Surface Spin Disorder in $NiFe_2O_4$ Nanoparticles

R. H. Kodama and A. E. Berkowitz
Physics Department, University of California at San Diego, La Jolla, California 92093

E. J. McNiff, Jr. and S. Foner
Francis Bitter National Magnet Laboratory, Cambridge, Massachusetts 02139
(Received 6 February 1996)

Nickel ferrite nanoparticles exhibit anomalous magnetic properties at low temperatures: low magnetization with a large differential susceptibility at high fields, hysteresis loops which are open up to 160 kOe, time-dependent magnetization in 70 kOe applied field, and shifted hysteresis loops after field cooling. We propose a model of the magnetization within these particles consisting of ferrimagnetically aligned core spins and a spin-glass-like surface layer. We find that qualitative features of this model are reproduced by a numerical calculation of the spin distribution. Implications of this model for possible macroscopic quantum tunneling in these materials are discussed. [S0031-9007(96)00628-X]

PACS numbers: 75.50.Tt, 75.30.Pd, 75.50.Gg, 75.50.Lk

Magnetic properties of nanoparticles are of great current interest, stemming in part from the development of high density magnetic storage media with nanosized constituent particles or crystallites. Spontaneous magnetization reversal in such particles is of particular interest, since this determines the stability of stored information and limits the ultimate storage density. As such, particles of magnetic oxides such as γ-Fe_2O_3 and ferritin have been the subject of basic studies of magnetic relaxation [1–4]. The present study points to surface spin disorder as an important factor in the relaxation behavior of magnetic oxide particles. Experimental evidence for surface spin disorder has been reported in several previous studies. Spin canting in ball-milled $NiFe_2O_4$ [5,6] and chemically precipitated γ-Fe_2O_3 [7] was demonstrated via Mössbauer spectroscopy as a mechanism for moment reduction. The initial study [5,6] of ball-milled ferrites additionally noted shifted hysteresis loops, and proposed "spin pinning" due to an organic surfactant coating. Recent polarized neutron scattering experiments on ball-milled $CoFe_2O_4$ particles were consistent with a core of aligned spins surrounded by a magnetically disordered shell [8]. Similar conclusions were made from a Mössbauer study of chemically precipitated $NiFe_2O_4$ particles [9]. The present results on ball-milled $NiFe_2O_4$ are also consistent with spin canting. We propose that the canted spins are in a surface layer and that they freeze into a spin-glass-like phase at temperatures below 50 K. Thus, the surface spins have multiple configurations for any orientation of the core magnetization. This model accounts for previously reported anomalous behavior, as well as the remarkable irreversibility and time-dependent moment in high fields that we report here. The model also provides an alternative to macroscopic quantum tunneling (MQT) for interpretation of our magnetization relaxation measurements at low temperatures [10].

There are several compelling reasons to expect surface spin disorder in ferrite nanoparticles. The superexchange interaction between the magnetic cations is antiferromagnetic. Bulk ferrimagnetic order arises since the intersublattice exchange is stronger than the intrasublattice exchange. Variations in coordination of surface cations result in a distribution of net exchange fields, both positive and negative with respect to a cation's sublattice. Since the interaction is mediated by an intervening oxygen ion, exchange bonds are broken if an oxygen ion is missing from the surface. Additionally, if organic molecules are bonded to the surface, the electrons involved can no longer participate in the superexchange. Both types of broken exchange bonds will further reduce the effective coordination of the surface cations. Our calculations show that broken exchange bonds are sufficient to induce surface spin disorder [11]. Finally, the superexchange is very sensitive to bond angles and lengths, which would likely be modified near the surface.

The fine particle samples were produced by grinding coarse powders of high purity $NiFe_2O_4$ in kerosene and oleic acid (organic surfactant). It was found that the oleic acid is strongly bonded to the surface, and could not be removed by chemical means. The average particle size as determined from x-ray diffraction line breadths was 65 Å. High resolution transmission electron microscopy studies on an identically prepared $CoFe_2O_4$ sample showed that the cubic spinel structure was preserved and that the particles are, for the most part, equiaxed single crystals [12].

High field magnetization measurements (0–200 kOe) were made using a water-cooled Bitter magnet with a vibrating sample magnetometer. Lower field measurements were made with a commercial SQUID magnetometer (0–70 kOe, 5–300 K). Corrections were made in the magnetization data for the surfactant and contaminant from the ball mill (see Ref. [6] for details). Samples are dry powders, immobilized in paraffin. The interparticle separation due to the surfactant coating is estimated to be 20 Å. Dipolar interaction fields are estimated to be <200 Oe. Figure 1

 0031-9007/96/77(2)/394(4)$10.00 © 1996 The American Physical Society

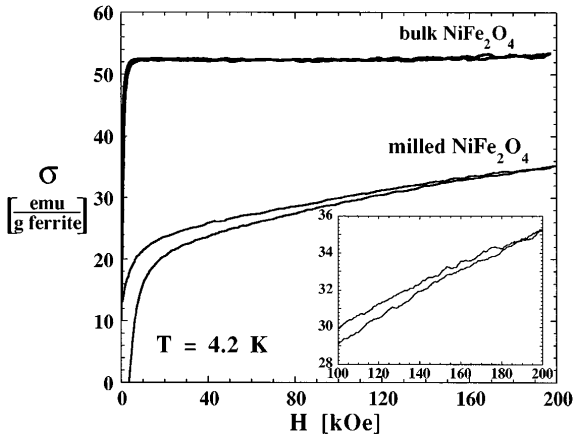

FIG. 1. ZFC magnetization hysteresis loops at 4.2 K for bulk and milled ($\langle D \rangle = 65$ Å) samples. Inset is the milled sample moment.

shows the first quadrant of magnetization hysteresis loops for the nanoparticles and for bulk $NiFe_2O_4$ measured at 4.2 K. The loop for the nanoparticles is open, with positive and negative field sweeps separated, up to approximately 160 kOe. This separation implies that some of the magnetic spins have a "switching field" of 160 kOe. Figure 2 shows moment vs temperature in 70 kOe applied field, in field cooled (FC) and zero field cooled (ZFC) states. This measurement cannot be directly compared to "conventional" FC and ZFC measurements on, e.g., spin glasses, done in a much lower field, typically <100 Oe. The separation between FC and ZFC curves indicates a nonequilibrium magnetization state below 50 K for the ZFC case. The FC-ZFC separation in 70 kOe and the open loop at 160 kOe can be described as "high field irreversibility." This irreversibility is remarkable for $NiFe_2O_4$ which has a bulk magnetocrystalline anisotropy field of only 400 Oe. We also find a hysteresis loop shift in the FC state which decreases with increasing temperature and vanishes near 50 K. We associate the onset of the loop shift and high field irreversibility at about 50 K with a "freezing" of disordered surface spins.

Magnetic moment vs time measurements were made by first cooling in zero field, then ramping the applied field to $+70$ kOe at 10 kOe per minute and then measuring every 30 s for 5000 s, ramping the field to -70 kOe, and measuring again for 5000 s. Finally, the field was ramped back to $+70$ kOe and measured again for 5000 s. A -0.03% instrumental background drift with time was determined using Ni and Gd_2O_3 standards. This background was 10% of the change in sample moment, and had the opposite sign. Figure 3 shows moment vs total elapsed time during this procedure. Absolute values of the moment are plotted on an expanded scale in order to compare $+70$ and -70 kOe curves. We note an upward creep in the moment. Also, subsequent iterations with positive and negative fields result in continually higher values of magnetization. The moment in $+70$ kOe was also taken after field cooling as rapidly as possible (1400 s) from 100 to 5 K (not shown). In that case the moment was constant with time, indicating that field cooling establishes an equilibrium magnetization state.

Sufficiently small magnetic particles are usually single domains, with atomic spins completely aligned by exchange interactions. The rotational barriers due to magnetocrystalline, magnetoelastic, and shape anisotropy can trap particles in two or more metastable orientations, giving rise to hysteresis. The persistence of hysteresis up to 160 kOe could be interpreted as resulting from anisotropy fields of 160 kOe. However, this is 400 times larger than the bulk magnetocrystalline anisotropy field. Our observation of shifted hysteresis loops suggests that the surface spins are spin-glass-like, having multiple configurations that become frozen below 50 K. Because of the exchange coupling between the surface and core spins, field cooling can select a surface spin configuration which favors the particle being magnetized in the field cooling direction, hence resulting in a shifted hysteresis loop below 50 K. The field required to force transitions between surface spin configurations can be very large since the exchange fields are approximately 5×10^6 Oe. Therefore,

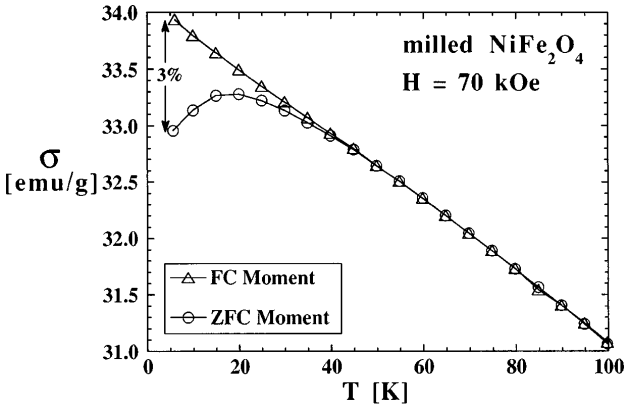

FIG. 2. ZFC and FC moment in 70 kOe applied field vs temperature. Lines are guides to the eye.

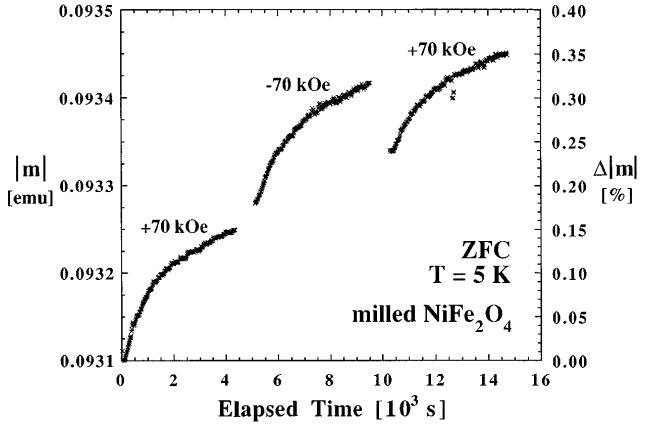

FIG. 3. Absolute value of ZFC moment vs time in $+70$, -70, and $+70$ kOe sequentially applied fields.

our interpretation is that the open hysteresis loop at high field is the result of irreversible changes between these surface spin configurations rather than reversals of particle magnetization as a whole. A 65 Å ferrite particle has 26% surface cations, so it is reasonable that the 3% change in moment upon field cooling (Fig. 2) arises from changes in the surface spin configuration.

Time-dependent magnetization of a fine particle system is usually modeled in terms of thermal activation of particles with two stable magnetization states. Within our surface spin disorder model, time-dependent magnetization may not *only* be due to particles reversing their orientation of magnetization, but also result from transitions between surface spin configurations. We attribute the measured time-dependent magnetization in 70 kOe to thermally activated transitions between these surface spin states. These transitions can involve a small fraction of the spins, so the activation energy is not proportional to the particle volume. This has significance in interpreting our recent measurements of the time decay of remanent magnetization for a similar $NiFe_2O_4$ sample [10]. We observed a temperature-independent viscosity parameter from 2.0 down to 0.4 K. Such a crossover into a temperature-independent regime is predicted for MQT of single domain particles [13]; however, it also has been shown that a distribution of energy barriers $n(E) \sim 1/E$ gives crossover behavior for thermal activation [14]. This type of barrier distribution is not consistent with single domain particles, but it *is* consistent with a spin-glass-like collection of surface spins, as demonstrated below.

A numerical model was developed to calculate the spin distribution within small $NiFe_2O_4$ particles and the energy barriers between surface spin states. The model assumptions were: (1) exchange constants derived from a mean field analysis of magnetization and Mössbauer data [15], (2) classical spins in an inverse spinel structure, (3) no anisotropy or dipolar interactions, and (4) a fraction of broken exchange bonds between surface spins (80% for the example below), with exchange bonds between surface and core spins unaffected. The algorithm used to calculate the equilibrium spin configurations was a three-dimensional generalization of one developed by Hughes [16]. The expression used for the total energy was

$$E = -\sum_{i}^{\{\text{all spins}\}} g_i \mu_B \hat{\mathbf{S}}_i \cdot \left[\vec{\mathbf{H}} + \frac{1}{2} \sum_{j}^{\text{n.n.}} \frac{2 J_{ij} S_j}{g_i \mu_B} \hat{\mathbf{S}}_j \right],$$

where $g_i \mu_B S_i$ is the magnitude of the ionic moment and the unit vector $\hat{\mathbf{S}}_i$ gives its direction. The second summation is over first and second nearest neighbors. The exchange constants [15] are the following (in units of K):

$$J_{AA} = -21.0, \quad J_{AB} = -36.0, \quad J_{AB'} = -28.1,$$
$$J_{BB} = -22.0, \quad J_{BB'} = +2.0, \quad J_{B'B'} = -8.6,$$

where $A = (Fe^{3+}$, tetrahedral site), $B = (Ni^{2+}$, octahedral site), $B' = (Fe^{3+}$, octahedral site). We define the spin unit vector as a function of (α_i, β_i) which corresponds to rotations in two orthogonal directions,

$$\hat{\mathbf{S}}_i(\alpha_i, \beta_i) = \frac{\hat{\mathbf{S}}_{0i} + \alpha_i \hat{\mathbf{e}}_{\alpha i} + \beta_i \hat{\mathbf{e}}_{\beta i}}{\sqrt{1 + \alpha_i^2 + \beta_i^2}},$$

where $\hat{\mathbf{S}}_{0i}$ is the initial spin direction and $\hat{\mathbf{e}}_{\alpha i}$ and $\hat{\mathbf{e}}_{\beta i}$ are chosen to make $(\hat{\mathbf{e}}_{\alpha i}, \hat{\mathbf{e}}_{\beta i}, \hat{\mathbf{S}}_{0i})$ a mutually orthogonal set. This choice of coordinates gives the following expressions for the derivatives of E (evaluated at $\alpha_i = \beta_i = 0$):

$$\frac{\partial E}{\partial \alpha_i} = -g_i \mu_B S_i \hat{\mathbf{e}}_{\alpha i} \cdot \vec{\mathbf{H}}_{\text{eff},i},$$

$$\vec{\mathbf{H}}_{\text{eff},i} = \vec{\mathbf{H}} + \sum_{j}^{\text{n.n.}} \frac{2 J_{ij} S_j}{g_i \mu_B} \hat{\mathbf{S}}_j,$$

$$\frac{\partial^2 E}{\partial \alpha_j \partial \alpha_i} = \begin{cases} +g_i \mu_B S_i \hat{\mathbf{S}}_{0i} \cdot \vec{\mathbf{H}}_{\text{eff},i}, & i = j, \\ -2 J_{ij} S_i S_j \hat{\mathbf{e}}_{\alpha i} \cdot \hat{\mathbf{e}}_{\alpha j}, & i \neq j. \end{cases}$$

Once the derivatives are known, the application of the conjugate directions method [16] is straightforward. Figure 4 shows a calculated spin configuration for a (111) cross section of a 25 Å $NiFe_2O_4$ particle (310 spins). This is smaller than the measured particles, but illustrates the general features we have proposed. We note that some of the surface spins are completely reversed from their normal orientation. The highly misoriented spins are indicated by dashed circles. Figure 5 shows the calculated net moment M (normalized to the aligned state, M_A) vs field at zero temperature for a 25 Å particle. Also shown is the magnetic order parameter (MOP), defined as the sum of the absolute magnitudes of each sublattice magnetization, normalized to the aligned state. The MOP gives a measure of the degree of spin alignment. The MOP is relatively insensitive to applied field, since the field increases one sublattice magnetization and decreases the other. Figure 6 shows a distribution of activation energies associated

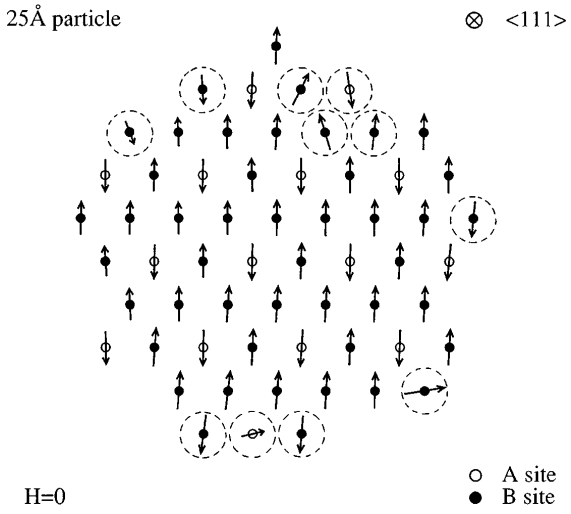

FIG. 4. Calculated spin configuration at $H = 0$ for a cross section of a 25 Å particle. Highly misoriented spins are circled.

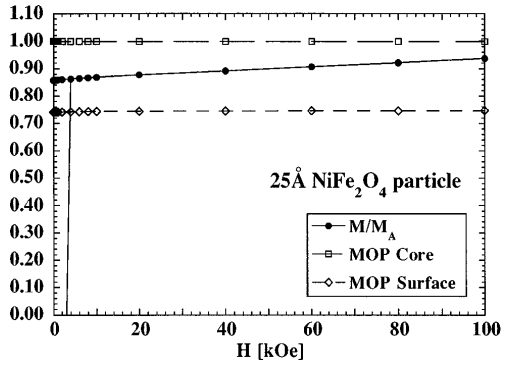

FIG. 5. Calculated moment and magnetic order parameter (as defined in the text) vs field for a 25 Å particle.

with the spin configurations of a 25 Å particle. States are found by perturbing an initial configuration with a random set of rotations. Each new state is tested for stability by applying a perturbation 3 times and checking that every time it converges back to the same state ($|\Delta\hat{\mathbf{S}}_i| < 0.02$). The "activation energy" is the perturbation required to put the particle in a different state. The dashed curve is a fit to $1/E$, implying that thermally activated relaxation of this system would be temperature independent at low temperatures [14].

In summary, we have observed high field irreversibility in the moment versus field and moment versus temperature of $NiFe_2O_4$ nanoparticles. The onset temperature of this irreversibility is near 50 K. It was previously established that there is spin canting in these particles. The appearance of shifted hysteresis loops leads us to propose that the canted spins are on the particle surfaces and have multiple stable configurations, one of which is selected by field cooling. We additionally propose that the open hysteresis loops and time-dependent moment are due to transitions between surface spin configurations, rather than magnetization reversals of whole particles. Our numerical model demonstrates the potential for surface spin disorder, arising from reduced coordination and broken exchange bonds between surface spins. Calculation of the energy barrier distribution between surface spin states is consistent with $n(E) \sim 1/E$ which has been shown to produce a *thermally activated* temperature-independent viscosity. Thus, a temperature-independent viscosity is not necessarily an indicator of MQT in fine particle systems where spin disorder is present.

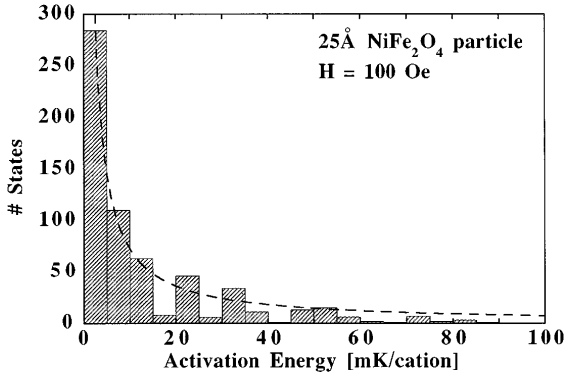

FIG. 6. Calculated activation energy distribution for a 25 Å particle. Dashed curve is a fit by a $1/E$ distribution.

This work was supported in part by the MRSEC Program of the NSF under Award No. DMR-9400439. The FBNML is supported by the NSF.

[1] E. Vincent, J. Hammann, P. Prené, and E. Tronc, J. Phys. I (France) **4**, 273 (1994).
[2] S. Mørup and E. Tronc, Phys. Rev. Lett. **72**, 3278 (1994).
[3] D. P. E. Dickson *et al.*, J. Magn. Magn. Mater. **125**, 345 (1993).
[4] D. D. Awschalom, J. F. Smyth, G. Grinstein, D. P. DiVincenzo, and D. Loss, Phys. Rev. Lett. **68**, 3092 (1992).
[5] A. E. Berkowitz, J. A. Lahut, I. S. Jacobs, L. M. Levinson, and D. W. Forester, Phys. Rev. Lett. **34**, 594 (1975).
[6] A. E. Berkowitz, J. A. Lahut, and C. E. VanBuren, IEEE Trans. Magn. **MAG-16**, 184 (1980).
[7] J. M. D. Coey, Phys. Rev. Lett. **27**, 1140 (1971).
[8] D. Lin, A. C. Nunes, C. F. Majkrzak, and A. E. Berkowitz, J. Magn. Magn. Mater. **145**, 343 (1995).
[9] A. H. Morrish and K. Haneda, J. Appl. Phys. **52**, 2496 (1981).
[10] R. H. Kodama, C. L. Seaman, A. E. Berkowitz, and M. B. Maple, J. Appl. Phys. **75**, 5639 (1994).
[11] "Broken exchange bonds" is distinct from the idea of "spin pinning" proposed in the initial study [5]. Our recent measurements on a sample milled without surfactant show all the same anomalous effects, differing quantitatively by less than a factor of 2. In conjunction with the results of our calculation, this leads us to believe that chemical species other than surfactants can bind to surface ions and break exchange bonds. Surfactant removal by heating as performed in the initial study incurs the possibility of sintering and surface oxidation, which can act to decrease the surface area and "heal" the broken bonds, thus reducing the surface spin disorder.
[12] A. C. Nunes, E. L. Hall, and A. E. Berkowitz, J. Appl. Phys. **63**, 5181 (1988).
[13] E. M. Chudnovsky and L. Gunther, Phys. Rev. Lett. **60**, 661 (1988).
[14] B. Barbara *et al.*, in *Studies of Magnetic Properties of Fine Particles*, edited by J. L. Dormann and D. Fiorani (Elsevier Science Publishers, New York, 1992), p. 235.
[15] A. A. Sidorov, V. P. Suetin, and V. G. Pokazan'ev, *IAdernyi rezonans v tverdofaznykh soedineniiakh d-metallov* (UNTs AN SSSR, Sverdlovsk, 1984), pp. 21–31.
[16] G. F. Hughes, J. Appl. Phys. **54**, 5306 (1983).