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Spin flop in goethite

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Abstract. A spin-flop transition is observed when a field of 20 T is applied parallel to the *b* axis of a specimen of natural goethite at 4.2 K. The goethite orders in a four-sublattice antiferromagnetic structure with the sublattice magnetizations inclined at ±13° to *b*, and an iron moment of 3.90 μ_B. There is a small net ferromagnetic moment of 0.004 μ_B along *b* which has the effect of more than doubling the threshold field for spin flop. The anisotropy field is deduced to be 0.11 T, corresponding to a uniaxial anisotropy energy $K = 6 \times 10^4$ J m^{-3}. The origin of the weak moment is discussed, and it is suggested that *mode superparamagnetism* may arise in non-collinear antiferromagnets when two transverse spin configurations are effectively degenerate.

1. Introduction

Goethite (α-FeOOH) and haematite (α-Fe_2O_3) are the most common antiferromagnetic materials in nature. Goethite has an orthorhombic structure with space group *Pnma*, shown in figure 1. Its Néel point is sample-dependent, usually falling in the range 325–405 K [1], and the spins lie essentially along *b* in an antiferromagnetic arrangement contained within the crystallographic unit cell [2].

Goethite was long regarded as a typical superparamagnet. Even quite well crystallized samples exhibit Mössbauer lineshapes at room temperature [3–5] which have been interpreted in terms of the Néel theory of magnetic thermal fluctuations [6]

$$\tau = \tau_0 e^{KV/kT} \tag{1}$$

or a variant of this theory which takes account interactions among the crystallites [7]. Here τ is the fluctuation time, V is the particle volume, K is an effective uniaxial anisotropy constant and τ_0 is a time of the order of 10^{-11} s. The anisotropy constant K has been estimated as 10^3 J m^{-3} [8]. An anisotropy field $B_a = K/M_{sl}$ is conventionally associated with the uniaxial anisotropy of an antiferromagnet, where M_{sl} is the sublattice magnetization.

This view is in doubt in a recent series of papers [1, 9, 10]. On the basis of fitting the lineshapes for Mössbauer spectra in large applied fields, Pankhurst and Pollard inferred that the anisotropy field $B_a = 0.41$ T at 4.2 K [10]. The corresponding uniaxial energy $K = 3.10^5$ J m^{-3} is similar to that of $BaFe_{12}O_{19}$, the common ceramic permanent magnet.

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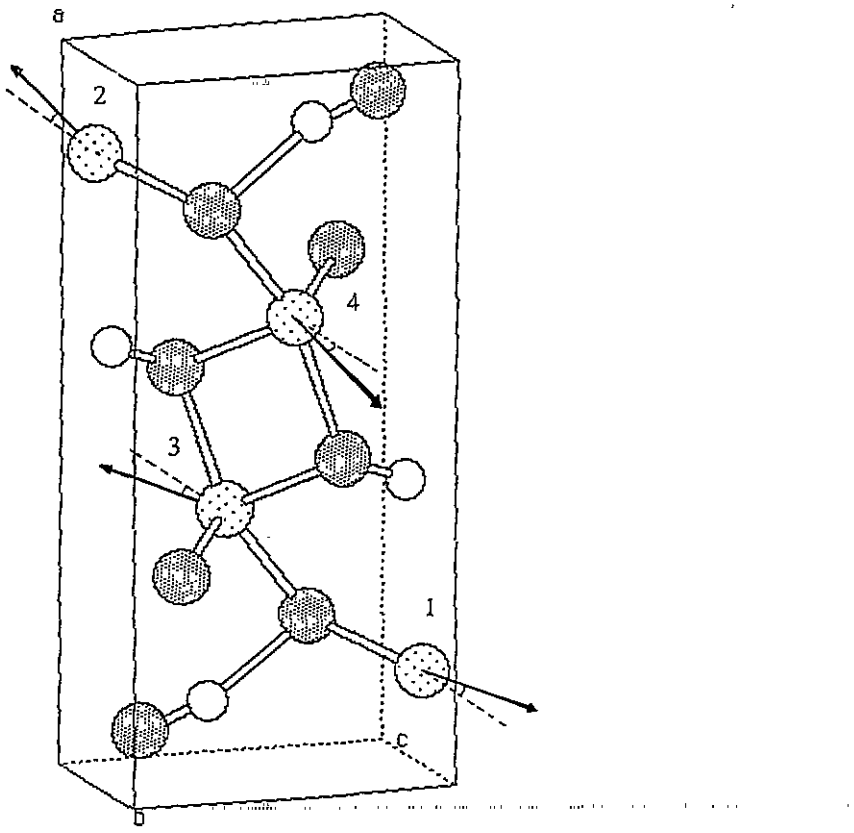

Figure 1. Crystal and magnetic structure of goethite, α-FeOOH, the four antiferromagnetic sublattices are inclined $\pm 13°$ to b.

Their view was supported by the argument that no spin flop transition has ever been observed in goethite in applied fields as high as 10 T [11]. Conventional antiferromagnets are expected to exhibit a spin flop to a state where the moments lie almost perpendicular to the applied field when a sufficiently large field B_{sf} is applied parallel to the antiferromagnetic axis. An elementary calculation of the spin flop field at $T = 0$ [12] gives

$$B_{sf} = \left(2B_{ex}B_u - B_a^2\right)^{1/2} \tag{2}$$

where B_{ex} is the exchange field, which may be inferred from the Néel temperature or the transverse susceptibility. The spin flop in haematite occurs at 6.8 T, from which it was inferred that $B_u = 0.02$ T [14].

Here we report the first observations of the spin-flop transition in goethite, and discuss the implications for the anisotropy and superparamagnetic properties of this compound.

2. Experimental results

The goethite sample was a natural one with a fibrous habit from Cary Mine, Ironwood, MI.

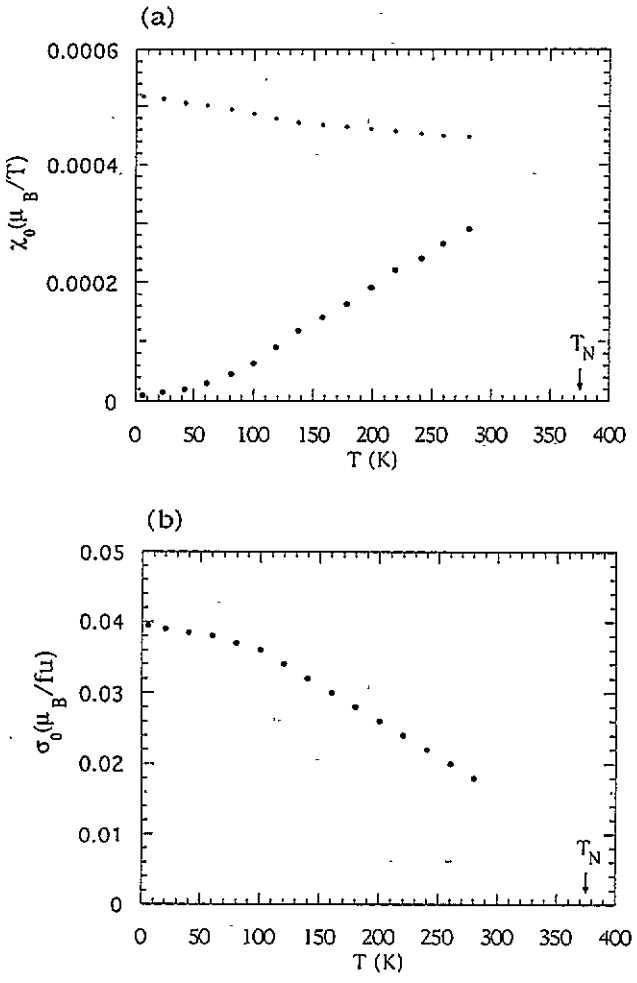

Figure 2. Temperature dependence of (*a*) susceptibility of goethite deduced from the slope of the magnetization curve from 1–7 T measured parallel and perpendicular to the *b* axis and (*b*) magnetization of goethite deduced by extrapolating the parallel magnetization curve to $B_0 = 0$.

It consists of large crystalline domains elongated in the *b* direction. Lattice parameters are $a = 9.949(1)$ Å, $b = 3.018(1)$ Å and $c = 4.600(1)$ Å. The formula deduced from electron microprobe analysis and weight loss on heating to 650 °C is

$$Fe_{0.95}Al_{0.01}Si_{0.03}(OH)_{1.02}O_{0.99}.$$

The Néel temperature was determined by AC susceptibility and thermomagnetic scans to be 375(2) K. The fibrous habit permits measurements to be made parallel or perpendicular to the *b* axis. All data were obtained on pieces or powders of the same material. A Mössbauer spectrum taken at room temperature on a thin absorber made of powder magnetically aligned perpendicularly to the plane of the absorber (parallel to the γ direction) and set in epoxy resin (figure 3(*a*)) showed that the moments lie essentially along *b*. Susceptibility measured parallel and perpendicular to *b* (figure 2(*a*)) also indicates that *b* is the antiferromagnetic axis.

The magnetic structure was determined in detail by powder neutron diffraction on the DN5 diffractometer at Siloë, CREN-Grenoble. The entire diffraction profile was fitted using the FULLPROF program, which refines the structural parameters and moment in spin modes, or combinations of spin modes compatible with the crystal symmetry. There are four possible configurations of the spins of the four iron atoms in the unit cell, one ferromagnetic

$$F = S_1 + S_2 + S_3 + S_4$$

and three antiferromagnetic

$$G = S_1 - S_2 + S_3 - S_4$$
$$C = S_1 + S_2 - S_3 - S_4$$
$$A = S_1 - S_2 - S_3 + S_4$$

and eight modes e.g. $(A_x 0 G_z)$, $(0 F_y 0)$ ... corresponding to the eight representations of the symmetry group D_{2h}. The best refinement is achieved with $(C_x A_y 0)$, and the fit parameters at 10 K are summarized in table 1. It should be noted that the ordered iron moment is only 3.90(4) μ_B, and the spin directions are inclined at $\pm 13°$ to *b*, as indicated in figure 1. The corresponding sublattice magnetization M_{sl} is 525 kJ T^{-1} m^{-3}. Earlier low-resolution neutron studies gave similar low values of the ordered iron moment [2, 9] (5.0 μ_B is expected for the Fe^{3+} ion).

Table 1. Fitted iron moments in goethite.

Temperature (K)	Mode	R_{mag}	m_x (μ_B)	m_y (μ_B)	m_z (μ_B)	m (μ_B)
10	$C_x A_y 0$	4.38	0.85(7)	3.81(3)	0	3.90(4)
274	$C_x A_y 0$	3.83	0.82(7)	2.87(3)	0	2.98(4)

Like many other natural goethites [15–17], our sample has a small magnetization along the *b* direction. The possible origin of this moment is discussed later, but here we provide experimental evidence that the weak magnetization is indeed a property of the goethite, rather than some associated impurity phase. The evidence is: (i) the moment falls to zero at the Néel point (figure 2(*b*)) and; (ii) when ground to a fine powder and oriented in a field of 0.6 T, the Mössbauer spectrum shows that the iron sublattice moments are effectively aligned in the direction of the applied field (figure 3). There is substantial hysteresis associated with this $(0 F_y 0)$ mode, even at room temperature (figure 4). The magnetization M_f is sample-dependent, but in the present goethite at low temperature it is 0.039 μ_B FU^{-1}, or just 2% of M_{sl}.

Magnetization curves measured in fields up to 36 T parallel and perpendicular to the *b* direction at 4.2 K are shown in figure 5. The high fields were generated at the pulsed-field faculty of SNCMP, Toulouse. Pulse duration was 1 s, and magnetization was measured using a field-compensated coil. The spin-flop transition begins at 20 T when the field is parallel to the *b*. Note that the small amount M_f is easily saturated when the field is applied along *b*, but *not in the transverse direction.*

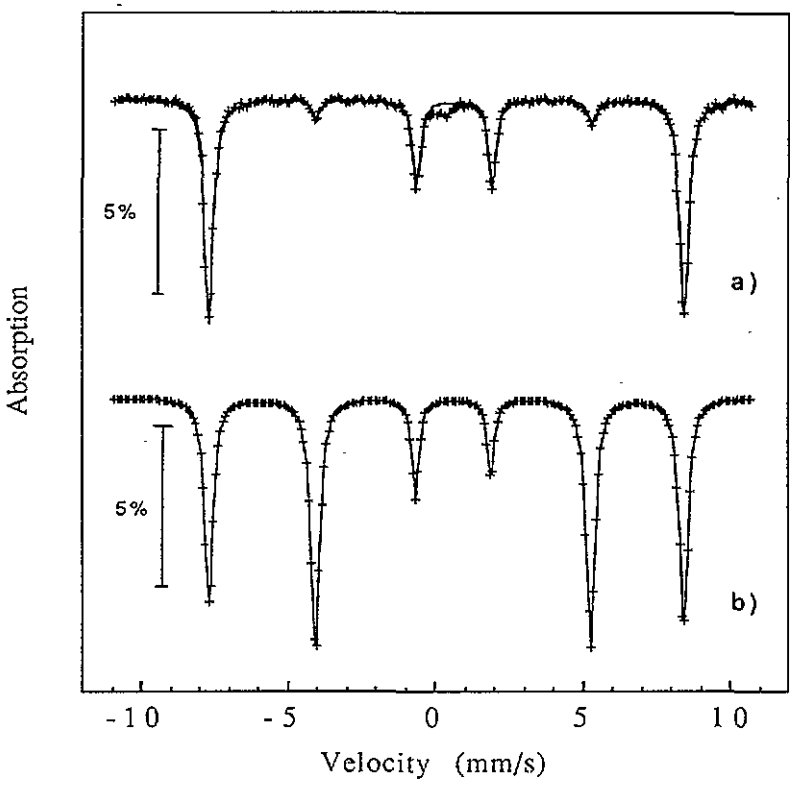

Figure 3. Low-temperature Mössbauer spectrum (20 K) of a goethite powder oriented in a 0.6 T field applied (*a*) perpendicular to the plane of the absorber and (*b*) parallel to the plane of the absorber, which is perpendicular to the γ direction.

3. Discussion

In order to analyse the spin flop, we need a value for the exchange field. A direct way to obtain one is to extrapolate the transverse magnetization curve to saturation, which gives $2B_{ex} = 780(50)$ T. Alternatively, B_{ex} may be inferred from the Néel temperature, using the mean-field theory result $T_N = B_{ex} g \mu_B (S+1)/3k$, which gives $B_{ex} = 284$ T for $T_N = 375$ K and $S = 1.95$. Bocquet *et al* [1] deduce $J_{ex}/k = 12.0$ K from the T^2 variation of the ^{57}Fe hyperfine field of a sample having $T_N = 347$ K, assuming $S = 5/2$, and infer $B_{ex} = 267$ T. A similar analysis for the present sample with $S = 1.95$ would yield $B_{ex} \simeq 370$ T. Since the mean field theory is known to overestimate T_N for a given value of B_{ex} and since it is the transverse susceptibility which actually enters in the spin-flop process, we will use the extrapolated value $B_{ex} = 390$ T.

A lower limit to the anisotropy can be deduced from the fact that there is no tendency for the ferromagnetic moment to align a transverse field (figure 5). Hence

$$K - M_f B_0 > -(1/2)\chi B_0^2$$

where χ is the perpendicular susceptibility. The transverse magnetization is equal to M_f when $B_0 = 7$ T, hence $K > 2 \times 10^4$ J m^{-3}.

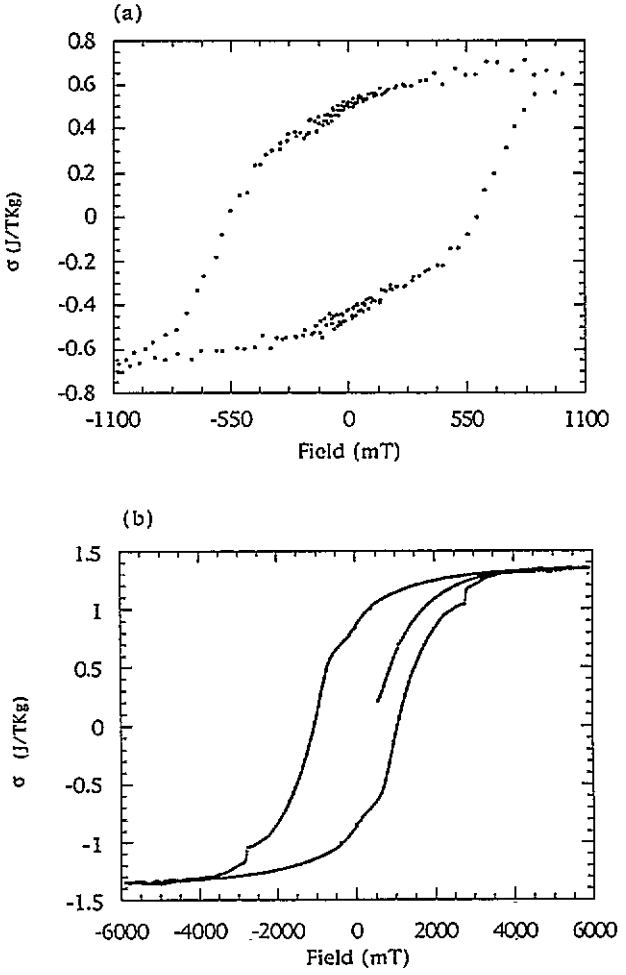

Figure 4. Hysteresis loops measured with the field applied along *b* (*a*) at 296 K and (*b*) at 4.2 K.

Calculation of the spin flop in the parallel direction in the presence of a small moment $m = M_f/M_{sl}$ for a collinear, uncompensated antiferromagnet gives

$$B_{sf} = mB_{ex} + \left[\left((mB_{ex}\right)^2 + 2B_aB_{ex}\right)\right]^{1/2} \tag{3}$$

when $m \ll 1$ and $B_a \ll B_{ex}$. Equation (3) is deduced by comparing the energy of the configuration with moments lying parallel and antiparallel to B_a, with the energy of the canted state. An equivalent expression has been given by Mørup [13]. Hence the observed value $B_{sf} = 20$ T, with $m = 0.02$ and $B_{ex} = 390$ T implies $B_a = 0.11$ T and $K = 6 \times 10^4$ J m^{-3}. If there were no weak ferromagnetic moment, the spin flop would occur at 9.3 T, but the small ferromagnetic moment more than doubles the threshold field. Assuming a M_{sl}^2 dependence, the value of the anisotropy at room temperature will be 3×10^4 J m^{-3}.

The observation of coercivity (figure 4(*b*)) is independent evidence for significant uniaxial anisotropy. In the Stoner–Wohlfarth model of uniform, coherent reversal, the

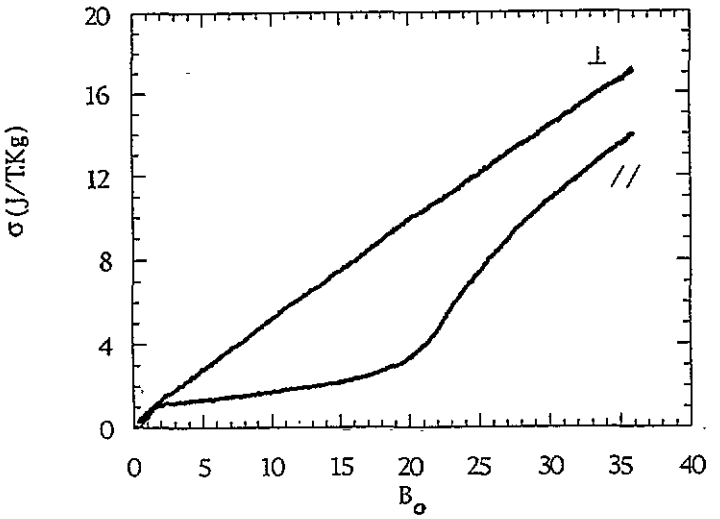

Figure 5. High-field magnetization curves measured for goethite at 4.2 K. The spin flop occurs in the parallel direction at 20 T.

coercivity, $\mu_0 H_c = 2K/M_f$. The value of 1.5 T at 4.2 K implies $K = 0.8 \times 10^4$ J m^{-3}. In practice, the Stoner–Wohlfarth model greatly overestimates the coercivity, so this value of K can be regarded as a lower limit.

Uniaxial anisotropy constants of order 10^5 J m^{-3} can reasonably be expected in ferric compounds. The anisotropy is the sum of contributions due to the classical dipole interaction and to the spin-orbit interaction in crystal-field-split excited states of the single ion [15]. In goethite, lattice sums have been used to estimate the dipolar contribution

$$B_{\text{dip}} = \sum_i \left(\mu_0 \mu_i / 4\pi r_i^3\right)\left(2\cos\theta_i r + \sin\theta_i \theta\right).$$

The lattice sums converge for a sphere of radius greater than 3 nm. The magnitude of the dipole field for the observed spin configuration is 0.16 T, but this field is due to the transverse C_x component $(++--)$, but not the main A_y component $(+--+)$. The corresponding anisotropy energy is effectively nil. It is more difficult to calculate the contribution which arises from deviations from octahedral symmetry of the crystal field at the iron site, but it may be inferred that the observed anisotropy is essentially of single-ion origin. The major axis of the electric field gradient was found to lie in the AC mirror plane, at an angle of $\pm 40°$ with c axis [2], so it is likely that the contributions for the total anisotropy for the four iron ions in the unit cell largely cancel each other. By contrast, the magnetic dipole and single ion contributions in haematite are quite large ($\sim$1 T) almost equal but opposite in sign [15]. They cancel exactly at the Morin (spin reorientation) transition.

There remains the question of why very small values of the anisotropy $K \simeq 0.1 \times 10^4$ J m^{-3} are inferred from the Mössbauer lineshapes for fine particles. From our measured anisotropy constant $K = 6 \times 10^4$ J m^{-3} (3×10^4 J m^{-3} at room temperature), it follows from (1) that superparamagnetic relaxation may be anticipated in magnetic measurements ($\ln(\tau/\tau_0) \simeq 25$) for particles smaller than 19 nm at room temperature, whereas for Mössbauer measurements ($\ln(\tau/\tau_0) \simeq 5$) the critical diameter is 11 nm. In fact, it seems that

much larger goethite particles exhibit line broadening or collapse of the magnetic hyperfine splitting at room temperature [4]. The intrinsic magnetic properties of goethite, including Néel temperature, ordered iron moment and spin configuration are quite sample-dependent [19], and inhomogeneities such as variable water/hydroxyl content, cation vacancies and hydrogen disorder may lead to a distribution of magnetic properties within a sample. Bocquet and Kennedy [9] have shown that synthetic goethite particles some 20 nm in size show a consistent magnetic ordering temperature of 358 K in measurements having quite different timescales. Weak interactions between [5, 7] or within [1] crystallites have been suggested as the origin of some of the relaxation lineshapes. In some cases interparticle interactions can actually reduce the relaxation time [20].

Here we make another suggestion. Although all the goethite samples we have examined have A_y as the main antiferromagnetic mode, they differ in the nature of the ordering in the AC plane. The present sample has C_x transverse order, whereas others have A_z [19]. This suggests that the two modes are almost degenerate, and raises the possibility of thermally excited collective excitations (or even tunnelling) between them. We call this *mode superparamagnetism*. The component of the antiferromagnetic order along the b axis is stable, but the component in the AC plane may fluctuate between C_x and A_z. Physically, this corresponds to the in-plane components rotating clockwise or anticlockwise, as indicated in figure 6. The in-plane anisotropy may be very much smaller than the effective uniaxial anisotropy K, so that the axial and transverse superparamagnetic fluctuations may occur on quite different timescales in non-collinear antiferromagnets like goethite.

Finally, we consider the origin of the weak ferromagnetic moment along the ferromagnetic axis. Three possible explanations are: (i) cation or cation vacancy order; (ii) finite size effects and (iii) hydrogen order. The first possibility was advanced by Hedley [16], who suggested that non-magnetic cations such as Al^{3+} or Fe^{3+} vacancies order preferentially on one of the antiferromagnetic sublattices, but it is difficult to understand why this should arise. The second possibility was raised by Rochette and Fillion [18]. The goethite structure consists of ferromagnetic chains of ions running parallel to b, and ferromagnetic planes perpendicular to b. The observation of a net amount of 1% of the ferromagnetic saturation requires that the size of coherent crystalline domains is quite small in the AC plane. Each cross section would have to contain approximately $n_c = 10^4$ chains, corresponding to a width of about 30 nm. The boundary delimiting they crystallite will naturally include a random imbalance of up and down chains, leading to a magnetization $(n_c)^{-1/2}M_s$. While this cannot be ruled out, we have seen no evidence in SEM or AFM images of the present sample for such limited crystalline perfection. The third possibility is attractive because hydrogen is mobile, and a superstructure of excess or deficit hydrogen could easily influence the net iron moment. Further experiments on deuterated or partly dehydrated samples are needed to resolve this issue.

4. Conclusion

We have observed a spin-flop transition in goethite when a magnetic field of 20 T is applied along the b axis at low temperature. The spin flop is driven to a high field by the small intrinsic moment along b, which may be attributed to a statistical imbalance in the number of up and down chains present in the small cross-section of the crystalline domains in the direction perpendicular to b, or to hydrogen order. The values of the anisotropy field $B_a = 0.11$ T and the anisotropy energy $K = 6 \times 10^4$ J m^{-3} deduced from the spin-flop field are typical for Fe^{3+} in an octahedral site, and they are supported by lower limits based

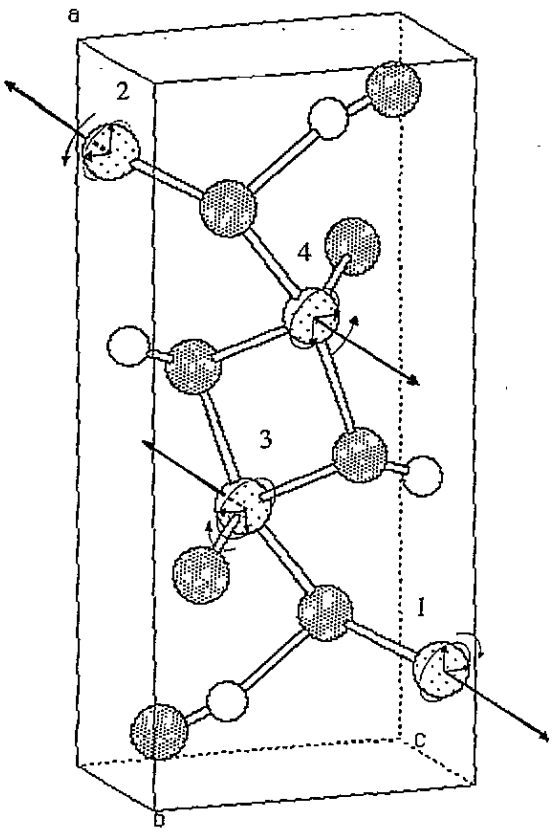

Figure 6. Possible transverse spin fluctuation which may be thermally excited in mode superparamagnetism. The components of the moments parallel to *b* are stable, but the components in the AC plane fluctuate in a clockwise or anticlockwise sense, as shown.

on two other magnetic properties, but they should not lead to superparamagnetic behaviour which is frequently observed for this material. Collective superparamagnetic fluctuations of the transverse magnetization (mode superparamagnetism) is proposed, but the idea needs to be investigated further in goethite and other non-collinear multi-sublattice antiferromagnets.

Acknowledgments

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