

Mössbauer study of intermediate superparamagnetic relaxation of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles

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Abstract In the present work, we have synthesized and characterized magnetic nanoparticles of maghemite $\gamma\text{-Fe}_2\text{O}_3$ to study their structural and magnetic properties. For the preparation, magnetite precursor, were oxidized by adjusting the pH = 3.5 at about 80 °C in an acid medium, The mean size of the maghemite particles calculated from the X-ray diffractogram was around 5.7 nm. Mössbauer spectroscopy measurements at room temperature show their superparamagnetic behavior. Furthermore, Mössbauer measurements were carried out at 77 K and 4.2 K in order to find the typical hyperfine fields of the maghemite. Magnetite phase was not found. FC and ZFC magnetization curves measured at 500 Oe indicate a blocking temperature of 105.3 K. The magnetization measurements also show almost zero coercivity at RT.

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TEM images show nanoparticles with diameter smaller than 10 nm, which are in good agreement with the X-ray pattern and the fitting of the magnetization data.

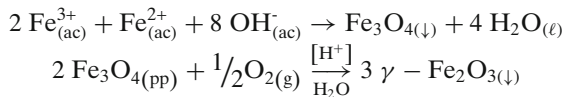
Keywords Nanomaghemite · Superparamagnetism · Blocking temperature · Mössbauer spectroscopy · ZFC · FC

1 Introduction

Currently magnetic materials at the nanoscale, such as γ -Fe₂O₃, have captured the attention of many researchers due to its important usefulness in different areas of the modern nanotechnology. Some applications are for instance, in ferrofluids, high density magnetic storage, high-frequency electronics, high performance permanent magnets, magnetic refrigerants, magnetic resonance imaging (MRI) contrast enhancement [1], biomagnetic separations, and hyperthermia treatment or magnetic drug targeting [2]. Moreover, maghemite nanoparticles are considered a significant field of investigation in medicine, since their surface can be modified (funcionalization), and they are easily controlled by an external magnetic field, so they can be driven inside blood vessels for cancer therapy [3]. In this work, we report the synthesis of γ -Fe₂O₃ nanoparticles less than 10 nm in size. Morphology and microstructure are discussed on the basis of TEM measurements, X-ray diffraction, and vibrational analysis. Besides, Magnetic studies are discussed with help of magnetic measurements and Mössbauer spectroscopy.

2 Experimental

Homogeneous maghemite nanoparticles were obtained by following the next reactions:



The synthesis of the magnetite (Fe₃O₄) nanoparticles was performed in aqueous solution without any surfactants. A stoichiometric mixture of Fe³⁺/Fe²⁺ in relation 2:1 from ferric chloride and ferrous chloride in a basic medium of pH = 11–12 was prepared. In addition, 0.85 mL of 12.1 N HCl and 25 mL of purified, deoxygenated water was added. Besides, 5.2 g of FeCl₃ and 2.0 g of FeCl₂ were dissolved in the solution with stirring. The resulting solution was dropped wise in 250 mL of 1.5 M NaOH solution under vigorous stirring. The last step generated a black precipitate (pH = 12). The paramagnetivity was checked in situ by placing a magnet near the black precipitate of the Fe₃O₄. The precipitate was isolated in the magnetic field, and the supernatant was removed from the precipitate by decantation.

Purified deoxygenated water was added to the precipitate and the solution decanted after centrifugation at 4,000 rpm. After repeating the last procedures three times, 500 mL of 0.01 M HCl solution was added to the precipitate with stirring in order to neutralize the anionic charges on the nanoparticles. Immediately, the oxidation of Fe₃O₄ into γ -Fe₂O₃ was carried out by adjusting the pH of Fe₃O₄ to a

pH of about 3.5 with hydrochloric acid for the moderate oxidation at about 80 °C for 30 min and with magnetic stirring with the objective to get the phase transition from magnetite to maghemite.

The sample was dried at about 40 °C with the aim of getting a reddish-brown powder [4].

The characterization was done by X-Ray Diffraction (XRD) in a Bruker D8 equipment and with the radiation $K_{\alpha 1}$ of copper ($\lambda = 1.54056 \text{ \AA}$) in the range from 8 to 80°, with a step of 0.02°, at room temperature (RT). The Mössbauer spectroscopy (MS) was performed with a conventional transmission Mössbauer spectrometer, operating with 1,024 channels and a Wissel INC. velocity module with a sinusoidal signal. The measurements were taken at room temperature (RT) and the obtained data were adjusted with the help of the program NORMOS [5]. In this program, the good fitting is controlled by the value of the χ^2 . The source employed was a ^{57}Co in rhodium matrix with strength 25 mCi. The Isomer shifts and the velocity scale were calibrated with respect to a $\alpha\text{-Fe}$ film at RT. The sample holder used has a diameter 1 cm and 26 mg mass which permitted to ascertain and quantify the small systematic effects of cosine smearing which usually occur in the folded Mössbauer spectra when relatively large collection solid angles are used. The data was collected at 77 K and 4.2 K the Mössbauer measurements at 4.2 K were taken in a bath cryostat in which both, the source and the absorber, are at 4.2 K. So there is virtually no SOD compared to measurements at room temperature.

Measurements of the magnetic moment vs. temperature were carried out in a DC MPMS-SQUID magnetometer in ZFC and FC modes, in a range of temperatures of 10 K to 290 K, with a magnetic field of 500 Oe. The magnetic hysteresis measurements were taken in a range of $-60,000$ Oe to $60,000$ Oe at the temperatures of 10 K and 290 K, respectively. For TEM measurements, we have used the Titan 80–300 kV microscope equipped with a special high-brightness Schottky-field emission electron source. The Raman spectrum was obtained using the Horiba LABRAM-HR equipment. The laser 532 nm Nd-Yag was used for excitation; it was calibrated with a line of Si in 521 cm^{-1} , and with a power on the sample of 0.5 mW.

3 Results and discussions

We have used Crystallographic Software to observe the mean peaks of diffraction, and we have indexed them with the PDF file 39–1346 with cubic symmetry (crystal space group $P4_132$), the average size of the nanocrystallites of $\gamma\text{-Fe}_2\text{O}_3$ was estimated from the wide of the diffraction peaks (Fig. 1) using Debye-Scherrer approximation: $d = \frac{k\lambda}{\beta \cos \theta}$, where λ is the wavelength ($\lambda = 1.54056 \text{ \AA}$) and θ is the Bragg angle. Assuming a spherical particle shape the particle diameter d is obtained by setting $K = 0.916$ when β is the full width at half maximum line breadth [6].

For the crystallographic plane (hkl) of the peaks in the XRD: we got grain sizes for (110)–4.2 nm, (220)–5.6 nm, (311)–5.88 nm, (400)–5.64 nm, (422)–6.41 nm, (511)–7.42 nm, (440)–6.71 nm and for (533) was 3.8 nm. The mean value of the grain size gives us a diameter of 5.7 nm.

The X-ray powder diffraction patterns show the presence of only one phase and widened peaks due to the nanometric size of the little crystallites.

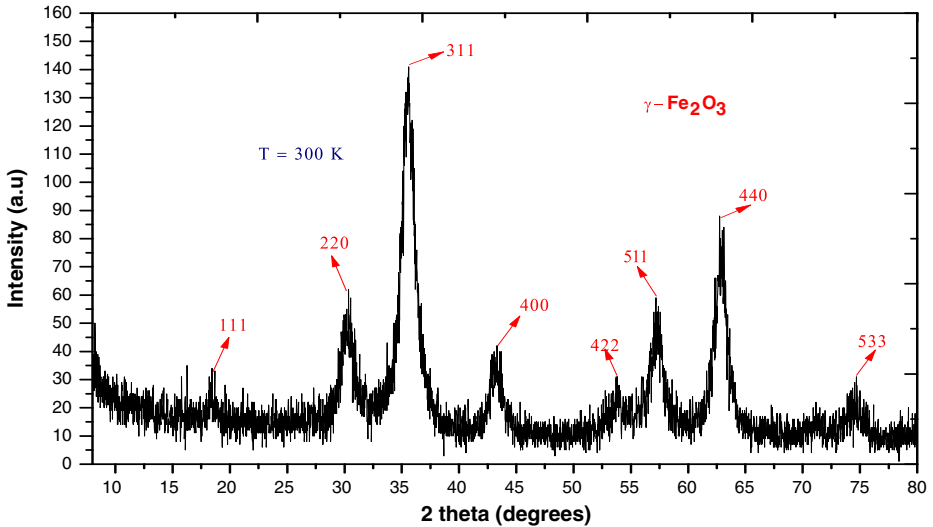


Fig. 1 X-ray powder diffraction pattern of maghemite nanoparticles

Recording that maghemite is a fully oxidized form of magnetite, has the structural formula $(\text{Fe}^{3+})_{\text{A}} \left[\text{Fe}_{5/3}^{3+} \right]_{\text{B}} \text{O}_4$ where represents again the vacancies on the octahedral sites. The corresponding Mössbauer spectrum consists of a somewhat broad-lined Fe^{3+} sextet, which is in fact composed of two non-resolved sextets from Fe^{3+} in tetrahedral and octahedral sites, respectively [7].

Figure 2 shows the MS at RT and 77 K of the nanometric $\gamma\text{-Fe}_2\text{O}_3$ (5.7 nm) sample and it reveals the intermediate superparamagnetic relaxation effect. At RT, the fitting was made using one distribution of hyperfine fields and one doublet representing the superparamagnetic particles. At 77 K, the spectrum was adjusted by using one distribution of the hyperfine fields of Fe^{3+} . It shows five peaks whose centers were calculated through five Gaussian curves obtaining 51.3, 48.6, 43.2, 23.4 and 17.1 T, respectively (see the right panel). In the Mössbauer spectra the blocking temperature (T_{B}) can be obtained when the area of the distribution is 50 %, of the superparamagnetic area [8, 9]. Thus, at 77 K the total area of the two principal peaks give 71.4 % assumed to maghemite without relaxation, and the remaining peaks give 28.6 %; then the T_{B} is nearly 100 K. This result is confirmed by the ZFC and FC measurement of the magnetization below. Since the initial sample consisted on magnetite and it was oxidized to obtain the maghemite, measurement at liquid helium were necessary to check if the entire sample was full oxidized. The Mössbauer spectrum of the sample obtained at 4.2 K is shown in Fig. 3. The spectrum is fitted with two magnetic fields of the characteristic maghemite, ie there was no magnetite component. Table 1 shows the Mössbauer hyperfine parameters obtained at RT, 77 K and 4.2 K.

Magnetic hysteresis loops with applied magnetic fields up to 60 kOe and at the temperatures of 10 K and 290 K (Fig. 4) reveal that the sample has superparamagnetic behavior, which is typical from nanosized magnetic particles. At nearly room temperature (290 K) which is well above the blocking temperature (T_{B}) the loop presents almost zero coercivity, which is caused by single magnetic domains. This

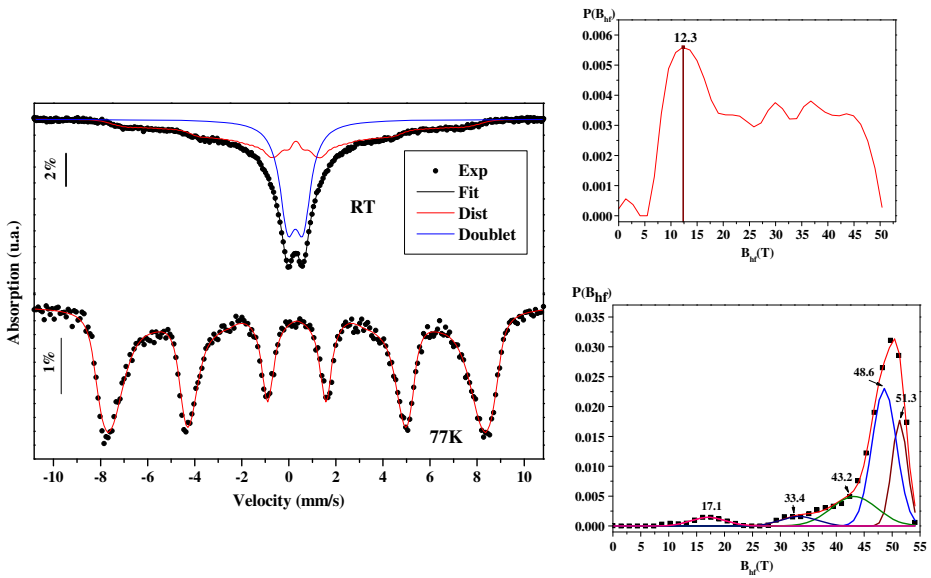


Fig. 2 Mössbauer spectra of maghemite nanoparticles at RT and 77 K. The hyperfine magnetic field distribution are on the right panel

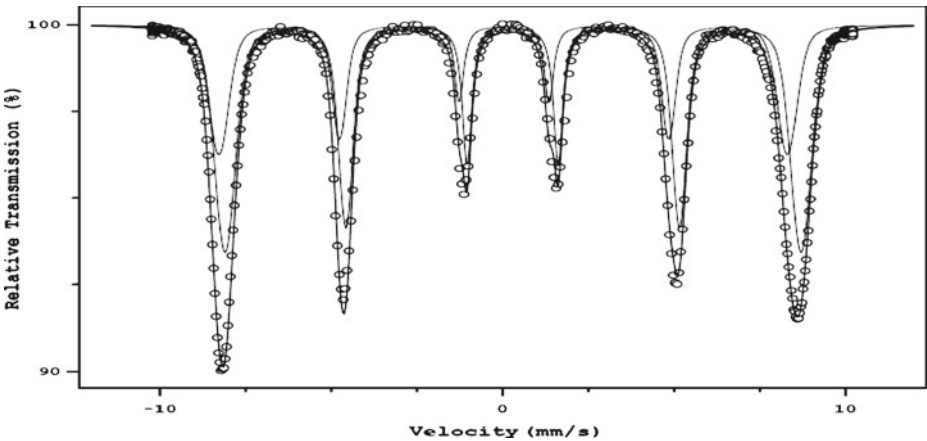


Fig. 3 MS at 4.2 K showing typical two magnetic fields of maghemite

kind of magnetic behavior means the loss of coercivity and remanence. The coercive field found at 10 K was 229 Oe indicating that the blocking temperature is much higher than this temperature.

The data obtained was fitted using the Langevin equation, $M(H) = M_S \left[\coth \left(\frac{M(R)\mu_0 H}{k_B T} \right) - k_B T / M(R)\mu_0 H \right] + \lambda \mu_0 H$, where $k_B = 1.38 \times 10^{-23}$ J/K, the measurement temperature $T = 290$ K. The integral nanoparticle moment is $M(R) = M_S V_{\text{mag}}$ where V_{mag} corresponds to the volume of the nanoparticle and M_S is the saturation magnetization, λ the excess susceptibility including a diamagnetic

Table 1 Mössbauer hyperfine parameters obtained at RT, 77 K and 4.2 K

Sites	Temp. (K)	δ (mm/s) \pm 0.03	ϵ, Δ (mm/s) \pm 0.02	B_{hf} (Tesla)(+)	Area (%) \pm 3
Fe ³⁺ distribution	RT	0.403	0.00	12.3	54.8
SP Doublet		0.397	0.71(*)		45.2
Fe ³⁺ Tetra (peak 1)	77	0.447	-0.002	48.6	48.1
Fe ³⁺ -Fe ²⁺ Oct (peak 2)		0.447	-0.002	51.3	23.3
Peak 3		0.477	-0.002	43.2	19.3
Peak 4		0.477	-0.002	33.4	5.0
Peak 5		0.447	-0.002	17.1	4.3
Fe ³⁺ (Tetra)	4.2	0.136	-0.014	51.4	35.4
Fe ³⁺ -Fe ²⁺ (Oct)		0.406	0.006	52.1	64.6

(*) Representing the superparamagnetic doublet

δ is the isomer shift relative to α -iron, ϵ and Δ are the quadrupole splitting and A is the spectral fraction as obtained from the fit

(+) B_{hf} is the most probable hyperfine field. SP Superparamagnetic

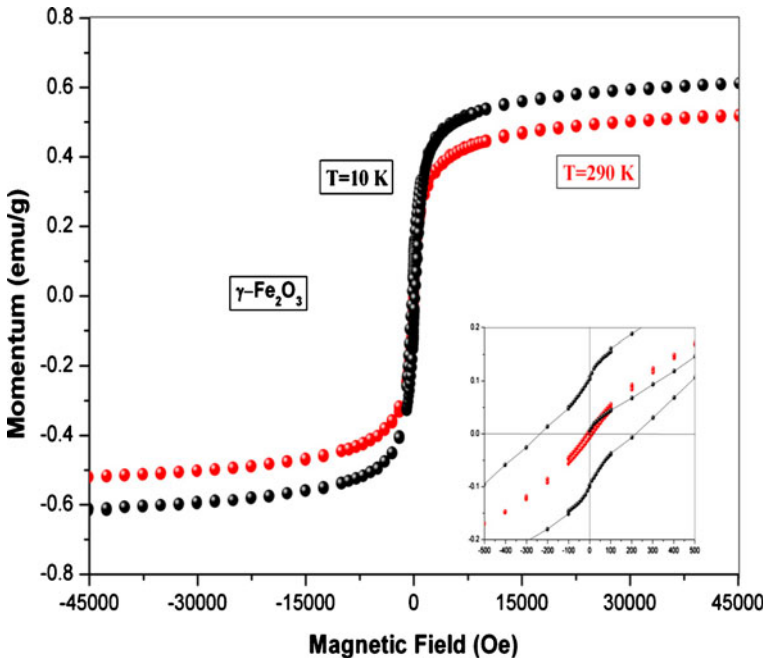


Fig. 4 Hysteresis loops of maghemite nanocrystallites with at 10 K and 290 K

contribution and $\mu_0 H$ the applied field with the permeability of the free space $\mu_0 = 4\pi \times 10^{-7} \text{ T}\cdot\text{m}/\text{A}$ [10]. From Fig. 5, the saturation magnetization is $M_s = 0.035 \text{ A}\cdot\text{m}^{-1}$. Three parameters with initial values of: $P1 = 0.035$, $P2 = 22.87$, $P3 = 0.0015$ were used reducing the Langevin equation into $y = P1 * (1/\tanh(P2*x) - 1/(P2*x)) + P3*x$, where $P1 = M_s$, $P2 = M_s V_{msg}/K_B T$, $\lambda = P3$ and $\chi = \mu_0 H$. Thus, the final

Fig. 5 Fit of the hysteresis loop at RT of maghemite nanoparticles with and applied field of 6 T at 290 K

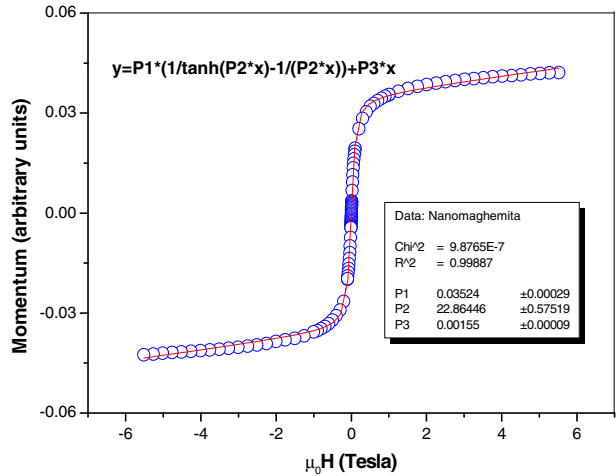
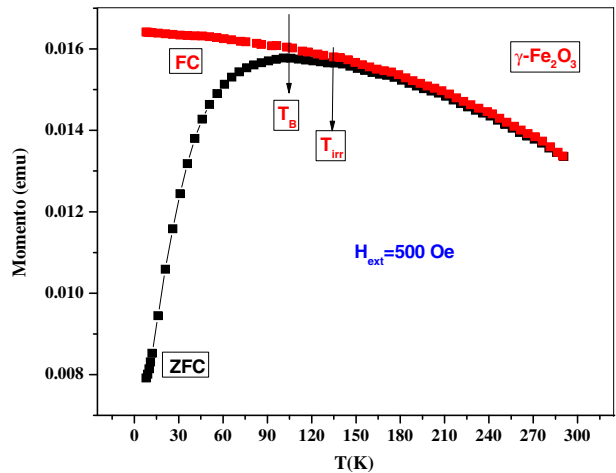


Fig. 6 Temperature dependence of the magnetic moment in the ZFC and FC cases with applied field $H = 500$ Oe for particles of 5.7 nm



values of the fitting parameters are: $P1 = 0.03524 \pm 0.00029$, $P2 = 22.86446 \pm 0.57519$, $P3 = 0.00155 \pm 0.00009$. The obtained V_{mag} is 261 nm^3 . Following the procedure of reference [11], assuming that all the particles are spherical without mutual interactions and taking into account that $V_{mag} = \pi D^3/6$, then the magnetic diameter is $D = 7.93 \text{ nm}$ which is closer to the size of the particle.

Figure 6 shows the zero-field-cooled (ZFC) and field cooled (FC) curves obtained by applying a magnetic field of 500 Oe showing a typical broad maximum in the ZFC curve of superparamagnetic particles. The blocking temperature (T_B) is defined as the temperature at which the ZFC curve exhibits a cusp, in our case T_B is 105.3 K [12]. Similar calculations of the blocking temperature are given for magnetic nanoparticles of maghemite in [13]. The FC curve shows irreversible behavior with respect to the ZFC curve until the temperature $T_{irr} = 135 \text{ K}$. When the T_{irr} is larger than T_m suggests the occurrence of moderate particle-particle interaction [14].

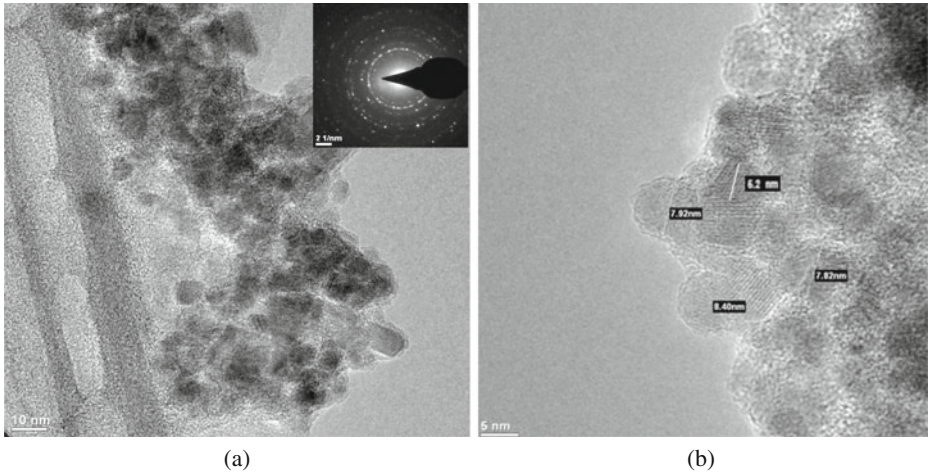


Fig. 7 **a** TEM image of γ -Fe₂O₃ nanoparticles with its respective electron diffraction pattern. Bar length of 10 nm. **b** TEM image of γ -Fe₂O₃ nanoparticles showing, different sizes of grain. Bar length of 5 nm

Fig. 8 Raman spectrum of maghemite nanoparticles

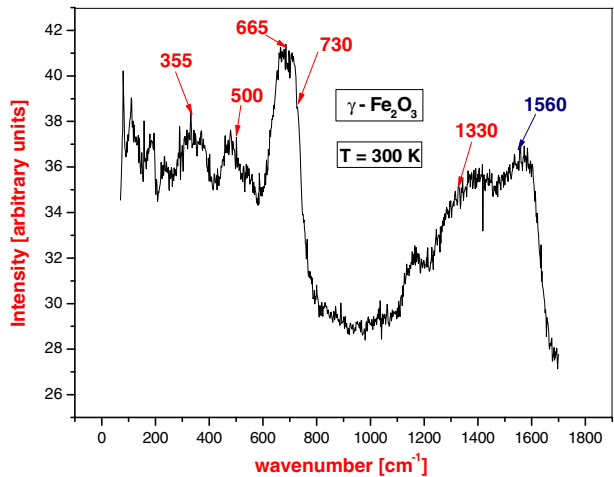


Figure 7a shows the distribution of γ -Fe₂O₃ nanoparticles. They are nearly spherical in shape, but without homogenous distribution. Our γ -Fe₂O₃ nanoparticles agglomerate. However, agglomeration could be prevented by using oleic acid [15, 16]. Figure 7b shows different diameters of γ -Fe₂O₃ nanoparticles, some highlighted are: 5.2 nm, 7.82, 7.92 and 8.4 nm. The mean grain size is 7.3 nm, which is closer to that obtained by the X-ray measurements above (5.7 nm)

The Raman spectrum (Fig. 8) of our synthetic maghemite nanoparticles was indexed taking the mean bands from the references [17, 18]. The phases are indexed by red arrows: 355, 500, 665, 730 and 1330 cm⁻¹, the last additional peak at 1,560 cm⁻¹ belongs to ferrihydrite [19–21].

4 Conclusions

Nanomagnetite with stoichiometric mixture $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the relation 2:1, Fe_3O_4 was oxidized to form maghemite nanoparticles of around 5.7 nm. The Mössbauer spectrum and the magnetic measurements indicate that the sample is superparamagnetic. Measurements of magnetic moment vs. temperature indicates blocking temperature of $T_B = 105.3$ K. At room temperature, it is difficult to identify whether the samples are magnetite or maghemite. However, the Mössbauer measurements at 77 K was fitted using hyperfine fields distribution and confirming the presence of two magnetic fields of maghemite (48.6 T for A site and 51.3 T for B site) and finally a 4.2 K the MS is well resolved with two magnetic fields sites. Despite the fact that TEM images show that the nanoparticles of $\gamma\text{-Fe}_2\text{O}_3$ are not well-dispersed, it reveals good crystallinity in agreement with the XRD.

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