

Magnetic fluid: Comparative study of nanosized Fe₃O₄ and Fe₃O₄ suspended in Copaiba oil using Mössbauer spectroscopy with a high velocity resolution

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Abstract. Comparative study of nanosized magnetite and magnetite suspended in Copaiba oil (biocompatible magnetic fluid) was made using Mössbauer spectroscopy with a high velocity resolution (spectra were measured in 4096 channels). The better fit of room temperature spectra was done using 15 sextets and 1 doublet employing different parameters while spectra measured at 90 K were better fitted using 15 sextets with different parameters. These component numbers were related to multi-domain structure and non-stoichiometry of magnetite. Observed differences of magnetic hyperfine fields and relative areas of spectral components for nanosized Fe₃O₄ and Fe₃O₄ suspended in Copaiba oil may be related to the effect of surface interactions of Fe₃O₄ and polar molecules of Copaiba oil.

1. Introduction

Biocompatible magnetic fluids are used and developed for instance as contrast agents for magnetic resonance imaging, as drug carriers and for drug delivery, for local hyperthermia effect in tumor therapy [1]. Typical magnetic fluids consist of iron-containing magnetic nanoparticles and may be well studied using Mössbauer spectroscopy [2]. Recently, new capabilities of Mössbauer spectroscopy with high velocity resolution were demonstrated in various biomedical researches [3]. Therefore, in this work we applied this technique to study native nanosized magnetite and nanosized magnetite suspended in Copaiba oil as a biocompatible magnetic fluid sample.

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2. Materials and methods

Magnetite nanoparticles were synthesized by co-precipitation of a heated mixture of ferrous and ferric chloride aqueous solution with concentrated ammonia (25 % v.v.), under vigorous stirring. After precipitation of nanosized Fe_3O_4 and repeated washing using hydrochloric acid a stable sol at pH 2, with nanoparticle volume fraction around 1%, was produced. Copaiba oil was collected from Copaifera tree (*Copaifera Langsdorffii Desf.*) in the Ji-Paraná region, Rondônia State, Brazil. Copaiba oil dispersed in cyclohexane was then added to the as-produced sol under stirring. The resulting suspension was dried to remove out the organic solvent whereas the precipitated sample (CO- Fe_3O_4) as well as native Fe_3O_4 were used for Mössbauer measurement. Both samples had effective thicknesses about 5 mg Fe/cm² and about 18 mg Fe/cm² for 295 and 90 K measurements, respectively.

Mössbauer spectrometric complex with a high velocity resolution and its characteristics were described in details in [3, 4]. Spectra were measured at 295 and 90 K, in 4096 channels, and computer fitted with the least squares procedure using UNIVEM-MS program (from Research Institute of Physics, Southern Federal University, Rostov-on-Don, Russian Federation) with Lorentzian line shape. This program realizes two methods: direct search by method of configurations (the Hook–Jives method) and gradient search by the Newton–Gauss algorithm, both for minimization of χ^2 . Therefore, minimization of χ^2 can be done using direct search firstly, then by gradient search. It is possible to use any number of spectral components and varied parameters for fitting spectra contained up to 4096 points. The Mössbauer parameters isomer shift δ , quadrupole splitting (quadrupole shift for magnetically split component) ΔE_Q , magnetic hyperfine field H_{eff} , line width Γ , subspectrum relative area S and statistical criterion χ^2 were determined. Magnetic sextets were fitted using the ratio $S_{16}:S_{25}:S_{34}=3:2:1$. Criteria of spectra fitting quality were χ^2 , differential spectrum and physical meaning of parameters. Hyperfine field distribution program was additionally used for comparison. The values of isomer shift are given relative to α -Fe at 295 K.

3. Results and discussion

Mössbauer spectra of nanosized native Fe_3O_4 and CO- Fe_3O_4 samples are shown in Figure 1. These spectra were fitted using various numbers of components up to 18 sextets. For instance, fitting of the native Fe_3O_4 spectrum at 295 K using 1 paramagnetic doublet and 13, 14, 15 and 16 sextets demonstrated the following variation of χ^2 values: 3.434, 3.392, 3.366 and 3.366, respectively. Fitting of the CO- Fe_3O_4 spectrum at 295 K using the same number of components showed variation of χ^2 values: 1.629, 1.621, 1.608 and 1.611. Therefore, comparison of χ^2 values, differential spectra and physical meaning of parameters permitted us to suggest the better fit of Mössbauer spectra using 15 magnetic sextets and 1 paramagnetic doublet for the room temperature and 15 magnetic sextets for 90 K. However, hyperfine parameters of these spectral components and its relative areas were different. Parameters of paramagnetic doublet for native Fe_3O_4 and CO- Fe_3O_4 were also different: $\delta=0.47\pm 0.02$ mm/s, $\Delta E_Q=1.19\pm 0.06$ mm/s and $\delta=0.52\pm 0.02$ mm/s, $\Delta E_Q=1.03\pm 0.04$ mm/s, respectively. Differences of the plots of magnetic hyperfine field versus isomer shift for spectral components are shown in Figure 2. Unfortunately, the reason of large number of components in Mössbauer spectra of nanosized magnetite samples is not clear yet. These magnetic components may be a result of particle structure variations from surface to the core region (multi-domain structure) or layers as well as the presence of A and B sites in magnetite and non-stoichiometry of magnetite. Moreover, it is possible that some variations of the δ values (see Figure 2) may be related to the A and B sites in magnetite that is in agreement with published data (see, for instance, [5]). However, the δ value of about 1.2 mm/s cannot be explained. The room temperature data for nanosized Fe_3O_4 and CO- Fe_3O_4 samples demonstrated differences which may be a result of the effect of surface interactions of Fe_3O_4 and polar molecules in Copaiba oil. These interactions may lead to reduction of spin off-orientations of Fe^{3+} and increase of internal magnetic field. Then surface changes of the internal field may affect deep layers or domains in nanoparticles. Differences of relative areas of sextets and the values of H_{eff} are shown in Figure 3, **a** and **b**. It should be noted that the hyperfine field distribution was not informative in comparison with

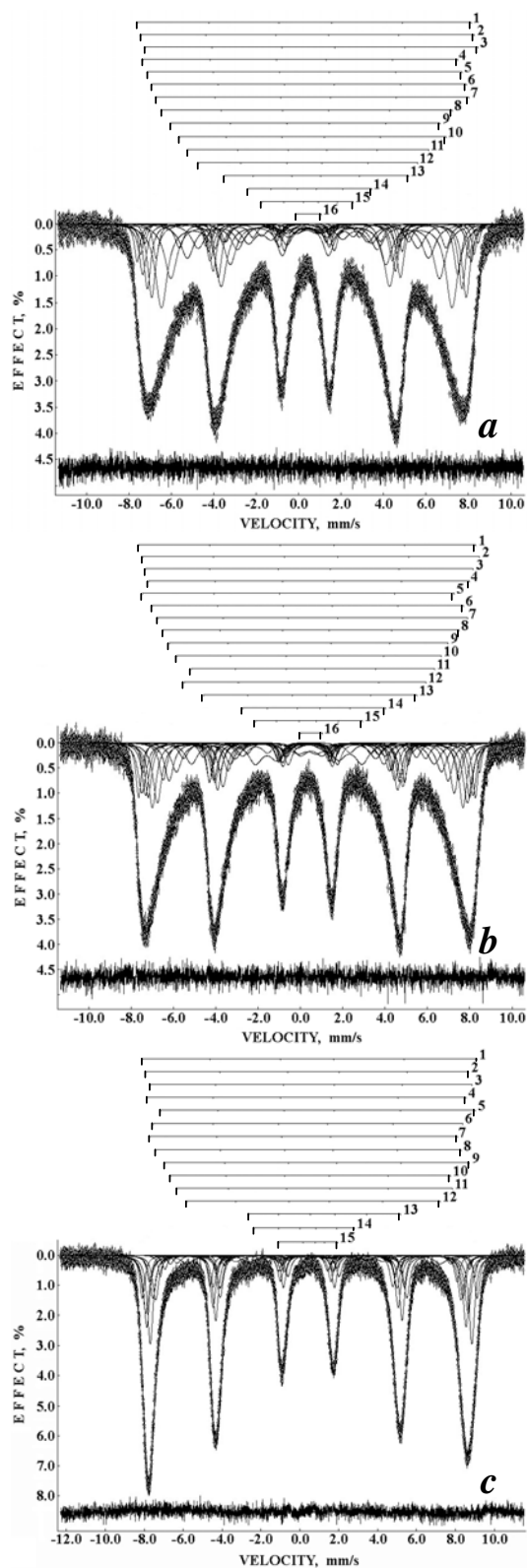


Figure 1. Mössbauer spectra of native Fe_3O_4 nanoparticles (*a*) and $\text{CO-Fe}_3\text{O}_4$ (*b*, *c*) measured in 4096 channels. Components are the results of the better fit. $T=295\text{ K}$ (*a*, *b*), $T=90\text{ K}$ (*c*).

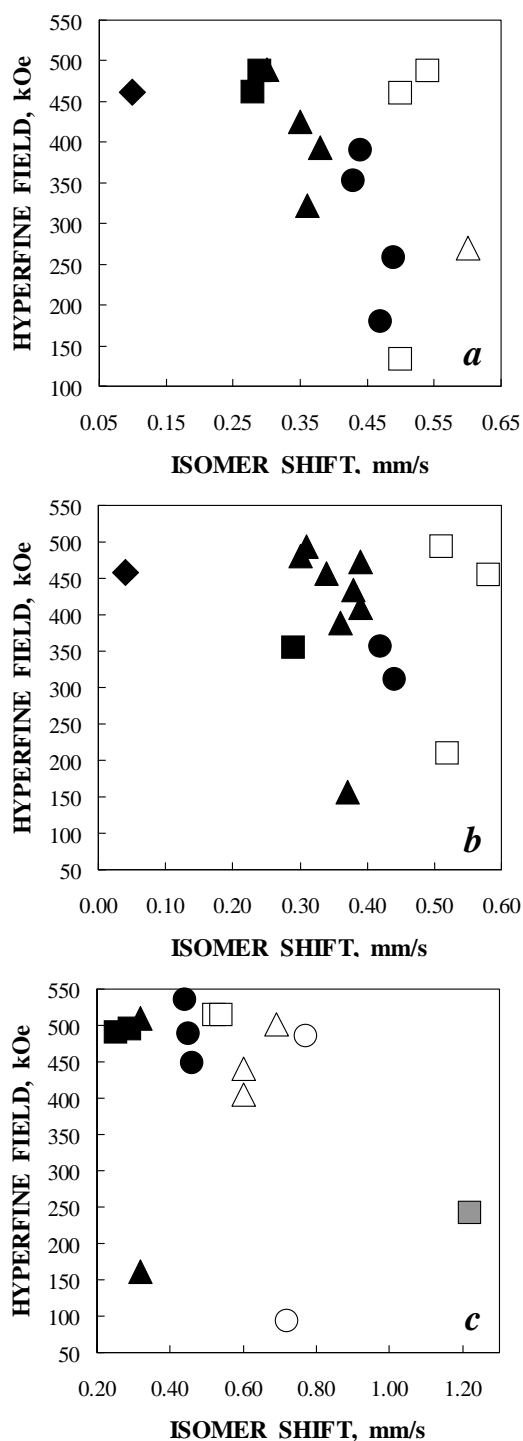


Figure 2. Hyperfine field versus isomer shift: \blacklozenge – for $\delta=0.0\text{--}0.1\text{ mm/s}$, \blacksquare – for $\delta=0.2\text{--}0.3\text{ mm/s}$, \blacktriangle – for $\delta=0.3\text{--}0.4\text{ mm/s}$, \bullet – for $\delta=0.4\text{--}0.5\text{ mm/s}$, \square – for $\delta=0.5\text{--}0.6\text{ mm/s}$, \triangle – for $\delta=0.6\text{--}0.7\text{ mm/s}$, \circ – for $\delta=0.7\text{--}0.8\text{ mm/s}$, \blacksquare – for $\delta=1.2\text{--}1.3\text{ mm/s}$. *a* – native Fe_3O_4 , $T=295\text{ K}$; *b* – $\text{CO-Fe}_3\text{O}_4$, $T=295\text{ K}$; *c* – $\text{CO-Fe}_3\text{O}_4$, $T=90\text{ K}$.

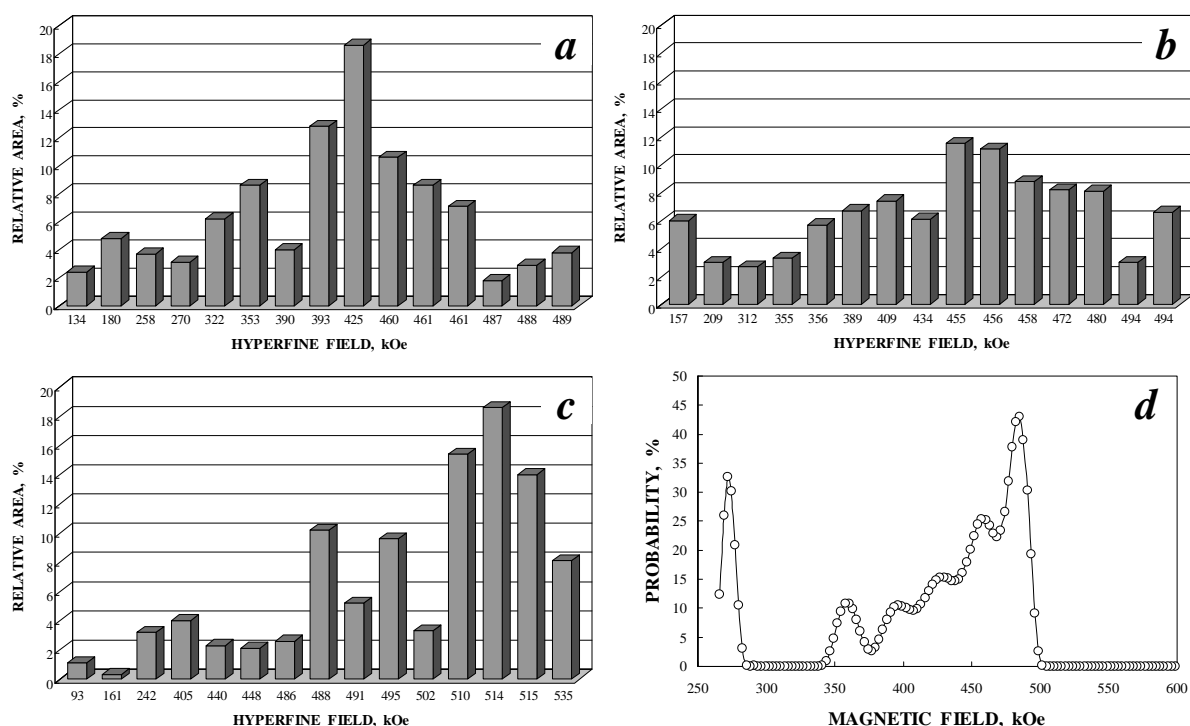


Figure 3. Differences of magnetic components relative areas versus hyperfine fields obtained from the better fit of Mössbauer spectra of native Fe₃O₄ nanoparticles at T=295 K (a) and CO-Fe₃O₄ at T=295 K (b) and T=90 K (c) measured in 4096 channels as well as result of hyperfine field distribution for Mössbauer spectrum of CO-Fe₃O₄ at T=295 K (d).

discrete fitting (Figure 3, b and d) and demonstrated less components in the spectrum. Comparison of room and low temperature data for nanosized Fe₃O₄ and CO-Fe₃O₄ samples demonstrated disappearance of paramagnetic doublet, changes of hyperfine parameters (compare Figure 2, b and c) and redistribution of relative areas of magnetic sextets (compare Figure 3, b and c). This fact may be a result of temperature dependent variation of nanoparticles' internal structure and multi-domain magnetic structure. Moreover, differences of Mössbauer parameters for nanosized Fe₃O₄ and CO-Fe₃O₄ were also found at 90 K.

4. Conclusion

Study of native nanosized Fe₃O₄ and biocompatible Fe₃O₄ nanoparticles suspended in Copaiba oil using Mössbauer spectroscopy with a high velocity resolution (in 4096 channels) at 295 and 90 K demonstrated complicated structure of nanoparticles. This may be a result of structural variations from surface to core region (multi-domain structure) or layers as well as the presence of A and B sites in magnetite and non-stoichiometry of magnetite. Differences between native nanosized Fe₃O₄ and CO-Fe₃O₄ may reflect the effects of uncoated nanoparticle surface-carrier liquid interaction. Temperature dependent variation of Mössbauer parameters for CO-Fe₃O₄ was also observed.

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