^{57}Fe Mössbauer spectrometry applied to magnetic nanostructures

J.M. Greneche

IMMM
Institut des Molécules et Matériaux du Mans

Le Mans Université

UMR CNRS 6283

Université du Maine, 72085 Le Mans Cedex 9, France

E-Mail : jean-marc.greneche@univ-lemans.fr

Universidad Nacional de Ingeniería

NATIONAL UNIVERSITY OF ENGINEERING, FACULTY OF SCIENCES, LIMA, PERU

XIX Meeting of Physics

24th-26th September 2020

ANIVERSARIO 1960 - 2020 FACULTAD DE CIENCIAS

Magnetic NPs applied in medicine

Targeted Drug Delivery

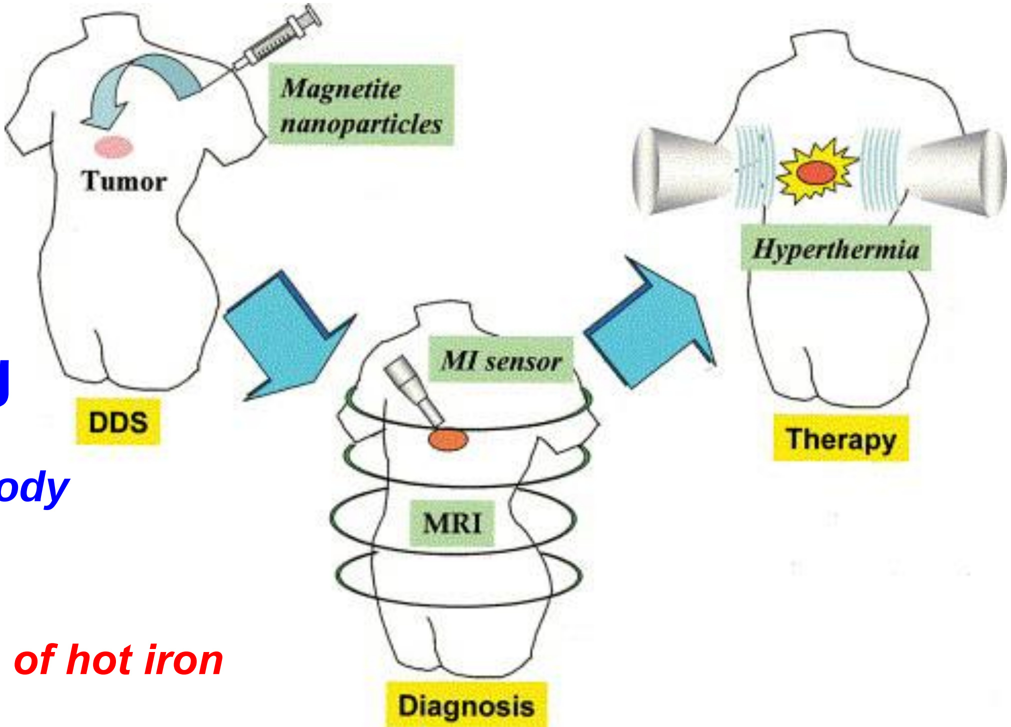
1891: Paul Ehrlich paradigm of drug Delivery; Transport of drugs appropriate concentration to the appropriate place in the appropriate time.

Magnetic Resonance Imaging

Non-invasive tomographic technique diagnostics: cross sections of the patient body

Magnetic Hyperthermia

Hippocrates "Father of Medicine" by means of hot iron



A. Ito, M . Shinkai, H. Honda,T. Kobayashi, Journal of Bioscience and Bioengineering, 100 (2005)

NPs ?: Size comparable to the dimensions of proteins (5 - 50 nm) or viruses (20 – 450 nm)

"NPs can act at the cellular and molecular level"

Theranostics and individual drug concept

Nanosciences and nanotechnology

Atomic scale analysis with local probe techniques

Magnetic Materials ?

Magnetic Energy

=

Exchange

+

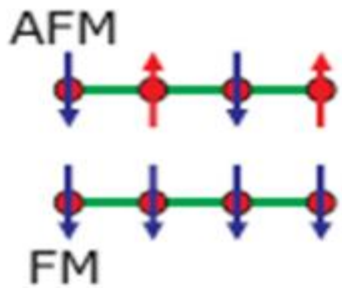
Anisotropy

+

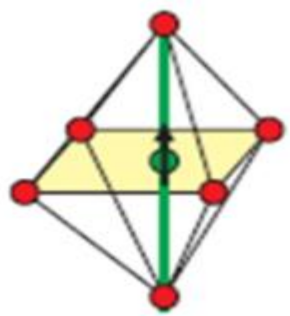
Dipolar

+

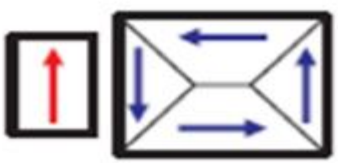
Zeeman



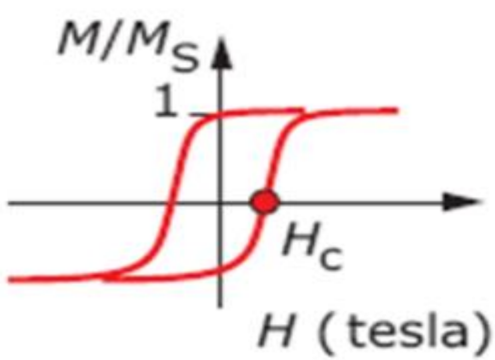
Magnetic moments
Magnetic order
Phase transitions
Mean field theory
Exchange interaction



Crystalline/Amorphous structure
Spin-orbit coupling
Magnetocrystalline anisotropy
Local anisotropy
Shape anisotropy

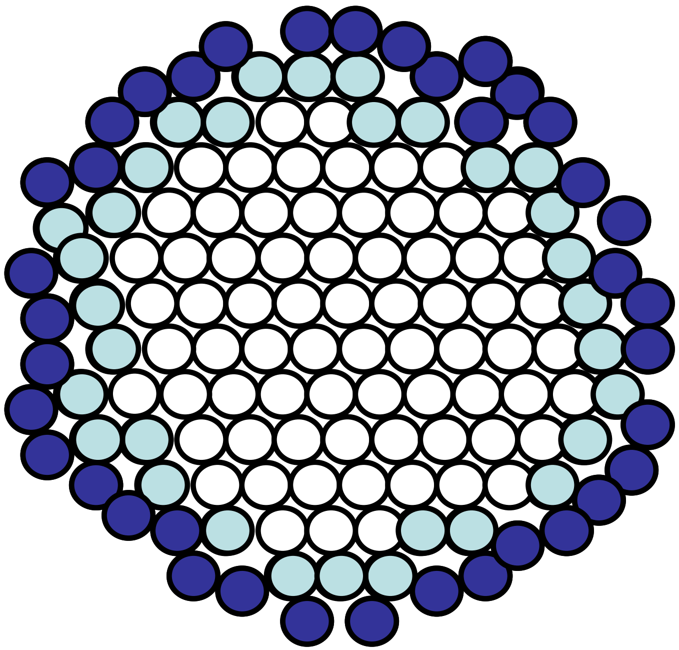


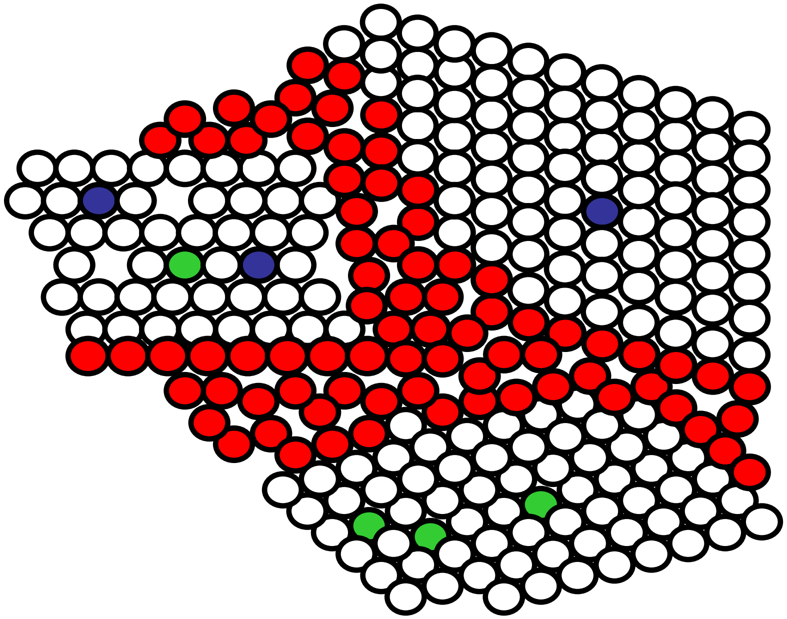
Long distance dipolar interaction
Magnetic domain
Bloch/Néel magnetic wall

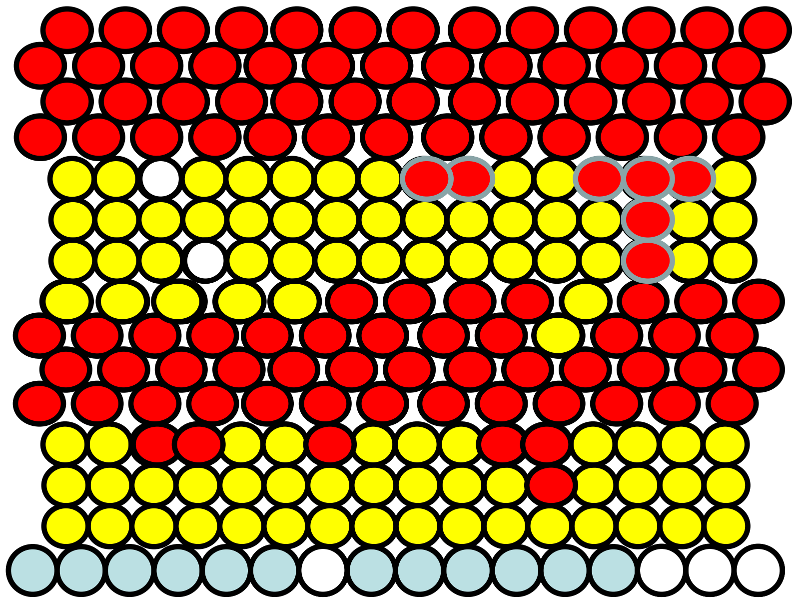


Hysteresis loop
Hard/soft Magnetic Material
Coercive field
Saturation magnetization
Remnant magnetic field

Nanostructures: Main Characteristics







Magnetic NanoMaterials ?

Magnetic moments
Magnetic order
Phase transitions
Mean field theory
Exchange interaction

Crystalline/Amorphous structure
Spin-orbit coupling
Magnetocrystalline anisotropy
Local anisotropy
Shape anisotropy

Dipolar interaction
Magnetic domain
Bloch/Néel magnetic wall

Hysteresis loop
Hard/soft Magnetic Material
Coercive field
Saturation magnetization
Remnant magnetic field

Surface/volume effect
Crystalline/amorphous structure
Surface structure
Exchange interactions
Magnetic frustration
Surface non colinear magnetic order

Surface anisotropy
Interface anisotropy

Single domain nanoparticle

Non/weak/strong interacting nanoparticles
Superparamagnetic relaxation phenomena

Competition Boltzmann/relaxation phenomena
Field cooling and zero-field cooling (FC-ZFC)
Reduction of coercive field
Saturation magnetization ?
Exchange bias

Tunelling effects – quantum description

Nanostructures: Examples

- ❖ Co-ferrite NPs
- ❖ Magnetite
- ❖ In-field MS
- ❖ Magnetic surface?
- ❖ Functionalized NPs
- ❖ Growth process
- ❖ Hollow γ-Fe_2O_3 NPs
- ❖ Surface anisotropies
- ❖ Core-shell-shell NPs

- ➢ Nanocrystalline alloys
- ➢ Ball milled Fe
- ➢ Ball milled FeNi alloys
- ➢ Ball milled ferric fluorides

- ○ Well controlled samples
- ○ Well characterized samples (X-ray, EXAFS, TEM, magnetic measurements, XMCD, …)

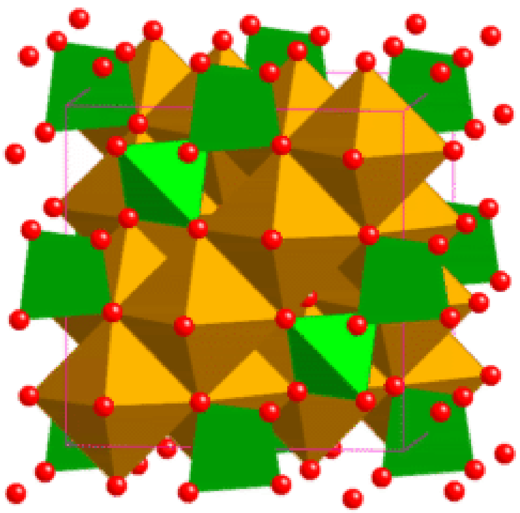
- ○ Contribution of zero-field and in-field
- ○ Mössbauer spectrometry
- ○ Input of computer modelling (Monte Carlo, *ab initio*, Molecular dynamics, …)

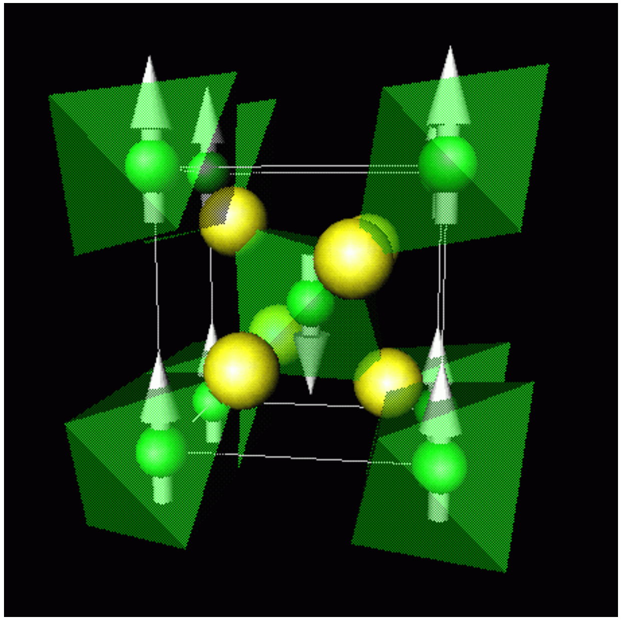
Ferrites: Spinel structure

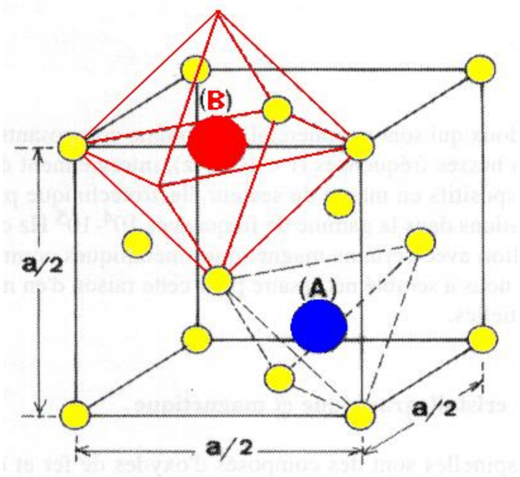
derived from $MgAl_2O_4$ $A^{2+}B^{3+}O_4$

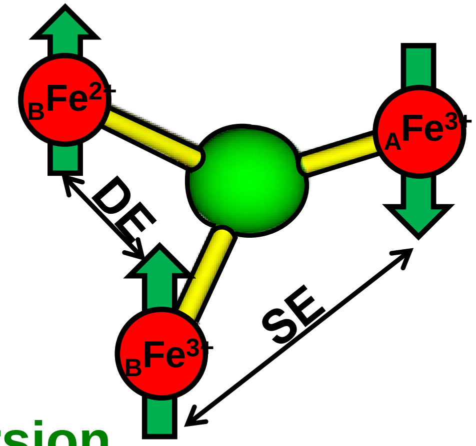
FCC structure with 16 octahedral B sites and

8 tetrahedral B sites







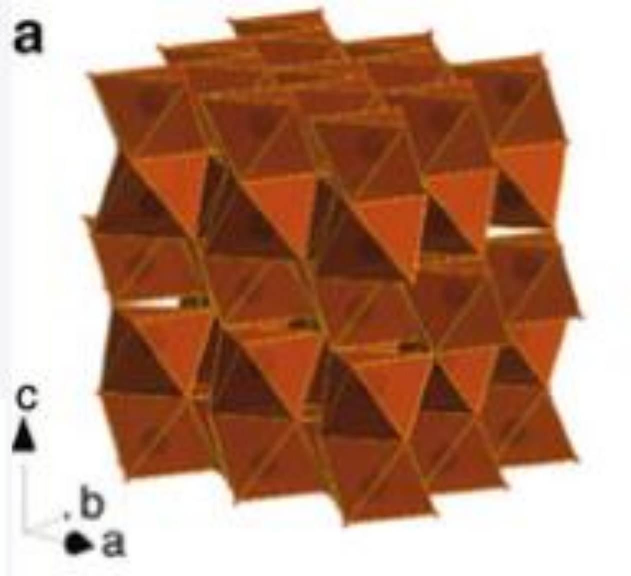


Magnetic behaviour ⇔ cationic distribution

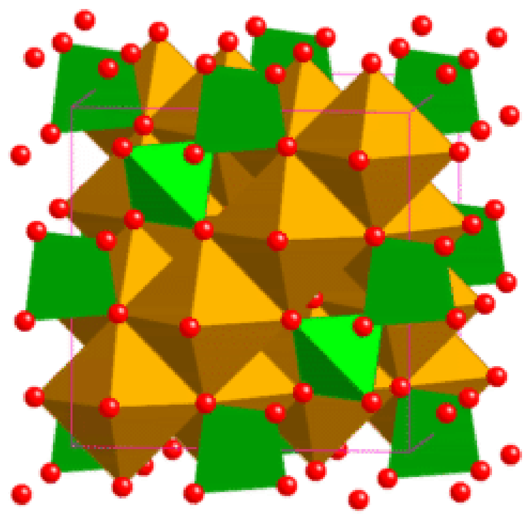
Magnetic frustration, spin-glass like, cationic inversion, reversed spins, …!

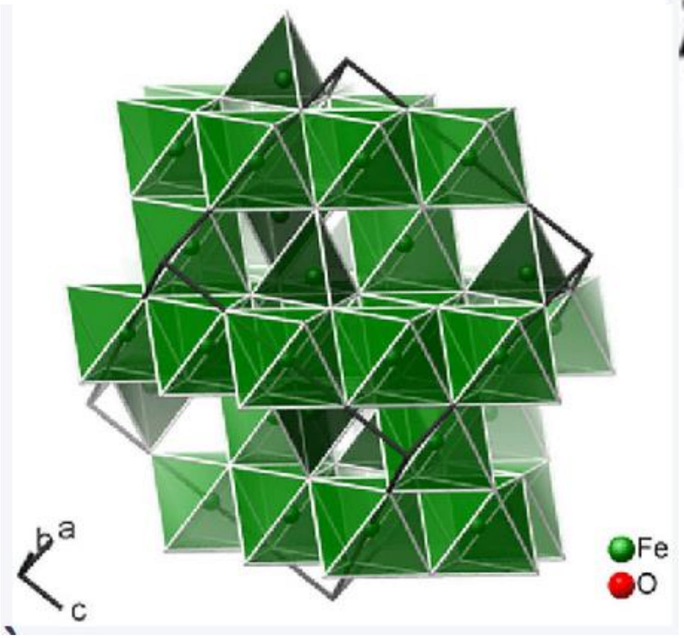
Some Iron Oxide crystalline phases

α-Fe_2O_3
T_N = 948 K, AF
Fe^{3+} Octa

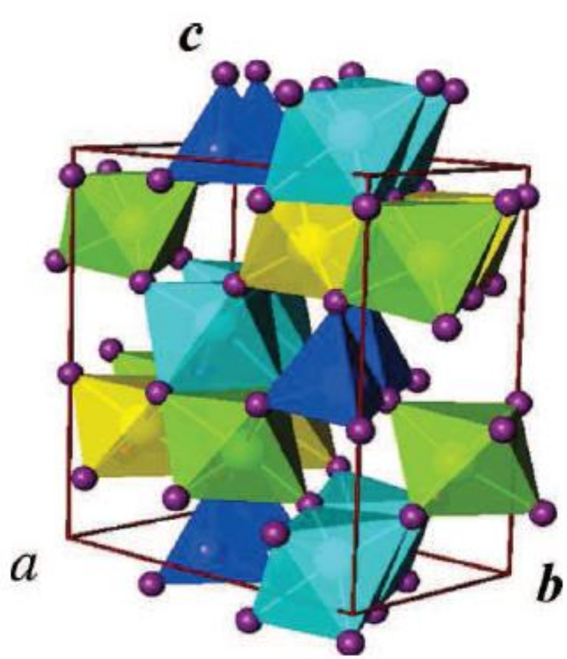


Fe_3O_4
T_c= 850 K, Fi
Fe^{2+} and Fe^{3+}
Tetra and Octa



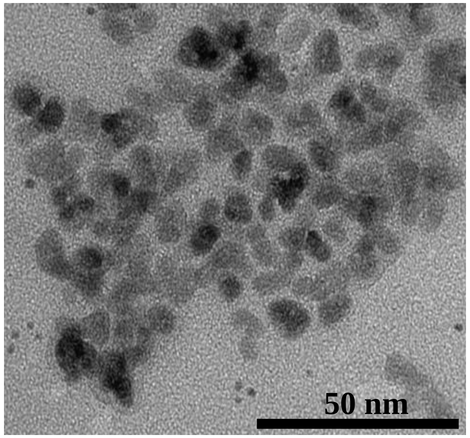


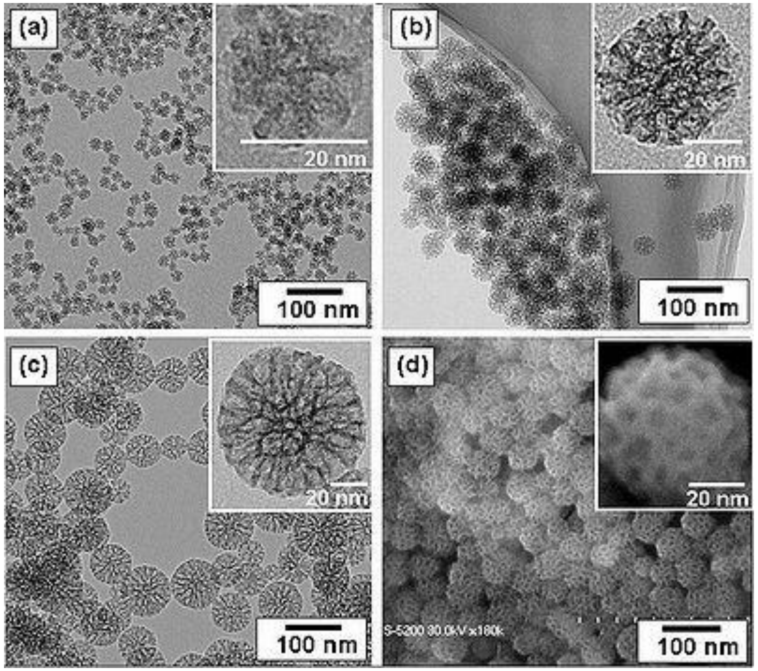
γ-Fe_2O_3
T_c= 950 K, Fi
Fe^{3+} Octa and Tetra

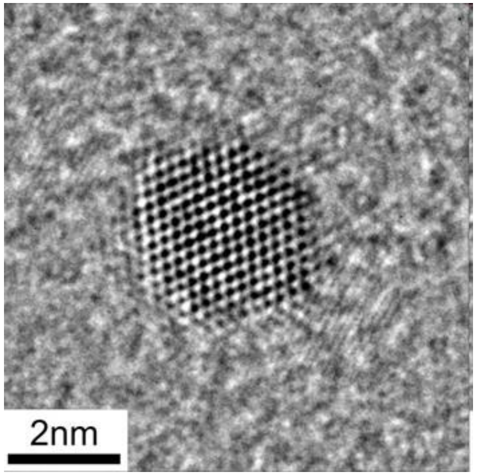


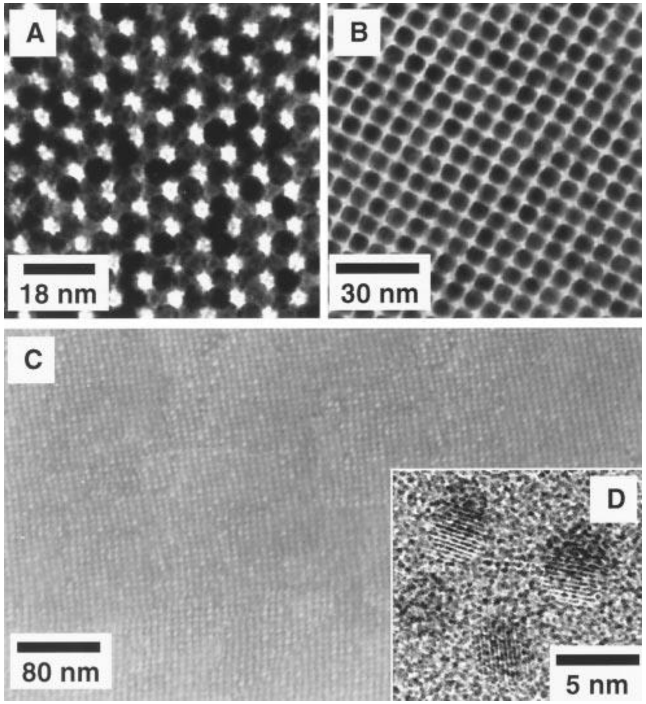
ε-Fe_2O_3
T_c = 485 K
complex structure
with Fe^{3+} T and O

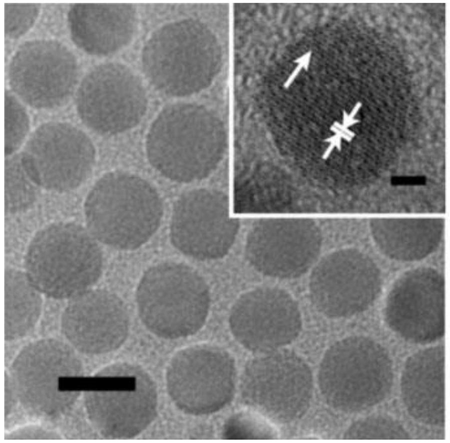
Nanoparticles: size? Morphology? Core-shell? Aggregates towards superlattice!

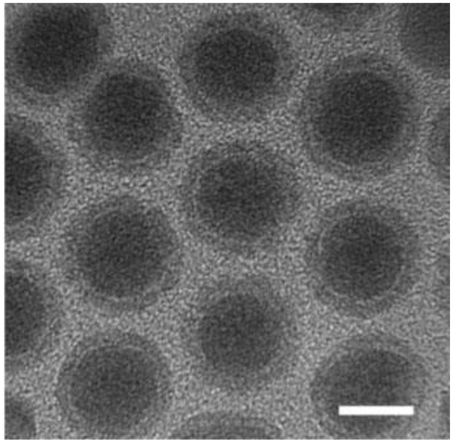




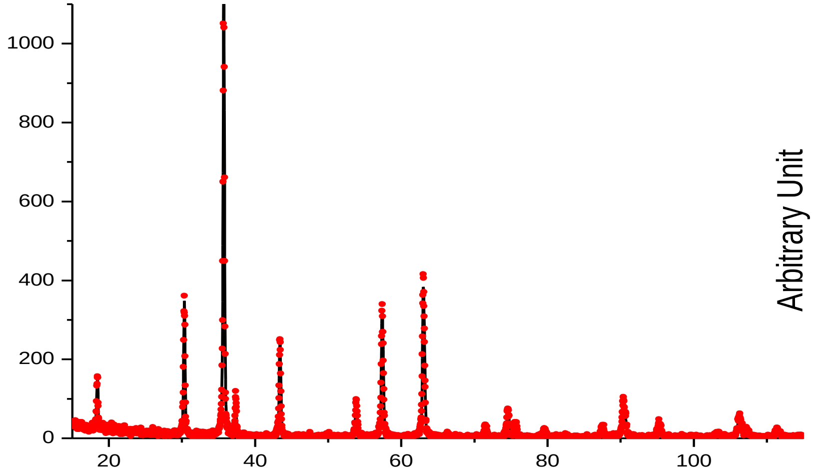


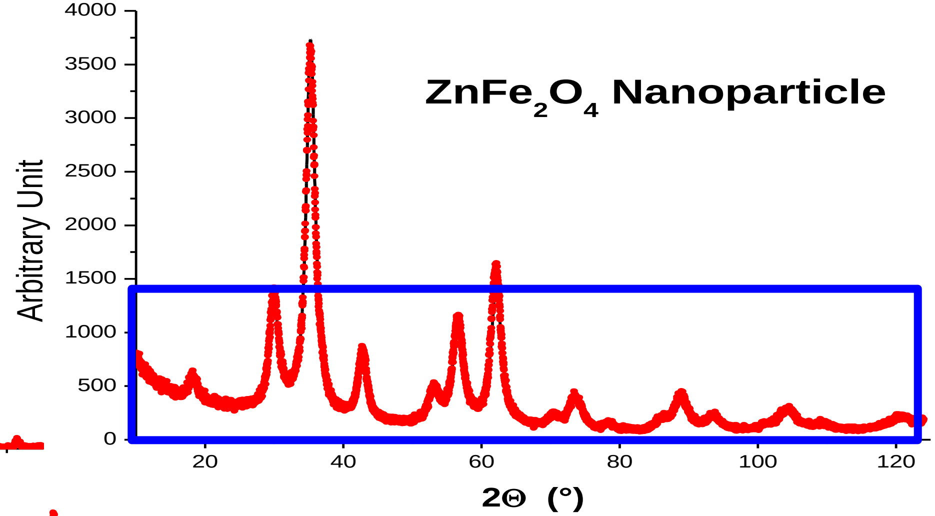


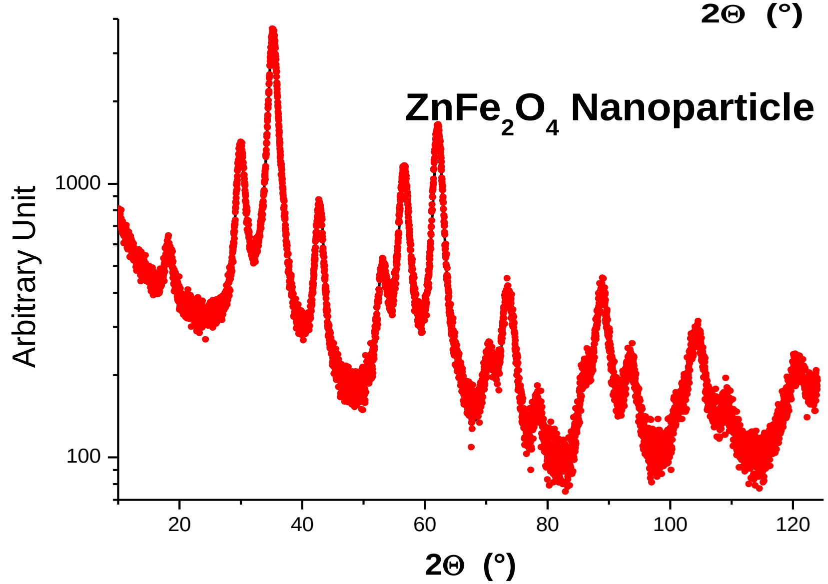




X-ray Diffraction



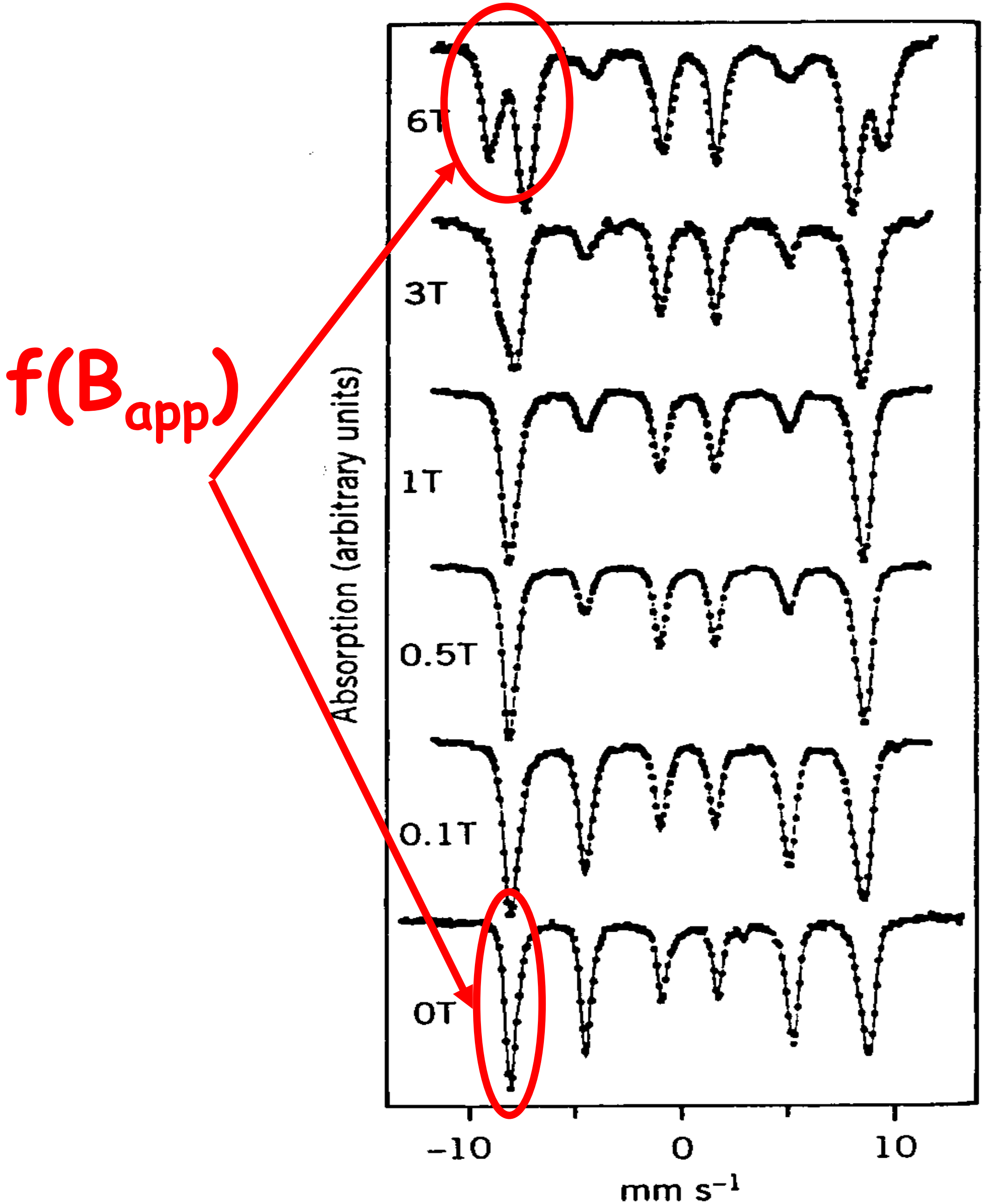


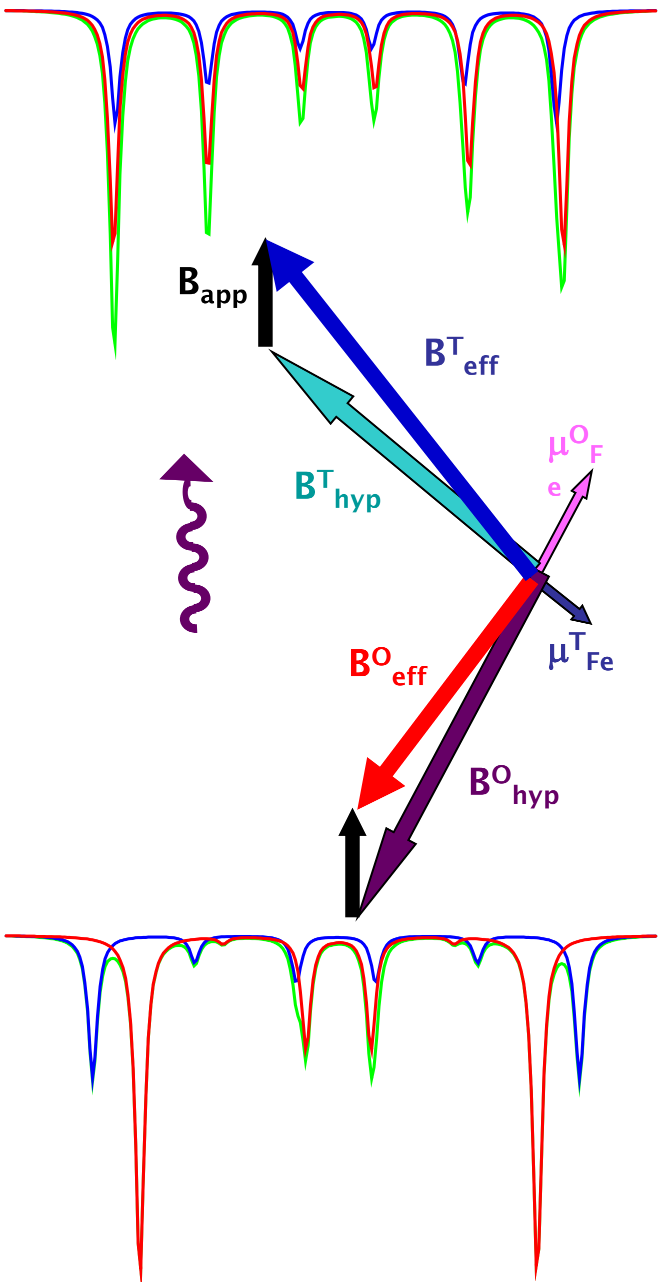


<a>, <b>, <c>, … and <d> ***(coherent diffraction domain)***

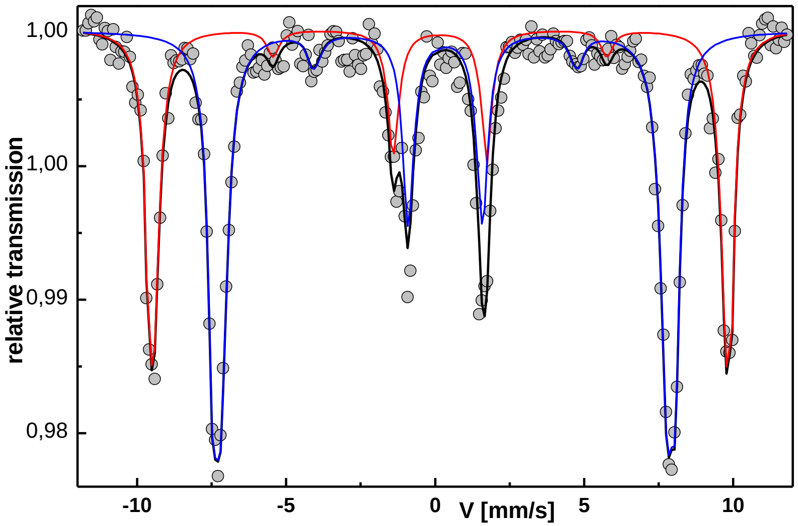
$\langle d_{nanoparticles} \rangle = 12.4386 \pm 0.0045$ nm

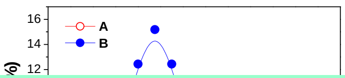
In-field ^{57}Fe Mössbauer *versus* Field of Fi

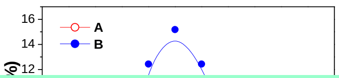




Chemical Homogeneity in $CoFe_2O_4$ NPs ?







Chemical Homogeneity

Chemical gradient of Fe and Co

Co-rich Core/Fe-rich shell

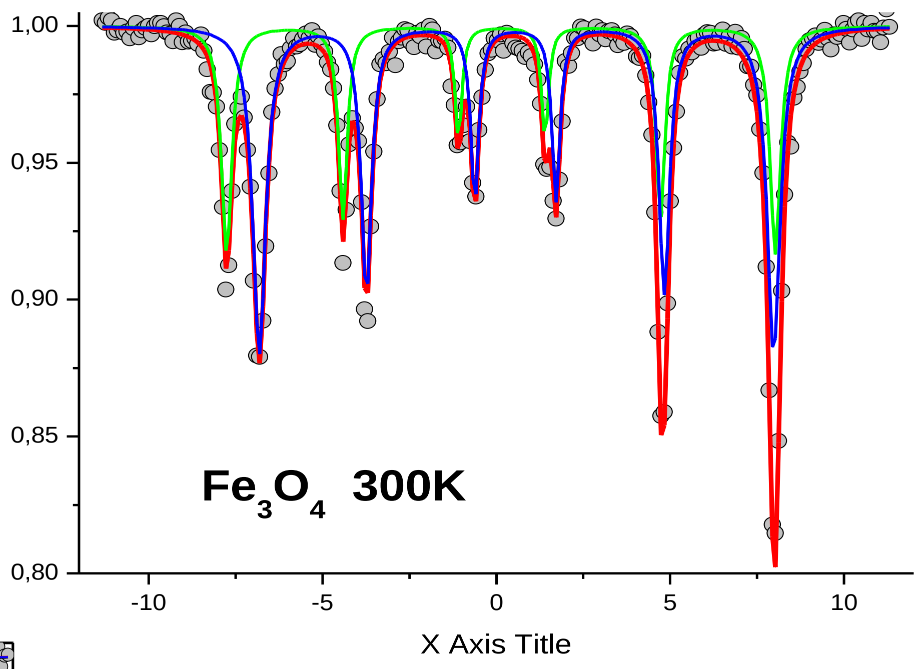
But also in other Ferrites, FePt, FeRh, …

D Peddis, N Yaacoub, M Ferretti, A Martinelli, G Piccaluga, A Musinu, C Cannas, G Navarra, J M Greneche and D Fiorani, *J. Physics: Condens. Matter 23 (2011) 426004*

M. Artus, L. Ben Tahar, F. Herbst, L. Smiri, F. Villain, N. Yaacoub, J.M. Grenèche, S Ammar and F. Fiévet, *J. Physics: Condens. Matter 23 (2011) 506001*

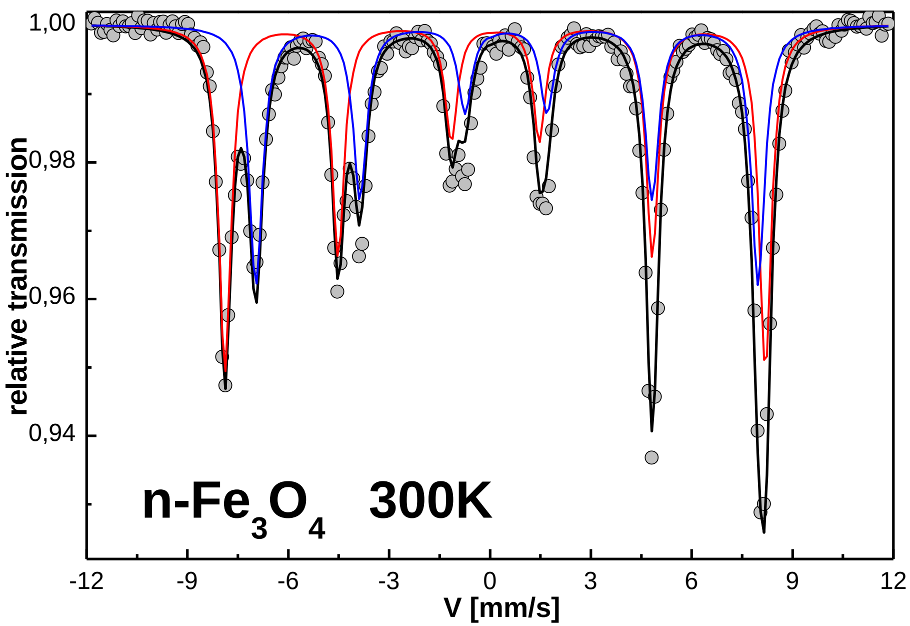
Single Phase Fe_3O_4 Nanoparticles ?

1/3 Tetra Fe^{3+} +
1/3 Octa Fe^{2+} +
1/3 Octa Fe^{3+}



1/3 Tetra Fe^{3+} +
2/3 Octa $Fe^{2.5+}$

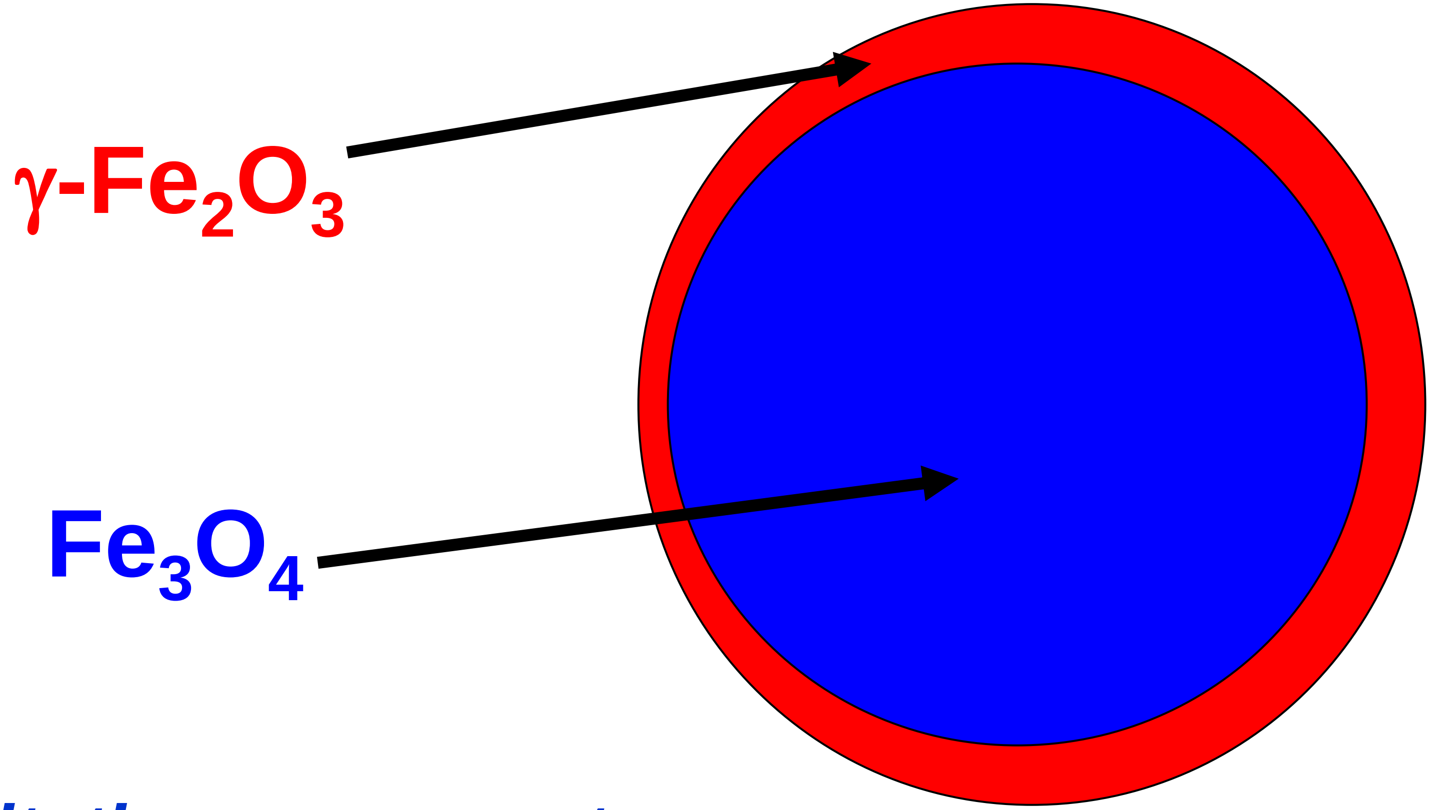
when $T>T_{Ver}$



~~**1/3 Tetra Fe^{3+} +**~~
~~**2/3 Octa $Fe^{2.5+}$**~~

~~**when $T>T_{Ver}$**~~

⇒ Core-Shell Structural Model



Qualitative agreement with EXAFS, XPS and magnetic measurements !

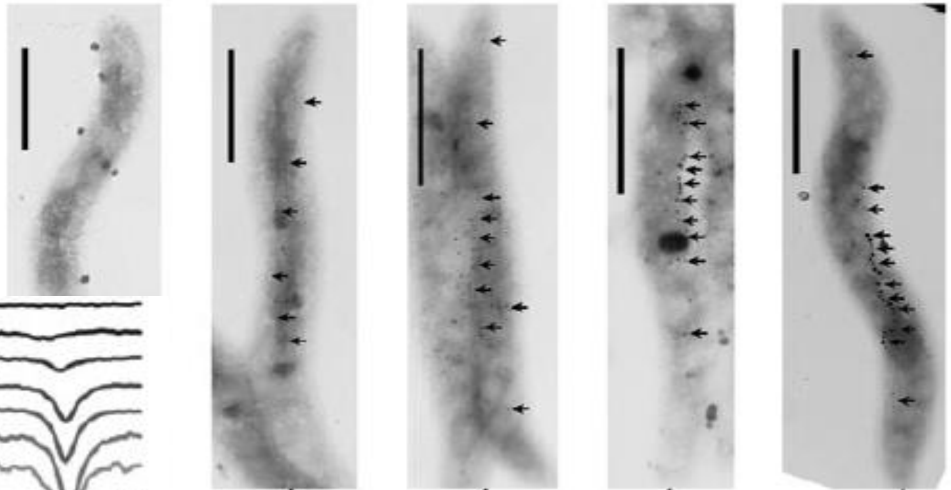
Ideal and Naïve view! Composition gradient from Fe_3O_4 to γ-Fe_2O_3

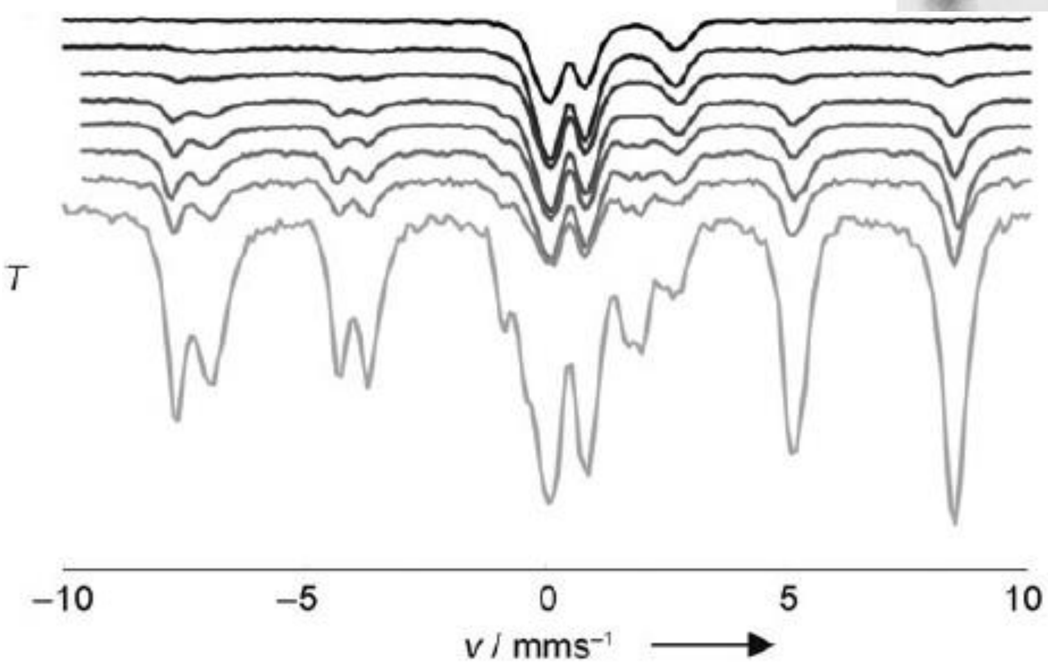
T. J. Daou, et al Chem. Mater. 2007, 19, 4494-4505

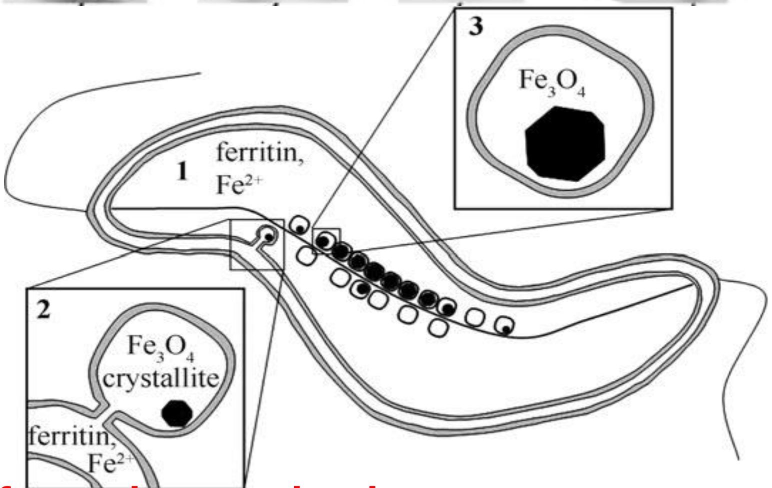
Biomineralization: NanoMagnetite!

Intracellular Magnetite Biomineralization in Bacteria

magnetosome formation after induction







Model of iron uptake and magnetite formation mechanism

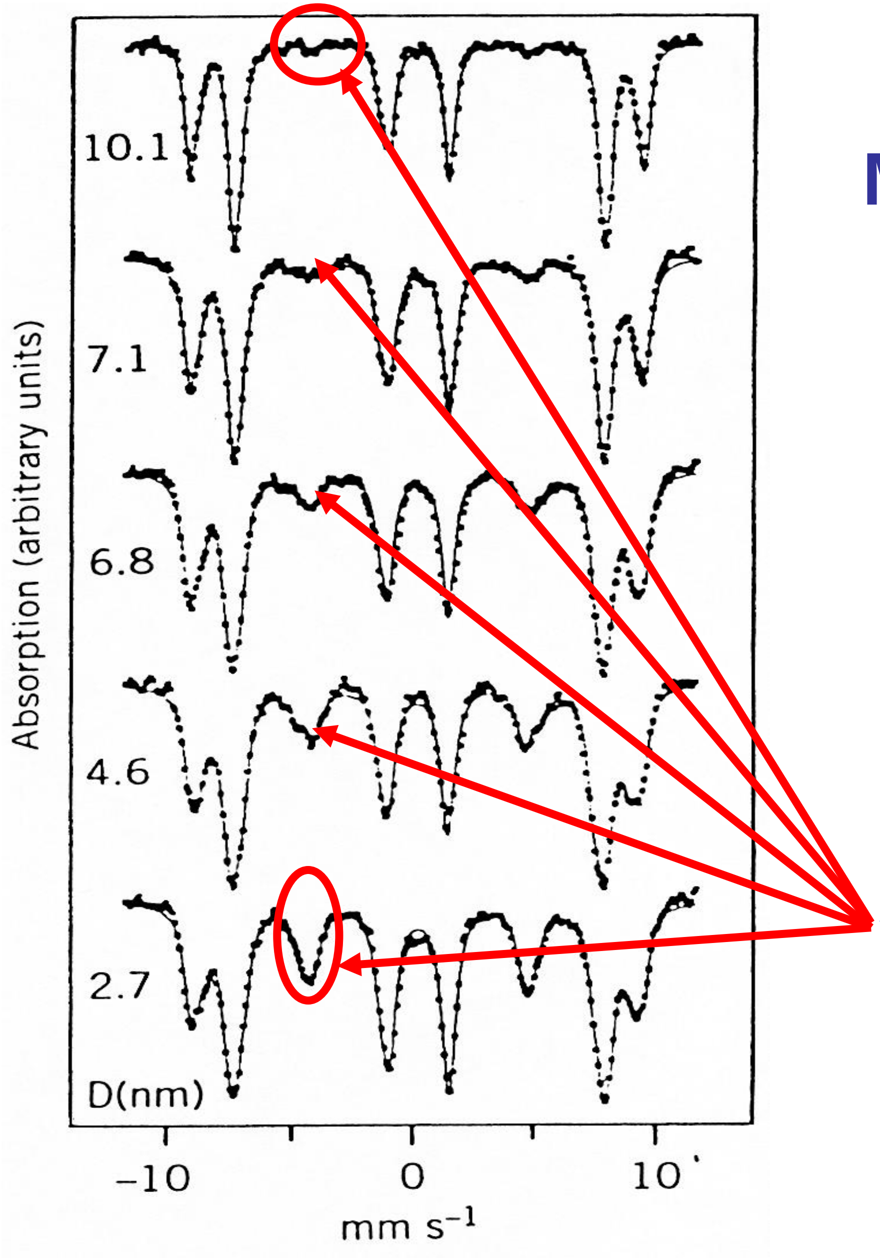
1 - biochemical pool of Fe is formed in cells, essentially of ferritin and Fe^{2+}

2 - transport of Fe^{2+} ions and ferritin into invaginated magnetosome vesicles where Fe^{2+}- Fe^{3+} ions coprecipitate

3- growth of magnetite to form mature magnetosomes

D. Faivre, L.H. Böttger, B.F. Matzanke, D. Schüler , Angew. Chem. Int. Ed. 2007, 46, 8495

In-field ^{57}Fe Mössbauer *versus* NP's size



Non-interacting Monodisperse Maghemite Nanoparticles:

HFMS

Canting angle increases when the size decreases:

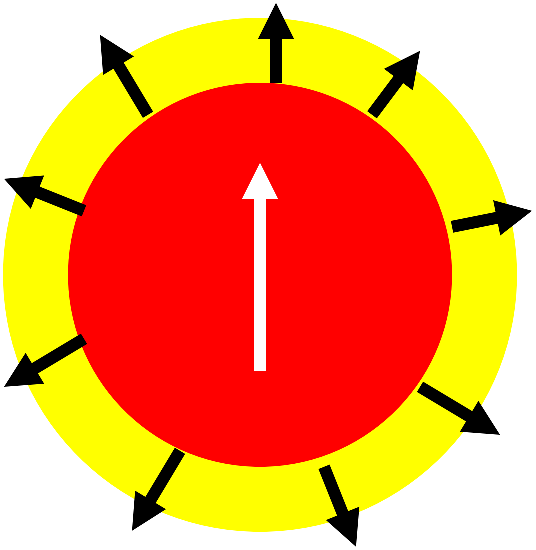
Surface Effects !

Core-Shell Magnetic Model

$$A_{2,5} = 1/2\,((1-q)\sin^2\Theta_{core} + q\sin^2\Theta_{shell})$$

$$= 1/2\,\sin^2\Theta \text{ (Mössbauer)}$$

with $q = 1-(1-e/r)^3$



$\Theta_{core} = 0$ (saturated) and $\Theta_{shell} = 54.7$ (random)

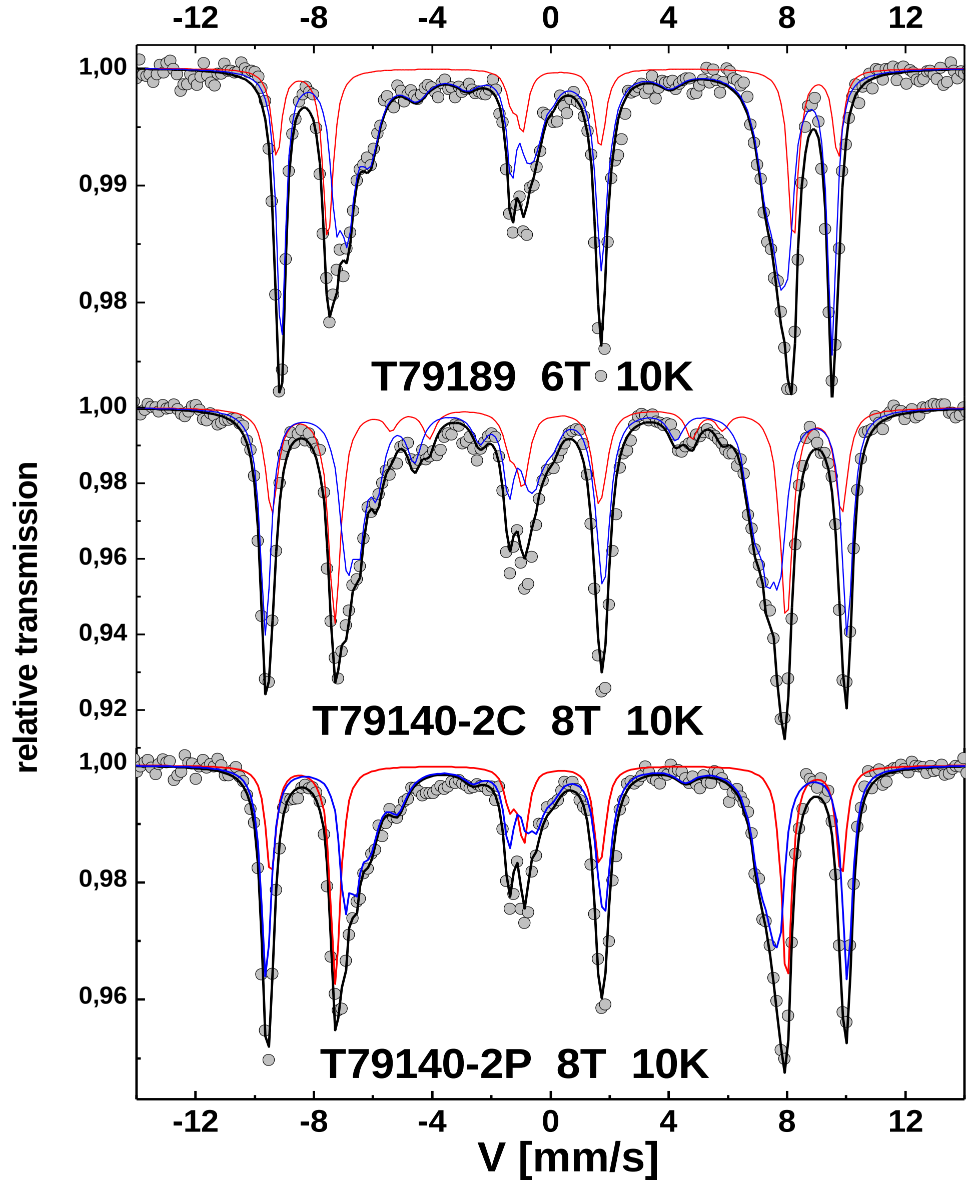
$$e = r/2\,\sin^2\Theta$$

~ 0.7 nm

~ 2 atomic layers

E. Tronc, P. Prené, J.P. Jolivet, J.L. Dormann and J.M. Greneche, Hyper. Int. 112 (1997) 97-100; E. Tronc, A. Ezzir, R. Cherkaoui, C. Chanéac, M. Noguès, H. Kachkachi, D. Fiorani, A.M. Testa, J.M. Grenèche, and J.P. Jolivet, J. Magn. Magn. Mater. 221 (2000) 63-79; E. Tronc, D. Fiorani, M. Noguès, A.M. Testa, F. Lucari, F. D'Orazio, J.M. Grenèche, W. Wernsdorfer, N. Galvez, C. Chanéac, D. Mailly, M. Verdaguer, J.P. Jolivet J. Magn. Magn. Mater 262 (2003) 6–14

Superficial magnetic layer ?

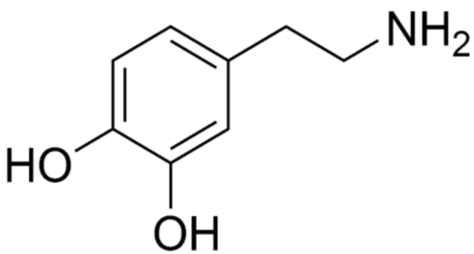


Functionalized NPs

- Ionic/Covalent Chemical Bond
- Magnetic Structure of NPs surface

T. J. Daou, J.M. Grenèche, G. Pourroy, S. Buathong, A. Derory, C. Ulhaq-Bouillet, B. Donnio, D. Guillon and S. Begin-Colin, Chem Mater 20 (2008) 5869–5875

Dopamine grafted NPs



77K	δ ($mm.s^{-1}$)	2ε ($mm.s^{-1}$)	B_{hf} (T)	%
As prepared (1)Fe^{3+}_{B} (2)(2) Fe^{3+}_{A}	 0.45 0.41	 0.00 -0.02	 51.7 49.4	 64 36
Grafted (1) Fe^{3+}_{B} (2) Fe^{3+}_{A} (3) Fe^{x+}_{B} (!) $2<x<3$	 0.46 0.41 0.50	 -0.01 -0.01 -0.04	 51.8 49.6 41.0	 53 38 9

J. Fouineau, K. Brymora, L. Ourry, F. Mammeri, N. Yaacoub, F. Calvayrac, S. Ammar-Merah, and J.M. Greneche, J. Phys. Chem. C 2013, 117, 14295−14302

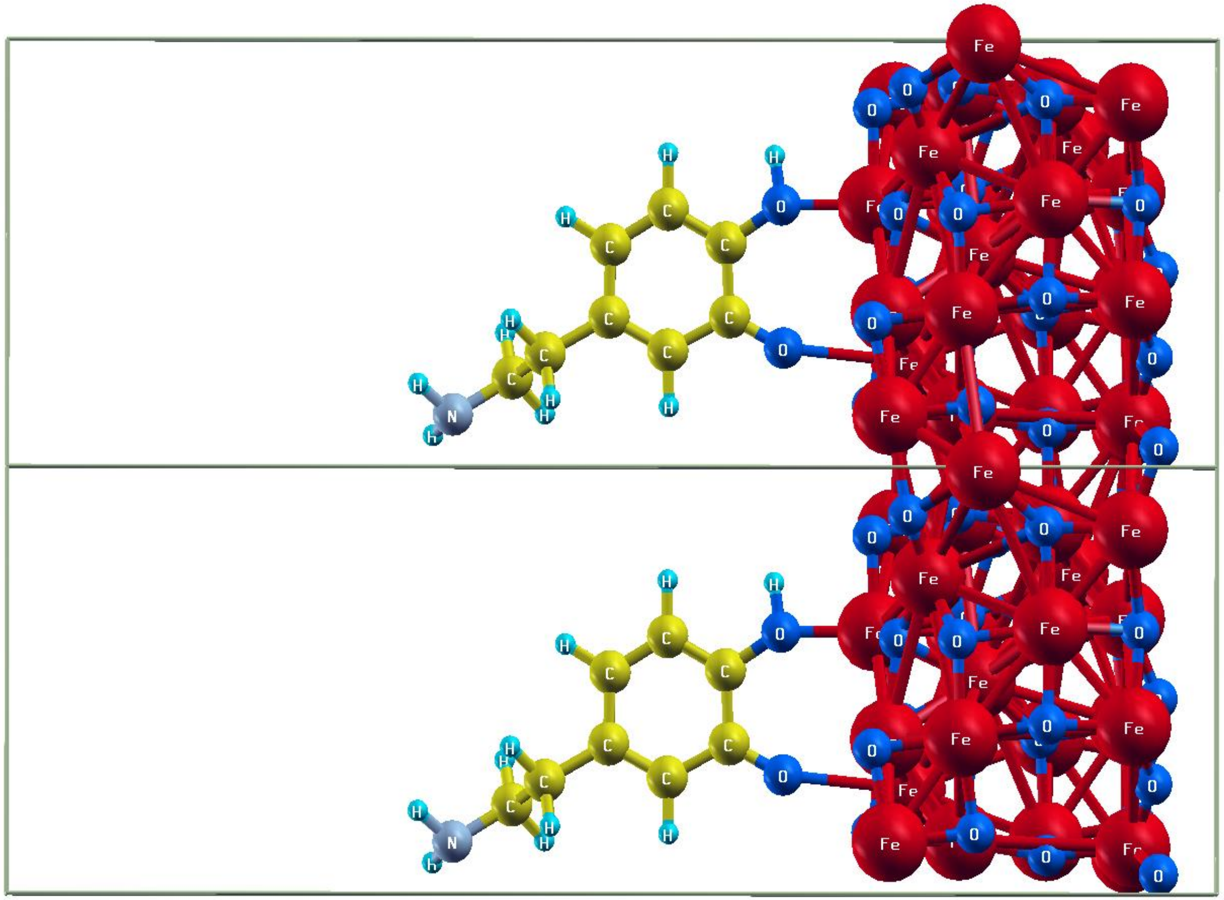
Ab initio modelling of dopamine-Fe oxyde NPs

Grafting through 2 O atoms with Octahedral Fe ions

π donor character of the ligand

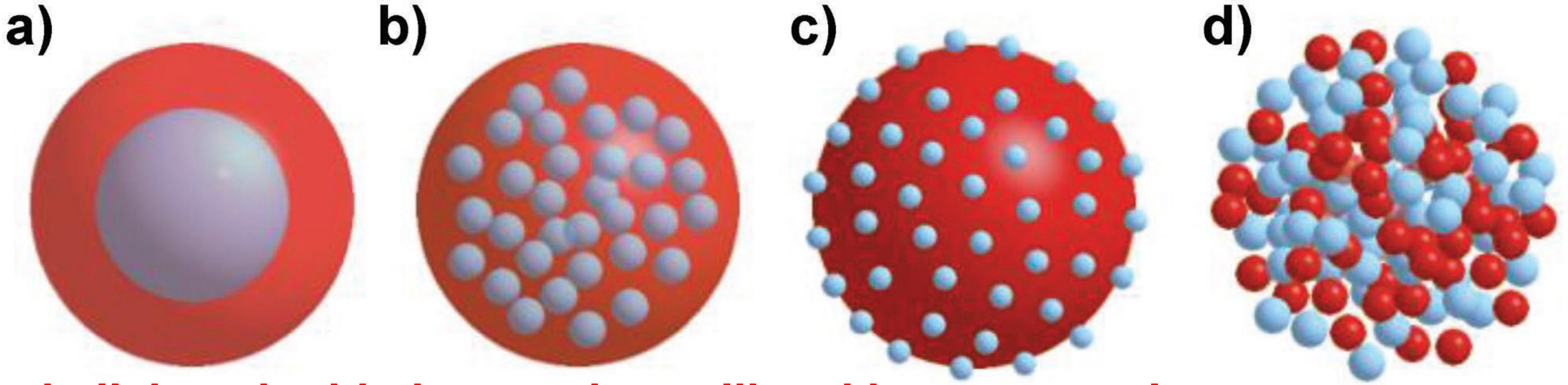
covalent bond

In agreement with hyperfine data!

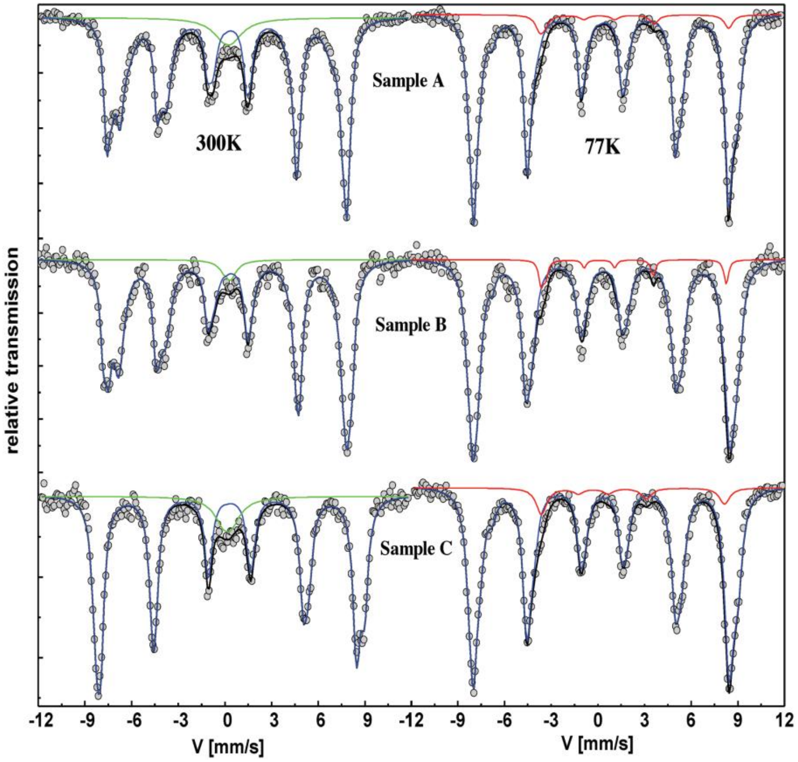


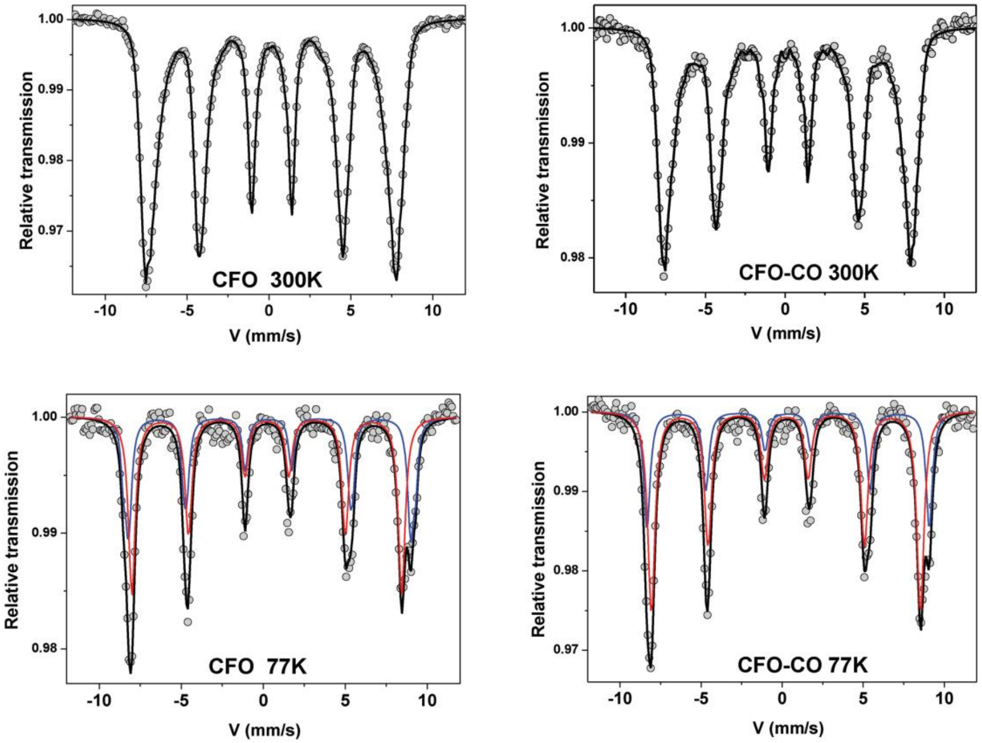
J. Fouineau, K. Brymora, L. Ourry, F. Mammeri, N. Yaacoub, F. Calvayrac, S. Ammar-Merah, and J.M. Greneche
J. Phys. Chem. C 2013, 117, 14295

$CoFe_2O_4$-CoO Nanoparticles



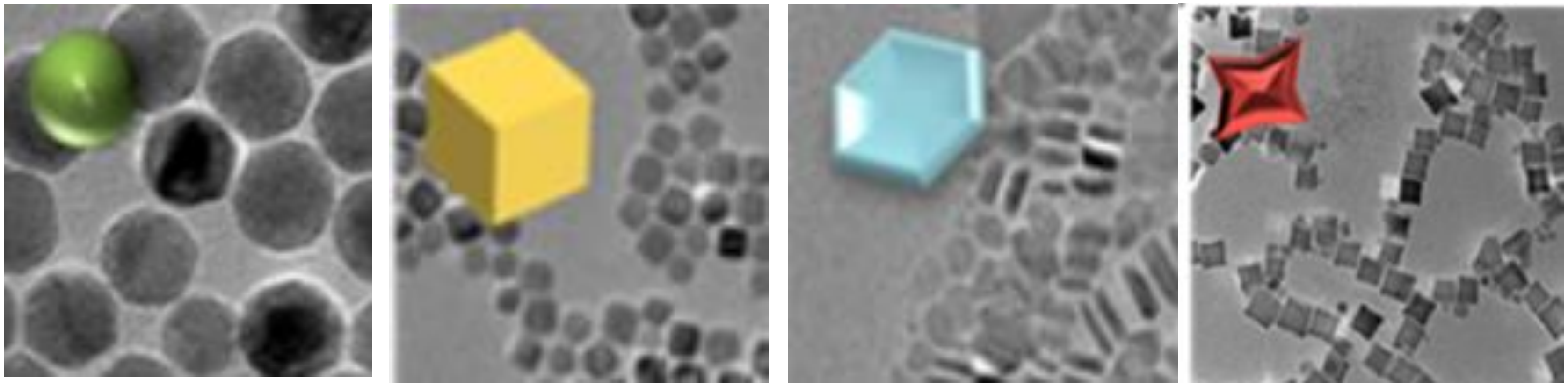
a core–shell, b embedded, c raspberry-like, d heterocoagulate or nanoaggregates

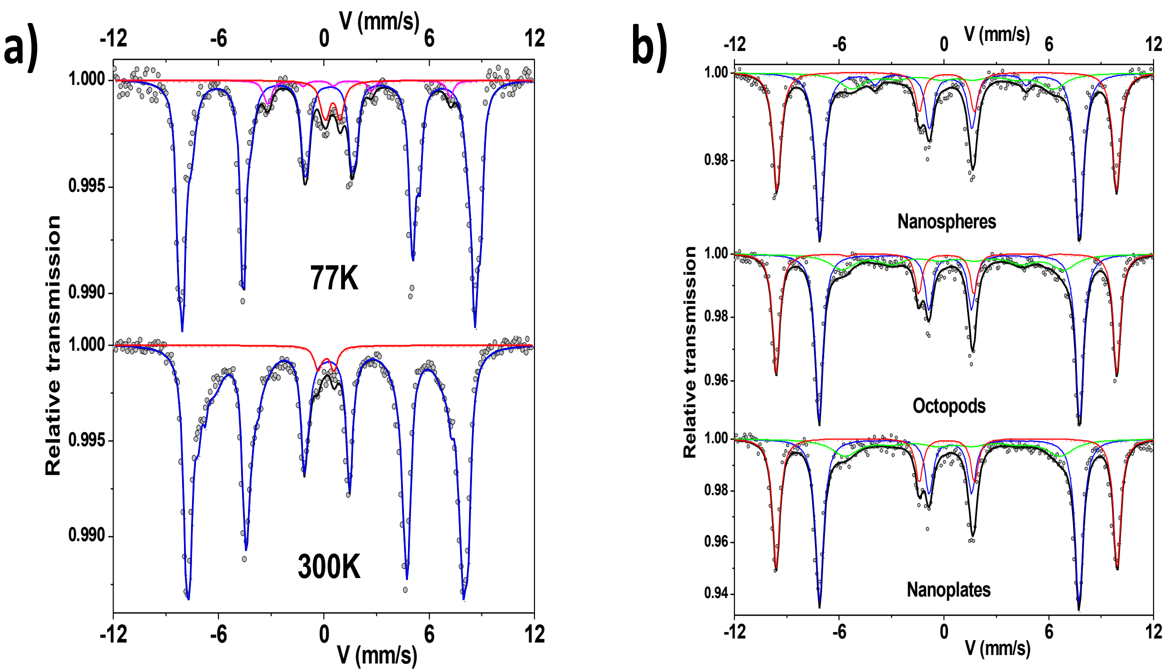




Part. Part. Syst. Charact. 2018, 35, 1800104; Part. Part. Syst. Charact. 2018, 1800290

Growth process of nuclei towards NPs

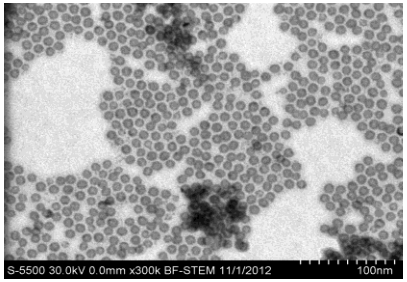


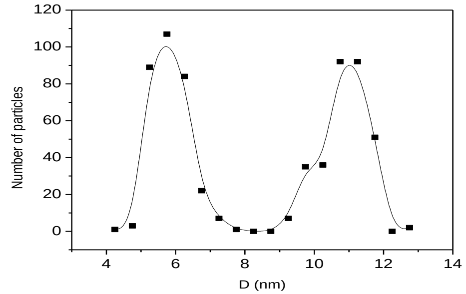


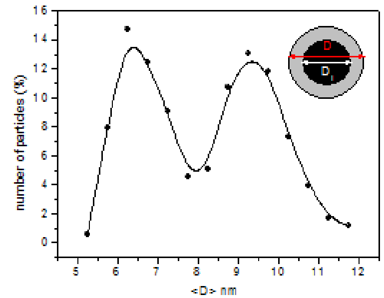
Comparison of hyperfine structures of Fe^{3+} and Fe^{2+} components $f(T, B_{app})$

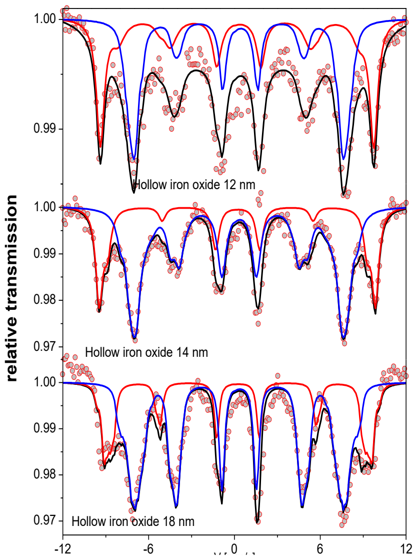
To be published

Hollow Magnetic Nanoparticles γ-Fe_2O_3



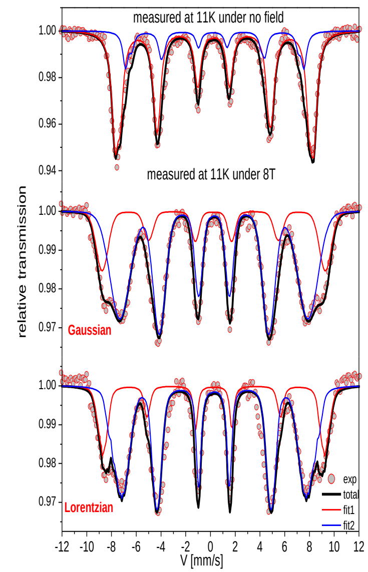


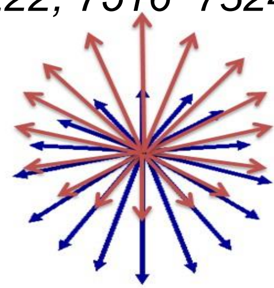


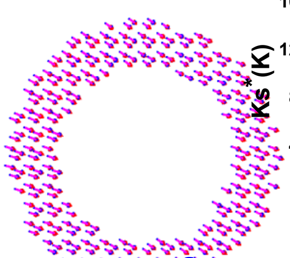


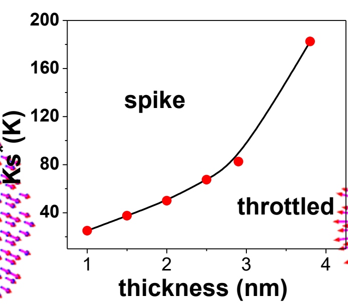
- 2 SP AF coupled due to Tetra and Octa Fe lattices
- IS (Octa and Tetra)
- Bhf (Octa <0 and Tetra >0)
- Octa:Tetra 80:20
- Octa = closing units as suspected in NPs

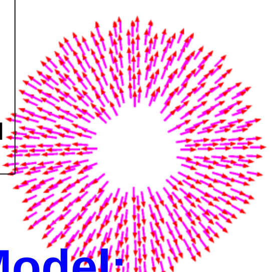
J. Phys. Chem. C (2018) 122, 7516−7524

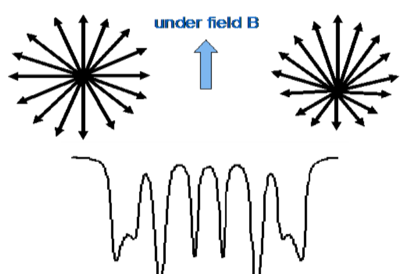


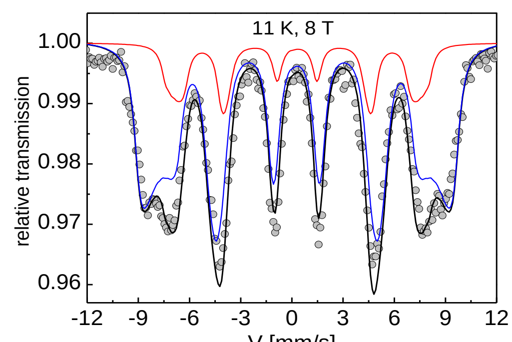












Surface Anisotropy Model; Néel or normal?

Conclusions

Crucial preliminary points:
High quality of samples with homogeneity and reproducibility

Collaboration with excellent chemists

Requirements:
Detailed structural and magnetic characterization

Fitting models established from numerous Mössbauer spectra in agreement with other results

Experimental Approaches to MNPs

- **X-ray & neutron D; TEM:<structural characteristics>; HRTEM-EFTEM: core-shell, grain boundaries ?**

- **EXAFS: atomic neighbouring; SAXS and GISAXS**
- **XPS: Valency states at the top layer; IR**
- **Local Probe Techniques (NMR, EPR, Mössbauer, …)**

- **FC-ZFC magnetic characteristics, T_B^{Mag}**
- **^{57}Fe MS: Fe valency states, magnetic phases, $T_B^{Möss}$**
- **In-field ^{57}Fe MS: towards blocked magnetic structures; canting angle of Fe moments; tetra/octa Fe sites; cationic inversion and local sensitivity**

- **XMCD: magnetic states and tetra/octa ratio**
- ***ab initio*, Monte Carlo, Molecular dynamics; Computer multiscale modeling**

Acknowledgements

- F. Sayed, Z. Nehmé, K. Brymora, M. Grafoute, B. Fongang,
R. Busselez, N. Yaacoub, N. Randrianantoandro, Y. Labaye, L. Berger, F. Calvayrac (Le Mans)
- E. Tronc, C. Chaneac, P. Prené, P. Jolivet (LCM Paris),
- T.J. Daou, B. Pichon, P. Rabu, S. Bégin-Colin, G. Pourroy (IPCMS Strasbourg)
- A. Karimi, F. Hindré, J.P. Benoit (CHU Angers), A. Roucoux (ISCR Rennes)
- S. Ammar, F. Fievet, R Brayner, M. Giraud (ITODYS Paris), Y. Prado, J. Fresnais (PHENIX Paris)
- F. Pelletier, J.G. Mattei, C. Amiens, M.J. Casanove (Toulouse)
- M. Rico, R. Rodriguez, J.F. Valderutten, L.E. Zamora, G. Perez, K. Garcia, J. Restrepo, C. Barrero (Colombia)
- J. Borrego, J. Blazquez, A. Conde (Sevilla), M.P. Fernandez, P. Gorria (Oviedo, Spain)
- A. Slawska-Waniewska (Warzaw), I. Idzikowski, Z Sniadecki (Poznan) (Poland)
- D. Peddis, D. Fiorani (Roma Italy)
- R. Valenzuela, S. Montemayor (Mexico)
- J.M.D. Coey (Dublin Ireland)
- J. Degmova, M. Miglierini (Bratislava), I. Skorvanek (SAS Kosice) (Slovakia)
- S. Alleg, A. Djekoun, A. Otmani, H. Moumeni, C. Djebbari, F. Z. Bentayeb (Annaba, Algeria)
- L.Z. Zhao (Hangzhou), Z.W. Liu (Guangzhou) (China)
- L. Ben Tahar, L. S. Smiri, A. Ben Ali, M. Smili, M. Khitouni, N. Rammeh (Tunisia)
- N. Ponpandian, A. Narayanasamy, C.N. Chinnasamy, N. Sivakumar, M. Kaur, R.J. Joseyphus (India)

Profesor (Cooperante) UNI 1981-1983

Colaboraciones actuales Le Mans-Lima:

Roberto Salazar & Domingo Aliaga Guerra (UNI)
Estudios de ortoferitas

Juan Adrián Ramos Guivar (San Marcos)
Estudios de nanopartículas magneticas funcionalizadas

Julio Fabián Salvador (San Marcos)
Estudio vinculado a la antigua metalurgia precolombina del Perú

jean-marc.greneche@univ-lemans.fr

Le Mans