Magnetic and Hyperfine Interactions in Systems of Antiferromagnetic Oxide Nanoparticles with Industrial Applications

S. G. MARCHETTI[1], R. A. BORZI[2], E. D. CABANILLAS[3], S. J. STEWART[2,4] and R. C. MERCADER[2]

[1] *CINDECA, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 N° 257, 1900 La Plata, Argentina*
[2] *Departamento de Física, IFLP, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CC 67, 1900 La Plata, Argentina*
[3] *Departamento de Materiales, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Av. del Libertador 8250, 1429 Buenos Aires, Argentina*
[4] *Department of Chemistry, The Open University, Walton Hall, Milton Keynes, MK7 AA6, United Kingdom*

Abstract. We report characterizations of systems of antiferromagnetic iron oxide particles of importance in catalysis where Mössbauer spectroscopy has played an essential role. We show that signals contributing to the Mössbauer spectra that arise from the surface or from non-crystalline environments still find difficulty in their assignment in spite of the large amount of research already done on hematite and similar antiferromagnetic systems.

1. Introduction

When oxide-supported hematite particles are reduced, they exhibit high activity and selectivity for the Fischer–Tropsch catalytic synthesis of hydrocarbons from CO and H_2. In this field, Mössbauer spectroscopy has been used as an essential non-destructive technique to assess very important parameters like the surface-to-volume ratio of the precursor particles. Recently, we have been able to monitor unwanted clustering of the iron oxide and metallic particles that can be produced in the preparation of the precursors and catalysts [1, 2].

Generally, the interpretation of the Mössbauer spectra of these complex systems is not straightforward because of the lack of an *a priori* knowledge of the inter-particle interactions and the influence of the microstructure on their physical and chemical properties. Moreover, if the system is made up of nanosized particles, the important fraction of surface atoms – which have different properties from those in the interior – are an additional difficulty. In particular, the complexity stems from the preparation-dependent surface morphology, the unavoidable distribution of sizes, the likely presence of more than one phase, the interface at the surface, the

interparticle interactions and the impurities or defects in the crystallites [3]. These factors, whose relative influence is difficult to assess in a particular system, have given rise to quite a few controversies in the past [4–6].

In our laboratory, we have gained experience in the study of systems of anti-ferromagnetic oxide nanoparticles that find applications as precursors of heterogeneous catalysts [1, 2, 7–11]. We have also been involved [12–14] in systems which have been claimed to be of potential use as gas sensors by Jiang *et al.* [15] and Zhao *et al.* [16]. Along this road, we have met systems of hematite nanoparticles supported on different oxides, or forming self-supporting nanoparticle systems of different sizes, or with several degrees of dilution in magnetic and non-magnetic materials.

In this work, through examples of our own and of the literature, we will show some controversial assignments of Mössbauer signals arising from iron oxide particles on diverse supports and of hematite particles in different states of aggregation.

2. Brief survey of signal assignments in nanosized iron oxides

The contribution of the surface atoms of hematite particles to the observed Mössbauer spectra was addressed firstly by van der Kraan [4] by enriching their surface layers in ^{57}Fe. An enriched sample of ≈ 7 nm size, exhibits a significant signal of ≈ 47 T – with a relaxation regime of its own – in the Mössbauer spectrum at 4.2 K. The author concluded that the behavior of Fe^{3+} ions at the surface of the crystallites depends on the particle size itself. Also, the negligible quadrupole shift of the surface component was assigned to the random orientation of the magnetization vector of the particle with respect to the principal component of the electric field gradient.

Dimitrov *et al.* [17] prepared α-Fe_2O_3/Ag multilayers by sputtering with oxide layers of different thickness. In this nanostructured material they assigned a signal with a substantial reduction of its hyperfine field to atoms on the surface. By simple calculations they concluded that the Néel model of uncompensated moments is not able to account for this reduction and that the reduction must be due to the bond breaks that occur to atoms sitting on the surface of the grains without the same number of near neighbors as in the bulk material. They also concluded that the surface spins were randomly oriented in a spin-glass-like arrangement. The surface component, of about 47 T at 17 K, contributed to approximately 50% of the total Mössbauer spectra regardless of the layer thickness.

A system of hematite particles of ≈ 5 nm average diameter embedded in a polymer solution of polyvinyl-pyrolidone was prepared by Vasquez-Mansilla *et al.* [18] by calcination of precipitated FeOOH particles by the sol-gel method. The magnetization and Mössbauer measurements showed a lack of compensation of the antiferromagnetic arrangement of moments located at the surface of the particles. If a core-shell picture of the particles was assumed, the disordered surface magnetic layer was found to be two atoms thick. The authors ascribe the observed magne-

tization and anisotropy energy as arising mainly from the surface uncompensation of the antiferromagnetic moments of hematite. Hence, the second component of $\approx$46 T at 4.2 K displayed in the Mössbauer spectrum was assigned to the atoms belonging to the surface magnetic layer.

A recent study of precipitated hematite nanoparticles of 16 nm average diameter [19], showed at 15 K a 48 T signal which was assigned to ferrihydrite and disappeared from the Mössbauer spectrum after oxalate washing the samples. However, the existence of uncompensated magnetic moments, of about 2% of ferrihydrite not washed away by the oxalate treatment, or the increase of the canting angle between the two antiferromagnetic sublattices of hematite, could not be discarded.

It is worth noting that a Mössbauer signal with a $\approx$47 T hyperfine field at low temperature was reported for amorphous Fe_2O_3 [20]. The authors interpret their data as arising from a sample displaying a purely amorphous phase. The usual reduction in the hyperfine field caused by the disorder of the surface layer in α-Fe_2O_3 nanoparticles would be produced, in this case, by the non-crystalline environments in which all the iron atoms are located.

Regarding ball-milled mixtures that involve hematite, Jiang *et al.* [21] have observed at 80 K a signal of reduced hyperfine field after prolonged milling of 25 mol% α-Fe_2O_3–SiO_2 powders in a closed container. It was ascribed to a fraction of smaller hematite particles produced over the milling. However, at room temperature, the hyperfine field reduction is in the limit that is usually caused by collective magnetic excitations. We believe that the disordered surface layer of the milled hematite may also contribute to that signal.

3. Catalysts

In this section we will describe how we have used Mössbauer spectroscopy to characterize iron catalysts supported on zeolite-L and on amorphous oxides. Another article of this volume [22] reports the preparation of iron catalysts supported on MCM-41.

To prepare zeolite-supported catalysts, the precursor iron oxide phases were supported on potassic (ZLK) and acidic (ZLH) zeolite-L. ZLH was obtained from ZLK – commercial form (Tosoh Corp.) of zeolite-L – after exchanging with a NH_4NO_3 solution as described in [1]. The solids obtained by dry impregnation with *ca* 5% w/w of iron (noted as Fe/ZLK and Fe/ZLH in the following) were dried in air and subsequently calcinated in a dry N_2 stream from room temperature up to 698 K at a heating rate of 0.33 K/min. Subsequently, they were kept at 698 K for 8 h.

Our results showed that a larger fraction of very small α-Fe_2O_3 superparamagnetic particles was located inside the channels of Fe/ZLK than in Fe/ZLH [1, 2]. We associate this difference to an "alkaline micro-injection" that can be described as follows. When the impregnation of ZLK takes place, K^+ ions belonging to the main channel zeolite walls exchange for Fe^{3+} at room temperature. This causes
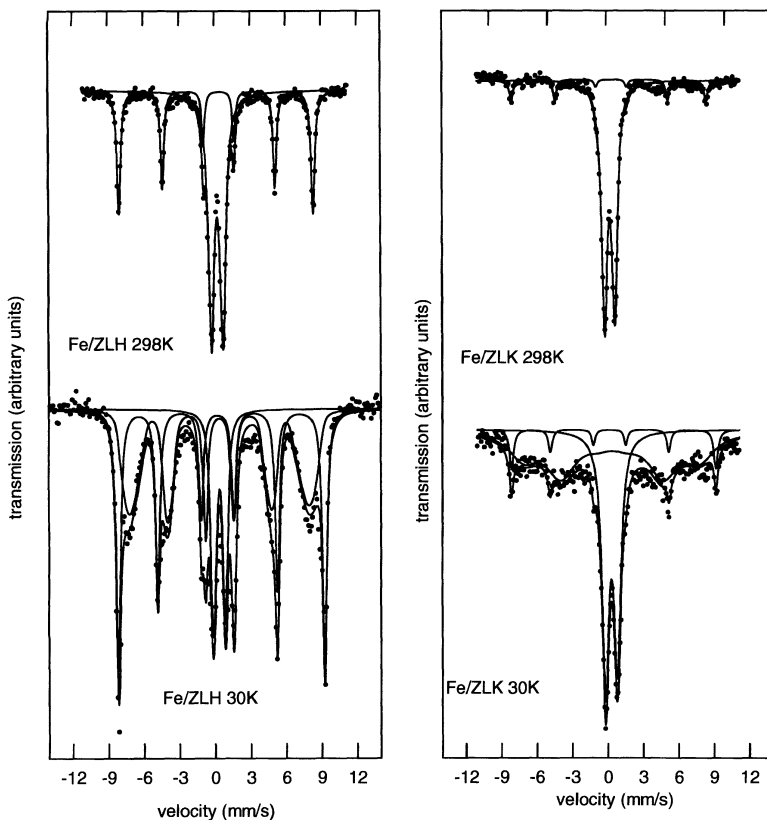
Figure 1. Mössbauer spectra of precursors of zeolite-L supported catalysts taken at the temperatures indicated in the figure. ZLK refers to the original zeolite, ZLH to the H^+-exchanged zeolite (see text).

an increase of the pH of the impregnating solution inside the channels of the zeolite matrix, that brings about the precipitation and "anchoring" of the forming ferrihydrite and/or goethite particles. These oxides are precursors to the smallest fraction of α-Fe_2O_3 microcrystals after calcination. The calcination conditions are enough to totally destroy any ferrihydrite and/or goethite species. The process cannot develop in ZLH since all the K^+ exchangeable ions have already been replaced by H^+.

In [1, 2] we assigned the broad magnetic sextet of $\approx$46 T to a fraction of very small α-Fe_2O_3 microcrystals. Notwithstanding that the overall conclusions of the works do not change, based on the evidences described in the previous section, we believe that the assignment might be wrong; this signal is displayed by iron-oxides systems with a particular surface-to-volume ratio irrespective of the support. In former works, we have prepared α-Fe_2O_3 microcrystals dispersed on amorphous supports like SiO_2, and changed the crystal sizes through modifications of the ther-
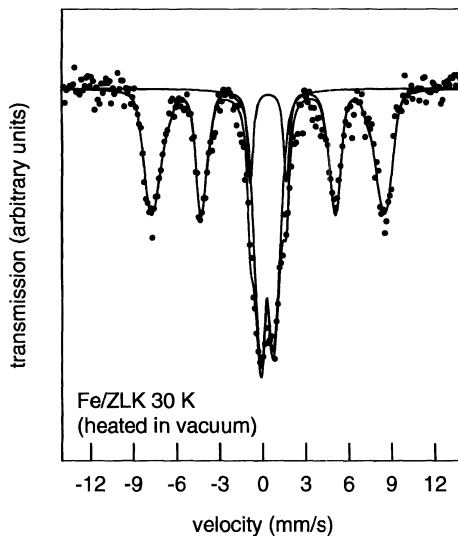
Figure 2. Mössbauer spectrum of Fe/ZLK heated in vacuum, kept for 9 h at 423 K and 1 h at 673 K, measured in ultra-high pure helium.

mal pretreatments [8, 9, 11]. The structural properties of the amorphous supports did not allow obtaining uniform-sized small crystals of iron oxides. However, in some of these systems it is also possible to distinguish the $\approx$46 T signal. Therefore, the presence of the $\approx$46 T signal in both Fe/zeolite systems could be attributed to a surface magnetic layer. The different percentage between the signals assigned to the "cores" and "shells" of the oxide microcrystals in Fe/ZLH and Fe/ZLK would indicate differences in the size of the α-Fe$_2$O$_3$ crystals.

The different behavior between Fe/ZLK and Fe/ZLH can disappear if the thermal pretreatment is not executed properly. For example, if Fe/ZLK is heated in vacuum (instead of in a N$_2$ atmosphere and with a correct heating program) the α-Fe$_2$O$_3$ microcrystals migrate outside the zeolite pores and sinterize to form larger particles. Thus, a broad hyperfine field distribution obscures the $\approx$46 T signal. The Mössbauer spectra of these solids (Figures 1 and 2) were essential to identify the iron species and their location in the zeolite structure.

4. Systems of self-supported hematite nanoparticles with different particle separation

To obtain nanoparticles with a narrow size distribution and low interparticle interaction, we have synthesized non-supported systems of iron-oxide-particles via micro-emulsion [23]. We selected a three-phase system composed of an aqueous phase, water + Fe(NO$_3$)$_3$ $\cdot$ 9H$_2$O, a hydrocarbon, 2-ethylhexanol, and a surfactant,
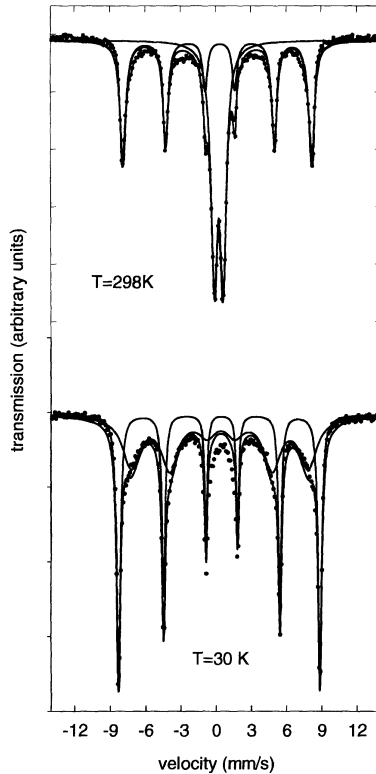
Figure 3. Mössbauer spectra recorded at the indicated temperatures of hematite nanoparticles obtained via micro-emulsion.

cetyl-trimethyl-ammonium bromide. The details of the preparation method will be described elsewhere [24].

The Mössbauer spectrum at 30 K (Figure 3) resembles that of [57]Fe-coated 7 nm α-Fe$_2$O$_3$ particles at 4.2 K of [4] and shows a *ca* 47 T hyperfine field signal. Preliminary dark-field transmission electron microscopy (TEM) images (Figure 4) show isolated particles of $\approx$14 $\times$ 40 nm^2. If the collective magnetic excitations model [25] is applied to the spectrum at room temperature (Figure 3), an average diameter of $\approx$13 nm is obtained – in agreement with the TEM observations.

In a recent experiment we subjected powders of pure hematite and of equimolar mixtures of α-Fe$_2$O$_3$ and CuO to ball milling for a fixed time of 10 h [13]. We obtained nanoparticles of hematite or of mixtures of nanostructured CuO and hematite, respectively. In both systems the hematite remained in the weak ferromagnetic state down to the lowest temperatures measured. The pure α-Fe$_2$O$_3$ particles were further subjected to different degrees of dilution and the results showing the existence of strong interparticle interactions were reported in [13]. Both "as-milled" systems show a high degree of particle clustering. Figure 5 shows

Figure 4. Transmission electron microscopy image of nanoparticles obtained via micro-emulsion. (*Top*) bright-field image. (*Middle*) electron diffraction pattern with the spot that gave rise to the dark field image indicated by a circle. (*Bottom*) dark-field image of the same particle as that at the top.

a dark field image of the pure hematite ball-milled sample, in which it can be seen that the crystallites are packed forming big agglomerates.

The size of α-Fe$_2$O$_3$ grains is ≈ 7 nm in the milled CuO/α-Fe$_2$O$_3$ mixture and no phases other than the initial ones are detected by accurate X-ray line profile Rietveld analysis. However, a broad Mössbauer sextet corresponding to an average magnetic field of 43 T, substantially lower than the bulk-type hematite one, is found at low temperatures for this sample (Figure 6). It coexists with the magnetically resolved hematite component and displays a relaxation behavior over the range of temperatures where the spectral area of the magnetically split bulk-type hematite contribution remains almost unchanged.

Magnetization measurements performed on this sample at low temperature showed magnetic hysteresis effects up to relatively high fields (≈ 3 T). Expressing
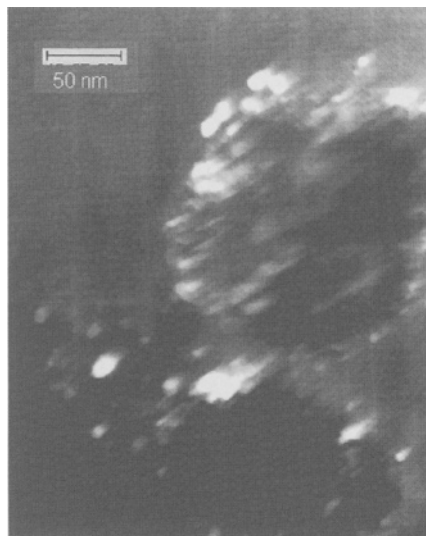
Figure 5. Transmission electron microscopy image of ball-milled hematite particles.

the high-field linear magnetization behavior as $M(H) = M_0 + \chi H$, we found $M_0 \approx 2.6$ emu/g at 10 K. This is much higher than the expected one for the hematite weak ferromagnetism, and one order of magnitude lower [26] than that expected if the broad sextet were related to $CuFe_2O_4$ spinel that might have formed along the milling process.

We associate these facts to the presence of a significant fraction of iron atoms located at grain boundaries. Due to crystallite agglomeration, the interface between α-Fe_2O_3 particles can be seen as an iron-rich Cu–Fe–O solid solution. The high relative area associated with the ferric oxide surface is related to the presence of a wide layer where the Fe atoms have a disordered environment, originated in the damage induced by the ball milling and, additionally, the irregularity introduced by the presence of Cu^{2+} ions with different spin, exchange constants and oxygen coordination. The measured magnetization magnitude would be the result of uncompensated moments, surface spin disorder [18, 19] (which would play an important role in magnetic hysteresis) and the weak ferromagnetism innate to hematite magnetism.

The Mössbauer spectra of ball-milled pure hematite at different temperatures are depicted in Figure 7. As we have shown in [13], the broad lines and the evidences of magnetic field distributions are due to the slowing down of the superparamagnetic relaxation arising from interparticle interactions. The normal doublet–sextet coexistence is observed only after the particles have been dispersed [13]. At 17.7 K only one hematite signal can be observed indicating that the disordered surface layer is not detected. The spin-disordered surface layer may no longer be noticeable because of the combination of several causes; a higher particle size ($D \approx 14$ nm), the uniform chemical phase (compared to the Cu–Fe–O system)
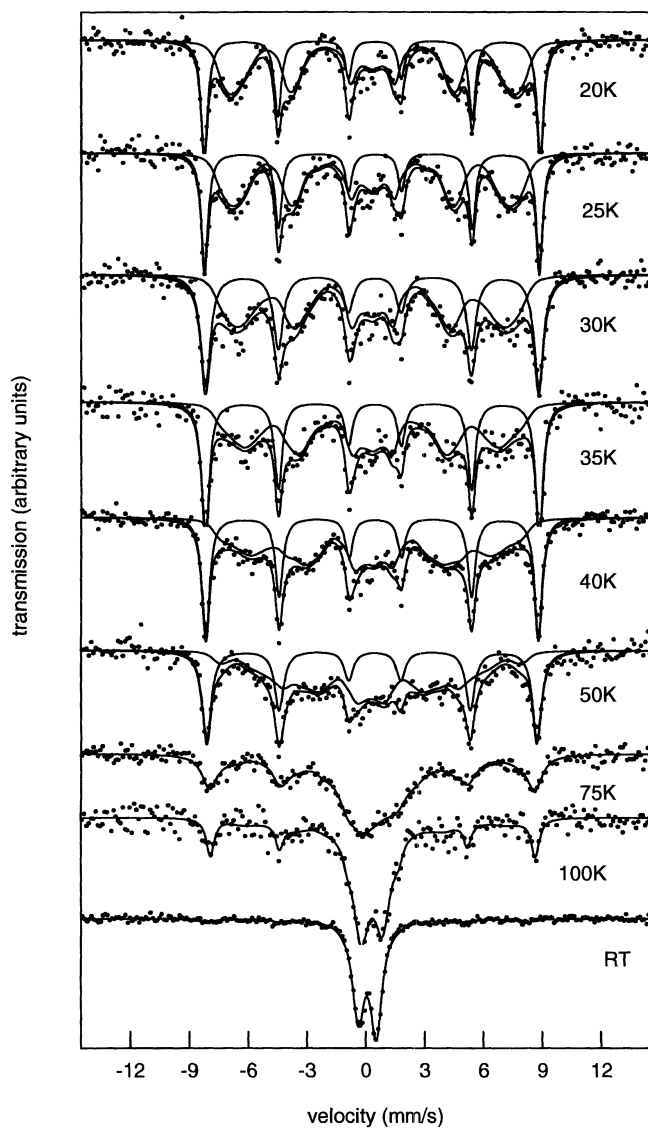
Figure 6. Mössbauer spectra of a ball-milled powder mixture of 33% CuO and 67% hematite at the temperatures indicated.
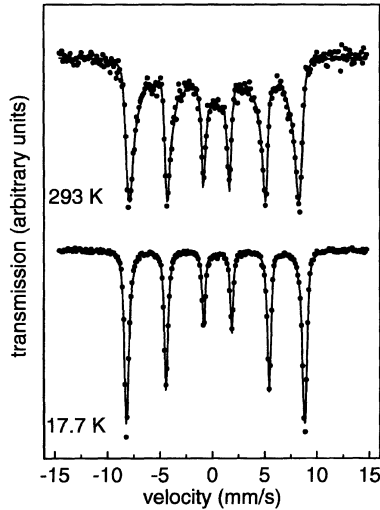
Figure 7. Mössbauer spectra of ball-milled pure hematite at RT and 17.7 K.

throughout the sample, and the particle agglomeration which leads to both the enhancement of the magnetic interactions and to the decline of well-defined interfaces (Figure 5). The different – strongly correlated – contributions to the surface magnetization of the nanoparticles are revealed in their Mössbauer spectra and cannot be separated in simple ways. They depend not only on the size of the particles but also on the type of material where the particles are immersed. We believe with Seehra *et al.* [27] that there is still a lack of a theoretical frame capable of predicting the general behavior of a system of antiferromagnetic nanoparticles.

5. Conclusions

The characterization of systems of antiferromagnetic iron oxide nanoparticles by Mössbauer spectroscopy is of great help in applications towards the development of better catalysts. Through several examples, we have shown that hematite nanoparticles display a disordered magnetic layer at the surface. This is mainly related to properties of the particles themselves, but is affected by the interactions between particles in a way that is highly dependent on the preparation conditions of the samples.

Acknowledgements

References

1. Marchetti, S. G., Alvarez, A. M., Bengoa, J. F., Cagnoli, M. V., Gallegos, N. G., Yeramián, A. A. and Mercader, R. C., *Hyp. Interact. C* **2** (1999), 61.
2. Marchetti, S. G., Cagnoli, M. V., Alvarez, A. M., Bengoa, J. F., Mercader, R. C. and Yeramián, A. A., *Appl. Surf. Sci.* **165** (2000), 91.
3. Morrish, A. H., In: J. L. Dormann and D. Fiorani (eds), *Magnetic Properties of Fine Particles*, North Holland, Amsterdam, 1992, p. 181.
4. van der Kraan, A. M., *Phys. Status Solidi A* **18** (1973), 215.
5. Dormann, J. L., Fiorani, D. and Tronc, E., *Adv. Chem. Phys.* **98** (1997), 283.
6. Morup, S. and Tronc, E., *Phys. Rev. Lett.* **72** (1994), 3278.
7. Alvarez, A. M., Marchetti, S. G., Cagnoli, M. V., Bengoa, J. F., Mercader, R. C. and Yeramián, A. A., *Appl. Surf. Sci.* **165** (2000), 100.
8. Cagnoli, M. V., Marchetti, S. G., Gallegos, N. G., Alvarez, A. M., Mercader, R. C. and Yeramián, A. A., *J. Catal.* **123** (1990), 21.
9. Gallegos, N. G., Alvarez, A. M., Cagnoli, M. V., Bengoa, J. F., Marchetti, S. G., Mercader, R. C. and Yeramián, A. A., *J. Catal.* **161** (1996), 132.
10. Spretz, R., Marchetti, S. G., Ulla, M. A. and Lombardo, E. A., *J. Catal.* **194** (2000), 167.
11. Marchetti, S. G., Cagnoli, M. V., Alvarez, A. M., Gallegos, N. G., Bengoa, J. F., Yeramián, A. A. and Mercader, R. C., *J. Phys. Chem. Sol.* **58** (1997), 2119.
12. Stewart, S. J., Borzi, R. A., Punte, G. and Mercader, R. C., *Phys. Rev. B* **57** (1998), 4983.
13. Borzi, R. A., Stewart, S. J., Punte, G., Mercader, R. C., Vásquez-Mansilla, M., Zysler, R. D. and Cabanillas, E. D., *J. Magn. Magn. Mater.* **205** (1999), 234.
14. Borzi, R. A., Stewart, S. J., Punte, G., Mercader, R. C., Curuchet, G. A., Zysler, R. D. and Tovar, M., *J. Appl. Phys.* **87** (2000), 4870.
15. Jiang, J. Z., Lu, S. W., Zhou, Y. X., Morup, S., Nielsen, K., Poulsen, F. W., Berry, F. J. and McMannus, J., *Mater. Sci. Forum* **235–238** (1997), 941.
16. Zhao, J., Huggins, F. E., Feng, Z. and Huffman, G. P., *Phys. Rev. B* **54** (1996), 3403.
17. Dimitrov, D. V., Hadjipanayis, G. C., Papaefthymiou, V. and Simopoulos, A., *J. Magn. Magn. Mater.* **188** (1998), 8.
18. Vasquez-Mansilla, M., Zysler, R. D., Arciprete, C., Dimitrijewits, M. I., Saragovi, C. and Greneche, J. M., *J. Magn. Magn. Mater.* **204** (1999), 29.
19. Bodker, F., Hansen, M. F., Koch, C. B., Lefman, K. and Morup, S., *Phys. Rev. B* **61** (2000), 6826.
20. Van Diepen, A. M. and Popma, T. J. A., *J. de Physique* **37** (1976), C6-755.
21. Jiang, J. Z., Zhou, Y. X., Morup, S. and Bender Koch, C., *Nanostruct. Mater.* **7** (1996), 401.
22. Marchetti, S. G., Cagnoli, M. V., Alvarez, A. M., Bengoa, J. F., Gallegos, N. G., Yeramián, A. A. and Mercader, R. C., *Hyp. Interact.*, this issue.
23. Ayyub, P., Multani, M., Barma, M., Palkar, V. R. and Vijayaraghavan, R., *J. Phys. C* **21** (1988), 2229.
24. Marchetti, S. G., Bengoa, J. F., Alvarez, A. M., Borzi, R. A., Cabanillas, E. D. and Mercader, R. C., to be published.
25. Morup, S., *Hyp. Interact.* **60** (1990), 959.
26. Cullity, B. D., *Introduction to Magnetic Materials*, Addison Wesley, Reading, 1972.
27. Seehra, M. S., Babu, V. S., Manivannan, A. and Lynn, J. W., *Phys. Rev. B* **61** (2000), 3513.