Magnetic properties of Co_3O_4 nanoparticles mineralized in *Listeria innocua* Dps

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Temperature-dependent magnetic measurements are reported for 4.34 nm antiferromagnetic Co_3O_4 nanoparticles mineralized in the *Listeria innocua* Dps protein cage. ac measurements show a superparamagnetic blocking temperature of roughly 5.4 K and give an extracted anisotropy energy density of $(7.6\pm0.4)\times10^4$ J/m^3. The Néel temperature for the Co_3O_4 nanoparticles, determined with dc magnetometry, was determined to be roughly 15 ± 2 K. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2163839]

I. INTRODUCTION

Recently magnetic nanoparticles have become the focus of many studies.[1–3] In particular, antiferromagnetic nanoparticles have shown a stunning array of emergent properties reminiscent of the variation of bulk materials when created as magnetic films.[1,4] In the case of magnetic thin films, low dimensionality and interface effects played a significant role. For magnetic nanoparticles, when the number of atoms that make up the surface become of the order that make up the remaining volume, the surface spins compete with the core spins, resulting in unusual magnetic properties with a multiple assortment of technological applications which include biomedical and hard-drive densifying technologies.[5,6]

In this study, biological containers of *Listeria innocua* Dps proteins, LDps, were used as the growth and constraining vessels for the synthesis of Co_3O_4 nanoparticles. Nanoparticles were synthesized inside of these biological containers in order to produce uniform and monodisperse spherical Co_3O_4 nanoparticles separated by a nonmagnetic buffer to help mute any magnetic interparticle interactions.

LDps is composed of 12 identical 18 kDa subunits, which self-assemble into an empty cage having a 2-3 symmetry.[7–10] LDps has an outer diameter of 8.5 nm and an inner diameter of 5 nm with 0.8 nm pores at subunit interfaces allowing molecular access to the interior. These pores allow Co ions to penetrate into the interior for the size constrained synthesis of Co_3O_4 nanoparticles. It has been found that protein cages can be emptied of their contents and mineralized with a multitude of different materials, forming monodisperse and highly uniform nanoparticles.[11–13]

In this article we present the temperature-dependent magnetization measurements for Co_3O_4 nanoparticles. (Other studies of the magnetic properties of biologically aided synthesis with native ferritin and γ-Fe_2O_3 mineralized ferritin have previously been reported.[12–14]) It is a traditional precursor of anode material in Li-ion rechargeable batteries[15] and is an effective catalyst in the reduction of SO_2 by CO,[16] and NO by methane.[17]

Co_3O_4 has a normal cubic spinel structure and is antiferromagnetic in the bulk with a Néel temperature, T_N, between 30 K (Ref. 18) and 40 K.[19] Co_3O_4 unit cell has a lattice constant of 8.08 Å and contains 8 Co^{2+} tetrahedral ions and 16 Co^{3+} octahedral ions. The Co^{3+} ions behave diamagnetically while the Co^{2+} ions are ordered antiferromagnetically with magnetic moments of roughly $3\mu_B$.[19]

II. EXPERIMENT

The expression and purification of the *Listeria innocua* Dps protein as well as the synthesis of the Co_3O_4 nanoparticles inside these protein cages are described in detail elsewhere.[10,20] Transmission electron microscopy (TEM) measurements showed Co_3O_4 spherical-like particles with an average diameter of roughly 4.34 ± 0.55 nm.[10] Electron diffraction measurements in the TEM showed these nanoparticles to have a similar structure and *d* spacings as Co_3O_4.[10]

The chemical environment of the Co atoms was also identified by x-ray absorption spectroscopy (XAS), acquired at the Co $L_{2,3}$ edges (770–800 eV). Measurements were performed on microgram quantities of Co_3O_4 mineralized cages dried out on formvar-coated TEM grids, at the Advanced Light Source beamline 4.01. Figure 1 shows the Co $L_{2,3}$ XAS measurements in transmission. The characteristic two-peak

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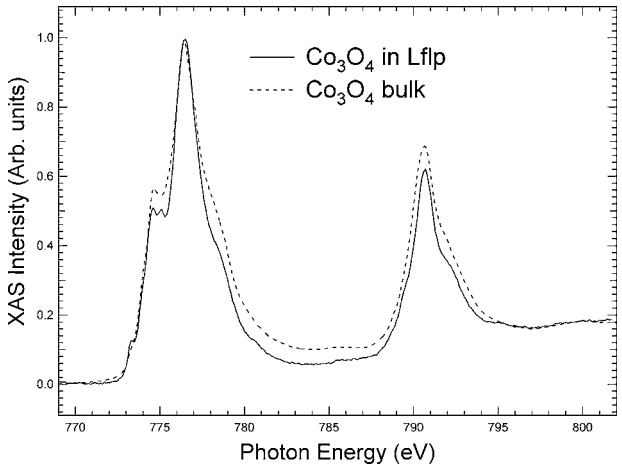

FIG. 1. XAS spectrum of the Co_3O_4 nanoparticles compared to a bulk Co_3O_4 spectrum. The multipeak in the L_3 edge is evidence for Co_3O_4.

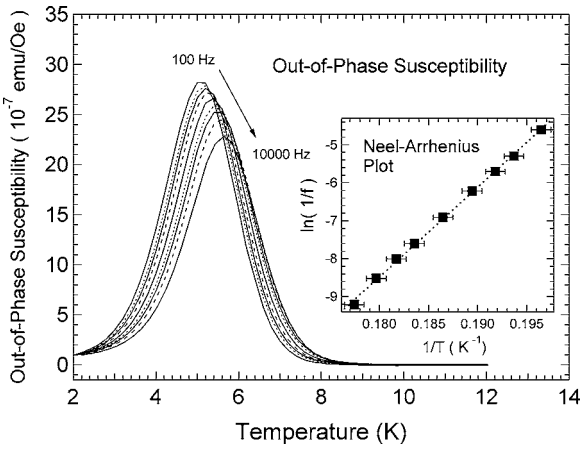

FIG. 2. The imaginary parts of the ac susceptibility of Co_3O_4 in LDps. The data shows multiple frequency curves taken from 100 to 10 000 Hz. Solid and dashed lines alternate between the different frequency curves. The inset shows the Néel-Arrhenius plot from which the properties are extracted.

structure in the L_3 cobalt edge is consistent with Co_3O_4.[21] For comparison, the $L_{2,3}$ XAS spectra for a bulk sample Co_3O_4, obtained from Sigma-Aldrich, is also shown. The small differences in the nanoparticle's spectrum compared to the bulk's may be due to the sudden termination of the Co_3O_4 structure on the surface. Since transmission XAS probes equally over all Co atoms, the sample is almost entirely Co_3O_4.

ac and dc magnetometry measurements were performed on 3.5 mg of dried out Co_3O_4 mineralized cages, immobilized with epoxy into a small pellet form, with the alternating current magnetic susceptometer (ACMS) and vibrating sample magnetometer (VSM) options for the Quantum Design physical properties measurement system. The ac magnetometry measurements were taken at 100, 200, 300, 500, 1000, 2000, 3000, 5000, and 10 000 Hz with an oscillation amplitude of 10 Oe, while being cooled in a zero dc field down to 2 K. The dc magnetometry measurements shown in this study were taken between 0 and 8 T at several temperatures between 2 and 15 K.

III. RESULTS AND DISCUSSION

Antiferromagnetic Co_3O_4 nanoparticles of the size used in this study are thought to possess single domains with small moments that have a collective superparamagnetic behavior. The Co_3O_4 nanoparticle moments are ascribed to uncompensated spins, which are attributed to structural inhomogeneities, defects, and finite size effects. For superparamagnetic particles thermal fluctuations flip the magnetization between two states along the anisotropy axis by overcoming an anisotropy energy barrier. The relaxation time, τ, between the two states is given by[22]

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right), \tag{1}$$

where τ_0 is the attempt time of the material, E_a is the anisotropy energy, k_B is Boltzmann's constant, and T is the temperature of the particle. There is typically a broad peak in the ac susceptibility, which is associated with the blocking temperature, T_B. Taking the log of Eq. (1) gives the Néel–Arrhenius relation, which has worked well for protein-encapsulated nanoparticles:[23]

$$\ln\left(\frac{1}{f}\right) = \ln\left(\frac{1}{\Gamma_0}\right) + \left(\frac{E_a}{k_b}\right)\left(\frac{1}{T_B}\right), \tag{2}$$

where f is the measurement frequency of the oscillating ac field, and $\Gamma_0 = \langle \tau_0^{-1} \rangle$ is the attempt frequency. Figure 2 shows the imaginary parts to the ac susceptibility at the different frequencies. The peaks shift down and to the right as the frequency increases, corresponding to higher extracted blocking temperatures for higher frequencies, a characteristic superparamagnetic behavior. By fitting the peak in the imaginary or out-of-phase susceptibility, we determine that the superparamagnetic blocking temperature of these particles at 1000 Hz is roughly 5.4 K.

Plotting the blocking temperatures with frequency, the anisotropy energy and attempt frequency can be determined from a Néel-Arrhenius plot. The insert in Fig. 2 shows this plot for the out-of-phase component of the ac susceptibility. E_a and Γ_0 were determined to be 3.3×10^{-21} J and 1.4×10^{23} Hz, respectively. E_a is the product of the anisotropy energy density, K, and the volume of the particles, V, which are taken to be spherical. Using an average diameter, determined by TEM to be 4.34 nm, the anisotropy energy density for the Co_3O_4 nanoparticles is $(7.6 \pm 0.4) \times 10^4$ J/m^3. This is slightly below the reported value of the anisotropy energy density of 9×10^4 J/m^3 measured on 3 nm Co_3O_4 nanoparticles with a SQUID magnetometer.[24] However, a difference in the anisotropy energy density is not unexpected since the affect of a reduced size on a magnetic material should enhance its anisotropy.[25,26]

Figure 3 shows initial magnetization curves of the Co_3O_4 nanoparticles from 2 to 30 K. The data was well fit to a simple Langevin model with an added offset and linear susceptibility term given by

$$m = m_R + m_s L(x) + \chi H, \tag{3}$$

where m is the measured magnetic moment of the sample, m_R is taken to represent the remnant moment, m_s is the saturation moment of the sample, χ is the linear susceptibility

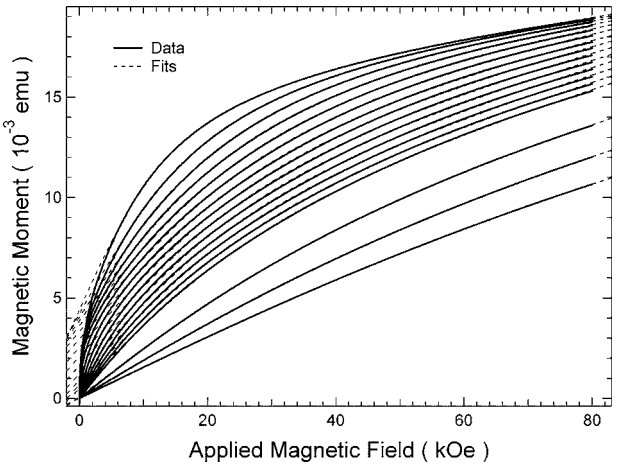

FIG. 3. Initial magnetization curves from 2 to 30 K. The magnetic properties are extracted by fitting the model to these curves above 5 kOe. The model fits very well and the fits are shown with dashed lines.

attributed to the antiferromagnetic nature and spin canting of the material, and

$$L(x) = \coth(x) - \frac{1}{x} \tag{4}$$

is the Langevin function, where $x = \mu H / k_B T$. μ is the magnetic moment of a single particle, H is the external applied magnetic field, k_B is Boltzmann's constant, and T is the temperature of the sample.

Figure 4 shows the susceptibility extracted from the fits. The peak in the susceptibility suggest a Néel temperature of 15 ± 2 K. This is significantly lower than the reported values for bulk Co_3O_4 (40 K),[23] for 20 nm Co_3O_4 particles (>25 K),[27] and for 8 nm particles (30 K).[28] The significantly lower Néel temperature can be accounted for by the effect of finite-size scaling that has been thought to change the critical ordering temperatures of both ferro- and antiferromagnetic nanoparticles[29] and thin films.[30] Quantitatively finite-size scaling can account for this reduction by using a characteristic length scale of roughly 2.6 nm and a correlation length

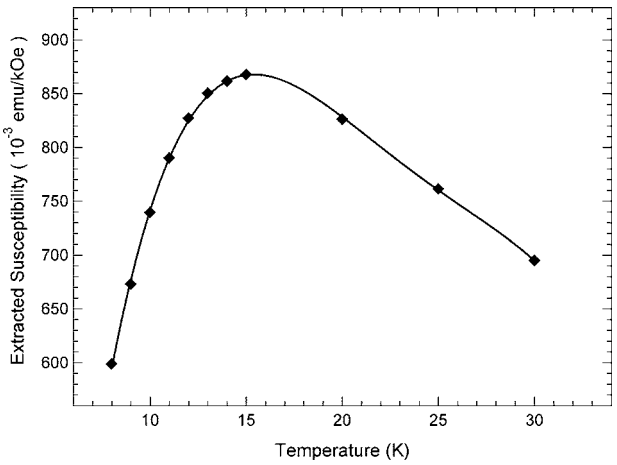

FIG. 4. The extracted susceptibility at different temperatures is shown. The 15 K peak is taken to be T_N. The solid line is a guide to the eye.

exponent of 0.8 in the finite-size scaling model. These values are similar to values found in other reduced systems.[29,30]

IV. CONCLUSION

Both an elevated anisotropy energy density and a lower Néel temperature point to surface or finite-size effects playing a major role in the magnetism of these antiferromagnetic Co_3O_4 nanoparticles. Further studies of the finite-size and surfaces effects on a multiple assortment of different size Co_3O_4 nanoparticles is needed in order to further probe and understand these interesting effects.

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