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LETTER TO THE EDITOR

A comment on the detection of speromagnetism in insulators by Mössbauer spectroscopy

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Abstract. The concept of 'speromagnetism' in insulators describes a state of matter in which the antiferromagnetic exchange interaction between neighbouring magnetic ions is frustrated, leading to a random, isotropic spin structure. The detection of speromagnetism has relied heavily on applied-field Mössbauer spectroscopy. We reconsider the Mössbauer data on three ferric insulators said to be speromagnetic, and find that they may be most simply modelled in terms of antiferromagnetism.

An important problem in magnetism is the nature of the magnetic ground state in disordered materials. In dilute alloys with little direct magnetic exchange between atoms, it is well understood that the RKKY interaction can lead to a spin-glass state. At low temperatures the moments freeze with random orientations. Magnetic clusters, within which direct exchange aligns the moments, are likely to form at higher magnetic concentrations.

The understanding of magnetism in disordered insulators is less advanced. Twenty years ago an amorphous insulator exhibiting 'speromagnetism' was discovered, in which the spin arrangement on an atomic-nearest-neighbour scale is disordered, despite the presence of strong antiferromagnetic exchange interactions [1]. This was regarded as a scientific breakthrough [2], and added a branch to the family tree of magnetism [3]. In the revised taxonomy, speromagnets are said to differ from spin glasses in that the random magnetic structure is the result of superexchange frustrated by topological disorder, rather than the absence of direct exchange.

The identification of speromagnetism is almost entirely a matter of scale. One must distinguish a random spin structure at the atomic level from a random structure at the level of domains, crystallites, small particles or large particles. In the former case, adjacent spins are uncorrelated in orientation. In the latter case, which is analogous to a cluster state in alloys, perfect collinear magnetic order may exist within a region of small or not so small dimensions. It is this distinction that we address.

The prototype speromagnet was a natural ferric gel containing fine particles ($\leq 100 \text{ \AA}$ in dimension) of amorphous $\text{Fe}(\text{OH})_3 \cdot 0.9\text{H}_2\text{O}$ in an organic matrix [1-4]. Bulk magnetic measurements (magnetization and susceptibility) of the substance indicated antiferromagnetism and a Néel temperature of $\sim 100 \text{ K}$. The Curie constant gave an unexpectedly small effective moment of $3.68\mu_B$ per iron atom, which was attributed

to the formation of 38% of the available iron into diamagnetic ferric dimers. A small remnant magnetization was observed below ~ 10 K. Similarly, magnetic order was observed in the ^{57}Fe Mössbauer spectra only at temperatures below ≈ 13 K. It was concluded that in the approximate range 10–100 K the material was exhibiting superparamagnetism.

By fitting the magnetization curves with a Langevin function, a spontaneous moment of $\approx 73\mu_{\text{B}}$ per particle was deduced. The origin of this net moment was attributed to the very small particle size, giving rise to relatively large surface areas and high concentrations of imperfections such as impurities and defects. It was assumed that a particle containing N magnetic atoms of moment m would have a net moment of $N^{1/2}m$ as a result of statistical fluctuations. Taking into account the 38% dimerization, this led to a predicted moment of $\approx 78\mu_{\text{B}}$ per particle, in agreement with the observations and justifying the model.

Although the statistical argument was used for spins arranged at random at three dimensions, the same argument applies to spins arranged at random in one dimension. In three dimensions the net moment is $0.92N^{1/2}m$, whereas in one dimension it is $0.79N^{1/2}m$ [5]. Consequently the bulk magnetic measurements, and the temperature-dependent Mössbauer spectra, all supported the conclusion that the material was a disordered antiferromagnet.

The proof that a new magnetic state was present rested on an interpretation of applied field Mössbauer spectra. These spectra, reproduced in figure 1, were recorded at 4.2 K in applied fields of 0, 1 and 5 T directed parallel to the γ -ray beam. It was argued that if the material contained antiferromagnetic particles, then in order that the weak net moment be accounted for, either (i) there was a statistical imbalance in the occupation numbers of the two oppositely oriented magnetic sublattices, or (ii) the sublattices were slightly canted away from being antiparallel, as in haematite above the Morin temperature.

In case (i) the net moment would be either parallel or antiparallel to the individual moments; so when the net moment was saturated by the external field B , it was expected that all the moments would be either parallel or antiparallel to B . It follows that the Mössbauer spectrum would exhibit two subspectra, with effective hyperfine magnetic fields equal to $B_{\text{hf}} + B$ and $B_{\text{hf}} - B$, and the $\Delta m_I = 0$ lines (the second and fifth lines in the spectrum) would vanish since their intensities depend on $\langle \sin^2 \theta \rangle$ where θ is the angle between the moments and B . Since this was not observed, case (i) was ruled out.

In case (ii), the net moment is nearly perpendicular to the individual moments, and it was expected that at saturation the moments would align nearly perpendicular to the applied field. The second and fifth lines in the spectrum would then increase in intensity (by up to twice as much), and no splitting of the spectrum would occur. Again this was not observed experimentally. It was concluded that the data were not consistent with any kind of antiferromagnetism, and the existence of speromagnetism was invoked.

We wish to point out that the expectation in case (i), that the individual moments would align exactly parallel or antiparallel to the applied field, is false. Even ferrimagnets with relatively large moments such as $\gamma\text{-Fe}_2\text{O}_3$ and $\delta'\text{-FeOOH}$ show incomplete alignment in applied fields [6, 7]. The response of the moments depends upon the strength of the magnetic interactions, the electrostatic environment, and the relative occupancies of the various lattice sites. A mean-field model has recently been used to analyse applied-field Mössbauer spectra, and has been applied successfully to a

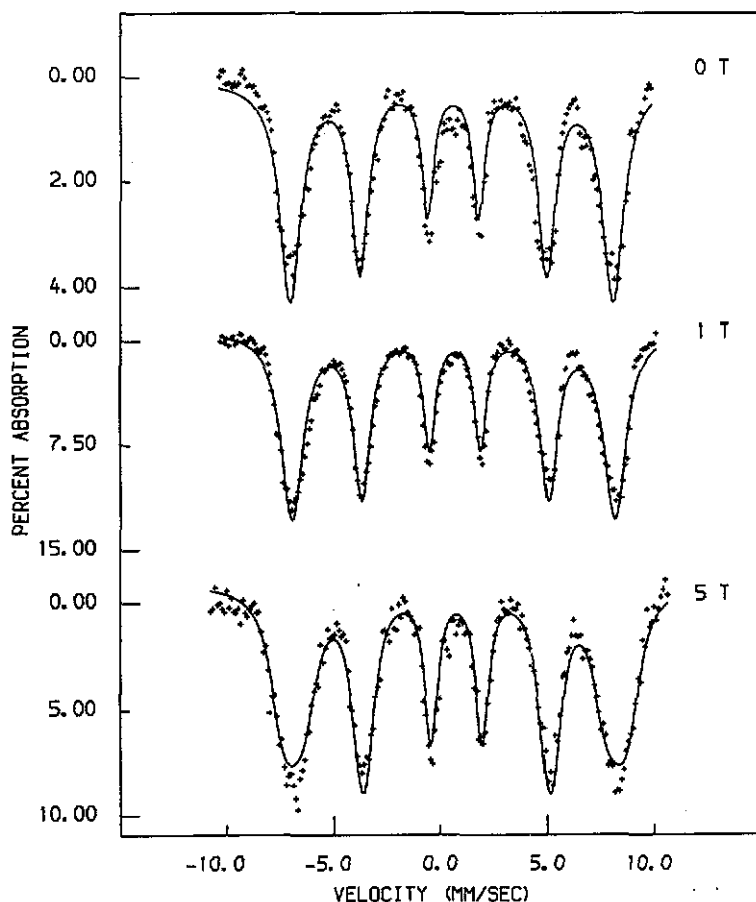


Figure 1. Mössbauer spectra, taken from figure 1 of [1] of a natural ferric gel cooled to 4.2 K. Magnetic fields, of the strength shown, were applied parallel to the γ -ray beam. The identification of speromagnetism was based upon the constancy of the intensities of the second and fifth lines with increasing applied-field strength. The solid lines show the results of a simultaneous least-squares fit made using a simple antiferromagnetic model.

variety of polycrystalline ferrimagnets and antiferromagnets [5-8]. It is of interest to see whether the applied-field behaviour of the prototype speromagnet has a simpler explanation than that put forward many years ago. This matter is important, since qualitative observations of applied-field spectra remain central to the identification of speromagnetism. To this end we reanalyse the original data.

The model is based on expressing the magnetic energy in terms of the orientations of the two-sublattice spins [8]. For the general case of a simple two-sublattice ferrimagnet

$$E = NSg\mu_B \left\{ B_E \xi \cos(\theta_1 - \theta_2) - \frac{1}{2} B_A [\cos^2(\theta_1 - t) + \xi^2 \cos^2(\theta_2 - t)] - B(\cos \theta_1 + \xi \cos \theta_2) \right\}. \quad (1)$$

Here N is the number of sublattice spins, S and ξS are the sublattice spins, B is the applied-field strength, B_A is the effective anisotropy field (which incorporates both crystalline and shape effects), and $B_E = -2JzS/g\mu_B$ is the exchange field. The

angles θ_1 , θ_2 and t are with respect to the local-field direction: θ_1 and θ_2 are for the sublattice spins and t is the direction of the easy anisotropy axis. For representative values of t (corresponding to different particle orientations), the equilibrium spin configuration may be determined numerically by minimizing E with respect to both θ_1 and θ_2 .

Data were obtained by electronically digitizing the published figure in [1], taking care to avoid any non-linear distortion. A cubic-spline algorithm was used to convert the data to equally spaced velocity channels to account for any small errors in the original plotting of the data or in the digitizing process. Tests of the procedure (by visual comparison with photographic enlargements and by independent digitizing) showed that both systematic errors and operator errors were absent. As a first approximation the spectra were modelled as a simple antiferromagnet ($\xi = 1$ in equation (1)). Variables in the fit were the exchange and anisotropy fields, the hyperfine field B_{hf} , the isomer shift, the quadrupole term $\frac{1}{2}eQV_{zz}$, the linewidth parameters Γ and $\Delta\Gamma$, and the total absorption area. Because the hyperfine field is expected to be distributed, the linewidths of the innermost, middle and outermost pairs of lines in the constituent sextets were taken to be Γ , $\Gamma + \Delta\Gamma$ and $\Gamma + 2\Delta\Gamma$ respectively. All three spectra were fitted simultaneously to restrain the fit within the physical model. V_{zz} was taken to be perpendicular to the easy anisotropy axis.

The results of this first approximation analysis are shown by the solid curves in figure 1 and the parameters are summarized in table 1. The observation that there is little effect of the applied field on the Mössbauer spectrum, apart from a broadening of the lines, is a consequence of the small net moment and the relatively large anisotropy. Better fits were obtained by allowing unequal sublattice occupancies (i.e. ferrimagnetism), and it was found that the data are consistent with imbalances of up to about 5%. Modelling distributions in the parameters, such as using an explicit $P(B_{\text{hf}})$ distribution, also gave improvement. However, such modifications introduce extra parameters which are of doubtful significance for the data concerned. Our present purpose is to consider the qualitative trends without involving unnecessary complexity.

Table 1. Summary of results for ferric gel and amorphous FeF_3 at 4.2 K. B_A is the anisotropy-field strength, B_E is the exchange-field strength, B_{hf} is the hyperfine-field strength, and $\frac{1}{2}eQV_{zz}$ is the quadrupole coupling. Uncertainties, determined for a 68% confidence level, are indicated in parentheses.

	Ferric gel	Amorphous FeF_3
B_A (T)	4.2(0.5) [†]	4.6(1.9) [†]
B_E (T)	166(20) [†]	128 [‡]
B_{hf} (T)	46.8(0.4)	55.2(0.4)
$\frac{1}{2}eQV_{zz}$ (mm s ⁻¹)	0.19(0.12)	0.02(0.16)

[†] Lower bound only; the upper bounds were ill-defined.

[‡] Not varied during least-squares fitting.

It is clear that there is qualitative agreement between the data and the predictions for antiferromagnetic particles (figure 1). The question arises of how a speromagnetic model would differ. To be realistic, it would have to include the effects of distributed and multiaxial anisotropy, and would therefore contain numerous parameters. If the anisotropy is high, little reorientation will occur; if some ions experience

low anisotropy, significant reorientation will occur. The calculations would be cumbersome. It is generally assumed that in speromagnets the anisotropy is large. In this case it is not possible, even in principle, to use Mössbauer spectroscopy to distinguish between speromagnetism and antiferromagnetism in randomly aligned particles, since there is no information present concerning the angle between adjacent moments. It is apparent (from table 1) that the anisotropy in this material is indeed large.

To proceed further, some other materials said to be speromagnetic should be considered. Broadly speaking there are three categories of such materials: (i) amorphous precipitates such as the prototype ferric gel and the precipitates found in ion exchange membranes [9]; (ii) amorphous ionic compounds such as FeF_3 [10] and NaFeF_4 [11]; and (iii) poorly crystalline minerals such as ferrihydrite [12]. Having discussed a representative of category (i), we now look at categories (ii) and (iii).

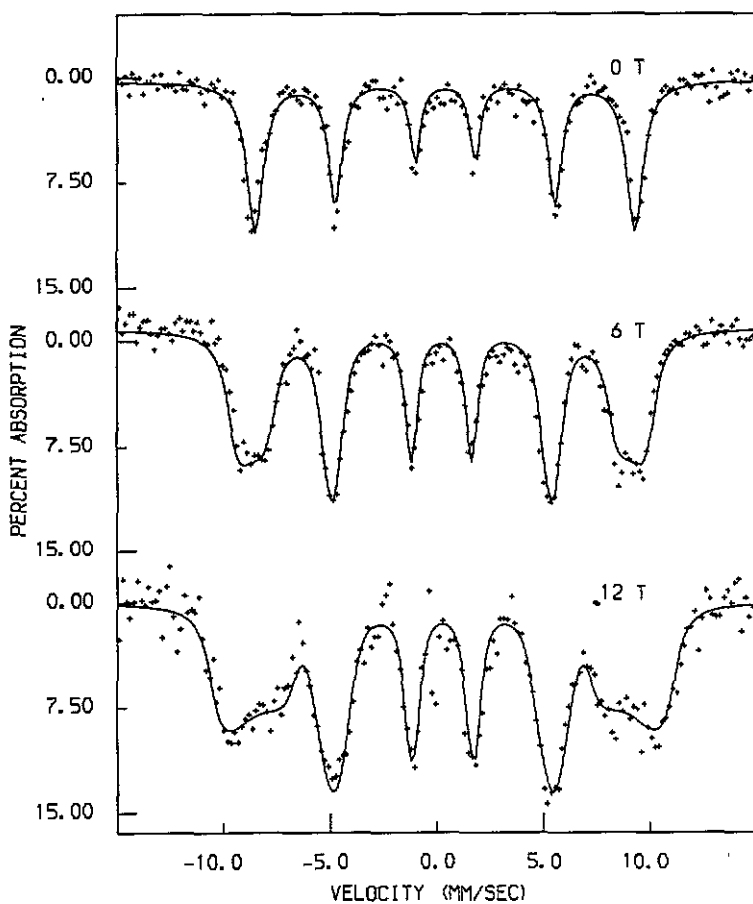


Figure 2. Mössbauer spectra, from figure 2 of [10], of amorphous FeF_3 at 4.2 K. The vertical axis scaling is arbitrary. The solid lines show the results of one least-squares fit to the three spectra using the model of antiferromagnetism.

Amorphous FeF_3 has strong antiferromagnetic exchange. The appearance of remanence and an irreversible susceptibility at temperatures below 29 K was taken as evidence of spin freezing, and a low value of the Curie constant measured at higher temperatures was explained as resulting from a distribution of exchange strengths

[10]. Applied-field Mössbauer spectra were said to demonstrate the presence of speromagnetic order. These spectra are reproduced in figure 2, along with curves fitted using the antiferromagnetic model. The parameters are given in table 1. Again somewhat better fits were obtained using unequal sublattice occupancies, but the dominant response exhibited in the spectra is that of a simple antiferromagnet. In amorphous NaFeF_4 the measured and theoretical spin-only values of the Curie constant were in excellent agreement [13]. Nevertheless an applied-field Mössbauer spectrum with broad lines was taken as sufficient evidence that the material is speromagnetic [11]. A subsequent analysis of zero-field Mössbauer spectra has shown that the distribution of exchange fields present in materials of this type is grossly different to that expected for randomly oriented spins, and that the nearest-neighbour spins are orientated such that their vector sum is small [14]. Nevertheless, the analysis also indicated that within this latter constraint the average nearest-neighbour spin is rotated by only a few degrees towards an antiparallel alignment from a random orientation. Within this average, much larger counterbalancing rotations of the spins were considered to be likely to be present, but further details of the spin orientations could not be deduced.

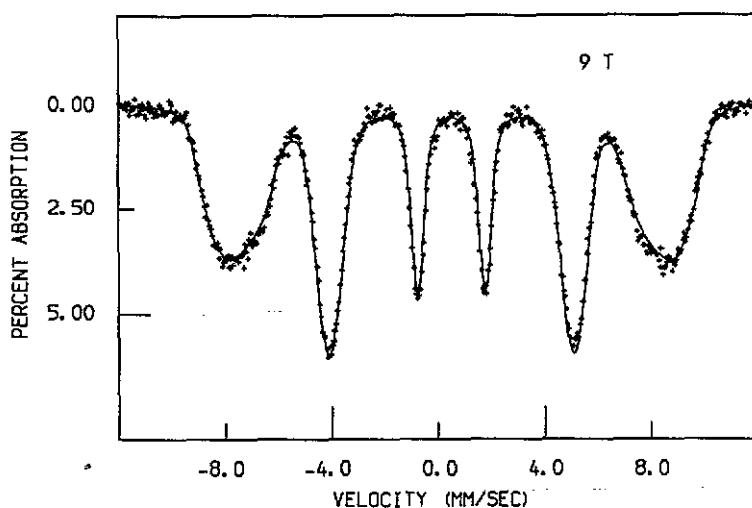


Figure 3. The Mössbauer spectrum of a synthesized sample of the mineral ferrihydrite, $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ at 4.2 K and in an applied field of 9 T parallel to the γ -ray beam. The solid line was fitted using the antiferromagnetic model.

The third class of material to be considered is represented by the mineral ferrihydrite, $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ [12]. We have studied the applied-field response of a synthetic sample of ferrihydrite; a detailed report is to be published elsewhere [15]. X-ray diffraction analysis of our sample showed six lines, with a breadth indicative of particle dimensions of order 6 nm. The 9 T applied-field Mössbauer spectrum is shown in figure 3, along with the solid curve expected for an antiferromagnet. The quality of the fit shows that antiferromagnetism is an adequate model.

A final consideration is the significance of applied-field Mössbauer spectra recorded at temperatures just above that at which magnetic splitting is observed in zero field [16]. At 80 K, a 3 T field applied to ferrihydrite induces a well developed hyperfine structure [12], perhaps because of a reduction in the superparamagnetic relaxation rate or an inducement of cluster ordering. It has been argued that if the

atomic moments are rigidly linked to the net particle or cluster moment, speromagnetic and antiferromagnetic states can be readily distinguished by the intensities of the $\Delta m_I = 0$ lines following the same reasoning as applied to low-temperature spectra [16]. The $\Delta m_I = 0$ lines for ferrihydrite at 80 K appear to be non-zero [12], and may be taken as evidence for speromagnetism. However, this behaviour would also follow from antiferromagnetic particles in which the net particle moment is small or in which the particles' anisotropy inhibits coupling to the applied field. It has been shown that anisotropy dominates in ferritin and haemosiderin particles at elevated temperatures [17].

Since it was first proposed in 1973, the term 'speromagnetism' has entered the taxonomy of magnetism [3]. However, the Mössbauer spectra of three ferric insulators said to be speromagnetic, including the prototype material, are consistent with simple antiferromagnetism in poorly crystalline or disordered insulators. Because Mössbauer spectroscopy is central to the identification of speromagnetism in these materials, we conclude that its use in detecting the existence of speromagnetism can be misleading. Of the categories considered, only the amorphous ionic compounds exhibit unusual magnetic behaviour, and even here the identification of speromagnetism from applied-field Mössbauer spectra is equivocal.

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