

# Mössbauer Resonance Study of Brown Ferric Oxyhydroxide Gel

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Brown ferric oxyhydroxide gel is found to be superparamagnetic down to 77 K. Samples heated to 200°, 250°, 270° and 290° indicate the dissolution of gel resulting in the formation of microcrystalline  $\alpha$ -FeOOH. Disintegration of  $\alpha$ -FeOOH at 325°C results in the formation of ultrafine dispersions of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> giving ordered spectrum at 77 K and superparamagnetic doublet pattern at 300 K. On further heating to 375° growth of particles results in sharp magnetically split spectrum both at 300 and 77 K.

MÖSSBAUER resonance studies of synthetic ferric oxyhydroxide gels have been reported by several workers<sup>1-7</sup>. Giessen<sup>1,2</sup> regarded these as either FeOOH.*n*H<sub>2</sub>O or Fe<sub>2</sub>O<sub>3</sub>.*n*H<sub>2</sub>O, consisting of incompletely compensated antiferromagnets in superparamagnetic state. A quasi-amorphous structure based on a hexagonal close packed oxygen lattice with ferric ions randomly distributed in the octahedral interstices was suggested by Okamoto *et al.*<sup>3</sup>. Study of hydrolysis products of FeCl<sub>3</sub> by Mössbauer and other techniques showed that short boiling time produced an amorphous gel while some poorly crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and FeOOH (ref. 4) were produced on longer boiling time and higher concentrations. Effect of poor crystallinity on HFS of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> formed by thermal decomposition of ferric oxide gel was investigated by Laseva *et al.*<sup>5</sup>. Srivastava and Singh<sup>7</sup> studied the thermal decomposition of ferric oxide hydrate gel heated in air for two hours in the range of 100° to 650°C (7).

Mössbauer spectra in the temperature range 300-77 K of brown ferric oxyhydroxide gel and the typical changes in the Mössbauer spectral features observed in order to investigate the character and sequence of structural and phase transformation that occur during the heat treatment of gel in the range of 60° to 875° are presented in this paper.

## Materials and Methods

Chemicals used for the preparation of absorbers were of AR quality. Brown ferric oxyhydroxide gel was obtained by adding ammonium hydroxide to a freshly prepared and continuously stirred solution of ferric chloride till pH 7.5 was indicated. The precipitate was repeatedly washed with water to free it from chloride ions. It was dried in air at 60° for 24 hr. Choice of the temperatures for heat treatment was guided by the differential thermal analysis data of the gel.

The Mössbauer spectra were recorded with a constant acceleration velocity transducer coupled to <sup>57</sup>Co in Pd-matrix in the standard transmission

geometry. The velocity calibration was done with the enriched iron foil. The temperature was measured by a copper constantan thermocouple and the temperature variation was achieved with the help Elscint temperature controller MTC-3 (accuracy better than 0.03°).

## Results and Discussion

Mössbauer spectrum of the gel heated to 60°, consists of a sharp well-defined doublet with  $\delta$ /Fe = 0.319 mm/s and  $\Delta E_Q$  = 0.539 mm/s at 300 K. These parameters characterize iron atoms in higher spin trivalent state incorporated in distorted octahedral sites in gel structure. Considering amorphous or microcrystalline state of gel particles the Mössbauer parameters (Table 1) are in good agreement with those reported previously<sup>1-7</sup>.

TABLE 1 — MÖSSBAUER PARAMETERS OF BROWN FERRIC OXYHYDROXIDE GEL HEATED IN AIR TO DIFFERENT TEMPERATURES FOR 24 HR.

Heat treatment (°C)	Temp. (K)	$\delta$ (mm/sec)*	$\Delta E_Q$ (mm/sec)	$H_n$ (kOe)
60	300	0.319	0.539	0
	77	0.433	0.680	0
100	300	0.319	0.736	0
	77	0.433	0.680	0
200	300	0.294	0.539	0
	77	Tendency of magnetic splitting		
250	300	0.363	0.631	0
	77	Tendency of magnetic splitting		
270	300	0.363	0.631	0
	77	Better tendency of magnetic splitting		
290	300	0.363	0.631	0
325	300	Tendency of magnetic splitting		
	77	0.510	0.121	531
375	300	0.360	0.090	507
	77	Well resolved magnetic splitting		
600	300	0.392	0.098	511
	77	0.498	0.182	537
875	300	0.367	0.098	513
	77	0.486	0.243	540

\*With respect to iron. Error in  $\delta$  and  $\Delta E_Q \pm 0.025$  mm/sec and  $\pm 0.036$  mm/sec respectively. Error over  $H_n$  value is  $\pm 03$  kOe.

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At liquid nitrogen temperature dehydration occurs without much disruption in the coherence of the gel. These variations and second order Doppler shift result in a  $\delta$  of 0.433 mm/s and  $\Delta E_0$  of 0.680 at 77 K for sample heated to 60°. Apparent broadening of resonance lines reflects the degree of randomness in relation to the incorporation of  $\text{Fe}^{3+}$  ions in gel environment. Relative magnitude of resonance effect in the spectra of gel samples heated to different temperatures up to 875° may show changes due to variation in bonding strength within the particles in different phases that appear on heat treatment of the gel. Line broadening shows an increase with heat treatment temperature till  $\alpha\text{-Fe}_2\text{O}_3$  multidomain crystallites are formed. Line intensity also show complex features associated with appearance and disappearance of different phases.

Textural variations in the gel may cause some distortions in symmetry around the iron ions as reflected from the increased quadrupole splitting in 300 K spectrum of gel heated to 100°. However parameters for spectrum at 77 K remain unaltered because of low temperature dehydration of the gel. On heating to 200°, transformations involving the rupture and rearrangement of hydrogen bonds in the gel and removal of capillary and adsorbed water molecules with partial dissolution of gel may presumably take place. Room temperature spectrum of the samples heated to 200° shows a doublet which indicates a more covalent bonding of iron in less distorted octahedral sites. Spectrum at 77 K for the same sample gives a single broadened line presumably due to unresolved magnetic splitting.

Spectra at 77 K of the samples heated to 250°, 278° and 29° are ill-defined, showing a better tendency of magnetic splitting as compared to the unresolved single broad line observed at 77 K the spectrum of the sample heated at 200°. However, unambiguous location of peaks for these spectra which spread over a magnetic field of about 360 to 450 kOe could not be assigned. Room temperature spectra of samples heated to 250°, 270° and 290° are typical quadrupole split doublets with isomer shift and quadrupole shift of the same magnitude for each of three spectra. These features indicate that a change from one structure to another seems less likely and a definite magnetic phase must be present in this thermal treatment temperature range. A comparison of the observed hyperfine interaction parameters with those previously reported<sup>8-11</sup> warrants the following conclusions: (a)  $\alpha\text{-FeOOH}$  particles are formed from the dissolution of the gel at temperature 200° and above as an intermediate phase. (b) Short range magnetic ordering as apparent from the ill-defined spin ordered spectra is a consequence of the poorly crystalline and small particle size effect in  $\alpha\text{-FeOOH}$  phase.

Similar observation of fluctuating hyperfine fields due to poor crystallinity and small particle size of

$\beta\text{-FeOOH}$  by Vorznyuk and Dubinin<sup>12</sup> further substantiates these conclusions.

During thermal treatment between 200° and 290° and above  $\alpha\text{-FeOOH}$  may be partially converted to at least poorly crystalline  $\alpha\text{-Fe}_2\text{O}_3$ . However, the coexistence of  $\alpha\text{-Fe}_2\text{O}_3$  with  $\alpha\text{-FeOOH}$  phase could not be identified distinctly in samples heated to 325°. Samples heated to 325° give an unresolved single broad line indicating motional narrowing of magnetic spectra at room temperature. At 77 K a reasonably well-resolved six-line pattern is discerned. These features are characteristics of superparamagnetic  $\alpha\text{-Fe}_2\text{O}_3$ . Mössbauer parameters at 77 K of samples heated to 325° nearly correspond to those reported for  $\alpha\text{-Fe}_2\text{O}_3$ . Samples heated at 375° give magnetic hyperfine splitting both at 300 and 77 K. Hyperfine field values in these samples are somewhat decreased as compared to that reported for  $\alpha\text{-Fe}_2\text{O}_3$ . Further heat treatment results in growth of small particles to large crystallites of  $\alpha\text{-Fe}_2\text{O}_3$ . Microstructural variations<sup>13</sup> involved in this growth cause slight variations in bonding and site symmetry of iron as indicated by the shifts and splittings of Mössbauer spectra. On heating to 600° and 875°C the hyperfine field shows an increase of about 2 to 3 kOe due to increase in the particle size of  $\alpha\text{-Fe}_2\text{O}_3$  crystallites.

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