The inadequacy of applied-field Mossbauer spectroscopy as a means of proving the existence

of speromagnetism

REPLY TO COMMENT

The inadequacy of applied-field Mössbauer spectroscopy as a means of proving the existence of speromagnetism

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Abstract. We reply to the suggestion that a two-sublattice collinear spin model employed by us to analyse applied-field Mössbauer spectra of various insulators yields impossibly large values for the uniaxial anisotropy constant and should therefore be disregarded in favour of a model of speromagnetism. We note that the value of the anisotropy constant obtained for antiferromagnetic goethite (α-FeOOH) using the collinear model, $K_1 \simeq 3 \times 10^5$ J m^{-3}, is consistent with both spin-flop measurements on bulk goethite and with independent theoretical calculations. The anisotropy constants of samples of the disordered iron oxyhydroxide feroxyhite (δ'-FeOOH), obtained with the collinear model, may be as high as $\sim 10 \times 10^5$ J m^{-3}. The anisotropy constants of three reputedly speromagnetic insulators, calculated using the collinear model, fall within this range, and are therefore not impossibly large. We reaffirm that there remains a fundamental misconception in the belief that applied-field Mössbauer spectroscopy may be employed to distinguish between speromagnetism and antiferromagnetism in randomly aligned particles and disordered materials.

In a recent letter [1] we pointed out that it is difficult, and perhaps impossible, to employ applied-field Mössbauer spectroscopy to distinguish between two different magnetic states of matter—that of speromagnetism, and that of antiferromagnetism in randomly aligned fine particles and disordered materials. A speromagnet is defined as a material in which the spin structure on an atomic level is random; the spin directions are isotropically distributed and are uncorrelated. In antiferromagnets an isotropic spin structure may appear at the aggregate level of domains, crystallites or particles, but adjacent spins within the constituent regions are antiparallel.

The concept of speromagnetism arose twenty years ago on the basis of applied-field Mössbauer measurements on a material described as a 'ferric gel' obtained from pools of water near springs on a marshy moor [2, 3]. This material is now thought to be the mineral ferrihydrite which occurs in fine-particle form and is frequently formed biologically [4, 5]. We have already discussed in detail the reasoning by which the new concept of speromagnetism was invoked [1]. In essence it was founded upon qualitative expectations: two conventional magnetic states in fine particles were considered, namely antiferromagnetism and canted antiferromagnetism (or parasitic ferromagnetism). These were both said to be inconsistent with the applied-field Mössbauer spectra [2, 3], and consequently a new type of magnetic order was instated [6]. No attempt was made to quantify the expectations for the well-known antiferromagnetic states.

The concept of speromagnetism was, *per se*, inadequate: to explain a weak net magnetic moment, the ferric gel was said to contain fine particles within which the order was speromagnetic. For both antiferromagnetism and speromagnetism, a random walk argument

shows that an uncompensated net moment is expected for fine particles: the uncompensated moment per ion is proportional to $n^{-1/2}$, where n is the number of magnetic ions per particle. Although the original work [2, 3] described the magnetic structure as 'sperimagnetic', this did not signify anisotropy in the distribution of spin directions, and in later work the term was revised to 'speromagnetic' [7].

Experimentally we found that the common iron oxyhydroxides goethite, akaganéite and lepidocrocite, as well as several samples of ferrihydrite, exhibit qualitatively similar applied-field Mössbauer spectra to those of the ferric gel, and so might appear speromagnetic [8]. Most of these materials are well known as antiferromagnets. We therefore calculated the results expected for conventional magnetic structures, starting from the simplest model of uniaxial antiferromagnetism in randomly oriented particles. Excellent agreement with the findings of alternate techniques was obtained for a range of materials: the results are consistent with estimates of the spin-flop transition field in both haematite and goethite [9], with high-resolution electron microscopy observations of the particle-size in ferrihydrite [10], and with the blocking temperature in fine-particle goethite [11].

The difficulty in using Mössbauer spectroscopy to distinguish between speromagnetism and antiferromagnetism arises because the spectra convey no information concerning the length of magnetic correlations within the material. Even for single crystals it is only in special cases that such information can be deduced, for example when all spins lie parallel or perpendicular to the direction of the γ-ray beam. Applying a magnetic field to a powder in which there is distribution of orientations of electric field gradients is similarly ambiguous with regard to the distribution of spin directions, unless all spins are either parallel or perpendicular to the applied field direction. In [1] we drew attention to these observations.

We also reexamined the evidence for speromagnetism in other insulating materials, since the qualitative reasoning originally applied has been taken up by other authors. Besides ferrihydrite [5] these materials include the precipitates found in ion exchange membranes [12], and the glassy insulators FeF_3 [13] and $NaFeF_4$ [14]. Application of a simple model to the glassy materials is less justified than it is to minerals, since there is no long-range order; nevertheless it is of interest to determine whether there is a need to invoke speromagnetism. In such materials one might argue that random exchange is expected, however the indications are that the nearest-neighbour spins are oriented such that their vector sum is small [15]. Our approach was therefore to apply the simplest possible model, and to progress to more complicated models only as the data required. In all cases either antiferromagnetism or ferrimagnetism provides an adequate explanation. We concluded that there is insufficient evidence to unambiguously identify speromagnetism from applied-field Mössbauer spectra, even for a material that is indeed speromagnetic.

Coey [16] takes issue with the values of anisotropy constants derived by least-squares fitting the parameters of the model, arguing that they are impossibly large and that antiferromagnetism or ferrimagnetism should therefore by disregarded in favour of speromagnetism. Coey derives values for the anisotropy energy per unit volume from the measured values of the local anisotropy field, B_A, and claims that these energies are unrealistic.

Excessive energies would be of concern if the model was said to be a complete and rigorous representation of the magnetism in the particles, or if the materials were perfect crystalline antiferromagnets. However, this is not so. Our interest was to see whether qualitative trends assumed to prove speromagnetism could have a simpler explanation. It is unreasonable to expect the anisotropy constants obtained from such a simple model to be absolute, especially since their effect on the experimental data is neither direct nor easily measured. In disordered insulators single-valued uniaxial anisotropy constants are

probably a gross simplification, although in minerals the limitations of the approach should be less severe. We have explicitly noted the limitations where appropriate, for example the neglected effects of incoherent magnetization reversal in ferrimagnets [17]. More recently it has been shown that interactions between ferrihydrite crystallites are significant [18].

Nevertheless, it is a reasonable question to ask how the anisotropy parameters derived compare with those measured by other techniques. The anisotropy fields, B_A, obtained using our model are shown in table 1 for the original 'ferric gel', glassy FeF$_3$, and ferrihydrite [1, 10], as well as for two polycrystalline two-sublattice antiferromagnets, namely powdered goethite and haematite [9]. For completeness, the anisotropy fields obtained using the analogous two-sublattice ferrimagnetic model to describe samples of feroxyhite (δ'-FeOOH) [19], cobalt surface-modified maghemite (γ-Fe$_2$O$_3$) [20] and barium ferrite (BaFe$_{12}$O$_{19}$) [21] are also given.

Table 1. Anisotropy fields, B_A, derived from least-squares fits for applied-field Mössbauer spectra recorded at liquid helium temperature for several materials using a simple two-sublattice antiferromagnetic or ferrimagnetic model, and the corresponding anisotropy energies per unit volume, K_1. The experimentally determined range of possible B_A values, ΔB_A, calculated to a confidence level of one standard deviation, are also shown. For materials that exhibit a ferrimagnetic character, the ratio of sublattice spin magnitudes, ξ, differs from unity.

Sample	B_A (T)	ΔB_A (T)	ξ	K_1 ($\times 10^5$ J m^{-3})	Reference
'ferric gel'	4.2	$\geqslant 0.5$	1	$\geqslant 2.1$	[1]†
a-FeF$_3$	4.6	$\geqslant 1.9$	1	$\geqslant 9.0$	[1]†
'two-line' ferrihydrite	0.6	0.5–0.7	0.92±0.05	3.1–4.4	[10]
'six-line' ferrihydrite	0.9	0.8–1.0	1	5.0–6.3	[10]
feroxyhite, sample 1	0.1	$\leqslant 0.2$	0.96±0.02	$\leqslant 1.5$	[19]
feroxyhite, sample 1	1.36	1.35–1.38	0.73±0.15	10.1–10.3	This work‡
goethite	0.41	0.34–0.54	1	2.5–4.0	[9]
haematite	0.02	0.019–0.022	1	0.18–0.20	[9]
Co:maghaemite	0.62	0.55–0.68	0.61	4.7–5.8	This work‡
barium ferrite	0.68	0.60–0.76	0.53	4.8–6.1	This work‡

† Ambiguous wording in the first footnote in table 1 in [1] may have led readers to believe the lower bounds on B_A were larger than tabulated here.
‡ To be consistent with the other data in this table, and to permit comparisons, the previously published spectra [19, 20, 21] were re-analysed under the assumption that the anisotropy constant K_1 was the same on each sublattice.

The way in which these anisotropy fields relate to experimentally measured anisotropy constants is not immediately obvious. Within the formulation of the model, the anisotropy term is included in the spin Hamiltonian as

$$\mathcal{H}_A = -K \sum_i \left(S_{zi}\right)^2 - K' \sum_j \left(S'_{zj}\right)^2 \tag{1}$$

where K and K' are effective anisotropy constants acting on the sublattice spins S and S', incorporating all anisotropy contributions. In an antiferromagnet $K = K'$ and $S = S'$, whereas in a ferrimagnet K and K' are not necessarily equal, and $\xi = S'/S$ is less than 1. If all the spins on a given sublattice move in unison, the anisotropy energy per unit volume is

$$E_A = -N S^2 \left(K \cos^2\theta + \xi^2 K' \cos^2\theta'\right) = \text{constant} + N S^2 \left(K \sin^2\theta + \xi^2 K' \sin^2\theta'\right) \tag{2}$$

where θ and θ' are the angles between the sublattice spins and the easy anisotropy axis, and N is the number of sublattice spins per unit volume. In the materials of interest in this work, the magnetic ions are Fe^{3+}, so that $S = 5/2$, and $N = \frac{1}{2}v_{Fe}^{-1}$, where v_{Fe} is the crystal volume per iron ion. It follows that anisotropy fields may be defined as $B_A = 2KS/g\mu_B$ and $B_A' = 2K'S/g\mu_B$, where $g = 2$ and μ_B is the Bohr magneton.

As Coey [16] points out, a common notation for the anisotropy energy per unit volume in uniaxial materials is

$$E_A = \tfrac{1}{2}K_1\left(\sin^2\theta + \sin^2\theta'\right) \tag{3}$$

which reduces to $K_1\sin^2\theta$ for a ferromagnet. Comparing (2) and (3) one obtains

$$K_1 = 2NS^2K = 2NS^2\xi^2K' \tag{4}$$

as the defining relationship between the two definitions. Clearly (2) is the more flexible form, in that it allows different anisotropies on the two sublattices. Nevertheless, since some experimental determinations of the anisotropy constant use the definition of (3), it is relevant to convert the measured anisotropy field to the corresponding K_1 values. Both equalities in (4) are satisfied in antiferromagnetic materials, where $B_A = B_A'$ and $\xi = 1$, but this is not so in ferrimagnetic-like materials where $B_A \neq B_A'$ and $\xi \neq 1$. To overcome this problem, the spectra of those materials that were modelled using ξ values of significantly less than one (namely feroxyhite (sample 2), Co:maghaemite and barium ferrite), were refitted using the assumption of (4). The resultant K_1 constants are given in table 1, where the values of v_{Fe} in [16] were assumed.

In comparing the values of K_1 (table 1) with those measured by other techniques, it is important to note that a collinear spin structure is in doubt only for the ferric gel, glassy FeF_3, and ferrihydrite. In these materials the extremely small particle size prohibits neutron diffraction measurements and, to our knowledge, small-angle neutron scattering experiments have not yet been performed. The remaining materials in table 1 are either collinear antiferromagnets or ferrimagnets.

Whereas it is relatively straightforward to measure the anisotropy of a fine particle ferrimagnetic system from bulk magnetization measurements, it is very difficult to do the same for antiferromagnetic particles. The best method for antiferromagnetic systems is to induce a spin-flop phase transition in a single crystal sample by applying a magnetic field along the easy anisotropy axis. The critical field is $B_{sf} \simeq (2B_E B_A)^{1/2}$, and is observed by a reorientation of the spins towards the perpendicular to the applied field direction. Other methods of estimating the anisotropy are indirect and less reliable. A case in point is fine particle goethite, where inferences of superparamagnetism from Mössbauer spectra lead to an anisotropy of 0.01×10^5 J m^{-3} [22]. Recent neutron diffraction, Mössbauer effect and SQUID magnetization measurements on a sample of fine-particle goethite showed that these three methods give the same magnetic ordering temperature, thereby proving that the material is not superparamagnetic [11,23]. In bulk goethite the spin-flop field exceeds 10 T [24], which corresponds to $B_A > 0.17$ T given an exchange field $B_E \simeq 290$ T. Using the formalism of table 1 this corresponds to $K_1 > 1.3 \times 10^5$ J m^{-3}. Theoretical estimates of the anisotropy in goethite support this, predicting values as high as 11×10^5 J m^{-3} [24].

The fitted K_1 value for goethite in table 1, $\simeq 3 \times 10^5$ J m^{-3}, compares favourably with that obtained from the spin-flop experiment. Similarly, the anisotropy constant fitted for haematite is in close agreement with bulk spin-flop measurements: $B_{sf} \simeq 6.2$ T is predicted, compared to 6.4 T observed in the single-crystal experiments [25]. The relatively small

anisotropy in haematite (compared to goethite) may be attributed to the same competition between magnetic dipole and single-ion anisotropy fields that gives rise to the Morin transition.

For the disordered iron oxyhydroxide feroxyhite, δ'-FeOOH, comparative data on the anisotropy field are not available. However, it is to be expected that the anisotropy in disordered fine-particle systems will be larger than that in bulk systems, since the effect of any vacancies, defects or dislocations in the structure, which 'pin' the spins against reorientation, becomes magnified as the particle size decreases. The amount of 'pinning' in a given sample may depend strongly on factors present at the time of the growth of the particles. This appears to be the case for the feroxyhite samples, which despite being of similar dimensions were chemically prepared in quite different ways: sample 2 has $K_1 \sim 10 \times 10^5$ J m^{-3} while the anisotropy in sample 1 appears to be small.

The anisotropy constant obtained for Co-modified maghemite at 4.2 K is $\simeq 5 \times 10^5$ J m^{-3}. In applied-field Mössbauer experiments on similar samples, anisotropies as high as 30×10^5 J m^{-3} have been reported [26]. From magnetization measurements at room temperature the anisotropy constant of the Co-adsorbed surface regions is greater than 2.3×10^5 J m^{-3} [27]. Our somewhat larger 4.2 K value may be distorted due to the assumption of coherent magnetization reversal; the value for barium ferrite may be similarly affected. A more complete analysis of magnetism in Co:maghaemite allows for the effects of an inhomogeneous chemical composition and an anisotropy field distribution [28].

For the materials of disputed magnetic structure, namely the ferric gel, a-FeF$_3$ and ferrihydrite, it is apparent from table 1 that the fitted anisotropy constants are all of the same order of magnitude as those observed in goethite and in feroxyhite. Given that the ferric gel and ferrihydrite are hydrated compounds which are structurally similar to disordered iron oxyhydroxides, this is not surprising. It is clear that the anisotropy constants obtained using the simple two-sublattice collinear spin model are not impossibly large for a disordered antiferromagnet. This conclusion is independent of the absolute accuracy of the anisotropy constants derived using the two-sublattice model.

In summary, we reiterate that the original proposal of the speromagnetic state, which added a branch to the taxonomy of magnetism [6, 29], was unnecessary and was based on unfounded qualitative expectations. Several authors have repeated the qualitative analysis and classified additional materials as speromagnets. Our experiments on well known antiferromagnetic iron oxyhydroxides cast doubt on the validity of these assignments, irrespective of the method of analysis. Applying a simple model of ordinary magnetism has resulted in quantitative agreement with results from independent measurements and alternate techniques. However, we do not assert that speromagnetism cannot or does not exist, nor even that the Mössbauer data is inconsistent with speromagnetism—merely that the unambiguous identification of speromagnetism in insulators on the basis of conventional applied-field Mössbauer spectroscopy is impossible. It will be necessary to employ other measurement techniques before the question of the existence or otherwise of speromagnetism in insulators is settled.

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