EXPERIMENTAL DESIGN OF HYSTERESIS LOOP MEASUREMENTS OF NANOSIZED ε-Fe$_2$O$_3$ – A STATISTICALLY-BASED APPROACH TOWARDS PRECISE EVALUATION OF ε-Fe$_2$O$_3$ HYSTERESIS LOOP PARAMETERS

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Abstract

Nanosized ε-Fe$_2$O$_3$ is one of the most remarkable iron(III) oxide polymorph exhibiting a giant room temperature coercivity, thus being recognized as a promising candidate in the field of high coercivity media. To apply it in practice, knowledge of its hysteresis loop parameters is highly required. In most case, from the mathematical viewpoint, hysteresis loop profiles are given in terms of the Langevin function. In this work, we report a statistically-based procedure to more accurately describe the ε-Fe$_2$O$_3$ hysteresis loop considering a suitably-planned measurement process. Employing the experiment design of hysteresis loop measurement, we get the most precise estimation of the ε-Fe$_2$O$_3$ hysteresis loop parameters and, consequently, evaluate the ε-Fe$_2$O$_3$ macroscopic magnetic properties.

Keywords: ε-Fe$_2$O$_3$, hysteresis loop, Langevin function, optimal experiment design, D-optimal efficiency.

1. INTRODUCTION

Out of all characteristics nanomaterials exhibit, magnetic properties deserve much scientific attention due to diversity of application fields where magnetic nanomaterials can be used. It is well-known that on lowering the size of a magnetic nanomaterial, new magnetic phenomena, not observed for its bulk counterpart, emerges as a result of finite-size and surface effects [1]. Thus, the nanomaterial becomes equipped with new magnetic properties driven by a single-domain state, superparamagnetism, collective magnetic excitations, spin canting, presence of interparticle magnetic interactions, colossal magnetoresistance, quantum tunneling of magnetization, etc. [2]. For a given application, some of these phenomena establish a desired magnetic behavior of the nanomaterial, whereas the others are found to be of a parasitic nature for which strategies to eliminate and/or partially suppress them are required to be applied.

Among application-appealing magnetic nanomaterials, iron oxides hold a prominent position empowered by a remarkable combination of magnetic and biochemical properties they possess [3]. Nowadays, 6 different crystalline forms of iron oxide are recognized [3]. Very often, they are classified in terms of type of iron valence state found in their crystal structure [3]: (i) FeO (i.e., wustite) with only Fe$^{2+}$ ions; (ii) Fe$_2$O$_3$ (ferric oxide, iron(III) oxide) with only Fe$^{3+}$ ions; and (iii) Fe$_3$O$_4$ (i.e., magnetite) having both Fe$^{2+}$ and Fe$^{3+}$ ions in its crystal structure. Most notably, ferric oxide shows a phase polymorphism; 4 different Fe$_2$O$_3$ phases have been described yet [4]: (i) α-Fe$_2$O$_3$ (i.e., hematite); (ii) β-Fe$_2$O$_3$; (iii) γ-Fe$_2$O$_3$ (i.e., maghemite); and (iv) ε-Fe$_2$O$_3$. While γ-Fe$_2$O$_3$, along with Fe$_3$O$_4$, currently strengthens its role in various biomedical branches [5], ε-Fe$_2$O$_3$ is being considered as a promising future candidate in technologically-based applications due recent discoveries of interesting material's properties it exhibits [6].

ε-Fe$_2$O$_3$, existing only in a nanosized form and firstly reported in 1934, had been left unexplored for a long time till 2004 when its huge room-temperature coercivity of ~2 T was discovered, turning back an attention of the scientific community to this extraordinary iron(III) oxide polymorph [6]. Shortly after that, ε-Fe$_2$O$_3$ was found to have coupled magnetoelectric properties [6] and to show a ferromagnetic resonance in a millimeter-wave region [6]. Thus, ε-Fe$_2$O$_3$ can be used not only in applications requiring high-coercivity media but also
as components of electric/magnetic field tunable devices and in communication systems for effective suppression of the electromagnetic interference and a stabilization of the electromagnetic transmittance. However, its introduction to such applications is being hampered by problems associated with its synthesis such as low yields, a lack of precise control of resulting product size, and presence of Fe\(_2\)O\(_3\) admixtures [6].

Mathematical statistics accompanied with a theory of experiment design offers a possibility of measurement process optimization. The main aim of the experiment design is to find points \(x \in X\), where \(X\) is an experimental domain, which are important for the measurement. The most important question is a choice of criterion function for particular experiment as the total utility of the design depends on correctly chosen criterion function. In this work, after proper physical characterization of the \(\varepsilon\)-Fe\(_2\)O\(_3\) sample, we exploit the D-optimal criterion function to find the optimal design of the \(\varepsilon\)-Fe\(_2\)O\(_3\) hysteresis loop measurement since this criterion function minimizes the confidence area of the estimates of the unknown parameters. This theory can be extended for another function describing hysteresis loop profile to make a general view on the statistical process of the hysteresis loop measurements.

2. EXPERIMENTAL AND METHODS

Sample preparation. \(\varepsilon\)-Fe\(_2\)O\(_3\), incorporated into an SiO\(_2\) matrix, has been prepared following the synthetic procedure firstly proposed by Jin and co-workers [7]. This synthetic approach is based on a combination of the reverse-micelle and sol-gel techniques and exploits SiO\(_2\) matrix and Ba\(^{2+}\) ions as a stabilizing and phase-purity agent, respectively, yielding a single-phased specimen of \(\varepsilon\)-Fe\(_2\)O\(_3\) origin without any admixtures of other iron(III) oxide polymorphs. So far, this preparation procedure is being widely recognized as the only one synthetic route leading to single-phased \(\varepsilon\)-Fe\(_2\)O\(_3\) samples (for a review of \(\varepsilon\)-Fe\(_2\)O\(_3\) synthetic routes, see recently published review work by Tucek and co-workers [6]).

Characterization techniques. 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. The 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 spectrum was recorded at 300 K with a home-made Mössbauer spectrometer operating in a constant acceleration mode and equipped with a 50 mCi \(^{57}\)Co(Rh) source. The values of the isomer shift are reported with respect to \(\alpha\)-Fe. A superconducting quantum interference device (SQUID, MPMS XL-7, Quantum Design) has been used for measuring the sample hysteresis loop at 300 and in external magnetic fields from \(-5\) T to \(+5\) T.

3. RESULTS AND DISCUSSION

3.1. Size, morphology, crystal, phase, and magnetic characteristics of \(\varepsilon\)-Fe\(_2\)O\(_3\)/SiO\(_2\) nanocomposite

TEM images (not shown) show that the prepared nanocomposite is predominantly composed of nanoobjects with a rod-like morphology (i.e., nanorods) having a length and width in the range from \(~80\) to \(~140\) nm and from \(~15\) to \(~40\) nm, respectively, in accordance with TEM observations in Ref. [7].

XRD pattern (not shown) of the investigated nanocomposite contains diffraction peaks positioned at 2θ angles characteristic of \(\varepsilon\)-Fe\(_2\)O\(_3\) (ICSD card No. 415250) without any XRD-detectable traces of other iron(III) oxide polymorphs and starting precursors; the Rietveld analysis identifies 4 crystallographically nonequivalent cation sites (i.e., Fe\(_{A}\), Fe\(_{B}\), Fe\(_{C}\), and Fe\(_{D}\) site) and gives values of lattice parameters, i.e., \(a = 5.071(8)\) Å, \(b = 8.730(6)\) Å, \(c = 9.428(8)\) Å, and \(\alpha = \beta = \gamma = 90^\circ\); being in accordance with those published previously for \(\varepsilon\)-Fe\(_2\)O\(_3\) [6]. The crystal structure of the studied nanorods has been most precisely refined within the \(Pna2_1\) space group that belongs to the orthorhombic crystal class, as also expected for \(\varepsilon\)-Fe\(_2\)O\(_3\) [6].

To further check the chemical origin and phase composition of the investigated sample, \(^{57}\)Fe Mössbauer spectroscopy has been employed. Mathematical processing of the room-temperature zero-field Mössbauer
spectrum (see Fig. 1a) yields 3 sextet components with the spectral area ratio of 2:1:1. This implies that nanorods are in a magnetically ordered state (for ε-Fe₂O₃, the Curie temperature is ~495 K [6]). Derived values of the Mössbauer hyperfine parameters (isomer shift – δ, quadrupole splitting – ΔE_Q, hyperfine magnetic field – B_hf) of all 3 sextets precisely (within the error of the Mössbauer technique) correspond with those expected for ε-Fe₂O₃ [4, 6]: (i) Sextet 1 with δ = 0.34 ± 0.01 mm/s, ΔE_Q = – 0.24 ± 0.01 mm/s, and B_hf = 44.9 ± 0.3 T belongs to the Fe_A and Fe_B sites, (ii) Sextet 2 with δ = 0.35 ± 0.01 mm/s, ΔE_Q = – 0.01 ± 0.01 mm/s, and B_hf = 39.9 ± 0.3 T belongs to the Fe_C sites, and (iii) Sextet 3 with δ = 0.22 ± 0.01 mm/s, ΔE_Q = – 0.14 ± 0.01 mm/s, and B_hf = 26.2 ± 0.3 T belongs to the Fe_D sites in the ε-Fe₂O₃ crystal structure. One would expect 4 sextets for ε-Fe₂O₃ to be observed. However, this is not possible due to very close room-temperature values of the Mössbauer hyperfine parameters for the Fe_A and Fe_B sites in the ε-Fe₂O₃ crystal structure [6]. To resolve sextet components associated with the Fe_A and Fe_B sites, an external magnetic field is necessary to be applied [6]. Since no other spectral components are observed in the Mössbauer spectrum, presence of other Fe₂O₃ polymorphs is unambiguously excluded.

![Fig 1. (a) Room-temperature zero-field Mössbauer spectrum and (b) room-temperature hysteresis loop of the ε-Fe₂O₃/SiO₂ nanocomposite. In panel (b), the mass magnetization is recalculated with regard to the Fe₂O₃/SiO₂ molar ratio (= 0.22) in the prepared nanocomposite.](image)

The room-temperature hysteresis loop of the ε-Fe₂O₃/SiO₂ nanocomposite, recalculated with respect to the ε-Fe₂O₃/SiO₂ molar ratio (= 0.22), is depicted in Fig. 1b. It exhibits a coercive field of ~1.9 T and saturation mass magnetization (after extrapolation of mass magnetization values beyond 5 T) of ~20 Am²/kg, being a typical hysteresis loop parameter values reported for ε-Fe₂O₃. Again, any presence of other Fe₂O₃ polymorphs has not been detected.

Thus, the above-presented experimental data confirm that in the SiO₂ matrix, only nanorods of ε-Fe₂O₃ nature are present. However, a slight modification of the synthesis conditions may lead to formation of other Fe₂O₃ polymorphs (i.e., α-Fe₂O₃ and γ-Fe₂O₃). From the magnetic viewpoint, mainly γ-Fe₂O₃ constitute unwanted admixture as it may drastically affect the magnetic properties of the ε-Fe₂O₃/SiO₂ nanocomposite and ε-Fe₂O₃ nanoobject assembly when freed from the SiO₂ matrix. Thus, knowledge of room-temperature values of ε-Fe₂O₃ hysteresis loop parameters is of significant importance. To get their values, a statistical approach using experimental design theory is found to be a powerful tool. Moreover, fitting the hysteresis loop experimental data with the defined function may reveal the presence of magnetic impurity the concentration of which can be then easily derived, evaluating thus the degree of purity of the prepared ε-Fe₂O₃ samples.

3.2. Design of experiment applied for measurement of the ε-Fe₂O₃ hysteresis loop

The main goal of this work is to find an optimal experimental design for the measurement of hysteresis loop of ε-Fe₂O₃ nanoobjects. The experimental domain \( X \) is the set of 150 points which represent the induction of the external magnetic field. We try to find the most important points \( x \in X \) for measurement in order to
estimate the unknown parameters of the Langevin function to describe magnetic response of \( \varepsilon \)-Fe\(_2\)O\(_3\) in applied magnetic fields. As the hysteresis loop of the measured \( \varepsilon \)-Fe\(_2\)O\(_3\)/SiO\(_2\) nanocomposite has an upper branch and a lower branch symmetric around the origin, it is sufficient to construct a mathematical model only for the upper branch of the hysteresis loop and to extend the validity of the as-obtained results for the lower branch of the \( \varepsilon \)-Fe\(_2\)O\(_3\) hysteresis loop.

In terms of statistical modeling, the Langevin function, describing the magnetic response of a (nano)material, is given by

\[
L(x, \theta) = \theta_1 \cdot \coth \left( \frac{\theta_2}{k_B \cdot T} (x + \theta_3) \right) - \theta_1 \cdot \frac{k_B \cdot T}{\theta_2} (x + \theta_3)
\]

where \( \theta = (\theta_1, \theta_2, \theta_3)^T \) are unknown physical parameters, \( k_B \) and \( T \) are known physical constants and \( x \) is the induction of the external magnetic field. We assume a nonlinear regression model in the form of

\[
y = L(x, \theta^*) + \epsilon
\]

where \( \theta^* = (\theta_1^*, \theta_2^*, \theta_3^*)^T \in \Theta \) is the true parameter, \( \Theta = \Theta_1 \times \Theta_2 \times \Theta_3 \) is the set of physically possible values of the parameters, \( x \in X \) is the design point, \( X \) is the experimental domain and \( \epsilon \) is the unobservable error with \( E(\epsilon) = 0 \) and \( D(\epsilon) = \sigma^2 \).

If \( \xi \) is an arbitrary design, then, in order to find a locally D-optimal experimental design \( \xi^{* \theta^*} \) to estimate \( \theta^* \) more exactly, we have to construct an information matrix \( M \) such that \( \det(M_\theta(\xi)) \) is minimum. As the model is nonlinear, we have to use the Taylor series expansion to linearize this model. Thus, we get a linear regression model with the information matrix \( M \) in the form of

\[
M_\theta(\xi) = \sum_{x, \xi(x) = 0} \xi(x) \left( \frac{\partial L(x, \theta)}{\partial \theta} \right) \left( \frac{\partial L(x, \theta)}{\partial \theta} \right)^T ; \theta \in \Theta
\]

where \( \xi \) is the design and \( \frac{\partial L(x, \theta)}{\partial \theta} \) is the partial derivative of the Langevin function at point \( \theta \).

The locally D-optimal design is dependent on the point \( (\theta_1, \theta_2, \theta_3)^T \) at which the nonlinear regression model was linearized. It is easy to verify that D-optimal design is independent on the value of parameter \( \theta_1 \) because

\[
\det \left( M_{\theta_1, \theta_2, \theta_3}(\xi) \right) = \theta_1^2 \cdot \det \left( M_{\theta_1, \theta_2, \theta_3}(\xi) \right)
\]

for \( \theta = (\theta_1, \theta_2, \theta_3)^T \in \Theta \) and any \( \xi \in \Xi \), where \( \Xi \) is the set of all designs on \( X \). It means that the D-optimal design for the hysteresis loop profile described by the Langevin function depends only on the values of parameters \( \theta_2 \) and \( \theta_3 \). A possible solution is to choose values \( \theta_2 \in \Theta_2 \) and \( \theta_3 \in \Theta_3 \) and construct the D-optimal design for these particular values. The problem is that the set of possible values of parameters \( \theta_2 \) and \( \theta_3 \) is too extensive and consequently, the locally D-optimal designs are too different. For this reason, we used the D-efficiency to measure the performance of a design \( \xi \) compared to that of the locally D-optimal design \( \xi^{* \theta^*} \) [8]. To get the value of D-efficiency, we exploited a relation in the form of

\[
\text{eff}_{\theta^*}(\xi) = \frac{\det \left( M_{\theta^*}(\xi) \right)^{\frac{1}{m}}} {\det \left( M_{\theta^*}(\xi^{* \theta^*}) \right)^{\frac{1}{m}}}
\]

where \( m \) is the number of unknown parameters (3 in our case).

Now we focus on problem of nonlinear locally D-optimal designs. If we consider design \( \xi \) where the parameters \( \theta = (1, \theta_2, \theta_3)^T \in \Theta \) are not close to the parameters \( \theta = (\theta_1^*, \theta_2^*, \theta_3^*)^T \in \Theta \), then the value of efficiency for design \( \xi \), i.e., \( \text{eff}_{\theta^*}(\xi) \), can be very small (see Fig. 2).
Fig 2. Locally optimal design for the measurement of upper branch of the $\varepsilon$-$\text{Fe}_2\text{O}_3$ hysteresis loop.

Another possibility is to construct a uniform design of experiment at all points of $X$. The value of efficiency of design $\xi$ with respect to $\theta^* = (\theta_1^*, \theta_2^*, \theta_3^*)^T \in \Theta$ is bigger, however, it is not effective as an experimenter has to reset the measuring device many times, which results in high costs of the experiment (see Fig. 3).

Fig 3. Uniform design for the measurement of the upper branch of the $\varepsilon$-$\text{Fe}_2\text{O}_3$ hysteresis loop.

The most efficient stable design over the entire set of possible values of the parameters $\theta_2$ and $\theta_3$ is the maximin efficient design defined by [9]

$$\xi_{\text{ME}}^* = \arg \max_{\xi \in \Xi} \left\{ \min_{\theta \in \Theta} \left[ \text{eff}_{\theta} (\xi) \right] \right\}.$$

To find this design we used the method of simulated annealing. In Fig. 4, one can see the best approximation $\xi_{\text{ME}}^*$ of $\xi_{\text{ME}}^*$ for which the efficiency value is at least 69.26% and is stable over the entire $\Theta$.

Fig. 4. Maximin efficient design for the measurement of the upper branch of the $\varepsilon$-$\text{Fe}_2\text{O}_3$ hysteresis loop.
From Fig. 4, it is evident that we need only 12 points for the measurement of the upper branch of the \( \varepsilon - \text{Fe}_2\text{O}_3 \) hysteresis loop to obtain the most exact estimate of the vector unknown parameter \( \theta = (\theta_1, \theta_2, \theta_3)^T \in \Theta \).

4. CONCLUSIONS

After proper physical characterization of the synthesized \( \varepsilon - \text{Fe}_2\text{O}_3/\text{SiO}_2 \) nano-composite sample checking its phase purity, we have proposed an optimal design of experiment for measuring the \( \varepsilon - \text{Fe}_2\text{O}_3 \) hysteresis loop securing the requirement that the derived values of \( \varepsilon - \text{Fe}_2\text{O}_3 \) hysteresis loop parameters are as precise as possible. It turns out that only 12 points at which the measurements are carried out are needed for accurate determination of \( \varepsilon - \text{Fe}_2\text{O}_3 \) hysteresis loop parameters. This approach can be generalized for other sigmoidal functions including the Brillouin function that appears to be more correct function for a description of the magnetic response of a nanomaterial. Thus, we present a universal tool for assessment of hysteresis loop profiles for any magnetic (nano)material, bringing a complex information on its macroscopic magnetic properties.

ACKNOWLEDGEMENTS

This study was funded by the Operational Program Research and Development for Innovations – European Social Fund (CZ.1.05/2.1.00/03.0058), the projects of the Ministry of Education of the Czech Republic (1M6198959201 and MSM6198959218), and the project of the Academy of Sciences of the Czech Republic (KAN115600801). J. T. deeply thanks prof. Shin-ichi Ohkoshi (Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan) for providing the \( \varepsilon - \text{Fe}_2\text{O}_3/\text{SiO}_2 \) nanocomposite sample.

LITERATURE