STRUCTURAL AND MAGNETIC PROPERTIES OF FERRIHYDRITE

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Abstract—[57]Fe Mössbauer spectra of two synthetic samples of ferrihydrite, recorded at 4.2 K in applied fields of up to 9 T, have been analysed by a mean-field model. The samples exhibit two and six X-ray diffraction peaks. It is shown that only one ferric ion site is present in the mineral, and that in this site the ions are octahedrally coordinated. The spectra show the presence of different magnetic states: ferrimagnetism in two-line ferrihydrite, and antiferromagnetism in six-line ferrihydrite. The ferrimagnetism in two-line ferrihydrite is analysed in terms of random fluctuations arising from the small numbers of ferric ions per particle, and it is shown that the different magnetic states may arise purely as a result of these fluctuations.

Key Words—Ferrihydrite, Ferrimagnetism, Antiferromagnetism.

INTRODUCTION

Ferrihydrite is a poorly crystalline hydrated ferric oxyhydroxide which is the growth precursor to more crystalline iron minerals such as hematite. It has the approximate composition $Fe_5HO_8 \cdot 4H_2O$. The poor crystallinity of ferrihydrite samples is evident in their X-ray diffraction patterns, which contain between two and six broad lines. Samples are described as, for example, two-line, four-line, or six-line ferrihydrites, as a means of indicating the degree of crystallinity.

Both the structural and the magnetic properties of ferrihydrite are currently the subject of vigorous debate. It is generally accepted that ferrihydrite has a structure based on that of hematite, with a hexagonal unit cell ($a = 5.08$ Å, $c = 9.4$ Å) and the iron in octahedral coordination (Towe and Bradley, 1967; Chukhrov *et al.*, 1973).

However, on the basis of X-ray diffraction, high-resolution transmission electron microscopy, and X-ray absorption edge data, Eggleton and Fitzpatrick (1988) propose that a new structural model based on a trigonal unit cell is more appropriate. They conclude that 36% of the Fe is present in tetrahedral sites, with the remainder in octahedral sites. This proposal has been disputed by Manceau *et al.* (1990). Eggleton and Fitzpatrick (1990) contend that as yet none of the proposed models for the structure of ferrihydrite, ranging from all tetrahedral to all octahedral Fe, have been either proved or disproved. In support of this they refer to the room temperature Mössbauer spectrum of six-line ferrihydrite, which can be modelled equally well with paramagnetic doublets corresponding to either 0% or 25% tetrahedral Fe (Cardile, 1988). Further, Murad (1988) analysed both the paramagnetic and magnetic Mössbauer spectra of a 'well-crystallised' ferrihydrite in terms of different distributions of hyperfine parameters, and inferred that two distributions were needed, and that they could be ascribed to the presence of both

octahedral and tetrahedral Fe. However, subsequent work on this 'well-crystallised' material (Bigham *et al.*, 1990) has shown that sulphur plays an important role, and that the material may in fact be an iron (III) oxyhydroxysulphate rather than ferrihydrite *sensu stricto*.

The magnetic state of ferrihydrite is also the subject of controversy. It is supposed to be 'speromagnetic', a state in which the atomic magnetic moments are individually oriented at random despite the presence of antiferromagnetic nearest-neighbour interactions. The prototype speromagnet was a natural ferric gel (Coey and Readman, 1973) now thought to have been ferrihydrite (Madsen *et al.*, 1986; Murad *et al.*, 1988) and which showed applied-field Mössbauer spectra similar to those of ferrihydrite (Madsen *et al.*, 1986).

We have recently pointed out (Pollard and Pankhurst, 1992) that although the applied field Mössbauer spectra of the prototype speromagnet were said to demonstrate the new magnetic state (despite contrary indications from bulk magnetic measurements which suggested antiferromagnetism), the original Mössbauer spectra can in fact be explained most simply as resulting from antiferromagnetic order in fine particles. Consequently, the nature of the magnetic order in ferrihydrite is thrown into some doubt.

Mössbauer spectroscopy offers the prospect of detailed analysis of both the crystallographic and magnetic states of ferrihydrite. The room temperature spectra are ambiguous because they comprise overlapping paramagnetic doublets; however, on cooling to temperatures below the ordering temperature, hyperfine magnetic splitting occurs which increases the resolution. Applying magnetic fields enhances the resolution further. In addition, the response of the material to the applied field indicates its magnetic state.

High-field (up to 9 T) spectra of two-line and six-line synthetic samples at 4.2 K have been recorded (Pollard *et al.*, 1992), but have not been analysed with
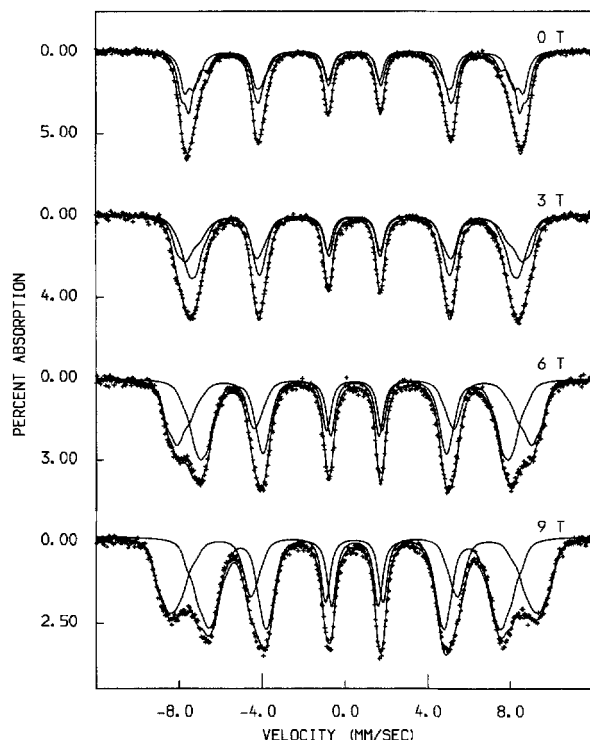
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Figure 1. ^{57}Fe Mössbauer spectra of synthetic two-line fer-rihydrite at 4.2 K in applied fields of 0, 3, 6, and 9 T directed parallel to the γ-ray beam. The solid lines show the least-squares fit to each sublattice, as well as the sum of these, obtained by simultaneously fitting the spectra with a mean field model of ferrimagnetism.

Figure 2. ^{57}Fe Mössbauer spectra of synthetic six-line fer-rihydrite at 4.2 K in applied fields of 0, 3, 6, and 9 T directed parallel to the γ-ray beam. The solid lines show the least-squares fit obtained by simultaneously fitting the spectra with a mean field model of antiferromagnetism.

a physical model. In this report we present detailed analyses of the spectra, and show for the first time that there is no appreciable contribution from Fe in tetra-hedral sites. Further, it is shown that two-line ferri-hydrite is a ferrimagnet and that six-line ferrihydrite is an antiferromagnet. In keeping with our recent re-evaluation of spectra of the prototype ferric gel, there is no evidence that ferrihydrite is speromagnetic.

EXPERIMENTAL

A detailed description of the sample synthesis and the experimental method is provided elsewhere (Pol-lard et al., 1992). Briefly, two-line ferrihydrite was precipitated from a solution of $Fe(NO_3)_3 \cdot 9H_2O$ at pH 7.5. Six-line ferrihydrite was prepared by hydrolysis of a $Fe(NO_3)_3 \cdot 9H_2O$ solution at pH 2.97, with subsequent flocculation at pH 8.0.

X-ray diffraction patterns were of lightly pressed powders using CoKα X-rays and a scanning rate of 0.5° in 2θ per minute. They conform to the expected pat-terns of two-line and six-line ferrihydrite. The breadth of the two-line peaks indicate particle dimensions of order 2–3 nm, while the six-line peaks correspond to dimensions of order 6 nm.

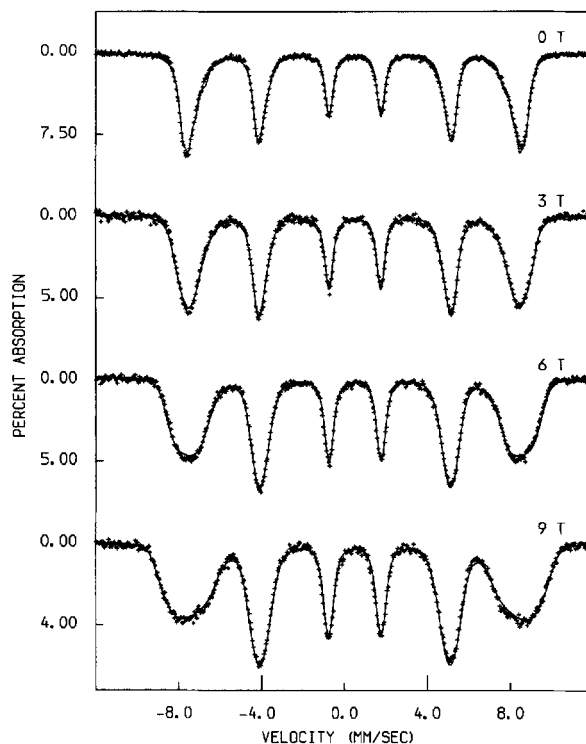Mössbauer absorbers were prepared by mixing the

samples with powdered starch and gently pressing the mixture between two nested plastic cups. The iron thickness was 5 mg/cm². The γ-ray source was ^{57}CoRh, and was Doppler modulated using a triangular wave-form. Counts were collected in 1000 channels; subse-quent folding produced 500 channel spectra with no baseline curvature. Velocity calibration was with re-spect to the centre of an iron foil spectrum at room temperature. Source and absorber temperatures were monitored using AuFe thermocouples referenced to a warm oil bath, and were always in the range 4–5 K. Magnetic fields were supplied by an Oxford Instru-ments solenoid, and were applied in a direction parallel to the collimated γ-ray beam.

RESULTS AND ANALYSIS

^{57}Fe Mössbauer spectra of the two samples, recorded at 4.2 K in applied fields of 0, 3, 6, and 9 T, are shown in Figures 1 and 2. It is clear that the two sets of spectra are markedly different. The spectra of two-line ferrihy-drite appear to split into two sextets as the applied field is increased, whereas the spectra of the six-line sample broaden, but do not split.

The appearance of two sextets for two-line ferrihy-drite has not been observed in spectra of other ferrihy-

drite samples. This may simply be due to insufficient applied field strength having been used; Madsen *et al.* (1986), looking at four-line ferrihydrite, used 4 T, while Coey and Readman (1973), looking at their ferric gel, used 1 and 5 T. By comparing Figures 1 and 2 it is apparent that both samples show a single broad sextet in fields of 0 and 3 T, and only in the 6 and 9 T spectra does the difference become marked.

It should be noted that the apparent splitting does not prove, *per se,* that the magnetic states are not simply antiferromagnetic, since even pure antiferromagnets can show a similar effect in applied fields (Pankhurst and Pollard, 1990). Quantitative analysis is required in order to determine whether the magnetic structures of the two samples are different. In general the applied-field spectra of magnetic powders are complex, since the applied field adds vectorially to the local hyperfine fields, and causes a rotation of the magnetic moments in a way that depends on details of the crystallographic and magnetic interactions.

Similarly, it should be noted that the non-zero intensity of the $\Delta m_I = 0$ lines (the second and fifth lines of a sextet) does not necessarily rule out the possibility that some form of ferrimagnetic order is present. It is a common misconception that as soon as a material exhibits the slightest net ferrimagnetic moment, this moment will dominate the response of the material to an external magnetic field. It is therefore commonly anticipated that large applied fields, such as those used in this work, will cause the atomic moments to align parallel and antiparallel to the field, and that the $\Delta m_I = 0$ lines will be suppressed. This is not the case. Many factors contribute to determining what will be the equilibrium moment orientations of a ferrimagnetic material in an applied field. Particularly important factors are the 'degree' of ferrimagnetism, characterised by the ratio of the magnitudes of the sublattice moments, and the strength of the crystallographic anisotropy. Such effects have been discussed in a recent paper on ferrimagnetism in fine feroxyhite particles (Pollard and Pankhurst, 1991).

The spectra were computer fitted to minimise the sum-of-squares parameter χ^2, using a uniaxial anisotropy mean field model designed to incorporate both ferrimagnetism and antiferromagnetism into a simple two-sublattice formalism. This model has been described in detail by Pankhurst and Pollard (1990) and by Pankhurst (1991). The main feature of the model is that it incorporates the competition between the relative strengths of the exchange, anisotropy and local fields, the ratio of the sublattice moments, and the powder summation of the angles between the applied field and the easy anisotropy axis of each crystallite. In this way the model provides a microscopic description of the factors determining the equilibrium orientation of representative ferric moments in the sample.

A second feature of the fitting procedure is that for each sample, the full set of 0, 3, 6, and 9 T spectra were analysed simultaneously. This method of fitting alleviates the problems associated with the interdependence of the fit parameters, since the exchange, anisotropy, and sublattice moment terms only affect the applied field spectra. The other parameters are independent of the applied field.

Although distributions of both isomer shift (δ) and quadrupole splitting (Δ) are expected as the result of local crystallographic variability, they were taken to be single valued. The major effect of such distributions is some field-independent line broadening, which was modelled by a larger than usual linewidth.

Three hyperfine fields (B_{hf}) of variable relative probability were allowed for each magnetic sublattice, to further account for the broad lines observed in zero applied field. Since the exchange field is a relatively insensitive parameter in the model, it was set to the value $B_E = 128$ T for both samples. Three extra parameters were varied to model the response to applied fields: the anisotropy field (B_A) on each sublattice and the ratio of sublattice moments (ξ).

The resultant fits are shown as the solid lines in Figures 1 and 2. For the six-line ferrihydrite a simple antiferromagnetic model, with $\xi = 1$ and the hyperfine fields set equal for each sublattice, provided a good fit ($\chi^2 = 2.4$). An isomer shift $\delta = 0.48(2)$ mms^{-1}, quadrupole splitting $\Delta = 0.11(4)$ mms^{-1}, mean hyperfine field $<B_{hf}> = 49.0(1)$ T, and anisotropy field $B_A = 0.9(1)$ T were determined. For the two-line ferrihydrite the antiferromagnetic model gave a poor fit ($\chi^2 = 3.8$), so a ferrimagnetic model was adopted, with ξ allowed to vary. The fit thus obtained (Figure 1) was better ($\chi^2 = 2.1$), with $\xi = 0.92(5)$ at 9 T. The other fitted parameters were $\delta = 0.48(2)$ mms^{-1}, $\Delta = 0.04(4)$ mms^{-1}, $<B_{hf}> = 49.7(1)$ T, and $B_A = 0.6(1)$ T on the sublattice with the larger moment, and $\delta = 0.46(2)$ mms^{-1}, $\Delta = -0.01(4)$ mms^{-1}, $<B_{hf}> = 48.4(1)$ T, and $B_A = 0.6(1)$ T on the sublattice with the smaller moment.

DISCUSSION AND CONCLUSIONS

Structurally, it is important that it was possible to model the applied field spectra using a single value of isomer shift, $\delta = 0.48 \pm 0.02$ mms^{-1}, for all the Fe sites. This value is characteristic of octahedrally coordinated Fe^{3+} at liquid helium temperatures. For two-line ferrihydrite the two values of quadrupole splitting Δ are equal within their uncertainties, and are therefore also consistent with one type of crystallographic environment. For six-line ferrihydrite Δ is single valued but is surprisingly high compared to the values reported by Murad (1988). Given that tetrahedral Fe(III) in ferrihydrite would have a quadrupole splitting and an isomer shift that was significantly different to that of octahedral Fe(III) in ferrihydrite, tetrahedral Fe should have been apparent as an asymmetry in the

zero field spectra. This asymmetry should have become more pronounced in the applied field spectra. Neither feature is apparent in the data. We therefore conclude that tetrahedral Fe is not present in appreciable quantities in either of the two-line and six-line ferrihydrite samples.

Magnetically, the spectra are satisfactorily fitted by assuming a model of two-sublattice ferrimagnetism for two-line ferrihydrite, and simple antiferromagnetism for six-line ferrihydrite. One curious result is that the mean hyperfine fields of the two samples are very similar, a feature that is evident on visual inspection of the zero applied field spectra. Naturally occurring two-line and six-line ferrihydrites have hyperfine fields that differ by between 2 and 3 T (Murad *et al.*, 1988). This is presumably a sample-dependent effect.

The origin of the ferrimagnetic moment in the two-line sample is intriguing, since although two-line and six-line ferrihydrite differ in their crystallinity and particle sizes, they are thought to possess the same crystallographic structure. It would therefore be anticipated that they would exhibit the same local magnetic structure. The ferrimagnetism may be due to the very small particle sizes which lead to relatively large surface areas and large uncompensated surface moments, or due to some degree of disorder which leads to uncompensated moments distributed throughout the particle. These effects are tantamount to statistical fluctuations in the numbers of moments occupying one of the two oppositely oriented sublattices. Consequently, the degree of ferrimagnetism which results can be estimated in magnitude. We use the term 'magnetic entity' to denote a portion of a particle within which the moments are parallel but aligned at random in one of the two sublattice directions. Since the fluctuations may be in the number of individual moments, or in the number of planes of moments, the entity may contain one or many magnetic moments.

A certain fraction (x) of the N magnetic moments per particle are assumed to occupy either sublattice at random, and the other moments are assumed to be perfectly paired. The number of moments per entity is k. It follows that the ratio of the sublattice occupancies (f_1/f_2) is $(N - R)/(N + R)$ where $R = 0.794(kxN)^{1/2}$ (Pollard *et al.*, 1991). Using $f_1/f_2 = 0.85(5)$ measured for two-line ferrihydrite shows that kx/N is in the range 0.004–0.02.

This result can be compared with the number of ferric ions per particle, as estimated by Eggleton and Fitzpatrick (1988) for ferrihydrites of similar dimensions. For two-line ferrihydrite there are about 100 ions, so kx is in the range 0.4–2.0. If the ferrimagnetism is due to fluctuations in individual moments $(k = 1)$, it follows that the degree of disorder is $x > 0.4$. Lesser disorder, with $x < 0.4$, would imply that the fluctuating magnetic entities contain more than a single magnetic moment.

It might be anticipated that similar fluctuations would be present in six-line ferrihydrite. In the Mössbauer analysis it was assumed that f_1/f_2 was equal to 1, but the lower limit is estimated to be 0.95. It follows that $kx/N < 0.001$, and using $N = 1500$ (interpolated from the data of Eggleton and Fitzpatrick) gives $kx < 1.5$. This condition is satisfied by all values of x for $k = 1$, but if the entities contain more than one moment, then a degree of pure antiferromagnetic order is implied. Thus, the observation of different magnetic ground states in two-line and six-line ferrihydrite may arise purely as a result of the different numbers of ferric ions in the individual particles.

ACKNOWLEDGMENT

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