Field-dependent Morin Transition and Temperature-Dependent Spin-flop in Synthetic Hematite Nanoparticles

Ihab M. Obaidat1,*, Sulaiman Alaabed2, Imad A. Al-Omari3, Venkatesha Narayanaswamy2, Bashar Issa4, and Abbas Khaleel5

1Department of Physics, United Arab Emirates University, Al-Ain 15551, UAE; 2Department of Geology, United Arab Emirates University, Al-Ain 15551, UAE; 3Department of Physics, College of Science, Sultan Qaboos University, P.O. Box 36, Muscat, PC 123, Oman; 4Department of Medical Diagnostic Imaging, College of Health Sciences, University of Sharjah, Sharjah, P.O. Box 27272, UAE; 5Department of Chemistry, United Arab Emirates University, Al-Ain 15551, UAE

Abstract: Background: In nano-size α-Fe2O3 particles, the Morin transition temperature was reported to be suppressed. This suppression of the $T_M$ in nano-size α-Fe2O3 was suggested to be due to high internal strain and to the enhanced role of surface spins because of the enhanced surface to volume ratio. It was reported that for nanoparticles of diameters less than 20 nm, no Morin transition was observed and the antiferromagnetic phase disappears. In addition, annealing of samples was reported to result in both an increase of $T_M$ and a sharper transition which were attributed to the reduction in defects, crystal growth, or both.

Objective: In this work, we investigated the role of applied magnetic field in $T_M$, the extent of the Morin transition, thermal hysteresis, and the spin-flop field in synthetic α-Fe2O3 nanoparticles of diameter around 20 nm.

Methods: Hematite nanoparticles were synthesized using the sol-gel method. Morphology and structural studies of the particles were done using TEM, and XRD, respectively. The XRD patterns confirm that the particles are hematite with a very small maghemite phase. The average size of the nanoparticles is estimated from both TEM images and XRD patterns to be around 20 nm. The magnetization versus temperature measurements were conducted upon heating from 5 K to 400 K and cooling down back to 5 K at several applied fields between 50 Oe and 500 Oe. Magnetization versus magnetic field measurements between -5 T and +5 T were conducted at several temperatures in the temperature range of 2-300 K.

Results: We report three significant findings in these hematite nanoparticles. Firstly, we report the occurrence of Morin transition in hematite nanoparticles of such size. Secondly, we report the slight field dependence of Morin transition temperature. Thirdly, we report the strong temperature dependence of the spin-flop. Zero-field-cooled magnetization versus temperature measurements were conducted at several applied magnetic fields.

Conclusion: From the magnetization versus temperature curves, Morin transition was observed to occur in all applied fields at Morin transition temperature, $T_M$ which is around 250 K with slight field dependence. From the magnetization versus magnetic field curves, spin-flop in the antiferromagnetic state was observed and found to be strongly temperature dependent. The results are discussed in terms of three components of the magnetic phase in our sample. These are the paramagnetic, soft ferromagnetic, and hard ferromagnetic components.

Keywords: Morin transition, soft ferromagnetic, ZFC, spin canting, exchange bias, nanoparticles.

1. INTRODUCTION

Metal oxides are involved in many fields of science and technology [1-3]. Iron oxides are an important part of metal oxides which also have many applications. Magnetic nanoparticles are iron oxide nanoparticles which have several magnetic phases. These nanoparticles have been extensively investigated for several potential applications [4-11]. One interesting iron oxide phase is hematite (α-Fe2O3) which is the most stable form of iron oxide. It is a common mineral in many natural samples that is found all over Earth. Both bulk
and nano-sized α-Fe₃O₃ were extensively studied [12-14]. α-Fe₂O₃ belongs to the antiferromagnetic class of magnetic materials where its two magnetic sublattices have equal and opposite (anti-parallel) magnetic moments. However, at temperatures above the Morin transition temperature, spin canting in the basal plane (perpendicular to the hexagonal c-axis) occurs making the spins not perfectly anti-parallel, leading to weak ferromagnetism.

At temperatures above 948 K (the Neel temperature, T_N) bulk α-Fe₂O₃ is paramagnetic. Above 260 K (and below 948 K) spin canting in the basal plane (perpendicular to the hexagonal c-axis) occurs making the spins not perfectly anti-parallel. Thus, bulk α-Fe₂O₃ in this temperature range is in a state called weakly ferromagnetic (WF) state which is an antiferromagnetic state (AF) but with slightly canted spins, resulting in a net magnetic moment. Below 260 K, the spins flip 90 degrees, where α-Fe₂O₃ becomes a pure AF. This magnetic transition from WF to AF is a first-order transition and is called the Morin transition and the temperature at which this transition occurs is called the Morin transition temperature, T_M (in bulk α-Fe₂O₃, T_M ≈ 260 K) [13, 14]. Morin transition is considered as one of the main diagnostic signatures of α-Fe₂O₃.

Studying magnetic properties and transitions of α-Fe₂O₃ is one of the methods generally used in palaeomagnetism where the record of the magnetic field of Earth is investigated in rocks, sediments, or archaeological materials. Natural α-Fe₂O₃ samples at high elevations, where the temperatures are around the T_M, may cycle many times through the Morin transition. Hence, for paleomagnetic interpretations it is essential to understand the changes of the magnetic properties of α-Fe₂O₃ around this temperature.

Because of its interesting electronic, catalytic and magnetic properties, α-Fe₂O₃ can be involved in several applications [15]. Nanoscale α-Fe₂O₃ has shown potential in a variety of fields, such as its photoelectrical properties [16-18]. Understanding the magnetism of α-Fe₂O₃ nanoparticles is expected to lead to an improved understanding of the material along with enhancing the α-Fe₂O₃ potential of applications. Nano-size α-Fe₂O₃ has been studied using several magnetic techniques such as the inelastic neutron diffraction where magnetic anisotropy constants were obtained and Morin transition was investigated [19-22].

The occurrence of Morin transition was attributed to the change of magnetocrystalline anisotropy as the temperature of the α-Fe₂O₃ is changed across T_M [13]. There are several factors that might determine the Morin transition in bulk α-Fe₂O₃ such as the grain size, cation substitution [23], lattice defects, pressure [24], and applied magnetic field [25]. For pure, stoichiometric α-Fe₂O₃ at 1 atm, the Morin transition temperature, T_M = 262K.

In nano-size α-Fe₂O₃ samples, Morin transition temperature was reported to be suppressed. This suppression of the T_M in nano-size α-Fe₂O₃ was suggested to be due to high internal strain [26] and to the enhanced role of surface spins because of the enhanced surface to volume ratio [25, 27, 28]. It was reported that for nanoparticles of diameters less than 20 nm, no Morin transition was observed and the antiferromagnetic phase disappeared [29, 30]. In addition, annealing of samples was reported to result in both an increase of T_M and a sharper transition which were attributed to a reduction in defects, crystal growth, or both [31].

In this work, we investigated the role of applied magnetic field on T_M, the extent of the Morin transition, thermal hysteresis, and the spin-flop field in synthetic α-Fe₂O₃ nanoparticles of diameter around 20 nm.

2. MATERIALS AND METHODS

2.1. Synthesis

Iron(III) oxide was prepared from iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O) dissolved in 2-propanol and propylene oxide was used as a condensation and gelation promoter. In a typical experiment, 10.7 g (26.4 mmol) of the precursor was dissolved in 100 ml 2-propanol and 25 mL (0.36 mol) propylene oxide was then added under continuous stirring. The mixture was stirred for 4 hours giving a redish-brown colloidal suspension and it was aged for an additional 24 followed by solvent removal by evaporation in a water bath at a temperature around 80°C. The obtained brown solid was washed with distilled water before drying at 120°C for one hour followed by calcination at 350°C and 500°C for 1 and 4 hours, respectively.

2.2. Structure and Morphology Characterization

The structure and morphology of the samples was characterized using the X-ray diffraction (XRD), and transmission electron microscopy (TEM). XRD characterization was performed on a Shimadzu-6100 powder XRD diffractometer with Cu-Kα radiation, λ = 1.542 Å. Diffraction data was collected in the 2θ range of 20-80 deg. at the rate of 1 deg./min. TEM images were obtained using a CM10 Philips electron microscope. The histograms extracted from the TEM images show the size distributions. The average sizes from the TEM are compared with the average sizes obtained from the XRD images using the Scherrer’s formula [32];

\[ D_p = \frac{0.94λ}{β \cos θ} \]

where \( D_p \) is the average crystallite size, \( λ \) is the X-ray wavelength, \( β \) is the full width at half maximum (FWHM) of the XRD line, and \( θ \) is the Bragg’s angle.

2.3. Magnetic Measurements

The dc magnetic measurements were carried out using a VSM in a Physical Properties Measurement System (PPMS) from Quantum Design. The zero-field cooled (ZFC) and field cooled (FC) temperature dependence of magnetization (M-T) measurements were carried out at several applied magnetic fields. ZFC field-dependence magnetization (M-H) measurements were conducted at several temperatures (5, 20, 50, 70, 100, 150, 200, 240, 250, 260, 270, 280, and 300 K) in the field range of -5T to +5T. In the ZFC M-T protocol, the temperature of the sample was cooled down from room temperature to the lowest temperature 2 K (or 4 K) in the absence of any applied magnetic field. After that, a small magnetic field (up to 500 Oe) was applied and the magnetic moment was measured as the temperature is increased up to 300 K. After that, the temperature was lowered down to 2 K (while the field is still applied) and the magnetic moment...
was recorded during this temperature decrease. This is called FC M-T protocol. In the ZFC M-H protocol, the temperature of the sample was cooled down from room temperature to a particular temperature in the absence of any applied magnetic field. After that, a magnetic field was applied and the magnetic moment was measured as the field increased from -5 T to +5 T.

3. RESULTS AND DISCUSSION

An XRD profile obtained from the α-Fe₂O₃ nanoparticles is shown in Fig. (1). It consists of the peaks corresponding to α-Fe₂O₃ and maghemite (γ-Fe₂O₃) phases, indicating the formation of mixed phases but the low intensity ratio of the γ-Fe₂O₃ peaks shows that the significant phase fraction is α-Fe₂O₃. The unit cell parameters were determined by using POWDER-CELL, the lattice dimensions are a = 5.0339 Å and c = 13.7866 Å with cell volume of 302.5545 (Å³). The calculated cell parameters have a close match with the reported values of bulk α-Fe₂O₃ in the literature. The average crystallite size of the nanoparticles is obtained by using FWHM of the highest intensity peak (110) corresponding to the α-Fe₂O₃ phase. Bright field TEM image of the nanoparticle is shown in Fig. (2). The nanoparticles possess somewhat distorted spherical shape and have large size distribution. From the XRD patterns, the average diameter of the nanoparticles is estimated to be around 20 nm. Although the sample has considerable size distribution with some nonspherical shapes, the average size estimated from several TEM images is roughly 20 nm. However, this TEM estimation can be considered good enough since it matches with the XRD calculations where the number of particles involved in the XRD measurement is very large.

![Fig. (1). X-ray diffraction pattern of α-Fe₂O₃ nanoparticles.](image)

ZFC and FC magnetization curves as a function of temperature at applied magnetic fields 100, 200, 350, and 500 Oe are shown in Fig. (3). Typical magnetization curves were also obtained at 50, and 150 Oe (not shown). The measurement consists of a zero-field cooling and warming of the nanoparticle while measuring the magnetisation. This curve is obtained after applying various magnetic fields starting the cyclic measurement from temperature 400 K, on cooling from 400 to 5 K and then back to 400 K. At all applied fields, the magnetization in the antiferromagnetic state is nearly constant (not zero) at temperatures below 200 K. As can be seen in Fig. (3), Morin transition is observed to occur at the Morin transition temperature, $T_M$. $T_M$ at a particular applied field was obtained as the maximum of the first order derivative $dM/dT$ of the heating curve. $T_M$ was found to slightly change between 248 K and 250 K depending on the applied field. The transition was not sharp and occurs in a large temperature range. The nonzero magnetization observed in the AF state can be attributed to the existence of a slight γ-Fe₂O₃ phase and to the surface spin effects which become significant at small particle sizes such as in our nanoparticles.

![Fig. (2). TEM bright field images of α-Fe₂O₃ nanoparticles illustrating the characteristic particle morphologies. (A higher resolution / colour version of this figure is available in the electronic copy of the article).](image)

The ratio of magnetisation value of the AF and WF portions in the sample is denoted as $n$. This ratio is obtained from the M-T curves at each particular applied field. The AF/WF fraction $n$ is plotted as a function of the applied magnetic field and is shown in Fig. (4a). As can be seen in this figure, $n$ has a nonmonotonic behaviour with the applied field. Below 200 Oe, $n$ increases slowly and almost linearly with the field. Above 200 Oe, $n$ decreases strongly and linearly with increasing the field. In addition, $n$ values are large compared with other reports on much larger nanoparticles [33-35]. The reason for this could be because of the enhanced role of surface spins and due to the existence of the slight γ-Fe₂O₃ phase in our sample.

The antiferromagnetic temperature, $T_{AF}$ is defined as the temperature at which heating and cooling trends of magnetisation start deviating from the overlap. The variation of $T_{AF}$ with the applied magnetic field is shown in Fig. (4b). A strong decrease of $T_{AF}$ is observed in this figure at field below 100 Oe and above 200 Oe. A very slight decrease of $T_{AF}$ is observed between 100 and 200 Oe. $T_{AF}$ is found to vanish above 350 Oe where the magnetization curves clearly
Fig. (3). ZFC and FC magnetization curves of α-Fe₂O₃ nanoparticles (a) at 100 Oe, (b) 200 Oe, (c) 350 Oe, and (d) 500 Oe. *(A higher resolution / colour version of this figure is available in the electronic copy of the article).*

Fig. (4). (a) Antiferromagnetic/ferromagnetic fraction, $n$ versus the applied magnetic field, and (b) $T_{AF}$ versus the applied magnetic field.
separate from each other. The non-vanishing magnetization below $T_{AF}$ is attributed to the existence of a very small $\gamma$-Fe$_2$O$_3$ phase.

The first derivative of magnetization with respect to temperature ($dM/dT$) is shown in Fig. (5a). The Morin transition temperature $T_M$ was obtained as the maximum of the first-order derivative $dM/dT$ of the heating curve. From Fig. (5a), we can see that Morin transition does not occur sharply but comprises a wide range of temperatures starting at $T_i$ and ending at $T_f$. Below $T_i$, the material is in a non-pure antiferromagnetic state with a small (nonzero) magnetization due to the existence of the $\gamma$-Fe$_2$O$_3$ phase and the surface spin effects (as mentioned earlier). Thermal hysteresis, $\Delta T_M$ which is the difference in $T_M$ obtained from the heating and cooling branches, is found to be around 15 K which can be considered as a large value. For the perfect single crystals without any defects, $\Delta T_M$ should be close to zero [33]. The high value of $\Delta T_M$ in our sample can be attributed to the surface spin canting and other surface effects of the nano-sized particles. The effects of the applied magnetic field on the Morin transition temperature, $T_M$ and on the thermal hysteresis $\Delta T_M$ are shown in Fig. (5b). As can be seen in this figure, both $T_M$ and $\Delta T_M$ display very small changes with the applied field. The $T_M$ values (between 248 and 250 K) are in good agreement with several reports on small particles [33, 34] but lower than the bulk value of 265 K. The extent of the transition, $\Delta T_h = T_f - T_i$ was found to vary from 43 K to 83 K. The dependency of $\Delta T_h$ on the applied magnetic field is shown in Fig. (5c). It is clearly seen in this figure that $\Delta T_h$ increases with the increase of the applied magnetic field. This large range in the extent of transition, $\Delta T_h$ can be attributed to the large size distribution of our nanoparticles, which is evident from the TEM image of our $\alpha$-Fe$_2$O$_3$ nanoparticles.

Magnetic nanoparticles were cooled under zero-field cooled state and magnetization at several temperatures (between 2-200 K) was measured as a function of the applied magnetic field. The branches of M-H curves where the field was increasing are shown in Fig. (6a). Magnetization measured can be attributed to the contributions of paramagnetic background, soft ferromagnetic, and hard ferromagnetic components [33]. We can see that all M-H plots (at all temperatures) are similar and exhibit a paramagnetic behavior. There is a slight change in the slope of M-H curves as the field increases. The field at which the slope of the M-H

![Fig. (5).](image-url) (a) $dM/dT$ plot, whose maximum is at Morin transition temperature, $T_M$. Temperatures $T_i = 210$ K and $T_f = 275$ K, the initial and final temperatures of the transition, respectively, are shown with dotted lines and arrows. (b) $T_M$ and $\Delta T_M$ versus the applied magnetic field. (c) $\Delta T_h$ versus the applied magnetic field. (A higher resolution / colour version of this figure is available in the electronic copy of the article).
curve starts changing is termed as the spin flop field, $H_{sf}$. It is evident that $H_{sf}$ is temperature-dependent as can be seen in Fig. (6c). The differential plots of the M-H curve are calculated to determine the magnetic susceptibility, $\chi$ and these are shown in Fig. (6b). From the ZFC M-H curves (Fig. 6a), it is clear that the spin-flop in the antiferromagnetic state ($T < 200$ K) exists and the field at which it occurs, $H_{sf}$ is strongly temperature-dependent (Fig. 6c) with values between 700 Oe to 20200 Oe. From Fig. (6b), we can see that the magnetic susceptibility at all temperatures in the antiferromagnetic region ($T < 200$ K) shows a narrow soft ferromagnetic behaviour (a sharp peak) and a wide and nearly flat paramagnetic region. The filed at which the peak in the differential $dM/dH$ occurs is termed the soft magnetic field, $H_{soft}$. $H_{soft}$ dependency in the temperature range of 2-200 K is shown in Fig. (7). The soft ferromagnetic contribution is noticed as a peak in $\chi$ centered at -150 Oe ($H_{soft}$) at $T = 2$ K, and then shifts further on the negative field with increasing temperature and becomes almost constant around -1000 Oe at temperatures above 100 K. As can be seen in Fig. (7), $H_{soft}$ is strongly temperature dependent at $T < 100$ K and nearly constant at (100 K $< T < 200$ K). The soft ferromagnetic contribution is attributed to surface spin canting. The paramagnetic phase has very small and temperature-independent susceptibility.

Fig. (6). (a) Magnetisation versus the applied magnetic field at $T = 2, 30, 50, 70, 100, 150$, and 200 K, and (b) the magnetic susceptibility, $\chi$ at $T = 2, 30, 50, 70, 100, 150$, and 200 K. (c) The spin flop field, $H_{sf}$ as function of temperature. (A higher resolution / colour version of this figure is available in the electronic copy of the article).
M-H plots under zero-field-cooled condition in the temperature range of 240-300 K are shown in Fig. (8a). Similar to the temperature range of 2-200 K, the M-H plots in the temperature range of 240-300 K indicate that α-Fe₂O₃ nanoparticles magnetization has a contribution from paramagnetic background and soft ferromagnetic component. In order to obtain the magnetic susceptibility values, first-order differential plots of M-H curve were calculated and shown in Fig. (8b). It is observed that in this temperature range (240 K < T < 300 K), in addition to the paramagnetic background and the soft ferromagnetic peak, another (hard) peak in the magnetic susceptibility occurs at large fields, $H_{\text{hard}}$ at all temperatures [33]. The hard peak is attributed to the spin flop of the antiferromagnetic phase around the Morin transition temperature.

The differential plots of M-H curve are calculated to determine the susceptibility in the temperature range 240-300 K. The field at which the sharp peak in the differential $dM/dH$ occurs is the soft magnetic field, $H_{\text{soft}}$. This is similar to the situation in the temperature range of 2-200 K but $H_{\text{soft}}$ switched to the positive field values. The field at which the wide peak in the differential $dM/dH$ occurs is the hard magnetic field, $H_{\text{hard}}$. $H_{\text{soft}}$ and $H_{\text{hard}}$ dependency on the temperature in the temperature range of 240-300 K is shown in Fig. (9). As can be seen in this figure, both $H_{\text{soft}}$ and $H_{\text{hard}}$ have a similar and nonmonotonic temperature dependent behaviour but with much larger values of $H_{\text{hard}}$.

The main magnetic components in the temperature range of 2-200 K are the soft ferromagnetic (SF) and paramagnetic (PM) components. In addition to these components, a hard ferromagnetic (HF) component exists in the temperature range of 240-300 K. The magnitude of the magnetic susceptibility, $\chi$ obtained from the deferential plots of M-H represents these three contributions and are shown in Fig. (10). As can be seen in Fig. (10a and b), $\chi$ in the PM background is nearly temperature independent with constant susceptibility, $\chi = 1.2 \times 10^{-5}$ emu/g Oe in the temperature range of 2-200 K and $2 \times 10^{-5}$ emu/g Oe in the temperature range of 240-300 K. We can also see that in Fig. (10a and b), $\chi$ of SF component has a nonmonotonic behavior with temperature in the whole temperature range of 2-300 K. However, the magnitude of $\chi$ of SF component is roughly around $10 \times 10^{-5}$ emu/g Oe at all temperatures except at 30 and 200 K where the values are larger. Fig. (10b) shows that $\chi$ of HF component (in the temperature range of 240-300 K) has a weak temperature dependence with an average value of nearly $2 \times 10^{-5}$ emu/g Oe.

**CONCLUSION**

Sol-gel method was used for the synthesis α-Fe₂O₃ nanoparticles of an average size of 20 nm and with a slight γ-Fe₂O₃ phase. Morin transition was observed at around 250 K with slight field dependence. The extent of the transition was observed and attributed to the considerable size distribution.
in our nanoparticles. The observed nonzero magnetization in the antiferromagnetic state was attributed to the γ-Fe₂O₃ phase and to the surface spin effects. The observed large thermal hysteresis was attributed mainly to the surface spin canting. Spin-flop in the antiferromagnetic state was found to be strongly temperature dependent with spin-flop field values between 700 Oe and 20200 Oe. In the antiferromagnetic region, soft ferromagnetic and paramagnetic behaviours were observed. The soft ferromagnetic was attributed to surface spin canting and the ferromagnetic contribution of the small γ-Fe₂O₃ phase. The paramagnetic region is very small, wide and nearly flat. In the transition region (240 K < T < 300 K), in addition to these two behaviours, a hard peak in the magnetic susceptibility was observed to occur in large fields. The hard peak was attributed to the spin flop in the antiferromagnetic phase.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE
Not applicable.

HUMAN AND ANIMAL RIGHTS
No Animals/Humans were used for studies that are the basis of this research.

CONSENT FOR PUBLICATION
Not applicable.

AVAILABILITY OF DATA AND MATERIALS
Not applicable.

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CONFLICT OF INTEREST
The authors declare no conflict of interest, financial or otherwise.

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Fig. (10). χ (Soft ferromagnetic and Paramagnetic) versus temperature (a) in the temperature range of 2-200 K and (b) in the temperature range of 240-300 K. (A higher resolution / colour version of this figure is available in the electronic copy of the article).
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