

Study of maghemite nanoparticles as prepared and coated with DMSA using Mössbauer spectroscopy with a high velocity resolution

M. I. Oshtrakh · M. V. Ushakov · V. A. Semionkin ·
E. C. D. Lima · P. C. Morais

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Abstract Study of maghemite nanoparticles, native and coated with DMSA as magnetic fluid for biomedical applications, was carried out using Mössbauer spectroscopy with a high velocity resolution at 295 and 90 K. The obtained results demonstrated differences in Mössbauer hyperfine parameters for uncoated and DMSA-coated nanoparticles which were related to the interactions of DMSA molecules with Fe^{3+} ions on maghemite nanoparticle's surface.

Keywords Mössbauer spectroscopy · Maghemite nanoparticle · Magnetic fluid

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M. I. Oshtrakh (✉) · M. V. Ushakov · V. A. Semionkin
Department of Physical Techniques and Devices for Quality Control,
Institute of Physics and Technology, Ural Federal University,
Ekaterinburg 620002, Russia
e-mail: oshtrakh@gmail.com

M. I. Oshtrakh · M. V. Ushakov · V. A. Semionkin
Department of Experimental Physics, Institute of Physics and Technology,
Ural Federal University, Ekaterinburg 620002, Russia

E. C. D. Lima
Instituto de Química, Universidade Federal de Goiás, Goiânia,
GO 74001-970, Brazil

P. C. Morais
Department of Control Science and Engineering,
Huazhong University of Science and Technology,
Wuhan 430074, China

P. C. Morais
Instituto de Física, Núcleo de Física Aplicada,
Universidade de Brasília,
Brasília, DF 70910-900, Brazil

1 Introduction

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles are currently used in the development of magnetic fluids for various biomedical applications [1–4]. To decrease interparticle interaction and reduce nanotoxicity while providing biological specificity nanoparticles are surface-coated with molecules like folic acid and dimercaptosuccinic acid (DMSA). Mössbauer spectroscopy is a key technique in the investigation of nanosized magnetic particles while suspended as magnetic fluid samples [5]. Therefore, in the present study we investigated and compared bare maghemite nanoparticles with DMSA-coated maghemite nanoparticles developed as magnetic fluids samples for biomedical purposes using Mössbauer spectroscopy with a high velocity resolution.

2 Experimental

Native maghemite nanoparticles were prepared using the as-synthesized native magnetite nanoparticles as the starting material. The oxidation of nanosized magnetite to maghemite was performed by dispersing the magnetite sample in boiling solution of 0.35 mol/L $\text{Fe}(\text{NO}_3)_3$ under stirring, for 1 h. The obtained reddish nanoparticulated sample was then washed with 2.0 mol/L HNO_3 aqueous solution and separated from the supernatant using a permanent magnet. As-prepared maghemite nanoparticles, with average size of around 8 nm, as well as the dimercaptosuccinic acid ($\text{HO}_2\text{CCH}(\text{SH})\text{CH}(\text{SH})\text{CO}_2\text{H}$) coated maghemite nanoparticles ($\gamma\text{-Fe}_2\text{O}_3\text{-DMSA}$) were studied. The $\gamma\text{-Fe}_2\text{O}_3\text{-DMSA}$ nanoparticles were produced and dispersed in aqueous medium according to the following procedure. Native and purified $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were treated with an aqueous solution of DMSA in order to obtain the DMSA-coated maghemite suspended in aqueous-based sol (surfacted magnetic fluid sample). The DMSA concentration used for surface coating the native nanosized maghemite runs in the range of 0.025–0.150 mol/L. The as-prepared sol was shaken for 12 h and then dialyzed for 12 h against deionized water to eliminate the free DMSA from the bulk dispersion. The pH was adjusted to 7.0–7.2 and large aggregates were removed out from the surfacted magnetic fluid (SMF) sample by centrifugation at 5,000 rpm, for 5 min. The produced aqueous-based SMF sample, with 0.100 mol/L DMSA concentration, revealed long-term colloidal stability.

The phase analysis of the native $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles sample was performed using X-ray powder diffraction (XRD) with a scanning rate of 0.025 °/s in 2Θ range from 20° to 120° using a Bruker D8 Advance diffractometer with Cu-K_α radiation. The morphology (shape and size) of the as-prepared $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles was studied by transmission electron microscopy (TEM) using a Jeol JEM-1010 system. Prior to TEM investigations, powders were crushed in a mortar, dispersed in ethanol, and fixed on a copper-supported carbon grid. Nanoparticles were also characterized using scanning electron microscopy (SEM) with energy dispersion spectroscopy (EDS) using Quanta 2000.

Mössbauer spectra were measured using an automated precision Mössbauer spectrometric system built on the base of the SM-2201 spectrometer with a sawtooth shape velocity reference signal formed using 4,096 bits. Details and characteristics of this spectrometer and the system were given elsewhere [6–8]. The 1.8×10^9 Bq ^{57}Co in rhodium matrixes (Ritverc GmbH, St. Petersburg) was used at room

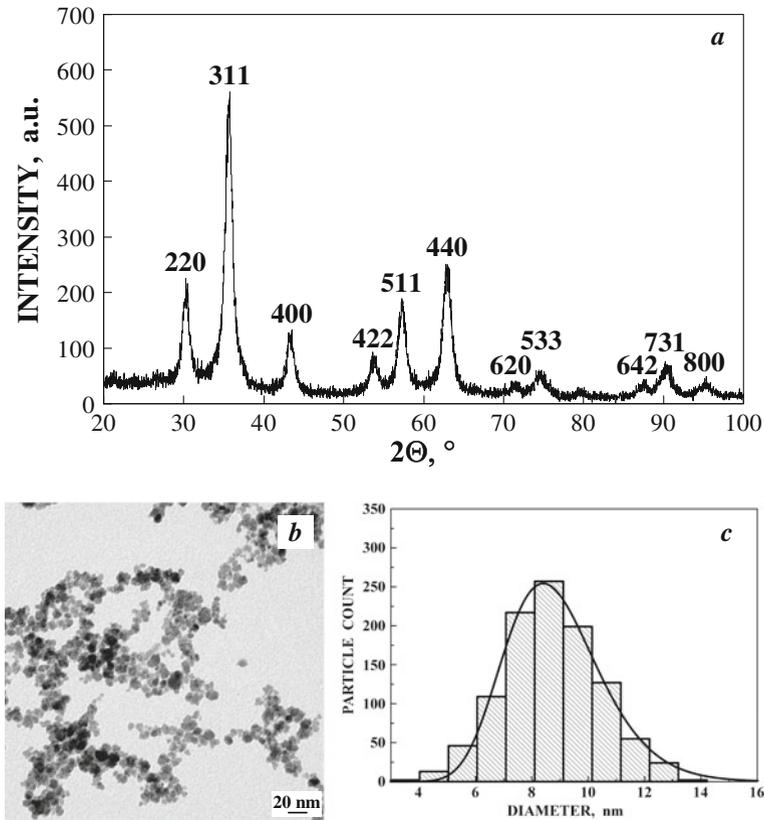


Fig. 1 Characterization of the native γ - Fe_2O_3 nanoparticles by X-ray diffraction (a) and transmission electron microscopy micrograph (b) with evaluation of particles size distribution (c)

temperature. The Mössbauer spectra were measured in transmission geometry with moving absorber in the cryostat at 295 and 90 K and recorded in 4,096 channels. Spectra of γ - Fe_2O_3 and γ - Fe_2O_3 -DMSA samples were measured in velocity range of about ± 12 mm/s. For their analysis, spectra were converted into 2,048 channels by a consequent summation of two neighboring channels. Statistical count rate in the 295 and 90 K spectra presented in 2,048 channels was in the range between $\sim 1.0 \times 10^6$ and $\sim 2.5 \times 10^6$ counts per channel and the signal-to-noise ratio was in the range from 22 till 53. The spectra were computer fitted with the least squares procedure using UNIVEM-MS program with a Lorentzian line shape. The spectral parameters such as: isomer shift, δ , quadrupole splitting (quadrupole shift for magnetically split spectra), ΔE_Q , magnetic hyperfine field, H_{eff} , line width, Γ , relative subspectrum area, S , and statistical quality of the fit, χ^2 , were determined. Magnetic sextets were fitted using the sextet peaks areas ratio $S_{1,6}:S_{2,5}:S_{3,4} = 3 : 2 : 1$. An instrumental (systematic) error for each spectrum point was ± 0.5 channel (the velocity scale), the instrumental (systematic) error for the hyperfine parameters was ± 1 channel. If an error calculated with the fitting procedure (fitting error) for these parameters exceeded the instrumental (systematic) error we used the larger error instead. Values of δ are given relative to α -Fe at 295 K.

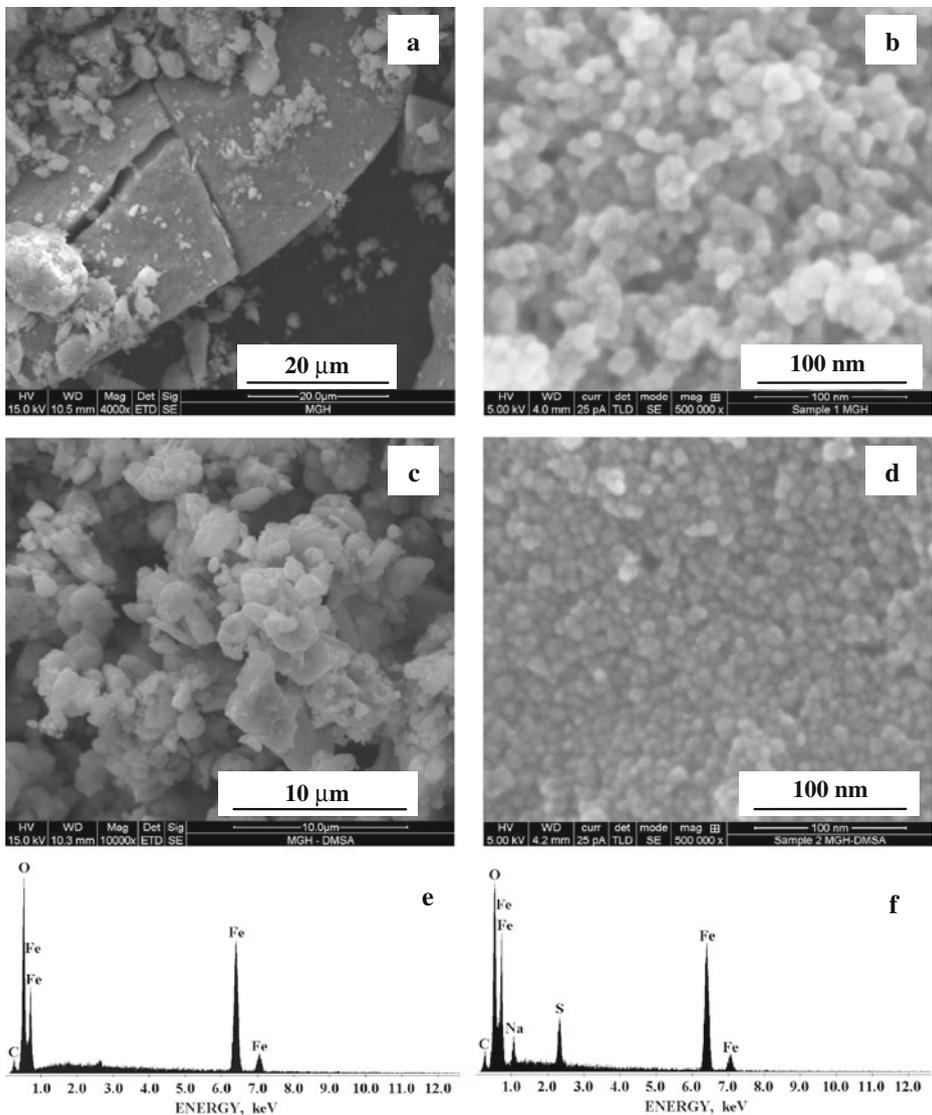


Fig. 2 Scanning electron microscopy (**a, d**) and high resolution scanning electron microscopy (**b, e**) images and energy dispersion spectra (**c, f**) for samples of the native γ - Fe_2O_3 (**a, b, c**) and γ - Fe_2O_3 -DMSA (**d, e, f**)

3 Results and discussion

A typical XRD pattern of the native γ - Fe_2O_3 nanoparticles sample is shown in Fig. 1a. XRD analyses of the γ - Fe_2O_3 sample showed spinel structure with space group $P4_3212$ (# 96) and lattice parameter $a = 8.3400 \text{ \AA}$. TEM micrograph of the native γ - Fe_2O_3 nanoparticles (Fig. 1b) reveals roughly spherically-shaped nanoparticles with an average size of 8.4 nm (log-normal distribution function fitting) with a

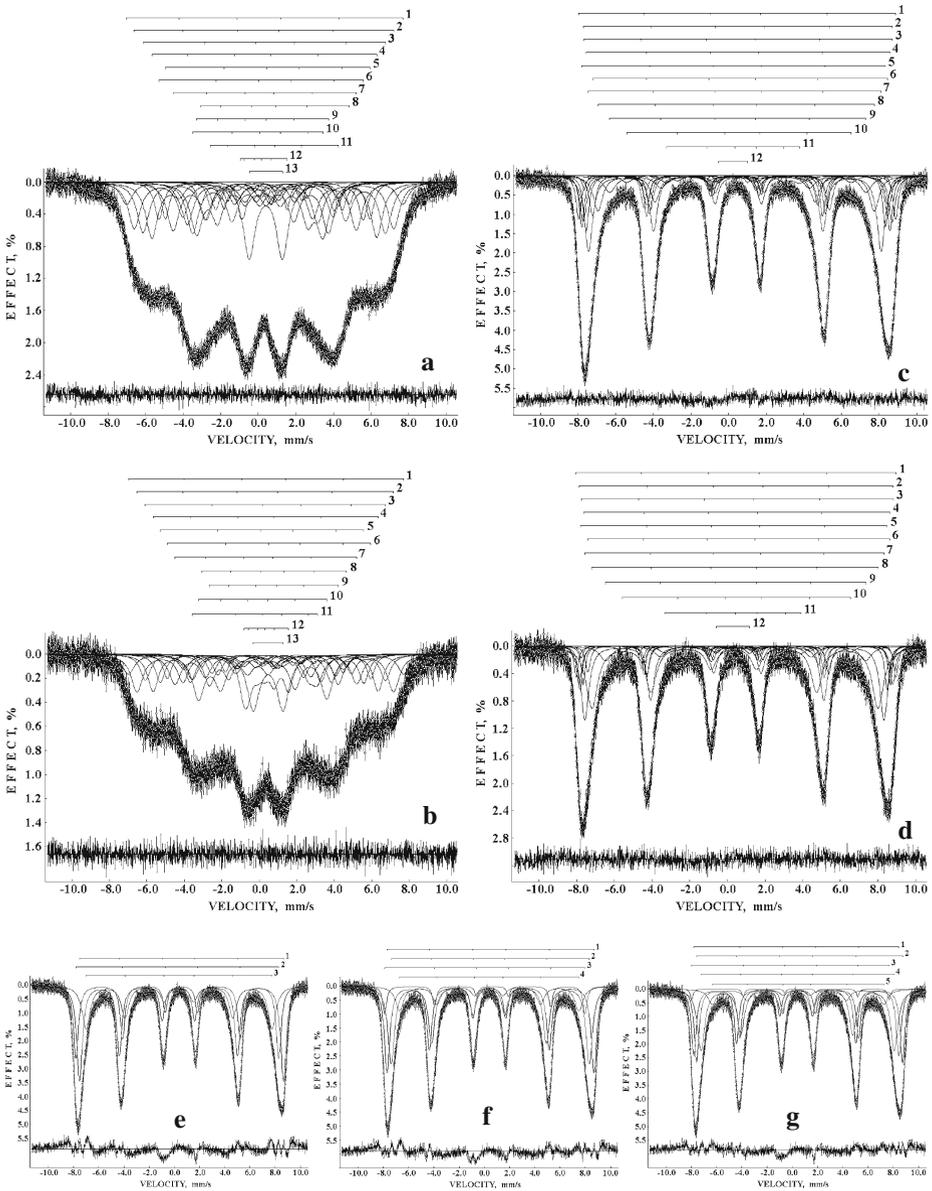


Fig. 3 Mössbauer spectra of the native $\gamma\text{-Fe}_2\text{O}_3$ (a, c, e, f, g) and $\gamma\text{-Fe}_2\text{O}_3\text{-DMSA}$ (b, d) nanoparticles measured at 295 K (a, b) and 90 K (c, d, e, f, g) and presented in 2,048 channels. Indicated components for the spectra a, b, c and d are the results of the better fits while indicated components for the spectra e, f and g are the results of poor fits using smaller numbers of magnetic sextets. Differential spectra are shown below

relatively narrow size distribution characterized by a size dispersion of 0.20 (Fig. 1c), ranging from 4 to 12 nm. SEM and high resolution SEM images of the native $\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3\text{-DMSA}$ nanoparticles with EDS results are shown in Fig. 2. For our

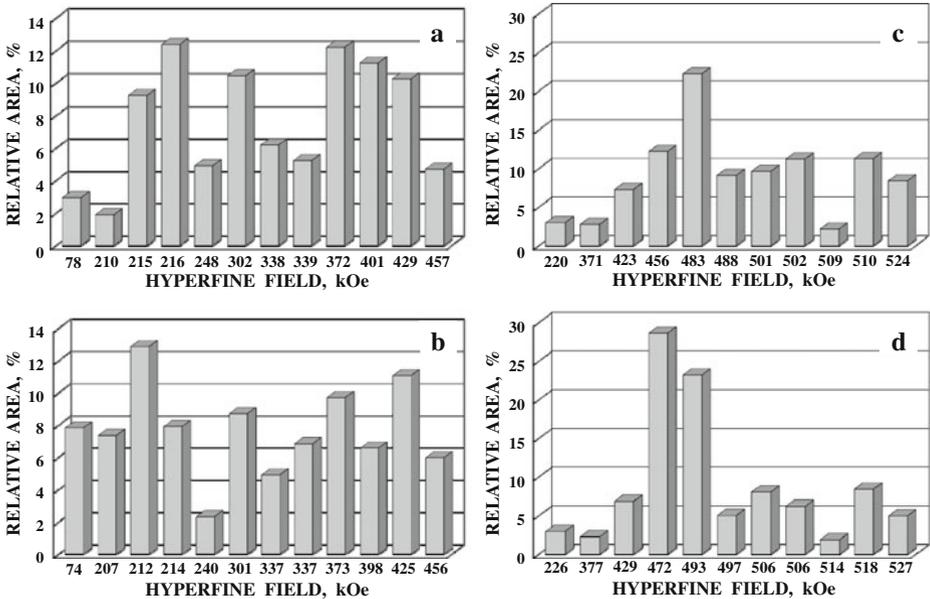


Fig. 4 Histograms of relative areas of components versus hyperfine fields obtained from the better fits of Mössbauer spectra of the native $\gamma\text{-Fe}_2\text{O}_3$ (**a, c**) and $\gamma\text{-Fe}_2\text{O}_3\text{-DMSA}$ (**b, d**) nanoparticles measured at 295 K (**a, b**) and 90 K (**c, d**)

purpose EDS data collected from the native $\gamma\text{-Fe}_2\text{O}_3$ sample are more precise as S from the DMSA ruled out from the data. Actually, stoichiometric maghemite present iron/oxygen mass ratio equals to 2.3. EDS data recorded from our $\gamma\text{-Fe}_2\text{O}_3$ sample provide iron/oxygen mass ratio equals to $[\text{Fe}]/[\text{O}] = 4.1$. These finding indicates non-stoichiometric maghemite.

Mössbauer spectra of the native $\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3\text{-DMSA}$ nanoparticles measured at 295 and 90 K with a high velocity resolution are shown in Fig. 3. These spectra demonstrated asymmetric six-line patterns which were significantly different at 295 and 90 K. Moreover, the 295 K spectra of the native $\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3\text{-DMSA}$ nanoparticles were also different. All these spectra were not fitted well using known physical model for maghemite accounting for the ^{57}Fe in the tetrahedral (A) and octahedral [B] sites. Therefore, we fitted these spectra with a larger number of components to reach the best fit similarly to our previous study of magnetite nanoparticles (see [9, 10]). In this case we obtained 12 magnetic sextets and 1 quadrupole doublet for the 295 K spectra and 11 magnetic sextets and 1 quadrupole doublet for the 90 K spectra. For comparison we added in Fig. 3 three models of the fit of the 90 K native $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles Mössbauer spectrum using 3, 4 and 5 magnetic sextets (Fig. 3e, f and g). Similar fits were used for Mössbauer spectra of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles measured at different temperatures in [11–14]. However, it is clearly seen that such fits of the native $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles Mössbauer spectrum demonstrate poor quality on the basis of differential spectra (similar results were obtained for other spectra shown in Fig. 3). Unfortunately, the reason of too many sextets needed for a good fit is not clear yet. Nevertheless, we can suppose that these components may be related to tetrahedral and octahedral iron-site occupancy, small

particles' size distribution, non-stoichiometry, possible interparticle interactions even in the case of DMSA-coated maghemite, complicated nanoparticle structure with surface and internal layers and/or nano-domains, etc. It was interesting that paramagnetic components remained at 90 K in both native γ -Fe₂O₃ and γ -Fe₂O₃-DMSA nanoparticle's spectra. Mössbauer parameters of paramagnetic doublet are related to the ferric compound. The relative area of paramagnetic component was about 5–6 % for both the native γ -Fe₂O₃ and γ -Fe₂O₃-DMSA spectra at 295 K while hyperfine parameters for this component were slightly different beyond the error. In contrast, the relative area of paramagnetic component decreased down to about 1 % at 90 K. These finding can show that the magnetic anisotropy energy barrier in the native γ -Fe₂O₃ and γ -Fe₂O₃-DMSA nanoparticles was slightly smaller than in the case of previously studied magnetite nanoparticles in [9, 10].

A comparison of histograms of relative areas for magnetic sextets obtained from the better fits versus hyperfine field is shown in Fig. 4. It is interesting to observe some differences in the histograms for the native γ -Fe₂O₃ and γ -Fe₂O₃-DMSA nanoparticles at both 295 and 90 K. This fact may be related to the effect of DMSA-coated and interaction of these molecules with Fe³⁺ ions at the nanoparticle's surface. If this interaction may decrease Fe³⁺ electron spin off-orientation at the nanoparticles surface, this may increase small magnetic hyperfine field at the surface layer with further effect on the internal layers or nano-domains.

4 Conclusion

Comparative study of the native γ -Fe₂O₃ and γ -Fe₂O₃-DMSA nanoparticles samples developed as magnetic fluids for biomedical aims using Mössbauer spectroscopy with a high velocity resolution demonstrated differences in magnetic hyperfine fields for both samples. This fact may be a result of the interaction of DMSA molecules with Fe³⁺ ions at the nanoparticle's surface. We can suggest that a large number of components in the high velocity resolution Mössbauer spectra of the maghemite samples required for the better fit may be a result of complicated nanoparticles' core structure, non-stoichiometry, small size distribution and the presence of nanoparticles' ensemble similar to previous suggestion for magnetite nanoparticles [9, 10].

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