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## REPLY

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

D Predoi, V Kuncser and G Filoti

National Institute for Physics of Materials, PO Box MG 07, 77125, Bucharest Magurele, Romania

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The paper published by Predoi *et al* [1] was not well understood in its main points by Tronc *et al*. In their comment, the authors make quantitative assumptions about sample composition and Mössbauer parameters without using specific procedures and based on not relevant data. There are also strong confusions in the interpretation of the Mössbauer spectra in relation to magnetic relaxation phenomena, leading finally to false arguments against the mentioned paper.

The aim of this response is only to point to the methodological validity of Predoi’s work on systems of ‘structurally defected’ nanoparticles with Fe distributed configurations giving rise in the <sup>57</sup>Fe Mössbauer spectra at low temperature to a distribution of hyperfine magnetic fields. A detailed point by point refutation of the comments made by Tronc *et al* will be presented in a separate paper [2].

Tronc *et al* build their main arguments against Predoi’s work on the supposition that the analysed samples contains, excepting the maghaemite phase, up to 33% (1:3) Fe in goethite form and another 20–30% of additional extra phases. In this respect they present four XRD spectra obtained in 1998 (immediately after the sample preparation) and four other spectra obtained in 2003 on samples stored in France. Taking into account that the Mössbauer data were collected in 1999, the XRD data obtained in 2003 are not appropriate for any corroboration with the reported Mössbauer results (it is not unexpected, depending on the storage conditions, to have an ageing process leading to some crystalline products over a couple of years). Additionally, among the four XRD patterns obtained in 1998, only patterns of sample 4N and 4S are relevant for correlation with Mössbauer data (samples 4ST and 4NT’ were not investigated by Mössbauer spectroscopy). The XRD pattern corresponding to sample 4N shows clearly the specific peaks of maghaemite, with very broad lines typical for a nanosized structural coherence length. The main 110 line of goethite is almost undistinguishable. This line appears in sample 4S but its integrated intensity is still very small compared with the main line of maghaemite. According to our knowledge, the typical procedure for a quantitative estimation of the phase composition starting from the XRD pattern should be based on a previous calibration performed on collected XRD spectra corresponding to the desired mixture ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> +  $\alpha$ -FeOOH in this case) with a controlled relative ratio of the components, followed by the analysis of the areas of suitable peaks of each of the two phases. Tronc *et al* made quantitative assumptions on the goethite content without using the mentioned typical procedure.

A simple XRD spectrum of a mixture of 20 wt% of goethite and 80 wt% of maghaemite as nanoparticles [2] proves that samples 4S and 4N (representative for the correlation with the Mössbauer data) present only very small fractions of goethite-like structure. Concerning the presence of additional extra phases (other than goethite) in sample 4N, Tronc *et al* present a deconvolution of the corresponding XRD pattern into components belonging to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and two additional very broad lines. It is worth mentioning that with so large XRD profiles a convenient fit may be obtained both with or without the two broad extra lines. Therefore this is not definite and relevant evidence for the presence of the 'extra phases'. On the other hand we have already considered in the original paper [1], that we deal with nanoparticles of defected maghaemite, that could be responsible for deviations from the typical structure of bulk very crystalline  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. There are strong arguments [2] that the analysed systems contain the same type of spherical nanoparticles with iron distributed positions (the phase configuration appears as belonging to each particle). From a physical point of view, the most probable and adequate situation seems to agree with the presence of nanoparticles with a better formed core of maghaemite and a very defected external shell presenting a graduate modification toward the limit of a quasi-amorphous configuration near the surface sensitive to water (corresponding to a so-called ferric gel).

Predoi's paper [1] emphasizes two methodological procedures (based on Mössbauer data) which are especially appropriate for systems of nanoparticles with defected structures. The first one deals with the distinction between 'bulk' and 'surface' states of Fe and their influence on the macroscopic magnetic properties, whereas the second one refers to a new method for the evaluation of the blocking temperature from the Mössbauer spectra collected at different temperatures.

The low temperature Mössbauer patterns of the analysed samples show very large sextets, providing a broad probability distribution of the hyperfine magnetic field. Each probability distribution consists of a main peak centred at about 52 T and a tail at lower fields. The main peak of the probability distribution was assigned to the iron placed in 'bulk states' and the tail of the probability distribution at lower fields to the iron belonging to 'surface states'. This assignment was also supported by the observation that the number of such Mössbauer defined 'surface states' (counted by the relative area under the tail of the probability distribution of the hyperfine field) increases almost proportionally with the water amount provided by each sample, as deduced by TGA. Therefore, only the surface states (corresponding to smaller hyperfine fields) are sensitive to the water presence, whereas the bulk states (main peak of the distribution) are the ones not affected by the water normally existing only on the particle surface. From the magnetic point of view, the analysed samples are clearly different by their relative number of the above defined 'surface' and 'bulk' iron sites.

The broad hyperfine field distribution obtained in the magnetic static regime has suggested from the very beginning a large distribution of the Fe positions in each particle. In the original paper, the data were interpreted in terms of a very defected maghaemite structure involving a continuous digression from the crystalline well formed  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and giving rise to hyperfine fields inside the same broad distribution. The proposed methodological approach provides the distinction between the macroscopic magnetic behaviour of systems of nanoparticles with the same mean size (or very close size distribution), via the area of the low field tail of the hyperfine field distributions at low temperature (related to the number of the 'surface' states). It can be generally applied, and is especially convenient in the case of defected structures. The behaviour of the hyperfine field distribution at low temperature is dependent on the hydration degree of the samples (and consequently on the number of 'surface states') and does not support the assumption of a large amount of anhydrous goethite in samples 4S and 4NT, as detailed in [2].

Excepting the above mentioned methodological problem implying the distinction between the ‘bulk’ and the ‘surface’ states, each with peculiar influence on the magnetic properties of the nanoparticle systems, the paper deals with another general methodological problem, namely, how to define more precisely the blocking temperatures from Mössbauer measurements in complex systems involving super-paramagnetic transitions. The proposed approach was to define the temperature corresponding to a drastic change in the hyperfine field distribution, namely that temperature where the main lobe in the probability distribution changes from high fields (static regime) to low fields (dynamic regime). The new procedure is less dependent on the fitting performances than the classical one. The distribution shapes are changing drastically over the transition range and therefore small errors in the fitting procedure do not influence the final estimations. As may be observed, this new proposed general procedure does not depend on a specific nanosystem, when it undergoes a super-paramagnetic transition. It is worth mentioning that it does not depend on the shape of each distribution, but only on its evolution versus temperature.

Tronc *et al* do not agree with this procedure for evaluating the blocking temperature, also because they do not recognize the superparamagnetic (SP) relaxation process in the analysed samples. Detailed arguments about a superparamagnetic transition in such systems will also be presented in [2]. Tronc *et al* claim the lack of co-existence of high- and low-field peaks in the hyperfine field distribution to rule out the SP relaxation. They do not observe this coexistence over a range of temperatures around the temperature where flat distributions are evidenced. Their expectation for a much larger temperature range is based on an improper exploitation of the particle size distribution graph: in their opinion, the particle diameter was considered to vary by a factor of eight, as stated in the comment. In our opinion, from the size distribution presented in figure 1 of the original paper, the significant variation of the particle sizes is by a factor of about 2.5 (the distribution width at half maximum should be considered, and that ranges between 2 and 5 nm).

Concerning the evaluation of  $T_{\text{bra}}$ , Tronc *et al* simply enlarge the scale of zero-field cooled (ZFC)–field cooled (FC) magnetization curves. Considering the physical meaning of  $T_{\text{bra}}$ , as the blocking temperature of the largest particle in the distribution, in correlation with the asymptotic dependence of the particle size distribution toward higher sizes, such a procedure is not scientifically appropriate in our opinion. Therefore, we used another procedure for the evaluation of  $T_{\text{bra}}$ . This procedure, leading to the reported values of  $T_{\text{bra}}$  in the original paper, is also detailed and exemplified in [2].

The well known two-level relaxation model is based on the theoretical case of a Dirac-type size distribution (involving a definite relaxation time). It is in principle very useful because it describes the collapsing process of the Mössbauer spectrum versus the relaxation time in the above limiting case, but is not helpful in real situations involving systems of nanoparticles with distributed sizes or with defected structure (involving a distribution of relaxation times), as in the reported case.

Another observation of Tronc *et al* is related to the blocking temperature which could be influenced either by the characteristics of the surface states or by the specific phase composition of the particles in the analysed systems. But, the linear dependence of the anisotropy constant versus the ratio  $T_{\text{max}}/T_{\text{bra}}$ , and especially the evolution of the blocking temperatures versus the number of the ‘Mössbauer defined surface states’, give support for a real contribution coming from the surface states.

There are also observations against the original paper which are not scientifically relevant, being connected with some limits in the graphical presentation of the Mössbauer data. We recognize these limits which are mainly due to either an inappropriate procedure for assembling spectra or to the reduced clarity in case of the representation of too many distributions (e.g. in

figure 7 were represented fewer exemplifications of distribution as compared with the available spectra; in contrast, in figure 10, all the computed mean hyperfine fields were plotted versus temperature).

The fitting procedure of the Mössbauer spectra of sample 4S deserves a special note. Details will be presented in [2]. Here we have to mention only that the probability distributions of the hyperfine field refer specifically to the amount of iron not sensing S in the neighbourhood. The paramagnetic component at 40 and 100 K in figure 5 contains both the contribution of Fe sensing S neighbours and Fe in superparamagnetic particles of lower size. In this respect, the spectral area of the doublet represented in figure 5 of the original paper cannot be exploited in terms suggested by the comment, as will be detailed in [2].

### **Acknowledgment**

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### **References**

- [1] Predoi D *et al* 2003 *J. Phys.: Condens. Matter* **15** 1797
- [2] Predoi D, Kuncser V and Filoti G 2005 *J. Phys.: Condens. Matter* to be submitted