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The spin-canting anomaly in ferrimagnetic particles

R J Pollard

Department of Physics, Monash University, Clayton, Victoria 3168, Australia

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Abstract. The spin-canting anomaly, in which fine ferrimagnetic iron oxide particles are not completely saturated by very large applied magnetic fields, is investigated by high-field Mössbauer spectroscopy. Until now it has been thought that randomly oriented moments near surfaces were responsible. High-quality data are used to repudiate this view. Ferric ions on A sites are collinear with the applied field, whereas those on B sites are not quite collinear. Further, it is shown that the likely presence of antiferromagnetic impurities greatly confounds the interpretation of earlier experiments.

1. Introduction

In a large applied magnetic field, one expects the net magnetic moment of ferrimagnetic particles to completely align in the field direction and the magnetisation to be saturated. However, it was shown many years ago that this is not true for fine $\gamma\text{-Fe}_2\text{O}_3$ particles in a 5 T field [1]. Since its discovery, the spin-canting anomaly has attracted numerous experimental studies and seems universal in fine iron oxide and ferrite particles. Comprehensive reviews of the work have been published by Morrish and Haneda [2] and Haneda [3]; the effect has been discussed in a general context by Coey [4].

Our present purpose is to show, from Mössbauer spectra of fine $\gamma\text{-Fe}_2\text{O}_3$ particles, that part of the observed effect is the result of impurities. X-ray and Mössbauer patterns of two different samples are consistent with the presence of hematite impurities; applied-field Mössbauer spectra show that there is no canting of the ferrimagnetic moments on A sites. This work differs experimentally from the previous studies only in that long γ -ray counting times, combined with 9 T applied fields, provided higher resolution.

The spin-canting phenomenon is of importance in magnetic recording, since it is expected to lead to decreased coercivities and remanences and is inconsistent with the simple models of magnetisation reversal commonly used [5]. Many of the investigations, including the present one, are made on acicular $\gamma\text{-Fe}_2\text{O}_3$ recording particles.

Coey [1, 4] proposes that the effect involves a random canting of the surface spins in a ferrimagnetic lattice, resulting from a different balance of competing exchange interactions at sites near the surface. Haneda [3] further suggests that the canting occurs at the surfaces of a number of crystallites within a particle; nevertheless it is evident that the effect is larger for particles with a higher specific surface, and that the magnitude of the effect does not vary markedly with applied-field strength [2]. A study of particles with superior surface morphology obtained similar degrees of canting to those of other samples [6]. Metallic particles (Fe, Fe–Co, and Fe–Ni) do not exhibit spin-canting, and

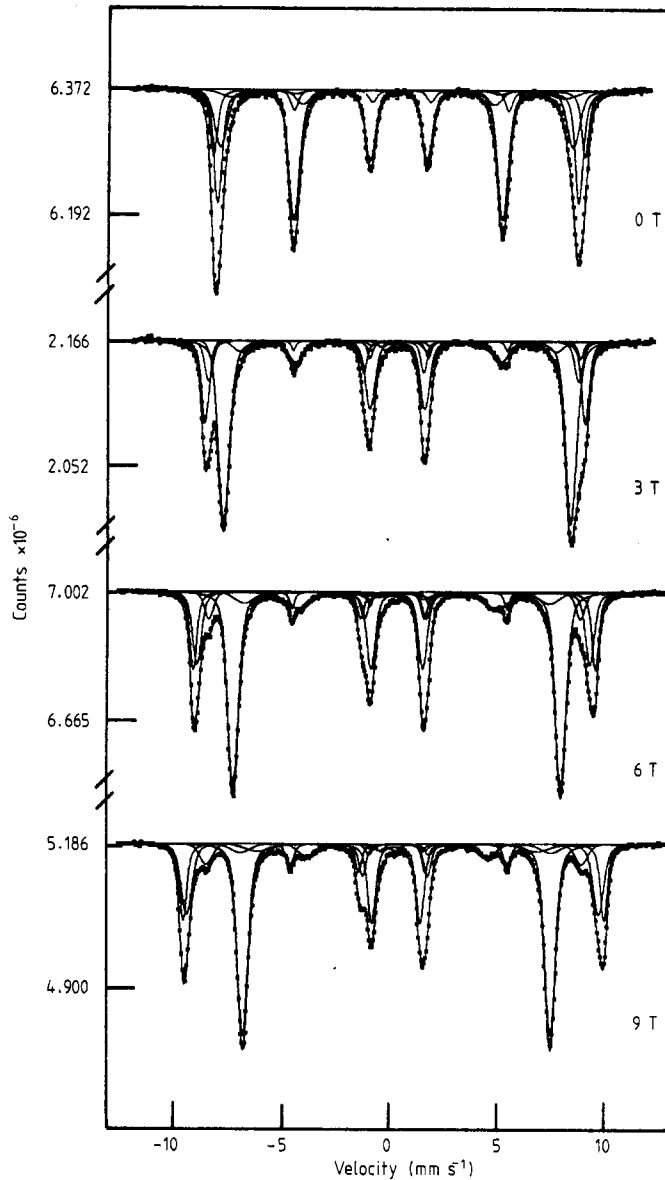


Figure 1. Mössbauer spectra of $\gamma\text{-Fe}_2\text{O}_3$ (maghaemite) particles at 4.2 K and subjected to the applied magnetic field strengths shown. The full curves show the individual Voigtian profiles and their sum obtained by least-squares fitting.

it has been suggested that this is a result of itinerant electrons acting to reduce anomalous exchange interactions near the surface [7, 8]. In all the studies on ferrites, the particles were assumed to be of homogeneous chemical composition, whereas in studies on metallic particles the results were interpreted with the knowledge that the particles were coated with oxide.

Although evidence for the effect is seen by a reduced and non-saturated magnetisation ([1] and [3] and references therein), most investigations have employed

Mössbauer spectroscopy. Randomly oriented particles are subjected to a 3–9 T field applied parallel to the collimated γ -ray beam. In principle the interpretation of the spectra is straightforward, since the electric field gradients (EFG) are small and any effects on line areas are usually neglected. For ferrites two magnetic sub-patterns are resolved: the applied field adds to the hyperfine magnetic splitting of Fe^{3+} in A sites and subtracts from that in B sites (see figure 1). Both the A- and B-site subpatterns occur as sextets; with lines numbered in ascending order with increasing γ -source velocity, the relative area of the second and fifth lines ($\Delta m_l = 0$ transitions) to the inner lines ($\Delta m_l = \pm 1$) depends only on the angle between the γ -ray beam and the magnetic moment (θ):

$$L_{25}/L_{34} = 4 \sin^2 \theta / (1 + \cos^2 \theta).$$

This quantity takes values between 0 and 4. For collinear spins it is 0, and for canted spins it is non-zero. Observations of spin-canting typically show L_{25}/L_{34} values in the range 0.1–0.6, which correspond to single-valued angles of non-collinearity in the range 13–30° [2]. For non-uniform spin directions an averaged quantity $\langle L_{25} \rangle / \langle L_{34} \rangle$ is measured, however in the case of zero EFG there is no dependence of the line positions on θ and the distribution of directions cannot be measured. The L_{25}/L_{34} ratio for microcrystalline antiferromagnetic substances is generally large; for a random orientation it is 2. In zero-applied-field experiments on acicular particles the easy direction is the particle long axis, and θ can be used as measure of the orientation of the particles. However, in spin-canting experiments the fields applied are larger than the demagnetising fields and the results are considered to be independent of particle orientation. Powder samples are used, in which the orientations of the particles are close to being random.

An earlier study investigated the positions of the $\Delta m_l = 0$ lines with 6 T fields applied to check for the effects of electric field gradients, which may be enhanced near the particle surface [9]. It was found that although electric field gradients do lead to non-zero L_{25} even when the spin arrangement is collinear, the magnitude of the interaction required seemed unreasonably large for this to be the only cause. The higher-field and higher-quality results now presented provide better resolution and an alternative interpretation.

Zero-applied-field Mössbauer spectra of $\gamma\text{-Fe}_2\text{O}_3$ show asymmetrically broadened lines; the degree of broadening varies from sample to sample and is temperature dependent. These effects and possible causes are discussed in [10].

2. Experimental details

Two samples of $\gamma\text{-Fe}_2\text{O}_3$ particles were studied that have been characterised in detail previously [9]. One sample consists of spindle-shaped monodispersed particles with a length of 350(60) nm and an axial ratio of 4.8(5). The other consists of partially dispersed rod-shaped 'non-polar' particles, having a length of 260(100) nm and an axial ratio of 7(3). The spectra shown are from the spindle-shaped particles, however both samples were investigated in equal detail.

A $^{57}\text{CoRh}$ source at 4.2 K was used, and velocity calibration is with respect to Fe foil at room temperature. Magnetic fields were applied parallel to the γ -ray beam. A triangular shaped velocity waveform was used, and spectra with 500 velocity channels were obtained after numerical folding.

3. Results

Mössbauer spectra taken with various applied field strengths are shown in figure 1. The weak lines centred near -4.5 and 5.5 mm s^{-1} are those normally associated with L_{25} ; they appear to lie close to the positions expected from non-zero intensity $\Delta m_l = 0$ transitions for the A- and B-site subspectra. However, at both 6 T and 9 T extra lines are seen for the first time. At 9 T they are positioned at $-8.36(2)$ and $9.10(2) \text{ mm s}^{-1}$; the corresponding hyperfine field (B_{HF}) is $54.4(1) \text{ T}$. These lines are identified as belonging to the outer lines of antiferromagnetic haematite ($\alpha\text{-Fe}_2\text{O}_3$), pure micrometre-sized particles of which show $\langle B_{\text{HF}} \rangle = 54.5(1) \text{ T}$ under the same conditions (these spectra are shown in figure 2). One difference is in the centroid of the lines: for haematite the mean position of the outer lines (isomer shift δ + quadrupole perturbation ϵ) is at $0.57(4) \text{ mm s}^{-1}$, whereas for the sub-spectrum in figure 1 it is at $0.37(4) \text{ mm s}^{-1}$ at 9 T. This difference can be understood in terms of the particle-size dependence of the Morin transition in haematite. For bulk material the Morin transition occurs at 263 K, whereas for particles smaller than 12 nm it is below 4.2 K [11]. The transition is manifested by a change in the sign and magnitude of the quadrupole splitting: ϵ is $0.21(2) \text{ mm s}^{-1}$ below the transition and $-0.11(2) \text{ mm s}^{-1}$ above the transition. These values were measured from zero-applied-field spectra at 4.2 K and room temperature respectively, however in 9 T the apparent quadrupole splitting is reduced since the particles are randomly aligned. For haematite subjected to fields of 9 T, ϵ is $0.09(2) \text{ mm s}^{-1}$ at 4.2 K and $-0.08(2) \text{ mm s}^{-1}$ at 298 K. Thus we expect a difference of $0.17(4) \text{ mm s}^{-1}$ at 4.2 K in the centroid of the outer lines for fine and large haematite particles at 9 T, which compares well with the $0.20(8) \text{ mm s}^{-1}$ difference obtained. Hence the extra lines have positions which are consistent with those expected from the outer lines of a sub-spectrum from fine haematite particles.

The corresponding $\Delta m_l = 0$ lines for this subspectrum are expected to lie at $-4.47(2)$ and $5.64(2) \text{ mm s}^{-1}$, and are therefore close to the lines hitherto identified with spin-canting. Figure 3 shows the experimental data in these regions. The characteristic which clearly identifies antiferromagnetism from both ferrimagnetism and ferromagnetism is the field dependence of the line positions. As illustrated in figure 2, haematite line positions change little with field. In this region (below the Morin transition) haematite is a pure antiferromagnet. In comparison, $\Delta m_l = 0$ lines from saturated ferri- and ferromagnetic components should change position by $0.093 \text{ mm s}^{-1} \text{ T}^{-1}$. It can be seen that the area fitted with the narrower line changes position by less than $0.015 \text{ mm s}^{-1} \text{ T}^{-1}$. This absorption is therefore of antiferromagnetic origin, and is of the correct area and position to correspond to $\Delta m_l = 0$ lines of a sub-spectrum from fine haematite particles.

Supporting evidence for the presence of haematite was obtained from x-ray diffractograms with a cobalt target. Although $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ have largely overlapping patterns, the (104) peak of $\alpha\text{-Fe}_2\text{O}_3$ was clearly discernible and the (102) peak could also be seen on the shoulder of a $\gamma\text{-Fe}_2\text{O}_3$ peak. All other peaks were identified as arising from $\gamma\text{-Fe}_2\text{O}_3$. The abundance of haematite was estimated to be $6.2(5)\%$ (spindle-shaped particles) and $2.7(3)\%$ (non-polar particles) from the Mössbauer line areas.

Inspection of figure 3 shows that there is no absorption which moves to higher absolute velocity with increasing field, which might arise from $\Delta m_l = 0$ transitions of ions on A sites. However, some absorption does change towards lower absolute velocity with increasing applied field: on average the shift is $0.10(1) \text{ mm s}^{-1} \text{ T}^{-1}$, which is consistent with ferromagnetism and ferrimagnetism. This absorption has a position close to that expected from B sites in $\gamma\text{-Fe}_2\text{O}_3$, however before an unambiguous identification of its origin can be made it is necessary to consider whether impurities might be responsible.

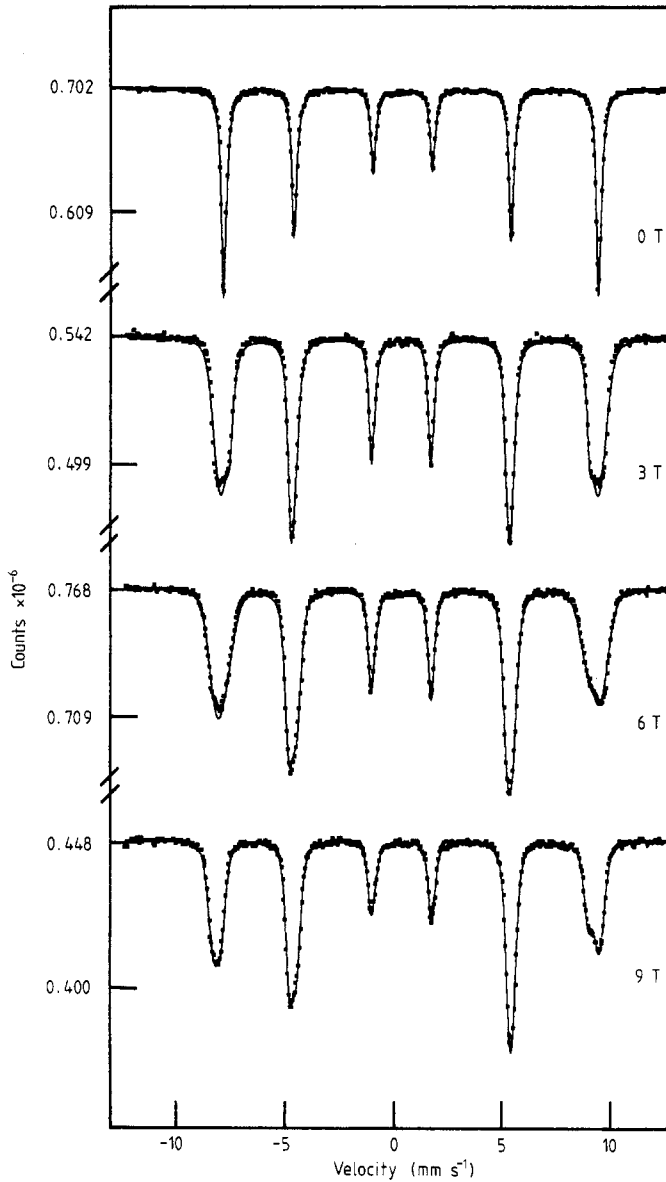


Figure 2. Mössbauer spectra of randomly oriented 1–10 μm sized haematite particles at 4.2 K subjected to the applied magnetic field strengths shown.

All known iron-oxides and oxyhydroxides were considered, however only $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ (ferrihydrite), Fe_3O_4 (magnetite), $\delta\text{-FeOOH}$, and $\delta'\text{-FeOOH}$ (ferroxihite) are not antiferromagnetic. Spectra of synthetic samples of these were taken for comparison at room temperature, 77 K, and 4.2 K. Fields of up to 9 T were applied at 4.2 K. In summary the $\Delta m_l = 0$ lines from ferrihydrite samples showing two and six x-ray peaks [12] change position by less than $0.01 \text{ mm s}^{-1} \text{ T}^{-1}$ in an applied field (ferrihydrite is speromagnetic), and the Fe_3O_4 patterns do not show absorption features in the velocity

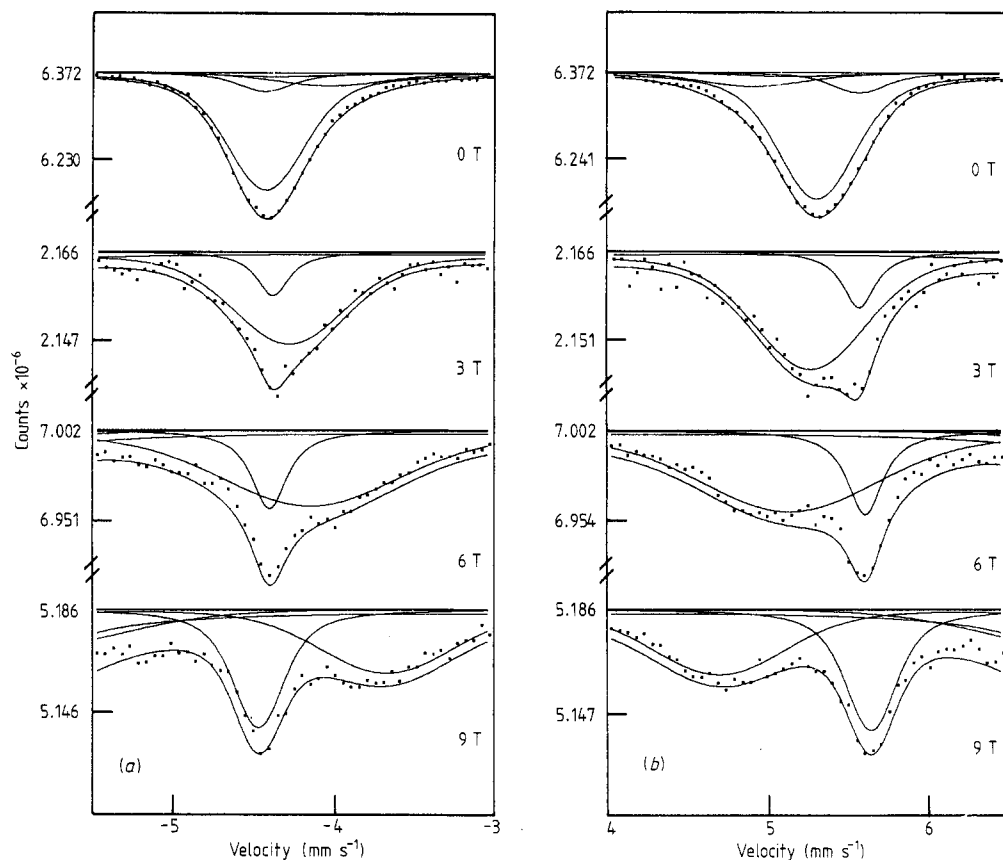


Figure 3. The spectra of figure 1, showing the experimental and calculated data in the velocity regions of the $\Delta m_I = 0$ lines.

range of concern. However, both δ and δ' -FeOOH are ferrimagnetic and their spectra provided a good fit at 77 K and at 4.2 K with and without a field applied. At room temperature and without a field applied, δ -FeOOH and δ' -FeOOH show either a severely reduced hyperfine field or a paramagnetic doublet. A doublet of sufficient area was not observed at room temperature; a very weak doublet was present but could be ascribed to iron impurities in the detector window. Paramagnetic impurities could only be present in the sample if their area reduced by a factor of at least two on warming from 4.2 K. Nevertheless, such a strong temperature dependence is commonly observed for very fine particles [8, 13, 14].

To test for the presence of δ -FeOOH or δ' -FeOOH, a spectrum of the spindle-shaped particles was taken with the sample temperature controlled at 298 K and with a 6 T magnetic field applied (figure 4). Lines from $\Delta m_I = 0$ transitions for two components are just resolved; their positions are consistent with haematite and a component with a hyperfine field close to that of the moments at B sites in γ -Fe₂O₃. Consequently neither δ -FeOOH nor δ' -FeOOH is responsible for the field-dependent absorption in figure 3.

In order to quantify the magnetic behaviour of the component with the field-dependent absorption, the 4.2 K spectra were least-squares fitted to sextets of Voigtian profiles.

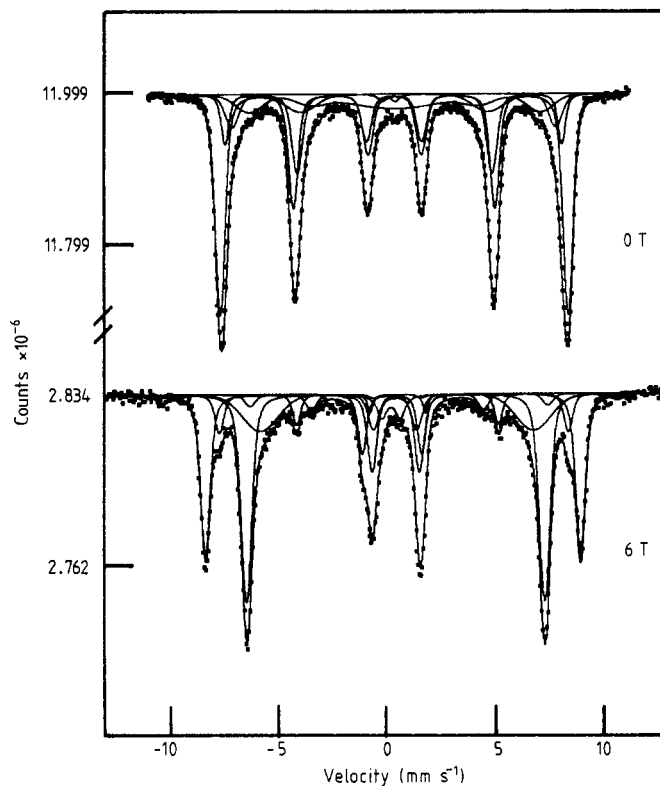


Figure 4. Mössbauer spectra of $\gamma\text{-Fe}_2\text{O}_3$ at 298 K, with and without a 6 T magnetic field applied. The quality of the 6 T spectrum is relatively poor because excessive liquid helium consumption restricted the counting time.

The requirement for a number of sextets of non-Lorentzian shape arises in part from asymmetric hyperfine distributions, and is discussed in [10]. Two sextets with areas of lines $L_1:L_2:L_3:L_4:L_5:L_6$ constrained in the proportions 3:0:1:1:0:3 were used to represent collinear ions at each of A and B sites. One sextet constrained to 3: h :1:1: h :3, where h is a parameter, was used to represent the haematite subspectrum, and one sextet constrained to 3: u :1:1: u :3 where u is a parameter was used for the unidentified component with non-zero L_{25} . The respective magnetic hyperfine fields obtained, labelled A_1, A_2, B_1, B_2, H , and U , are plotted in figure 5. It can be seen that component U follows the trend of B_1 quite closely, indicating that its origin is from nearly collinear B-site ions. Furthermore, at 9 T the positions of the $\Delta m_I = 0$ lines for U are $-3.67(3)$ and $4.69(3)$ mm s^{-1} , and the outer line positions for B_1 are $-6.67(2)$ and $7.65(2)$ mm s^{-1} . The two components can be reconciled by one component with $B_{\text{HF}} = 44.6(2)$ T, $\varepsilon = -0.01(2)$ mm s^{-1} , and $\delta = 0.50(2)$ mm s^{-1} at 9 T.

The values u and h obtained at 9 T were 4 and 2.2(5) respectively. The former value is quite uncertain as in the analysis only the $\Delta m_I = 0$ lines were resolved. However the latter value indicates that the moments of component H are close to random, and therefore verifies that this area has been properly treated as arising solely from haematite.

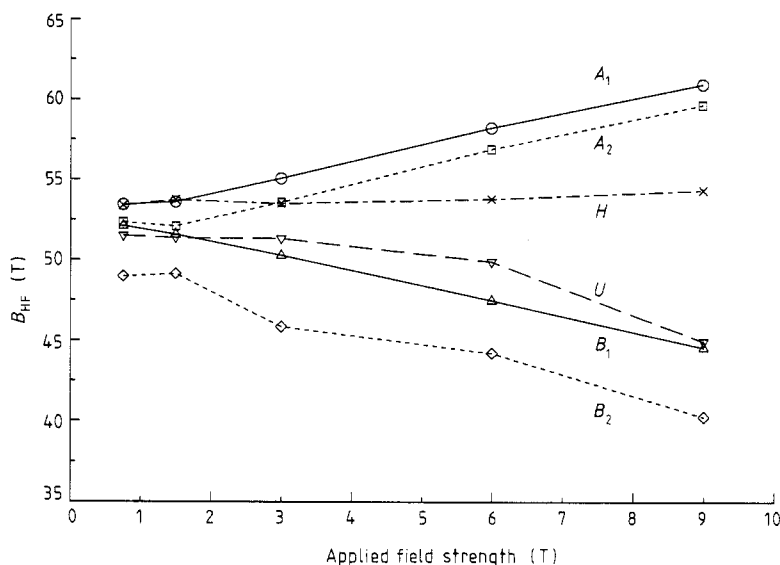


Figure 5. The variation of the magnetic hyperfine fields in $\gamma\text{-Fe}_2\text{O}_3$ at 4.2 K with applied magnetic field. The major A- and B-site components are A_1 and B_1 respectively, H represents the haematite sub-spectrum, and U represents non-collinear moments.

4. Discussion and conclusions

It has been shown that there is no evidence for A site spin-canting in $\gamma\text{-Fe}_2\text{O}_3$. Unless high quality data are taken at fields at or above 6 T, haematite impurities may be mistaken for spin-canting of the ferrimagnetic moments. The presence of anti-ferromagnetic surface impurities explains the apparent particle size dependence of the earlier results which led to the hypothesis of surface spin-canting. Toney *et al* have shown by x-ray depth profiling of thin films that a 9 nm thick layer of haematite forms during oxidation of Fe_3O_4 in the preparation of $\gamma\text{-Fe}_2\text{O}_3$ [15]. Since magnetic recording particles are produced by oxidation of Fe_3O_4 , and since both samples examined here show haematite, the presence of a haematite coating on the surface of fine particles is likely to be pervasive.

Fine oxide crystallites on the surface of a particle are known to exhibit strongly decreasing zero-phonon fractions at temperatures increasing from 4.2 K to room temperature [8, 13, 14], an effect which explains the two-fold reduction in the apparent spin-canting effect for $\gamma\text{-Fe}_2\text{O}_3$ with a 5 T field applied at 300 K compared to 4.2 K [16].

The $\Delta m_l = 0$ lines for B sites appear to have non-zero intensity, but change position under the influence of an applied field in the manner expected of a collinear magnetic structure. If the lines arose from randomly oriented pinned magnetic-moments, their positions would not change. We can understand these results if the applied field forces the A-site moments to align completely antiparallel to the field direction, and the B-site moments are not quite completely aligned parallel. From the line areas of spectra from spindle-shaped particles at 4.2 K, the angle between the field direction and the B-site moments is such that $\langle \sin^2\theta \rangle = 0.11(1)$ and $0.072(8)$ at 6 T and 9 T respectively. If the angles are not distributed then the corresponding θ -values are $19(1)^\circ$ and $16(1)^\circ$. For the non-polar sample under the same conditions, θ is $12(1)^\circ$ and $10(1)^\circ$ respectively.

Consequently the collinearity of the B-site ions appears to improve slightly with increasing field strengths. For the spindle-shaped particles at 298 K, θ was $16(3)^\circ$, showing that there is little temperature dependence of the spin-canting effect.

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