

CHARACTERIZATION OF FeOOH POLYMORPHS AND FERRIHYDRITE USING LOW-TEMPERATURE, APPLIED-FIELD, MÖSSBAUER SPECTROSCOPY

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(Received 21 March 1991; revised 9 July 1991)

ABSTRACT: Mössbauer spectroscopy obtained with the sample at low temperatures and subject to large magnetic fields is discussed in terms of its use in analysing the naturally occurring polymorphs of FeOOH and the common growth precursor, ferrihydrite. Experiments on well-characterized synthetic samples provided benchmark results. A relatively simple means of quantitative analysis was used, in which sextets of Voigtian-shaped lines were summed and least-squares fitted. The results are discussed in terms of the magnetic structures of each compound.

Fine-grained iron oxides and oxyhydroxides in soils and sediments can often be best identified using Mössbauer spectroscopy, since their X-ray diffractograms are complicated by small crystallite size-broadening and the iron phases may constitute a relatively small proportion of the sample. Several excellent reviews of the work have been published (Bowen, 1979; Murad & Johnston, 1987; Murad 1988a; De Grave *et al.*, 1990; Vandenberghe *et al.*, 1990; Murad, 1990). The last study was directed towards soil scientists without expertise in Mössbauer spectroscopy.

However, a frequent problem in characterizing iron compounds using Mössbauer spectroscopy is that although the patterns of individual compounds are generally available, the patterns and any derived results are generally not directly comparable. This is because they depend on the source and sample temperatures, the calibration reference, and the method of fitting. Further, unless the experiments are performed at low temperatures, the effects of small particle size and isomorphous substitution (especially Al in natural samples) are frequently pronounced. This makes the task of identifying phases difficult and, in some cases, impossible.

A set of reference Mössbauer spectra of iron oxides and oxyhydroxides with and without magnetic fields applied is available to enable visual identification of iron phases (Pollard, 1991). Compounds which exhibit very similar zero applied-field Mössbauer patterns show distinctive patterns when a field is applied, partly because the magnetic structures are diverse and include ferrimagnetism and antiferromagnetism. The response of such magnetic systems to applied fields is a subject of contemporary interest, and the results can be of use to soil scientists to aid identification. Ferrihydrite and “ferric gels” are of particular interest, since their Mössbauer patterns have been used to identify a novel type of magnetic order, speromagnetism (Coey & Readman, 1973a,b).

The aim of this report is to present low-temperature and applied-field Mössbauer spectra

of synthetic iron oxyhydroxide and ferrihydrite soil components for identification purposes, in order to establish a reference against which natural samples may be compared. Strong magnetic fields, up to 9 T, were used, since the spectral resolution increases with field strength. In this respect our data is of a significantly higher grade than that reported previously, in which 4–6 T fields were used. A relatively simple method of least-squares analysis was used which does not correspond to particular physical models but which enables a simple comparison of parameters.

We report experiments on goethite, akaganéite, lepidocrocite and feroxyhite (α -, β -, γ - and δ' -FeOOH), and on two ferrihydrite (\sim Fe₅HO₈.4H₂O) samples which exhibit two and six X-ray diffraction (XRD) lines. Iron oxides are not included in the study, as a quantitative analysis of low-temperature and high-field iron-oxide spectra has been reported (Pollard, 1990).

SAMPLE SYNTHESSES

Goethite was prepared by dissolving 20 mmol of Fe(NO₃)₃.9H₂O (8.08 g) in 80 ml of distilled water and slowly raising the pH to 7.5 by the addition of 20 ml of 3 M KOH. After storage for 3 h, the sediment was washed four times to remove KNO₃, then re-suspended in distilled water (100 ml) and added to 150 ml of 0.5 M KOH to give a final suspension of 0.3 M in free OH⁻. The suspension was stored at 20°C, with occasional shaking, for five years before finally washing free of alkali and drying at 50°C.

Akaganéite was prepared by allowing solid AR grade FeCl₂.4H₂O to hydrolyse by storage in contact with moist air for several months. The brown product was freed from residual FeCl₂ by repeated washing with distilled water and then dried at 50°C.

Lepidocrocite was prepared by dissolving 3 mmol of FeCl₂.4H₂O (0.6 g) in 150 ml of N₂-saturated 0.2 M NaCl solution. With stirring and N₂ bubbling, the pH was adjusted to 6.0 by the addition of 1 M NaOH from a Radiometer Autoburette. After the pH had stabilised, the bubbling N₂ was replaced by air (at 15 ml/min) whilst maintaining the pH at 6.0 throughout the 2.5 h oxidation period. The sample was washed and dried at 50°C.

Feroxyhite was prepared by saturating a solution of 50 ml of 0.045 M FeCl₂ with N₂ for one hour, and then raising the pH to 8.5 by the addition of NaOH. Rapid oxidation was *via* addition of 1 ml of 30% H₂O₂. The pH decreased to 3.5 but was returned to 8.5 by the addition of NaOH within one minute. The product was stirred for 45 min before washing and drying at 50°C.

Two-line (XRD) ferrihydrite was formed by dissolving 5 mmol of Fe(NO₃)₃.9H₂O (2.02 g) in 500 ml of distilled water (Fe³⁺ at 10⁻² M) and the pH raised to 7.5 by the addition of 15 ml of 1 M NaOH. The precipitate was aged at pH 7.5 for 18 h and then washed and dried at 50°C.

Six-line (XRD) ferrihydrite was prepared by dissolving 3 mmol of Fe(NO₃)₃.9H₂O (1.2 g) in 3 l of distilled water at 33°C to give a solution of Fe³⁺ = 10⁻³ M at a pH of 2.97. During hydrolysis, protons were liberated, but by automatic addition of 1 M NaOH the pH was not allowed to fall below 2.7. Two further 1.5 mmol measures of Fe(NO₃)₃.9H₂O were added when the Fe³⁺ concentration decreased to <10% of the initial value. The final product was flocculated by increasing the pH to 8.0 and the resultant sediment was washed and dried at 50°C.

X-RAY ANALYSIS

Powders were lightly pressed into a holder, and were scanned using Co- $K\alpha$ radiation with a post-diffraction monochromator at a speed of $0.5^\circ 2\theta$ per min. By reference to data in the JCPDS files and other authoritative literature, all samples gave patterns which were consistent with a single phase component. X-ray line-widths were measured in units of 2θ and are the full width at half peak intensity.

For goethite the peaks ranged in width from 0.30° to 0.88° . Appropriate peaks were selected for estimates of the crystallite dimensions using the Scherrer formula¹ appropriate for Cauchy profiles given by Klug & Alexander (1974). The dimensions of the orthorhombic laths were approximately 12 nm and 90 nm along the a and b axes, respectively. Transmission electron microscopy showed that these dimensions correspond well to the particle dimensions, and that the length along c (which could not be determined from XRD) was 100–200 nm.

Apart from the sharpest 002 reflection, most peaks from akaganéite had a common width of $0.6 \pm 0.03^\circ$ which corresponds to lengths of 22–24 nm along a , and 38 nm along c in the tetragonal crystal. These sizes are consistent with the spindle or rod shapes observed by Childs *et al.* (1980) in electron micrographs.

For lepidocrocite the diffractograms indicated rhombohedral laths with the length a being no smaller than 33 nm and the length along b being 10 nm. The peak used to determine the a length is an unresolved composite of 200 and 051 reflections, hence only a minimum value could be determined. These dimensions are smaller than the particle sizes reported for this sample using electron microscopy, in which the laths were $\sim 60 \times 15$ nm in cross-section and had an average length of 300 nm (Lewis & Farmer, 1986).

Peaks of feroxyhite and the two ferrihydrite samples were much broader than for the other samples, with widths of up to 5° . For feroxyhite only four peaks were observed, and we infer that the crystallite dimensions are 15 nm along a and 4–5 nm along c . This is in accord with electron microscope observations of very thin flakes in similar samples (Feitknecht *et al.*, 1969; Carlson & Schwertmann, 1980).

For 2-line ferrihydrite, the peaks indicated a dimension of 2–3 nm. Electron micrographs of similar products usually show aggregated clumps of small spheres (e.g. Eggleton & Fitzpatrick, 1988). The 6-line ferrihydrite sample exhibited 100 and 300 peaks which indicate a dimension of ~ 6 nm. The other, broader peaks correspond to dimensions of 2–3 nm. Electron microscopy on a sample with a very similar six-line X-ray pattern showed well-faceted crystals of diameter 1.5–6 nm (Eggleton & Fitzpatrick, 1988).

MÖSSBAUER EXPERIMENTAL TECHNIQUE

Absorbers were made by diluting the samples with powdered starch to achieve 5–7 mg/cm² of iron. Mössbauer spectra were recorded at room temperature (RT, ~ 293 K), 77 K, and 4.2 K. The source was at RT, except for the 4.2 K runs for which the source temperature was between 4.2 K and 6 K. Both source and absorber temperatures were monitored with AuFe thermocouples referenced to a warm oil bath and calibrated in liquid nitrogen and liquid helium. In the spectra denoted 4.2 K, the absorber temperature was in the range 4.2–5 K.

¹ $L_{hkl} = 0.9\lambda/(b\cos\theta)$, where L_{hkl} is the crystallite dimension normal to hkl , λ is the X-ray wavelength, b is the peak-width corrected for instrumental broadening (in radians), and θ is the Bragg angle.

The γ -ray source was $^{57}\text{CoRh}$ which was moved via a triangular velocity waveform, and γ -counts were collected in 1000 channels. Numerical folding of the spectra was performed subsequently, and produced 500-channel spectra without baseline curvature. Calibration was with respect to the centre of the room temperature spectrum of α -Fe foil. Magnetic fields were applied parallel to the γ -ray direction.

MÖSSBAUER DATA ANALYSIS TECHNIQUE

The applied-field Mössbauer spectra of magnetic powders appear complex: each spectrum is the superposition of subspectra which correspond to different orientations of the particles in the powder absorber. For each orientation the effective hyperfine field is the vector addition of the external and internal fields, and the dominant effect is a severe broadening of the profiles. Further, the magnetic moments partially reorient in reaction to the field, depending on the balance of the magnetic exchange and magnetocrystalline anisotropy interactions which are characteristic of the crystallographic structure. Consequently, the effective hyperfine field is distributed, and in general there is a distribution of orientations present for particular values of the effective hyperfine field.

Two different methods of detailed analysis are available. In one, the magnetocrystalline anisotropy is assumed to be uniaxial and a mean-field model is used to determine the equilibrium orientations of the moments. Spectra taken with different strength applied fields are simultaneously fitted (Pankhurst & Pollard, 1990; Pankhurst, 1991). The influence of the applied field is considered for representative orientations of the particles (~ 20) and the weighted subspectra are summed. This leads to a large number of calculations, typically 10^9 floating point operations per fit.

The second technique is said to be model independent. It involves a transformation of the Mössbauer data into bi-dimensional probability distributions of the hyperfine magnetic field and the orientation of the magnetic moments (de Bakker *et al.*, 1990). Although these distributions are also characteristic of the sample, they are difficult to compute and interpret, and because they necessarily contain many values the degree of data reduction (the ratio of the number of velocity channels in the spectrum to the number of adjustable parameters in the fit) is small.

A relatively simple method of least-squares fitting was used in order to enable a straightforward analysis. Subspectra comprising six lines were summed. The number of sextets used was chosen to be the minimum required in order to obtain a good fit as measured by χ^2 . Because the broadened profiles in applied fields result from relatively narrow distributions of randomly oriented internal fields convoluted with the applied-field, to a good approximation each sextet arises from moments with a similar effective field. The aggregated orientation of those moments is simply related to the area ratios of the lines in each sextet, and it is the relationship between field and orientation which is a characteristic of a material. This model is therefore a realistic approximation; a similar method has been demonstrated to provide physical information which is consistent with that obtained from model-independent bi-distribution analyses (Bowen *et al.*, 1990).

Each line in a sextet was modelled by a Voigtian profile. Such profiles arise when the Fe sites are not quite equivalent (crystallographically or magnetically), but each site contributes a Lorentzian-shaped line such that the probability distribution of the various line positions follows a Gaussian distribution. This is the case when a number of independent perturbations are present, a result which follows from the central limit

theorem of statistics, and is expected to be most appropriate in applied-field spectra of powders.

It is noted that asymmetric internal hyperfine field distributions are common for soil samples. Cooling to 4.2 K minimises the asymmetry. Further, such distributions are masked by the applied field since they are convoluted with the effects of the summation with the applied field, and the inclusion of more than one sextet permits asymmetry in the calculated spectral shapes.

Voigtian lines-shapes can be written as the real part of the complex error function (Posener, 1959)

$$H(a, v) = (2\pi)^{-\frac{1}{2}} \operatorname{Re} \left[\exp(z^2) \int_z^\infty \exp(-t^2) dt \right]$$

where $z = a + iv$, $v = 2(v - v_0)/\Delta v'_G$, the line centre is v_0 , $\Delta v'_G = (\ln 2)^{-\frac{1}{2}} \Delta v_G$, Δv_G is the Gaussian half-width (the half-width that the line would have in the limit of a zero-width Lorentzian component), $a = \Delta v_L/\Delta v'_G$ and Δv_L is the half-width of the Lorentzian component. The error function was evaluated numerically following the rapidly computed algorithm specified by Gautschi (1969) and Kölbig (1972).

In least-squares fitting, Δv_G and an area parameter were allowed to vary for each line, subject to the constraint that the widths and areas of line pairs in a sextet were equal, i.e., the pairs (1,6), (2,5) and (3,4) where the lines are numbered in order of increasing velocity. The value of Δv_L was assumed to be equal to that obtained by fitting natural Fe-foil spectra with Lorentzian lines (0.13 mm s^{-1}), and was not varied.

Within each sextet, the line positions were constrained to be consistent with the positions calculated from magnetic splitting of the nuclear states, and perturbed to first order by the electric quadrupole interaction (e.g. Eibschütz & Lines, 1982). For each sextet the variable positional parameters were the hyperfine magnetic field B_{hf} , the isomer shift δ , and the first-order quadrupole shift ϵ .

In the approximation of small quadrupole interaction and thin absorber, the area of the second and fifth lines relative to that of the first and sixth lines in each subspectrum depends on the ratio $A_{25}/A_{16} = \langle 4\sin^2\theta_{\text{hf}} \rangle / 3 \langle 1 + \cos^2\theta_{\text{hf}} \rangle$, where θ_{hf} is the angle between the effective hyperfine field and the γ -ray beam. The ratio A_{34}/A_{16} always equals 1/3. The total area of a subspectrum is independent of θ_{hf} (because the γ -ray absorption cross-section is isotropic), and hence increases in A_{25} are accompanied by decreases in A_{34} and A_{16} and *vice versa*. In fitting, A_{25}/A_{16} was constrained within the physical upper bound of 4/3.

MÖSSBAUER RESULTS

Spectra of goethite (α -FeOOH, Fig. 1) show increasing line-broadening as the applied field strength is increased. The first and sixth lines broaden most and become asymmetric, whereas the second and fifth lines remain symmetric and broaden less. Approximating the spectra with three Voigtian profiles led to very good fits as shown by the solid lines in Fig. 1. The parameters obtained are summarized in Table 1.

The behaviour can be understood from the response of the antiferromagnetically coupled

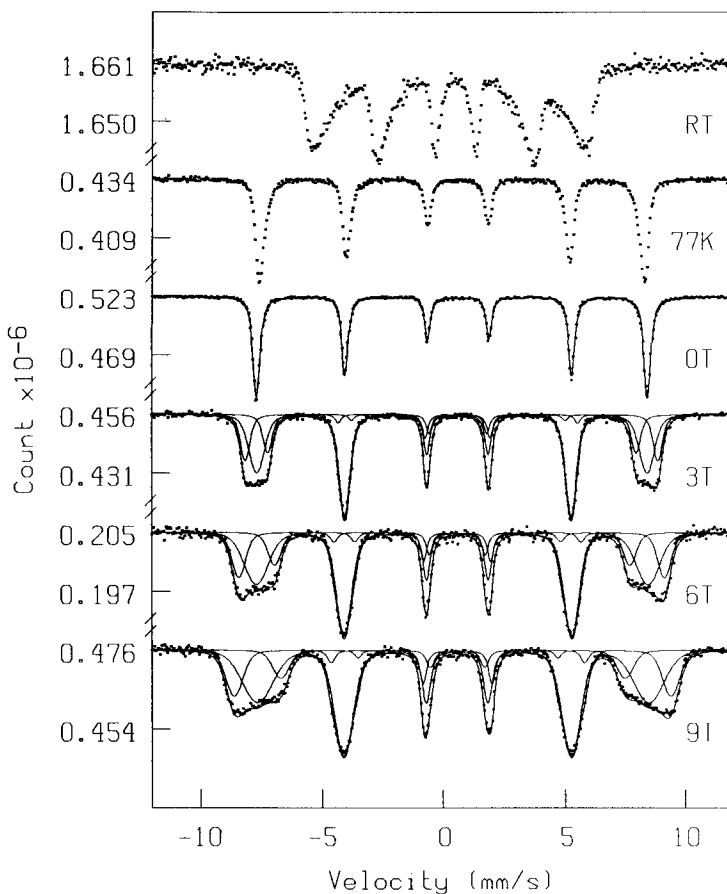


FIG. 1. Mössbauer spectra of goethite at the temperatures indicated. The 4.2 K spectra are labelled 0, 3, 6 & 9 T, indicating the strength of the field which was applied along the γ -ray beam. The solid lines indicate the separate sextets of Voigtian lines, and the sum of the sextets, obtained by least-squares fitting.

moments to the applied field (Pankhurst & Pollard, 1990). Depending on the relative strengths of the exchange interaction and the magnetocrystalline anisotropy, the moments will be partially reoriented by the applied field. If the exchange is large, moments on the two magnetic sub-structures retain antiparallel orientations in applied fields. If the anisotropy is weak, the net moment of a particle is free to rotate under the influence of the applied field.

For a ferrimagnet with strong exchange and weak anisotropy the second and fifth lines in the Mössbauer spectrum vanish as the net moment is aligned by the applied field, whereas for an antiferromagnet the moments 'flop' towards directions perpendicular to the applied field and A_{25}/A_{16} is between $2/3$ and $4/3$. For materials with strong anisotropy and strong exchange, little re-orientation occurs. In this case, moments close to the γ -ray direction exhibit the extreme effective fields, $B_{hf} - B_{app}$ and $B_{hf} + B_{app}$. These moments have $\langle \sin^2 \theta_{hf} \rangle \approx 0$, and therefore contribute very little intensity to the second and fifth lines and consequently dominate the outer line-shapes.

TABLE 1. Summary of parameters determined by least-squares fitting the 4.2 K Mössbauer spectra of FeOOH polymorphs.

Sample	B_{app} (T)	B_{hf} (T)	δ (mms ⁻¹)	ϵ (mms ⁻¹)	A_{25}/A_{16}	A (%)	Δv_G (mms ⁻¹)	χ^2	
α -FeOOH	0	50.3	0.49	-0.12	0.72	100	0.09	2.3	
		3	53.2	0.48	-0.12	0.13	19	0.15	1.3
			50.3	0.49	-0.11	1.30	65	0.30	
		47.5	0.49	-0.13	0.11	16	0.14		
	6	54.8	0.47	-0.11	0.13	19	0.26	1.2	
		50.4	0.48	-0.11	1.33	66	0.52		
		45.8	0.48	-0.11	0.18	15	0.24		
	9	56.2	0.49	-0.10	0.14	20	0.35	1.5	
		50.4	0.49	-0.08	1.31	68	0.68		
		44.3	0.49	-0.10	0.13	12	0.33		
	β -FeOOH	0	48.9	0.50	0.00	0.66	43	0.17	1.3
				47.9	0.47	-0.14	0.78	28	
			47.5	0.49	-0.28	0.70	29	0.35	
9		54.5	0.49	-0.10	0.10	22	0.42	1.3	
		48.1	0.49	-0.10	1.33	65	0.68		
		41.6	0.51	-0.10	0.16	13	0.35		
γ -FeOOH	0	45.7	0.49	0.01	0.77	54	0.14	1.7	
			44.0	0.51	0.06	0.77	46		0.51
	9	51.3	0.48	0.02	0.06	18	0.45	1.2	
			45.2	0.49	0.02	1.30	71		0.68
			38.4	0.50	0.05	0.06	11		0.42
	δ' -FeOOH	0	53.2	0.50	0.08	0.66	22	0.17	1.2
			51.6	0.49	0.02	0.66	46	0.29	
			49.3	0.48	-0.03	0.66	32	0.44	
3		55.5	0.49	0.02	0.22	31	0.33	1.8	
			49.1	0.49	0.00	0.42	69		0.43
6		58.6	0.52	0.00	0.07	19	0.32	1.3	
			55.3	0.47	0.00	0.24	18		0.43
			48.8	0.53	0.02	1.33	31		0.87
			46.3	0.49	0.00	0.05	32		0.33
9		60.9	0.51	0.02	0.05	15	0.33	1.3	
			58.0	0.48	-0.01	0.21	23		0.55
			49.1	0.50	0.01	1.33	31		0.83
			44.1	0.49	0.00	0.09	31		0.33

The hyperfine field B_{hf} is that observed at the nucleus, and includes the effect of the applied field B_{app} , δ is the isomer shift relative to α -Fe at RT, ϵ is the quadrupole shift of the lines, i.e. $(L_1 + L_6 - L_2 - L_5)/4$, A_{25}/A_{16} are the areas of the second and fifth lines relative to the outer lines, A denotes the proportion of spectral area included in each sextet, Δv_G is the half-width of the outer-line Gaussian profiles convoluted with a natural-width Lorentzian line, and χ^2 is the goodness-of-fit measure normalized by the number of degrees of freedom of the fit.

Goethite is characterized by strong antiferromagnetic exchange and reasonably large anisotropy (Meagher *et al.*, 1986; Pankhurst & Pollard, 1990). Replacement of Fe by Al in goethite leads to an increased asymmetry of the outer lines of applied-field spectra, and is thought to indicate Al-induced ferrimagnetism (Bowen *et al.*, 1990).

Akaganéite (β -FeOOH) spectra are shown in Fig. 2. This is also antiferromagnetic, but the zero-field spectrum at low temperatures shows three distinct magnetic components. The origins of these have been discussed at length (De Grave *et al.*, 1990). We found it necessary to include three sextets to obtain an acceptable fit at 4.2 K. As with goethite, applying a magnetic field broadens the lines, and details of subspectra cannot be resolved. A spectrum taken with a 6 T field applied has been presented by De Grave *et al.* (1990) which was fitted with two sextets; the 9 T spectrum in Fig. 2 shows substantially broader asymmetric features and three sextets provided an acceptable fit.

Lepidocrocite (γ -FeOOH) is antiferromagnetic, and in the absence of an applied field the 4.2 K spectrum exhibits asymmetrically broadened lines. These have been analysed in terms of a continuous distribution of hyperfine fields, but detailed analysis is complicated by the necessity of properly accounting for significant quadrupole perturbations (De Grave *et al.*,

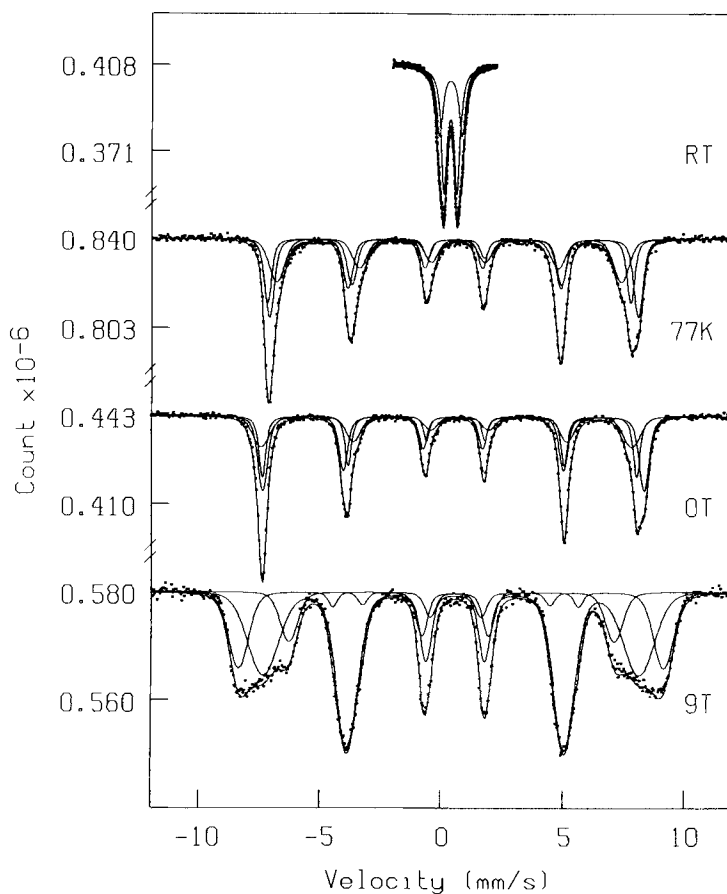


FIG. 2. Mössbauer spectra of akaganéite.

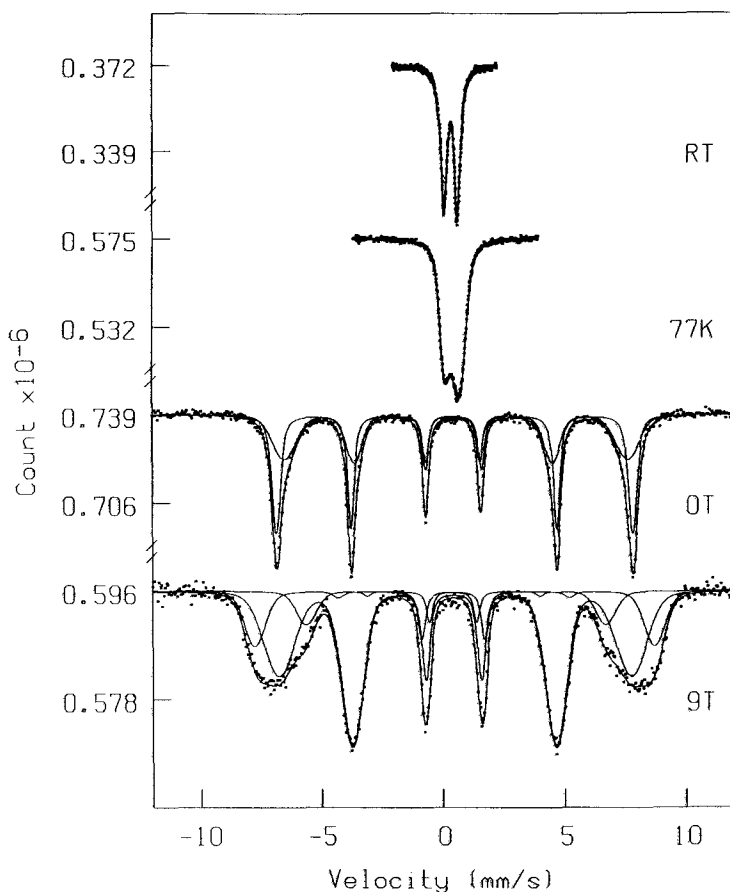


Fig. 3. Mössbauer spectra of lepidocrocite.

1990). Nevertheless, two Voigtian sextets are sufficient to describe the zero-field spectrum. With a 9 T field applied, it can be seen from Fig. 3 that the outer lines became rounded, and three sextets are required.

For goethite, akaganéite, and lepidocrocite, inspection of Table 1 shows that the sextets with the extreme effective hyperfine fields have small A_{25}/A_{16} values. These arise from moments aligned almost parallel and antiparallel with the applied field. Consequently, these three compounds are characterized by strong antiferromagnetic exchange and significant anisotropy, and show similar applied-field spectra.

Ferrihydrite (δ' -FeOOH) is ferrimagnetic, and consequently the spectra show two patterns which are separated by the applied field (Fig. 4). The longitudinal applied field partially rotates the moments parallel and antiparallel to the γ -ray direction, and hence the second and fifth lines reduce in intensity. The incomplete alignment of the moments indicates a reasonably significant anisotropy, originating from the structure itself, from defects in the structure, or from a higher anisotropy experienced by magnetic ions near the surface. A study of the closely related compound δ -FeOOH, using 4 T fields, has favoured the latter explanation, in which ferric ion coordinations near the surface are deformed

(Persoons *et al.*, 1986). Madsen *et al.* (1985) have observed that the magnetic state is strongly affected by particle size at temperatures in the intermediate temperature range 80–300 K.

Fitting the 6 T and 9 T spectra of ferroxhyte (Fig. 4) required four sextets, whereas in the lower resolution zero-field spectrum, three sextets were sufficient. At 3 T, a fortuitous overlap of components allows a satisfactory fit with only two components. Even at 9 T the pattern cannot be unambiguously decomposed into sextets corresponding to ferric ions in two distinct sites, but as higher applied field strengths become available this should be possible.

With no field applied, even well-crystallized ferrihydrite shows distributed hyperfine parameters at 4.2 K (Murad, 1988b), and the distributions evolve with increasing temperature (Murad *et al.*, 1988). The zero-field 4.2 K spectra are well approximated by two Voigt profiles (Figs. 5 and 6), and the parameters derived are given in Table 2.

Ferrihydrite provided the first example of a speromagnetic structure in which the moments are aligned in random, isotropic directions (Coe & Readman, 1973a,b). The magnetic behaviour was unexpected, and therefore is important to the magnetic

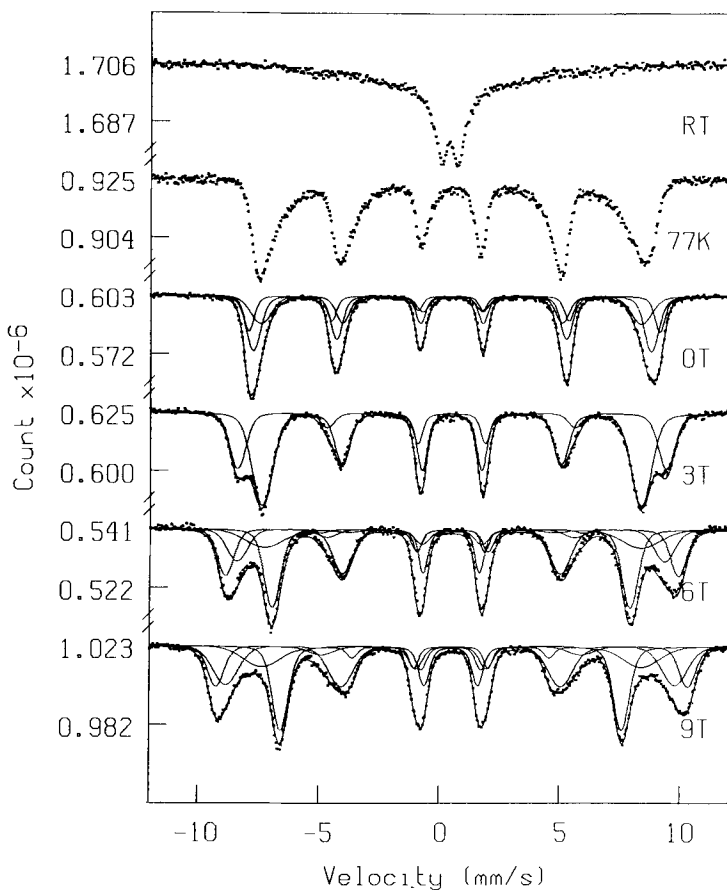


FIG. 4. Mössbauer spectra of ferroxhyte.

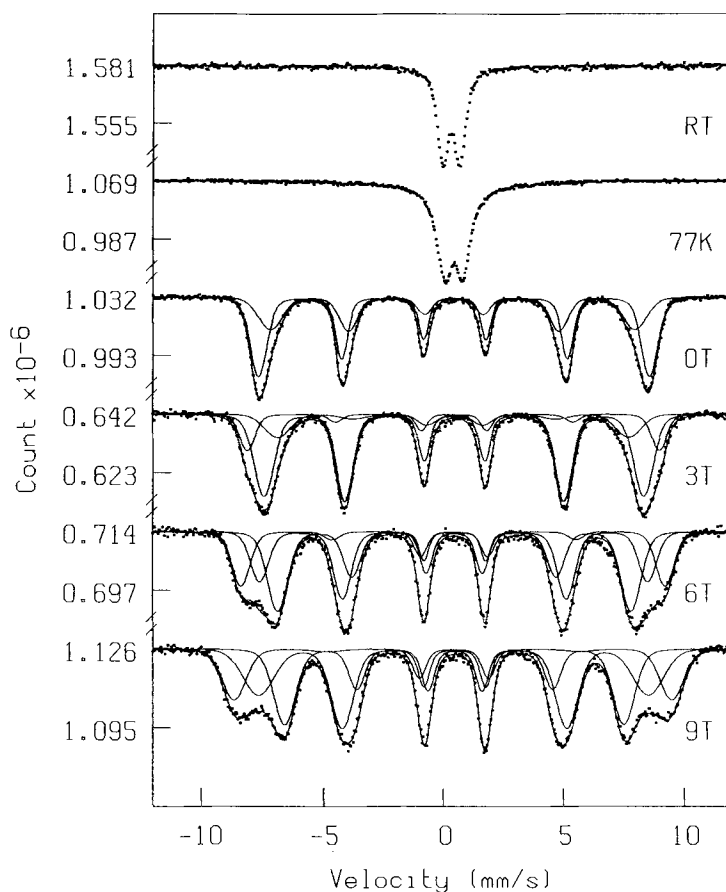


Fig. 5. Mössbauer spectra of a ferrihydrite sample exhibiting a 2-line X-ray pattern.

characterization of Fe-containing components (e.g. De Grave *et al.*, 1990). In the remainder of this section the behaviour is discussed in detail.

The sample examined by Coey & Readman (1973a,b) was a natural ferric gel, and exhibited a non-zero (but weak) net magnetic moment. Madsen *et al.* (1986) later measured the strength of the magnetic moment per ferrihydrite particle by applying fields of up to 4 T at 80 K, and inferred that the moment was likely to arise from uncompensated moments near the particle surface. It is noteworthy that fine goethite particles also exhibit a non-zero magnetic moment, even though it is well understood that in the core of the particles the magnetic arrangement is antiferromagnetic (e.g. Brož *et al.*, 1989).

Coey & Readman's identification of speromagnetism was based upon a 5 T spectrum, in which the constancy of the second and fifth lines with increasing field strength was taken as evidence that the magnetic structure is neither antiferromagnetic, with a slight canting of the sub-structures, nor ferrimagnetic. If the magnetic structure was that of a canted antiferromagnet, an example of which is hematite above the Morin transition, the second and fifth lines might increase in intensity upon applying a longitudinal field (e.g. Pollard, 1991). If a ferrimagnet, the applied field was expected to re-orient the moments along the

γ -ray direction, and consequently the second and fifth lines would vanish. As neither phenomenon occurred, the moments were thought to be arranged nearly at random with a distribution of angles between adjacent moments, i.e. without a long-range antiferromagnetic axis.

The same phenomenon observed by Coey & Readman (1973a,b) can be seen in the synthetic 2-line and 6-line ferrihydrite samples (Figs. 5 and 6, respectively). The method of fitting employed provides accurate (± 0.01) measurements of the ratio of the areas of the second and fifth lines (A_{25} in Table 1) relative to the other lines ($A_{16} + A_{34}$). Random moments are expected to give a ratio of 0.50. For two-line ferrihydrite the ratio is 0.51 at 0 T, 0.46 at 3 T, 0.45 at 6 T, and 0.44 at 9 T (a decrease of 14% from 0 T to 9 T). For 6-line ferrihydrite a reverse trend is observed: 0.50 at 0 T, 0.53 at 3 T, 0.55 at 6 T, and 0.56 at 9 T (an increase of 12%).

However, antiferromagnets also show little variation in the ratio: for example, from the goethite spectra in Fig. 1 the ratios are 0.53 at 0 T, 0.53 at 3 T, 0.57 at 6 T, and 0.58 at 9 T (an increase of 9%). This trend can be understood in terms of the spin-flop transition of antiferromagnets in applied fields, in which the moments rotate away from the applied field

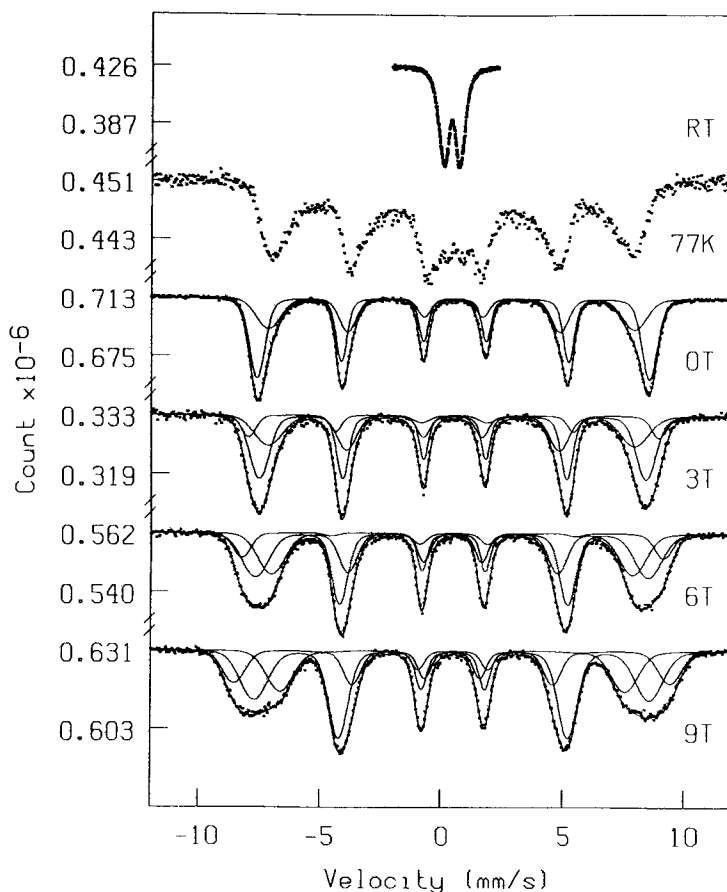


Fig. 6. Mössbauer spectra of a ferrihydrite sample exhibiting a 6-line X-ray pattern.

TABLE 2. Parameters determined by least-squares fitting the 4.2 K Mössbauer spectra of two ferrihydrite samples identified by the number of peaks in the X-ray diffractograms.

Sample	B_{app} (T)	B_{hf} (T)	δ (mms ⁻¹)	ϵ (mms ⁻¹)	A_{25}/A_{16}	A (%)	$\Delta\nu_G$ (mms ⁻¹)	χ^2
2-line	0	50.6	0.48	0.00	0.61	61	0.34	1.3
		47.2	0.43	-0.02	0.83	39	0.51	
	3	53.2	0.45	-0.01	0.21	16	0.30	1.2
		49.1	0.47	0.00	0.93	67	0.41	
		45.5	0.46	-0.03	0.21	17	0.55	
	6	54.7	0.45	-0.01	0.13	22	0.37	1.5
		50.2	0.47	-0.01	1.33	35	0.36	
		45.8	0.48	0.01	0.50	43	0.42	
	9	56.5	0.44	-0.01	0.07	21	0.51	1.2
		50.4	0.46	-0.02	1.32	44	0.67	
		44.0	0.48	-0.01	0.41	35	0.46	
	6-line	0	50.5	0.50	-0.03	0.61	61	0.31
47.1			0.42	-0.04	0.80	39	0.53	
3		52.8	0.51	-0.01	0.62	13	0.29	1.1
		49.7	0.49	-0.04	0.67	51	0.41	
		47.1	0.43	-0.02	0.83	36	0.62	
6		54.2	0.49	-0.02	0.11	12	0.36	1.1
		50.5	0.48	-0.04	1.03	49	0.59	
		46.4	0.46	-0.01	0.69	39	0.59	
9		56.0	0.48	-0.03	0.07	16	0.49	1.1
		50.8	0.47	-0.03	1.31	53	0.61	
		44.3	0.47	0.00	0.56	31	0.59	

direction (e.g. Pankhurst *et al.*, 1986). Consequently, from its Mössbauer spectra, 6-line ferrihydrite behaves like an antiferromagnet, and 2-line ferrihydrite shows evidence of a mild rotation of the moments towards the applied field direction.

With a 9 T field applied, structure has developed in the outer lines for 2-line ferrihydrite but not for 6-line ferrihydrite. This difference may indicate that the anisotropy is stronger in the 2-line sample, perhaps a result of the greater crystallographic disorder, and is the subject of continuing research.

CONCLUSIONS

Spectra have been presented which should aid in the identification of iron oxyhydroxides on the basis of their 4.2 K zero-field and applied-field Mössbauer spectra. It is evident that the similarity of the patterns of the antiferromagnetic (but not ferrimagnetic) oxyhydroxides precludes analysis of various mixtures of these compounds based solely on their 4.2 K spectra. However, the patterns are sufficiently different to those of iron oxides to enable quantitative analysis. An advantage of using low-temperature, applied-field data for identification purposes, rather than Mössbauer spectra taken at higher temperatures, is that

it minimizes the effects of small particle sizes and poor crystallinity, and hence enables a more reliable comparison with the reference data presented. The method of fitting described permits a physically-based, but not model specific, quantitative analysis.

It has been shown that Mössbauer spectra of ferrihydrite subject to applied fields do not provide a unique identification of speromagnetism. Mössbauer spectra are sensitive to the alignment of moments, being comprised of subspectra superimposed with a weighting in proportion to the abundance of a particular alignment, but not to the angle between adjacent moments.

Differences in the applied-field spectra of iron oxyhydroxides depend primarily upon the exchange and anisotropy interactions. These are modified by the presence of impurities such as Al, and hence applied-field spectra provide a means of measuring impurity concentrations as an alternative to the variations of hyperfine fields employed previously (Murad, 1988a).

ACKNOWLEDGMENTS

We thank Q.A. Pankhurst for criticisms of this manuscript, and E. Murad for encouraging its writing. RJP is grateful to C.E. Johnson for support during the writing of this paper at the University of Liverpool. We acknowledge the Australian Research Council for financial support. The fitting program was written by B. Maguire.

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