BNL 32685

Conf-830619--1

February 1983

BNL--32685

DE83 010015

Polarized Neutron Study of the Magnetization Density Distribution Within a $CoFe_2O_4$ Colloidal Particle (Magnetization Density in a Colloidal $CoFe_2O_4$ Crystallite).

A. C. Nunes

C. F. Majkrzak

A. E. Berkowitz

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

The submitted manuscript has been authored under contract DE-AC02-76CH00016 with the Division of Basic Energy Sciences, U.S. Department of Energy.
Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Submitted to the

THIRD INTERNATIONAL CONFERENCE
ON
MAGNETIC FLUIDS

28-30 June 1983

POLARIZED NEUTRON STUDY OF THE MAGNETIZATION DENSITY DISTRIBUTION WITHIN A $CoFe_2O_4$ COLLOIDAL PARTICLE*

(MAGNETIZATION DENSITY IN A COLLOIDAL $CoFe_2O_4$ CRYSTALLITE)

A.C. Nunes, C.F. Majkrzak, A.E. Berkowitz†

KEY WORDS: Neutron, $CoFe_2O_4$, particle

*Work supported by (ACN) NSF Grant DMR-8024662; (CFM) DOE Contract DE-AC02-76CH00016; (AEB) ONRL Contract N00014-81-C-0751

†A.C. Nunes, Physics Dept., University of Rhode Island, Kingston, RI 02881, USA.
C.F. Majkrzak, Physics Dept. Brookhaven Nat. Lab., Upton, NY 11973, USA
A.E. Berkowitz, G.E. Corporate Research Laboratory, Schenectady, NY 12301, USA

ABSTRACT

Magnetization and Mössbauer data suggest that a magnetically anomalous region exists within finely divided $CoFe_2O_4$ particles when coated with oleic acid [1]. We have undertaken an x-ray and a polarized neutron powder diffraction study of these samples with and without the surfactant coating in an attempt to locate and characterize this anomalous zone. The shape of neutron scans of the (4,0,0) reflection are independent of polarization indicating that the reflecting crystallites are uniformly magnetized. Magnetization calculated from the peak flipping ratio is characteristic of uncoated rather than coated particles in both cases. Scan widths of both x-rays and neutrons are narrower for the sample from which the chemisorbed surfactant has been largely removed indicating an increase in the size of the coherent lattice of a crystallite. These observations are consistent with the existence of a highly strained surface layer roughly 10 Angstroms thick characterized by pinned spins associated with the presence of oleic acid, which relaxes to a more normal lattice structure upon boiling off the surfactant.

I. INTRODUCTION

We wish to present preliminary findings of an investigation into the magnetization density distribution within very finely divided $CoFe_2O_4$ particles (diameter $\sim$ 100 Å) employing x-ray and polarized neutron powder diffraction line shape analysis. Berkowitz, et al. [1] report magnetization and Mössbauer data taken on these samples which suggests that a magnetically anomolous region exists within the particles when coated with a chemisorbed surfactant, oleic acid. This anomalous region, presumed to exist at the ferrite-surfactant interface, may comprise nearly half of the ferrite volume of the particle and is characterized by pinning of the spins. These "pinned spins" are still present, but are unable to follow an externally applied field (up to 68 KOe!). In the present work, we investigate the magnetization density distribution within and crystallite size of the ferrite particles with the surfactant intact, and after having driven off much of the surfactant by heating. Through this, we gain further insight into the atomic events which give rise to the observed magnetic behavior.

Two questions are addressed here. First, is the magnetically anomolous behavior localized at the particle-surfactant interface or is the entire volume of the particle somehow affected? Second, to what extent is the crystal structure of the ferrite modified by the presence of the surfactant?

II. METHOD

We are employing polarized neutron powder line shape analysis to determine the radial distribution of the magnetization density within a tiny magnetic particle. To our knowledge, this is the first such study and so deserves some elucidation.

Consider an unstrained spherical crystal of radius R. It can be shown [2] that the intensity scattered at an angle $\delta\theta$ from a Bragg reflection (scattering angle = $2\theta_o$) will be proportional to

$$I(q) = (F(h,k,\ell)G(R,q))^2 \qquad (1)$$

where $F(h,k,\ell)$ is the structure factor associated with the Bragg reflection identified by the Miller indices h,k, and ℓ. $G(R,q)$ is the spherical Bessel function given by

$$G(r,q) = 4\pi R^3\left(\frac{\sin Rq}{(Rq)^3} - \frac{\cos Rq}{(Rq)^2}\right) \qquad (2)$$

and

$$q = \frac{4\pi(\sin(\theta_o+\delta\theta) - \sin\theta_o)}{\lambda} \qquad (3)$$

When plotted I(q) is approximately a Gaussian whose width Δq is inversly proportional to R; thus from Δq (the powder line width corrected for instrumental broadening) one can determine the size of the crystallite in Angstroms from

$$R = 3.652/\Delta q \qquad (4)$$

where Δq is the full width at half maximum of I(q) expressed in $\mathring{A}^{-1}$.

If the particles are ferromagneric, and polarized perpendicular to the scattering plane, and the incident neutrons are also polarized parallel (+) or antiparallel (-) to the sample magnetization, the structure factor becomes the sum of magnetic $\pm F_M$ and a nuclear F_N parts [3]

$$F(h,k,\ell) = F_N(h,k,\ell) \pm F_M(h,k,\ell). \qquad (5)$$

If the magnetization is evely distributed throughout the crystal, then the magnitude only, not the width of I(q), will vary with the neutron polarization state (sign of F_M). If the magnetization is restricted to a spherical core, leaving a non magnetic spherical shell of thickness ΔR then Eqn. (1) becomes

$$I(q) = [(F_N \pm F_M)G(R-\Delta R,q) + F_N(G(R,q) - G(R-\Delta R,q))]^2 \qquad (6)$$

which simplifies to

$$I(q) = (F_N G(R,q) \pm F_M G(R-\Delta R,q))^2 \qquad (7)$$

This is also true if the outer layer is paramagnetic or composed of randomly oriented pinned spins, in which case there will be magnetic scattering from the shell, but it will be incoherent and will not contribute to the Bragg intensity. Note that now not only the magnitude but also the shape of I(q) is dependent on the sign of the neutron polarization. If R is 50 Angstroms and ΔR is 10 Å, using nuclear and magnetic structure factors determined by Prince [4] one finds that the width of the (4,0,0) reflection of $CoFe_2O_4$ (for which $|F_M| \simeq |F_N|$) should vary by more than 10% with a change in neutron polarization. Also the integral flipping ratio, given by

$$\mathcal{R}(h,k,\ell) = \frac{\int I_+(q)dq}{\int I_-(q)dq} \qquad (8)$$

will be approximately 6 as opposed to $\mathcal{R}_o(4,0,0) = 97$ for a uniformly magnetized sample. The fraction specific magnetization of the particle (total magnetization relative to the saturation value) is found from

$$M = \frac{F_N}{F_M}\left[\frac{\mathcal{R}_o+1\pm2\sqrt{\mathcal{R}}}{\mathcal{R}-1}\right] \qquad (9)$$

Eqn. (9) has two solutions and one must choose the most physically sensible.

It should be noted that if one replaces the structure factor with a scattering density, and performs the experiment at $(h,k,\ell) = (0,0,0)$ all formulae remain otherwise unchanged, however, the experiment is often called "small angle" rather than powder scattering. Magnetic small angle scattering experiments have been reported on nickel [5] and cobalt [6], however interparticle interference terms can be very important, especially

if chaining or particle agglomeration is significant [7,8] and cannot be ignored. Interparticle interference is usually unimportant in Bragg scattering, as the very stringent lattice coherence requirement between two particles for such interference in a powder reflection renders the probability of such events extremely small.

Additional complications are introduced in the real world by the fact that the particles are not perfectly spherical nor monodispersed. Electron micrographs [1] show particle images which are irregular but approximately spherical. This has the effect of altering the constant in equation (4) by at most a few percent (see particle shape dependence of the Scherrer constant, Table X.1, James [2]). Electron micrographs also show the particle size to be log normally distributed [9]

$$P(R) = N_o e^{-\frac{1}{2}\left[\frac{\ell nR-\ell nR_o}{\ell n\sigma}\right]^2} \tag{10}$$

with approximate parameters $R_o \sim 50$ Å, $\ell n\sigma \gtrsim 0.2$. To include this quantity, equation (7) becomes

$$I(q) = \int_{R=0}^{\infty} (F_N G(R) \pm FMG(R-\Delta R))^2 P(R)dR \tag{11}$$

The effect of properly including P(R) is to change the constant of equation (4) from 3.65 to 2.71 and to increase the sample flipping ratio (to ∿10). However, the magnitude of the change in Δq with neutron polarization is little altered.

Therefore, from measurements of $I_+(q)$ and $I_-(q)$ for certain powder reflections, one should be able to determine sample magnetization (as a fraction of the saturation value given by Eqn. (9) and, from the polarization dependent widths Δq_+ and Δq_-, determine R and ΔR of the particle.

III. SAMPLE PREPARATION

Samples were prepared by prolonged grinding in a ball mill in kerosene and oleic acid, followed by centrifugation and washing as described in reference [1]. Chemical analysis reveals contaminants from the mill and mill balls are present [1]. In seeking evidence of these contaminants in x-ray powder patterns of two samples, one $CoFe_2O_4$ and the other MgO (both prepared in the same way), we found none. We conclude that the contaminants do not contribute significantly to the observed Bragg peaks, but rather to the background scatter.

After grinding and centrifuging at 17 Kg's for 20 minutes, the suspended material remaining was dried and washed with methylene chloride leaving particles coated with one to two monolayers of oleic acid [1]. A portion of this was then heated in air for 10 minutes at 300 °C, which removed more than 80% of the remaining surfactant.

IV. SCATTERING EXPERIMENTS

Polarized neutron scattering experiments were performed at the High Flux Beam Reactor at Brookhaven National Laboratory. The monochromator was a bent pyrolytic graphite crystal. Polarization analysis of the scattered beam was performed with a heusler alloy crystal analyser. The instrumental flipping ratio was measured to be 41 with a Heusler crystal as sample. The sample was mounted in a flat aluminum sample holder in a 4.5 KOe field perpendicular to the scattering plane. No depolarization of the beam transmitted through the sample could be detected in a separate measurement employing a Heusler monochromator as well as a Heusler analyser crystal.

X-ray powder data was taken on a θ-2θ diffactometer at the University of Rhode Island. The results of both neutron and x-ray scans of the (4,0,0) reflection of $CoFe_2O_4$ are summarized in Table 1. Peak widths Δq have been corrected for instrument resolution.

SAMPLE	NEUTRON-SAMPLE POLARIZATION	NEUTRON SCAN q WIDTH $\Delta q_N (\mathring{A}^{-1})$	FLIPPING RATIO R	% MAGNETIZATION M	X-RAY q WIDTH $\Delta q_x (\mathring{A}^{-1})$	PARTICLE RADIUS $R_o = \frac{2.71}{\Delta q_x} (\mathring{A})$
$CoFe_2O_4$ + Oleic Acid	↑ ↑	0.085±.003	3.4±0.3	(37±1)%	0.092±.003	29±1
	↑ ↓	0.085±.003				
$CoFe_2O_4$ after heating	↑ ↑	0.069±.001	3.8±0.1	(39±1)%	0.065±.001	42±0.6
	↑ ↓	0.070±.002				

Table 1. Summary of experimental results of polarized neutron and x-ray study of the (4,0,0) Bragg reflection of $CoFe_2O_4$ colloidal particles in a magnetic field or 4.5 KOe.

V. DISCUSSION

There are three striking features of these data. First, the percent magnetization of the ferrite derived from the flipping ratio is unchanged by boiling off the surfactant, and its value is approximately that derived from magnetization experiments on the uncoated particles (ref. [1]). Second, the neutron scan widths are, within statistics, polarization independent, indicating that the magnetization is uniformly distributed throughout the coherently scattering part of the crystallite. Third, the size of the coherently scattering region of the particle R_o is significantly increased by boiling off the surfactant. As it seems unlikely that annealing $CoFe_2O_4$ at 300 °C for 10 minutes can result in significant melting and recrystallization we tentatively interpret this apparent "particle growth" as a relaxing of a seriously strained surface back to normal ferrite lattice positions with the removal of the surfactant.

These observations and those of reference [1] are consistent with a model in which the chemisorption of oleic acid on the surface of $CoFe_2O_4$ causes spin pinning at the surface and simultaneously distorts the surface region of the ferrite such that those moleucles can no longer participate in the Bragg scattering from the crystallite. This surface layer is approximately 10 Å (∿ two molecules) thick. The percent magnetization of the inner unstrained region of the particle is lower than that measured for bulk $CoFe_2O_4$, and while it is consistent with magnetization measurements on very small particles this indicates that when even uncoated, no region of these tiny particles is truly "bulk like" in character.

In these respects, these results are similar to recently reported NMR studies of chemisorption on tiny platinum particles [10], leading to the questions: how large must a particle be to be "bulk like"? how

do material characteristics depend upon particle size? Is the surface of a large particle similar to that of a very small one, or is the curvature of the surface as, or more important than the simple density discontinuity? The need for more work, both theoretical and experimental is indicated.

REFERENCES

1. A.E. Berkowitz, J.A. Lahut and C.E. Van Buren, IEEE Trans. MAG-16 (1980), 184.

2. R.W. James, "The Optical Principles of the Diffraction of X-rays", Cornell University Press, Ithaca, NY, (1965), 528-540.

3. G.E. Bacon, "Neutron Diffraction", 2nd ed., Oxford, (1962), 179.

4. E. Prince, Phys. Rev., 102, No. 3, (1956), 674.

5. M. Sato and H. Hirakawa, J. Phys. Soc. Japan, 39, No. 6, (1975), 1467.

6. D.J. Cebula, S.W. Charles, and J. Popplewell, Colloid Polym. Sci., 259, (1981), 395.

7. D.A. Krueger, IEEE Trans. MAG-16, (1980), 251.

8. J.B. Hayter and R. Pynn, Phys. Rev. Lett., 49, No. 15, (1982), 1103.

9. G.F. Neilson, J. Appl. Cryst., 6, (1973), 386.

10. H.E. Rhodes, P.K. Wang, H.T. Stokes, C.P. Slichter and J.H. Sinfelt Phys. Rev. B26, No. 7 (1982), 3559.