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Electrical Properties of Ferric Oxyhydroxides

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The electrical conductivity of α-FeOOH, β-FeOOH, and γ-FeOOH was measured in dry air at room temperature in the frequency range of dc to 10 MHz under various pressures of 9—150 kg/cm^2. The logarithm of conductivity, log σ, shows a linear relationship with the ratio of true density to apparent density, d_0/d', of the samples compressed at different pressures. σ_1 at 7 MHz, determined by extrapolating the log σ *vs.* d_0/d' plots to unity of d_0/d', is proportional to the number of the nearest iron atoms with identical spin. The conductivity increases with increasing frequency f. The ac conductivity σ_{ac} which equals σ minus σ_{dc}, where σ_{dc} is the dc conductivity, is proportional to f^s $(0.6<s<0.8)$ in the lower frequencies than 1 MHz. This behavior is presumed to be due to the hopping of a *d*-electron in the t_{2g}-orbital of Fe^{2+} to the t_{2g}-orbital of adjacent Fe^{3+}, through a slight overlapping of t_{2g}-orbitals of Fe^{2+} and Fe^{3+}.

The oxide film formed on transition metal surfaces in atmospheric environments consists of minute crystals of particular oxides and oxyhydroxides together with some amorphous polynuclear complexes. The mechanism of oxide formation under ambient atmospheric conditions has not been sufficiently established. The corrosion process of iron could be better understood if one investigates the correlation between the structure and the physico-chemical properties of the constituent substances of the oxide film. Information on the electrical conductivity of these oxides and oxyhydroxides is desirable, since it is apparent that the transport of electrons and ions plays an important role in the formation of oxide film. Although the electrical conductivity of pure iron oxides such as α-Fe_2O_3, Fe_3O_4, and FeO has been studied to a certain extent, the study on ferric oxyhydroxides (iron hydroxide oxides) is insufficient, possibly because of the difficulty to eliminate the contact resistance between oxyhydroxide crystals by means of sintering at a high temperature, since ferric oxyhydroxides unavoidably decompose around 300 °C.[1] Okamoto, Furuich, and Sato[2] measured the electrical conductivity of hydrous ferric oxides, so-called ferric hydroxides, by compressing at 1 kg/cm^2 with the dc-method, but not that of pure ferric oxyhydroxides, which is necessary.

In the preceding paper[3] the frequency dependence of the conductivity of unignited fine crystals of α-Fe_2O_3 was reported in the frequency range of dc to 30 MHz under various pressures of 9—150 kg/cm^2, and the results were discussed from the viewpoint that the electrical conductivity variations with respect to pressure and frequency reflect the intrinsic structure and imperfection of α-Fe_2O_3. The experimental procedures proposed appear to enable elimination of the contact resistance between fine crystals in general.

The same method has been applied to three forms of ferric oxyhydroxide known, α-FeOOH, β-FeOOH, and γ-FeOOH, which occur widely in the atmospheric corrosion products of iron. The relationship between structure and electrical conductivity of these three types of ferric oxyhydroxide is discussed.

Experimental

Samples. α-FeOOH was prepared by hydrolyzing 0.6 M ferric sulfate solution at 50 °C for 30 hr, the pH being adjusted to 13.6 with 0.1 M KOH solution. α-FeOOH filtered was washed with water until no sulfate ion was detected and dried at 100 °C for 3 hr.[4] β-FeOOH was prepared by the following procedure. One liter of 0.1 M $FeCl_3$ containing 60 g urea was heated to 98 °C within 1 hr and kept at this temperature for additional 5 hr. The filtered precipitates were washed with water until no Cl^- was detected and dried at 100 °C for 3 hr.[5] γ-FeOOH was obtained by warming at 60 °C for 50 min a mixed solution of 500 ml 0.2 M $FeCl_2$, 100 ml 2 M hexamethylenetetramine, 13.5 ml concentrated HCl, and 100 ml 1 M sodium nitrite. Preparation of γ-FeOOH was performed in a stream of nitrogen. The precipitates obtained were washed with water until no Cl^- was detected and dried at 60 °C for about 10 hr.[6]

Examination of Samples. The X-ray diffraction patterns were obtained by the powder method with an automatic diffractometer (Geigerflex 2001, Rigaku Denki Co.) by use of Mn-filtered FeK_α (30 kV, 10 mA). The BET surface-area was determined with a Shibata Surafce-area meter using N_2 adsorption at liquid nitrogen temperature.

The ferrous ion content was determined by titration with 0.005 N cerium sulfate solution in the presence of ferroin as an indicator, after the samples had been dissolved in hydrochloric acid by heating in a stream of carbon dioxide. The total iron content in β-FeOOH was determined by titration with 0.05 N $K_2Cr_2O_7$ solution. The chlorine content in β-FeOOH was determined by the Volhard method. The amount of cation impurities was determined by emission spectroscopy.

Electrical Measurements. Electrical conductivity in the frequency range of dc to 10 MHz under various pressures 9—150 kg/cm^2 at room temperature was measured by the method described in the preceding paper[3] in air dried with silica gel. Samples were dried at 100 °C for 1 hr prior to conductivity determination. The conductivity change with the adsorption of water on α-FeOOH and γ-FeOOH was negligible during the measurements but an increase of approximately 10% in conductivity was observed for β-FeOOH. The conduction was found to be approximately ohmic with applied voltage in the range ~200—~4000 V/cm.

The sign of Seebeck voltage of compressed samples dried at 100 °C for 1 hr was measured in air with a μV-meter (Oyo Denki Co.) in order to determine the sign of the predominant charge carrier.

Results

Properties of Samples. Each sample prepared gave X-ray diffraction patterns of crystalline α-FeOOH,

β-FeOOH, and γ-FeOOH, structures of which have been reported elsewhere.[7-9] In Table 1 are given the crystallite size calculated by the Scherrer formula for the half-value width of the principal lines, the specific surface area (S_{N_2}) and the ratio of iron atoms exposed to crystal surface to the total iron atoms, which was estimated by assuming that only the developed face area of crystals contributes to the specific surface area. The instrumental broadening in diffraction lines was subtracted by use of patterns of magnetite crystals. The ratio of chlorine to iron for β-FeOOH was found to be 9.5 atomic%. The content of cation impurities is given in Table 2. The amount of ferrous iron, providing the carrier, was found to be 0.06 wt% for all samples. The Fe^{2+}/Fe ratio was hence calculated as approximately 0.1 atomic%.

TABLE 1. PROPERTIES OF SAMPLES

	Crystallite size (Å)	S_{N_2} (m^2/g)	Surface Fe (%)
α-FeOOH	210	65	13
β-FeOOH	470	34	6
γ-FeOOH	63	124	32

TABLE 2. CATION IMPURITIES OF SAMPLES (wt%)

Cation	α-FeOOH	β-FeOOH	γ-FeOOH
Ferrous iron	0.06	0.06	0.06
Ca	0.002	0.001	0.001
Co	<0.005	<0.005	<0.005
Cr	0.01	0.001	<0.001
Cu	0.001	0.006	0.002
Mg	0.002	0.001	0.001
Mn	0.2	<0.005	<0.005
Mo	<0.01	<0.01	<0.01
Ni	0.05	0.004	0.001
Al	0.01	0.002	0.001
Si	0.3	0.1	0.001
Sn	<0.002	<0.002	<0.002
Ti	0.005	0.005	0.001
Zr	<0.005	<0.005	<0.005
Nb	<0.005	<0.005	<0.005
V	0.005	0.005	0.001

Electrical Conductivity and Compression of Powder Sample. The logarithm of electrical conductivity log σ and the ratio of the true density to the apparent density d_0/d' of the compressed specimen show linear relationships as in the case of α-Fe_2O_3.[3] The relationships for α-FeOOH, β-FeOOH, and γ-FeOOH at different measuring frequencies are shown in Figs. 1 and 2.

The values of σ_i at dc and 7 MHz, determined by extrapolating the linear relationship between log σ and d_0/d', are shown in Table 3. The density values found in literature were used for the calculation: α-FeOOH, 4.28;[10] β-FeOOH, 3.0;[8] and γ-FeOOH, 4.07.[9]

Frequency Dependence. The frequency dependence of conductivity and dielectric constant of α-FeOOH as the representative of three forms of oxyhydroxide is shown in Fig. 3. β-FeOOH and γ-FeOOH gave a frequency dependence similar to that of α-FeOOH. The frequency dependence of σ_i is also shown in Fig. 3. The dielectric constant decreases with the frequency below 10 kHz and becomes constant above 10 kHz. It increases slightly with pressure in the whole frequency range. The electrical conductivity increases with fre-

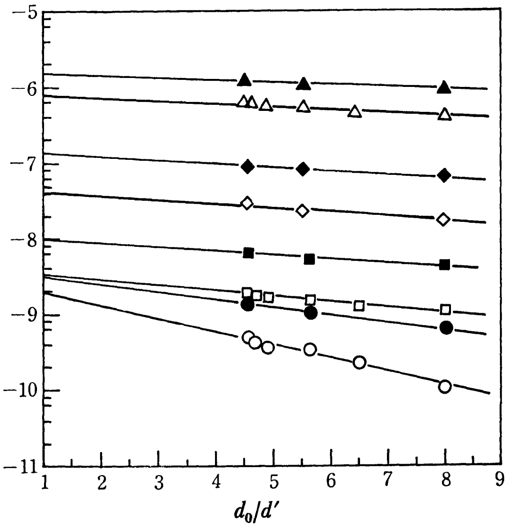


Fig. 1. Changes of conductivity with the ratio of the true density d_0 to the apparent density d' for α-FeOOH. ○: dc, ●: 400 Hz, □: 1 kHz, ■: 10 kHz, ◇: 100 kHz, ◆: 900 kHz, △: 7 MHz, ▲: 10 MHz.

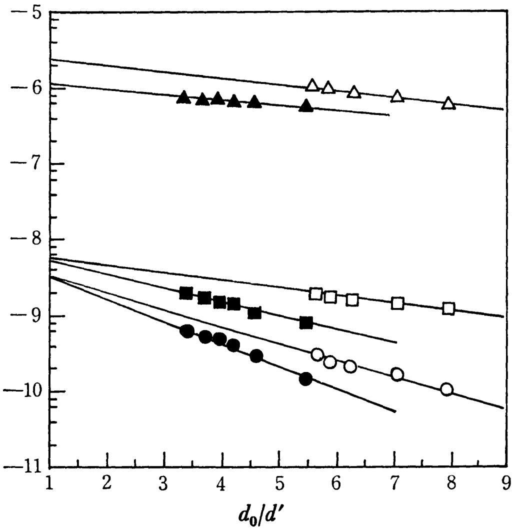


Fig. 2. Changes of conductivity with the ratio of the true density d_0 to the apparent density d'. Filled symbols denote the changes for β-FeOOH and open symbols denote the changes for γ-FeOOH. (●,○): dc, (■,□): 1 kHz, (▲,△): 7 MHz.

TABLE 3. σ_i AND z

	α-FeOOH	β-FeOOH	γ-FeOOH
σ_i at dc $\Omega^{-1}cm^{-1}$	2×10^{-9}	3×10^{-9}	3×10^{-9}
σ_i at 7 MHz $\Omega^{-1}cm^{-1}$	8×10^{-7}	1.5×10^{-6}	2.3×10^{-6}
z	2	4	6

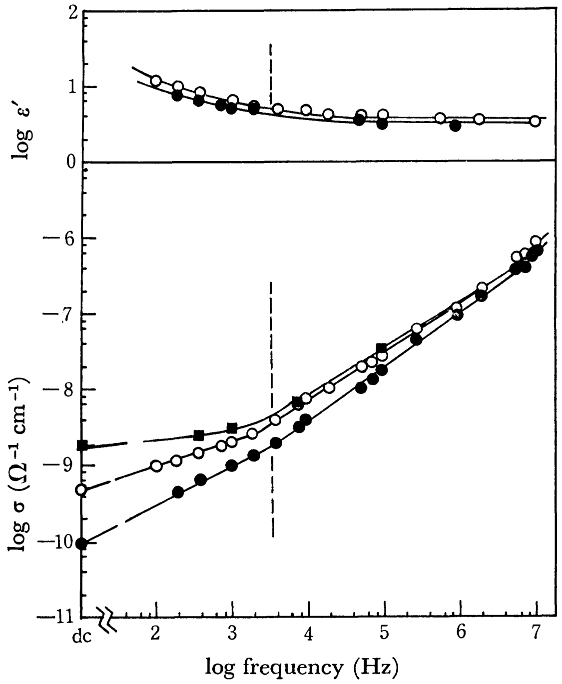


Fig. 3. Frequency dependence of conductivity σ and dielectric constant ε′ for α-FeOOH compressed at 9 kg/cm² (●) and 150 kg/cm² (○). The frequency dependence of σ_i is denoted by ■.

quency in the frequency range below 10 kHz and more steeply above 10 kHz. The dispersion of electrical conductivity in the lower frequency range becomes less recognizable with the increase of pressure and is influenced by humidity. On the other hand, the dispersion in the higher frequency range is slightly affected by compression.

In the frequency range below 1 MHz, the ac conductivity (σ_{ac}) which equals σ minus σ_{dc}, where σ_{dc} is the dc conductivity, has the relation with frequency (f) as given by,

$$\sigma_{ac} \propto f. \qquad (1)$$

The exponents s range from 0.6 to 0.8 and are almost independent of the pressure (Table 4).

The steepest increase of conductivity was observed with the frequency above 1 MHz.

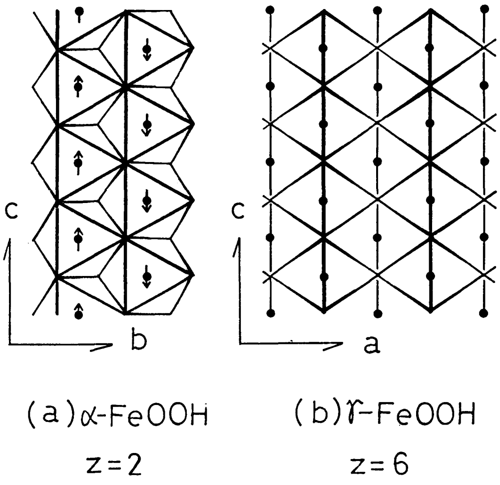
TABLE 4. EXPONENTS (s)

	At 9 kg/cm²	At 150 kg/cm²	σ_i
α-FeOOH	0.7	0.7	0.7
β-FeOOH	—	∼ 1k 0.5 2k ∼ 1M 0.8	—
γ-FeOOH	0.7	0.6	0.7

Sign of Carriers. The sign of carriers in both α-FeOOH and γ-FeOOH is presumed to be negative, judging from the sign of the cold probe due to the Seebeck voltage observed in the preliminary experiments. The adsorption of water molecules on crystals made it difficult to conclude the exact carrier sign for β-FeOOH, but it appears to be also negative.

Discussion

Frequency Dependence. The frequency dependence of electrical conductivity in the lower frequency range greatly depends on the pressure. The dispersion observed in the lower frequency range seems to be ascribed to the heterogeneity in the specimen, namely the intergranular gaps. The frequency dependence of dielectric constant agrees with that of the two-layer condenser which consists of two admittances in series.[11] Each layer consists of a resistance and a capacitance in parallel. The conductivity above 10 kHz does not become constant but exhibits a pronounced dispersion, though the two-layer condenser consisting of the frequency-independent admittance of crystals and that of gaps suggests that the conductivity of the system should be invariable with respect to the frequency in the frequency range above 10 kHz where the dielectric constant is unchangeable. The dispersion of conductivity occurs in both cases of 150 kg/cm² and σ_i. The dispersion seems to be due to the frequency-dependent conductivity of crystals. The two-layer condenser model could be extended to the inhomogeneous system consisting of the crystals with frequency-dependent conductivity and of the intergranular gaps as in the case of α-Fe_2O_3.[3] The frequency-dependent conductivity in the frequency range above 10 kHz is much higher than σ_{dc} and almost equals σ_{ac}. The ac conductivity given by Eq. (1), in which s is 0.8, was obtained by Pollack and Geballe[12] for the impurity conduction due to hopping processes in doped silicon at low temperature. The chemical analysis indicates that all ferric oxyhydroxides examined are non-stoichiometric having a general composition of $Fe^{II}_{3\delta}$ $Fe^{III}_{1-2\delta}$ OOH where δ is much smaller than 1. In view of the fact that the sign of carriers by the Seebeck voltage measurement is negative, the electrical conduction in ferric oxyhydroxides is attributed to the hopping of excessive d-electrons in Fe^{2+} to Fe^{3+} rather than to that of protons. Fe^{2+} ions are randomly distributed spatially and have an energy differing by about kT. The hopping occurs mainly between a pair of Fe^{2+} and the adjacent Fe^{3+}. Thus the electrical conductivity of ferric oxyhydroxides exhibits a frequency-dependence similar to the impurity conduction at low



(a)α-FeOOH z=2 (b)γ-FeOOH z=6

Fig. 4. Crystal structure of α-FeOOH (a) and γ-FeOOH (b). Filled circles denote iron ions and arrows the spin direction of iron ions. O and OH ions are located at the corners of octahedrons.

temperature.

The increase of conductivity with the frequency observed above 1 MHz may be due to the hopping processes with the different mechanism from the above-mentioned processes.

Structure and Hopping Conduction. In ferric oxyhydroxides, Fe^{3+} ions are surrounded octahedrally by six oxygen atoms. These octahedral units form a binuclear complex by sharing edges. In α-FeOOH[13,14] and β-FeOOH,[8,15] the dimers are stacked parallel to the c-axis and the strings are further joined by sharing corners and by hydrogen bonds, as illustrated in Fig. 4(a). In γ-FeOOH, on the other hand, the dimers form layers parallel to the ac-plane by sharing edges (Fig. 4(b)) and each layer links together with hydrogen bonds.[9] It is characteristic of β-FeOOH to embrace chlorine in tunnels parallel to c-axis. The Fe–Fe distance between the nearest neighbors is about 3 Å for each form of oxyhydroxides and there seems no appreciable interaction among iron atoms except nearest neighbors. The distortion at the surface of fine crystals is so predominant as to disturb the periodic potential and to give more localized d-electrons, since much surface Fe exists as shown in Table 1. The state of d-electrons in ferric oxyhydroxide crystals may be regarded approximately as that of "octahedral complex molecules." The d-electron level of a central metal splits into t_{2g} having a small contribution of the $2p_\pi$ orbital of oxygen and e_g having a small contribution of the sp-hybrid orbital of oxygen in molecular orbital of an octahedral complex.[16]

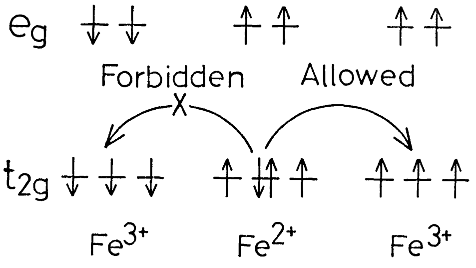


Fig. 5. Electron configurations on the occasion of the hopping of a d-electron in Fe^{2+} to Fe^{3+}.

A charge transfer occurs by the mechanism where a d-electron in the t_{2g}-orbital of Fe^{2+} hops to the adjacent site, t_{2g}-orbital of Fe^{3+}, through a slight overlapping of t_{2g}-orbitals of Fe^{2+} and Fe^{3+}. So long as no magnetic perturbation is present, the spin state of an electron before hopping must be in accord with that of an electron after hopping[17] (Fig. 5). Consequently the transfer probability is proportional to the number z of the nearest iron atoms in the same spin state. In the case of slight interactions among the partners, the transfer probability under an oriented electric field would also be proportional to z for the powdery crystals in various directions. It is noteworthy that the value of σ_i at 7 MHz is proportional to that of z at room temperature (Table 3). The preceding paper[3] showed that the σ_i at 7 MHz reflects the inner structure. This proportionality seems to be caused by the difference in the number of the nearest hopping-partners, since the amount of Fe^{2+} for each form of oxyhydroxide is equal.

All oxyhydroxides are antiferromagnetic and their Néel temperatures T_N found in previous works are as follows: β-FeOOH, 270 K;[18] γ-FeOOH, 50 K[18] or 70 K.[19] For α-FeOOH, different values ranging from 330 to 403 K have been reported.[14,20] The value of z at room temperature (Table 3) was estimated on the assumption that spins can be converted freely above T_N.

State of Chlorine in β-FeOOH. The sample of β-FeOOH examined in this work contains 9.5 atomic % chlorine which cannot be removed by washing with abundant distilled water until no Cl^- was detected with $AgNO_3$ solution. The presence of free chlorine ions would result generally in an increase of conductivity. The results obtained, however, indicate that the influence of chlorine is not remarkable and that chlorine may be immobile and does not seriously distort the electronic structure of iron. For a more definitive discussion on the chlorine effect the β-FeOOH samples with different contents of chlorine should be examined.

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