SPIN CANTING OF $\gamma$-Fe$_2$O$_3$ NANOPARTICLES AND ITS EVALUATION EMPLOYING A
STATISTICAL APPROACH

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Abstract

Nanosized $\gamma$-Fe$_2$O$_3$ is one of the most remarkable iron(III) oxide polymorph with extensive applications in practice. However, its exploitation in nanosized form is limited by presence of parasitic magnetic phenomena emerging if the size of $\gamma$-Fe$_2$O$_3$ nanoobjects falls below a certain threshold value. One of them is a spin canting negatively reflecting in a capability of these nanoobjects to be easily controlled by an external magnetic field. Knowledge of all parameters affecting spin canting may shed light into understanding of this parasitic phenomenon, thus enabling its prevention. For a study of spin canting, in-field $^{57}$Fe Mössbauer spectroscopy is widely recognized as the most powerful experimental tool allowing qualitative and quantitative determination of the degree of this phenomenon. In this work, we study the parameters having an impact on spin canting phenomenon occurring in the two $\gamma$-Fe$_2$O$_3$ nanoparticle systems exhibiting different average particle size and particle size distribution. It turns out that the spin canting phenomenon significantly depends on the temperature and its thermal evolution is influenced by average particle size and particle size distribution of a $\gamma$-Fe$_2$O$_3$ nanoparticle assembly. For smaller nanoparticles, diminishing of spin canting is assisted by collective magnetic excitations. Moreover, we propose a statistically-based procedure testing the nature and site-occurrence of spin canting phenomenon in the studied $\gamma$-Fe$_2$O$_3$ nanoparticle systems. The presented approach, combining physical and statistical methods, could bring a more sophisticated picture of spin canting phenomenon in all magnetic nanosystems.

Keywords: Gamma-Fe$_2$O$_3$, maghemite, spin-canting, in-field $^{57}$Fe Mössbauer spectroscopy, regression models.

1. INTRODUCTION

Nanomaterials are interesting for their physico-chemical properties that are diametrically distinct from those exhibited by their bulk counterparts [1]. Among these nanomaterial’s properties, magnetic characteristics significantly attract the attention of the scientific community due to a variety of practical fields where magnetic nanomaterials can be exploited. Formally primarily used in areas of magnetic recording and storage of information (i.e., magnetic pigments in recording media), some of these magnetic nanomaterials have been found effective in medicine improving diagnostic procedures (e.g., contrast agents in nuclear magnetic resonance) and/or giving rise to new treatment methods (e.g., labeling and magnetic separation of cells, targeted drug delivery, magnetic-field assisted hyperthermia, etc.) [2, 3]. Beside this, they have been used as modeling systems for theoretical studies explaining significant magnetic phenomena occurring in “nanoworld” (e.g., superparamagnetism, quantum tunneling of magnetization, etc.) [4].

Iron oxides, especially Fe$_3$O$_4$ and Fe$_2$O$_4$ (magnetite), belong to the most remarkable magnetic nanomaterials [5]. Beside their application-promising magnetic properties such as superparamagnetism, they are notable for their appealing biochemical properties, mainly nontoxicity, biodegradability, and biocompatibility [5]. This classifies them as one of leading agents in the fields of medicine where utilization of external magnetic field is highly required for diagnostic and/or treatment purposes. We distinguish 4 structural forms of crystalline iron(III) oxide [5]: (i) $\alpha$-Fe$_2$O$_3$ (i.e., hematite); (ii) $\beta$-Fe$_2$O$_3$; (iii) $\gamma$-Fe$_2$O$_3$ (i.e., maghemite); and (iv) $\epsilon$-Fe$_2$O$_3$. 
They all have the same chemical properties, however, their physical properties markedly differ. For practical purposes, nanosized $\gamma$-Fe$_2$O$_3$ is the most application-suitable Fe$_2$O$_3$ polymorph as it can be used in all above-mentioned fields. However, its exploitation in nanosized form is limited by presence of parasitic magnetic phenomena emerging if the size of $\gamma$-Fe$_2$O$_3$ nanoobjects falls below a certain threshold value [6].

A spin canting is one of these parasitic phenomena; it negatively reflects in a capability of nanoobjects to be easily controlled by an external magnetic field [4, 6]. It is governed by finite size effects (presence of defects or vacancy in the crystal structure) and surface effects (increasing number of atoms present in the surface layers on decreasing the nanoparticle size). The spin canting has a static and dynamic character and causes, along with other factors, unsaturated values of magnetization in relatively low applied magnetic fields. For a study of spin canting, in-field Mössbauer spectroscopy is widely recognized as the most powerful experimental tool as it allows to qualitatively and quantitatively determine the degree of this phenomenon [4, 6]. From the intensity of the 2nd and the 5th spectral lines, it is possible to derive an angle reflecting a degree of spin canting.

In this work, we study parameters influencing spin canting, particularly average size of nanoparticles in their assembly and temperature. To do so, we used two samples made up of $\gamma$-Fe$_2$O$_3$ nanoparticles with different average particle size and particle size distribution. In order to shed light into the occurrence and nature of spin canting in $\gamma$-Fe$_2$O$_3$, employing a statistical theory of regression models, we have constructed a model allowing evaluating the degree of spin canting at both crystallographically non-equivalent sites in the $\gamma$-Fe$_2$O$_3$ crystal structure. It turns out that a combination of physical and statistical methods could bring a more sophisticated picture of spin canting phenomenon in all magnetic nanosystems.

2. EXPERIMENTAL AND METHODS

In this work, spin canting phenomenon has been studied for two nanoparticle systems of $\gamma$-Fe$_2$O$_3$ origin, denoted as the Sample A and Sample B. The Sample A is a commercially-synthesized $\gamma$-Fe$_2$O$_3$ powder which has been bought from Nanophase Technologies Corporation (U.S.A.) under the name NanoTek® Iron Oxide (Product No. Fe-0800-007-025). For study of spin canting, the Sample A has been used as-received without any further chemical modification. On the contrary, the Sample B has been prepared following the synthetic (mechanochemical) route published by Lu and co-workers [7]. This synthetic procedure has been modified with respect to the reaction yield. For the preparation of the Sample B, following precursors have been used: (i) iron(II) chloride tetrahydrate (FeCl$_2$·4H$_2$O – 99 %); (ii) iron(III) chloride hexahydrate (FeCl$_3$·6H$_2$O – 99 %); (iii) potassium chloride (KCl – 99.5%), and (iv) potassium hydroxide (KOH – 99%). All precursors have been bought from Sigma Aldrich Company (U.S.A.) and used as received without any further chemical modification. For the synthesis, mixed powders of 1.35 g FeCl$_3$·6H$_2$O, 0.50 g FeCl$_2$·4H$_2$O and 3.90 g KCl were ground in a mortar at room temperature for 30 minutes; this resulted in an yellow paste. Subsequently, 1.22 g of KOH powder has been added in to the reaction mixture followed by grinding at room temperature for another 30 minutes; the color of the mixture changed from yellow to dark brown. Finally, the sample has been ultrasonificated and washed by double deionized water to remove Cl$^-$ ions. To dry the sample, it has been left under air atmosphere at room temperature.

Transmission electron microscopy (TEM) images were obtained using a JEM2010 microscope operated at 200 kV with a point-to-point resolution of 1.9 Å. X-ray powder diffraction (XRD) experiments were performed with a PANalytical X`Pert PRO instrument (CoK$_\alpha$ radiation) equipped with an X`Celerator detector.

Zero-field Mössbauer spectra of the Sample A and B have been recorded at 5 K in a constant acceleration mode with a 50 mCi $^{57}$Co(Rh) source. The values of the isomer shift are reported with respect to $\alpha$-Fe. In-field Mössbauer measurements were performed in a constant acceleration mode when the sample was placed in a cryomagnetic system (Oxford Instruments) at a temperature of 5, 100, 200, and 300 K and exposed to an external magnetic field of 5 T, applied parallel to the direction of the $\gamma$-rays (i.e., parallel experimental setup).
3. RESULTS AND DISCUSSION

3.1 Evaluation of spin canting by in-field Mössbauer spectroscopy

Before Mössbauer measurements, structural, size and morphology characteristics and phase composition of both samples have been checked by XRD, TEM, and Mössbauer spectroscopy. XRD patterns of both samples (not shown) contain only traces of γ-Fe₂O₃ (diffraction peaks with accordance with the JCPDS card No. 19-0629) without any detectable admixtures of other Fe₂O₃ polymorphs and/or starting precursors; for both samples, the lattice parameters \( a = b = c \) were found to be equal to 8.3277(5) and the crystal structure has been refined within the \( P4_{1}32 \) space group. From TEM images, we observed that both samples are composed of spherical-like nanoparticles; for the Sample A, the diameter of γ-Fe₂O₃ nanoparticles ranges from 5 to 80 nm whereas for the Sample B, γ-Fe₂O₃ nanoparticle diameter varies from 1 to 5 nm. The average particle diameter was found to be ~22 nm and ~3 nm for the Sample A and B, respectively, in accordance with the average values of coherent domains derived from XRD pattern employing the Scherrer formula [8]. Both samples exhibit different particle size distribution; while lognormal distribution function is used to describe particle size distribution of the Sample A, the Gaussian distribution function is applied for the Sample B (see Fig. 1).

Moreover the sample purity was evaluated by Mössbauer spectroscopy. At 5 K, the zero-field spectrum of both samples consists of one asymmetric sextet with hyperfine parameter values close to those frequently reported for γ-Fe₂O₃ [5]. The deconvolution of the recorded Mössbauer spectra of both studied samples has been performed on the basis of analysis of respective Mössbauer spectra collected at the same temperature and in an external magnetic field of 5 T, enabling to distinguish the two spectral components typical for γ-Fe₂O₃ (one component for tetrahedral sites – Sextet A – and one for octahedral sites – Sextet B – in the spinel crystal structure of γ-Fe₂O₃) [5, 6]. Again, there are no signs of presence of other Fe-bearing phases; both samples are single phased of γ-Fe₂O₃ origin based on XRD and Mössbauer spectroscopy results.

Fig 1. Particle size distribution for the Sample A and B derived from mathematical analysis of TEM images (left) and Mössbauer spectra of the Sample A and B recorded at a temperature of 5 K and in zero applied magnetic field (right), where \( \delta \) (± 0.01 mm/s) is the isomer shift, \( \Delta E_Q \) (± 0.01 mm/s) represents the quadrupole splitting and \( B_{hf} \) (± 0.3 T) denotes the hyperfine magnetic field.
To get a deeper insight into understanding of spin canting phenomenon, in-field $^{57}$Fe Mössbauer spectroscopy (IFMS) has been exploited. It is well known that for Fe$^{3+}$-containing compounds like $\gamma$-Fe$_2$O$_3$, IFMS conveys important information on orientation of Fe atomic magnetic moments ($\mu$) inside (nano)materials, i.e., it can monitor orientation behavior of $\mu$ in external magnetic fields. To do so, for both samples, we have measured Mössbauer spectra in 5 T at temperatures of 5, 100, 200, and 300 K (see Fig. 2). At 5 K in-field Mössbauer spectrum of both samples can be mathematically deconvoluted with two sextet components, reflecting the presence of two crystallographically nonequivalent (tetrahedral and octahedral) sites. For an ideal ferromagnetic (F) and ferrimagnetic (FI) (nano)material and in parallel experimental setup, zero values of intensities of the 2$^{nd}$ and 5$^{th}$ resonant lines ($A_{2,5}$) are expected due to alignment of $\mu$ to the direction parallel or antiparallel with respect to the orientation of external magnetic field ($B_{\text{ext}}$). If $A_{2,5}$ are not zero, it implies a non-complete alignment of $\mu$ inside F and FI (nano)material and thus presence of spin canting phenomenon [4, 6]. The more intense $A_{2,5}$ are, $\mu$ are more disordered which is reflected in a higher degree of spin canting. Looking at in-field Mössbauer spectra of both samples at 5 K, we can deduce that spin canting is more pronounced for Sample A than for Sample B, conforming thus its dependence on particle size. As the temperature rises, spin canting phenomenon progressively decreases due to its dynamic character. With an increase in temperature, transverse component of $\mu$ increases due to enhanced
fluctuations of $\mu$. When the temperature is sufficient enough, transverse component of $\mu$ overcomes an anisotropy barrier separating two different spin canted states of $\mu$. As the temperature increases, spin canting becomes a relaxation phenomenon, thus vanishing at a certain temperature. As it is evident from Fig. 2, the degree of spin canting decreases in a different manner for both samples. In the case of Sample A, spin canting completely vanishes at temperature higher than 200 K whereas for the Sample B, spin canting is not detectable at temperatures higher than 100 K. This implies that the dynamic character of spin canting is dependent on particle size and particle size distribution; the smaller the particles are the more rapidly spin canting fades away with temperature. In addition, the dynamic character of spin canting is empowered by collective magnetic excitations that dominate the magnetic behavior of nanoparticle system at temperatures close to its blocking temperature. This is clearly evident for the Sample B for which collective magnetic excitations affect more drastically the spin canting phenomenon. In this case, the presence of collective magnetic excitations is reflected by non-Lorentzian resonant lines bent towards the spectrum center [4, 6].

Note that spin canting phenomenon occurs in different degree at both $\gamma$-Fe$_2$O$_3$ crystal sites. It is evident that spin canting is dominant at octahedral (B) sites in comparison to its degree at tetrahedral (A) sites. However, there have been certain studies reporting that spin canting occurs at the same degree at both sites of $\gamma$-Fe$_2$O$_3$ crystal structure [6]. To confirm our fitting model, we employ a statistical theory of non-regression models.

3.2 Spin canting assessed by non-linear regression models

In order to shed light into the occurrence and nature of spin canting phenomenon in $\gamma$-Fe$_2$O$_3$ nanoparticles, we have constructed a non-linear regression model enabling to quantify the exact estimates of Lorentzian curve describing the $\gamma$-rays resonance in the Mössbauer effect [9]. To do this, we have only considered the region at the velocity scale where the 2$^{nd}$ sextet line is likely to occur. For $\gamma$-Fe$_2$O$_3$, 2 Lorentzian curves are used, one for tetrahedral sites and one for the octahedral sites. The proposed model is then in the form of

$$Y = f(\beta)$$

where $Y$ is the observation vector (i.e., experimental data) and $f(\beta)$ is the weighted sum of the 2 Lorentzian functions given by

$$f(x, \beta) = \beta_0 \left( \frac{\beta_1 + \frac{2\beta_2}{\pi} \frac{\beta_3}{4(x-\beta_5)^2 + \beta_6^2}}{1 - \beta_4} \right) + (1 - \beta_4) \left( \frac{\beta_5 + \frac{2\beta_6}{\pi} \frac{\beta_7}{4(x-\beta_8)^2 + \beta_6^2}}{1 - \beta_4} \right)$$

with unknown parameters $\beta = (\beta_0, ..., \beta_8)^T$. Here, $\beta_0$ is the weight coefficient reflecting the portion of individual Lorentzian curves in their sum. Thus, the precise knowledge of $\beta_0$ along with $\beta_0$ and $\beta_6$ (intensities of individual Lorentzian curves) enables to quantify the degree of spin canting phenomenon at individual $\gamma$-Fe$_2$O$_3$ crystallographic sites.

In the case of the Sample B, we get $\beta_0 \approx 0.768$, $\beta_2 \approx -0.038$ and $\beta_6 \approx -0.089$. Based on these derived values of function parameters, we can deduce the spectral intensity of the 2$^{nd}$ line of the 2 sextets for $\gamma$-Fe$_2$O$_3$ samples. Comparing the intensity value of the 2$^{nd}$ sextet line with the intensity value of the 3$^{rd}$ sextet line for the 2 sextets, it turns out that spin canting is more pronounced at the octahedral sites for the Sample B. Employing analogous mathematical procedure for the Sample A, we also find that at the octahedral sites, the spin canting manifests itself in a higher degree compared to that derived for the tetrahedral sites. This also implies that for both samples, the spin canting phenomenon is rather a manifestation of surface effects than finite-size effects although the impact of finite-size effects on the spin canting cannot be unambiguously excluded at this stage.

Exploiting the theory of non-linear regression models for the weighted sum of the Lorentzian functions provides precise determination of unknown function parameters including the weight coefficient. This mathematical procedure can be further improved by using the multi-stage regression models with constrains
[10] as this approach enables to impose relevant conditions on individual parameters of a given fitting function. This would allow to describe the nature of spin canting more correctly for both studied samples.

4. CONCLUSIONS

We have shown that spin canting phenomenon, being a parasitic effect in $\gamma$-Fe$_2$O$_3$ and thus limiting its applications in certain fields, significantly depends on the temperature. As the temperature rises, spin canting vanishes due to its dynamic character. It turns out that the temperature evolution of spin canting phenomenon is affected by average particle size and particle size distribution of $\gamma$-Fe$_2$O$_3$ nanoparticles in their assembly. Moreover, its fading is assisted by collective magnetic excitations that become dominant as the temperature approaches the blocking temperature characteristic of particular $\gamma$-Fe$_2$O$_3$ nanoparticle system. Based on the statistical analysis employing theory of non-linear regression models, we demonstrate that spin canting occurs in different degree at individual crystallographic sites of $\gamma$-Fe$_2$O$_3$, being more pronounced at the octahedral sites. The presented approach, combining physical and statistical methods, could thus bring a more sophisticated picture of spin canting phenomenon in all magnetic nanosystems. This would require exploitation of multi-stage regression models to construct a more precise model. However, our study does not unambiguously confirm if the temperature evolution of spin canting at both $\gamma$-Fe$_2$O$_3$ crystallographic sites has similar character or if at one site, spin canting diminishes more rapidly than at the other site with the rise in temperature. This needs a further investigation with more $\gamma$-Fe$_2$O$_3$ nanoparticle assemblies having different average particle size.

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LITERATURE