

## Ultrafine maghemite particles: II. The spin-canting effect revisited

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**Abstract.** The magnetic structure of ultrafine maghemite particles was studied by Mössbauer spectroscopy. We have compared the degree of spin alignment obtained in applied magnetic fields in particulate samples with different frozen-in orientational distributions of the easy directions of the magnetization. Full alignment of the spins was not obtained even in large applied fields (4.35 T). The degree of alignment with the applied field was found to be independent of the orientation of the easy directions in the sample when the applied field was larger than 0.75 T. This result shows that the incomplete alignment of the spins in ultrafine maghemite particles subjected to large applied fields is not due to incomplete alignment of the net particle magnetization due to large magnetic anisotropy, but rather stems from a canting of individual spins.

### 1. Introduction

The magnetic properties of ultrafine ferrimagnetic metal oxide particles have been intensively studied over the last three decades, because of the great technological importance of such materials in magnetic recording media and ferrofluids. It is well established that the magnetic properties of such materials are affected by finite-size effects [1]. The saturation magnetization of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> ultrafine particles has been found to be smaller than that of the bulk material [2, 3]. An explanation of this phenomenon was suggested more than twenty years ago by Coey [4], who studied 6 nm maghemite particles by in-field Mössbauer spectroscopy. He found that even in very large magnetic fields (5 T), some of the atomic moments were pinned and did not align with the field. He ascribed the non-collinear spin structure to random canting of the surface spins, being caused by competing antiferromagnetic exchange interactions,  $J_{AA}$  and  $J_{AB}$ , at the surface. Later Mössbauer spectroscopy studies of ultrafine  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles, enriched with <sup>57</sup>Fe or <sup>57</sup>Co in the surface, indicated that the spin canting in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is a surface effect [5–7]. Recently, this kind of experiment was repeated by Parker and co-workers [8], who studied acicular maghemite particles (25 × 200 nm) coated with <sup>57</sup>Fe. In contrast to the earlier work, Parker and co-workers [8] found that the spin canting in maghemite is not a surface property. Incomplete alignment of the magnetic moments in large magnetic fields has also been found in fine particles of NiFe<sub>2</sub>O<sub>4</sub> [9, 10], CoFe<sub>2</sub>O<sub>4</sub> [9, 11] and CrO<sub>2</sub> [12]. Reviews of the work in this field are given in [1, 13].

Recently the *a priori* assumption that a ferrimagnetic particle will saturate in a large magnetic field has been questioned by Pankhurst and Pollard [14]. They considered a

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two-sublattice spin system in a homogeneous magnetic field. The spins were coupled by antiferromagnetic exchange between the sublattices, and a uniaxial anisotropy was associated with each sublattice. By minimizing the total energy they calculated the spin orientation as a function of applied field. They found that extremely large fields are necessary to ensure full alignment of the net magnetization with the field; the interaction with the applied field is too weak to overcome the sublattice anisotropy. Hence, they ascribed the lack of a full alignment of the spins in ultrafine particles in a large magnetic field, and the consequent reduced magnetization, to incomplete alignment of all the spins. This is in contrast to the concept of spin canting, where the lack of full alignment is ascribed to a fraction of the spins being canted relative to the direction of the net magnetization. On the basis of this model the authors were able to explain experimental results of in-field Mössbauer spectroscopy studies of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles with adsorbed Co [14].

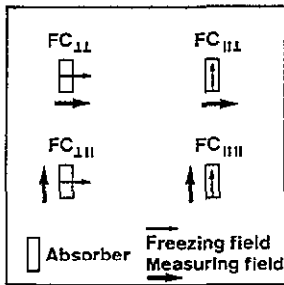
It is the aim of this work to clarify whether incomplete field-alignment of the spins in ultrafine ferrimagnetic particles is an effect of specific spins being canted in random directions or, as suggested by Pankhurst and Pollard, that it stems from incomplete alignment of all the spins due to the inability of the applied field to overcome the particle anisotropy. We have devised a simple experiment to test the latter hypothesis. If the full alignment of the magnetic moments is hindered by the anisotropy, the degree of alignment will depend on the angle between the easy axis of the anisotropy and the field [14]. The angles between the easy axes and the direction of an applied field are randomly distributed in a powder sample. A sample with a magnetic texture (non-random distribution of the easy axes) can be made by freezing a ferrofluid in a magnetic field [15, 16]. In this way the easy axes of the sample will be oriented around the direction of the freezing field. It is thus possible to test the hypothesis of Pankhurst and Pollard, by measuring the degree of spin alignment in field-cooled ferrofluids in large magnetic fields applied perpendicular to, or parallel with, the direction of the freezing field.

In this paper we report the results of investigations of the behaviour of samples with different magnetic textures in large magnetic fields. The degree of spin alignment along the magnetic field was determined by Mössbauer spectroscopy. The samples were (frozen) suspensions of ultrafine maghemite particles (9 nm). The samples were characterized in detail in part one of this study [16], where the magnetic anisotropy constant of the particles was determined and where we described how the magnetic texture was introduced in the samples.

## 2. Experimental

The samples investigated were made from a suspension of ultrafine oleic acid coated maghemite particles in heptane. The maghemite particles were prepared by a chemical precipitation method (see [16] for details). Analysing electron micrographs and magnetization measurements of the sample, assuming a log-normal particle size distribution, a median diameter of 9 nm and a standard deviation of  $\sigma_v = 1.05$  was found. (This refers to the volume-weighted particle volume distribution). The anisotropy energy constant of the particles was determined in [16] to be of the order of  $(1 - 2) \times 10^4 \text{ J m}^{-3}$ .

In-field Mössbauer spectra were obtained at 15 and 80 K. A 50 mCi source of <sup>57</sup>Co in rhodium was used and isomer shifts are given relative to  $\alpha$ -iron at room temperature. The low-temperature Mössbauer spectra were obtained in a liquid helium cryostat equipped with a superconducting solenoid allowing Mössbauer spectra to be obtained in magnetic fields up to 4.35 T. The 80 K Mössbauer spectra were obtained in a conventional liquid nitrogen



**Figure 1.** Illustration of the notation characterizing the direction of the freezing and measuring fields relative to the sample plane. The geometry of the 15 K measurements is shown in the two upper illustrations and the geometry of the 80 K measurements in the two lower.

cryostat with the possibility of applying magnetic fields up to 0.75 T. In the 15 K setup the magnetic field was applied parallel to the direction of the  $\gamma$  beam, while in the 80 K setup the magnetic field was applied perpendicular to the  $\gamma$  beam. The samples were contained in disk-shaped plexiglass containers. When placed in the spectrometers the sample plane was perpendicular to the  $\gamma$  beam. Magnetic texture was introduced in the samples by freezing them in a magnetic field [16]. The geometry of the in-field measurements on the field-cooled samples is indicated by subscripts; a field-cooled (FC) sample that was frozen in a magnetic field perpendicular to the sample plane, and where the magnetic field applied during measurement was parallel to the sample plane is labelled  $FC_{\perp\parallel}$ . The notation is illustrated in figure 1.

### 3. Results

We have investigated the extent to which it is possible to align the magnetic moments in the textured samples along an applied magnetic field at 15 and 80 K. We compare the Mössbauer spectra obtained in different magnetic fields of three samples; one zero-field cooled (ZFC) with a random distribution of easy axes, one cooled in a field perpendicular to the sample plane, and one cooled in a field applied in the sample plane. The degree of alignment of the easy directions obtained by the field cooling was discussed in [16].

Mössbauer spectra, obtained at 15 K with different fields (0.00 T, 0.05 T, 0.75 T and 4.35 T) applied along the  $\gamma$  direction for the  $FC_{\parallel\perp}$  ( $\Delta$ ) and  $FC_{\perp\perp}$  (line) samples, are shown in figures 2 and 3. The samples were cooled in a freezing field of 4.35 T. The difference between the spectra of the two samples obtained in the same external field is shown underneath the spectra. When calculating the difference the two spectra have been scaled such that the intensities of lines 3 and 4 are the same in both spectra. In zero field the different orientations of the magnetic moments in the two samples are clearly revealed by a large difference in the absorption in lines 2 and 5. This illustrates the induced texture in the samples. A small difference (on the scale of the statistical scatter) between the absorption in lines 1 and 6 in the two spectra is also seen. This is due to different sample thicknesses; the  $FC_{\perp\perp}$  sample is slightly thicker than the  $FC_{\parallel\perp}$  sample, and hence the area ratio  $A_{16}/A_{34}$  is slightly smaller in the  $FC_{\perp\perp}$  sample than in the  $FC_{\parallel\perp}$  sample due to saturation effects. As the applied field increases the relative areas of lines 2 and 5 decrease due to the orientation of the magnetic moments along the field direction. The difference between the two spectra diminishes with increasing applied field, and at 0.75 T the two spectra are, except for the thickness effect, identical within the experimental uncertainty. Increasing the applied magnetic field to 4.35 T only leads to a small reduction of the area fraction in lines 2 and 5 relative to the spectra obtained in 0.75 T. Full alignment of the

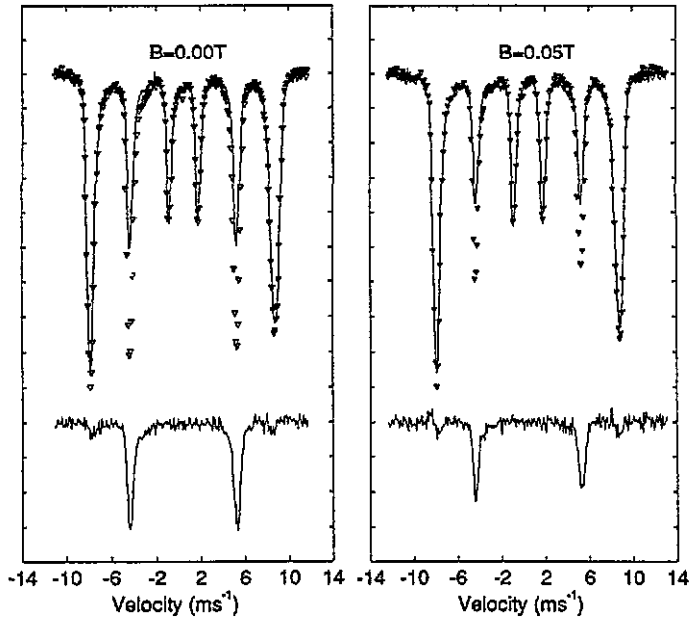


Figure 2. Mössbauer spectra of samples with frozen-in magnetic texture obtained at 15 K in zero field and in a field of 0.05 T applied along the  $\gamma$ -beam direction. The spectrum of the sample that was frozen in a field of 4.35 T perpendicular to the sample plane ( $FC_{\perp\perp}$ ) is illustrated with a full curve. The spectrum of the sample that was frozen in a field parallel to the sample plane,  $FC_{\parallel\perp}$  is given by the triangles. The full curve in the lower half of the figure is the difference between the two spectra, calculated after scaling the spectra to the same intensity in lines 3 and 4.

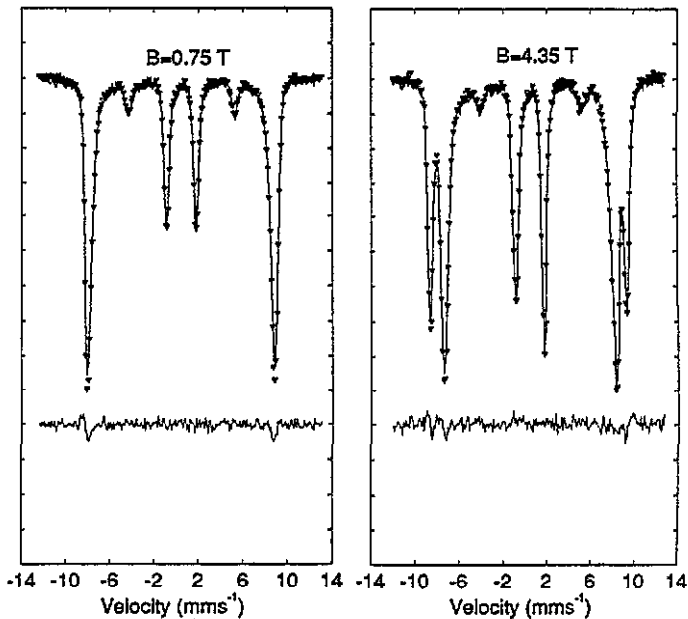


Figure 3. Mössbauer spectra of the textured samples obtained at 15 K in fields of 0.75 and 4.35 T applied parallel to the  $\gamma$ -beam. The spectra of the  $FC_{\perp\perp}$  sample are drawn as full curves and the  $FC_{\parallel\perp}$  spectra are given by triangles. The differences between the spectra (after scaling to equal intensities for lines 3 and 4) are shown in the lower half of the figure.

magnetic moments in the two samples is thus not obtained even at this large field. The only difference in the spectra of the  $FC_{\perp\perp}$  and  $FC_{\parallel\perp}$  samples obtained in a magnetic field of 4.35 T is the previously mentioned thickness effect.

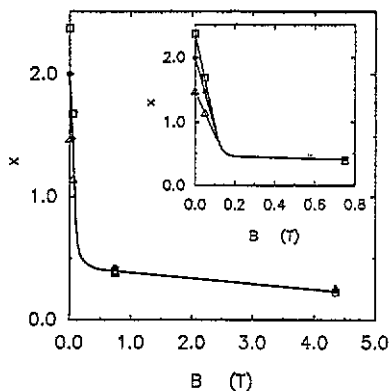


Figure 4. The area ratio  $x = A_{25}/A_{34}$  of the Mössbauer spectra obtained at 15 K in different magnetic fields of three samples; ZFC ( $\bullet$ ),  $FC_{\parallel\perp}$  ( $\square$ ) and  $FC_{\perp\perp}$  ( $\triangle$ ). The area ratios are derived from a best fit to the experimental spectra using two sextets of Lorentzian lines. The full curve is a guide to the eye and is drawn on the basis of the measurements made at 80 K.

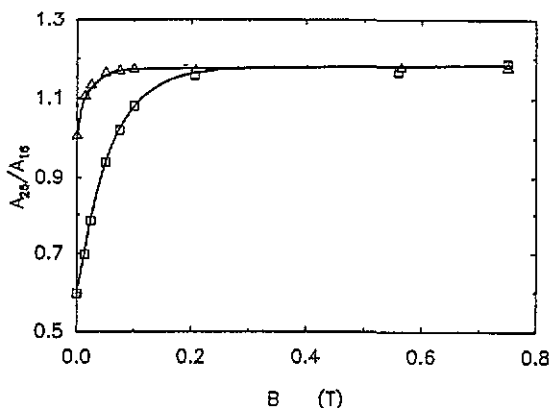


Figure 5. The area ratios  $A_{25}/A_{16}$  in the Mössbauer spectra obtained at 80 K in different magnetic fields applied perpendicular to the  $\gamma$ -beam for the samples  $FC_{\perp\perp}$  (squares) and  $FC_{\parallel\perp}$  (triangles).

We have fitted the spectra obtained at 15 K (figures 2 and 3) using a simple model including an A-site sextet and a B-site sextet. The area ratio of the line-pairs 1, 6 and 3, 4 was constrained to be  $A_{16}/A_{34} = 3$ . To limit the number of free parameters we further constrained the area fraction,  $x = A_{25}/A_{34}$ , to be the same for both subspectra ( $x_A = x_B$ ) and the relative abundance of the A and B-site sextets to be like that extracted from a fit of the 4.35 T spectrum (where the two components are well separated). In figure 4 the calculated values of  $x$  are plotted as a function of the applied magnetic field for a zero-field cooled sample as well as for the two field-cooled samples. The figure summarizes the behaviour already discussed when considering the spectra. The full curves are guide lines to the eye, and are drawn exploiting the information obtained from measurements at 80 K.

Results of the measurements performed at 80 K are summarized in figure 5, where the area ratios of lines 2 and 5 to lines 1 and 6 are plotted for the two field-cooled samples

as a function of the applied field. The spectra obtained at 80 K have broadened lines due to magnetic relaxation and are thus difficult to fit with a simple model. The area ratios have instead been derived from a direct integration of the experimental area of the individual lines. The spectra are, however, so strongly influenced by magnetic relaxation that the lines are partially overlapping and this complicates the analysis. We have taken the points of minimum absorption between them as the separation point between the lines when integrating the area.  $A_{25}/A_{16}$  is less dependent on relaxation effects than  $A_{25}/A_{34}$  and, thus, we use this ratio as a measure of the orientation of the magnetic moments in this series. To overcome the problems with overlapping lines when determining the line areas we tried to sharpen the spectra using Afanas'ev's method [17]. In general, we found good agreement between the values of the area ratios determined from the as-measured spectra and from the sharpened spectra. At high fields ( $B > 0.2$ , T) the area ratios determined from the sharpened spectra are about 5% larger than those found from the untreated spectrum.

The texture induced by the field cooling is revealed by the zero-field spectra, where the area ratio  $A_{25}/A_{16}$  is clearly different in the two samples, being largest in the FC<sub>||</sub> sample. As the applied field is increased the magnetic moments gradually orient in the direction of the applied field resulting in increasing values of  $A_{25}/A_{16}$ . At 0.2 T the spectra of the two samples have the same area ratio, and the aligning action of the applied field is seen to saturate. The area ratio  $A_{25}/A_{16}$  at 0.75 T is about 1.18, and hence all the spins are not fully aligned in this field, as this would result in an area ratio  $A_{25}/A_{16}$  of 4/3.

#### 4. Discussion

From the measurements on the textured samples (figures 4 and 5) it is clear that the frozen-in orientation of the easy axes in the sample is only important to the orientation of the magnetic moments when the applied field is small ( $< 0.2$  T). When larger fields are applied the spectra are identical regardless of the frozen-in orientation of the easy directions. Hence, the reason that full alignment of the spins is not obtained in large applied fields ( $x > 0$  in the 15 K setup and  $A_{25}/A_{16} < 4/3$  in the 80 K setup) cannot be that the magnetic volume anisotropy of the particles hinders the alignment. The results are consistent with the concept of spin canting; the net magnetic moment is easily aligned with the magnetic field, but some spins remain at an angle with the field even in very large applied fields.

Mørup and co-workers [18] have considered the minimum energy orientation of the magnetic moment in a single-domain particle with uniaxial magnetic anisotropy under the influence of a magnetic field,  $B$ , applied at an angle to the easy direction. When the Zeeman energy is the dominating energy term, and the angle between the direction of the applied field and the easy direction is less than  $\pi/2$ , the minimum energy orientation of the magnetic moment is given by

$$\cos \beta = \left[ 1 - \left( \frac{KV}{2\mu B} \right)^2 \sin^2 \alpha \cos^2 \alpha \right]^{1/2} \quad (1)$$

where  $\alpha$  is the angle between the easy direction and the magnetic moment,  $\beta$  is the angle between the applied field and the magnetic moment,  $K$  is the magnetic anisotropy energy constant,  $V$  the particle volume and  $\mu$  is the magnetic moment of the particle. Inserting typical values for the investigated samples ( $\mu \approx 1.4 \times 10^{-19}$  J T<sup>-1</sup>,  $K \approx 1 \times 10^4$  J m<sup>-3</sup>) into (1) shows that  $\cos \beta$  is larger than 0.96 at a field of 0.2 T and larger than 0.997 at 0.75 T

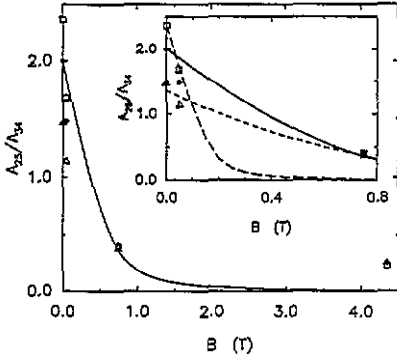


Figure 6. The field dependence of the area ratio  $x = A_{25}/A_{34}$  in the Mössbauer spectra obtained at 15 K for the three samples ZFC ( $\bullet$ ),  $FC_{\parallel}$  ( $\square$ ) and  $FC_{\perp}$  ( $\triangle$ ) as well as best fit curves of the data (ZFC (full curve),  $FC_{\parallel}$  (dashed) and  $FC_{\perp}$  (long-dash broken curve)) using the model described in appendix 1. For the ZFC sample the best fit was obtained for  $K = 1.6 \times 10^5 \text{ J m}^{-3}$  and for the field-cooled samples best accordance was found for  $K = 1.9 \times 10^5 \text{ J m}^{-3}$  and  $K = 3.8 \times 10^4 \text{ J m}^{-3}$  for the  $FC_{\perp}$  and the  $FC_{\parallel}$  samples, respectively. The experimental uncertainty on the area ratios is of the same order of magnitude as the size of the symbols.

for all values of  $\alpha$ . This seems in good agreement with the observed behaviour, where the aligning action of the applied field is also seen to saturate at about 0.2 T.

The field dependence of the obtained degree of spin alignment is inconsistent with the assumption that the alignment is determined only by the orientation of the net magnetization in the particles. This is illustrated in figure 6, where the experimental values of  $A_{25}/A_{34}$  at 15 K for the three samples are plotted. Also shown are best-fit curves obtained from the model suggested by Pankhurst and Pollard, with the anisotropy energy constant being treated as a fitting parameter. A short description of this model, and details of the calculations are given in appendix 1. From figure 6 it is clear that the model cannot account for both the strong aligning action of small applied fields, and the lack of full alignment in large fields. To describe the low-field behaviour a small anisotropy energy constant is required and to describe the high-field response a large value of the anisotropy energy constant is necessary. The best fits using the Pankhurst and Pollard model were obtained for values of the anisotropy constant which are from 5–15 times larger than the experimentally determined value of  $K$  [16].

There are other experimental observations that seem inconsistent with the hypothesis that the lack of full alignment of the spins in large fields is caused by the volume anisotropy. We shall discuss these below.

Pankhurst and Pollard expressed the influence of the anisotropy in their model through effective anisotropy constants  $K_A$  and  $K_B$  felt by the spins in the A and B sublattices, respectively. By fitting the Mössbauer spectra obtained in large fields they derived the values of  $K_A$  and  $K_B$ . In order to compare the importance of the anisotropy in their sample with the anisotropy in the sample studied here, we must calculate the effective volume-specific anisotropy constant,  $K_e$ , that corresponds to these  $K_A$  and  $K_B$  values. Since the exchange interaction among the spins is much stronger than the interaction with the effective anisotropy fields [14], the spins will reverse by coherent rotation in a thermally driven magnetization reversal. The energy barrier that must be surmounted when the magnetization reverses must thus be equal to the sum of the sublattice anisotropy energy barriers:

$$E_{\text{bar}} = N_B S_B^2 (K_B + \xi^2 K_A) \quad (2)$$

where  $N_B$  is the total number of B-sublattice spins,  $S_B$  the spin at the B-sites and  $\xi$  the ratio of the number of A-site spins to B-site spins times the ratio of the magnitude of the spins. The effective volume specific anisotropy constant,  $K_e$ , is related to the energy barrier defined above by

$$K_e = \frac{E_{\text{bar}}}{N_B v_B} \quad (3)$$

where  $v_B$  is the volume per B-site spin (in maghemite  $v_B = 4.425 \times 10^{-29} \text{ m}^3$ ). Inserting the values for  $K_A$ ,  $K_B$ ,  $\xi$  and  $S_B$  found by Pankhurst and Pollard [14] ( $K_A = 1.22 \times 10^{-23} \text{ J}$ ,  $K_B = 1.48 \times 10^{-25} \text{ J}$ ,  $\xi = 0.61$  and  $S_B = 5/2$ ) we find  $K_e \approx 6.6 \times 10^5 \text{ J m}^{-3}$ . This value is about 50 times larger than the value found for the sample investigated here, which was determined using three different methods [16]. Still, the remaining area fraction in lines 2 and 5 in large applied fields is larger in our sample than in the sample studied by Pankhurst and Pollard. Considering the relative magnitude of the magnetic anisotropy energies in the two systems, this is inconsistent with the suggestion that it is the magnetic volume anisotropy that accounts for the incomplete spin alignment.

When fitting the 15 K spectra shown in figures 2 and 3 we noticed that, whereas lines 2 and 5 of the spectra are well fitted at 0 and 0.05 T by the two-sextet model, the positions of lines 2 and 5 of both the A and the B-site sextet at 0.75 and 4.35 T are inconsistent with the experimental spectrum. If lines 2 and 5 are instead fitted separately we find (for the 0.75 T spectrum) that the hyperfine field calculated from the splitting of these lines is about 1 T (2%) smaller than that calculated from the position of lines 1 and 6. This is in agreement with earlier investigations by Morrish [19]. The canted spins, which give rise to the absorption in lines 2 and 5 of the Mössbauer spectrum, are thus distinguishable from the majority of aligned spins. No explanation of this observation can be given by the model where the incomplete alignment is ascribed to incomplete alignment of all spins [14].

On the basis of the above discussion it seems reasonable to assume that the Mössbauer spectra obtained in large fields ( $B > 0.7 \text{ T}$ ) consist of two components: one component accounting for the majority of spins that are fully aligned with the applied field, and one component accounting for the canted spins. If we assume that the canting angles of the canted spins are random we can calculate the fraction of spins that are canted from the measured area ratios. Analysing the 15 K Mössbauer spectra in this way, (assuming them to be made up of a sextet with the area ratio  $A_{16} : A_{25} : A_{34} \sim 3 : 2 : 1$  and a sextet with the area ratio  $A_{16} : A_{25} : A_{34} \sim 3 : 0 : 1$ ), the fraction of spins that are canted is found to be 0.27 and 0.17 in applied fields of 0.75 T and 4.35 T, respectively. At 80 K the fraction of spins that are canted in an applied field of 0.75 T is found to be 0.18. The fraction of spins that are canted thus decreases with increasing temperature, in agreement with earlier experimental findings [7, 8].

## 5. Conclusion

The present experimental studies lead to the conclusion that the incomplete alignment of the spins in maghemite particles in large magnetic fields is not caused by incomplete alignment of all the spins due to large magnetic volume anisotropy as suggested in a recent publication [14]. This is ruled out by several observations, such as the demonstrated independence of the observed degree of alignment in large magnetic fields on the orientation of the easy directions in the samples.

Our observations are all compatible with the concept of spin canting. The majority of the spins are easily aligned with an applied magnetic field but a fraction of the spins are canted and remain at an angle to the applied field even in very large fields. This picture can also account for the observation that the hyperfine field of lines 2 and 5 measured in large fields is different from the hyperfine field of the other line pairs.



## Appendix 1.

Pankhurst and Pollard have presented a model [14] for calculating the orientation of the magnetic moments in a two-sublattice spin system in a magnetic field. It includes the exchange energy, the Zeeman energy and a magnetic anisotropy energy associated with each sublattice. The following energy must be minimized to find the equilibrium moment orientation:

$$E = S \left[ B_E \xi \cos(\theta - \theta') - \frac{1}{2} B_A \cos^2(\theta - t) - \frac{1}{2} B'_A \xi^2 \cos^2(\theta' - t) - B(\cos \theta + \xi \cos \theta') \right]. \quad (\text{A1})$$

Here  $S$  is the total spin moment,  $B_E$  and  $B$  are the exchange and local fields,  $B_A$  and  $B'_A$  are the sublattice anisotropy fields and  $\xi$  is the sublattice spin ratio. All angles are measured with respect to the applied field direction:  $\theta$  and  $\theta'$  are the two sublattice moment directions and  $t$  is the easy direction of magnetization.

We used a bisection method to determine the values of orientation of the sublattice moments that minimize  $E$ . When a realistic value of the exchange energy is used (about 1000 T for maghemite according to Pankhurst and Pollard), the exchange energy term becomes so large as to dominate  $E$  and  $\theta'$  is found to be anti-parallel to  $\theta$ , to within  $0.4^\circ$ . Hence, in all further calculations we assumed  $\theta' = \theta - 180^\circ$ .

This leads to a further simplification, in that the two-sublattice anisotropy fields will effectively be the same because the sublattice with the smaller anisotropy field will be forced to be antiparallel to that with the larger anisotropy. Hence we let  $B'_A = B_A$ .

For the anisotropy field, Pankhurst and Pollard use a value of 1.0 T which is considerably higher than the value we expect for our particles. Instead of assuming a value for  $B_A$ , we used this as the unknown quantity which was varied until the best fit to the experimental data was found.

In figure 1 of the Pollard and Pankhurst paper [14], we see the lattice angle  $\theta$  with increasing local field for various orientations of the easy axis. The discontinuities occur because for large particles, with long relaxation times, the energy minimum in which the system is found will be the minimum closest to the original state of the system. However, for our much smaller particles, we expect to see complete relaxation so that the global minimum of the system will determine the orientation of the sublattice orientations, not the local minimum.

A density of states,  $P(t)$ , of easy-axis angles was calculated for each of the freezing-field orientations by the method described in [16]. For simplification the density of states was calculated only for the median particle size. The theoretical values of line areas 2 and 5, and 3 and 4, were determined by finding  $\theta$  for each easy-axis angle and weighting the contributions to the line areas by the appropriate density:

$$\left. \frac{A_{25}}{A_{34}} \right|_B = \frac{\sum_i 4P(t_i) \sin^2 \theta(t_i, B_A)}{\sum_i P(t_i) [1 + \cos^2 \theta(t_i, B_A)]}. \quad (\text{A2})$$

We assumed that the local field was equal to the applied field, which ranged from 0–4.35 T. A second bisection loop was used to find the anisotropy field which gave the best fit to the experimental line area ratios for the different applied fields. The other values used were those given by Pankhurst and Pollard for maghemite:  $\xi = 0.60$  and  $B_E = 1000$  T.

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