

The Magnetic Properties of the Synthetic Iron Oxyhydrates

Naoichi YAMAMOTO*

Received September 14, 1968

Pure and large crystals of three modifications of the α -, β - and γ -FeOOH were synthesized and their magnetic properties were studied. These iron oxyhydrates were antiferromagnetic with the Néel temperature being 400°K, 237°K and 50°K for α -, β - and γ -FeOOH, respectively. The direction of the electron spin axis was found from the Mössbauer effect to be parallel to the c-axis of the crystals for all these iron oxyhydrates.

I. INTRODUCTION

Three modifications of the iron oxyhydrate, α -, β - and γ -FeOOH, are known. Mineral names of α - and γ -FeOOH are goethite and lepidrocrite. The crystal structures of α - and γ -FeOOH are orthorhombic, belonging to the space groups of Pbnm and Bbmn, respectively^{1,2)}. The crystal structure of β -FeOOH is tetragonal or pseudotetragonal³⁾. In these compounds, however, positions of the hydrogen atoms have not been determined.

In recent years many Mössbauer and other magnetic studies have been done on these iron oxyhydrates⁴⁻¹²⁾. However, the published data on β - and γ -FeOOH are still few. As to α -FeOOH, there are great discrepancies between the results published on temperature dependence of the magnetic susceptibility, Mössbauer spectrum and Néel temperature. These discrepancies may be attributed to the difference in chemical purity and particle size between the samples used in the measurement.

The present work reports the magnetic susceptibility measurement of the synthetic iron oxyhydrates particles which are as pure and large as possible and the spin structures determined by the Mössbauer effect analysis.

II. EXPERIMENTAL

1. Sample Preparation

A. α -FeOOH The samples of α -FeOOH were prepared as follows.

(a) Stamped powder of the electrolytic iron, 31.5 g in weight was poured into 1 l of 0.125 M-H₂SO₄ solution. The solution containing the iron powder was oxidized by bubbling the air therein at the rate of 1000 l per hr at 70°C. After all of iron powder was oxidized, the resultant yellow precipitate was filtered, washed with distilled water and dried at 90°C.

(b) 500g of FeSO₄·7H₂O was dissolved in 2 l of distilled water and after 1 l of 6N-NaOH solution was added diluted to 3.5 l with distilled water. The alkaline suspension containing Fe(OH)₂ precipitate was oxidized at 40°C by bubbling the air therethrough. After 60 hr Fe(OH)₂ was oxidized perfectly and converted to α -FeOOH precipitate. The precipitate was filtered, washed with water and dried at 90°C.

* 山本 直一: Laboratory of Solid State Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

B. β -FeOOH 500g of $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$ and 100g of NH_4Cl were dissolved in 3 l of distilled water. The solution was oxidized by bubbling the air at the rate of 200 l per hr at 70°C. After 5 hr of this procedure, yellow colored precipitates, the mixture of α -FeOOH and β -FeOOH were deposited in the vessel. In this stage pH value of the solution was about 1.2. The yellow precipitate was separated from the solution by filtration. The filtrate was again oxidized at the same condition as above for 60 hr. The precipitate thus obtained from the second solution was pure β -FeOOH. After filtration the precipitate was subjected to electro dialysis to get off Cl^- ions contaminating in the crystal lattice.

C. γ -FeOOH (a) Stamped powder of electrolytic iron, 50 g in weight, was poured into 500 ml of 0.15 M acetic acid solution. The suspension was oxidized by bubbling the air at the rate of 1000 l per hr at 50°C. After 7 hr iron powder was perfectly consumed and orange yellow precipitate of γ -FeOOH was deposited. (b) 500g of $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$ was dissolved in 2 l of the distilled water and to this solution was added the alkaline solution in the amount of 0.4 equivalents of the acid radical. After total volume of the solution was diluted to 3.5 l with water, the resultant white suspension was oxidized by bubbling the air for 50 hr at 20°C. The precipitate of γ -FeOOH thus obtained was filtered, washed with water and dried at 90°C.

The precipitates of α -, β - and γ -FeOOH obtained in this way were affirmed by x-ray diffraction patterns and infrared spectra to be pure specimens. Impurity contents were checked with usual chemical methods. As an example the analytical result of α -FeOOH prepared by the first method is given in Table 1. Chemical analysis proved that these samples were extremely pure and reliable in the magnetic measurement.

Table 1. Impurity Contents of α -FeOOH
(prepared by the first method)

Impurities	Atomic %
Si (as SiO_2)	>0.01
S (as SO_3)	>0.5
Mn (as Mn_2O_3)	>0.01
Co (as Co_3O_4)	>0.01
Cu (as Cu_2O)	>0.01

The particle shapes and sizes of these iron oxyhydrates were observed on the electronmicrographs. Fig. 1, 2 and 3 are electronmicrographs of α -, β - and γ -FeOOH particles, respectively.

2. Magnetic Measurements

Magnetic susceptibility, χ was measured with an ordinary magnetic torsion balance above the liquid nitrogen temperature and by A-C Hartshorn bridge method from liquid helium temperature to liquid nitrogen temperature. Mössbauer effect was measured with the TMC multichannel type apparatus.

III. RESULT AND DISCUSSIONS

1. Magnetic Susceptibility

In Fig. 4 the temperature dependence of χ of three iron oxyhydrates are given.



Fig. 1. Electronmicrographs of α -FeOOH, acicular shape of the particles is shown.



Fig. 2. Electronmicrograph of β -FeOOH.

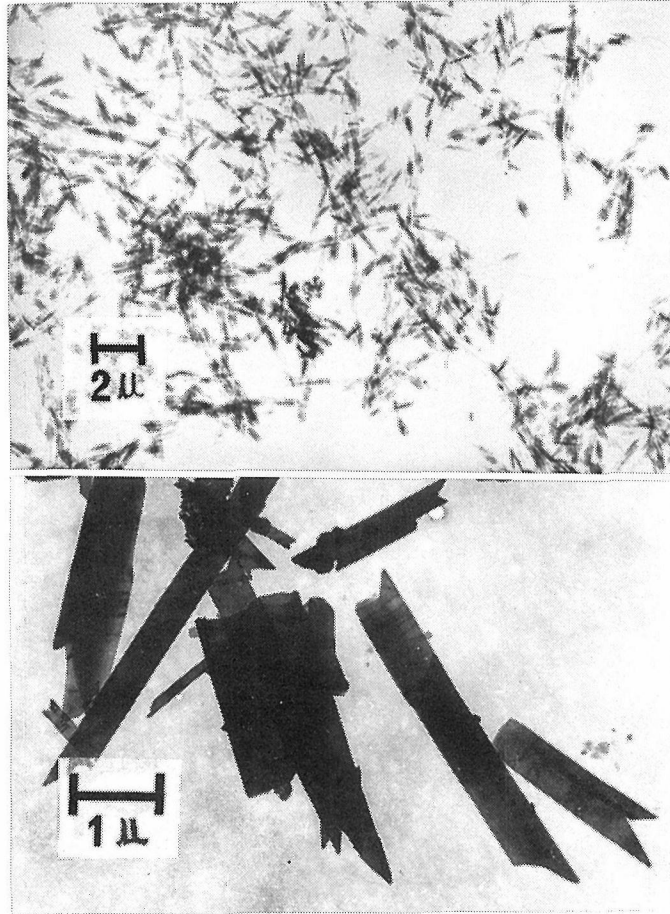


Fig. 3. Electronmicrographs of γ -FeOOH.

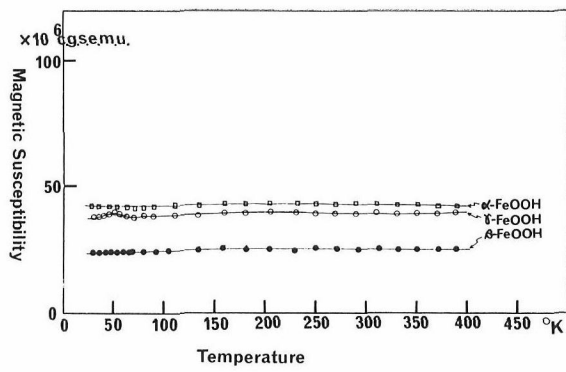


Fig. 4. Temperature dependence of the magnetic susceptibilities of three iron oxyhydrates.

χ of α -FeOOH was measured from 1.2°K to 440°K, where α -FeOOH decomposes to α -Fe₂O₃. χ shows the value of 46×10^{-6} c.g.s.e.m.u. at room temperature and exhibits no temperature dependence. As previously reported, the Néel temperature of this sample was determined to be 400°K from the temperature dependence of the internal field of the Mössbauer spectrum.

χ of β -FeOOH is also temperature independent and the value is 25×10^{-6} c.g.s.e.m.u.. The Néel temperature of this compound was found to be 273°K both from the temperature dependence of the internal field of the Mössbauer spectrum and by the thermal differential analysis. This value is in good agreement with the value reported by Dézsi *et al.*¹⁰⁾

χ of γ -FeOOH is 40×10^{-6} c.g.s.e.m.u. at room temperature and small broad peak was observed at near 50°K. As shown on the Mössbauer spectrum in Fig. 5, the magnetic hyperfine splitting is observed at liquid helium temperature. It should be noted that only quadrupole splitting was shown on the previously reported spectrum at liquid nitrogen temperature. These result confirms that γ -FeOOH is antiferromagnetic below 50°K.

χ of a single crystal of mineral goethite was reported by Oosterhout, properties of which may be representative of those of a Heisenberg antiferromagnet with $S=5/2$. On the other hand temperature dependence of χ observed in the present experiment was different from that of normal antiferromagnet of a powder specimen, that is, χ showed no peak at the Néel temperature and was temperature independent below the Néel temperature. These curious magnetic behaviors, which are observed also in the case of β -FeOOH, seem to be caused by some kind of the size effect although precise discussion is impossible. Theoretical explanation of the temperature independent χ of γ -FeOOH above the Néel temperature is also obscure.

2. Spin Structures

The spin structures of these iron oxyhydrates were determined by the Mössbauer effect with utilizing the strong anisotropic particle shapes of the samples. The angular dependences of the Mössbauer transition probabilities are expressed as $9/4 (1 + \cos^2 \theta)$ for peak 1 and 6, $3 \sin^2 \theta$ for 2 and 5, $3/4 (1 - \cos^2 \theta)$ for peak 3 and 4, where θ represents the angle between the incident gamma ray and the magnetic hyperfine field direction and the peak number is given in the order from the lower to the higher energy peak. In the case where magnetic hyperfine field direction is random against incident gamma ray, relative peak intensities of six peaks will become 3:2:1:1:2:3. When the direction of the magnetic hyperfine field is parallel or perpendicular to the incident gamma ray, the relative intensities will be 3:0:1:1:0:3 or 3:4:1:1:4:3. Therefore, if the correlation between the crystal axis and the incident gamma ray is given, the relative peak intensities of the Mössbauer spectrum make it possible to determine the spin axis of the sample.

As shown in Fig. 1, 2 and 3 the particle shapes of the iron oxyhydrates are acicular. Because of these crystal shapes the samples are easily inclined to take such an oriented state as the longest axes are in a plane. Previous electronmicroscopic studies clarified the longest axis of a particle is in coincidence with the crystal c-axis in each iron oxyhydrate.^{13,14,15)}

In practice oriented samples were made as follows. The oxyhydrates were suspended in water and the suspensions were filtered slowly through the Membran filteres. After drying the samples, these were pressed with uniaxial pressure of 10^3

kg/cm². Random oriented samples were made by mixing powder well with silicone grease. The relative peak intensities of the x-ray powder pattern showed that the c-axis of a sample was in good oriented state, perpendicular to the pressed direction. The preferred oriented sample was set so as for the pressed plane of the sample to be perpendicular to the incident gamma ray.

In Fig. 5 is given the spectra of α -FeOOH at room temperature. The spectrum of the random oriented sample has the ratio of the peak intensities of 3:2:1:1:2:3,

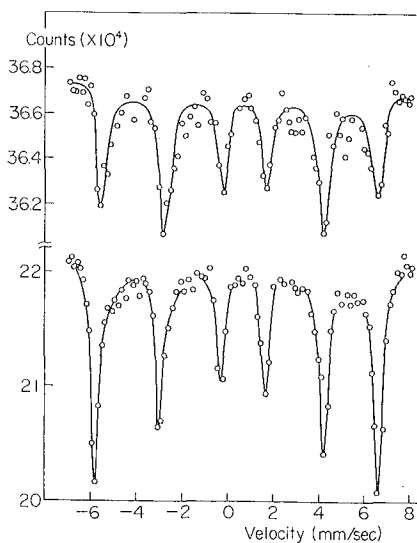


Fig. 5. Mössbauer spectra of α -FeOOH at room temperature, preferred oriented sample (above) and random oriented sample (below).

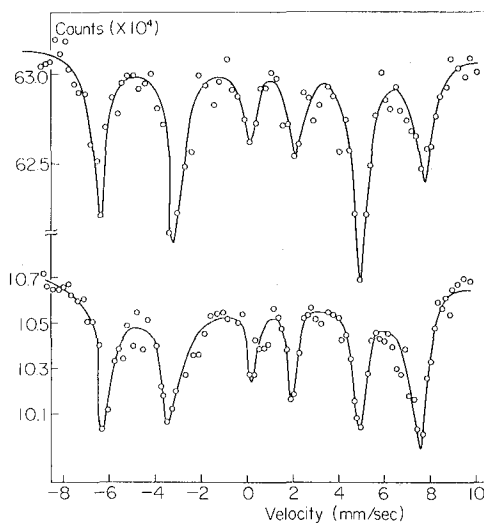


Fig. 6. Mössbauer spectra of β -FeOOH at liquid nitrogen temperature, preferred oriented sample (above) and random oriented sample (below).

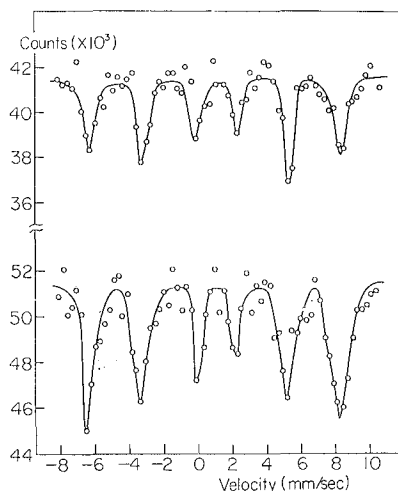


Fig. 7. Mössbauer spectra of γ -FeOOH at liquid helium temperature, preferred oriented sample (above) and random oriented sample (below).

the expected value of the completely random sample, whereas the ratio of the peak intensities observed on the preferred oriented sample is close to the value of 3:4:1:1:4:3. In such a sample that all the c-axes of particles are in same plane but other a- and b-axes are completely random, the observed ratio of the peak intensities is obtained only when the spin axis is perpendicular to the incident gamma ray. It is obvious from the simple calculation another spin arrangement will give same spectrum which is observed in the random oriented case. Therefore the antiferromagnetic spin axis of α -FeOOH is parallel to the c-axis. The result is in good agreement with that of Oosterhout who determined the spin axis to be parallel to the c-axis from the temperature dependence of the magnetic susceptibilities perpendicular and parallel to the c-axis, using the mineral single crystal specimen.

The relation of Mössbauer spectra with the particle orientation can be discussed quite analogously with the previous case of α -FeOOH. From the observed Mössbauer spectrum it is concluded that the spin axes of β - and γ -FeOOH are parallel to the c-axes in both compounds. Mössbauer spectra of β - and γ -FeOOH are shown in Fig. 6 and 7, at liquid nitrogen and liquid helium temperature, respectively.

IV. CONCLUSION

It is apparent from the above experimental results that three kinds of iron oxyhydrates α -, β - and γ -FeOOH are antiferromagnets, and spin axis of each compound is parallel to the crystal c-axis. Other results are summarized in Table 2. The magnetic susceptibilities of these samples show somewhat peculiar behavior, but satisfactory explanation of which is not given at the present time.

Table 2. Observed values of the magnetic hyperfine splitting, quadrupole splitting, isomer shift and Néel temperature of α -, β -, γ -FeOOH.

samples	magnetic hyperfine splitting at liq He temp.	quadrupole splitting (paramagnetic state)	isomer shift	Néel temperature	spin axis
α -FeOOH	530 KOe	0.60 mm/sec	0.5 mm/sec	400°K	[001]
β -FeOOH	490 KOe	0.60 mm/sec	0.56 mm/sec	273°K	[001]
γ -FeOOH	470 KOe	0.51 mm/sec	0.5 mm/sec	50°K	[001]

ACKNOWLEDGEMENT

The author would like to thank Prof. T. Takada for prominent guidance during the course of this work. He also wishes to thank Drs. Y. Bando, M. Kiyama and T. Shinjo for fruitful suggestions and discussions.

REFERENCES

- (1) Wyckoff, *Crystal Structure*, John Wiley and Sons, **1**, 291, 293.
- (2) J. D. Bernal, D. R. Dasgupta and A. L. Mackay; *Clay Minerals Bull.*, **4**, 15 (1959).
- (3) M. J. Rossiter and E. A. M. Hadgson, *J. Inorg. Nuclea. Chem.* **27**, 63 (1965).
- (4) F. Van der Woode and A. J. Dekker, *Phys. Stat. Sol.*, **13**, 181 (1966).
- (5) A. Z. Hryniewicz and D. S. Kulganecuk, *Acta. Phys. Polo.*, **24**, 689 (1963).
- (6) A. Z. Hryniewicz, D. S. Kulganecuk and K. Termala, *Phys. Letters (Netherlands)* **17**, 93 (1965).
- (7) G. E. Van Oosterhout, *Proc. Int. Con. on Magnetism, Nottingham England September* (1964).
- (8) A. Szytuza, A. Burewicz, K. Dyperk, A. Hryniewicz, D. Kulganecuk, Z. Obuszko, H. Rzany and A. Wanic, *Phys. Stat. Sol.*, **17**, K195 (1966).

- (9) T. Takada, M. Kiyama, Y. Bando, T. Nakamura, M. Shiga, T. Shinjo, N. Yamamoto and Y. Endo, *J. Phys. Soc. Japan* **19**, 1744 (1964).
- (10) I. Dézsi, L. Keszthelyi, D. Kulganecuk, B. Mcinr and N. A. Eissa, *Phys. Stat. Sol.*, **22**, 617 (1967).
- (11) M. J. Rossiter and E. A. M. Hadgson, *J. Inorg. Nuclea. Chem.* **27**, 63 (1965).
- (12) C. L. Herzenberg and D. Tomas, *J. Geophys. Res.* **71**, 2661 (1966).
- (13) J. H. L. Watson and P. R. Cardell Jr., *J. Phys. Chem.*, **66**, 1757 (1962).
- (14) T. Takada, M. Kiyama and S. Shimizu, *Bull. Inst. Chem. Res, Kyoto Univ.*, **42**, 505 (1964).
- (15) G. E. Van Oosterhout, *Acta. Cryst.*, **13**, 932 (1960).