Modeling of the magnetic behavior of γ-Fe_2O_3 nanoparticles mineralized in ferritin

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The temperature dependent initial magnetization of γ-Fe_2O_3 (maghemite) mineralized inside ferritin protein cages has been investigated with a vibrating sample magnetometer up to 8 T. The data are fit to different magnetic models to extract values of the magnetic moment of each cluster. It is found that the application of a simple Langevin model with a first and second order term in the susceptibility greatly enhances the quality of the fit to the data suggesting that the inclusion of crystalline anisotropy is important in extracting the magnetic moment of each core. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1669211]

I. INTRODUCTION

The synthesis of monodisperse and highly uniform magnetic nanoparticle sized structures has been made more possible with the help of biological containers as constraining vessels. Native ferritin, an iron-storage protein found nearly ubiquitously in nature, has a spherical shell with an external diameter of 12 nm and an inner core diameter of 8 nm.[1] A fully loaded, naturally occurring mammalian ferritin protein will possess an antiferromagnetic 8 nm iron oxyhydroxide core [Fe(O)OH] with roughly 4500 Fe atoms.[2] These cores form a noninteracting monodispersed, superparamagnetic system, but because of the presence of structural defects and uncompensated surface moments, each iron oxyhydroxide particulate will possess a net magnetic moment arising from unpaired Fe spins. It has been found that the ferritin protein, and other similar protein cages, can be emptied of its contents and mineralized with a multitude of different materials, forming highly uniform nanoparticles.[3–5]

In this article the temperature dependent initial magnetization curves of γ-Fe_2O_3 mineralized in ferritin is modeled. A similar behavior in native ferritin has previously been studied.[6,7] Each maghemite core possesses a net magnetic moment arising from the ferrimagnetic structure of the material and from additional uncompensated iron spins, which are due to defects and finite size effects. Since the mineralized cores are roughly the same size as the native ferritin but with a larger moment per core, they have a higher superparamagnetic blocking temperature, $T_B = 24\,\mathrm{K}$, compared to 15 K for the native.[8]

II. MODELING

The magnetization of single domain ferrimagnetic nanoparticles arises from the unequal magnitude of the spins associated with the two sublattices, as well as unpaired spins in the particles. In order to model the behavior of an ensemble of these nanoparticles, both a simple Langevin model, $L(x)$, with an added linear susceptibility term, $\chi^{(1)} \times H$, and a random magnetic orientations model,[9] $G(x)$, also with the added linear susceptibility term, $\chi^{(1)} \times H$, are used. Both these two models are further modified with the inclusion of a second order term, $\chi^{(2)} \times H^2$ to include the presence of crystalline anisotropy.

The Langevin model assumes an ensemble of noninteracting isotropic magnetic moments. With the inclusion of a paramagnetic linear susceptibility term (due to the mineralized cores, the filled and unfilled protein cages, and the embedding media) the simple magnetization model that is called here the Langevin model, $m_{\mathrm{LAN}}(T)$, is

$$m_{\mathrm{LAN}}(T) = m_S \times L(x) + \chi^{(1)} \times H, \tag{1}$$

where m_S is the saturation moment, $\chi^{(1)}$ is the linear susceptibility, the Langevin function $L(x) = \coth(x) - 1/x$ and $x = \mu(T)H/k_BT$, with $\mu(T)$ as the magnetic moment of each nanoparticle core.

Since our ferrimagnetic particles might not follow a strictly Langevin behavior, it may be useful to compare the Langevin model with a model for small antiferromagnetic particles determined by Néel[10–12] and shown in recent articles to describe superantiferromagnetic particles.[8,9] This model, based on an Ising model, takes into account random magnetic orientations by assuming the uncompensated moments of the spins in a particle fluctuate between two antiparallel directions along the antiferromagnetic axis. This axis can assume a random orientation with respect to the applied field and the moment is treated as an Ising spin pointed along that axis. In this model there is a linear term, $\chi^{(1)} \times H$, associated in part with the antiferromagnetic susceptibility, which accounts for weak canting of the two sublattices. This model will be called the random magnetic orientations model

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[(RMO) model] and the magnetic moment, $m_{\mathrm{RMO}}(T)$ is given by

$$m_{\mathrm{RMO}}(T) = m_S \times G(x) + \chi^{(1)} \times H,$$
$$G(x) = \tfrac{1}{2}\int_0^{\pi} \sin\theta \cos\theta \tanh(x \times \cos\theta) d\theta, \tag{2}$$

where x is again $x = \mu(T)H/k_BT$, except $\mu(T)$ is now more specifically the moment due to the uncompensated spins in each core, and θ is the random direction of the axis with respect to the applied field. The $G(x)$ function is similar to the Langevin function but saturates at half the value.

A major shortcoming of both these models is that they fail to take into account the crystalline anisotropy of the particles to a high enough degree. In fact the Langevin model includes no anisotropy and the RMO model assumes extremely large anisotropy for the Ising model. To incorporate this concept into the models another susceptibility term, $\chi^{(2)}$, second order in field is added. A Taylor series expansion in the applied magnetic field of the anisotropy energy would create terms of first and second order in the field. The first order term is added to the susceptibility term leaving only the second order term in the field: an added $\chi^{(2)} \times H^2$ term to Eqs. (1) and (2). This term neither reflects the full contribution of anisotropy, nor is anisotropy the only effect contributing to this parameter. However, it provides a starting point for including magnetic anisotropy.

In order to compare the quality of the fits of different models with different numbers of parameters and data points, it is useful to compare the reduced chi squared of the fits. Reduced chi squared is, $\chi^2_{\mathrm{red}} = \chi^2/(N-p)$, where N is the number of data points and p is the number of free parameters.

III. EXPERIMENT

Commercial apo-ferritin, from Sigma-Aldrich, was used as the growth chamber for the ferrimagnetic γ-Fe_2O_3 (maghemite) nanoparticles, which were mineralized, precipitated, and then dried out. The detailed preparation of the samples has been described in detail elsewhere.[13] DC magnetization measurements, running between ± 8 T, were taken at several temperatures from 5 to 300 K and were performed on a 1.89 mg quantity of sample, pressed into a small pellet, using the vibrating sample magnetometer option of the Quantum Design PPMS. Rough core sizes of 5–7 nm were determined with transmission electron microscopy.

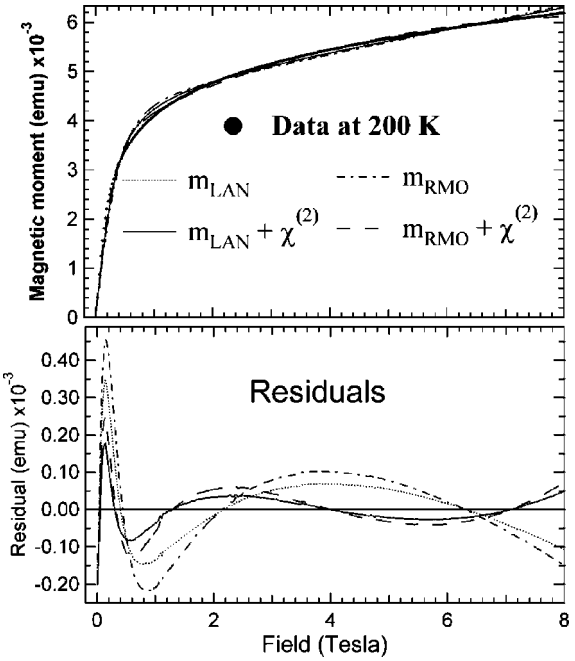

FIG. 1. Top: Initial magnetization curve at 200 K for γ-Fe_2O_3 artificially mineralized in ferritin fitted to the four models. The dotted, solid, dash-dot, and dash–dash curves represent, respectively, the Langevin model, Langevin model with second order susceptibility, RMO model, and RMO model with second order susceptibility. Bottom: Residuals of the four models illustrating the deviation from experimental results. The residuals show that the fit is in poorest agreement with the data at low fields.

IV. RESULTS AND DISCUSSION

Vibrating sample magnetometry measurements were made on the maghemite nanoparticles at several different temperatures. Shown in Fig. 1 is an initial magnetization curve at 200 K.[14] The plot of residuals shows that, of the four different models, the Langevin with the second order term provides the best fit. This plot also reveals the significant contribution to χ^2 incurred between zero and 0.4 T. This field range is where anisotropy would have its greatest affect as shown by Hanson, Johansson, and Mørup.[15]

Previous articles have reported good fits to the native ferritin using both the Langevin or RMO models without second order susceptibility terms.[7,9] However, it should be noted that the data presented in this manuscript were taken out to significantly higher field values. If truncated at the high field limit used in other articles (2–5 T), high quality fits can be obtained without need for the second order term. Only by including this high field data, is the poor fit at low

TABLE I. Extracted best fit parameters of the saturation moment, m_s, the moment per core, $\mu(T)$, and the first and second order susceptibilities, $\chi^{(1)}$ and $\chi^{(2)}$, for the four models. Also shown is the total χ^2_{red} for the four fits.

	$m_s(\times 10^{-3}$ emu)	$\mu(T)$ (μ_B)	$\chi^{(1)}(\times 10^{-4}$ emu/T)	$\chi^{(2)}(\times 10^{-5}$ emu/T^2)	χ^2_{red} (emu$^2\times$T)
m_{LAN}	4.71±0.02	2040±30	2.09±0.03	NA	6.01×10^{-9}
$m_{\mathrm{LAN}}+\chi^{(2)}$	4.21±0.01	2590±25	4.27±0.06	−2.23±0.06	1.31×10^{-9}
m_{RMO}	8.76±0.03	993±20	2.46±0.03	NA	12.6×10^{-9}
$m_{\mathrm{RMO}}+\chi^{(2)}$	7.62±0.03	1330±20	5.33±0.07	−3.05±0.08	2.85×10^{-9}

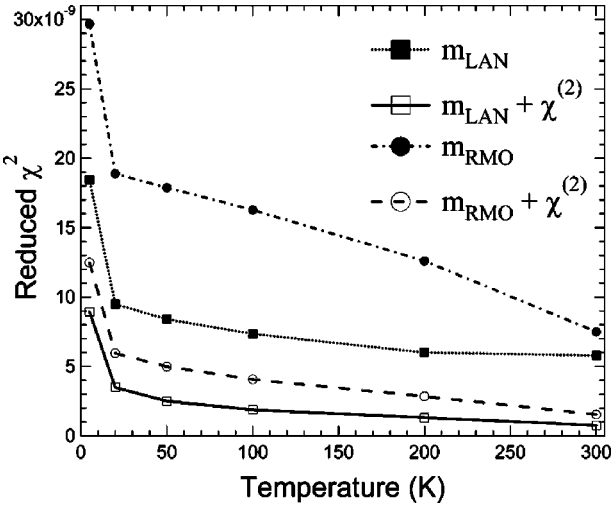

FIG. 2. χ^2_{red} of the four models at various temperatures are shown. The Langevin model with the second order susceptibility term consistently gives the best fit to the measured data.

field uncovered (in addition to different parameters then being extracted).

It is seen in Table I that χ^2_{red} is smallest for the Langevin model with the inclusion of the second order term. It is interesting to note that the two susceptibility terms are nearly independent of which function is used—Langevin or the RMO model. More interesting to note is the fact that while the saturation moments produced by fitting the Langevin models are roughly half the values extracted from the random orientation models, the moments per core extracted from the Langevin models are about double the random orientation values.

The effects of temperature on the fits were also studied. Figure 2 shows χ^2_{red} versus temperature for the four models. The Langevin model with the second order term consistently produced the best fit. This graph also shows a poorer fit for all the models at lower temperatures, which agrees with the claim that these models are most appropriate above the blocking temperature.

V. CONCLUSION

The field dependent magnetic behavior of γ-Fe_2O_3 (maghemite) mineralized inside ferritin protein cages was fit to four models. The best fit, over a wide temperature range, was consistently produced by a Langevin function together with a first and second order susceptibility term, suggesting that the inclusion of a crystalline anisotropy energy is critical. The requirement of the inclusion of crystalline anisotropy confirms the single crystal nature of the mineralized cores.

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