

Synthesis of iron oxide-based magnetic nanomaterials and composites

Jean-Pierre Jolivet*, Élisabeth Tronc, Corinne Chanéac

'Chimie de la matière condensée', UMR CNRS 7574, université Pierre-et-Marie-Curie, 4, place Jussieu, 75252 Paris cedex 05, France

Received 3 June 2002; accepted 9 October 2002

This article corresponds to a lecture presented at the meeting *Synthetic Strategies for New Spin Topologies*, organised by D. Gatteschi, H. Ratajczak, A. Müller, M. Verdaguer, and V. Marvaud on 7–9 March 2002, at the Scientific Centre of the Polish Academy of Sciences in Paris.

Abstract – Various properties of spinel iron oxide nanoparticles are reviewed in relation to the control of the particle size and the control of their dispersion in a variety of matrices. The deep knowledge of the different synthesis parameters and the interfacial oxide–solution characteristics allow us to prepare a large variety of materials like calibrated nanoparticles and inorganic or hybrid nanocomposites. *To cite this article: J.-P. Jolivet et al., C. R. Chimie 5 (2002) 659–664* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

spinel iron oxide nanoparticles / oxide–solution interface / nanocomposites

Résumé – Différentes propriétés de nanoparticules d'oxyde de fer de structure spinelle ont été examinées du point de vue du contrôle de la taille des particules et de leur dispersion dans diverses matrices. La connaissance approfondie des différents paramètres de synthèse et des caractéristiques de l'interface oxyde–solution nous permet de préparer une large variété de matériaux, comme des nanoparticules calibrées et des nanocomposites inorganiques ou hybrides. *Pour citer cet article: J.-P. Jolivet et al., C. R. Chimie 5 (2002) 659–664* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

nanoparticules d'oxyde de fer de structure spinelle / interface oxyde–solution / nanocomposites

1. Introduction

Ferro- and ferrimagnetic materials have been receiving a growing interest for both technological and theoretical reasons, especially in the context of magnetic recording. However, the properties of finely divided magnetic materials closely depend on the size of the particles and their state of dispersion and aggregation [1]. It is therefore very important to carefully control the synthesis of particles and their surface state.

Various chemical techniques [2] for controlling the particle size consist in limiting the space available for

the particle growth, by precipitating ions in micro-emulsions, vesicles or polymer solutions. However, such methods raise difficulties in getting out particles free from polymer, surfactant or ligands mostly inducing surface effects influencing the magnetic behaviour of the particles. Other techniques often used are gel impregnation [3] and sol–gel methods [4], involving aqueous metal ions and subsequent thermal treatment. In these conditions, well-defined materials regarding the crystal structure, the mean particle size, the size distribution, the morphology and the state of dispersion appear very difficult to obtain, because it is difficult to control the reactions.

* Correspondence and reprints.

E-mail address: jpj@ccr.jussieu.fr (J.-P. Jolivet).

Precipitation or coprecipitation of cations in aqueous solutions is an easy and cheap route of synthesis of metal oxide particles [5]. Thus, spinel iron oxides (magnetite Fe_3O_4 , maghemite $\gamma\text{-Fe}_2\text{O}_3$ and substituted magnetites, MFe_2O_4 with $\text{M} = \text{Fe}, \text{Co}, \text{Ni}\dots$) are easily formed by coprecipitating Fe^{3+} and M^{2+} ions. However, the physicochemistry of the systems have to be carefully controlled to adjust the characteristics of particles. Our studies showed that the particle size can actually be calibrated over one order of magnitude in the nanometer range, and that the aqueous dispersions of maghemite particles can be used to elaborate a variety of nanocomposites where the particle dispersion is controlled.

2. Synthesis and tailoring of iron oxide nanoparticles

Magnetite is easily obtained by coprecipitating aqueous Fe^{3+} and Fe^{2+} ions. At the stoichiometry $\text{Fe}^{2+}/\text{Fe}^{3+} = 0.5$, crystallisation of spinel phase is quasi-immediate at room temperature. The mean par-

ticle size is monitored by the conditions of the medium: pH and ionic strength, I , imposed by a salt. Typical experimental conditions [6, 7] are: 2.5 ml of a solution containing a mixture of FeCl_2 (1 mol l^{-1}) and $\text{Fe}(\text{NO}_3)_3$ (2 mol l^{-1}) were slowly, automatically injected into 25 ml of a solution of NaNO_3 at a concentration in between 0.5 and 3 mol l^{-1} . The pH of the medium was fixed and kept constant ($\Delta\text{pH} \approx 0.1$) by addition of NaOH , using an automatic potentiometric device. All solutions were carefully de-aerated with nitrogen, which was continuously bubbled during the precipitation. Ageing of the suspensions was achieved under argon atmosphere. Various samples were prepared in the range $8.5 \leq \text{pH} \leq 12$ and $0.5 \leq I \leq 3 \text{ mol l}^{-1}$.

Electron micrographs (Fig. 1) show spheroidal particles whatever the synthesis conditions, but with very different mean sizes. X-ray Diffraction (XRD) patterns (Fig. 2) are typical of the spinel phase. The line positions are the same for all samples, indicating no significant structural variation between the samples.

Fig. 3 shows the influence of the precipitation conditions on the mean size of the particles after 8-day

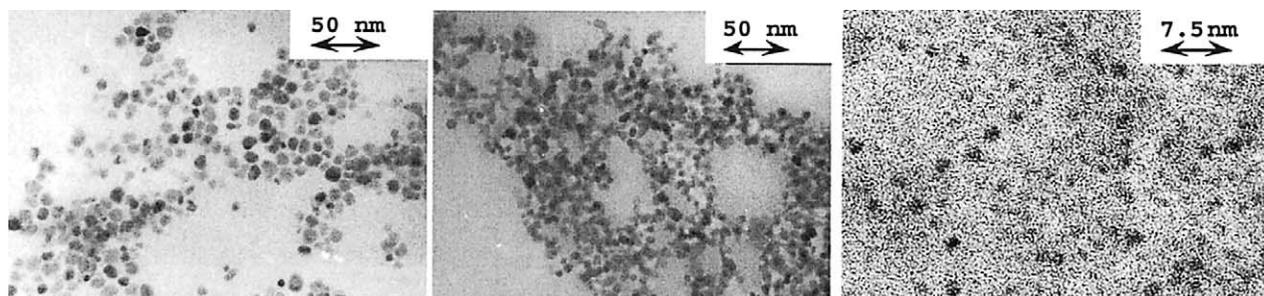


Fig. 1. Transmission Electron Micrographs (TEM) of particles synthesised under various conditions: (a) $\text{pH} = 9$, $I = 0.5 \text{ mol l}^{-1}$ [$D = 12.5 \text{ nm}$; $\sigma(D) = 2.5 \text{ nm}$]; (b) $\text{pH} = 12$, $I = 0.5 \text{ mol l}^{-1}$ [$D = 6.5 \text{ nm}$; $\sigma(D) = 1 \text{ nm}$]; (c) $\text{pH} = 12$, $I = 3 \text{ mol l}^{-1}$ [$D = 1.6 \text{ nm}$; $\sigma(D) = 0.2 \text{ nm}$] ($T = 25^\circ\text{C}$; 8-day aged suspensions).

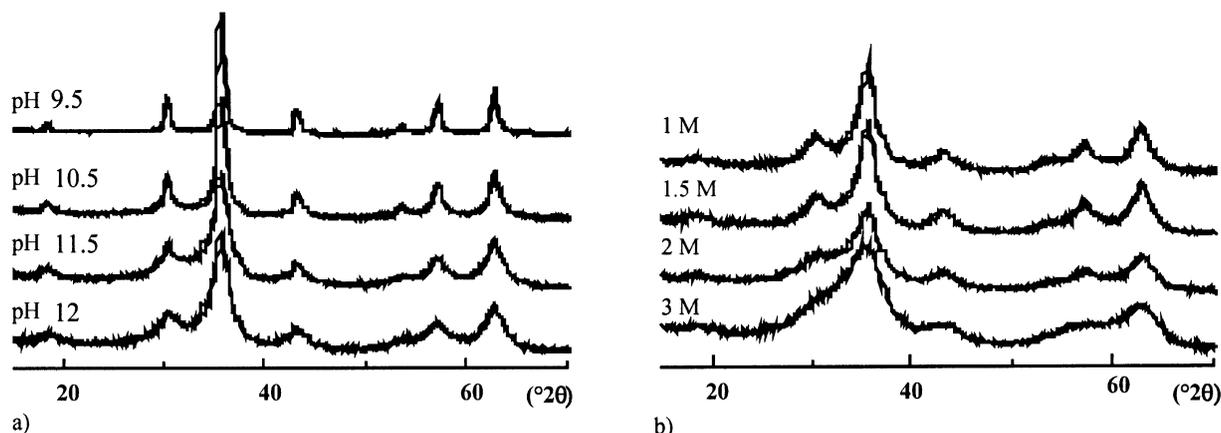


Fig. 2. X-ray diffraction patterns ($\lambda_{\text{Cu K}\alpha} = 1.5406 \text{ \AA}$) of particles synthesised (a) at different pHs with $I = 1 \text{ mol l}^{-1}$ and (b) at $\text{pH} = 12$ with different ionic strengths ($T = 25^\circ\text{C}$; 8-day aged suspensions).

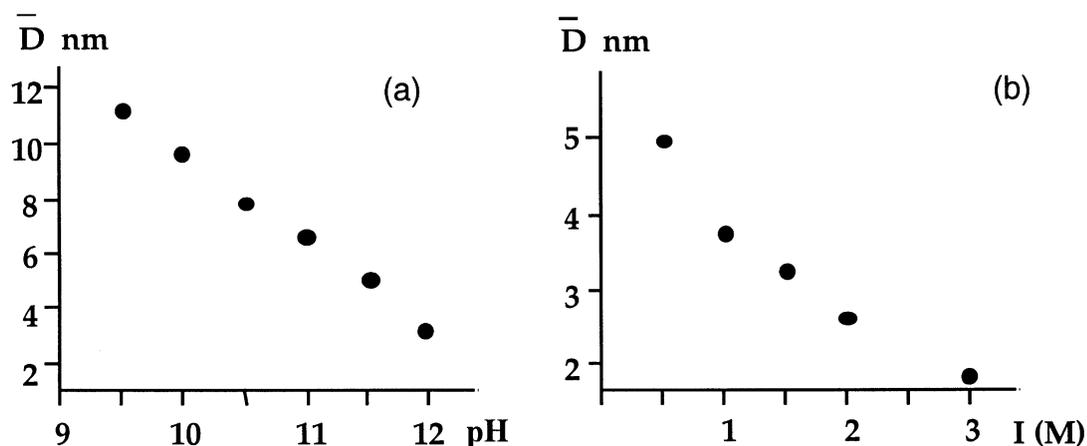


Fig. 3. Mean diameter of particles after 8-day ageing (a) as a function of pH (NaNO_3 1 mol l^{-1}) and (b) as a function of ionic strength ($\text{pH} = 12$) ($T = 25^\circ \text{C}$).

ageing. The mean size is strongly dependent on the acidity and the ionic strength of the precipitation medium, and clearly decreases with increasing pH and I .

It is interesting to observe that such an influence of acidity on the particle size is relevant to thermodynamics rather than kinetics (nucleation and growth processes) [7, 8]. The pH acts on protonation–deprotonation equilibriums of surface hydroxylated groups and, hence, on the electrostatic surface charge. The ionic strength carries out more or less electrostatic screening between charged groups and, then, at fixed pH, the electrical charge increases with I . Consequently, a change in the surface electrical charge due to pH leads to a change in the chemical composition of the interface, inducing a decrease of the interfacial tension, γ , as stated by Gibbs’s law, $d\gamma = -\Gamma_i d\mu_i$, where Γ_i is the density of adsorbed species i with chemical potential μ_i . Finally, the surface contribution, $dG = \gamma dA$ (A is the surface area of the

system) to the free enthalpy of the formation of particles is lowered, allowing the increase in surface area of the system [9].

Maghemite $\gamma\text{-Fe}_2\text{O}_3$ does not form directly in solution by precipitation of ferric ions, but a small proportion of Fe^{2+} ($x \geq 0.1$) induces the crystallisation of all the iron to spinel. Studies of the early precipitate revealed that all Fe^{2+} ions were incorporated into a Fe^{2+} -ferrihydrite and gave rise to high electron mobility, as evidenced by Mössbauer spectroscopy [10, 11]. This mixed valence material transforms with time into spinel by two simultaneous competing pathways: (i) solid state reaction with dehydration and spinel ordering at short range without particle size variation; (ii) dissolution of $\text{Fe}^{2+}\text{-Fe}^{3+}$ complexes from the surface, followed by crystallisation of spinel oxide (Ostwald ripening), this process taking place with considerable particle growth. The endproducts of the coprecipitation are single phase only for $x \geq 0.33$, process (ii) seeming dominant during the evolution from the ini-

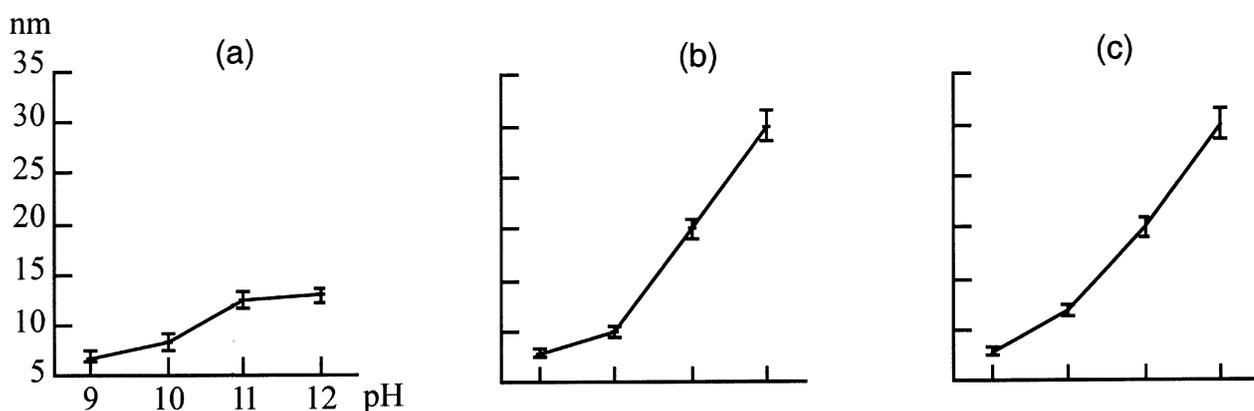


Fig. 4. Mean diameter of particles of (a) CoFe_2O_4 , (b) MnFe_2O_4 , (c) NiFe_2O_4 after 24-h ageing at 100°C of suspensions as a function of pH.

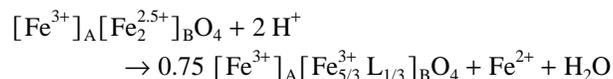
tial stage of precipitation, as noticeable growth of particles is observed.

The comparison with the cases where M^{2+} is different from Fe^{2+} emphasises the role of electron mobility between Fe^{2+} and Fe^{3+} ions in the crystallisation process. Mobility in the bulk presumably drives a local cubic close-packed ordering, made possible by the loose structure of the early material. This local ordering gradually extends to the whole fine particles (process (i)) and to the growing particles by process (ii). With the other divalent cations, intervalence transfers are generally negligible and a spinel ferrite forms only by process (ii) (dissolution–crystallisation) [11]. Nevertheless, a control of particle size is possible on a wide range, because the solubility of the solid is strongly dependent on the pH of the medium [12] (Fig. 4).

3. Oxidation of magnetite particles.

Formation of aqueous sols of maghemite

Due to the high electron mobility in the bulk, the magnetite nanoparticles are very unstable against oxidation, leading, at term, to maghemite. Different mechanisms [13] involving ionic and/or electronic interfacial transfers are implicated, depending on the pH of the suspension. In basic medium, the oxidation of Fe^{2+} ions proceeds by oxygen reduction at the surface of particles (electron transfer only) and coordination of oxide ions, while in acidic medium and anaerobic conditions, surface Fe^{2+} ions are desorbed as hexaaquo complexes in solution (electron and ion transfer) according to:



where A and B stand for tetrahedral and octahedral sites, respectively, and L represents a vacancy.

Maghemite nanoparticles, bearing a high positive charge density ($\sigma \approx 0.3 \text{ C m}^{-2}$ at pH 2, and low ionic strength, $10^{-2}/5.10^{-2} \text{ mol l}^{-1}$), can easily be dispersed in acidic water, forming cationic sols practically free from aggregation [14–16]. On raising the pH, σ decreases, the repulsions between particles weaken, the degree of agglomeration increases. Aggregation remains limited provided that $pH < PZC$. The aggregate configuration, dependent on the pH, ranges from small chain-like clusters of a few particles to branchy chains of more than ca 50 particles. In every case, the

structure is loose and the particles are not in close contact. At $pH \sim PZC$, $\sigma \sim 0$, a floc forms. At $pH > PZC$, the particle re-disperse, but aggregation is generally more significant than at $pH < PZC$, because the surface is less solvated.

4. Dispersion of maghemite nanoparticles in polymers and silica glasses. Nanocomposites

The particles synthesised and dispersed in aqueous medium can be trapped in different solid matrices keeping their dispersion state.

By adding a hydrosoluble polymer in the sol and drying of the mixture, solid samples were obtained. The oxide/polymer mass ratio determines the average distance between the objects existing in the sol, isolated particles or aggregates. This technique was used to prepare series of composites made up of maghemite particles with the same size distribution and different aggregation/dispersion states in polyvinyl alcohol, typically isolated particles with volume concentration ranging from ~1 to 20%, clusters of varying length and flocs, in order to study the magnetic properties of noninteracting particles and the interparticle interaction effects [1, 15, 17–19]. Such materials allowed us to give the first demonstrative experimental verification of the Néel–Brown model for superparamagnetic relaxation [17]

Composites made up of well-dispersed maghemite particles in an epoxy resin were obtained by polymerisation of the resin inside an organosol of particles [20]. The transfer of particles from aqueous medium to an organic solvent (sulfolane, propylene carbonate, hexamethylphosphorus-triamide) needs the adsorption of a coupling agent such as a phosphonic acid (phenylphosphonic acid, PPA). The head of the molecule, the phosphate group, strongly adsorbs onto particles, as evidenced by infrared and Mössbauer spectroscopies. The room temperature Mössbauer spectra of uncoated and coated particles are shown in Fig. 5. The quadrupole doublet observed for the coated particles demonstrates the formation of a paramagnetic surface complex, due to the strong complexing ability of PPA for iron [21].

The hydrophobic tail (phenyl group) of the coupling agent allows the dispersion in the organic solvent and prevents aggregation of the particles forming a kinetically stable organosol, as indicated by light scattering. The components of CIBA–GEIGY epoxy resin (araldite LY556, hardener HY917 and accelerator DY070) introduced in the sol form a homogeneous hybrid composite material after heating at 60 °C for 24 h. The materials were examined as thin slices by transmission electron microscopy (Fig. 6).

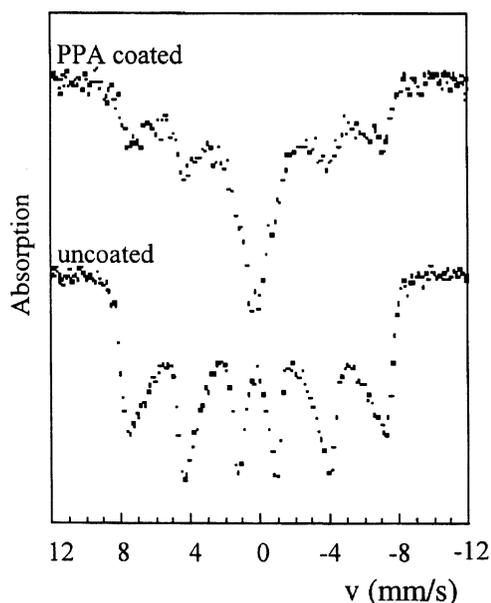


Fig. 5. Mössbauer spectra (at room temperature) of uncoated and PPA coated maghemite particles (9.0 nm).

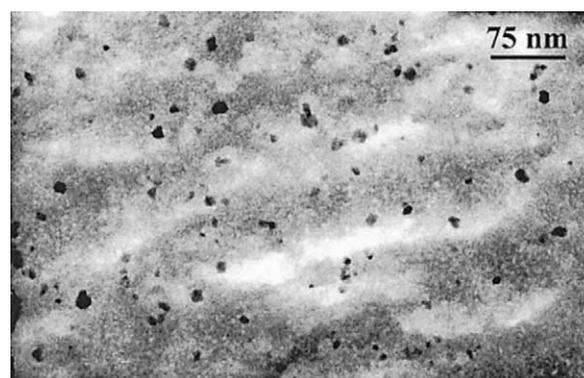


Fig. 7. TEM micrograph of a maghemite-silica composite (18 wt% Fe₂O₃).

Silica composites were prepared by polymerising silicic acid or alkoxysilanes inside the aqueous sol [22, 23]. Hydrolysis and condensation of the precursors take place in situ and the reactions yield a gel that leads, after drying at room temperature, to a transparent monolithic glass. Such a procedure leads to homogeneous solid composites (Fig. 7), containing up to 40 wt% Fe₂O₃. In both cases, infrared, near-infrared and Mössbauer spectroscopies indicate no detectable Fe–O–Si bond. In fact, the ‘dispersability’ of particles into the silica matrices results from solvation of silanol groups of the matrix by associated-water layers surrounding the particles, without other chemical surface interactions. The silica matrix acts as an antisintering agent, which stabilises the maghemite

particles against the thermal transformation into hematite. Whereas with powdered uncoated particles, the $\gamma \rightarrow \alpha$ -Fe₂O₃ transformation starts below 300 °C and is generally complete at 400 to 500 °C, in composites with sufficiently low particle concentration, no transformation occurs as long as the matrix prevents the migration and coalescence of particles that is, up to around 1000 °C, the temperature at which the glass softens or starts crystallising [24].

5. Conclusion

The aqueous chemistry of spinel iron oxide nanoparticles offers broad possibilities for tailoring materi-

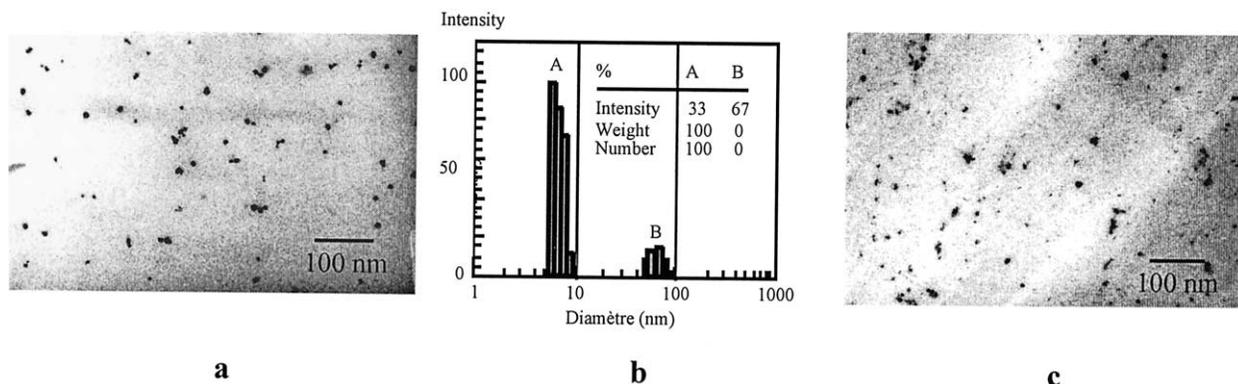


Fig. 6. Transmission electron micrographs (a) and quasi-elastic light scattering observation (b) of maghemite particle (4.7 nm) dispersed in hexamethylphosphorus triamide; micrographs of magnetic composites (4.7 nm maghemite particle-epoxy resin, thin slice) (c).

als for a wide range of utilisation. The careful control of the size and degree of dispersion of the particles in

composite materials can allow one to reveal unexpected phenomena.

Acknowledgements. We are deeply grateful to our magnetician colleagues, M. Noguès, LMOV, University of Versailles, France, D. Fiorani, IC-Mat, CNR, Monterotondo Staz., Italy, F. Lucari and F. D'Orazio, Università L'Aquila, Italy, for appreciating our materials and to M. Laverigne, UPMC, Paris, France, for electron microscopy observations.

References

- [1] J.-L. Dormann, D. Fiorani, E. Tronc, *Adv. Chem. Phys.* 98 (1997) 283.
- [2] A.J.I. Ward, S.E. Friberg, *Mater. Res. Sci. Bull.* 14 (1989) 41.
- [3] C.R.F. Lund, J.A. Dumesic, *J. Phys. Chem.* 85 (1981) 3175.
- [4] G. Ennas, A. Musinu, G. Piccaluga, D. Zedda, D. Gatteschi, C. Sangregorio, J.L. Stanger, G. Concas, G. Spano, *Chem. Mater.* 10 (1998) 495.
- [5] J.-P. Jolivet, *Metal Oxide Chemistry and Synthesis: from Solution to Solid State*, Wiley, Chichester, 2000.
- [6] J.-P. Jolivet, L. Vayssières, C. Chanéac, E. Tronc, *Mater. Res. Symp. Proc.* 432 (1997) 145.
- [7] L. Vayssières, C. Chanéac, E. Tronc, J.-P. Jolivet, *J. Colloid Interface Sci.* 205 (1998) 205.
- [8] R. Aveyard, *Chem. Ind.* 474 (1987).
- [9] C. Froidefond, C. Chanéac, E. Tronc, J.-P. Jolivet (to be published).
- [10] J.-P. Jolivet, P. Belleville, E. Tronc, *Clays Clay Miner.* 40 (1992) 531.
- [11] E. Tronc, P. Belleville, J.-P. Jolivet, *J. Livage, Langmuir* 8 (1992) 313.
- [12] A. Pottier, C. Chanéac, E. Tronc, J.-P. Jolivet (to be published).
- [13] J.-P. Jolivet, E. Tronc, *J. Colloid Interface Sci.* 125 (1988) 688.
- [14] J.-P. Jolivet, R. Massart, J.-M. Fruchart, *Nouv. J. Chim.* 7 (1983) 325.
- [15] P. Prené, et al., *IEEE Trans. Magn.* 29 (1993) 2658.
- [16] J.-P. Jolivet, C. Chanéac, P. Prené, L. Vayssières, E. Tronc, *J. Phys. IV France 7 C* (1997) 1–573.
- [17] E. Tronc, et al., *Hyperf. Interact.* 95 (1995) 129.
- [18] J.L. Dormann, F. d'Orazio, F. Lucari, E. Tronc, P. Prené, J.-P. Jolivet, D. Fiorani, R. Cherkaoui, M. Noguès, *Phys. Rev. B* 53 (1996) 14291.
- [19] J.-L. Dormann, L. Spinu, E. Tronc, J.-P. Jolivet, F. Lucari, F. d'Orazio, D. Fiorani, *J. Magn. Magn. Mater.* 202 (1999) 251.
- [20] C. Chanéac, E. Tronc, J.-P. Jolivet, *Mat. Res. Soc. Symp. Proc.* 628 (2000) CC641.
- [21] E. Tronc, J.-P. Jolivet, *Hyperf. Interact.* 525 (1986) 28.
- [22] C. Chanéac, E. Tronc, J.-P. Jolivet, *Nanostruct. Mater.* 6 (1995) 715.
- [23] C. Chanéac, E. Tronc, J.-P. Jolivet, *J. Mater. Chem.* 6 (1996) 1905.
- [24] E. Tronc, C. Chanéac, J.-P. Jolivet, *J. Solid State Chem.* 139 (1998) 93.