

Structural and Mössbauer studies of nanocrystalline Mn²⁺-doped Fe₃O₄ particles

K. S. Al-Rashdi¹ · H. M. Widatallah¹ · F. Al Ma'Mari¹ · O. Cespedes² · M. Elzain¹ · A. Al-Rawas¹ · A. Gismelseed¹ · A. Yousif¹

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Abstract Nanocrystalline Mn^{2+} -doped magnetite (Fe₃O₄) particles of the composition $Mn_x Fe_{3-y}O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5; y = $\frac{2x}{3}$), prepared using chemical precipitation under reflux with the Mn^{2+} ions substituting for Fe^{3+} ions rather than Fe^{2+} ones, are characterized mainly with XRD and ⁵⁷Fe Mössbauer spectroscopy. All samples were found to have spinel-related structures with average lattice parameters that increase linearly with the Mn^{2+} concentration, x. The particle size for the samples varied from ~ 8 nm to 23 nm. The oxidation of Fe²⁺ to Fe³⁺ at surface layers of the Fe_3O_4 nanoparticles leading to the formation of maghemite $(\gamma - Fe_2O_3)$ was found to considerably weaken with increasing Mn²⁺ concentration. The percentage of the nanoparticles that exhibit short range magnetic ordering due to cationic clustering and/or superparamagnetism increases from 17% to 32% with increasing x. The dependence of isomer shifts of the 57 Fe nuclei at the tetrahedral and octahedral sites on dopant Mn²⁺ concentration is emphasized. The electric quadrupole shifts indicate that the $Mn_xFe_{3-y}O_4$ particles undergo Verwey transition. The effective hyperfine magnetic fields at both crystallographic sites decrease with increasing Mn^{2+} concentration reflecting a size effect as well as a weakening in the magnetic superexchange interaction. The Mössbauer data indicate that for $x \le 0.2$, the dopant Mn²⁺ ions substitute solely for octahedral Fe³⁺ ions whereas for x > 0.2 they substitute for Fe³⁺ at both tetrahedral and octahedral sites.

Keywords Magnetite \cdot Maghemite \cdot Doping \cdot Defects \cdot Nanocrystalline particles \cdot Mössbauer spectroscopy \cdot XRD

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H. M. Widatallah hishammw@squ.edu.om

¹ Physics Department, College of Science, Sultan Qaboos University, Al-Khoudh, Muscat 123, Oman

² School of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, UK

1 Introduction

Magnetite (Fe₃O₄) is one of the most extensively studied ferrites due to its interesting magnetic and other physical properties and related technological applications [1–7]. The material crystallizes in an inverse spinel-related FCC structure where the cationic distribution over the tetrahedral sites (A) and the octahedral sites (B) is represented by the formula $(Fe^{3+})^{A}[Fe^{2+}, Fe^{3+}]^{B}$ O₄ [2, 3, 8–11]. Around 119 K, referred to as the Verwey temperature (T_V), the material exhibits a transition from the high symmetric cubic structure to the lower symmetric monoclinic crystal structure due to ordering in cationic distribution over the octahedral sub-lattice [2, 12, 13].

Fe₃O₄ is ferrimagnetic, where the moments at the A- and B-sub-lattices are antiferromagneticlly coupled and the dominant contribution to magnetization comes from the B-sites Fe²⁺/Fe³⁺ ions [13]. Hence the magnetic and other properties of magnetite are sensitive to the presence of dopant impurities at both sites [5, 6]. In this perspective various investigations were devoted to changing the magnetic and electric properties of Fe₃O₄ to suit specific applications through the modification of the structure via doping with transition metal cations such V³⁺, Cr³⁺, Mn²⁺, Co²⁺, Ni²⁺, Ti⁴⁺, Sn⁴⁺ and Cu²⁺ [2, 6, 11–13].

When produced at the nanometer scale, magnetite nanoparticles exhibit a variety of novel magnetic properties relative to bulk Fe₃O₄, that are mainly governed by their large surface area-to-volume ratios and the size-dependent magnetic anisotropy [14, 15]. One drawback of producing Fe₃O₄ nanoparticles is the large surface area to volume ratio that enhances the oxidation of Fe²⁺ to Fe³⁺ resulting in the formation of non-stoichiometric magnetite which may be thought of as a single-phased solid solution of Fe₃O₄ and the iso-structural γ -Fe₂O₃ in which electron hopping takes place between the Fe²⁺ and Fe³⁺ at the B-sites [13, 16]. According to Topsøe et al for a given Fe²⁺/Fe³⁺ ratio the Mössabuer spectrum of non-stoichiometric magnetite and that of a mixture of γ -Fe₂O₃ and Fe₃O₄ phases in which the A-site Mössbauer sub-spectrum of Fe₃O₄ coincide with that of γ -Fe₂O₃ have the same tetrahedral-to-octahedral spectral area ratio [8]. This magnetite-to-maghemite transformation, whether in the form of a single-phased solid solution of γ -Fe₂O₃ and Fe₃O₄ or a mixture of both compounds, could pose a serious problem in certain application as both materials have different physical properties [15].

Many routes have been utilized for the synthesis of cation-doped nanocrystalline Fe₃O₄ particles including hydrothermal, precipitation, sol-gel, micro-emulsion, and thermal decomposition techniques [1-3, 5, 9]. In most studies that involved the introduction of divalent dopant ions in nanocrystalline Fe₃O₄, the intension has been the substitution of Fe²⁺ cations, rather than Fe^{3+} ones, leading to the compositional formula $M_xFe_{3-x}O_4$, where M^{2+} is the dopant divalent cation [11, 17]. Of particular importance to the present study are those in which the dopant Mn^{2+} cations were found to preferentially substitute for Fe²⁺ at low Mn^{2+} concentration and occupy both A- and B-sites at high Mn^{2+} concentration in $Mn_xFe_{3-x}O_4$ [6, 9, 11, 18–20]. It is of interest to study the influence of substituting Fe³⁺ cations in Fe₃O₄ with Mn²⁺ cations. This is because, unlike the substitutional Mn²⁺ impurities introduced when Fe^{2+} cations are substituted, charge balance necessitates an additional type of defects, namely interstitial Mn²⁺ impurities when Fe³⁺ cations are substituted. In the present study we use x-ray diffraction (XRD), transmission electron microscopy (TEM) and Mössbauer spectroscopy to structurally investigate nanocrystalline Mn²⁺-doped Fe₃O₄ particles prepared using the simple technique of precipitation under reflux where the Mn²⁺ cations substitute for Fe^{3+} rather than Fe^{2+} .



Fig. 1 The XRD patterns of the $Mn_x Fe_{3-y}O_4$ (y = 2/3 x) samples

2 Experimental

Samples of Mn²⁺-doped Fe₃O₄ with the composition Mn_xFe_{3-y}O₄ where (y = 2/3x) and (x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) were synthesized using the simple precipitation under reflux technique. Aqueous ammonia was added to aqueous mixtures of FeCl₃.6H₂O (Sigma; \geq 99%), FeCl₂.4H₂O (Fluka; \geq 99%), and MnCl₂.4H₂O (Sigma-Aldrich; \geq 99%) until a PH value of ~8.5 was obtained. The mixtures were boiled under reflux (5 h). The precipitates were removed by filtration, washed with distilled water and ethanol, and dried under a yellow light lamp. XRD data were obtained using an X'Pert PRO PANalytical diffractometer with CuK α radiation ($\lambda = 1.54056$ Å) in the 2 θ range of 20°–90° and steps of 0.014°. A JEM 2100F high resolution transmission electron microscope (HRTEM) operating at a voltage of 200 kV was used. Images were recorded using a digital camera. Mössbauer measurements were carried out at 298 K and 78 K using constant acceleration Mössbauer spectrometer with 25 mCi ⁵⁷Co/Rh source. Isomer shifts are quoted relative to the centroid of metallic iron at 298 K. The Recoil-Mössbauer Spectral Analysis Software for windows was used for quantitative evaluation of the Mössbauer spectra [21].

3 Results and Discussion

The XRD patterns recorded of the obtained $Mn_xFe_{3-y}O_4$ samples are shown in Fig. 1. The broad reflection peaks, that are typical of nanocrystalline compounds, confirm that



Fig. 2 The variation of the lattice parameter *a* with *x* for the Mn_xFe_{3-v}O₄ (y = 2/3 x) samples

all samples have a spinel-related cubic structure. The reflection peaks systematically shift toward smaller 2θ values as x increases indicating the progressive incorporation of the Mn²⁺ ions. The average lattice parameter of non-doped sample (a = 8.3438 Å) is lower than that reported for nano-magnetite (8.391 Å) [22]. While reduction in the average lattice parameter could imply higher strain or surface effects in the nanoparticles, it also may be indicative of the presence of a γ -Fe₂O₃ phase (lower lattice parameter a = 8.334 Å) that has developed due to surface oxidation of Fe^{2+} cations [23]. The determination of the percentage of this γ -Fe₂O₃ component could be quite intricate using the XRD as both compounds are iso-structural [24]. However as both compounds have distinct hyperfine parameters their relative amounts could be assessed using the Mössbauer technique. Figure 2 shows the average lattice parameter (a) to increase with the dopant content, x, in a linear fashion according to the Vegard's law [25]. This result reflects that the inserted larger Mn²⁺ cations, with tetrahedral ionic radius of (0.81 Å) and octahedral ionic radius of (0.80 Å) have replaced the smaller Fe³⁺ cation with corresponding ionic radii of (0.63 Å) and (0.69 Å) [26]. The actual cationic distribution over the tetrahedral (A) and octahedral (B) sites will be inferred from the 78 K Mössbauer spectra of the samples to be discussed shortly. The HRTEM images of the Mn_xFe_{3-v}O₄ compounds with x = 0.0 and x = 0.5 (Fig. 3) show them to be composed of nearly spherical and highly crystalline nanoparticles. The particle size for the sample with x = 0.0 was found to vary from ~ 8 nm to ~ 21 nm whereas that for x = 0.5 varied from ~ 10 nm to 23 nm. The ⁵⁷Fe Mössbauer spectra recorded at 298 K and 78 K from the $Mn_xFe_{3-v}O_4$ nanoparticles are shown in Figs. 4 and 5, respectively. The corresponding fitted values of the hyperfine parameters are given in Table 1. It is well documented that assuming site-independent Mössbauer recoilless fractions, the 298 K ⁵⁷Fe Mössbauer spectrum of stoichiometric bulk or nanocrystalline Fe₃O₄ could be resolved into two sextets due to Fe ions at the A- and B-sites with areas in the ratio of 1: 2, respectively [11, 13]. As for stoichiometric Fe₃O₄, the 298 K Mössbauer spectrum of the non-doped sample (x = 0.0) features two resolved six-line patterns. However, the difference between this spectrum and that of stoichiometric Fe_3O_4 [11, 13] is that in the present spectrum the inner six-line pattern is broader and the outer one is more intense (Fig. 4). Consequently, this spectrum was not amenable to satisfactory fitting using the above model used for stoichiometric Fe_3O_4 .

Fig. 3 TEM images of the $Mn_x Fe_{3-y}O_4$ samples with x = 0.0 (top) and x = 0.5 (bottom)





The best fit for this spectrum was attained using the model of Topsøe et al, described earlier [8], where three sextets, namely M, A and B(Table 1), with spectral area ratio of 0.22, 0.26 and 0.56, respectively, were used. The isomer shift values obtained in this fit are typical of Fe²⁺ and Fe³⁺ cations with high spin state [27].

The sextet M is attributed to the maghemite (γ -Fe₂O₃) phase which, as discussed earlier, develops due to fast oxidation of the Fe^{2+} cations at the nanoparticles' surface layers. Sextets A and B with relative spectral area ratio of exactly 1: 2 are associated with the Fe^{3+} cations at the A-sites and the ensemble of Fe^{2+} and Fe^{3+} ions at the B-sites in Fe_3O_4 respectively. These results agree with previous reports on magnetite nanoparticles with size <30 nm [8, 9, 11, 13]. At 78 K, which is below Verwey temperature (T_V), the Mössbauer spectral features for the Fe₃O₄ nanoparticles (x = 0.00) (Fig. 5) change considerably. The best fit was attained, following Dézsi et al, with six partially overlapping magnetic sextets (Table 1) [13]. The sextet M is attributed to the γ -Fe₂O₃ phase with similar spectral ratio to that found for the 298 K spectrum. The components A and B1, with isomer shifts typical of Fe³⁺ ions, were assigned to Fe³⁺ cations at the A-sites and B-sites respectively. Sextets B2, B3 and B4, with isomer shifts characteristic of Fe^{2+} ions, are attributed to Fe^{2+} cations at non-equivalent sites in the octahedral sub-lattice of the monoclinic crystal attained below T_V. These assignments which, within experimental error, lead to equal amounts of Fe^{3+} and Fe^{2+} at the B-sites of Fe_3O_4 , are in agreement with those published [13, 28]. The quadrupole shifts in the spectrum recorded at 298 K of the non-doped sample are almost zero implying an almost cubic structural symmetry. The higher quadrupole shifts obtained at 78 K for the B₃ and B₄ subspectra reflect the low monoclinic symmetry expected below the



Fig. 4 The ⁵⁷Fe Mössbauer spectra collected from the $Mn_x Fe_{3-y}O_4$ (y = 2/3 x) samples at 298 K



Fig. 5 The ⁵⁷Fe Mössbauer spectra collected from the $Mn_x Fe_{3-y}O_4$ (y = 2/3 x) samples at 78 K

Table 1	The ³⁷ Fe Mössbauer para	ameters for the $Mn_x Fe_{3-y} O_{x}$	$_{4}$ (<i>y</i> = 2 / 3 <i>x</i>) samples at 298 K	, and 78 K (between brackets	and in italics)	
x	Sub-spectrum	δ± 0.02 (mm/s)	$2\varepsilon/\Delta\pm$ 0.02 (mm/s)	$\Gamma\pm$ 0.02 (mm/s)	$H_{eff.}\pm$ 0.1 (T)	Area Ratio \pm 3 (%)
0.0	W	0.30 (0.45)	-0.10(-0.03)	0.60(0.48)	47.8 (51.2)	22 (22)
	A	0.35(0.43)	0.10(0.04)	0.50~(0.54)	47.9 (52.6)	26 (26)
	BI	0.49(0.43)	-0.03(-0.02)	0.60(0.48)	45.3 (50.4)	52 (26)
	B2	(0.53)	(-0.06)	(0.63)	(48.2)	(13)
	B3	(0.85)	(-0.06)	(0.90)	(46.0)	(8)
	B4	(1.50)	(0.71)	(0.56)	(41.1)	(5)
0.1	D	0.33	4.98	6.10		17
	Μ	0.17~(0.44)	-0.02(0.03)	0.45(0.43)	47.7 (51.1)	15 (19)
	Α	0.41 (0.46)	0.03 (0.00)	0.52~(0.50)	47.8 (52.5)	26 (31)
	BI	0.43 (0.40)	-0.02(-0.03)	0.66(0.51)	44.5 (50.7)	23 (24)
	B2	0.52(0.42)	0.00(-0.04)	(0.99 (0.47)	41.3 (48.7)	18(13)
	B3	(0.66)	(-0.24)	(1.14)	(43.0)	(6)
	B4	(1.43)	(1.10)	(0.73)	(41.0)	(4)
0.2	D	0.30	5.76	7.02		19
	Μ	0.17(0.43)	-0.05(-0.03)	0.49 (0.60)	47.1 (51.1)	13 (13)
	А	0.42 (0.44)	0.01 (0.05)	0.65(0.98)	47.5 (51.8)	28 (37)
	BI	0.42(0.40)	0.00(-0.03)	0.56~(0.47)	44.4 (49.8)	13 (20)
	B2	0.50~(0.45)	-0.03(-0.07)	0.93 (0.71)	41.0 (48.2)	26 (14)
	B3	(0.68)	(-0.23)	(0.84)	(42.2)	(11)
	B4	(1.40)	(0.80)	(0.82)	(40.7)	(5)
0.3	D	0.23	5.77	9.90		21
	Μ	0.17~(0.44)	-0.03(-0.04)	0.37~(0.44)	47.2 (51.1)	11 (11)
	А	0.43(0.43)	0.00 (0.02)	0.45(0.45)	47.4 (51.5)	18 (23)
	BI	0.40(0.39)	-0.01(-0.01)	0.80~(0.44)	44.1 (49.9)	30 (26)

Table 1	(continued)					
x	Sub-spectrum	δ± 0.02 (mm/s)	$2\varepsilon/\Delta\pm$ 0.02 (mm/s)	$\Gamma\pm$ 0.02 (mm/s)	$H_{eff.}\pm$ 0.1 (T)	Area Ratio \pm 3 (%)
	B2	0.49 (0.45)	-0.03 (-0.05)	1.08 (0.63)	40.6 (48.0)	21 (25)
	B3	(0.60)	(-0.32)	(I.44)	(41.7)	(10)
	B4	(1.43)	(1.00)	(0.55)	(40.6)	(5)
0.4	D	0.34	6.85	5.82		24
	Μ	0.17 (0.44)	-0.01(-0.16)	0.36(0.31)	47.0 (51.0)	8 (7)
	Α	0.43 (0.43)	0.02 (0.02)	0.43(0.35)	47.2 (51.4)	15 (22)
	BI	0.36 (0.39)	-0.01(0.02)	0.77~(0.40)	44.0 (49.7)	34 (28)
	B2	0.43 (0.43)	-0.02(-0.06)	0.93(0.57)	39.2 (47.5)	19 (29)
	B3	(0.46)	(-0.50)	(1.22)	(41.3)	(8)
	B4	(1.41)	(1.10)	(0.49)	(40.3)	(9)
0.5	D	0.25	6.60	8.26		32
	Μ	0.17 (0.44)	-0.04(0.19)	0.40(0.20)	46.7 (51.1)	6 (4)
	Α	0.40 (0.42)	0.01(-0.02)	0.42(0.19)	46.8 (51.3)	13 (21)
	BI	0.39 (0.38)	-0.02(-0.03)	0.76(0.31)	43.7 (49.8)	30 (30)
	B2	0.42(0.43)	-0.01(-0.06)	0.94(0.77)	39.1 (47.5)	19(38)
	B3	(1.37)	(0.88)	(0.79)	(40.9)	(4)
	B4	(0.42)	(-1.43)	(0.80)	(39.8)	(3)
$D: dou $ $\delta: isome$	blet; $M : \gamma$ -Fe ₂ O ₃ ; Ais the x shift, 2ε : quadrupole shift	a A-sub-lattice in Fe ₃ O ₄ ; <i>B1</i> , ft, Δ : quadrupole splitting, <i>I</i>	. B2, B3, B4 are the B-sub-lattic.	e of Fe ₃ O ₄ , and relative spectral areas		

Verwey transition [2, 12, 13]. The effective hyperfine magnetic fields obtained at both temperatures within experimental uncertainty are in agreement with those reported for γ -Fe₂O₃ and Fe₃O₄ nanoparticles [13, 16].

We now turn to the 298 K Mössbauer spectra of the $Mn_xFe_{3-y}O_4$ ($x \neq 0.0$) nanoparticles (Fig. 4). These spectra exhibit broad magnetic splitting patterns flanked on a very broad central doublet. The absorption lines, specifically those of inner part of the six-line pattern, gradually broaden with increasing x value. Each spectrum was fitted using a central broad doublet (*D*) and four magnetic sextets *viz. M*, *A*, *B1* and *B2* (Table 1). The central doublet whose contribution to the total spectral area increases from 17% at x = 0.1 to 32% at x = 0.5 disappears in the corresponding 78 K spectra (Fig. 5). This is clearly a manifestation of a superparamagnetic behavior by ~17% to ~32% of all the nanoparticles with blocking temperatures (T_B) given by 78 K <T_B< 298 K as x increases from 0.1 to 0.5. The sizes of these nanoparticles could be significantly less than the average size of the samples. It is also possible that the central doublet arises from local ionic environments within the nanoparticles where the magnetic Fe²⁺/Fe³⁺ions are coupled with neighboring dopant Mn²⁺ ions in a complex manner that weakens the magnetic anisotropy energy leading to random spin orientations at 298 K.

The first magnetic sextet M is, as before, ascribed to the γ -Fe₂O₃ phase resulting from the oxidation of the Fe^{2+} cations. The isomer shift of this sextet is lower than that obtained for the sample with x = 0.0 implying the possible incorporation of the Mn²⁺ ions in the resulting γ -Fe₂O₃ nanoparticles. The spectral area of the sextet M decreases gradually with increasing x from 22% (x = 0.0) to 4-6% (x = 0.5) suggesting that the progressive presence of the Mn^{2+} dopant ions suppresses the magnetite-to-maghemite phase transformation observed in Fe₃O₄ nanoparticles at ambient conditions [13, 16]. However, the actual mechanism whereby the Mn^{2+} dopant ions affect the oxidation process of the Fe²⁺ cations requires more investigation. Sextet A in all spectra is assigned to Fe^{3+} ions at the A-site whereas sextets B1 and B2 attributed to the Fe^{3+}/Fe^{2+} ions at the B-site of Fe_3O_4 . Generally, the 298 K isomer shifts of these three sextets decrease as x increases. This behavior could be related to gradual change in the electron density at the sites of the Fe nuclei due to the presence of increasing number of Mn²⁺ ions in their vicinities leading to covalency effects between the Fe^{3+}/Fe^{2+} ions and the attached ligands that reduce the isomer shift [29]. The quadrapole shifts of all spectra at 298 K are almost zero reflecting the high cubic symmetry of the spinel attained even in the presence of Mn^{2+} cations.

The values of hyperfine magnetic fields, H_{eff} , associated with⁵⁷Fe nuclei at the A-and B-sites decrease as the Mn²⁺ content (*x*) increases implying weakened Fe_A-O-Fe_A and Fe_A-O-Fe_B magnetic exchange interactions. Recalling that in these Mn_xFe_{3-y}O₄ (y = 2/3x) nanoparticles, more Mn²⁺ than the expelled Fe³⁺ were introduced and that both Mn²⁺ and Fe³⁺ have similar magnetic moments [30], one envisages a complex magnetic coupling between the Fe²⁺/Fe³⁺ ions and the impurity Mn²⁺ ions. Accordingly, the magnetic moments at both sites are not expected to remain strictly parallel to each other and spin canting could take place leading to the observed progressive weakening of H_{eff} with increasing x. A similar behavior was reported by Soresco et al for Mn_xFe_{3-x}O₄ where the Mn²⁺ substituted for Fe²⁺ rather than Fe³⁺ as in the present study [11].

The 78 K Mössbauer spectra of the $Mn_x Fe_{3-y}O_4$ ($x \neq 0.0$) nanoparticles (Fig. 5) and the corresponding hyperfine parameters Table 1 show similar trends to that of the sample with x = 0.0 discussed above. In particular, the Mössbauer spectral features, for all compositions ($x \neq 0.0$) (Fig. 5), changed considerably. Each spectrum was fitted, as before, with six magnetic components similar to those used for the sample with x = 0.0 due to Fe²⁺/Fe³⁺

occupying inequivalent lattice sites. This, in turn, implies that the Verwey transition has not been suppressed when the Fe₃O₄ nanoparticles were doped with Mn^{2+} ions. The values of the isomer shifts, quadrupole shifts and hyperfine magnetic fields, and the way in which they varied with increasing x are easily explicable using the reasoning given in the preceding discussion of the Mössbauer data. Finally, we note that the relative intensities (spectral areas) of the sextets in the Mössbauer spectra could be used to qualitatively trace up the cationic distribution assuming similar recoilless fractions for the Fe nuclei at the A- and Bsites. The results generally indicate that the Mn^{2+} cations substitute solely for octahedral Fe³⁺ cations for $x \le 0.2$. For higher x values the Mn^{2+} ions apparently occupy both sites. The Mössbauer technique, of course, cannot trace the interstitial sites occupied by the extra Mn^{2+} ions required to charge-balance the substituted Fe³⁺ cations.

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