

MAGNETIC NANOPARTICLES AND MAGNETIC NANOSTRUCTURES

J.M. Greneche

*Laboratoire de Physique de l'Etat Condensé LPEC, UMR CNRS 6087,
Université du Maine, 72085 Le Mans, Cedex 9, France.
greneche@univ-lemans.fr*

During the last ten years, increasing attention has been devoted to the preparation and the study of the magnetic nanostructures including multilayers, nanocrystalline alloys, nanoparticles and nanostructured powders and the search of new nanoarchitectures. Indeed those nanostructures exhibit unusual fundamental properties and are very promising because of technological interests in magnetic recording and storage (spintronics), catalysis, and biomedicine after subsequent functionalization of some nanoparticles.

The methods of synthesis based on either chemical or physical concepts allow the structural and microstructural properties of these materials to be highly controlled and to be well reproduced. Indeed, the present objectives in nanosciences and nanotechnology are to prepare monodisperse nanoparticles, chemically homogeneous nanoparticles and their dispersion into a matrix to control the physical properties while the understanding of the mechanism of synthesis would allow to correlate the synthesis conditions and the chemical composition to tune structural and physical characteristics. In addition, it is important to emphasize the relevant contribution (increasing atomic fraction) of the surface because of the symmetry breaking, and the grain boundaries in the case of nanoparticles and nanostructured powders, respectively, as illustrated in Figure 1.

The role of these contributions on the chemical and physical properties starts to be rather clarified, favouring thus the applications of these nanostructures to be developed and further new architectures based on nanoparticles to be designed.

The applications of the different types of magnetic nanomaterials will be first reviewed. Attention will be then devoted to the individual and collective magnetic properties expected in the case of assembly of nanoparticles as a function of their size and their dispersion. Indeed, the properties of magnetic nanoparticles are strongly

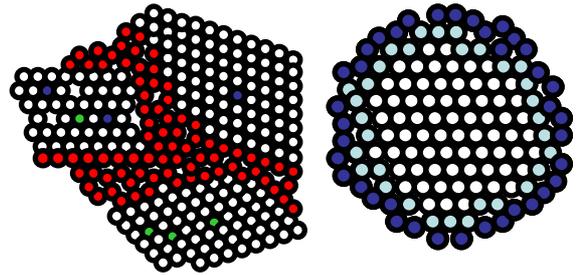


Figure 1: schematic representation of the grain boundaries in nanostructured system (left) and the surface in nanoparticle (right).

dominated by finite-size and interaction effects: The smaller the particle, the higher the surface-to-volume ratio, the stronger are these effects. In addition, the competition between surface and core magnetic properties determines the spin structure in the particle, which may thus be altered with respect to that in the bulk material. Thus, one can easily conclude that non interacting particles behave as superparamagnets contrarily to dense assembly of nanoparticles where dipolar interactions will prevail on the relaxation phenomena, originating thus a spin cluster glass collective state. The intermediate situation corresponding to assembly weakly interacting nanoparticles remains difficult to be modelled. These three classes of assemblies of magnetic nanoparticles can be easily experimentally investigated [1, 5].

Illustrations on the basis of recent studies will be then presented in order to understand the magnetic properties for as-prepared nanoparticles, subsequently annealed and functionalized nanoparticles as nanoferrites, as well as densified nanoparticles. Attention will be also previously paid to a complete description of the structural properties as obtained using experimental features combining X-ray diffraction, EXAFS, and Transmission Electron Microscopy to demonstrate the relevance of these complementary techniques.

Once this structural characterization is well achieved, static and dynamic magnetic properties will be investigated by also using complementary techniques as ac and dc magnetic measurements (with Field Cooled and Zero Field Cooled procedure), microsquid, XMCD and ^{57}Fe Mössbauer spectrometry (as a function of temperature and external applied field). The complementarity is particularly due to the time scale sensitivity scanning which finally provides a unique way to characterize and then to understand the dynamics of assemblies of magnetic nanoparticles.

Among experimental routes, it is important to emphasize that the contribution of ^{57}Fe Mössbauer spectrometry will be emphasized in the case of Fe-based nanomaterials. It is clear that the local probe sensitivity makes zero field and intense magnetic field Mössbauer spectrometry an excellent tool to characterize the structural and magnetic properties through the hyperfine parameters. In addition the characteristic time measurement in the nanosecond range allows the superparamagnetic fluctuations to be evidenced and to study the magnetic dynamics as a function of temperature.

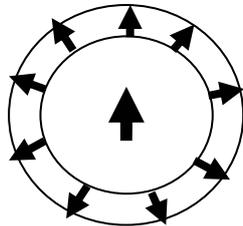


Figure 2: Schematic representation of the magnetic core-shell model of a nanoparticle.

A first result proposed in 70's [6] and recently confirmed [4, 7] evidences the core-shell magnetic structure as illustrated in Figure 2 from Mössbauer studies performed on monodisperse nanoparticles of maghemite dispersed into a matrix (Figure 3). Different studies on nanostructured ferrites prepared by mechanical milling and chemical route will demonstrate the role of the grain boundaries compared to that of dipolar interactions to understand the collective magnetic properties. We will emphasize that the chemical composition of nanoparticles might affect the magnetic properties when cationic inversion occurs as in the case of ferrite [8-13] and when it differs from the centre and the periphery. Morphology is also an important

parameter which influences the surface magnetic properties which is evidenced to be canted, as resulting from the symmetry breaking.

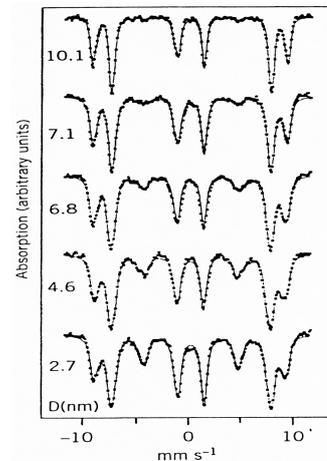


Figure 3: Evolution of in-field Mössbauer spectra on maghemite nanoparticles with different dispersion rates (from 7)

In the case of Fe oxides, attention will be paid to the exact nature of nanoparticles, which have to be described as a core-shell structural model resulting from both magnetite and maghemite like phases, respectively [14, 15]. This view results from Mössbauer spectra, magnetic XPS measurements (see figure 4). Finally, the study of functionalized oxides nanoparticles with different types of molecules allows to characterize the chemical nature at the interface nanoparticle-molecule (see figure 5 and 6) or the occurrence of a new shell interface (see figure 7) [15, 16], preventing thus this system to be applied as drug delivery or for magnetohyperthermy applications.

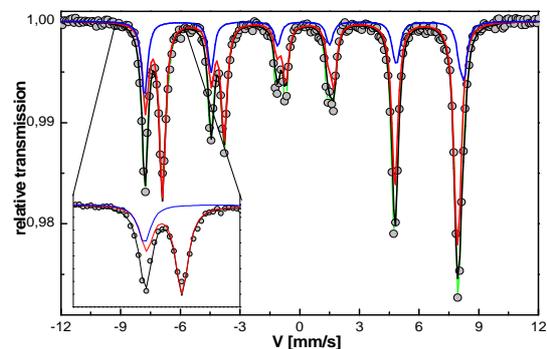


Figure 4: Room temperature Mössbauer spectrum recorded on maghemite nanoparticles decomposed into 2 components which are magnetite and maghemite (inset corresponds to a zoom with the two resolved lines)

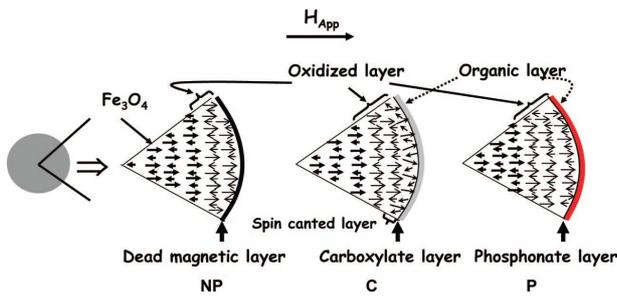


Figure 5: Schematic representation of the magnetic surface of as-prepared (NP) and functionalized C and P nanoparticles [15]

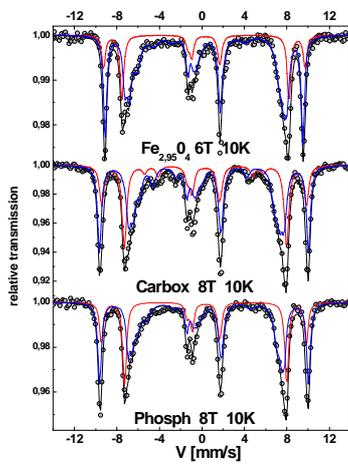


Figure 6: In-field Mössbauer spectra recorded on as-prepared (NP) and functionalized (Carboxylate and Phosphonate) nanoparticles [15]

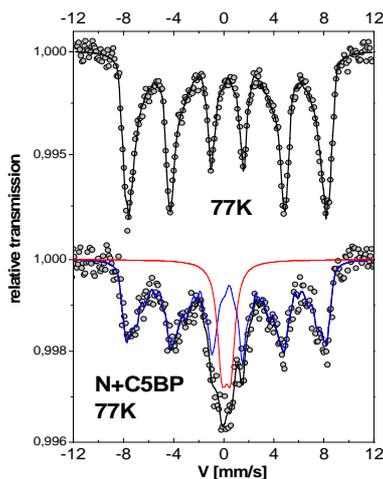


Figure 7: Mössbauer spectra at 77K of magnetic nanoparticles (top) and of these nanoparticles after vectorization (bottom): one clearly observes the occurrence of an additional quadrupolar component.

Nanostructured magnetic oxide powders will be also discussed on the basis of results obtained on nanostructured ferric fluoride powders prepared by ball milling route from the rhombohedral FeF_3 crystalline phase [17-19]. Indeed, this later system allows better to evidence the role of grain boundaries on the whole system by comparing their thickness to the magnetic correlation length. In addition, ^{57}Fe Mössbauer spectrometry allows to follow both the individual and collective magnetic behaviour of the crystalline grains and the grain boundaries (as illustrated in Figure 8) because these later behave as speromagnet which strongly differs from antiferromagnetic crystalline grains. This section will be reported at the end to discuss the magnetic properties of nanoarchitectures based on metallic and oxides.

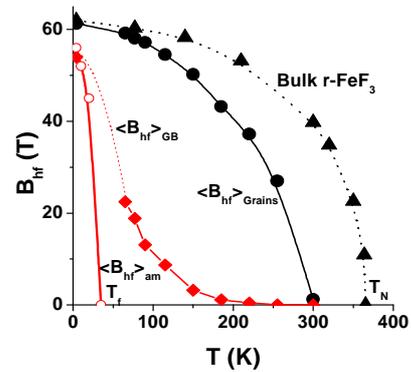


Figure 8: Temperature dependencies of the mean hyperfine field characteristics of grain boundaries (♦) and crystalline grains (●) of nanostructured ferric fluoride powders, compared to those of amorphous (○) and crystalline (▲) ferric fluorides, respectively.

This review aims to define clearly first the nanomaterials and their main structural and chemical characteristics and then to give great attention on the origin of the unusual physical properties of confined systems, particularly in the case of magnetic systems. We will also stress how the chemical and/or physical routes to prepare such nanoarchitectures have to be well controlled in order to prepare homogeneous, chemical stability and reproducible systems, allowing their physical properties to be tuned. Magnetic models in the case of assemblies of nanoparticles will be illustrated on the basis of experimental studies performed on nanostructured powders and nanoparticles of as-prepared and functionalized ferrites by means of complementary techniques

(including microscopy, diffraction techniques, surface sensitive tools and local probe spectroscopies and time scale sensitive techniques for magnetic systems where dynamics prevails on static effects).

Finally the computer simulation approach will be also underlined to illustrate how it does contribute in predicting physical properties of complex nanoarchitectures. Indeed, the first step consists in the atomic modelling of the nanoparticles where the surfaces are in an out of equilibrium metastable state, as well as the grain boundaries in the case of nanostructured powders which can be described by the mismatch of the individual crystalline structure of the grains far from the interfaces. In the case of magnetic systems, Monte-Carlo simulated annealing technique can provide models describing how the surface anisotropy strongly influences the intrinsic magnetic structure of a ferromagnetic spherical nanoparticle assumed. Great care has to be taken into the simulations with the choice of the method either molecular dynamics or Monte Carlo and then of the physical and non physical parameters.

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References:

- 1 J.L. Dormann, D. Fiorani, E. Tronc, *Adv. Chem. Phys.* 98 (1997) 283.
- 2 J.L. Dormann, L. Bessais, D. Fiorani, *J. Phys. C* 21 (1988) 2015.
- 3 J.L. Dormann, D. Fiorani, E. Tronc, *J. Magn. Magn. Mater.* 202 (1999) 251.
- 4 J.L. Dormann, L. Spinu, E. Tronc, J.P. Jolivet, F. Lucari, F. D'Orazio, D. Fiorani, *J. Magn. Magn. Mater.* 183 (1998) L225.

- 5 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
- 6 J.M.D. Coey *Phys. Rev. Letters* 17 (1971) 1140
- 7 E. Tronc, P. Prene, J.P. Jolivet, J.L. Dormann, J.M. Grenèche, *Hyperfine Interactions* 112 (1998) 97.
- 8 N. Ponpandian, A. Narayanasamy, C.N. Chinnasamy, N. Sivakumar, J.-M. Grenèche, K. Chattopadhyay, K. Shinoda, B. Jeyadevan, and K. Tohji, *Appl. Phys. Lett.* 86, 192510 (2005)
- 9 S. Ammar, N. Jouini, F. Fiévet, Z. Beji, L. Smiri, P. Molinié, M. Danot and J.M. Grenèche *J. Phys.: Condens. Matter* 18 (2006) 9055–9069
- 10 N. Sivakumar, A. Narayanasamy, N. Ponpandian, J.-M. Grenèche, K. Shinoda, B. Jeyadevan, and K. Tohji, *J. Phys. D: Appl. Phys.* 39 (2006) 4688–4694
- 11 C.N. Chinnasamy, A. Narayanasamy, N. Ponpandian, K. Chattopadhyay, H. Guérault and J.M. Grenèche *J. Physics: Condensed Matter* 12 (2000) 7795-7805
- 12 Z. Beji, N. Yaacoub, L. Smiri, J.M. Grenèche, N. Menguy, S. Ammar, F. Fiévet, submitted
- 13 T. J. Daou, G. Pourroy, S. Bégin-Colin, J.M. Grenèche, C. Ulhaq-Bouillet, P. Legare, P. Bernhardt, C. Leuvrey, and G. Rogez *Chem. Mater.* 2006, 18, 4399-4404
- 14 T.J. Daou, S. Bégin-Colin, J.M. Grenèche, F. Thomas, A. Derory, P. Bernhardt, P. Legare, and G. Pourroy *Chem. Mater.* 2007, 19, 4494-4505
- 15 T. J. Daou, J.M. Grenèche, G. Pourroy, S. Buathong, A. Derory, C. Ulhaq-Bouillet, B. Donnio, D. Guillon and S. Bégin-Colin *Chem Mater* 20 (2008) 5869–5875
- 16 A. Karimi, B. Denizot, G. Tanguy, F. Hindré, R. Filmon, J.M. Grenèche, S. Laurent, T.J. Daou, S. Bégin-Colin, A. Roch, J.J. LeJeune submitted
- 17 H. Guérault and J.M. Grenèche *J. Physics: Condensed Matter* 12 (2000) 4791-4798
- 18 H. Guérault, M. Tamine and J.M. Grenèche, *J. Physics : Condensed Matter* 12 (2000) 9497-9508
- 19 H. Guérault, B. Bureau, G. Silly, J.Y. Buzaré and J.M. Grenèche, *J. Non-Cryst. Solids* 287 (2001) 65-69