Synthetic scientific report

concerning the implementation of the project IDEI 75/2011 "Advanced approach of magnetic relaxation", October 2011- December 2014

Fe-based magnetic nanoparticle systems represented in the last years research topics of high interest, both scientific and application related (microelectronics, biomedicine and sensors). The remarkable specific properties of the magnetic nanoparticle systems are the result of three major contributions, sometimes interconnected: (i) intrinsic properties of the components, (ii) size effects and (iii) interphase or intercomponent interactions. The magnetic properties of a nanoparticle system depend on magnetic properties of constituent nanoparticles, which depend on the phase structure of each nanoparticle, on the nanoparticle sizes (assuming all to be 0-dimensional) and on the existing interactions. The nanoparticle size significantly influences the magnetic response through two major effects: superparamagnetic relaxation and disordered spin structure introduced at the nanoparticle surface. 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). For that purpose, different parameters such as composition and stoichiometry, phase structure, size distribution, morphology, couplings among magnetic entities, surface effects, will be taken into consideration in the attempt to correlate the mechanism of relaxation to all and every specific parameter related to nanoparticles.

1. Material parameters evidenced by means of a very powerful method: Mossbauer spectroscopy.
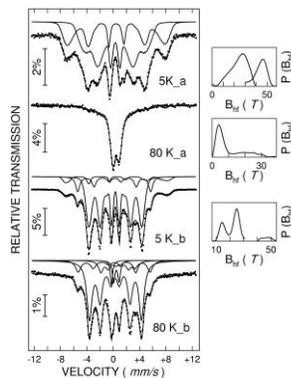
Fig.1. Mossbauer spectra obtained at 5 K and 80 K, on samples a, and b (set 1).

In order to exclude the dynamic magnetic effects (magnetic relaxation), very low temperature measurement regime was used (static regime). A topic of high interest was approached in the study of the nanoparticle systems, regarding differences in crystalline structure/phase composition and magnetic structure of the components, after subtle changes of preparation/processing conditions of the systems. The preparation methods have been laser pyrolysis and chemical methods, respectively. Metallic Fe nanostructures are extremely oxidazible when manipulated in normal conditions and can not be stabilized in this state unless protected by various matrices. Even in these conditions, partial oxidation occurs and completely or oxidated structures can be obtained, depending on the nanoparticle size, most probably presenting an oxidation gradient (rather reduced structure in the core and more oxidated, towards surface). From the point of view of the oxidation degree, hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) are to be mentioned among typical iron oxides, both containing only Fe^{3+} ions. The most probable combination for these oxide systems corresponds to the evolution from magnetite (in the core of the nanoparticle) to maghemite (towards surface). In the case of nanoparticles, the presence of

surface positions can induce a higher structural (and, implicitly, magnetic) disorder degree, affecting considerably the magnetic moment associated to the nanoparticle. An extremely powerful local technique, suitable for these systems, is the Mossbauer spectroscopy, offering information on the local symmetry, valence state and spin state of the iron ions on various positions, as well as on the spins/magnetic moments.

Two sample types are exemplified in this report: set 1 and set 2, prepared by laser pyrolysis, using acetilene (set 1) and air (set 2) as the confining agent. The Mossbauer spectra obtained at low temperatures (5 K and 80 K) on samples in the first set are shown in fig. 1. Very large patterns are observed, specific to defect structures, typical to nanoparticles with sizes lower than 10 nm. The spectra obtained at 5 K have been fitted with two distributions of magnetic hyperfine field. The two magnetic sublattices are assigned to an iron oxide phase with spinelic structure (mixture of magnetite and maghemite) and, respectively, an Fe-C/cementite phase. Fig. 2 shows the evolution of the Mossbauer spectra, of sample d (set 2), after applying hydrogenation treatments (20 bar, H_2 at 200 C/1-st hydr and 300 C/2-nd hydr). The first treatment induces a slight reduction, while the second treatment reduces completely the metallic iron powder.

2. Involved relaxation phenomena and magnetic behavior specific to all nanoparticle systems (NPs).

The synthesis conditions induced the formation of magnetic nano-composites of various sizes and phase compositions. The low temperature Mossbauer spectroscopy evidenced the existence of three nanoparticle types: i) spinelic oxides (solid solutions of maghemite and

Fig.2. Mossbauer spectra obtained at 5 K, after hydrogenation (sample d, set 2).

magnetite) (4-5 nm), ii) nanoparticles with Fe-bcc type phases (13-16 nm) and iii) mixture of carbides: Fe_3C, Fe_5C_2 and Fe_7C_3. (6-7 nm). Mossbauer spectroscopy measurements have been performed at different temperatures (between 4.2 K and 250 K) on the samples S1- S4. At 4.5 K, the first two magnetic phases have been assigned to Fe oxide (mixture of γ-Fe_2O_3 and Fe_3O_4 phases) NPs and to metallic Fe (bcc structure) NPs. In full agreement to XRD results, the third sextet was assigned to a carbide mixture (Fe_3C, Fe_5C_3 or Fe_7C_3). When increasing the temperature, the activation of a relaxation process specific only to the NPs is suggested. In order to study the relaxation phenomena in the S1-S4 systems, the temperature

Fig. 3. Temperature dependence of the average hyperfine magnetic field for sample S1.

evolution of the magnetic field is envisaged. An example of the sample S1 is shown in Fig. 3, and the relaxation of the three distinct phases (Fe oxide, Fe bcc and Fe-C) is evidenced.

The linear decrease of the average hyperfine magnetic field with temperature (observed in the case of metallic Fe and Fe-C phases) is specific to the collective excitations regime, while the sharp vanishing of the magnetic hyperfine field (specific to Fe oxide phases) corresponds to the superparamagnetic transition. An experimental criterion for the determination of the blocking temperature (T_B) is proposed, by means of Mössbauer spectroscopy. In the case of Fe or Fe-C nanoparticles, no decrease of the magnetic hyperfine field to half the initial value was observed in the experimental temperature range (5-260 K), for which T_B was not able to be determined through Mossbauer spectroscopy. In the case of Fe oxide NPs, the lowest T_B was observed for the sample

S2 (T_B=25 K), while the samples S1, S3 and S4 had $T_B \sim 60$ K. The mean size of the Fe oxide NPs is of approximately 5 nm in samples S1, S3 and S4, and 4 nm for sample S2, respectively.
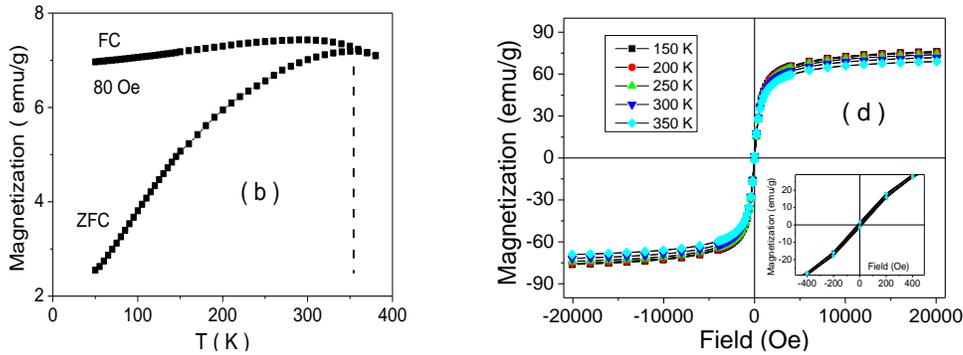
Fig. 4: ZFC-FC magnetization curves (left) and temperature dependent hysteresis loops (right) for surfacted NPs.
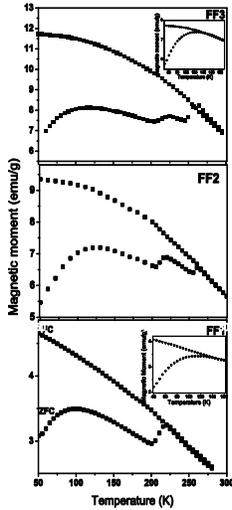
Fig.5. ZFC-FC magnetization curves for three different ferrofluid samples of volume fractions ranging from 0.04 (F1) to 0.20 (F3).

3. New methodology for determination of the anisotropy energy distribution of the NPs, applied in the comparative study of magnetic relaxation of the non-surfacted and dopamine surfacted magnetite NPs, for bio-medical applications. By combining magnetic and Mossbauer spectroscopy measurements, it was shown that dopamine surfactation induces the selection of NPs with larger sizes and lower size dispersion (fig.4). The issue of estimating the interactions between particles was approached in the case of the magnetic relaxation phenomena in three ferrofluids with increasing volume fractions. It was shown, considering both magnetic and Mossbauer spectroscopy measurements, that increase of the dipolar particle interactions induces the T_B of the systems and the magnetic anisotropy energy per nanoparticle - fig. 5. Different defrosting processes, related to the volume fraction, may be observed. The anisotropy energy barrier was determined from the specific evolution of the magnetic hyperfine field and the corresponding barrier increase was explained as being related to stronger dipolar magnetic interactions. Also, a new methodology of accurate experimental determination of the specific absorption rate in NP systems with different dispersions (fig. 6) and the calculation procedure of heat transfer per time unit, considering the energy loss mechanism due both to the imaginary part of the susceptibility, as well as due to hysteresis loss, was elaborated.

The following studies, having a significant contribution in the clarification of the electronic mechanisms and magnetic parameters, with direct influence on the magnetic relaxation phenomena, are to be mentioned:

- 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 relaxation phenomena are also considerably influenced by the inter- particle or intra- particle interactions. In the second case, the following situations may exist: (i) the particles are in contact in a range less lower than their circumference and (ii) one of the particles is completely embedded in the material of the second phase (core-shell type configuration, in which the interfacial interaction is maximized due to maximization of the contact surface of the two nanometer phases), NPs composed of two magnetic phases in direct interaction forming in both cases. The magnetic relaxation phenomena in the case of the nanoparticles formed from the two phases that are in interaction, become extremely complex, because in addition to the relaxation mechanism, related to the anisotropy energy per nanoparticle, a relaxation effect, implying the interfacial interaction energy, is superposed.

Fig. 6 Primary curve of temperature increase under the influence of the oscillating magnetic field and temperature decrease after stopping the applied field (left); adiabatic curve of temperature increase, obtained based on the proposed methodology (right).

Fig 7: Magnetic relaxation curves.

4. Superparamagnetic relaxation in the independent and identical NP systems

This case is treated theoretically, in an independent particle model (considering that the magnetic relaxation is related to the thermal activation process of the magnetic moments of the NPs over the magnetic energy barrier). Performing magnetic relaxation measurements on the NP system in various conditions can lead to obtaining a complete set of material parameters (τ_0, KV and M_S) (Fig. 7). In order to obtain the initial magnetization, the system is cooled from the superparamagnetic state to a very low temperature, in the absence of an applied field (zero field cooling), in which $M_0=0$. The temperature evolution of the relative magnetization, $M(t)/M_S$, with the deviation from the M_0 state in 3 different time values (after 10^{-4} s, 10^{-3} s and 10^{-2} s, equivalent to 3 different time windows) and measured in an applied field that induces a potential asymmetry Δ, of a thousandth KV, is shown in Fig 8.

Fig 8: Temperature dependence of the relative magnetization, corresponding to 3 different time windows.

5. Superparamagnetic relaxation in NP systems with long-range interactions.

The interaction energy in this case is of dipolar nature and, in consequence, the case when each NP is not only under the influence of an applied field (if any), but also under the influence of an effective (internal) field due to neighbors can be considered. In the absence of an applied field (the case of Mossbauer spectroscopy), the internal field is randomly oriented, and randomly leading to the amplification of one of the two energetic minima on the NP. All NPs will feel an average potential barrier directly proportional to the interaction between NPs. As a consequence, the NP interaction can be quantified in the Mossbauer spectroscopy by increasing the potential barrier

(implicitly, increasing the blocking temperature), simultaneous with increasing the interaction. On the other hand, in the case of magnetic measurements, by applying the measuring field, a quantifying axis is introduced in the system. It can be shown that the dipolar interaction favors an antiparallel orientation (antiferromagnetic nature) of the magnetic moments of the NPs, which induces overall a negative magnetization of the system, as if it would be under the influence of a negative internal field, directly proportional with the NP interaction.
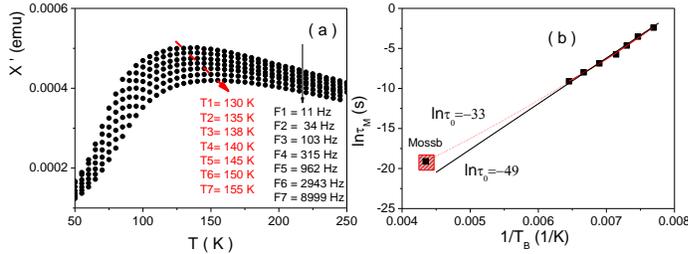
Fig.9: Temperature dependence of X' for a low volume fraction ferrofluid, at different frequencies (a) and the experimental dependence of $\ln \tau_M$ relative to $1/T_B$ (b).

Fig.10 Magnetic measurements obtained on the NP systems attached to the graphene foils. The ZFC curve is shown in the inset.

Finally, a last method to estimate the long range interaction between NPs can be based on the evaluation of the dependence between the time window of the method (the inverse of the oscillating field frequency in an ac measurement) and the blocking temperature corresponding to that temperature. In fig. (4), the temperature dependence of X' for a system of NPs dispersed in a fluid (ferrofluid) of low volume fraction (T_B can be deduced from the X' maximum) for different frequencies, and the experimental dependence of $\ln \tau_M$ relative to $1/T_B$ (b). Both parameters can be accurately determined only if the dependence is completed with the result on an extreme time window (given by Mossbauer spectroscopy). Concerning the long range NP interactions, of a

Fig.11. Presence of exchange bias at 5 K suggests the presence of a core (metallic phase) - shell (oxidic phase) type structure of the nanoparticles containing iron and magnetite/maghemite phases.

nature different than dipolar, in the case of oxidized graphene foils functionalized with NPs, the superparamagnetic behavior of the functionalized NPs is observed (peak in the ZFC curve, Fig. 10) and also the existence of a long range interaction between the NPs, mediated by the oxidized graphene foil.

6. Effect of interfacial intra-particle interaction: if the NP is composed of two different magnetic phases, the interfacial interaction between the two phases can induce two interesting effects, depending on the magnetic nature of the two phases in contact. A very interesting case is when one of the phases is ferromagnetic and the other is antiferromagnetic or implies internal antiferromagnetic couplings, in other words exchange bias (example in Fig. 11).

Project manager,
Victor Kuncser