IDEI 75/2011 : Advanced approach of magnetic relaxation

Abstract:
The project proposes a suite of tools and methodologies for a comprehensive characterization of the magnetic response and the magnetic relaxation process in real systems of interacting non-identical nanoparticles, to be applied in different domains (from biomedical applications to nanoelectronics and spintronics). The accomplishment of the project objectives will lead to a deeper knowledge of relaxation mechanisms in nanoparticles and to derived possibilities of controlling the relaxation process. It will be taken into consideration composition and stoichiometry, phase structure, size distribution, morphology, couplings among magnetic entities, surface effects in the attempt to correlate the mechanism of relaxation to all and every specific parameter related to nanoparticles. Theoretical and experimental approaches will be developed and permanently corroborated. A new possibility for adjusting the magnetic relaxation of nanoparticulate systems via molecular control over distances between particles and surface ligands through a new class of bio-inspired architectures is also proposed. Ways to develop self-assembly approaches for the controlled encapsulation of magnetic nanoparticles in viral protein cages are envisaged. The tuning of magnetic relaxation through inter-particle interactions or by increasing the anisotropy energy of each particle via non-spherical shapes or intra-particle interfacial couplings in core-shell configurations will be considered.

Objective I: *Deep investigation via low temperature and applied field Mössbauer spectroscopy for a comprehensive characterization of the nanoparticulate systems*.
Objective II: *Versatile theoretical models involving mainly physical and numerical solutions, linking the temperature dependent magnetic response obtained by Mössbauer spectroscopy and magnetometry to magnetic relaxation parameters.*
Objective III: *Developing suitable methodologies proving the strength of the inter-particle interactions*.
Objective IV: *Studying the relaxation mechanisms responding for the blocking temperature in superparamagnetism and, respectively, exchange bias in case of core-shell nanoparticle systems.*
Objective V: *Controlling the magnetic relaxation in a new class of bio-inspired architecture for bio-medical applications*.

The work-plane assumes the existence of 4 stages. Along each stage will be accomplished parts of different objectives. The time commitment runs along the objectives. Sharing activities along the stages are:
Stage I: Complex investigations, including low temperature and applied field MS of spinel-like nanopowders
Stage II: Complex investigations, including temperature/field dependent MS and magnetometry, of nanoparticles for bio-medical applications. VNPs are also envisaged. Modeling magnetic relaxation for MS and magnetometry.
Stage III: Studying interparticle interactions. Comparative study of relaxation phenomena in SPM and exchange bias effects on core-shell nanoparticles
Stage IV: Investigation of interparticle interactions in packing nanosystems. Studying the magnetic response of newly prepared VNPs and bio-inspired nanostructures.

Some results:

- Studying magnetism of Fe-oxide nanoparticles obtained by Laser pyrolysis (e.g. spin configurations in Fe-oxide nanoparticles with spinel structure. Evidence for the antiferromagnetic coupling and spin disorder degree by in field Mossbauer measurements and evidence of increased crystallization via hydrogenation treatment:

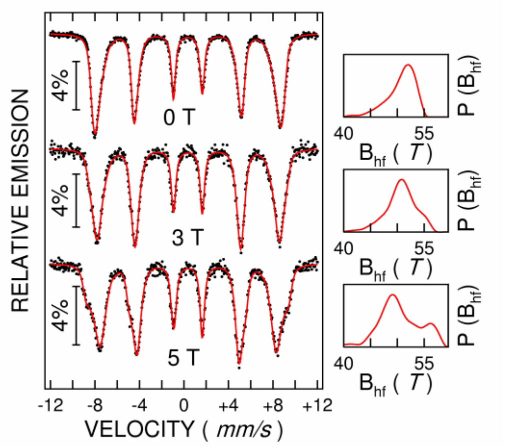


Fig.1. Mossbauer spectra obtained at 3 K in applied magnetic field, on Fe oxide nanoparticles of average size of about 5 nm. The evolution of the hyperfine magnetic field distribution evidence clearly both the antiferromagnetic coupling and a certain degree of spin disorder on each nanoparticle.

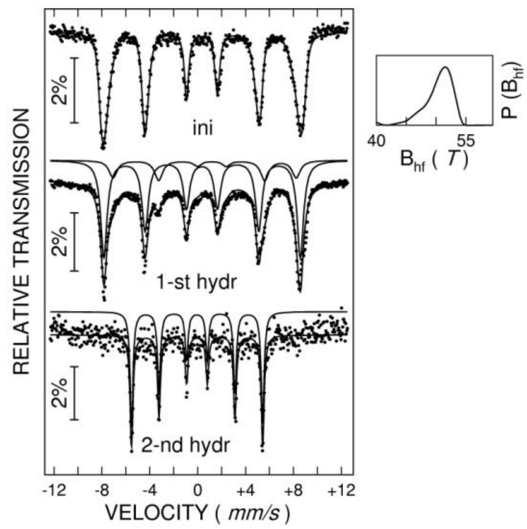


Fig.2. Mossbauer spectra collected at 5 K before and after hydrogenation of Fe oxide nanoparticles, evidencing the improved crystallinity and higher particle size induced by hydrogenation.

- Studying magnetic relaxation and phase composition in Fe carbide composites obtained by laser pyrolysis:

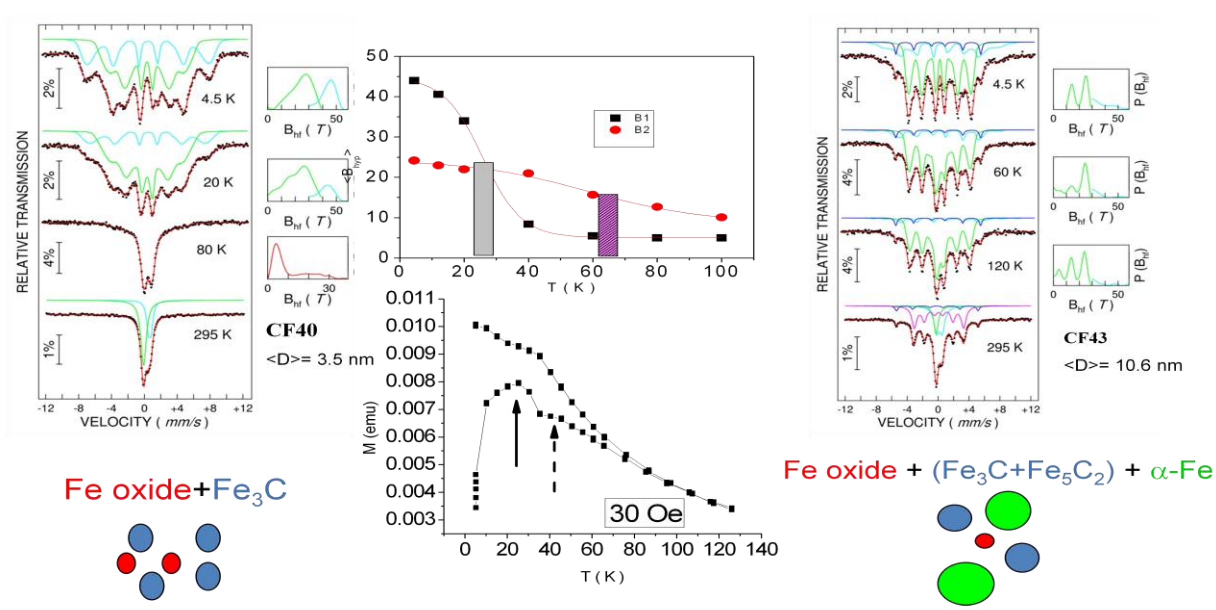
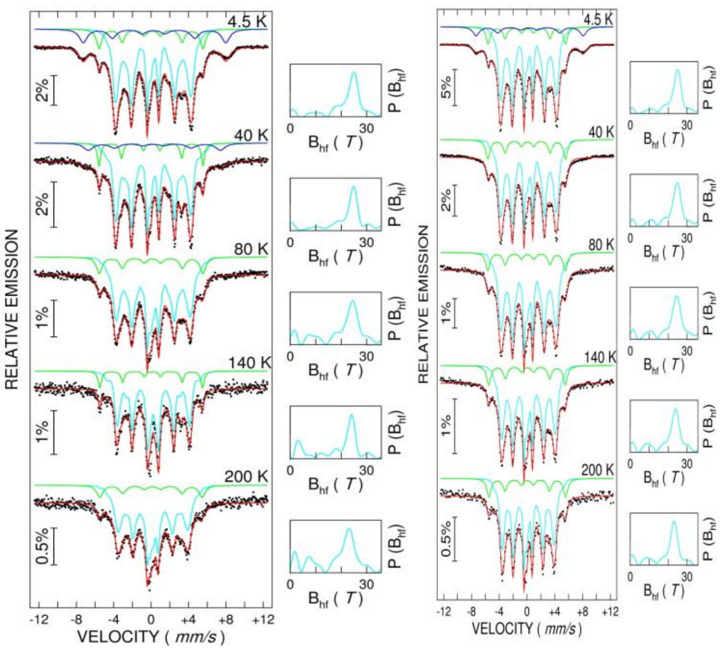


Fig.3. Mossbauer spectra and zero field cooled-field curve magnetization curves providing information of the Fe phase composition in different samples prepared by laser pyrolysis and evidencing a mixture of monophase NPs.

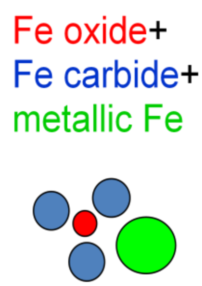
- A new methodology based on corroborating energy dispersive spectroscopy, magnetometry and temperature dependent Mossbauer spectroscopy data was elaborated in order to distinguish between nanoparticles of core-shell structure or a mixture of different mono-phase nanoparticles. In the range of a few nm average size, neither HRTM is able to provide such complex information:

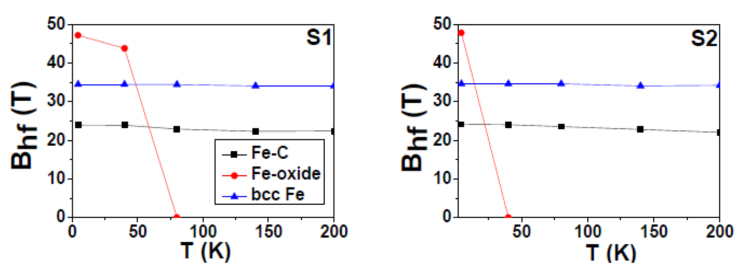
Sample	C_2H_4/$Fe(CO)_5$ vol.%)	C_2H_4 middle (sccm)	Ar middle (sccm)	C_2H_4/Ar mixture (vol.%)	Central nozzle diameter (mm)	T Flame (^{0}C)	P laser (W)	EDS elemental estimation (at%)		
								Fe	C	O
S1	10	130	0	100	0.9	680	75	29	66	5
S2	10	65	65	50	0.9	687	75	39	54	7



$$\tau_M = \tau_0 e^{\frac{KV}{kT}}$$

$$B_{hf} = B_0(1 - \frac{k_B T}{2KV})$$





Sample Fe phase	S1 %	S2 %
Fe-Carbide	72(1)	76(1)
Fe-Oxide	14(2)	11(2)
Metallic Fe	13(1)	13(1)

Sample	KV_{Fe-C} (10^{-20}J)	KV_{Fe-bcc} (10^{-20}J)	D_{Fe-C} (nm)	D_{Fe-bcc} (nm)
S1	1.28	5.75	8.00	13.20
S2	1.46	10.90	8.35	16.33

Fig.4.Temperature dependent Mossbauer spectra of other two different samples obtained by laser pyrolysis (see table on top for preparation conditions) and related procedures based on magnetic relaxation phenomena followed by Mossbauer spectroscopy, to determine phase composition, average size and anisotropy energy of each type of nanoparticle in the composite samples

- Studying magnetic relaxation in naked (MPs) and dopamine surfacted magnetite (MF-MPs) nanoparticles for biomedical applications. Elaboration of a new procedure for estimation of the magnetic size dispersion:

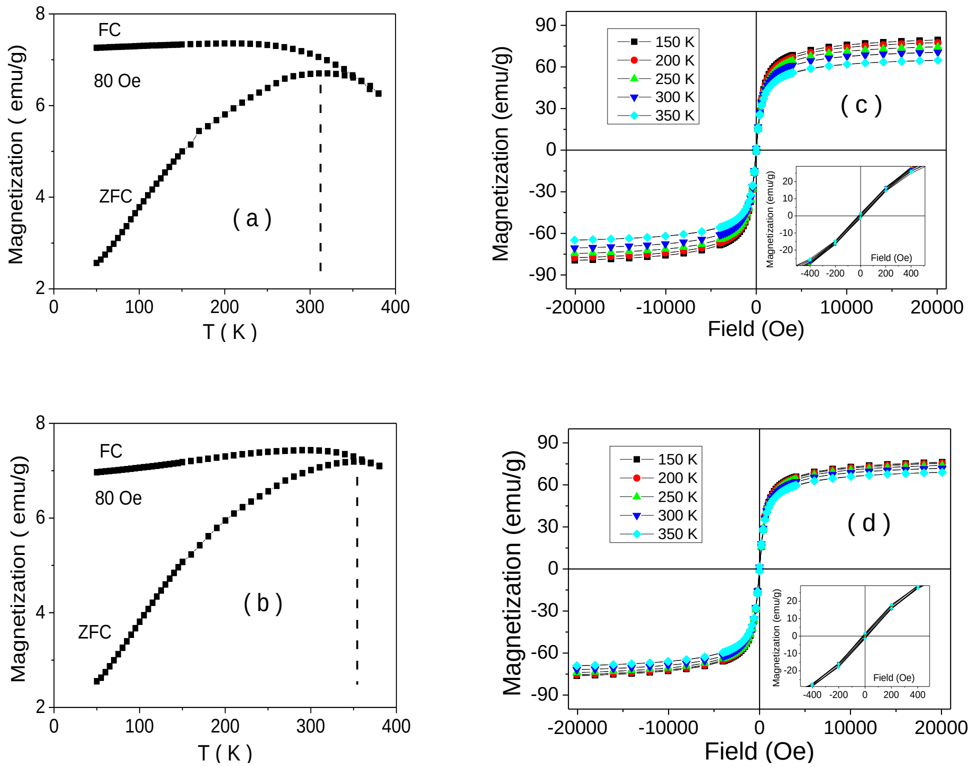


Figure 5: ZFC-FC magnetization curves (left hand images) and temperature dependent hysteresis loops (right hand images) for naked MPs (up) and MF-MPs (down).

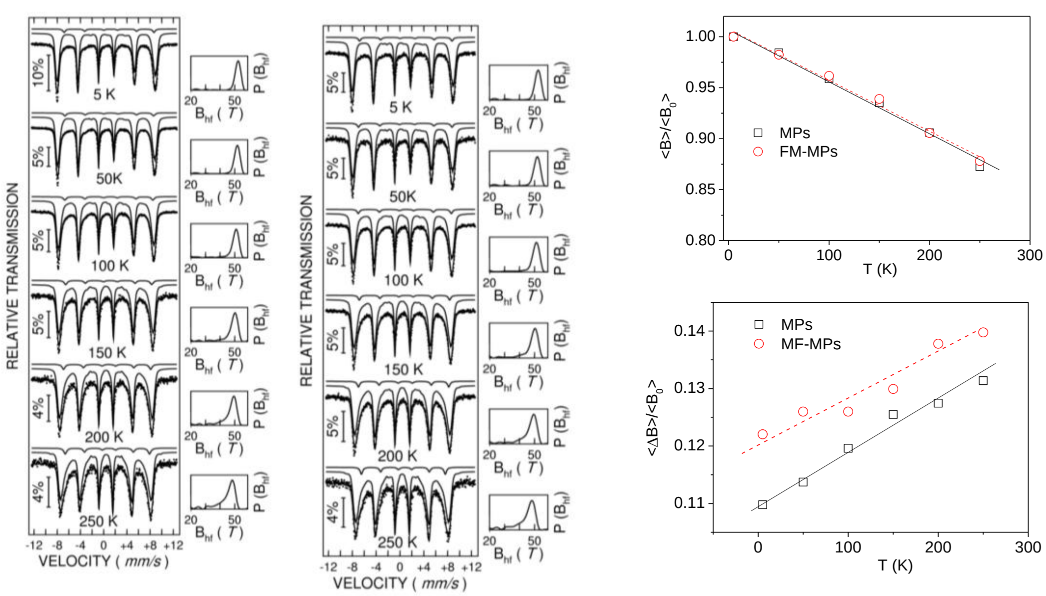
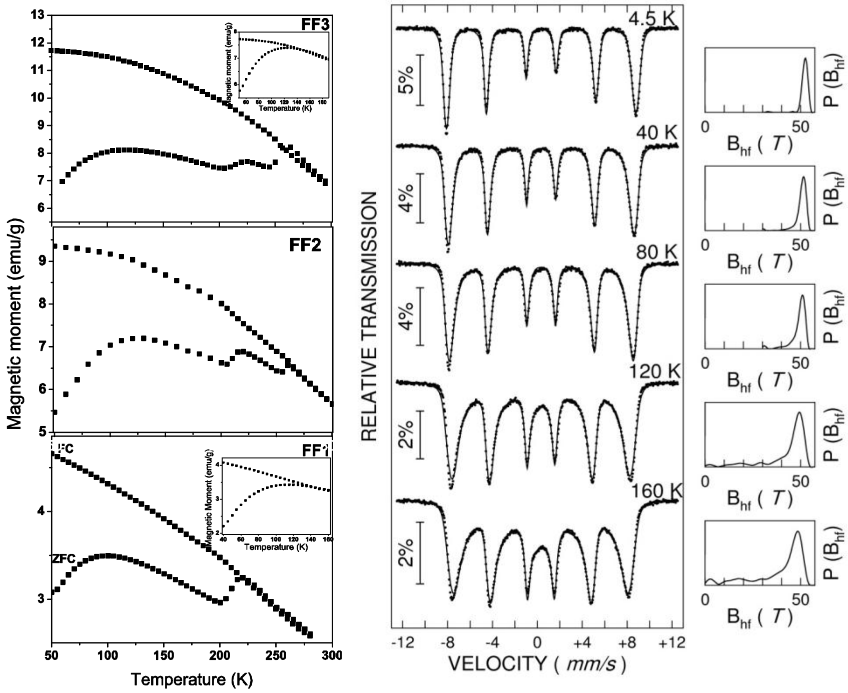


Fig.6: Temperature dependent Mossbauer spectra of MPs and MF-MPs systems and the resulted linear dependencies B_{hf}/B_0 and $\Delta B/B_0$ providing slopes SL1 and SL2. Size dispersion is given as: $\delta D/D = -SL2/3SL1$.

- Studying magnetic relaxation phenomena and interparticle interactions in ferrofluids.



$$B_{hf} = B_0\left(1 - \frac{k_B T}{2KV}\right)$$

$$E_D = \frac{\mu_0}{4\pi d^3}\mu^2$$

Sample	KV (10^{-20}J)	KV (K)	ΔE_D (K)
FF1	0.66	480	-
FF2	0.76	550	
FF3	0.79	570	65-90

Fig. 7: Zero field cooling-field cooling magnetization curves for three different ferrofluid samples of volume fractions ranging from 0.04 (F1) to 0.20 (F3). Different defreezing processe might be observed as function of the volume fraction. The anisotropy energy barrier was determined from the specific evolution of the hyperfine field and the corresponding increase of the barrier was explained as being related do increased dipolar magnetic interactions.

Additional non-detailed studies have been considered:

- Making difference between local magnetism due to magnetic nanoclusters and long range magnetic order in diluted magnetic oxides
- Studying the intrinsic magnetic properties of half metallic magnetic materials by DFT calculations
- Local electronic phenomena and atomic configuration in perovskite based nanoparticles with catalytic applications
- Magnetic anisotropy and peculiar spin configuration in metallic nanowires grown by the template method
- Superparamagnetic relaxation in magnetite-polymer nanocomposites

The dissemination was based on the following publications in well coted international journals as well as by the following presentations at international conferences and seminars, all of them including acknowledgements to the project (75/2011):

Publications (at the middle of the project)

[1] Superparamagnetic magnetite-divinylbenzene-maleic anhydride copolymer nanocomposites obtained by dispersion polymerization; D.Donescu, V.Raditoiu, C.I.Spataru, R.Somoghi, M.Ghiurea, C.Radovici, R.C.Firescu, G.Schinteie, A.Leca, V.Kuncser, European Polymer Journal 48 (2012) 1709-1716
[2] Half-metallic state and magnetic properties versus the lattice constant in Ti_2CoSn Heusler compound: An ab initio study; A.Birsan, P.Palade, V.Kuncser, Solid State Communications 152 (2012) 2147-2150
[3] Magnetic properties of iron-carbon nanocomposites obtianed by laser pyrolysis in specific configurations; G.Schinteie, V.Kuncser, P.Palade, F.Dumitrache, R.Alexandru, I.Morjan and G.Filoti, Journal of Alloys and Compounds 564 (2013) 27-34
[4] Iron Oxide Magnetic Nanoparticles with versatile surface functions based on dopamine anchors; M. Mazur, A. Barras, V. Kuncser, A. Galatanu, V. Zaitzev, P. Woisel, J. Lyskawa, W. Laure, A. Siriwardena, R. Boukherroub and S. Szunerits, Nanoscale, 5 (2013) 2692-2702
[5] Microstructure related magnetic properties in Co implanted ZnO thin films; L.C.Nistor, C.Ghica, V.Kuncser, D.Pantelica, J.J. Grob and M.Dinescu, J.Phys.D: Applied Physics, 46 (2013) 065003 (10pp)
[6] Magnetic nanophases: from exchange coupled multilayers to nanopowders and nanocomposites; V.Kuncser, O.Crisan, G.Schinteie, F.Tolea, P.Palade, M.Valeanu, G.Filoti, (book chapter) in Modern Trends in Nanoscience, M.Balasoiu and G.M. Arzumanyan eds., Ed. Academiei Romane, Bucuresti, 2013

[7] Spectroscopic Investigation of Iron Substitution in EuCoO3 : Related Impact on the Catalytic Properties in the High Temperature N2O Decomposition; Wu, Yihao; Dujardin, Christophe; Granger, Pascal; Tiseanu, Carmen; Sandu, Simona; Kuncser, V.;Parvulescu, Vasile, accepted at J.Phys.Chem: C
[8] Magnetic configurations of Ni-Cu alloy nanowires obtained by the template method; E. Matei, Ionut Enculescu, M.E. Toimil-Molares, A. Leca and V.Kuncser, accepted at J. Nanoparticle Research
[9] Volume fraction dependent magnetic behaviour of ferrofluids for rotating seal applications; G Schinteie, P Palade, L Vekas , N Iacob , C Bartha and V Kuncser, accepted at J.Phys.D: Applied Physics

Presentations at international conferences/seminars:

1. Mossbauer Spectroscopy –a powerful tool for investigation of local electronic phenomena and interactions in nanomaterials; V. Kuncser, invited lecture at national Physical Laboratory, London, 2012
2. Complex carcterization of magnetic configurations in multiphase nanoparticulate systems; V.Kuncser, G.Schinteie, G.Filoti, A.Birsan, R.Alexandrescu, I.Morjan; oral presentation at SIWAN5-5th Szeged International Workshop on Advances in Nonoscience, 2012
3. Perovskite based catalysts studied by Mossbauer spectroscopy and magnetic measurements, V.Kuncser, oral presentation at the International Symposium of the Romanian Catalysis Society, Cluj-Napoca, 2013
4. Distribution of potential barriers via temperature dependent 57Fe Mossbauer spectroscopy, V.Kuncser, G.Schinteie, P.Palade and G. Filoti, accepted as oral presentation at the International Conference on the Mossbauer Effect, Croatia, 2013