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## COMMENT

## Comment on ‘Magnetic relaxation phenomena and inter-particle interactions in nanosized $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> systems’

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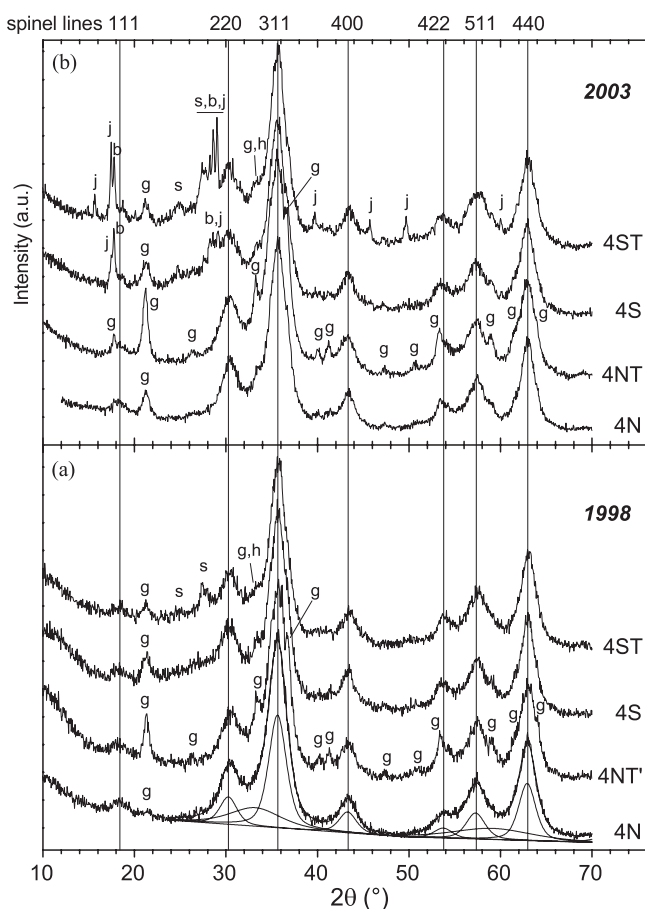
### Abstract

Predoi *et al* (2003 *J. Phys.: Condens. Matter* **15** 1797) analysed Mössbauer spectra of powders of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles with a varying degree of hydration or with sulfate coating in terms of surface effects, superparamagnetic relaxation, and inter-particle interactions. We show that the paper is based on an incorrect presentation of the materials and the reported analyses are misleading throughout.

### 1. Introduction

Predoi *et al* [1] report investigations of the magnetic behaviour of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particle powders by Mössbauer spectroscopy supported by x-ray diffraction (XRD), electron microscopy, thermal gravimetric analysis (TGA), and zero-field-cooled ( $M_{ZFC}$ ) and field-cooled ( $M_{FC}$ ) magnetization data. Two of us, Tronc and Noguès, dissociate ourselves from the authorship of the work in question. We believe that the results are unreliable, in particular those relating to the XRD studies, the surface iron states, and the magnetic relaxation.

The materials [2, 3] were fabricated in 1997 at the LCMC by Predoi (Prodan) (grant MENESR No 96P0079-191704H) using established chemical methods [4–6]. The first results were [2] in qualitative accord with known features. Additional magnetization measurements (0–5.5 T, 4.2–300 K; LMOV) [3] showed irregular variations with applied field and temperature and a problematic scaling for all samples, suggesting heterogeneous systems. This was confirmed by additional XRD studies (figure 1(a)) and complementary work (figure 1(b)). The structural complexity of the materials, at variance with all observations [5–10] on powders of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles obtained using the same methods, without or with coating, including sulfate



**Figure 1.** X-ray diffraction patterns (Cu  $K\alpha$ ) for Predoi's  $\gamma$ - $\text{Fe}_2\text{O}_3$  4 nm particle samples at the LCMC in (a) 1998; (b) 2003 after ageing under ambient conditions. g, h, s, j, and b stand for goethite (JCPDS file No 29-712), haematite (No 33-663),  $\text{FeOH}_2\text{SO}_4$  (No 21-928), jarosite (No 31-650), and butlerite (No 25-409) lines, respectively; — —, calculated curve (4N) and  $\alpha_1$  peaks (computing program WinPLOTR, May 2000/LLB-LCSIM: [www-llb.cea.fr/fullweb/winplotr](http://www-llb.cea.fr/fullweb/winplotr)). The patterns for samples 4NT and 4NT', presumably analogous in 1998, are similar in 2003.

coating, as prepared, heated up to conversion into haematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ), or aged for 10–20 years, is not considered in [1].

## 2. XRD studies

Predoi *et al* show (figure 1 [1]) an XRD pattern for sample 4N (LCMC, 1998); no pattern is given for the other two samples (4NT, 4S). In figure 1(a) we show the patterns for samples 4N, 4S, 4NT' (4N treated at 200 °C) [2, 3], and 4ST (4S treated at 250 °C) [3] in 1998; the pattern for sample 4NT (4N treated at 150 °C), presumably analogous to that of sample 4NT', was not recorded. These data make clear the presence of goethite,  $\alpha$ - $\text{FeOOH}$ , and disordered phases in all systems.

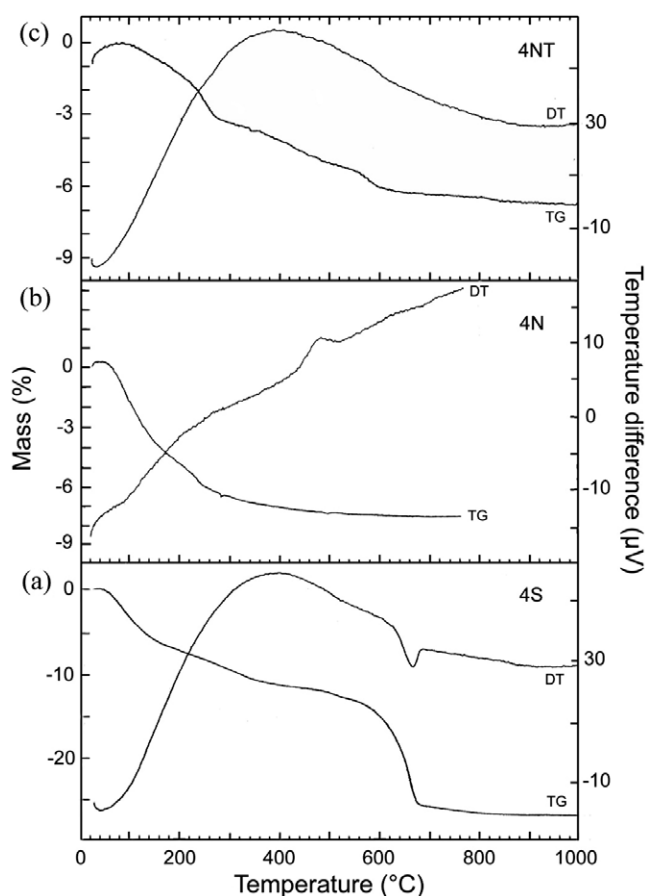
Because goethite cannot form [11–13] from the spinel iron oxide, its presence indicates contaminated preparation of the  $\gamma$ - $\text{Fe}_2\text{O}_3$  particle sol. Polynuclear species and/or a ferrihydrite-like phase must have nucleated in the sol, for an unknown reason. They could have adsorbed

onto the spinel particles and/or could have grown a separate nanophase, could have evolved under pH changes, and should have reacted with  $\text{H}_2\text{SO}_4$ . The resulting poorly crystalline phases in the powders manifest themselves through their crystalline products of dehydration by heating (figure 1(a)) or under ageing (figure 1(b)): the formation of goethite in samples 4N and 4NT (4NT') under heating or ageing suggests a disordered oxyhydroxide with goethite-like order at short range rather than a two-line ferrihydrite; the formation in sample 4S(4ST) of  $\text{FeOHSO}_4$  by heating, of a mixture of butlerite,  $\text{FeOHSO}_4 \cdot 2\text{H}_2\text{O}$ , and jarosite,  $\text{H}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$ , under ageing, indicates a disordered  $\text{Fe}^{\text{III}}$  hydroxy-sulfate phase with heterogeneous  $\text{Fe}/\text{OH}/\text{SO}_4/\text{H}_2\text{O}$  composition. All features (figure 1) are in accord with known properties [11] of iron oxides, but contrast with expectations [6–10] for surface properties of  $\gamma\text{-Fe}_2\text{O}_3$  particles. In the aged 4NT sample (figure 1(b)), the fractions of iron as crystalline goethite and maghemite are in the ratio of approximately 1:3, as indicated [14] by the integrated intensities of the goethite 110 ( $2\theta \sim 21^\circ$ ) and spinel 220 lines. Thus, the extra phases make up at least 25% of the iron content in all the samples. The spinel iron fraction should be the same in all samples, unless some dissolution occurred during the preparation of sample 4S.

### 3. Surface iron states

For the 7.2 K Mössbauer spectrum of sample 4S (figure 5 [1]), Predoi *et al* attribute the quadrupole doublet to paramagnetic surface  $\text{Fe}^{\text{II}}(\text{SO}_4)_2$  groups and the six-line pattern to non-sulfated  $\text{Fe}^{\text{III}}$  species. The stated isomer shifts are  $\text{IS} \sim 0.9$  and  $0.5 \text{ mm s}^{-1}$ , respectively. This does not conform to the experimental spectrum and the calculated one, which both indicate that the two IS values are very close to each other and typical of  $\text{Fe}^{3+}$  ions [15]. Predoi *et al* do not establish the doublet that accounts for all sulfated Fe species, so assigning the six-line pattern to non-sulfated species is unfounded. The  $T$  dependence of the doublet parameters was determined, as shown (figure 5 [1]) by fits, but the results are not reported. The  $T$  dependence of the six-line pattern is reported (figure 7(c) [1]), but without scaling the relative area with respect to 7.2 K and without accounting for the central part of the spectrum at  $T \leq 100 \text{ K}$ , unlike at  $T \geq 140 \text{ K}$ , which is illogical. In fact, the doublet at 7.2 K ( $\text{IS} \sim 0.5 \text{ mm s}^{-1}$ ; splitting  $\text{QS} \sim 1.2 \text{ mm s}^{-1}$ ), inconsistent [11, 16] with goethite and uncoated or sulfate-coated [6]  $\gamma\text{-Fe}_2\text{O}_3$  particles, can be attributed [17–19] to (super)paramagnetic  $\text{Fe}^{\text{III}}$  hydroxy-sulfates (section 2). This doublet, with slight changes in the IS and QS values, accounts (figure 5 [1]) for the paramagnetic components at 40 and 100 K, unlike at 200 K; its spectral area is  $\sim 0.25$  at 40 K and  $\sim 0.5$  at 100 K, compared with 0.12 [1] at 7.2 K. Therefore, the  $\text{Fe}^{\text{III}}$  hydroxy-sulfate phase contains  $\sim 50\%$  of the total iron, assuming the same recoilless fraction for all Fe atoms; it makes up  $\sim 40\%$  of the Fe atoms contributing to the six-line pattern at 7.2 K, and its magnetic ordering (with possible relaxation) influences the  $T$  dependence of the magnetic pattern. Then, the comparison (table 2 [1]) of the Mössbauer and TGA data for sample 4S is unjustified and the whole analysis [1] of the Mössbauer spectra of this sample is incorrect.

Predoi *et al* fit a distribution of the hyperfine field,  $B_{\text{hyp}}$ , to the low-temperature six-line pattern for each sample (figures 3–6 [1]) and attribute the distribution tail to surface states. Predoi *et al* adjust the symmetric patterns (one IS value, quadrupole shift  $\varepsilon = 0$ ) to spectra that are visibly asymmetric, involving [15] components with different isomer shifts and  $\varepsilon \neq 0$ , so the  $B_{\text{hyp}}$  distribution tails have no physical meaning. Thus, the iron fractions deduced are meaningless and the comparison (table 2 [1]) with TGA data is unfounded. Predoi *et al* assert that ‘the above surface states have to correspond to iron ions sensing the hydroxyl groups ( $\text{OH}^-$ ), which were not removed by the drying procedure’ ( $35^\circ\text{C}$  for samples 4N and 4S,  $150^\circ\text{C}$  for sample 4NT), and that all the water loss determined by TGA is due to dehydroxylation. Predoi *et al* do not mention studies on the thermal behaviour and surface properties of  $\gamma\text{-Fe}_2\text{O}_3$



**Figure 2.** Thermogravimetric (TG) and differential thermal (DT) analysis of Predoi's samples (a) 4S, (b) 4N, and (c) 4NT in 1997.

or metal oxides. They indicate [9, 11, 12, 20] that, under ambient conditions, all surface Fe atoms should achieve their coordination number and all surface O atoms should be present as OH, that dehydroxylation occurs above  $\sim 200^\circ\text{C}$ , and that all fine-grained materials normally contain adsorbed water, which is released below  $\sim 200^\circ\text{C}$ . Predoi *et al* confuse hydration (physisorbed, chemisorbed, structural) water and hydroxylation water and distribute it all among a number of OH groups at some surface sites, which does not make sense.

Predoi *et al* do not show the TGA curves. Those obtained in 1997 are given in figure 2. Predoi *et al* set the endothermic peak related to the loss of  $\text{SO}_3$  'before the transition  $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$  taking place at  $500^\circ\text{C}$ '. This peak occurs (figure 2(a)) around  $660^\circ\text{C}$ , in accord with known properties [6, 21] of the  $\text{SO}_4$  anion. The temperature,  $T_{\gamma\alpha}$ , for the  $\gamma$ -to- $\alpha$  conversion, exothermic, cannot be assessed without structural studies, which are not reported. The  $T_{\gamma\alpha}$  value given corresponds to sample 4N (figure 2(b));  $T_{\gamma\alpha}$  will increase [6, 9, 10] according to the thermal stability of anti-sintering agents, because the conversion is driven by particle growth. Predoi *et al* report that sample 4NT loses water 'only above  $150^\circ\text{C}$ ' with a loss (table 1 [1]) about half that found for sample 4N, at variance with observations (figures 2(b), (c)). The curves (figures 2(b), (c)) indicate [11] that the hydration (most of the weight loss below  $\sim 220^\circ\text{C}$ ) is reduced in sample 4NT compared with 4N, that the pre-heating

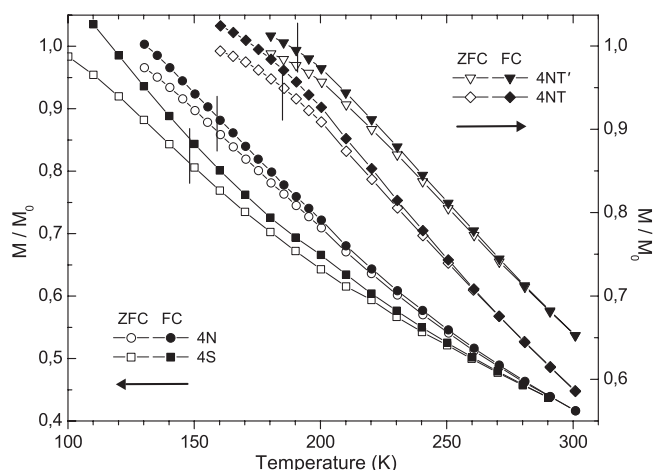
also caused crystallization of goethite (dehydroxylated around 240 °C), in accord with the XRD data (figure 1), and microstructural changes that obstruct dehydroxylation (weight loss above ~260 °C) of the disordered phase and/or formed haematite and/or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> grain surfaces, and shift the  $\gamma \rightarrow \alpha$ -Fe<sub>2</sub>O<sub>3</sub> conversion by about 100 °C (the exotherm at ~580 °C).

#### 4. Magnetic relaxation

Predoi *et al* determine the blocking temperature as the temperature,  $T_B$ , at which the  $B_{\text{hyp}}$  distribution fit to Mössbauer spectra at different temperatures shows a change of regime. For each sample the determination of  $T_B$  is somewhat problematic. For instance, for sample 4S the  $B_{\text{hyp}}$  distribution (figure 7(c) [1]) misrepresents the spectral evolution (figure 5 [1]), as noted above (section 3): the plots in figures 8–10 [1] are meaningless; for sample 4N the  $\langle B_{\text{hyp}} \rangle$  versus  $T$  variation (figure 10 [1]) is not in accord with the  $B_{\text{hyp}}$  distributions (figure 7(a) [1]):  $\langle B_{\text{hyp}} \rangle = 50$  T at 60 K is clearly overestimated, and a result is reported for  $T$  between 60 and 130 K whereas all corresponding data (figures 3, 7(a), 8, 9 [1]) are missing.

Predoi *et al* do not establish that the superparamagnetic (SP) relaxation determines the spectral evolution, so identifying  $T_B$  with a blocking temperature is unfounded. Predoi *et al* do not compare the observed evolutions (figure 7 [1]), showing no coexistence of peaks at high (low- $T$  sextet) and low (high- $T$  doublet)  $B_{\text{hyp}}$  values at intermediate temperatures, with those reported (references [13, 18–20, 22] in [1]) [22] for particle systems with established SP relaxation: they all show coexistence over a significant  $T$  range, if the size distribution is not narrow. Predoi *et al* apply a law (equation (2) [1]) giving the SP relaxation time,  $\tau$ , of a particle of volume  $V$ , but do not apply it to the size distribution (figure 2 [1]): since the diameter varies by a factor of ~8, since  $\tau$  varies exponentially with  $V/T$ , and since the hyperfine field of bulk  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> varies little with temperature, only a reduced fraction of the particles can have relaxation times in the critical range at temperature  $T$ ; thus, the patterns of blocked and unblocked particles will coexist in varying proportions over a significant  $T$  range, in contradiction with the observations (figure 7 [1]). Predoi *et al* discuss the median blocking temperature (sextet and doublet/singlet of equal areas), but do not comment on its irrelevance to the observations. Predoi *et al* do not mention cases where the SP relaxation is not present. Studies [23] of powdered  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles showing a collective dynamical regime report a  $B_{\text{hyp}}$  distribution evolving somewhat as described in [1]. Studies of goethite particles [16, 24] and FeOH<sub>2</sub>SO<sub>4</sub> [19] report spectral shapes associated with magnetic ordering; but each sample in [1] is multiphase, so each spectral evolution is a global feature. Considering the data (figures 3–5, 7 [1]), the bulk-like component observed (figure 4 [1]) for sample 4NT at 230 and 260 K appears to be the only magnetically split pattern that can be reliably assigned, because the magnetic splitting (~40 T) and  $\varepsilon \neq 0$  are inconsistent [7, 11, 15, 16] with maghemite but typical [11, 15, 16, 24] for goethite, which limits the amount of information attainable [1] on the magnetic relaxation.

Most statements [1] relating to the blocking temperature are problematic. Distribution effects are generally altered or discarded. For instance, Predoi *et al* consider one particle and state that ‘in spite of the clear phenomenological definition of the blocking temperature, different procedures for finding the experimental temperature where  $\tau = \tau_m$  are proposed, depending on the experimental technique’, which does not make sense. Predoi *et al* write ‘for a given nano-particle size (...). The blocking temperature as obtained from Mössbauer spectra taken at different temperatures is proposed to coincide with the temperature where the non-collapsed part of the spectrum (sextet) equals the already collapsed one (doublet or singlet)’, which does not make sense either. The effective problem (e.g., references [19, 20] in [1]) [22], i.e., to find, given the particle size distribution and the experimental technique,



**Figure 3.** Thermal behaviour of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization,  $M$ , relative to the magnetization,  $M_0$ , at the maximum of the ZFC curve for Predoi's samples in 1998; the applied field of 1.5 mT is parallel to the plane of the disc-shaped sample. Bars mark the temperatures at curve branching as estimated in [25] and used in [1].

the relevant particle volume,  $V$ , and measuring time,  $\tau_m$ , to be associated with a measured characteristic temperature to identify it with a blocking temperature,  $T_b(V, \tau_m)$ , is shifted to the measurement—unrealistic—of  $T_b$  for a given  $V$ . Moreover, for a given  $V$ ,  $T_b$  as obtained from Mössbauer spectra is not unique, owing to the  $\tau_m$  window, and what one obtains depends on the procedure used for the determination, which also determines  $\tau_m$ . Predoi *et al* define  $T_B$  as the blocking temperature at ‘The transition from the blocked to the relaxed regime’ (the appearance of a collapsed spectral part;  $\tau_M = 5 \times 10^{-9}$  s) and associate it (equation (4) [1]) with the mean particle volume,  $V$ . As all particles of volume smaller than  $V$  will contribute to the collapsed spectral part at  $T = T_B$ , it cannot be just appearing. The transition considered should be associated with the smallest particle volume, assuming that the effective anisotropy energy constant does not vary with particle volume and temperature, which is not valid for interacting particles (references [19, 20] in [1]) [22].

Predoi *et al* consider the blocking temperature  $T_B$ , the temperature,  $T_{\max}$  [2], at the maximum of the  $M_{ZFC}$  versus  $T$  curve, and the temperature,  $T_{\text{bra}}$  [25], at the  $M_{ZFC}$  and  $M_{FC}$  curve branching. The data [1] are  $T_B = 89\text{--}95$ ,  $110\text{--}125$ , and  $165\text{--}180$  K,  $T_{\max} = 89$ ,  $108$ , and  $146$  K,  $T_{\text{bra}} = 148$ ,  $159$ , and  $185$  K for samples 4S, 4N, and 4NT, respectively. Predoi *et al* find the values of  $T_B$  and  $T_{\max}$  for each sample ‘in quite good agreement (...) if the different time windows of the two methods are taken into account’, but do not give the time window for  $T_{\max}$ . Since it is of the order of  $10^2\text{--}10^3$  s (reference [19] in [1]) [22] compared with  $\tau_M = 5 \times 10^{-9}$  s [1] for  $T_B$  and since  $T_B$  is associated [1] with the mean size (4 nm), the data cannot be in accord with the SP relaxation. Predoi *et al* discuss the ratio  $R = T_{\max}/T_{\text{bra}}$  and relate (figure 11 [1]) the variations of  $T_B$  ( $K_{\text{eff}}$ ) and  $R$  between samples. The  $T_{\text{bra}}$  values are not in accord with the measurements, as can be seen in [25] and in figure 3 using another scale. The measurements indicate  $T_{\text{bra}} \sim 280$ ,  $280$ , and  $260$  K for samples 4S, 4N, and 4NT, respectively (290 K for 4NT' compared with 191 K [25]). Therefore, the set of  $T_{\text{bra}}(R)$  values [25] is incorrectly estimated.

Finally, we note that [1] reports on surface effects and mentions no article relevant to surface properties; reports on dipolar inter-particle interaction effects in powders and mentions only articles on dispersed systems; reports on the SP relaxation, lists many articles, and makes

no use of their content. Not any assumptions or results are compared to independent works; the Mössbauer spectra are attributed to unreal materials and every one of the reported analyses is meaningless.

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