IDEI 75/2011 : Advanced approach of magnetic relaxation

Website address of the project : http://www.infim.ro/projects/advanced-approach-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: Modeling and parameter-setting of interphase and interparticle interaction

Stage V: The control of relaxation phenomena in nanoparticle systems for biomedical applications

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:

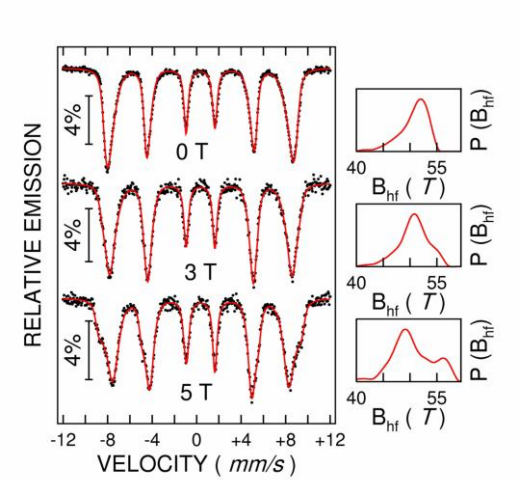


Fig.1. Mossbauer spectra obtained at 3 K in applied magnetic field, on Fe oxide nanoparticles of average size of about 5 nm. The evolution of the hyperfine magnetic field distribution evidence clearly both the antiferromagnetic coupling and a certain degree of spin disorder on each nanoparticle.

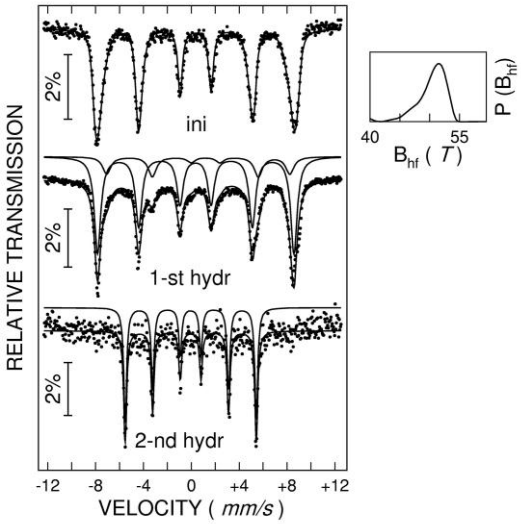


Fig.2. Mossbauer spectra collected at 5 K before and after hydrogenation of Fe oxide nanoparticles, evidencing the improved crystallinity and higher particle size induced by hydrogenation.

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

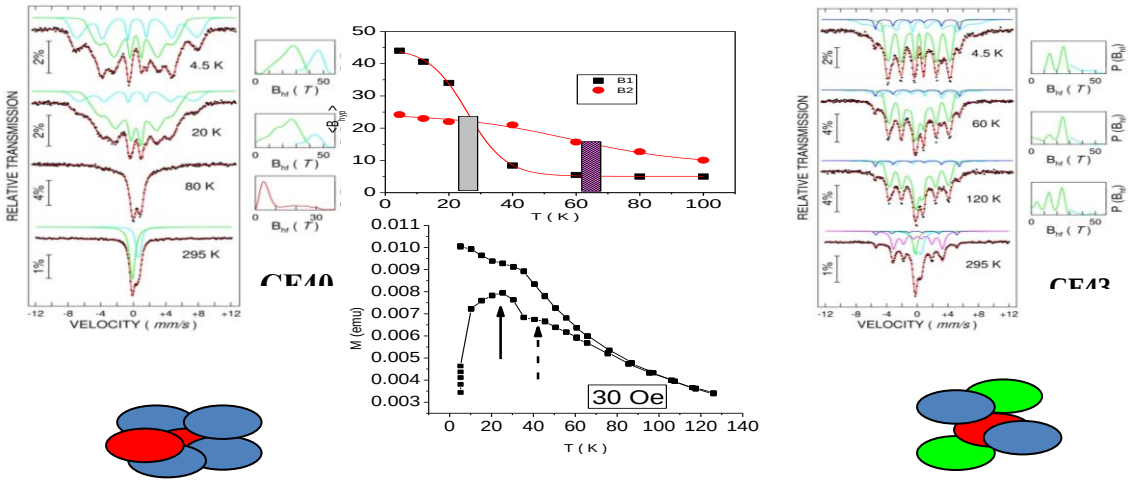


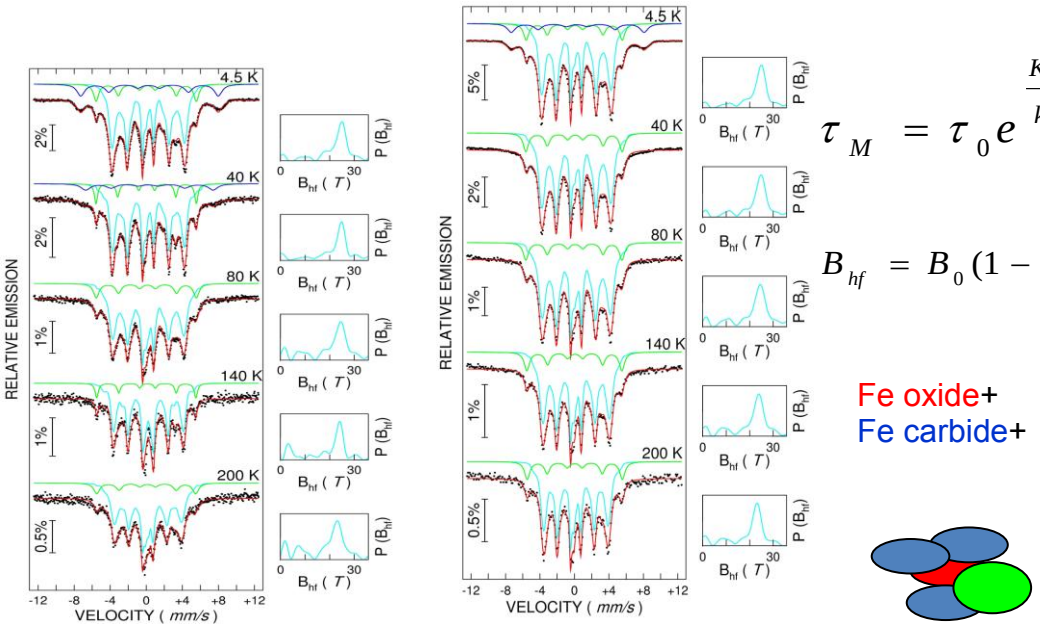
Fig.3. Mossbauer spectra and zero field cooled-field curve magnetization curves providing information of the Fe phase composition in different samples prepared by laser pyrolysis and evidencing a mixture of monophase NPs.

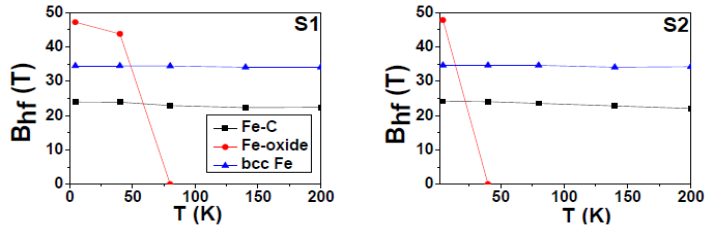
- A new methodology based on corroborating energy dispersive spectroscopy, magnetometry and temperature dependent Mossbauer spectroscopy data was elaborated in order to distinguish between nanoparticles of core-shell structure or a mixture of different mono-phase nanoparticles. In the range of a few 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

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

Sample	KV_{Fe-C}	KV_{Fe-bcc}	D_{Fe-C}	D_{Fe-bcc}
S1	1.28	5.75	8.00	13.20
S2	1.46	10.90	8.35	16.33





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:

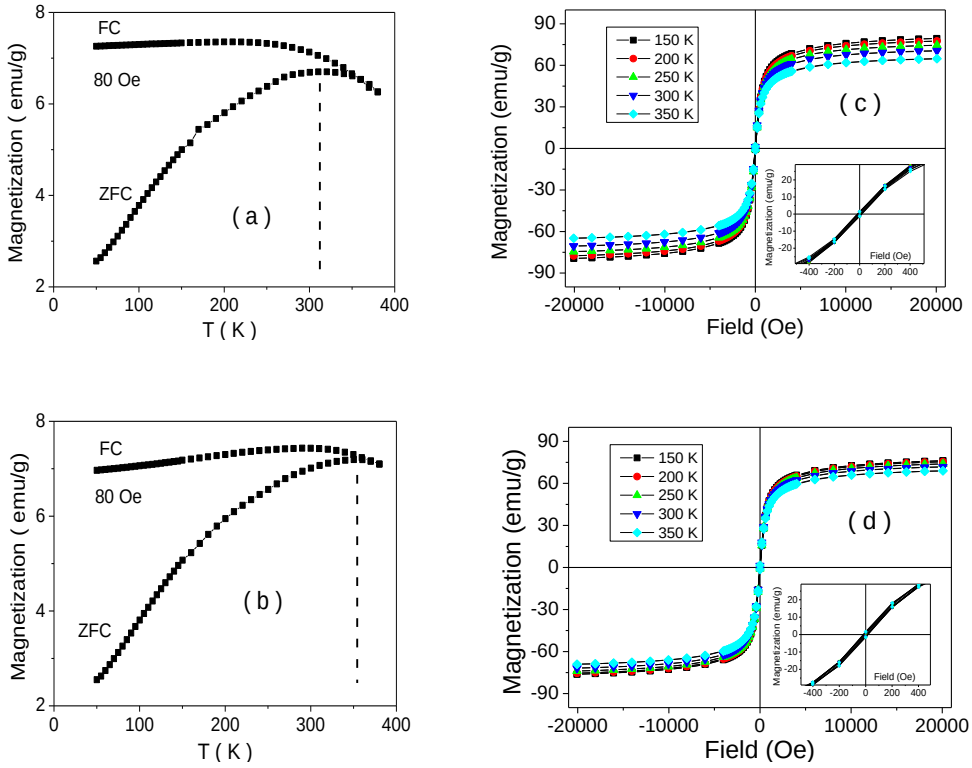


Figure 5: ZFC-FC magnetization curves (left hand images) and temperature dependent hysteresis loops (right hand images) for naked MPs (up) and MF-MPs (down).

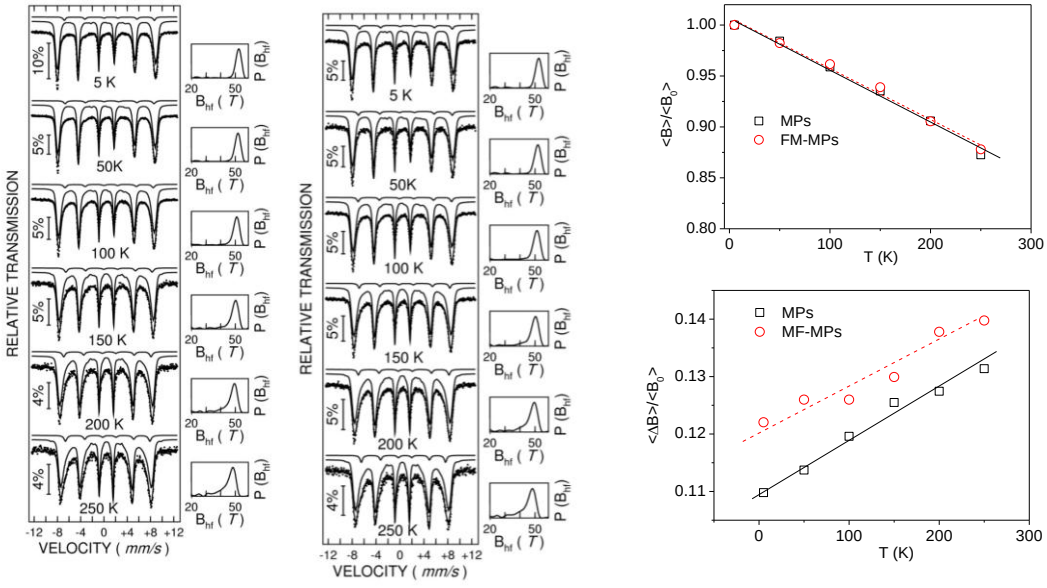


Fig.6: Temperature dependent Mossbauer spectra of MPs and MF-MPs systems and the resulted linear dependencies B_{hf}/B_0 and $\Delta B/B_0$ providing slopes SL1 and SL2. Size dispersion is given as: $\delta D/D$=-SL2/3SL1.

- The analytic expression of the relaxation phenomena for a system of identical independent nanoparticles and its critical examination with respect to the initial conditions. Demonstration of M(t) sensitivity on both material parameters and initial conditions. Obtaining the temperature dependences of the magnetization in different time intervals:

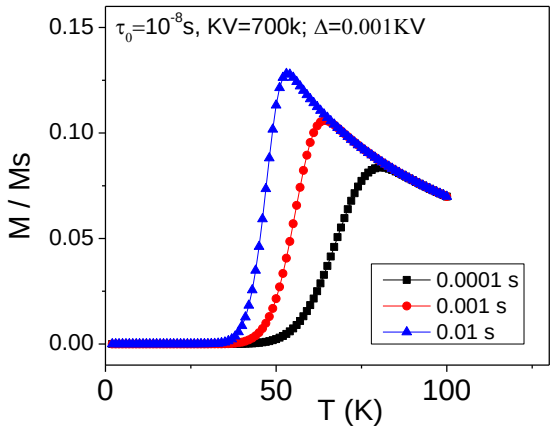


Fig 7: The relative magnetization dependence on temperature, corresponding to 3 different time measuring intervals, shown in the figure legend. Simulation conditions**:** M_0/M_S =0, τ_0=10^{-8}s, *KV*=700k, Δ=0.001KV.

Study of the magnetic relaxation phenomena in real systems, taking into account dimension distributions and inter-particle interactions.

The nature of the interactions appearing in nanoparticle systems is directly related to the mean mutual distance between particles (in this way, it is dependent on the NPs concentration) and to the NPs possibility to be or not in contact or to involve a direct or indirect electron exchange (depending on the medium type in which these are dispersed).

If the particles are in direct contact, the most probable interactions are the exchange interactions implying the magnetic atoms electrons situated on the particle surface or the exchange interactions mediated by the atoms of the nonmagnetic matrix in which the nanoparticles are immersed. Alternatively, if the nanoparticles are immersed in a metallic matrix, interactions mediated by conduction electrons can occur (Ruderman–Kittel–Kasuya–Yosida–RKKY-type interactions). Except these electron mediated interactions, which manifest on very short distances, in a nanoparticle system long range magnetic interactions, called dipolar magnetic interactions, occur.

Regarding the medical applications, the magnetic nanoparticles are functionalized by covering them with an organic surfactant (polymeric layer), which besides a specific functional role, it is able to prevent the physical contact between particles, their aggregation and sedimentation. Even in these special conditions, under a certain temperature, dipolar magnetic interactions can appear, especially when the NPs concentration is not negligible. From this point of view, the discussion continues supposing interparticle interactions with increasing intensity.

Further, it is supposed that nanoparticle interactions may lead on a hand to the modification of the system energy (and implicitly of the potential barrier) and on the other hand to the modification of the magnetic phase transitions (and implicitly of certain characteristic temperatures).

These two parameters of interest could be determined experimentally if both the implicit relaxation time and the temperature at which the relaxation time equals the measuring time interval would be known. Consequently, different interaction regimes would imply several relaxation time expressions, as a function of energetic parameters and magnetic transitions.

For small volume ratios, $\eta \sim 10^{-3}$, the distribution of monodomain particles in a ferrofluid keeps the independent SPM character of each particle. Increasing the concentration, the mutual dipolar interactions will grow in intensity and the characteristic relaxation time will depend on the presence of the other particles in the system, a collective magnetic behavior being assigned to the system (the system which phases from a superparamagnetic phase to an independent particles type phase implies the so called modified SPM, unlike the system which passes from the SPM state in a collective magnetic state).

Various approaches regarding the states generated by the magnetic interactions, from the modified superparamagnetism to superspin-glass (SSG) states or superferromagnetism (SFM) can be found in references [1,2, 5-7]. In accordance with these results, the magnetic relaxation process, described by the Neel-Brown relation, undergoes different modifications depending on the mutual magnetic interactions intensity:

(i)in the case of sufficiently weak dipolar interactions, only the anisotropy energy barrier modifies

$$\tau = \tau_0 \exp(\Delta^*/k_B T) \quad (3)$$

(ii) increasing the intensity of magnetic interactions (small interparticle distances), supposing a disordered magnetic spins orientation, a real transition from the SPM state in the SSG state under a certain transition temperature (T_g);

$$\tau = {\tau_0}^* \left(\frac{T-T_g}{T_g}\right)^{-zv} \quad (4)$$

where zv is a critic exponent. In these expression the form of the magnetic relaxation law is modified, the characteristic time constant having a distinct signification.

(iii) Finally, at very high nanoparticle concentrations, the magnetic interactions can create special conditions for a similar behavior with the ferromagnetic one in which the spatial arrangement of the magnetic spins is produced under a critical transition temperature (T_c);

In the present studies only the cases with medical significance were addressed, cases which resume in general to the modified SPM situation, the relaxation time being described by the equation (3).

It is to be mentioned the existence of two magnetic relaxation regimes, namely:

(i) collective oscillation regime (which appears when the heating energy is considerably lower than the width of the barrier introduced by the anisotropy energy KV of the NP) and

(ii) the superparamagnetic relaxation regime (which occurs at thermal activation energy comparable to the width of the KV barrier), respectively.

The arguments and methodologies developed by both relaxation regimes were applied in various situations.

- The discussion of the non-identical particles case and the problem solving possibilities for obtaining the volume distributions probabilities via magnetometric measurements and Mossbauer spectroscopy, respectively.

A first exemplification refers to the establishment of the dimension distribution of magnetite nanoparticles from two types of paleosols (one specific to the Mircea Voda region and the other specific to Costinesti region), collected from various depths, corresponding to various interglaciar periods. The Mossbauer spectra obtained at different temperatures for these two samples (MV indicative for Mircea Voda and C indicative for Costinesti) are presented in Fig. 1.

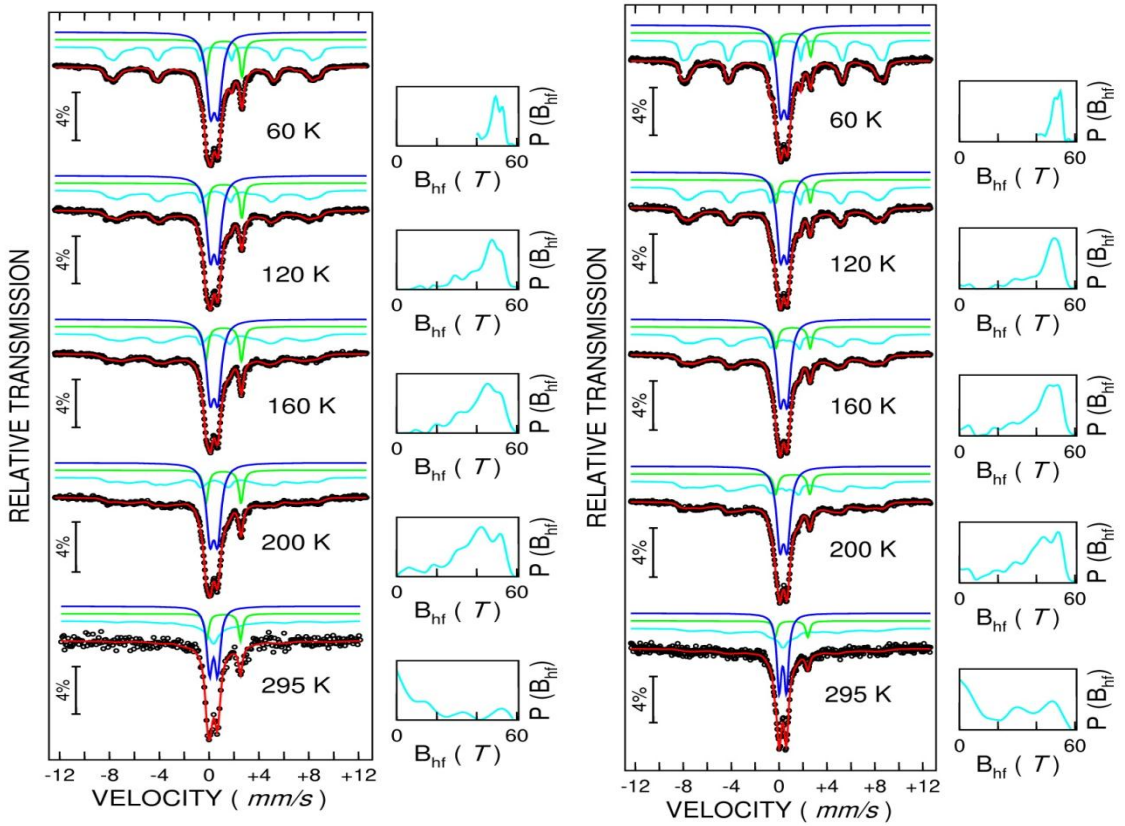


Fig.8. Mossbauer spectra dependent on temperature, coresponding to S3 MV sample (left) and S3 C sample (right), respectively

In all analyzed samples the presence of two paramagnetic spectral components (assigned to Fe ions dispersed in silicate matrix) and two magnetic components, their relative weight depending on sample, is emphasized at low temperatures (5K, inclusively).

The investigation of magnetic relaxation on each magnetic phase (magnetite and haematite) can be done based on Mossbauer methodology corresponding to collective excitations regime.

The mean hyperfine magnetic field distribution and the field distribution width (in the magnetite NPs case) are shown below, for each one of the samples:

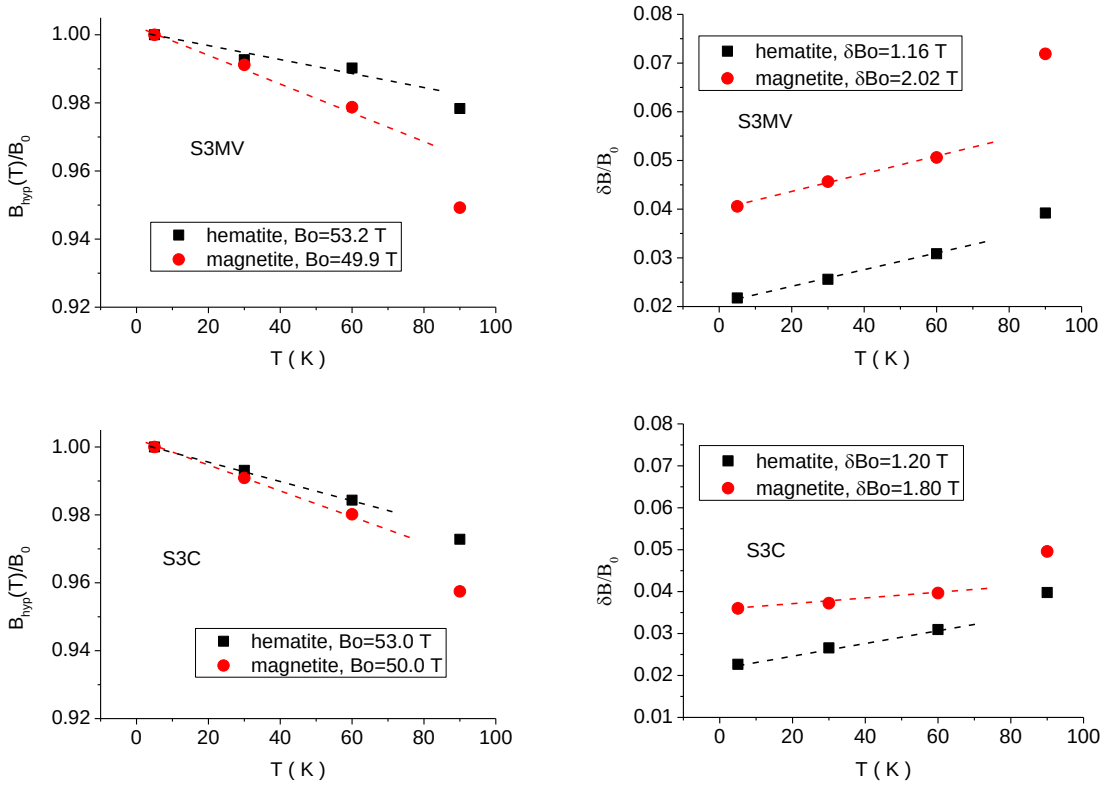


Fig.9. The temperature dependence of the hyperfine magnetic field and of the distribution width of the hyperfine field (proportional to the spectral line width), both relative to the hyperfine field in static regime.

The width of the potential barrier and the relative dispersion of the potential barrier (the relative dimension dispersion of the nanoparticles, considered spheres of diameter D), respectively are presented in the tables below, for each type of NP:

Haematite

Sample parameters	SMV3	SC3
Δ/k_B (K)	2430(30)	1790(20)
$\delta\Delta/\Delta$	0.82(3)	0.55(3)
$\delta D/D$	0.27(2)	0.18(2)

Magnetite

Sample parameters	SMV3	SC3
Δ/k_B (K)	1200(20)	1390(20)
$\delta\Delta/\Delta$	0.43(3)	0.20(3)
$\delta D/D$	0.14(2)	0.07(1)

In order to use the more accurate dimensions/volumes terminology, the involved anisotropy constants have to be determined, which could be achieved in general via magnetometry measurements (hystreresis cycle) in static regime.

The dependence of coercive fields on $T^{1/2}$ for four of the analyzed samples (S2MV, S3MV, S2C and S3C)is illustrated below. One observes a linear decrease of the coercive field as a function of $T^{1/2}$ for temperatures above 25 K. Supposing that this decrease is strictly related to the thermal activation processes over the one-particle potential barrier (the anisotropy constant and the material specific constant being constant with the temperature), the temperature dependence of the coercivity is given by the equation $Hc=Hc^0(1-T^{1/2}/T_B^{1/2})$ with Hc^0 expressed with the ratio K/M_s^* (Ms^* is the spontaneous magnetization).

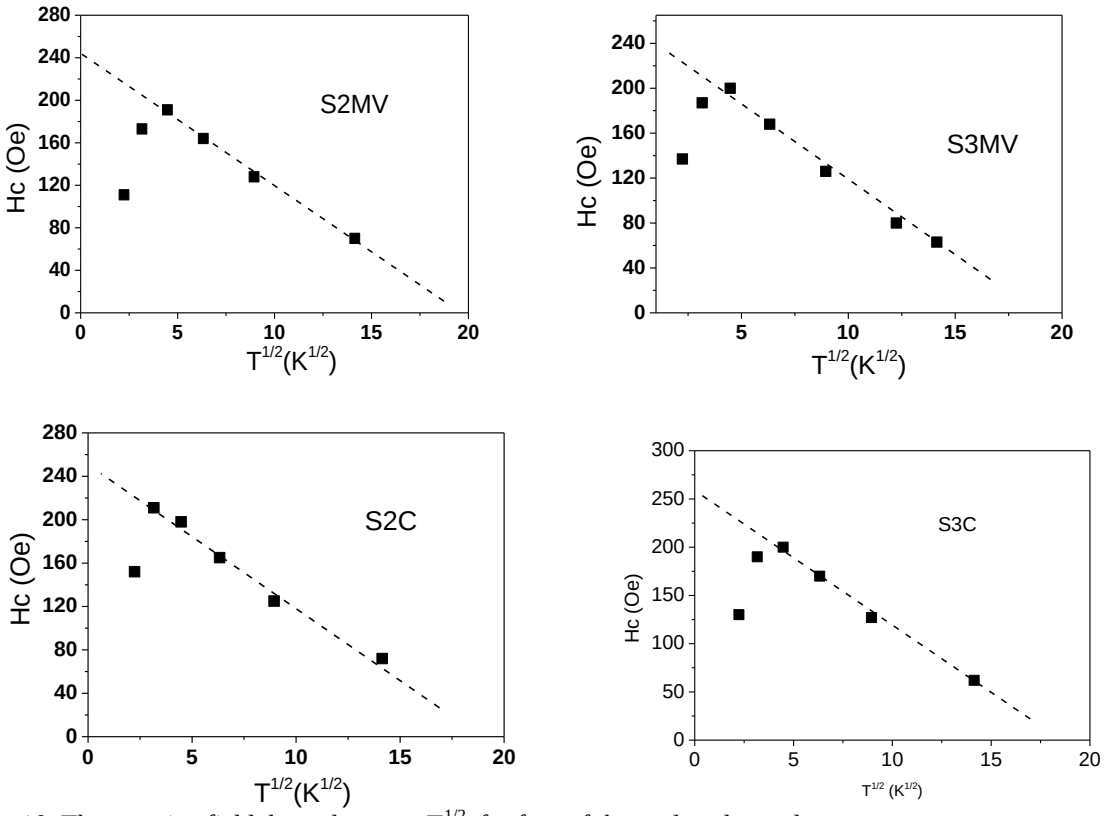


Fig.10. The coercive field dependence on $T^{1/2}$ for four of the analyzed samples

Finally, the anisotropy constant is obtained and further, using the slopes SL_1 and SL_2 from Fig 10 (only dependences corresponding to magnetite), the mean dimension and the relative dispersion of the samples S3MV and S3C, Mossbauer investigated, can be obtained:

sample	$\overline{D}$ (nm)	δD (nm)	FSMS maximum D (nm)
S3MV	14	2.25	17
S3C	14	0.81	17

It is to be mentioned that the dimension distribution of the magnetite nanoparticles can be also earned using a methodology based on magnetic susceptibility measurements in a.c. as a function of frequency (called frequency spectrum magnetic susceptibility –FSMS). It can be demonstrated that the so derived distribution overestimates the real dimensions of the nanoparticles. For example, the nanoparticles mean dimension derived from FSMS is 20% higher than the dimension derived from Mossbauer spectroscopy (see table above), pointing therefore the limits induced by the magnetometry method.

- Description and critical discussion of analysis and characterization methodologies of long range particle interactions (dipolar interactions and interactions transmitted through substrate, respectively).

Exemplification of methods for obtaining the information related to the NPs interactions can be done for a magnetic ferro-fluid set, with distinct volume ratios (the volume ratio η being defined as the ratio between the volume associated to the solid part and the volume of the ferro-fluid; similarly, the ferro-fluid density can be evaluated based on the relation $\rho_{FF} = \rho_{NPs}\,\eta + \rho_{TO}\,(1-\eta)$) given in the table below:

Sample code	ρ_{FF} (g/cm^3)	η
FF1	1.04	0.04
FF2	1.53	0.15
FF3	1.73	0.20

The Mossbauer spectra dependent on temperature for the FF1 sample are illustrated in Fig. 11, where the evolution of the mean hyperfine field with the temperature can be seen also for all the three studied samples.
One observes a much slower decrease of the high density (high volume ratio) ferrofluid samples with the temperature, which is equivalent to higher energetic barriers for these samples.

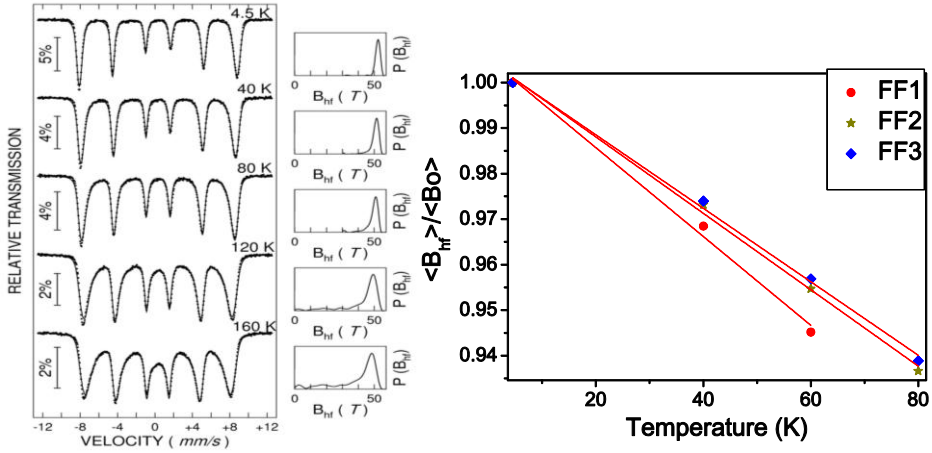


Fig.11. Mossbauer spectra in the collective excitations domain for the FF1 sample (left) and the temperature dependence of the reduced mean hyperfine magnetic field, for all 3 analyzed samples, respectively.

As the only difference between the samples is the volume ratio, the values obtained for the anisotropic energies using relation (8) and the experimental slopes SL_1 from Fig.11 increase with the volume ratio from the 480 K value in FF_1 to the 570 K value in FF3.

Other approached aspects, which were not detailed here, referred to:

- Analytical expression of the relaxation curve for independent and identical nanoparticles and critical discussion with respect to initial conditions and material parameters.
- Discussions on susceptibility components with emphasis on provided information (blocking temperature-by the in phase component and dissipated power by out of phase component) and theirs connections to magnetic hyperthermia applications.
- Description and critical discussion of methodologies providing evidence of inter- and intra-particle interactions
- 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 high-ranking international journals, as well as on the following presentations at international conferences and seminars, all of them including acknowledgements to the project (75/2011):

Publications:

[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, J.Phys.Chem: C 117 (2013) 13989-13999

[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

[**10**] Engineering magnetic properties of nanoparticles via size effects and interphase interactions, V. Kuncser, P. Palade, A. Kuncser, S. Greculeasa, G. Schinteie, (book chapter) in "Size effects in nanostructures:Basics and Applications, V.Kuncser and L.Miu eds., Springer-Verlag Berlin Heidelberg 2014

[**11**] Ferromagnetic behavior of bismuth germinate oxides glass-ceramic materials, S.Polosan, R.Negrea, I.C.Ciobotaru, G.Schinteie, V.Kuncser, J. Alloys and Comp. accepted, (2014)

[**12**] Insulin loaded magnetic nanoparticle-graphene oxide composites:synthesis, characterization and application for in vivo delivery of insulin, K.Turcheniuk, M.Khanal, A.Motorina, P.Subramanian, A.Barras, V.Zeitsev, V.Kuncser, A.Leca, A.Martoriati, K.Cailliau, J-F.Bodart, R.Boukherroub and S. Szunerits, RSC Advances, 4, 865 (2014)

[**13**] Approach for an improved experimental evaluation of the specific absorption rate in magnetic fluid hyperthermia, N.Iacob, G. Schinteie, P.Palade and V. Kuncser, Journal of Nanoparticle Research 17(4) 2015 190

[**14**] Reconstruction of superparamagnetic particle grain size distribution from Romanian loess using frequency dependent magnetic susceptibility and temperature dependent Mossbauer spectroscopy, Necula, C., Pamaiotu, C.,.Schinteie, G., Palade, P., .Kuncser, V., Global and Planetary Change 131 (2015) 89-103

[**15**] Magnetic nanocomposites for an efficient valorization of biomass, Kuncser , V., Coman, S., Kemnitz, E, Parvulescu, V., J. Appl.Phys. 117(17) (2015) 17D724

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
5. Magnetic relaxation of nanoparticulate systems in relation to bi-medical applications, V.Kuncser, N.Iacob, G.Schinteie, P.Palade, A.Leca and G. Filoti, Fifth Seeheim Conference on Magnetism, Octombrie 2013.
6. Specific magnetic response of functionalized Fe oxide nanoparticles in relation to bio-medical applications, V.Kuncser, N. Iacob, G.Schinteie, P.Palade, A.Birsdan, A.Kuncser, C.Ghica, A.Leca, S.Suneritz, invited lecture at 4th International Conference on Superconductivity and Magnetism, Turkey, 2014
7. Magnetic nanostructures and bio-medical applications, V. Kuncser, N. Iacob and G. Schinteie, Advanced workshop in solar energy conversion and nanophysics, Magurele-Bucharest, 2014

8. National conferences: Specific aspects of magnetic relaxation in nanoparticulate systems, V.Kuncser, oral presentation at Bucharest University Faculty of Physics 2013 Meeting