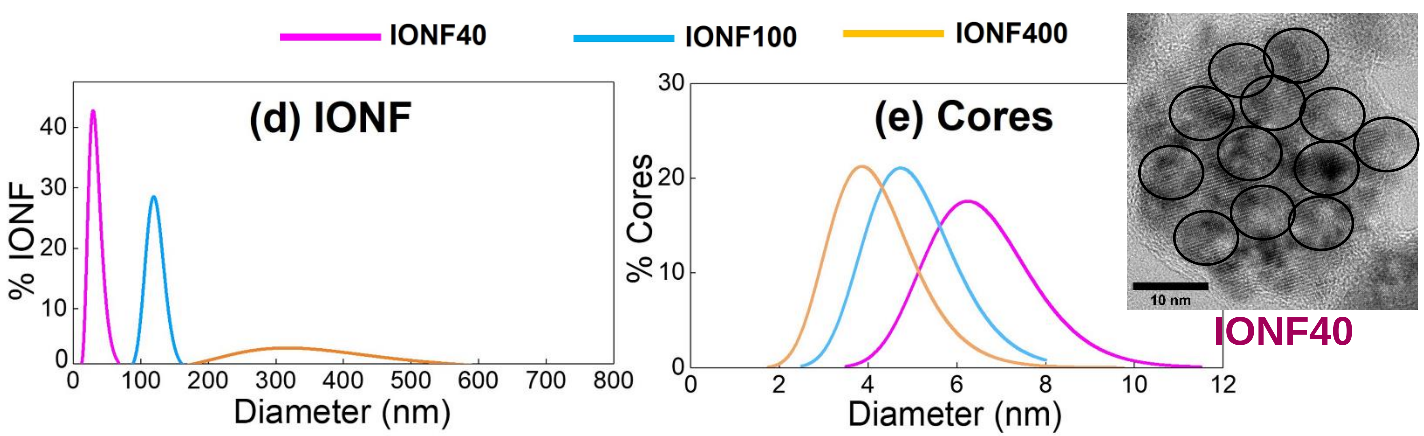




Materials for Medicine and Biotechnology Group (MaMBIO)

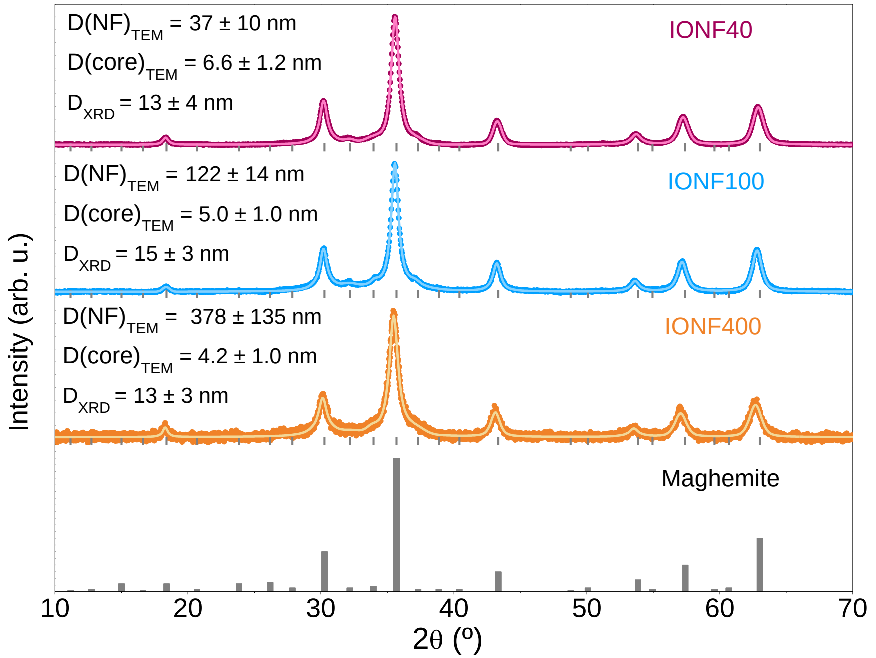
Gallo-Cordova, A. *et al. J. Clean. Prod.* **308**, 127385 (2021).



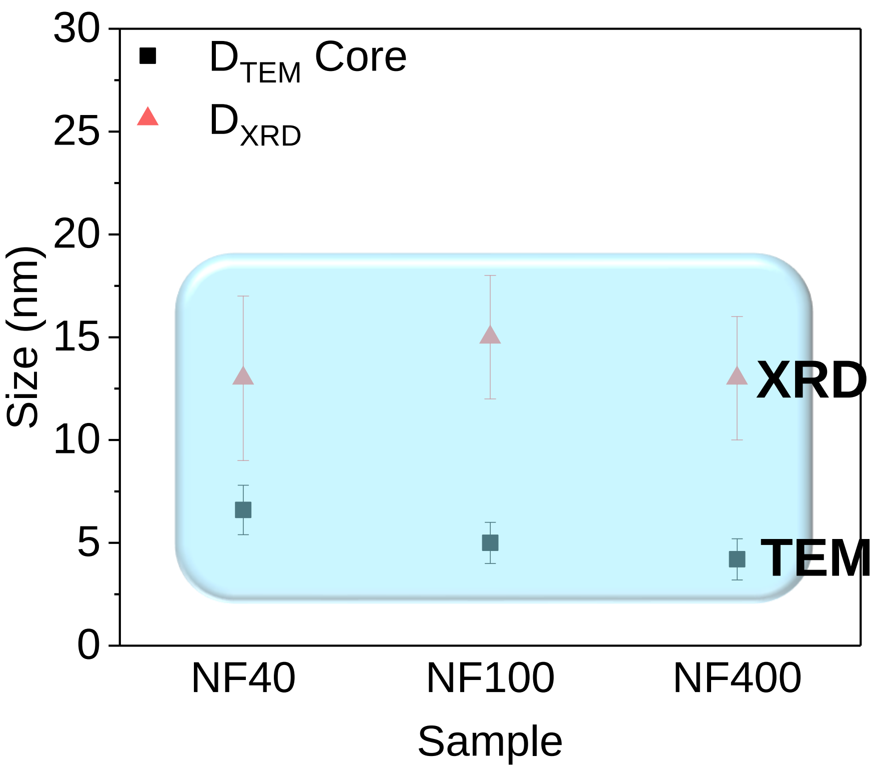


Structural features

XRD spectra

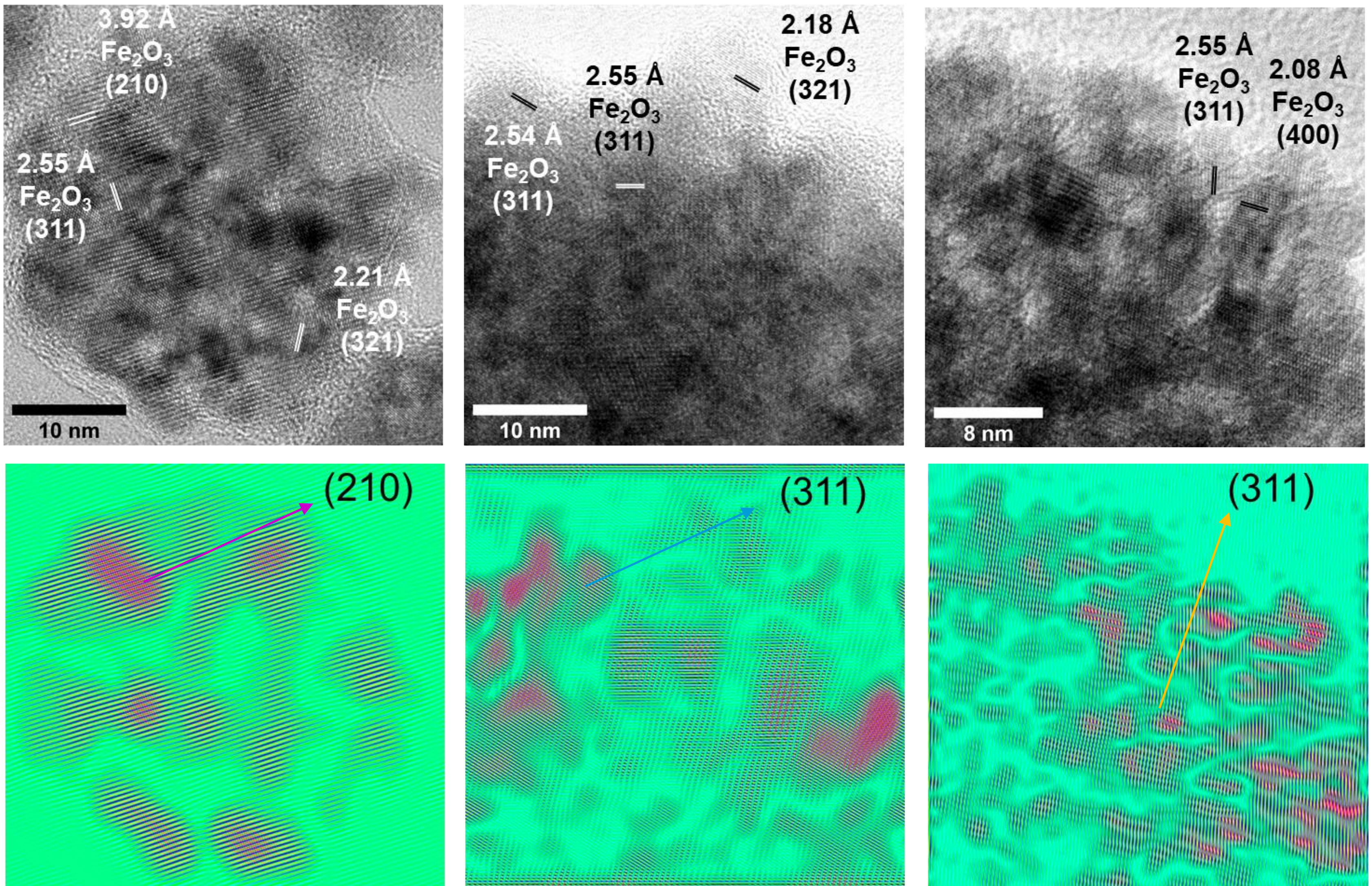


Crystal size (XRD) well above twice the core (petal) size (TEM)



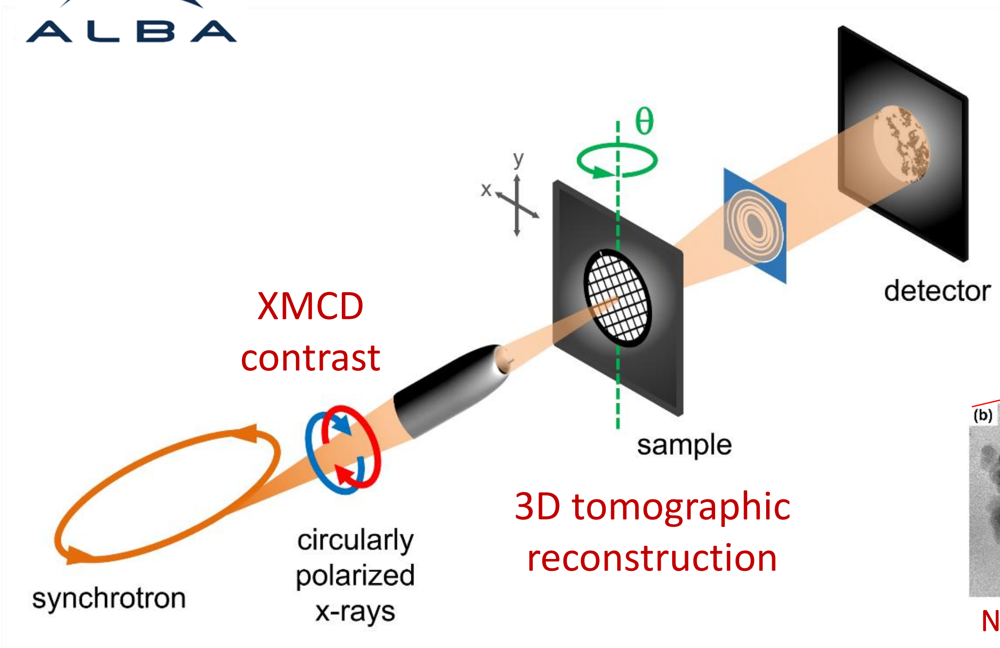
Structural features

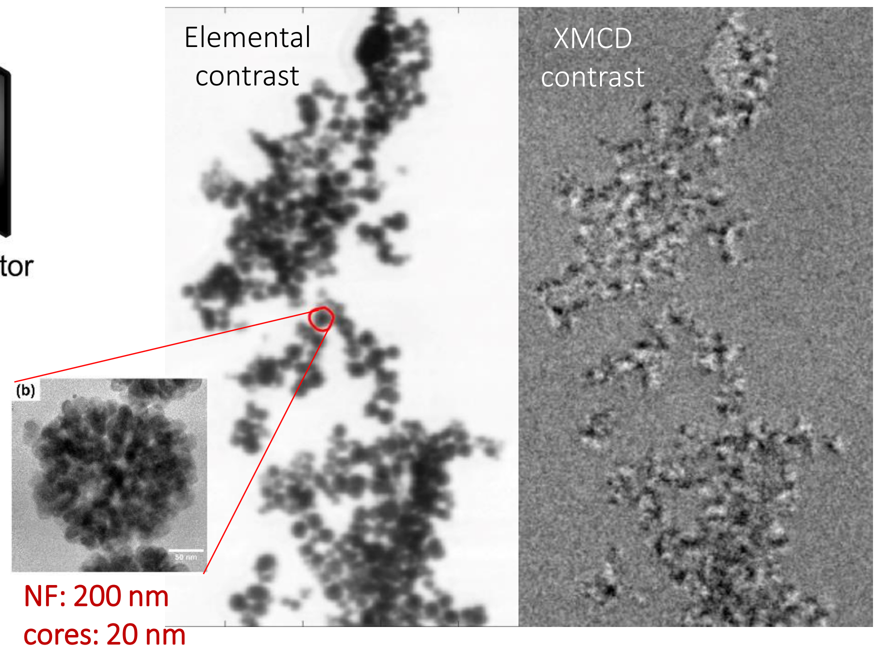
IONF40 IONF100 IONF400



Spin texture of individual IONF

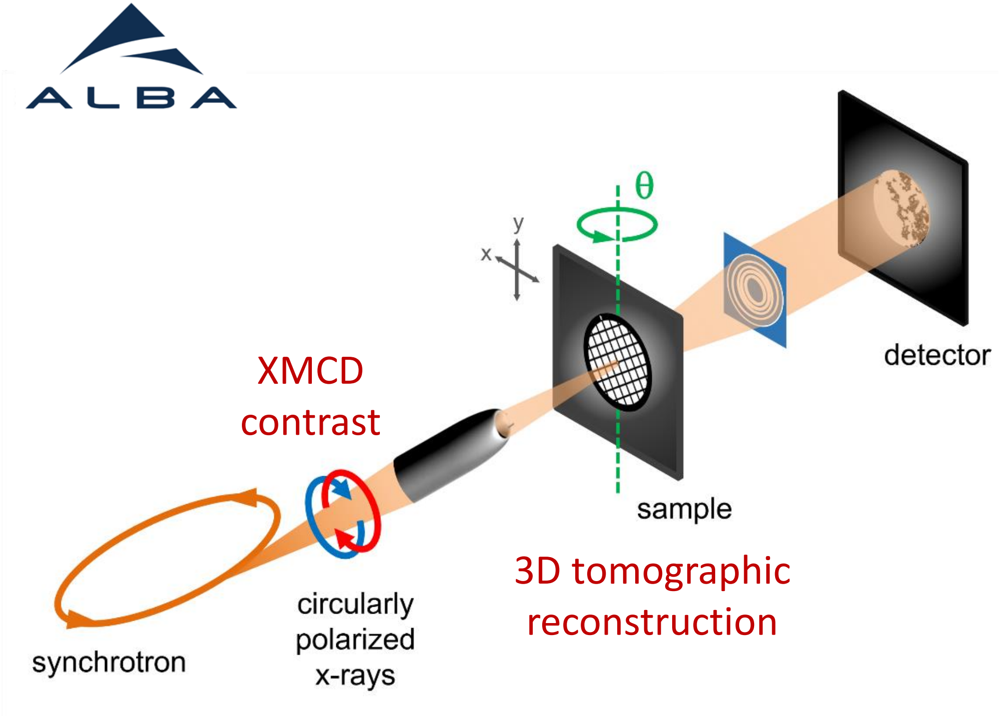
Magnetic Transmission X-ray Microscopy (M-TXM)

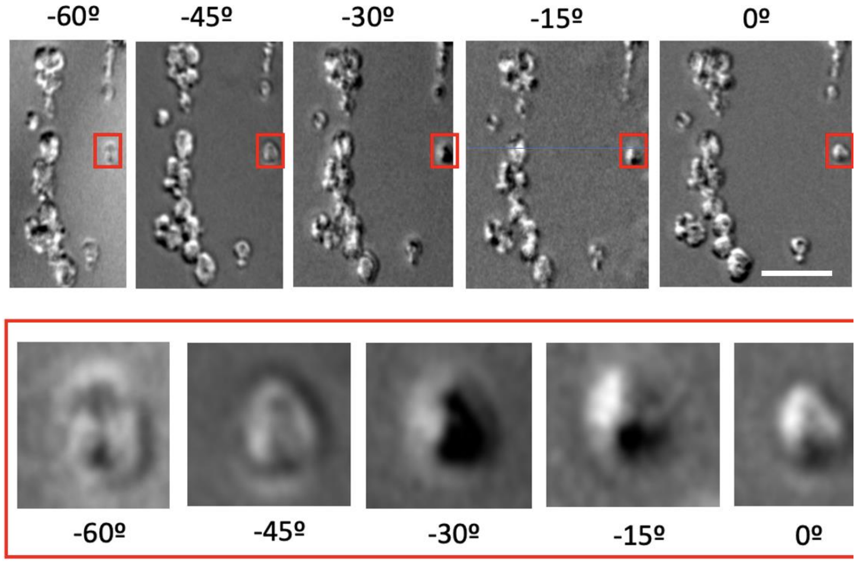




Spin texture of individual IONF

Magnetic Transmission X-ray Microscopy (M-TXM)



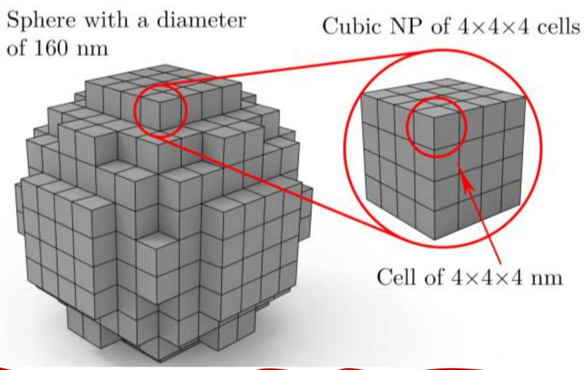


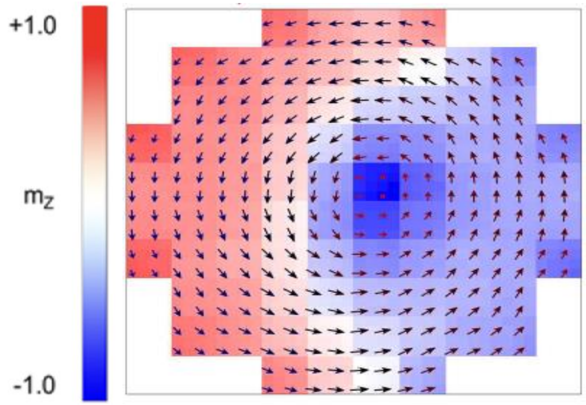
Statistical analysis <u>up to several tens of</u> individual IONF

C. Moya *et al.*, Nanoscale 16, 1942 (2024)

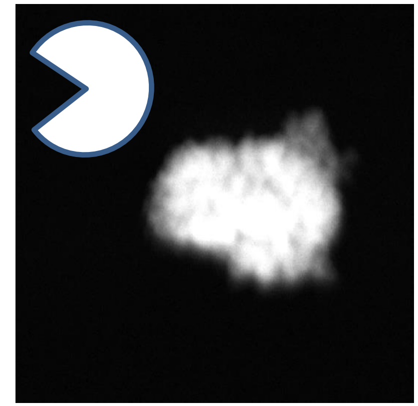
3D Tomographic reconstruction of the spin texture

OOMMF simulations

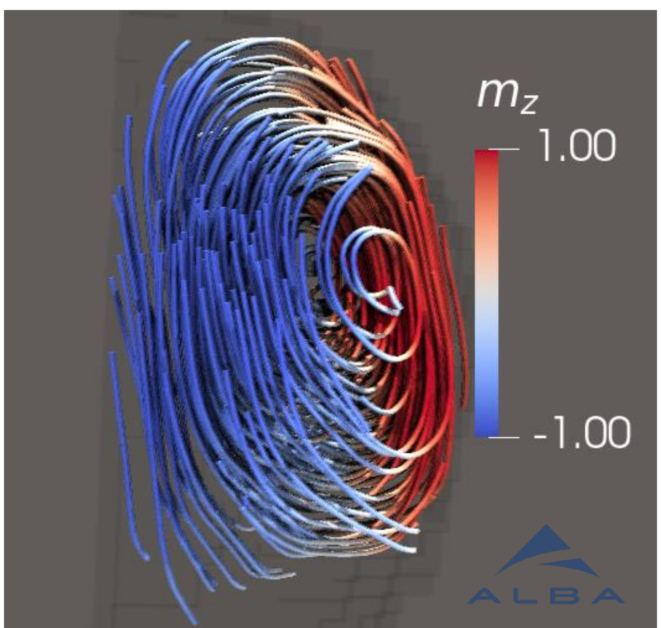


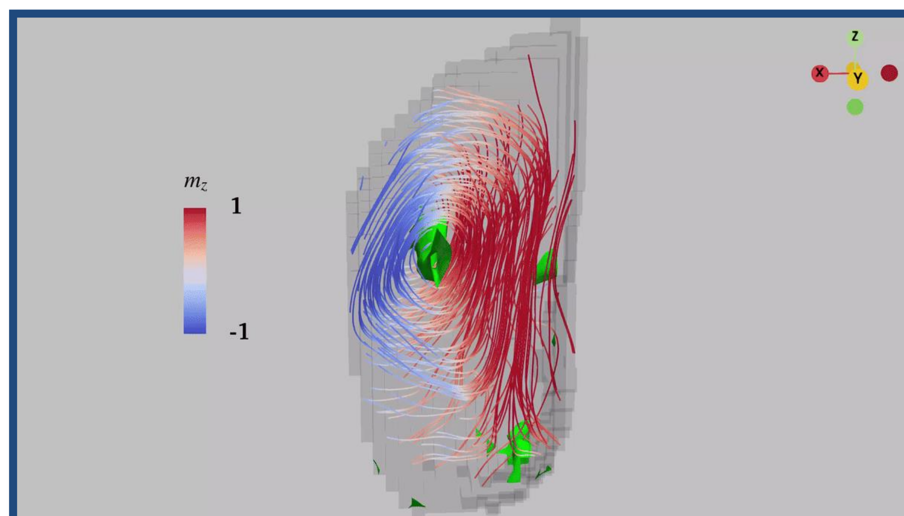


Electron microscopy Tomogram



X-ray microscopy Tomogram





Work in collaboration with Estela Herguedas and Aurelio Hierro-Rodríguez (Universidad Oviedo, Spain)

Conclusions: From the outside to the inside!

- **(Nano)structure sets function: The magnetic nanoparticle iceberg**
  - ✓ The quality of the crystalline structure determines physical properties.
  - ✓ Control nanostructuring and use of complementary advanced correlative, single-particle, (subnanometer) microscopic analysis (XAS, XMCD, PEEM, TMX, EELS, EMCD,..) picks up hidden features at different length scales.

- **Single domain nanoparticles:**
  - ✓ Magnetic NP larger than a few nm with high crystalline quality show bulk-like properties.
  - ✓ Magnetic NP with increasing defective structure show progressive worsening of the magnetic performance due to the frozen magnetic disorder.

- **Multi-core iron oxide nanoflowers:**
  - ✓ Crystalline correlations extending beyond the core determine 3D spin textures with high vorticity, leading to an *effective* superparamagnetic behavior (*supra-ferromagnetism*)