STOICHIOMETRY ISSUE OF IRON(III) OXIDE NANOMATERIALS BY MÖSSBAUER SPECTROSCOPY

Jana HAVLÁKOVÁ, Jiří TUČEK, Radek ZBOŘIL

Regional Centre of Advanced Technologies and Materials, Departments of Experimental Physics and Physical Chemistry, Faculty of Science, Palacký University Olomouc, Czech Republic, EU
jana.havlakova@upol.cz

Abstract

Iron oxides, especially the Fe_3O_4 and γ-Fe_2O_3 phases, play a significant role in potential applications of nanomaterials due to their suitable features such as biocompatibility, magnetic and optoelectronic properties. Moreover, it is convenient to use Fe_3O_4 for some applications, such as Li-ion batteries, because of its combined valence states of iron. Therefore, it is highly desired to distinguish the two, otherwise similar, iron oxide phases and to evaluate the degree of Fe_3O_4 stoichiometry. Genuinely, a proper characterization of these compounds can be problematic due to their similar structures and the common occurrence of non-stoichiometric iron oxide forms and their mixtures in the nanosystems. In this respect, [57]Fe Mössbauer spectroscopy is regarded as a powerful tool for the identification of different forms of iron oxides as well as for the distinguishing between core-shell structures and mixtures. The present contribution is focused on theoretical [57]Fe Mössbauer spectra of Fe_3O_4, γ-Fe_2O_3 and their different degrees of stoichiometry, with regards to the correct evaluation of the spectra. [57]Fe Mössbauer spectra of two distinct levels of non-stoichiometric γ-Fe_2O_3 and Fe_3O_4 were modelled and discussed. Furthermore, theoretical examples of [57]Fe Mössbauer spectra of Fe_3O_4/γ-Fe_2O_3 mixture of 1/1 particle ratio and a core-shell structure, where Fe_3O_4 core takes up 75 % of the particle's volume, are presented.

Keywords: γ-Fe_2O_3, Fe_3O_4, stoichiometry, mixtures, [57]Fe Mössbauer spectroscopy

1. INTRODUCTION

Iron oxides are considered as intriguing nanomaterials due to their importance in fundamental research as well as their convenient physicochemical properties such as nontoxicity, biocompatibility, outstanding magnetic, electronic and optoelectronic features together with relatively low-cost production possibilities, that offer a wide application potential [1-4]. They are frequently classified into two main groups - hydrated (i.e., hydroxides and oxide-hydroxides) and non-hydrated phases; in non-hydrated forms, iron ions are present in divalent (FeO), trivalent (Fe_2O_3) or both states (Fe_3O_4). Additionally, ferric oxide exhibits polymorphism; five crystalline (α-Fe_2O_3, β-Fe_2O_3, γ-Fe_2O_3, ε-Fe_2O_3, and ζ-Fe_2O_3) structures and amorphous Fe_2O_3 are known to date, from which Fe_3O_4 (mineralogically known as magnetite) and γ-Fe_2O_3 (mineralogically known as maghemite) are the two leading phases regarding applications [4,5].

When the particle size decreases, it generally becomes difficult to distinguish between Fe_3O_4 and γ-Fe_2O_3, because of the presence of their mixtures and nonstoichiometric structures [6]. Moreover, the degree of stoichiometry can affect particle's physical and chemical properties such as reduction potential, conductivity, coercivity and saturation magnetization, etc. [3]. For some applications, e.g., in lithium-ion batteries, it is crucial to use materials with mixed valence states, and therefore to know and evaluate the degree of their stoichiometry. These factors could raise an issue - how to sufficiently characterize these oxides and their stoichiometry? The solution can be to employ [57]Fe Mössbauer spectroscopy; a powerful tool which can provide the information about the present phases as well as the degree of their stoichiometry, i.e., the quantification of Fe^{2+}/Fe^{3+} ratio.

In the present contribution, we focus on theoretical simulation of nanoparticulate assembly composed of nonstoichiometric Fe_3O_4, γ-Fe_2O_3, Fe_3O_4/γ-Fe_2O_3 mixture and a core-shell structure. Furthermore, we predict their Mössbauer spectral features which can be related to the experimental data of nanosystems with particle size not smaller than ~10 nm (below such threshold size limit, ultrafine nanoparticles adopt amorphous nature). The ^{57}Fe Mössbauer spectra were simulated with the help of *MossWinn* programme with the input data from our vast knowledge on iron oxide nanoparticle systems [1,7]. The only variables in modelling of the spectra involved the degree of stoichiometry and the phase volume ratio for mixture and core-shell structure while the rest of the parameters (e.g., particle size distribution, morphology, temperature fluctuations, etc.) were not considered. Therefore, we accept possible slight differences between theoretical spectra modelled here and those experimentally observed.

2.   γ-Fe₂O₃, Fe₃O₄ AND THE EVALUATION OF THEIR STOICHIOMETRY

The two phases of non-hydrated iron oxide, γ-Fe_2O_3 and Fe_3O_4, are not trivial to distinguish as mentioned earlier, which is due to their nearly identical crystal structures [8]. γ-Fe_2O_3 has a cubic crystal structure of an inverse spinel with a lattice parameter a = 8.35 Å and two non-equivalent cation positions. Tetrahedral (A) sites are occupied solely by Fe^{3+} ions and octahedral (B) sites are divided between ferric ions and vacancies. Ferric ions occupy A- and B-sites in stoichiometric γ-Fe_2O_3 in the ratio of 1/1.67 and its formula can be written as $(Fe^{3+})^A (Fe^{3+}_{5/3} \square_{1/3})^B O_3$, where the symbol $\square$ means vacancies [9-11]. The space group of γ-Fe_2O_3 is $Fd\overline{3}m$ if the vacancies are distributed over B-sites randomly, $P4_132$ with partially ordered vacancies and tetragonal $P4_32_12$ when the vacancies are fully ordered [11]. Magnetic moments of ferric ions in A- and B-sites are not equal and are in antiparallel alignment with respect to each other, therefore γ-Fe_2O_3 is a collinear ferrimagnet. Additionally, the experimental measurement of the Curie temperature is not possible due to the transformation to thermodynamically more stable α-Fe_2O_3 (hematite), in nanomaterials possibly via a rare phase ε-Fe_2O_3.

Fe_3O_4 has a cubic crystal structure of an inverse spinel as well as γ-Fe_2O_3 but the lattice parameter a is slightly increased, i.e., a = 8.39 Å. Stoichiometric Fe_3O_4 has tetrahedral (A) sites and octahedral (B) sites occupied in the ratio of 1/2 since the B-sites are split between both Fe^{2+} and Fe^{3+} ions equally [3,8]. Nonetheless, Fe_3O_4 often exists in non-stoichiometric form due to oxidization, which causes formation of vacancies and therefore shifting of the A/B ratio towards γ-Fe_2O_3. Its formula can be therefore written as $Fe_{3-\delta}O_4$, where the degree of stoichiometry δ can vary from 0 to 1/3, while zero value represents stoichiometric Fe_3O_4 and δ = 0.33 implies γ-Fe_2O_3 [2]. Moreover, if we account for the distribution of vacancies and their ratio to Fe^{2+} and Fe^{3+} ions, then the structural non-stoichiometric formula can be written as $(Fe^{3+})^A (Fe^{2+}_{1-2\delta} Fe^{3+}_{1+2\delta} \square_\delta)^B O_4$, where the symbol $\square$ stands for vacancies [2,3]. Fe_3O_4 is a collinear ferrimagnet as well as γ-Fe_2O_3 with the Curie temperature of ~850 K. At room temperature, Fe_3O_4 exhibits a conductive behaviour due to the fast electron hopping between octahedral cations. As the temperature decreases to ~124 K, Fe_3O_4 undergoes the Verwey transition; a structural distortion from cubic to orthorhombic symmetry accompanied with a rapid drop in conductivity [8,12-14].

Crystal structures of stoichiometric γ-Fe_2O_3 and Fe_3O_4 are shown in **Figure 1a,b** together with their typical powder X-ray diffraction (XRD) patterns (see **Figure 1c,d**) and typical ^{57}Fe Mössbauer spectra, with isomer shift values referred to δ-Fe at room temperature and zero applied field (see **Figure 1e,f**), while their Mössbauer hyperfine parameters are listed in **Table 1**. The ^{57}Fe Mössbauer spectrum of stoichiometric γ-Fe_2O_3 consists of two spectral components corresponding to ferric ions in the A-sites and in the B-sites. The stoichiometric form of Fe_3O_4 is in Mössbauer spectrum manifested by two spectral components, one originating from Fe^{3+} ions in the A-positions and the other from Fe^{2+} and Fe^{3+} ions in the B-positions with effective valence state of 2.5+ due to the fast electron hopping above the Verwey temperature [3,12].
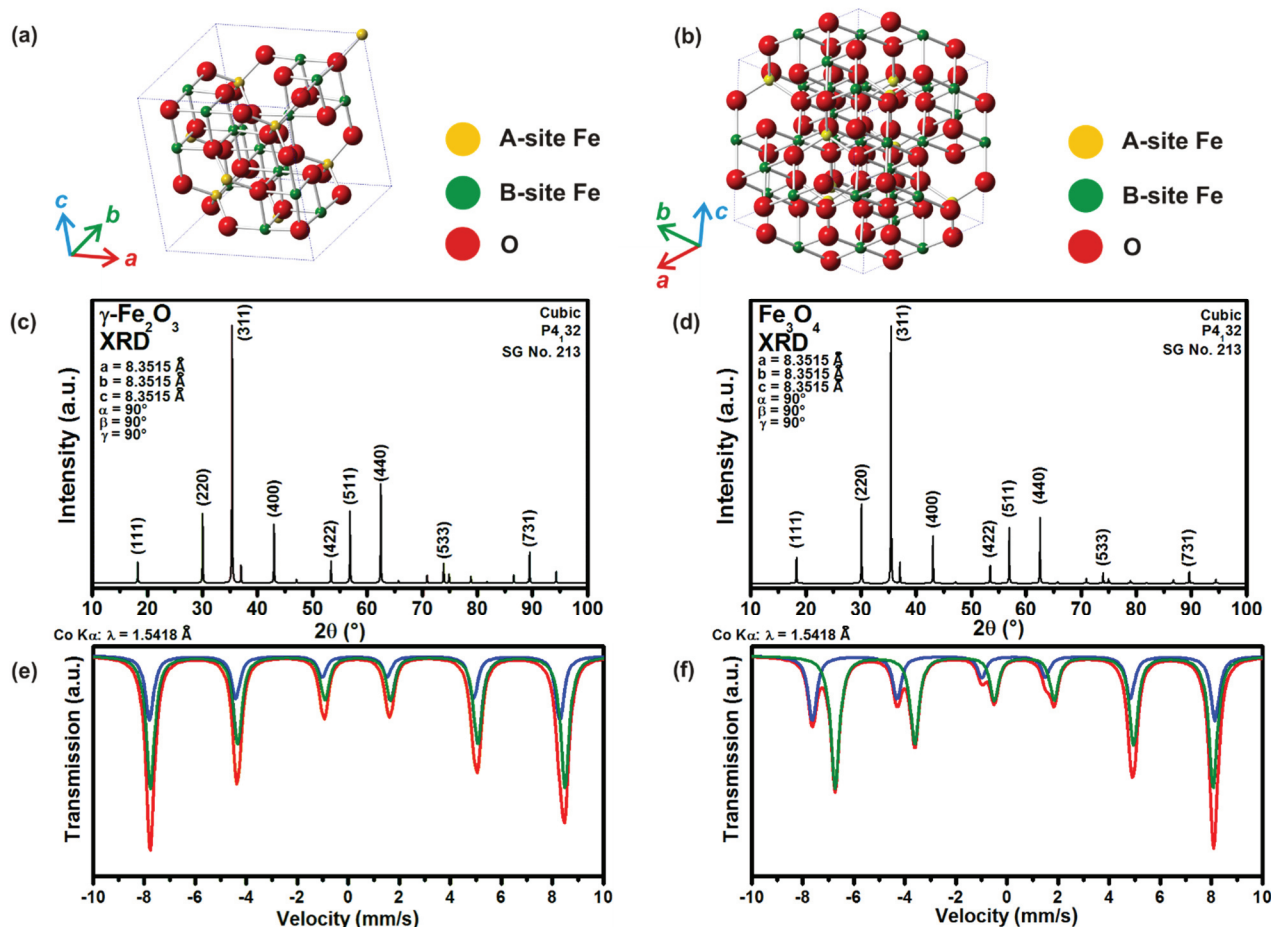
Figure 1 Crystal structures and typical XRD patterns and ^{57}Fe Mössbauer spectra of (a, c, e) γ-Fe_2O_3 and (b, d, f) Fe_3O_4, on the right-hand side. In the Mössbauer spectra, the red line is corresponding to the overall fit, the blue line corresponds to ions in the A-sites and the green line refers to ions in the B-sites. Panel (a) is reprinted with permission from [1].

Table 1 ^{57}Fe Mössbauer hyperfine parameters typical for ideally stoichiometric forms of γ-Fe_2O_3 and Fe_3O_4, where $δ_{Fe}$ is the isomer shift, $ΔE_Q$ is the quadrupole splitting, B_{hf} is the hyperfine magnetic field and RA is the relative spectral area. The isomer shift values are referred to metallic δ-Fe at room temperature

phase	$δ_{Fe}$ (mm/s)	$ΔE_Q$ (mm/s)	B_{hf} (T)	RA (%)	Assignment
γ-Fe_2O_3	0.25	0.00	50.0	37.5	Fe^{3+} A-site
	0.37	0.00	50.5	62.5	Fe^{3+} B-site
Fe_3O_4	0.25	0.00	48.9	33.3	Fe^{3+} A-site
	0.65	0.00	45.7	66.7	$Fe^{2.5+}$ B-site

Additionally, in the non-stoichiometric $Fe_{3-δ}O_4$, Fe^{3+} ions also occur as isolated in the B-positions, which are not involved in the electron hopping effect and are manifested in the Mössbauer spectra by the presence of the additional third sextet. The degree of stoichiometry of $Fe_{3-δ}O_4$ can be described also by the ratio x_m of structural amount of Fe^{2+} and Fe^{3+} ions, given by the following relationship stated by Gorski and Scherer [3]:

$$x_m = \frac{Fe^{2+}}{Fe^{3+}} = \frac{1-3\delta_m}{2+2\delta_m}.$$ (1)

The stoichiometry x_m can vary from 1/2 for stoichiometric Fe_3O_4 to zero corresponding to completely oxidized form (i.e., γ-Fe_2O_3). The value of x_m is obtained from ^{57}Fe Mössbauer spectra as a ratio of relative areas of spectral components corresponding to Fe^{2+} and Fe^{3+} ions by the following equation [3]:

$$x_m = \frac{Fe^{2+}}{Fe^{3+}} = \frac{\frac{1}{2}^B Fe^{2.5+}}{\frac{1}{2}^B Fe^{2.5+} + ^{A+B} Fe^{3+}}.$$ (2)

As the degree of stoichiometry shifts towards γ-Fe_2O_3, the amount of Fe^{2+} decreases; at some point, there is not enough Fe^{2+} ions to be detected by ^{57}Fe Mössbauer spectroscopy, therefore the $Fe^{2.5+}$ sextet is not resolved in the spectrum and x_m cannot be evaluated. Nevertheless, these assemblies are rather closer to the structure of γ-Fe_2O_3 and their degree of stoichiometry can be estimated as the occupancy ratio of B/A sites, since we know that for stoichiometric γ-Fe_2O_3, the spectral ratio is equal to 1.67 [9].

We addressed this issue by modelling ^{57}Fe Mössbauer spectra of two systems with different degrees of stoichiometry; one closer to the Fe_3O_4 and the other one closer to γ-Fe_2O_3, as can be seen in **Figure 2**. The theoretical ^{57}Fe Mössbauer spectrum of non-stoichiometric Fe_3O_4 consists of three spectral components, corresponding to Fe^{3+} in A-sites, isolated Fe^{3+} in B-positions and $Fe^{2.5+}$ in B-sites. The spectrum of the non-stoichiometric γ-Fe_2O_3 consists of two spectral components corresponding to Fe^{3+} ions in A-sites and Fe^{3+} ions in B-sites. Their predicted hyperfine parameters are listed in **Table 2**. We estimated the degree of stoichiometry according to the B/A relative spectral areas ratio as $\delta_1 = 0.14$ and $\delta_2 = 0.26$. On the other hand, when we follow equation (2) and then equation (1) to obtain the value of δ_m (this procedure can be employed only for the non-stoichiometric Fe_3O_4), then $\delta_{m1} = 0.22$. The vast difference in values δ_1 and δ_{m1} can be caused by the applicability of equations (1) and (2) to structures close to stoichiometric Fe_3O_4. This brings us to several issues and questions: (i) What is the threshold value of δ (or x_m) when the structure cannot be considered Fe_3O_4-like and hence becomes non-stoichiometric γ-Fe_2O_3 illustrated by the grey area in **Figure 2**?; (ii) How to correctly evaluate the degree of stoichiometry in the close proximity of this threshold value?
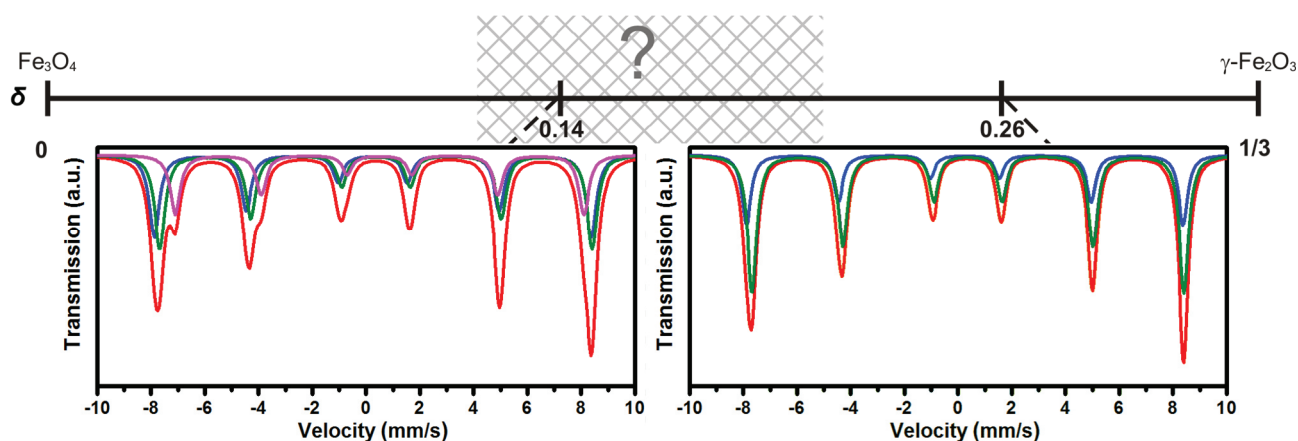

Figure 2 Theoretical ^{57}Fe Mössbauer spectra of Fe_3O_4 particles with different degrees of stoichiometry δ; the blue lines correspond to Fe^{3+} in A-sites, the green lines refer to Fe^{3+} isolated in B-sites, the pink line corresponds to $Fe^{2.5+}$ in B-sites and the red lines represent the overall fits

The second modelled situation is the difference between Mössbauer spectra of Fe_3O_4/γ-Fe_2O_3 mixtures and core-shell assemblies, which is shown in **Figure 2**. The theoretical Mössbauer spectrum of a 1/1 mixture consists of four spectral components of which two are assigned to Fe_3O_4 particles, hence Fe^{3+} ions in A-sites

and $Fe^{2.5+}$ ions in B-sites. The other two components refer to Fe^{3+} in A-sites and Fe^{3+} in B-sites in $\gamma\text{-}Fe_2O_3$. The theoretical spectrum of a core-shell assembly, on the other hand, consists of three spectral components. The first and second component is assigned to the Fe_3O_4 core and its Fe^{3+} ions in A-sites and $Fe^{2.5+}$ ions in B-sites, respectively. Since the core takes-up 75 % of the particle's volume, the $\gamma\text{-}Fe_2O_3$ surface layer is extremely thin, hence the spectral components referring to $\gamma\text{-}Fe_2O_3$ cannot be resolved separately and are seen as one component.

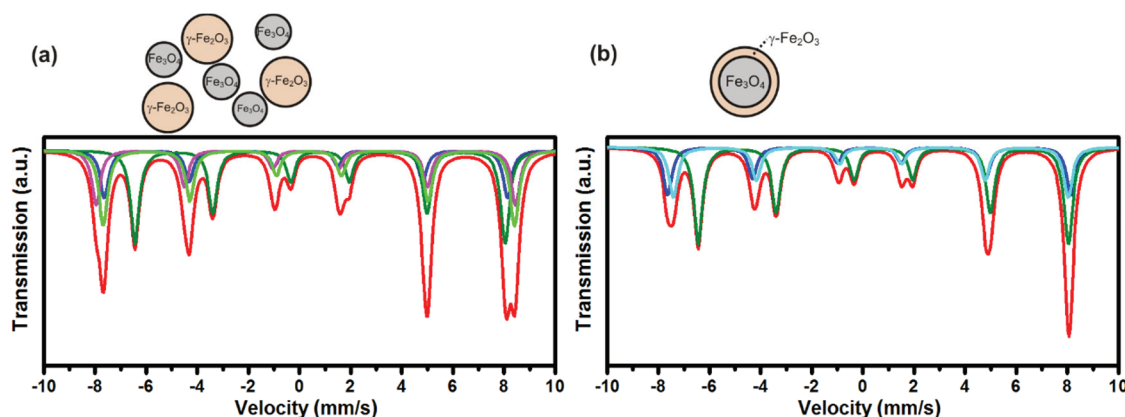**Figure 3** Theoretical ^{57}Fe Mössbauer spectra of (a) a 1/1 mixture $Fe_3O_4/ \gamma\text{-}Fe_2O_3$; (b) core-shell particles $Fe_3O_4/ \gamma\text{-}Fe_2O_3$ of 3/1 ratio, where the red lines correspond to the overall fit, the blue lines refer to the Fe^{3+} ions in A-sites, the dark green lines represent $Fe^{2.5+}$ in B-sites, the light green line refers to isolated Fe^{3+} in B-sites and the blue line represents the sum of Fe^{3+} in A- and B-sites.

Table 2 ^{57}Fe Mössbauer hyperfine parameters modelled for non-stoichiometric forms of $\gamma\text{-}Fe_2O_3$, Fe_3O_4, $\gamma\text{-}Fe_2O_3/ Fe_3O_4$ and of a core-shell $Fe_3O_4/\gamma\text{-}Fe_2O_3$ structure, where δ_{Fe} is the isomer shift, ΔE_Q is the quadrupole splitting, B_{hf} is the hyperfine magnetic field and RA is the relative spectral area. The isomer shift values are referred to metallic δ-Fe at room temperature.

phase	δ_{Fe} (mm/s)	ΔE_Q (mm/s)	B_{hf} (T)	RA (%)	Assignment
non-stoichiometric Fe_3O_4	0.25	0.00	50.0	35	Fe^{3+} A-site
	0.37	0.00	50.0	40	Fe^{3+} B-site
	0.50	0.00	47.2	25	$Fe^{2.5+}$ B-site
non-stoichiometric $\gamma\text{-}Fe_2O_3$	0.25	0.00	48.9	33.3	Fe^{3+} A-site
	0.65	0.00	45.7	66.7	Fe^{3+} B-site
$Fe_3O_4/\gamma\text{-}Fe_2O_3$ 1/1 mixture	0.25	0.00	49	17.5	Fe^{3+} A-site
	0.80	0.00	45	34.5	$Fe^{2.5+}$ B-site
	0.25	0.00	51	20	Fe^{3+} A-site
	0.37	0.00	50	28	Fe^{3+} B-site
$Fe_3O_4/\gamma\text{-}Fe_2O_3$ core-shell	0.25	0.00	49	25	Fe^{3+} A-site
	0.80	0.00	45	50	$Fe^{2.5+}$ B-site
	0.31	0.00	48	25	Fe^{3+} A-sites + B-sites

3. CONCLUSION

In the present contribution, we theoretically addressed the topic of distinguishing between non-stoichiometric forms of $\gamma\text{-}Fe_2O_3$, Fe_3O_4 and between $Fe_3O_4/\gamma\text{-}Fe_2O_3$ mixtures and core-shell assemblies by ^{57}Fe Mössbauer

spectroscopy. Some approaches to determine and quantify the degree of $Fe_{3-\delta}O_4$ stoichiometry have been proposed. Nevertheless, non-stoichiometric $Fe_{3-\delta}O_4$ materials can exist in a wide range of stoichiometry degrees δ varying from zero (Fe_3O_4) to 1/3 (γ-Fe_2O_3), when, in some cases, the procedures of stoichiometry determination, suggested in the literature so far, fail to some extent in terms of identifying the correct phase nature. In other words, here we highlight a peculiar situation frequently occurring in experimental samples, when the non-stoichiometry of the two iron oxide forms is in between or close to the middle δ value and it is hard to state if this phase carries the structural features of Fe_3O_4 or γ-Fe_2O_3. Therefore, it is an issue of further research to find the threshold value of stoichiometry degree δ (or x_m) between the two structures Fe_3O_4 and γ-Fe_2O_3. A possible solution is viewed in employing ^{57}Fe Mössbauer spectroscopy with an applied magnetic field, which would provide better resolution of individual spectral components and, hence, more precise determination of the stoichiometry parameter. Such information could then be related with data from XRD technique in terms of changing the lattice parameters values with vacancy ordering upon oxidation from Fe_3O_4 to γ-Fe_2O_3 as frequently observed in the literature [1].

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