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Field response of surface spins on Co-adsorbed γ-Fe_2O_3

F. T. Parker and A. E. Berkowitz
Center for Magnetic Recording Research, University of California, San Diego, La Jolla, California 92093-0401

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The Mössbauer effect has been employed to determine spin orientations at the surface and in the core of magnetic recording particles in applied fields. The samples consisted of a partially reduced γ-Fe_2O_3 (A), A coated with ^{57}Fe (B), B coated with Co (C), and a sample (D) obtained by coating A with natural Fe followed by Co. About one-half of the Mössbauer signal of samples B and C thus came from atoms on the surfaces of the particles. Samples C and D showed the strong enhancement of coercivity typical for Co-coated surfaces. In 60 kOe longitudinal applied field at 4.2 K, sample C showed much less canting than expected from the previously hypothesized random spin surface. First-quadrant moment versus field data obtained at 296 K were analyzed within the Stoner-Wohlfarth model to obtain anisotropy field distributions. Samples C and D showed nearly identical distribution parameters. The Mössbauer spectra of sample D and the surface-enriched sample C exhibited essentially the same canting in a 1.8-kOe transverse applied field at 296 K. The similarity of low-field anisotropy parameters and Mössbauer canting angles is again inconsistent with the random-spin surface-shell model. Using the experimental data, simple free-energy minimization calculations were done for a linear chain of ferrimagnetically coupled atoms in external fields applied along the hard axis. These show that a high-anisotropy Co shell will cause a parabolic dependence of sublattice spin angle versus position along the chain, with the maximum deviation from collinearity a few degrees, as observed. Coercivities calculated from the anisotropy field distributions assuming coherent rotation are only about 10% larger than experimental values. The Co coating reduces the hyperfine-field tailing found on the particulate surface. We report a Mössbauer spectrum characteristic of slightly reduced γ-Fe_2O_3.

INTRODUCTION

Co adsorption onto recording media particles of γ-Fe_2O_3 leads to large increases in coercivity (H_c). The large Co orbital moment results in a uniaxial magnetocrystalline anisotropy additive to the shape anisotropy,[1] but the mechanism whereby this is induced by the approximate monolayer of Co is unknown.[2] The Mössbauer effect in ^{57}Fe can be used to determine the characteristics of this layer, especially the differential response to applied magnetic field of the core versus the surface layer. The direct way is to coat the particles with the radioactive parent, ^{57}Co, and study the B-site characteristics.[3,4] The indirect method is employed here, with a thin enriched ^{57}Fe surface underlayer coated before the Co is adsorbed.

From the relative areas of the six lines in a magnetically split Mössbauer spectrum the angle (θ) between the hyperfine field or magnetic moment and the γ-ray propagation direction can be determined. For a single particle with a single moment direction, the polarization (p) is defined as $p=2\sin^2\theta/(1+\cos^2\theta)$.[5] The limits of p are 0, for moments along the propagation direction, and 2, for moments perpendicular to this direction. For applied fields along the propagation direction, most small-particle iron-containing oxides show moments canting away from the field direction,[6] even in fields much larger than the anisotropy fields. Since the canting increases as mean particle size decreases, a canted surface structure has been hypothesized. From results of experiments in which ^{57}Fe-coated γ-Fe_2O_3 showed an increased canting,[7] this hpypothesis was assumed validated, thus leading to a model with surface spins assumed random.[6]

Co-adsorbed γ-Fe_2O_3 is known to show high-field canting.[8] The high-anisotropy shell might be expected to increase the shell-core differential canting. In this paper, samples studied included a precursor of partially reduced γ-Fe_2O_3, and those prepared by coating the precursor with successive layers of natural or isotopically enriched Fe followed by Co coating. First, one sample is examined by Mössbauer spectroscopy at low temperature in large applied field. Then, Mössbauer data obtained in small field at 296 K are presented. To explain the differences in low-field moment angles, the anisotropy field parameters are needed. These are determined by first quadrant moment versus field data least-squares fits to log-normal anisotropy distributions within the Stoner-Wohlfarth[9] model. The results are then used to model the spin angle as a function of lattice position.

EXPERIMENTAL DETAILS

Partially reduced γ-Fe_2O_3 particles (about 250 Å diameter by 2000 Å) were coated in sequence by either natural Fe (^{nat}Fe, 2.2 at. % ^{57}Fe) or isotopically enriched ^{57}Fe (95 at. % ^{57}Fe), followed by a Co coating. The ^{57}Fe solution was prepared by acid dissolution of the metal. ^{nat}Fe and Co solutions were obtained from divalent sulfates. The Fe coatings (2 metal at. % Fe surface layer) were obtained at 100 °C for 2 h in a 3.6M NaOH solution, with all procedures involving Fe done under Ar. The Co coatings (initially 17 metal at. % Co) were done in basic solution in sealed stainless-steel containers at 105 °C for 22 h. The original sample will be denoted as sample A, sample B has the ^{57}Fe coating, sample C is the result of coating sample B with Co, and sample D is the product of Co on ^{nat}Fe on sample A. Magnetic separation of the cobalt-coated products yielded a nonmagnetic pink precipitate in addition to the magnetic materials. Chemical analysis of the separated sample D indicated 6 metal at. % Co. X-ray diffraction of the separated sample C showed no impurity phases. Mössbauer spectra were obtained on samples dispersed in benzophenone. Measurements in applied fields (H_a) were obtained either in a superconducting magnet Dewar, with the field along the γ-ray propagation direction (longitudinal) or in a 1.8-kOe field from a permanent magnet perpendicular to the γ-ray propagation direction (transverse). The isomer shift reference is Fe metal at 296 K. Magnetization measurements were obtained with a vibrating sample magnetometer on powders tightly wrapped in Ag foil.

MÖSSBAUER DATA FITTING PROCEDURES

Each spectrum was fit with a distribution $P(H)$ in magnetic hyperfine field (H). All subspectra had a common polarization, and all lines had pseudo-Lorentzian shapes with common exponent. The fits were slightly improved by allowing a small amount of preferential broadening in the outer subspectral lines, through addition of a fit term proportional to the distance of a line from the center of its subspectrum to the common half-width at half maximum (HWHM) parameter. Typically, a 10% relative increase of the outer lines HWHM was found. The height parameters of each line were renormalized to leave the area unchanged. For one particular subspectrum observed at 296 K, the linewidth parameter used was substantially different, as will be noted below.

For calculations with data obtained in 60-kOe applied field (parallel to the γ-ray propagation), the hyperfine fields and isomer shifts (IS) of the two most intense subspectra (denoted by "main") were free variables. The other subspectra in the fits (denoted by "tail") were on two fixed distributions beginning 26 kOe above and below the field H for each main subspectrum. The IS of the tail subspectra were set equal to those of the corresponding main subspectra. For correcting saturation, the main subspectra 1-6 line intensities were scaled by a separate free fit variable, about 0.95. These outer lines thus do not enter directly into calculation of p.

For spectra obtained in $H_a = 1.8$ kOe transverse, the tailing subspectra were placed on a single distribution in H beginning 26 kOe above and below the values obtained for the highest H and lowest H main subspectra, respectively. The IS of these tailing subspectra were fixed at the weighted average obtained for the main subspectra. To account for saturation on the outer lines, all inner 3-4 line intensities were multiplied by a free fit parameter, typically 1.05, since the dominant 1-6 and 2-5 lines are of approximately equal height. These inner lines thus do not enter directly into the fitting of p.

For spectra obtained at 296 K, subspectra showing the presence of divalent Fe were observed. One subspectrum had about the normal hyperfine parameters of the Fe_3O_4 B site ($H = 460$ kOe, IS $= 0.66$ mm/s). Since the area was a small percentage of the total, the hyperfine parameters were fixed. This subspectrum arises from fast electronic relaxation between Fe^{2+} and Fe^{3+} ("$Fe^{2.5}$"), and will be denoted $B^{2.5}$. Note this is easily discernible from subspectra belonging to Fe^{3+} B sites in the γ-Fe_2O_3 environment, which form part of the main peaks ($H \sim 500$ kOe, IS ~ 0.35 mm/s) and associated tailing.

A second subspectrum had the same isomer shift as $B^{2.5}$, but a lower hyperfine field (~ 400 kOe). This subspectrum, denoted B′, has been observed in all partially reduced γ-Fe_2O_3 samples studied which contain about 7 metal at. % Fe^{2+}. Some preliminary work has been done on larger particle (0.2×1 μm) materials, where the tailing is much less severe. The characteristics of the B′ site include an apparently small quadrupole splitting, the same IS as $B^{2.5}$, a very broad HWHM (about 2.5 times that of the main peaks), and, as a function of oxidation of the particles, a relatively constant Mössbauer area. For example, a sample with 6.7 metal at. % Fe^{2+} (measured by colorimetry) exhibited 1.0% of the total area in the $B^{2.5}$ subspectrum and 11.5% in the B′ subspectrum, giving a total divalent-related area of 12.5%. This is in good agreement with the expected 13.4%, assuming fast $Fe^{2+} \leftrightarrow Fe^{3+}$ relaxation for Fe in both B′ and $B^{2.5}$. The height of the B′ subspectrum is never more than about 4% of the sum of all heights, and the large HWHM tends to make fitting difficult. Since the hyperfine parameters may vary in different environments, for the present samples the values of H, IS and HWHM for B′ were free variables. The line-broadening factor was not used on this subspectrum. No tailing was included for the $B^{2.5}$ and B′ sites, since their heights are very small. Thus the descriptions of tailing that follow refer only to purely trivalent Fe.

RESULTS AND DISCUSSION

Mössbauer data are shown in Fig. 1, and $P(H)$ curves in Fig. 2. At 296 K, the Mössbauer area per milligram of sample for sample B is double that for the original, sample A. No evidence of superparamagnetic impurities was seen in these spectra or in spectra obtained at 296 K in zero applied field. The presence of the main A-site and B-site peaks for sample C at 4.2 K in 60 kOe indicates that the added ^{57}Fe is on the particles, and in the form of γ-Fe_2O_3 or $CoFe_2O_4$. The polarization for this spectrum is 0.09, which yields an equivalent single moment canting angle relative to the applied field direction of 17°. The ^{57}Fe oxide coating is very thin, about 1.3 Å in thickness, if uniform. Assuming these surface Fe spins were random in direction and the core aligned in field, a composite p of 0.40 would be obtained, far larger than observed. A major difference in these results from the previous Fe coating experiments[6] lies in the existence of nonmagnetic hyperfine peaks at room temperature in the previous work. These indicate fast superparamagnetic relaxation and the presence of very small particles. These smaller particles cant more strongly than the larger particles at low temperature where they are magnetically stable.

It does not seem possible with the current data to determine the chemical identity of the Co-^{57}Fe oxide surface layer in sample C. The $CoFe_2O_4$ A-site and B-site hyperfine parameters in large applied fields are very similar to those of γ-Fe_2O_3, although variable due to partial randomization of Co and Fe on the A and B sites dependent on preparation conditions.[10] Moreover, the present samples have only a partial surface-coated layer, and the hyperfine parameters could be different from bulk parameters. One of the most consistent characteristics of $CoFe_2O_4$ is the broad linewidth of the B-site lines due to fluctuation in the number of Co neighbors of the octahedral Fe, leading to nearly equal heights in the main A and B subspectra.[10] For sample C, the 60-kOe data B/A height ratio with the common HWHM employed is 1.33(5), somewhat less than the value 1.5 we typically ob-

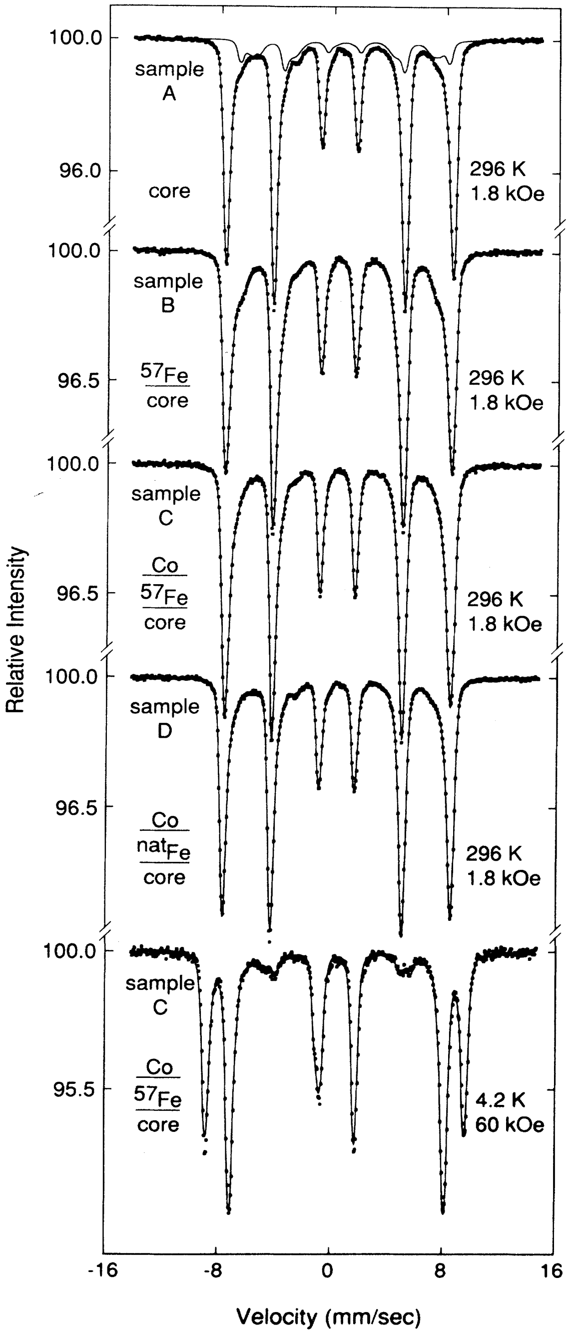

FIG. 1. Selected Mössbauer data and fits (solid lines). The measurements were obtained in 1.8-kOe transverse field, and 60-kOe longitudinal field. The figure keys denote the coating sequence, e.g., Co/^{57}Fe/core. The curve above the top spectrum denotes the fit contributions of the $B^{2.5}$ (outer) and B' subspectra to that fit.

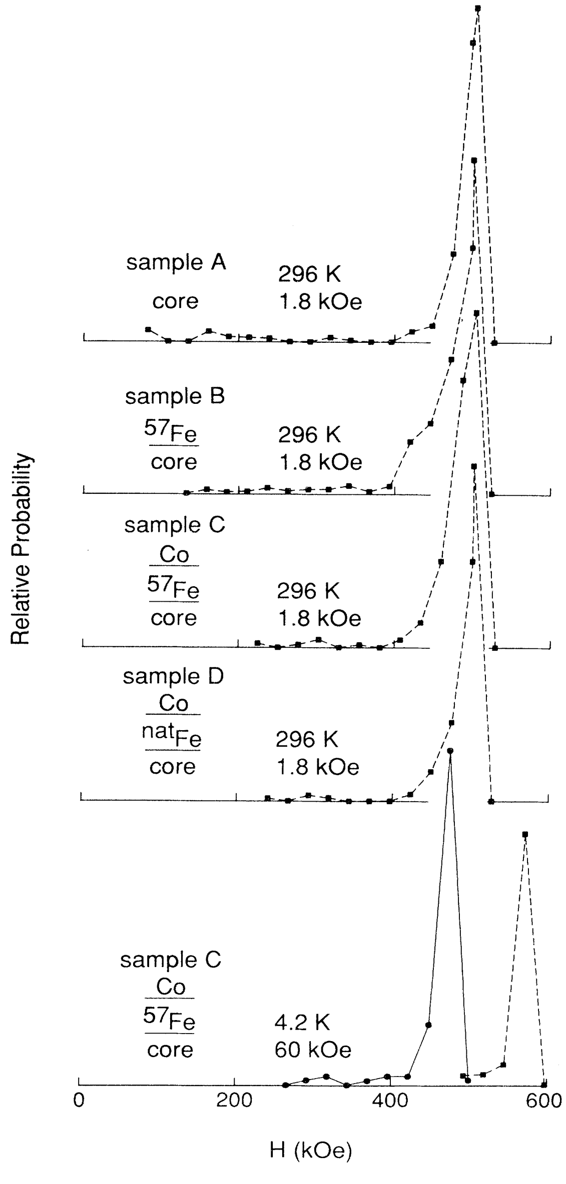

FIG. 2. Mössbauer data hyperfine field probability distributions. Only the relative probabilites for the trivalent subspectra are shown. The 60-kOe applied field data were obtained in longitudinal field, the other data in transverse field.

serve with γ-Fe_2O_3, but the relative contributions from the partially reduced core are unknown.

Some of the parameters from the 296-K Mössbauer data fits are shown in Table I. The polarization shows the expected sharp decrease with Co coating. The B′-site hyperfine parameters show little variation and agree with the larger particle results. The "area %" of B′ shows some variation, since the ^{57}Fe coat is trivalent, and decreases the relative Mössbauer area of the core. Note that this parameter cannot be used to determine the amount of Fe coated on the particles, since the Fe^{2+} content decreases with time, and these spectra were obtained over a year-long interval. For example, sample A originally exhibited an area for the $B^{2.5}$ subspectrum of 11.0% and for B′, 12.8%. Thus, over a period of about a year in benzophenone, the $B^{2.5}$ area decreased, while the B′ area showed little change, consistent with the observations on the oxidation of the larger particles.

As can be seen from $P(H)$ distributions obtained at 296 K (Fig. 2), all distributions are asymmetric with narrow tails to the low-H side of the fields obtained for the main subspectra. Sample B shows larger Fe^{3+} tailing than the uncoated sample A, with the peak H of the excess tailing occurring about 12% below the fields for the main subspectra. The increased tailing is due to lower surface coordination and weaker exchange of the ^{57}Fe atoms coated on the surface of the particles. A similar reduction in H at 296 K was found[11] from a Mössbauer study of ^{57}Fe obtained from the ^{57}Co parent coated on the surface of γ-Fe_2O_3, with the temperature dependence of H indicating an exchange field reduced from that of the core. The Co coating reduces the tailing of the ^{57}Fe-coated particles, although not that of the ^{nat}Fe-coated particles. The Fe^{3+} tail parameter is the only one in Table I that is markedly affected by the uncertainties in the main subspectra hyperfine parameters. For example, the sample-C spectrum showed a difference in main subspectra hyperfine fields of 16 kOe, which is large compared to the other fits. Nearly as good a fit was obtained with the difference in the main field parameters similar to the other fits, and the Fe^{3+} tailing increased from 19 to 23%.

One possibility for the cause of the reduction in tailing after Co coating the ^{57}Fe coated sample might simply be due to surface annealing during the extended time used in treating the powders with Co. A set of subsidiary experiments was performed to test this hypothesis. ^{57}Fe (2.8 metal at. %) was coated on the partially reduced γ-Fe_2O_3. After 2 h at 100 °C, an aliquot was treated similarly to the Co-coated samples by cooking in the sealed stainless steel container at 105 °C for a further 22 h. The trivalent tailing was 40% after the 2-h treatment, and (statistically) unchanged at 38% after the 22-h treatment. For comparison, the same sequential procedure was also performed on similar-sized particles of purely trivalent γ-Fe_2O_3. The corresponding Fe^{3+} tailing fractions were 43% after 2 h, and 42% after the 22-h treatment. Thus, the tailing is essentially independent of annealing time, and the Co coating does reduce the Fe^{3+} tailing of the ^{57}Fe coated sample.

The experimental values of polarization obtained in 1.8-kOe transverse applied field at 296 K are essentially independent of the existence of ^{57}Fe surface coating. That is, the polarization values for samples A and B are similar, and those for samples C and D are also very close. If there were a random surface layer, for the ^{57}Fe coated materials of each sample pair the polarization would decrease sharply towards unity, the value for random spins. Since the polarization at given applied field is known[5] to be dependent on the particles' magnetic anisotropy, the experimental anisotropy parameters were determined as described below.

Moment versus field measurements in the first quadrant were least-squares fit to log-normal distributions in anisotropy fields (H_K) using the Stoner-Wohlfarth model for coherently rotating, single domain, randomly oriented uniaxial particles. Some modifications were made to the method as previously reported.[1] A paramagnetic term was added to the fit moment, and the saturation moment was treated as a fit variable. About 700 terms were included in the H_K distribution. Some moment versus field data and fits at 296 K are shown in Fig. 3, and fit parameters in Table II. $\langle H_K \rangle_G$ and σ denote the geometric mean anisotropy fields and geometric standard deviations. Samples C and D are quite closely matched, showing similar values of $\langle H_K \rangle_G$ and σ, with $\langle H_K \rangle_G$ increasing markedly from the untreated sample A. Extending the Stoner-Wohlfarth calculations into the second quadrant and using the computed H_K distributions, similar model values of H_C are found, as expected, for samples C and D (Table II). Both are only about 10% greater than experimental values, so that reversal within the particles probably occurs coherently. The large observed values of σ yield anisotropy distribution full widths at half-maximum slightly greater than $\langle H_K \rangle_G$ for each of the samples. Model coercivities calculated from a single value of H_K, $\langle H_K \rangle_G$, would be about 55% greater than

TABLE I. Some parameters from least-squares fits to Mössbauer data obtained in 1.8-kOe transverse field at 296 K. The polarization is denoted by p. Fe^{3+} tail represents the fraction of all purely trivalent Mössbauer area in the tail. The area fractions of $B^{2.5}$ and B′ are relative to total Mössbauer area. The last three rows refer to B′ hyperfine parameters. Statistical errors p, ±0.005, $B^{2.5}$ percent area, ±0.2; H, ±2 kOe; IS, ±0.04 mm/s; HWHM, ±0.03 mm/s.

Sample	A	B	C	D
p	1.496	1.537	1.336	1.363
Fe^{3+} tail %	20	35	19	18
Area %				
$B^{2.5}$	5.4	0.7	2.2	2.2
B′	13.1	10.0	8.7	12.1
B′ parameters				
H (kOe)	399	399	403	400
IS (mm/s)	0.69	0.54	0.55	0.66
HWHM (mm/s)	0.70	0.70	0.70	0.74

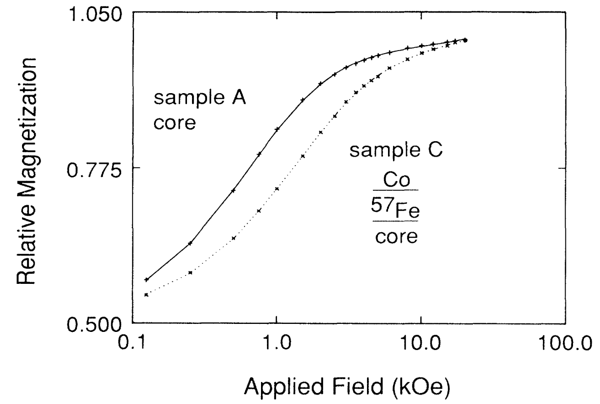

FIG. 3. Least-squares fits to selected first-quadrant 296-K magnetization data. The fit for sample A is shown as the solid line, and the fit for sample C as a dotted line.

those with the computed σ. Since room-temperature remanence ratios are close to 0.5, the anisotropy is predominantly uniaxial. However, there could be a small admixture of nonuniaxial anisotropy;[12] this would still leave the remanence ratio at 0.5.[13] The resultant effects on the model calculations are unknown.

For the previous hypothesis of a random moment shell, we model a hypothetical sample C by assuming a core with the polarization given by that of the magnetically closely matched sample D and a random spin shell provided by the sample C ^{57}Fe surface. Summing the equivalent single angle δm_i intensities from each layer and taking the ratio, one finds a hypothetical $p=1.17$, far less than the experimental 1.34 observed in $H_a=1.8$ kOe. Thus, both large-field and small-field data show the surface spins are far from randomly oriented.

There is a substantial discrepancy between the experimental values of polarization (p_e) and those deduced from the $\langle H_K \rangle_G$ values (p_d). For example, for sample D one calculates[5] $p_d=1.56$, while $p_e=1.36$. One possibility for the discrepancy is the distribution in anisotropy fields. A calculation employing the distribution for sample D yields only a slight change, $p_d=1.55$. The most likely source of the discrepancy is in some misalignment of the source-detector axis relative to the magnetic field axis from the 90° orientation. This misalignment should yield $p_e < p_d$ for all samples, as observed. For example, for sample D, p_d (single H_K) yields an equivalent single $\theta=69.4°$, while p_e gives 64.2°, a difference of only 5°. Because of this possible source of error, Mössbauer data for samples C and D were obtained consecutively without changes in experimental geometry.

TABLE II. Least-squares fit parameters to moment vs field data obtained at 296 K. All fields are in oersteds except $\langle H_K \rangle_G$, in kilo-oersteds. f_{par} denotes the fractional paramagnetic moment in 20-kOe applied field.

Sample	A	C	D
$\langle H_K \rangle_G$	1.17(1)	2.47(3)	2.32(2)
σ	2.16(5)	2.24(6)	2.13(5)
f_{par}	0.022(2)	0.023(4)	0.020(3)
H_C:			
Model	366	760	732
Experimental	305	700	660

FERRIMAGNETIC CHAIN MODEL

Of great importance for consideration of possible reversal mechanisms is the differential canting of spins on the surface relative to those in the center of the particles in weak fields. We consider below the case of applied field H_a perpendicular to the shape easy axis of an elongated single domain particle with a high-anisotropy shell of Co on the surface. To model this, we construct a linear chain of interacting spins which corresponds to those within the particle. The total number N of atoms is 121, approximately as found in the mean diameter of the current particles (250 Å). The spins are taken to be ferrimagnetically coupled. The angles θ_i of the spins in H_a (first quadrant) referred to the easy shape axis are calculated by minimizing the system free energy,

$$\varepsilon=\varepsilon_{\text{ex}}+\varepsilon_{\text{MH}}+\varepsilon_{\text{SH}}+\varepsilon_{\text{SU}} ,$$

where the terms denote exchange, applied field interaction, shape anisotropy, and surface anisotropy, respectively. These terms are obtained from experimental data on these and similar particles.

The exchange interaction is estimated from the temperature response of the magnetic hyperfine interaction in γ-Fe_2O_3 at 10-kOe applied field.[14] Boltzmann distribution mean-field sums were employed, with $g=2$, $S=\frac{5}{2}$. With the reduction in moments of the two sites averaging about 5% at 296 K compared to those at 4.2 K, one finds the mean molecular field at room temperature to be about 5000 kOe. Then, per magnetic ion, $E_{\text{ex}}=\varepsilon_{\text{ex}}/k=1680$ K (with the conversion factor $\mu_B/k=0.0672$ K/kOe). Thus, for the chain

$$E_{\text{ex}}=840\sum_i[\cos(\theta_i-\theta_{i+1})+1] \text{ K}$$

(all succeeding energy units E will be in degrees Kelvin). Note that the end points have only half the exchange interaction of the core. Unity is added to reduce computer truncation error due to this dominant term.

For ferromagnetically aligned moments, the external field interaction would give

$$E_{\text{MH}}=-0.336H_aN ,$$

H_a in kilo-oersteds. Since the moment of γ-Fe_2O_3 is 23% of the ferromagnetic equivalent, we arbitrarily devise an effective ferrimagnet by increasing/lowering the spin up/down moments of the equivalent antiferromagnet by 23%. Thus,

$$E_{\text{MH}}=-0.413H_a\sum_{\text{odd}}\sin\theta_i-0.259H_a\sum_{\text{even}}\sin\theta_i .$$

The shape-anisotropy field for γ-Fe_2O_3 is nominally about 2 kOe. Dividing the associated energy by the atom density for the linear chain, one finds

$$E_{SH} = -0.077 \sum_i \cos^2(\theta_i)$$

with local dipolar fields ignored.

For an estimate of the surface anisotropy, a previous calculation for Co-coated particles is employed.[5] Basically, H_K increases about 1.2 kOe with Co adsorption. For calculating the number density of anisotropic Co atoms, a $CoFe_2O_4$ shell was assumed. This gave a shell anisotropy of 2.3×10^6 ergs/cm^3; then the anisotropy K_e per Co atom is 1.29 K. Since the previous calculations assumed 4 at. % Co on the surface, and the present linear model only allows about 2 at. % Co, this number is doubled to $K_e = 2.58$ K:

$$E_{SU} = -2.58\cos^2\theta_1 - 2.58\cos^2\theta_{121} .$$

The moment ratio in the field direction is given by

$$\frac{M}{M_S} = \left| \frac{\sum_i M_i \sin\theta_i}{M_u N_u - M_d N_d} \right| ,$$

where the subscripts refer to the up and down spins, and the anisotropy field H_K is given by

$$H_K = H_a/(M/M_S) .$$

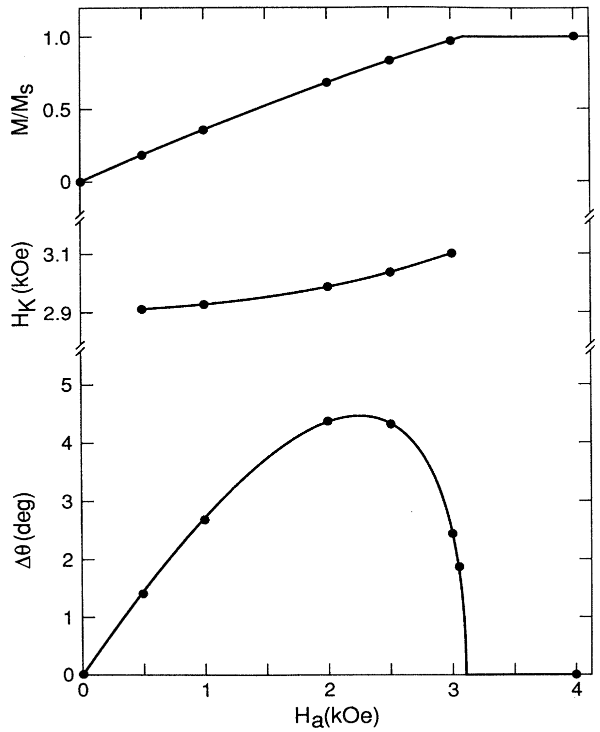

FIG. 4. Some calculated parameters from the linear ferrimagnetic chain model, as a function of applied field, with endpoint anisotropy energy $K_e = 2.58$ K. Solid curves are visual guides.

TABLE III. Model calculations of ferrimagnetic chain H_K and center-edge spin deviation $\Delta\theta$ at $H_a = 0.5$ kOe, with end spin anisotropy K_e variable.

K_e (K)	H_K (kOe)	$\Delta\theta$ (deg)
0	1.93	−0.14
2.58	2.91	1.41
5.16	3.72	2.06

The difference in canting angles θ_i between the middle and end spins is found as

$$\Delta\theta = \theta_{60} - \theta_1 - \pi .$$

The free energy was minimized numerically. Some results are given in Fig. 4 and Table III, and a typical curve of spin angle versus position is shown in Fig. 5. One sees that exchange does indeed dominate, with the incremental angle between spins very small in Fig. 5 (note that π has been subtracted from alternate spins). The end spins lag the center spins for end-spin anisotropy energies $K_e \neq 0$. They very slightly lead the center if $K_e = 0$, presumably because of weaker exchange. For the case with the surface anisotropy energy derived from experimental data ($K_e = 2.58$ K), the calculated H_K has increased from 1.9 to about 2.9 kOe, as expected, with some variation in H_K with H_a. The end-center differential canting depends on H_a, and peaks at about 4.5° (Fig. 4).

Comparing the polarizations for samples C and D (Table I), one finds in $H_a = 1.8$ kOe a difference in canting angles of only about 0.7° (assuming a single canting angle for each sample). If one adjusts for the slightly greater $\langle H_K \rangle_G$ for sample C, the difference would be even less. The model calculations are in good agreement with the experimental results, since only half the Mössbauer signal comes from the surface of sample C, and the model calculations only considered the case of easy axis perpendicular to the field direction. Note also that the effective an-

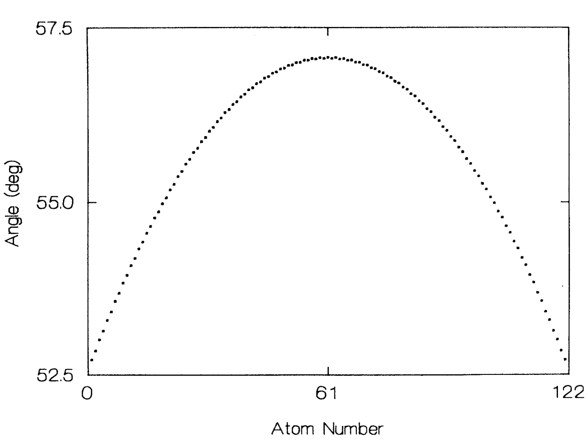

FIG. 5. Spin angle vs position, with $K_e = 2.58$ K, $H_a = 2.5$ kOe. π has been subtracted from alternate points.

gle for the chain based on the model calculations would be determined from an average over the calculated values, and would be sharply lower than the maximum $\Delta\theta$ of 4° calculated for $H_a = 1.8$ kOe. Thus, the results of the calculations show that the surface anisotropy causes the surface spins to deviate only slightly from the core spins, certainly not enough to agree with the previous random-shell surface-spin model. Furthermore, the experimental Mössbauer data are in good agreement with these calculations.

CONCLUSION

Mössbauer spectroscopy on partially reduced γ-Fe_2O_3 coated with Co has shown that the high-field canting is far less than can be attributed to a surface shell of randomly oriented spins. Furthermore, the mean spin orientation in low applied field is essentially the same at the surface as in the core of the particles, even with a high-anisotropy shell. These data indicate the high-field canting has its origins in the volume of small particles. First quadrant moment versus field data were used to obtain anisotropy field distributions. As expected, the Co-adsorbed materials showed much higher mean anisotropy fields than the untreated precursor, although the width parameters σ were unchanged. For the Co-adsorbed materials, model-calculated H_C values are only slightly greater than experimental, suggesting coherent rotation for the reversal mechanism. A linear-chain ferrimagnet model calculation shows that the differential spin canting in 1.8 kOe between the Co shell and the center of the basically γ-Fe_2O_3 particle should be only a few degrees, consistent with the experimental Mössbauer polarization data. A subspectrum characteristic of slightly reduced γ-Fe_2O_3 exhibits an isomer shift similar to that produced by fast electronic hopping on the B-site between Fe^{2+} and Fe^{3+}, but with a magnetic hyperfine field only 80% of the normal $B^{2.5}$ subspectrum and a very broad linewidth. The ^{57}Fe-treated material exhibits a sharply reduced hyperfine field tailing after Co coating, indicating increased surface exchange for the Fe^{3+} atoms.

ACKNOWLEDGMENT

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