

## Origin of the Spin-Canting Anomaly in Small Ferrimagnetic Particles

Q. A. Pankhurst<sup>(1)</sup> and R. J. Pollard<sup>(1),(2)</sup>

<sup>(1)</sup>Department of Physics, University of Liverpool, Liverpool L69 3BX, England

<sup>(2)</sup>Department of Physics, Monash University, Clayton, Victoria 3168, Australia  
(Received 6 March 1991)

The spin-canting anomaly, in which fine ferrimagnetic iron-oxide particles are not completely saturated by large magnetic fields, is usually attributed to noncollinear surface moments. Using a simple mean-field model we show that the anomaly is in fact a routine manifestation of the response of a uniaxial ferrimagnetic powder to an applied field. This view is supported by the modeling of <sup>57</sup>Fe Mössbauer spectra of Co-adsorbed  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> recorded at 4.2 K in applied fields of 6.0 and 7.6 T.

PACS numbers: 75.50.Gg, 75.60.Jp, 76.80.+y

Over the past few years there has been considerable interest in the magnetic properties of very small atomic clusters. The interest stems from improved methods of preparation which allow a high degree of control over the number of atoms per cluster, from technological uses of magnetic particles, and from a variety of interesting physical phenomena exhibited by the clusters [1]. Most recent studies have been on metallic systems. However, it has long been known that even relatively large ferrimagnetic oxide particles exhibit anomalous magnetic behavior [2] which is absent in metallic particles [3]. This behavior has been ascribed to finite-particle-size effects, and is of special interest because the same particles are used extensively in the magnetic recording industry. In light of the recent studies, it is timely to reconsider the evidence for the anomalous magnetism in ferrimagnetic particles.

It is commonly assumed that in a large magnetic field the net magnetic moment of a ferrimagnetic iron-oxide particle should become completely aligned in the direction of the applied field, and that the magnetization should become saturated. However, almost twenty years ago this was found to be not true for fine particles (diameter  $\sim 60$  Å) of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in an applied field of 5 T [2]. This "spin-canting anomaly" was attributed to a random canting of the surface spins due to a differing balance of exchange interactions at sites near the surface. Subsequently, the spin-canting anomaly has been observed in a number of both natural and synthetic ferrimagnetic iron oxides, oxyhydroxides, and ferrites, and the concept of surface spin canting has become widely accepted. Several reviews of this work have been published [4–7].

In this Letter we point out that the initial assumption is erroneous, and that it cannot be supposed, *a priori*, that a given ferrimagnetic particle will be saturated by a large applied field. Several parameters determine the degree to which the net moment of the particle will be aligned with the field: the ratio of the sublattice moments, the relative strengths of the exchange, anisotropy, and local fields, and the angle between the applied field and the easy anisotropy axis. The theoretical justification for this, which follows, is an extension of our recent work on antiferromagnetic powders in applied fields [8] and on anisotropy

field measurements in barium ferrite powders [9].

The Hamiltonian of a two-sublattice ferrimagnet with a nearest-neighbor exchange constant  $J$ , sublattice anisotropy constants  $K$  and  $K'$ , and sublattice spins  $\mathbf{S}$  and  $\mathbf{S}'$  is

$$\mathcal{H} = -2J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - K \sum_i (S_{zi})^2 - K' \sum_j (S'_{zj})^2 - g\mu_B \mathbf{B} \cdot \left( \sum_i \mathbf{S}_i + \sum_j \mathbf{S}'_j \right). \quad (1)$$

$\mathbf{B}$  is the local field at an atomic site, which in SI units for the case of cubic symmetry is given by

$$\mathbf{B} = \mathbf{B}_{\text{app}} - \mu_0 \left( N_{\parallel} - \frac{1}{3} \right) \mathbf{M}, \quad (2)$$

where  $N_{\parallel}$  is the demagnetization factor parallel to the direction of magnetization and  $\frac{1}{3} \mu_0 \mathbf{M}$  is the Lorentz cavity field. Using the mean-field approximation the energy of the system can be expressed in terms of the orientations of the sublattice spins:

$$E = NSg\mu_B [ B_E \xi \cos(\theta - \theta') - \frac{1}{2} B_A \cos^2(\theta - t) - \frac{1}{2} B'_A \xi^2 \cos^2(\theta' - t) - B(\cos\theta + \xi \cos\theta') ]. \quad (3)$$

Here  $N$  is the number of sublattice spins, and  $\theta$ ,  $\theta'$ , and  $t$  are the polar angles of the two-sublattice spins and the easy anisotropy axis with respect to the local-field direction.  $\xi = S'/S$  is the ratio of the spin magnitudes,  $B_E = -2JzS/g\mu_B$ , where  $z$  is the number of nearest neighbors,  $B_A = 2KS/g\mu_B$ , and  $B'_A = 2K'S/g\mu_B$ . In this formalism  $K$  and  $K'$  are effective anisotropy constants which incorporate both crystalline and shape anisotropy terms.

For a given  $t$  the equilibrium spin configuration is obtained by solving the simultaneous equations  $\partial E / \partial \theta = \partial E / \partial \theta' = 0$ . In a powder the angle  $t$  is sampled continuously from 0 to  $2\pi$ , with the range 0 to  $\pi$  encompassing all unique solutions. The variation of  $\theta$  as a function of increasing  $B$  is shown in Fig. 1 for a number of values of  $t$  (initial values of  $\theta$ ) between 0 and  $\pi$ , for the case  $B_E = 1000$  T,  $B_A = B'_A = 1$  T, and  $\xi = 0.6$ . Since the exchange is large, the sublattice spins remain almost antiparallel throughout. For  $t > \pi/2$  abrupt changes occur as the net ferrimagnetic moment is reoriented towards  $\mathbf{B}$ ;

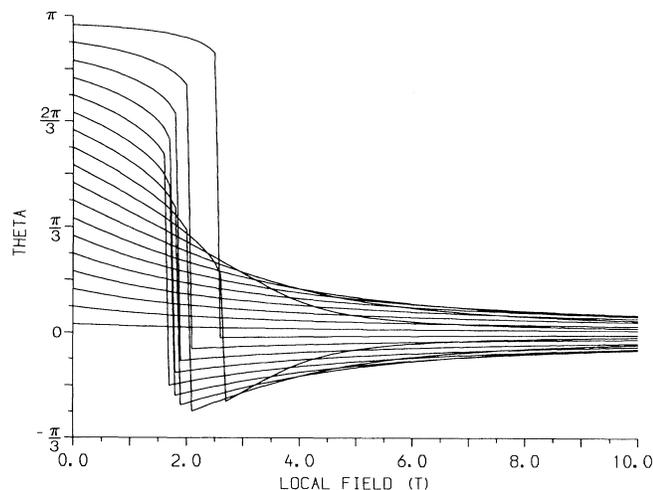


FIG. 1. Variation, as a function of local field  $B$ , of the angle  $\theta$  between  $\mathbf{B}$  and the major spin  $\mathbf{S}$  of a two-sublattice uniaxial ferrimagnet with exchange field  $B_E = 1000$  T, sublattice spin ratio  $\xi = S/S' = 0.60$ , and anisotropy fields  $B_A = B'_A = 1$  T.

this is tantamount to a model of coherent magnetization reversal. Although the magnetization-reversal mechanism is known to be incoherent in many ferrimagnetic powders [10], the coherent reversal approximation is sufficient to describe the near-saturation response of the system to large applied fields. In Fig. 1 it is clear that at large  $B$  the spins approach  $\theta = 0$ , but are not completely aligned. It is this incomplete alignment that accounts for the spin-canting anomaly. Experimental verification of this result follows.

Co-adsorbed  $\gamma\text{-Fe}_2\text{O}_3$  particles are a commonly used magnetic recording medium. Surface doping of  $\text{Co}^{2+}$  ions enhances the coercivity of  $\gamma\text{-Fe}_2\text{O}_3$ , and avoids the complications due to the formation of surface layers of antiferromagnetic  $\alpha\text{-Fe}_2\text{O}_3$  during the oxidation of  $\text{Fe}_3\text{O}_4$  into  $\gamma\text{-Fe}_2\text{O}_3$  [11,12].  $^{57}\text{Fe}$  Mössbauer spectra of a sample of Co: $\gamma\text{-Fe}_2\text{O}_3$  particles (Hercules Chemical Corporation) recorded at 4.2 K are shown in Fig. 2. Applied fields of 0, 6.0, and 7.6 T were directed parallel to the  $\gamma$ -ray beam. High signal-to-noise ratios were obtained by prolonged data accumulation: Using a 16-mCi  $^{57}\text{CoRh}$  source, counting times were between two and three weeks per spectrum.

The spectra were modeled by choosing a suitable number (twenty) of representative values of  $t$ , and calculating and summing the resulting subspectra. Possible preferred orientation in the sample was allowed for by taking the probability of sampling  $t$  to be proportional to the radial function of a prolate ellipsoid, multiplied by the usual  $(\sin t)$ -weighting factor:

$$P(t) = (\sinh^2 u + \cos^2 t)^{1/2} \sin t. \quad (4)$$

Spin  $S = \frac{5}{2}$  was assigned to the  $B$ -site  $\text{Fe}^{3+}$  ions, and a smaller effective spin  $S' = \xi S$  to the  $A$ -site ions. The spin

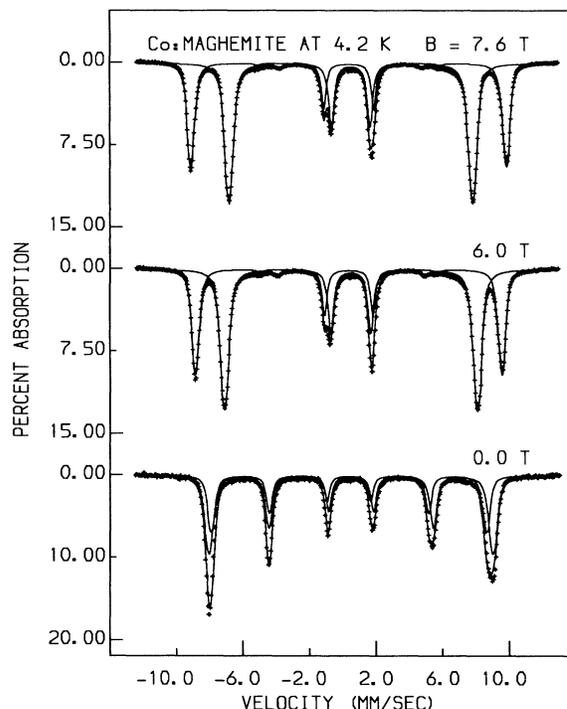


FIG. 2.  $^{57}\text{Fe}$  Mössbauer spectra of Co-adsorbed  $\gamma\text{-Fe}_2\text{O}_3$  at 4.2 K in applied fields of 0.0, 6.0, and 7.6 T directed parallel to the direction of  $\gamma$ -ray propagation. Velocity calibration is with respect to the center of the room-temperature spectrum of  $\alpha\text{-Fe}$ .

ratio was related to the observed hyperfine field at each site via

$$\xi = f_A B_{\text{hf}}^A / f_B B_{\text{hf}}^B, \quad (5)$$

where  $f_A$  and  $f_B$  are the fractional occupancies of the  $A$  and  $B$  sites. The exchange field was determined from the Curie temperature  $T_c$  of the sample using [9]

$$B_E = \frac{3k_B T_c}{2g\mu_B} \frac{S^2 + S'^2}{S'[S(S+1)S'(S'+1)]^{1/2}}. \quad (6)$$

Published values of  $T_c$  in maghemite range from 820 to 985 K; we assumed  $T_c = 900$  K.

The demagnetization and Lorentz fields were estimated from the room-temperature saturation magnetization,  $M_S \approx 4 \times 10^5 \text{ Am}^{-1}$ , measured in similar samples [13]. Transmission electron micrographs showed that on average the particles are acicular, with dimensions  $\sim 250 \text{ nm} \times 35 \text{ nm}$ . Demagnetization factors were calculated using the approximation for a slender prolate ellipsoid [14], giving  $N \approx 0.033$  along the long axis.

All three spectra were simultaneously least-squares fitted. Simultaneous fitting alleviates the problems associated with the interdependence of the fit parameters. Since the exchange and anisotropy fields have almost no effect on the  $B_{\text{app}} = 0$  spectrum, fitting that spectrum determines the isomer shift  $\delta$ , quadrupole splitting  $\Delta$ ,

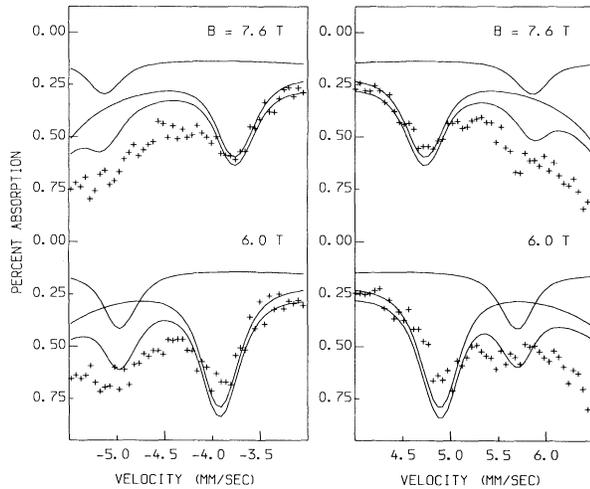


FIG. 3. The  $B_{\text{app}} \neq 0$  spectra of Fig. 2, showing the experimental and calculated data in the velocity regions of the  $\Delta m_l = 0$  lines.

linewidth  $\Gamma$ , and hyperfine field  $B_{\text{hf}}$  at each site. (Three separate  $B_{\text{hf}}$  values were associated with each site as a means of taking into account microstructural inhomogeneity.) Subsequently,  $\xi$  and  $B_E$  may be computed from Eqs. (5) and (6), leaving  $B_A$  and  $B'_A$  as the only free parameters used to fit the  $B_{\text{app}} \neq 0$  spectra.

The resultant fit is shown as the solid lines in Fig. 2. The following parameters were obtained:  $u=0.48$ ,  $\xi=0.61$ ,  $B_E=979$  T,  $B_A=0.04$  T (for the  $B$  site), and  $B'_A=3.30$  T (for the  $A$  site). A confidence level of 68% was estimated for the anisotropy fields by monitoring the goodness-of-fit parameter  $\chi^2$ . The extrema of the confidence region were found to be  $B_A=0.0$  T,  $B'_A=3.7$  T and  $B_A=1.2$  T,  $B'_A=0.5$  T.

The overall quality of the fit is good. In the region of the  $\Delta m_l = 0$  lines (see Fig. 3), whose intensities depend on  $\langle \sin^2 \theta \rangle$  and  $\langle \sin^2 \theta' \rangle$  [2,4], it is clear that the model successfully predicts nonzero line intensities, and that the predicted line positions compare well with the observed data. The misfit apparent in Fig. 3 is largely attributable to the misfit of the shoulders of the more intense lines at velocities  $\sim -6$  and  $\sim 7$   $\text{mms}^{-1}$ , and points to the inadequacy of using only three hyperfine fields to model the distribution of hyperfine parameters in the sample. It is also expected that there is a distribution of anisotropy fields experienced by the ferric ions in the sample, so that the assumption of only one anisotropy constant for each sublattice may account for some of the misfit.

The observation of nonzero  $\Delta m_l = 0$  line intensities, such as those shown in Fig. 3, is therefore seen to be consistent with the response of a simple uniaxial ferrimagnetic powder to a large external field. Previously the obser-

vation of such nonzero line intensities has been interpreted as the result of surface spin canting; however, it is now apparent that surface effects are not needed to explain the "spin-canting anomaly." The zero  $\Delta m_l = 0$  line intensities observed for metallic particles [3] result from the saturation of the magnetization at relatively low fields, whereas in oxide particles the combination of opposing sublattice orientations and relatively large anisotropy hinders complete alignment.

The effects of exceedingly small particle size upon magnetism in insulators, such as the iron oxyhydroxides and hydrated oxides, are made apparent by applying our technique to several samples with different particle sizes [15]. Marked differences in the degree of ferrimagnetism and in the anisotropy fields have been observed, and can be most simply understood in terms of local disorder and statistical fluctuations in the magnetic sublattice occupancies. However, in all cases the behavior is consistent with the mean-field predictions.

This work was financially supported by the Australian Research Council.

- [1] J. Merikoski, J. Timonen, M. Manninen, and P. Jena, *Phys. Rev. Lett.* **66**, 938 (1991); W. A. de Heer, P. Milani, and A. Chatelain, *Phys. Rev. Lett.* **65**, 488 (1990); W. P. Halperin, *Rev. Mod. Phys.* **58**, 533 (1986); D. M. Cox, D. J. Trevor, R. L. Whetten, E. A. Rohlfing, and A. Kaldor, *Phys. Rev. B* **32**, 7290 (1985).
- [2] J. M. D. Coey, *Phys. Rev. Lett.* **27**, 1140 (1971).
- [3] A. H. Morrish and K. Haneda, *J. Magn. Magn. Mater.* **15-18**, 1089 (1980); A. H. Morrish and R. J. Pollard, *Adv. Ceramics* **16**, 393 (1986).
- [4] A. H. Morrish and K. Haneda, *J. Magn. Magn. Mater.* **35**, 105 (1983).
- [5] J. M. D. Coey, *Can. J. Phys.* **65**, 1210 (1987).
- [6] K. Haneda, *Can. J. Phys.* **65**, 1233 (1987).
- [7] E. De Grave, R. E. Vandenberghe, and L. H. Bowen, in *Condensed Matter Studies by Nuclear Methods*, edited by J. Stanek and A. T. Pedziwiatr (World Scientific, Singapore, 1990), Vol. 2, pp. 186-239.
- [8] Q. A. Pankhurst and R. J. Pollard, *J. Phys. Condens. Matter* **2**, 7329 (1990).
- [9] Q. A. Pankhurst, *J. Phys. Condens. Matter* **3**, 1323 (1991).
- [10] For example, M. E. Schabes and H. N. Bertram, *IEEE Trans. Magn.* **67**, 5149 (1990).
- [11] M. F. Toney, T. C. Huang, S. Brennan, and Z. Rek, *J. Mater. Res.* **3**, 351 (1988).
- [12] R. J. Pollard, *J. Phys. Condens. Matter* **2**, 983 (1990).
- [13] F. T. Parker and A. E. Berkowitz, *IEEE Trans. Magn.* **25**, 3647 (1989).
- [14] J. A. Osborn, *Phys. Rev.* **67**, 351 (1945).
- [15] R. J. Pollard, Q. A. Pankhurst, and P. Zientek (to be published); Q. A. Pankhurst and R. J. Pollard (to be published).