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COMMENT

Interpretation of the Mössbauer spectra of speromagnetic materials

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Abstract. A reinterpretation by Pankhurst and Pollard of the Mössbauer spectra of amorphous ferric compounds in terms of an antiferromagnetic model requires uniaxial anisotropy $K_1 \sim 2 \times 10^6 \text{ J m}^{-3}$. This is two orders of magnitude greater than usual for ferric oxides, and comparable with the anisotropy of rare earth permanent magnet materials. In the absence of any physical justification for such huge uniaxial anisotropy, the original interpretation in terms of a speromagnetic model stands.

1. Introduction

Speromagnetism is a variety of magnetic order in amorphous or disordered materials where the atomic spins are frozen in essentially random orientations with an isotropic probability distribution [1]. This type of magnetic order was originally established in 1973 from consideration of the magnetic properties and Mössbauer spectra of a finely divided, amorphous natural ferric gel [2]; further evidence was provided by a study of amorphous synthetic FeF_3 [3] and related compounds. The spectra taken in a large applied field indicate random alignment of the spins in an ensemble of ultrafine particles (figure 1(a)), and it was concluded that the spins within each particle were also randomly aligned with respect to their resultant moment. The experiment provided the first demonstration of random spin freezing in an amorphous material on the atomic scale. Speromagnetism is closely related to the random spin canting found in disordered crystalline insulators, and it follows naturally from the frustration of antiferromagnetic superexchange interactions that arises in a topologically disordered lattice [4].

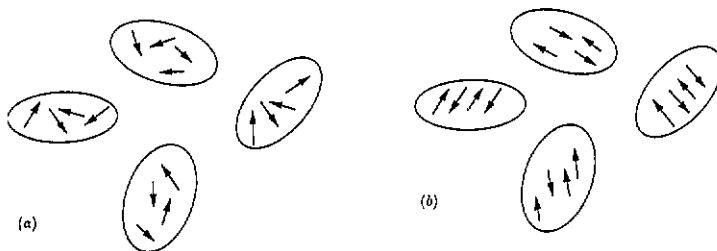


Figure 1. Schematic illustration of particles of (a) a speromagnet and (b) a uniaxial antiferromagnet. The arrows represent the orientations of the atomic spins in each particle.

Recently, Pollard and Pankhurst (PP) published Mössbauer spectra of ferric oxides and hydroxides in a number of different journals [5–9]. Data at 4.2 K in applied fields of up to 9 T were fitted using a simple antiferromagnetic or ferrimagnetic model where the atomic spins in each particle are subject to an exchange field and an anisotropy field directed along a unique axis in each particle. These anisotropy axes are randomly distributed for the particles in a powder (figure 1(b)). PP have also applied their model to reanalyse the original Mössbauer data on the amorphous natural ferric gel [2] and $\alpha\text{-FeF}_3$ [3], claiming that the spectra of these materials are most simply modelled in terms of antiferromagnetism [9]. They therefore suggest that the original identification of speromagnetism from applied-field Mössbauer data was equivocal. We wish to refute that claim.

PP consider the following energy for a two-sublattice ferrimagnet

$$E = Ng\mu_B S \{ B_E \xi \cos(\theta_1 - \theta_2) - (B_A/2) [\cos^2(\theta_1 - t) + \xi^2 \cos^2(\theta_2 - t)] - B(\cos \theta_1 + \xi \cos \theta_2) \}. \quad (1)$$

Here N is the number of magnetic atoms per sublattice, 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 is the exchange field. The angles θ_1 , θ_2 and t define the directions of the two-sublattice magnetizations and the easy anisotropy axis with respect to the local-field direction. For a given value of t , corresponding to a particular particle orientation, the equilibrium spin configuration is determined by minimizing E with respect to both θ_1 and θ_2 . Three parameters in the model are therefore the exchange field B_E (which can be compared with values deduced from the high-field susceptibility or the magnetic ordering temperature), the sublattice imbalance $1 - \xi$ (which can be compared with the net magnetization; the antiferromagnetic case is $\xi = 1$) and the anisotropy field B_A .

Applying this model to an amorphous material begs the question of how a unique antiferromagnetic axis is to be defined in an amorphous particle, and disregards the consequences of topological frustration of the antiferromagnetic interactions. But here we will restrict our criticism to showing that the values of the anisotropy fields required by PP to fit the Mössbauer data are unrealistically large.

First, it should be noted that the anisotropy field B_A in equation (1) differs from that normally encountered in ferrimagnetic materials,

$$B'_A = 2K_1/M \quad (2)$$

where K_1 is the anisotropy energy per unit volume and M is the net magnetization. The anisotropy given by equation (1) in zero applied field is $K_1 = -Ng\mu_B S B_A (1 + \xi^2)/2$, hence

$$B_A = 2K_1 / (M_{sl}(1 + \xi^2)) \quad (3)$$

where M_{sl} is the majority sublattice magnetization. For an antiferromagnet, this reduces to K_1/M_{sl} . The difference between B_A and B'_A may be illustrated by considering the hexagonal ferrite $\text{BaFe}_{12}\text{O}_{19}$, which is widely used for permanent magnets. Here we take $M = 480 \text{ kA m}^{-1}$ ($\mu_0 M = 0.6 \text{ T}$), $K_1 = 3 \times 10^5 \text{ J m}^{-3}$ and $\xi = 0.5$, hence $M_{sl} = 960 \text{ kA m}^{-1}$ and $B'_A = 1.25 \text{ T}$, whereas $B_A = 0.5 \text{ T}$.

The anisotropy energy K_1 is known for most uniaxial magnetic materials. It may be measured from the magnetization or torque curves of a single crystal or oriented powder. Another approach is to analyse the behaviour of superparamagnetic ultrafine particles, which

Table 1. Uniaxial anisotropy of some magnetic materials.

	K_1 (10^5 J m $^{-3}$)
α -Fe $_2$ O $_3$ (haematite)	0.08–0.5
γ -Fe $_2$ O $_3$ (maghemite)	0.1
α -FeOOH (goethite)	0.01
β -FeOOH (akaganeite)	0.03
a-Fe(OH) $_3$ nH $_2$ O (amorphous gel)	0.4–0.5
BaFe $_{12}$ O $_{19}$ (barium ferrite)	3
Nd $_2$ Fe $_{14}$ B	54

gives an effective uniaxial anisotropy constant, even for cubic materials, which includes all contributions (magnetocrystalline, shape, surface...) [10]. In table 1, we present a compilation of anisotropy constants for some representative ferric oxides, including the speromagnetic ferric gel. Values depend somewhat on temperature and particle size, so ranges are given, mostly taken from [10] and [11], and papers cited therein. Typical ferric compounds have anisotropy somewhere between 0.01 and 0.5×10^5 J m $^{-3}$. The anisotropy of barium ferrite, 3×10^5 J m $^{-3}$, is exceptional for a ferric oxide. Also included is the room-temperature value for Nd $_2$ Fe $_{14}$ B, a rare earth permanent magnet material where the spin-orbit interaction in the neodymium 4f shell provides strong magnetocrystalline coupling. This mechanism is inoperative in Fe $^{3+}$ to first order because there is no orbital moment for the 3d 5 configuration. Hence the low values of K_1 in ferric compounds.

Table 2 shows the results obtained by Pankhurst and Pollard from their analysis of high-field Mössbauer spectra. The published anisotropy fields B_A are listed, together with the corresponding anisotropy constants K_1 deduced from equation (3). Since the structures and densities of some of these materials are not known precisely, we deduced the volume per iron ion v_{Fe} by assuming crystalline close packing of the oxygen ions ($r = 0.14$ nm) for ferrihydrite and feroxyhite, and random close packing for the anions in a-FeF $_3$ and the amorphous ferric gel a-Fe(OH) $_3$. The iron moment is taken as $5\mu_B$. The volumes per iron ion and the sublattice magnetizations M_{sl} are included in the table. The latter is $2.5\mu_B/v_{Fe}$ for all except the ferrimagnetic barium ferrite.

A comparison of K_1 values in tables 1 and 2 reveals that the uniaxial model works well for certain materials. The anisotropy of α -Fe $_2$ O $_3$ falls in the right range, and that of BaFe $_{12}$ O $_{19}$ is in satisfactory agreement with the magnetocrystalline anisotropy constant,

Table 2. Uniaxial anisotropy deduced by fitting applied-field Mössbauer spectra with a uniaxial antiferromagnetic or ferromagnetic model.

	v_{Fe} (nm 3)	M_{sl} (kA m $^{-1}$)	B_A (T)	K_1 (10^5 J m $^{-3}$)	Reference
<i>Amorphous</i>					
a-Fe(OH) $_3$ · 0.9H $_2$ O	0.054	427	4.2	18	[9]
a-FeF $_3$	0.049	471	4.6	22	[9]
<i>Poorly crystallized</i>					
Fe $_5$ HO $_8$ · 4H $_2$ O (ferrihydrite—2-line)	0.037	623	0.6	4	[8]
Fe $_5$ HO $_8$ · 4H $_2$ O (ferrihydrite—2-line)	0.037	623	0.9	6	[8]
δ FeOOH (feroxyhite) Sample 1	0.031	748	0.1	0.7	[7]
δ FeOOH (feroxyhite) Sample 2	0.031	748	1.3	10	[7]
<i>Well crystallized</i>					
α -Fe $_2$ O $_3$ (haematite)	0.025	925	0.02	0.2	[6]
α -FeOOH (goethite)	0.031	748	0.41	3	[6]
BaFe $_{12}$ O $_{19}$ (barium ferrite)		960	1.07	4	[10]

considering that there may be a significant contribution related to particle shape in materials with a net magnetization. The value of K_1 for one of ferroxyhite samples also falls close to the high end of the ferric range. Surprisingly, the anisotropy derived for goethite is wrong by two orders of magnitude, which suggests that this material may not have a collinear antiferromagnetic structure, as generally supposed. Furthermore, the PP analysis of Co-adsorbed $\gamma\text{-Fe}_2\text{O}_3$ [13] yields an anisotropy energy $K_1 = 11 \times 10^5 \text{ J m}^{-3}$ that is ten times larger than measured from torque on oriented samples [14], or four times larger than deduced from the magnetization curve [15], suggesting that their uniaxial, collinear model is again inapplicable.

The most striking disaccord however is found when the antiferromagnetic model is applied to amorphous materials. The anisotropy needed to fit the applied-field Mössbauer spectra of $\alpha\text{-Fe}(\text{OH})_3 \cdot 0.9\text{H}_2\text{O}$ and $\alpha\text{-FeF}_3$ are six or seven times greater than that of barium ferrite, and two orders of magnitude greater than for the other ferric oxides in table 1. The fit value for the prototype speromagnet is 36 times as great as measured from the superparamagnetic properties of the same sample [2]. The anisotropies required to fit amorphous materials with the antiferromagnetic model approach that of $\text{Nd}_2\text{Fe}_{14}\text{B}$.

We conclude that the antiferromagnetic model is quite inappropriate for the amorphous materials in table 2, and questionable for some of the others. The intensities of the $\Delta m = 0$ transitions and lineshapes of Mössbauer spectra in an applied field indicate that the spins are frozen under the influence of an interaction that is stronger by an order of magnitude or more than anisotropy. That interaction is exchange.

Over the past twenty years, examples from many areas of magnetism have accumulated to show that frustrated exchange interactions may lead to non-collinear spin structures [4]. Most of this information was unavailable in 1972, when the original work to establish random spin freezing on an atomic scale was carried out. The analysis of Pollard and Pankhurst actually serves to consolidate the original speromagnetic interpretation by showing that an antiferromagnetic model leads to unreasonably large ferric anisotropy. Their work underlines the need to consider the physical meaning of parameters used to fit spectra, not just the statistical quality of the fits.

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