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Adsorption of Water on FeOOH as Studied by Electrical Conductivity Measurements

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Changes in the electrical conductivity of synthetic α-, β-, and γ-FeOOH crystals with the amount of adsorbed water were measured at 30 °C and various frequencies (dc, 100—10 MHz). The conductivity variations of water-adsorbed FeOOH with temperature were also examined over the range from −140 to 140 °C. For the adsorption coverages between 0 and 0.5, the electronic conduction increased with the coverage due to the transfer of electrons from chemisorbed water molecules to the FeOOH crystal. The decrease in activation energy for conduction with chemisorption was observed. The conductivity increase due to the chemisorption is related to the characteristic surface structure of each FeOOH polymorph. In the coverage range 0.7—2, protons in the adsorbed water layer transport electrical charges. The linear relationships between the logarithm of conductivity and the logarithm of the relative pressure of water vapor suggest the presence of clusters of physisorbed water molecules on FeOOH surfaces. A steep change in protonic conductivity by a factor of 10^2—10^4 was observed at a temperature close to −5 °C. The change seems to be caused by an order-disorder transition of protons in the adsorbed water layer.

Both O and OH on the surfaces of semiconductors and metal oxides play an important role in chemisorption.[1,2] Iron hydroxide oxide (FeOOH) crystal containing O and OH offers an ideal system for investigating the mechanism of chemisorption, since the geometrical positions of the surfaces O and OH can be derived by X-ray diffraction[3–5] and neutron diffraction[6–8] in crystallographic studies. α-, β-, and γ-FeOOH are found as minerals and as the main components in atmospheric corrosion products of iron. Electronmicroscopic observation reveals the presence of the predominant plane for each FeOOH, the index of which has been determined by selected-area electron diffraction.[9] With reference to these results, the surface characteristics of each FeOOH can be discussed by examining the structure of the predominant plane. It is anticipated that the adsorption sites for gaseous molecules are the characteristic O and OH on the predominant planes.

FeOOH is produced through an electrochemical process on the iron surface in the atmospheric environments, when water film of necessary thickness exists. The rust formed further promotes the adsorption of water on the iron surface. There is no doubt that water exhibits a particular activity to the FeOOH surface.

Kaneko *et al.* examined the adsorption process of water molecules on synthetic α-, β-, and γ-FeOOH by dielectric measurements.[10] They postulated that water molecules are adsorbed on two kinds of OH in (100) planes for α-FeOOH, OH and tunnels for β-FeOOH, and OH in (010) planes for γ-FeOOH; the adsorbed water layer forms a regular structure. The adsorption process was supported by thermodynamic study.[11] However, they were unable to discuss the electronic factors in the water adsorption. In the present work, the changes in electrical conductivity of synthetic FeOOH crystals with the amount of adsorbed water have been measured in order to elucidate the mechanism of chemisorption and the structure of adsorbed water.

Experimental

α-, β-, and γ-FeOOH were synthesized by procedures similar to those described in an earlier paper.[12] The X-ray diffraction of the samples gave patterns of pure, well-crystallized crystals. The BET surface areas obtained by use of N_2 adsorption at liquid nitrogen temperature were 69, 34, and 66 m^2/g for α-, β-, and γ-FeOOH, respectively.

Adsorption of Water and Electrical Conductivity. Sample disks made by applying a pressure of 150 kg/cm^2 were set between silver-plated brass electrodes in a glass cell of 215 cm^3. The sample disk was evacuated under a pressure of 10^{-5} Torr at 100 °C for 14 h prior to the adsorption measurement. The amount of adsorbed water was measured at 30 °C with use of a conventional volumetric apparatus with a silicone-oil manometer in the range of relative pressure 0—0.7. The water vapor was evolved from $BaCl_2 \cdot 2H_2O$. It took an hour to reach the adsorption equilibrium. Variations of electrical conductivity with the amount of adsorption at 30 °C and various frequencies (dc, 100—10 MHz) were measured by the same method as reported previously.[13] The conductivity of water-adsorbed FeOOH was also examined at different temperature in the range −140—140 °C. For the dc conductivity measurements, voltage in the range 0.1—100 V was applied. The current-voltage relationship for samples with submonolayer-adsorbed water obeyed Ohm's law, while that for samples with adsorbed water exceeding the monolayer deviated from the law.

Results and Discussion

FeOOH crystals exhibit an n-type electronic conduction *in vacuo*,[14,15] *i.e.*, the negative sign in Seebeck voltage and a conductivity decrease caused by introducing oxygen. The conductivity of samples with adsorbed H_2O of the coverage below 0.5 decreased by more than 25% of the initial value within a minute after the introduction of oxygen. The decrease is an evidence of electronic conduction. On the other hand, the exposure of samples with H_2O coverage above 0.7 to the oxygen gas brought about an instantaneous increase in conductivity. A fact of particular interest is that the water-adsorbed β-FeOOH (coverage 1.0) evolved hydrogen gas by applying dc 100 V at 30 °C for 265 h, which was detected by a mass spectrometer (Hitachi RMU-7M). No hydrogen gas was evolved from the water-adsorbed γ-FeOOH under the same conditions as those for the above-mentioned β-FeOOH specimen. No evolution of H_2 seems to be due to the progress of the reductive reaction of γ-FeOOH to Fe_3O_4 consuming the protons at the specimen-electrode interface.[16] Thus, the protonic conduction is assumed for water-adsorbed FeOOH of coverage above 0.7. In view of the facts mentioned above as well as the dependence of conductivity on frequency, temperature, and adsorption of water described later, it is suggested that the electrical transport in the water-adsorbed FeOOH consists of electronic and protonic conductions. The total electrical conductivity of the specimen is assumed to be the sum of the electronic conducitivity σ_{el} and the protonic one σ_p.

$$\sigma = \sigma_{el} + \sigma_p. \tag{1}$$

σ is nearly equal to σ_{el} for the samples of adsorption coverage less than 0.5. In the coverage range 0.7—2, σ is close to σ_p. In the range 0.5—0.7, σ_{el} is comparable to σ_p.

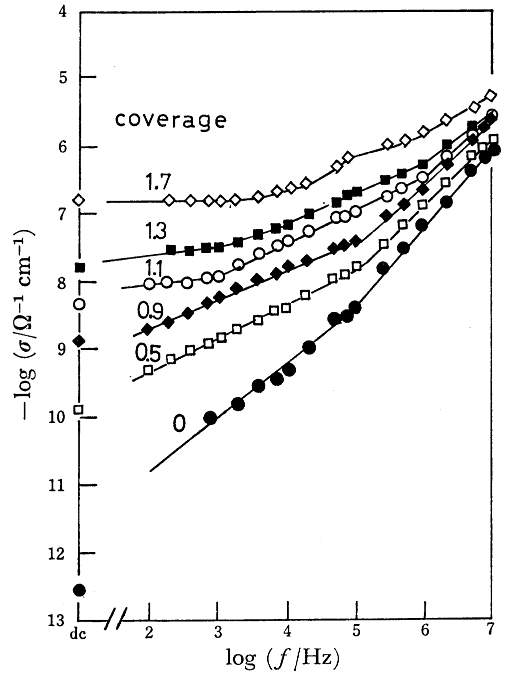

Fig. 1. Frequency dependence of electrical conductivity of γ-FeOOH at 30 °C at various coverages of adsorbed water (●: $\theta=0$, □: $\theta=0.5$, ◆: $\theta=0.9$, ○: $\theta=1.1$, ■: $\theta=1.3$, and ◇: $\theta=1.7$).

The frequency dependence of conductivity of γ-FeOOH measured at 30 °C for different values of coverage θ of adsorbed water is shown in Fig. 1. The logarithm of conductivity of pure γ-FeOOH ($\theta=0$) shows linear dispersion with the logarithm of frequency, suggesting the hopping of d-electrons in the t_{2g}-orbital of Fe^{2+} to that of adjacent Fe^{3+}.[17,18] In the coverage range 0.5—1, it appears that the more water is adsorbed, the more vague is the dispersion in the lower frequency range, probably because of the contribution of the protonic conduction to the dc conduction. The dispersion of conductivity in the lower frequency range disappeared for samples with adsorbed water exceeding the monolayer; dc protonic conduction through adsorbed water layer overwhelms the dc electronic conduction. Water molecules seem to be partly chemisorbed in the coverage range 0—0.5, and physisorbed in the coverage range 0.7—2. Discussion is given in two parts, chemisorption and physisorption.

Chemisorption

Change of Physisorption to Chemisorption. The excess d-electrons of Fe^{2+} in pure FeOOH crystals move in a hopping process with mobility proportional to $\exp(-W_H/kT)$, where W_H is the hopping energy. The activation energy E for conduction of pure FeOOH crystals is nearly equal to the hopping energy W_H, if the Fe^{2+} concentration n does not change with temperature. Taking into account the interaction between Fe^{2+} ions, E can be given by

$$E \approx W_H = W_H^\circ - c\frac{e^2}{d}, \tag{2}$$

where W_H° is the hopping energy in the case where there is no interaction between carriers, e the electronic charge, c a constant, and d the average Fe^{2+}–Fe^{2+} distance. The value d is approximately given by[14]

$$d = 2\left(\frac{3}{4\pi n}\right)^{1/3}. \tag{3}$$

It is accepted that the water molecule with negative electron affinity is apt to give an electron to the oxide surface.[19,20] A portion of water molecules physisorbed on the FeOOH crystals by hydrogen bonding can be chemisorbed through a charge-transfer interaction.[21] The chemisorbed water molecule donates an electron to the t_{2g} orbital of Fe^{3+} according to the thermal excitation process:

$$H_2O\ \text{(chemisorbed)} \longrightarrow H_2O^+\ \text{(chemisorbed)} + e(t_{2g}), \tag{4}$$

where $e(t_{2g})$ denotes the electron in the t_{2g} orbital. The ionization energy of the chemisorbed water molecule is denoted by E_i hereafter. The electron-transfer from water to the FeOOH surface results in an increase of the carrier concentration n; the activation energy for conduction decreases with increase in the amount of chemisorption owing to shallowing of the polarization-well of the carrier. The Fe^{2+}–Fe^{2+} distance d (Eq. 2) changes with the chemisorption of water. When the initial number of carriers, n_0, is much larger than the number of electrons donated from chemisorbed water, the hopping energy for the water-chemisorbed FeOOH is given by

$$W_H = W_H^\circ - \frac{ce^2}{2}\left(\frac{4\pi n_0}{3}\right)^{1/3} - \frac{ce^2}{6}\left(\frac{4\pi}{3n_0^2}\right)^{1/3} N_m\theta \exp(-E_i/kT), \tag{5}$$

where N_m is the number of adsorbed water molecules in monolayer at 30 °C. Equation 5 can be simplified to

$$W_H = W_H(\text{none}) - g\theta, \tag{6}$$

where W_H(none) is the hopping energy for FeOOH without water-chemisorption,

$$W_H(\text{none}) = W_H^\circ - \frac{ce^2}{2}\left(\frac{4\pi n_0}{3}\right)^{1/3}, \tag{7}$$

and g is given by

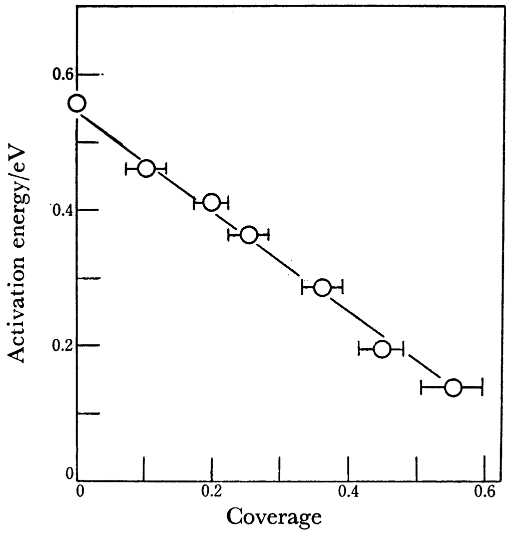

Fig. 2. Relationship between the activation energy and the coverage of adsorbed water for γ-FeOOH.

$$g = \frac{ce^2}{6}\left(\frac{4\pi}{3n_0^2}\right)^{1/3} N_m \exp(-E_i/kT). \tag{8}$$

Equation 6 shows that the hopping energy decreases in proportion to the coverage θ at a certain temperature.

Equation 6 holds for γ-FeOOH (Fig. 2); the activation energy for dc conduction at 30 °C decreases linearly with coverage; the slope of the straight line gives a g value of 0.71 eV. Taking the values $c=0.6$, $n_0=2\times10^{20}$ cm^{-3}, and $N_m=7\times10^{14}$ cm^{-2} in Eq. 8 we obtain $E_i=0.03$ eV. Thus, it is concluded that water molecules less than 15% of monolayer give electrons to γ-FeOOH at 30 °C, since the factor of $\exp(-E_i/kT)$ is about 0.3 and the upper limit of coverage for the chemisorption is 0.5.

Effect of the Surface Structure. Equation 6 requires a linear relationship between the logarithm of conductivity, $\log \sigma$, and coverage θ, since $\log \sigma$ is proportional to the activation energy E ($\log \sigma \propto (W_H - g\theta)/kT$). Figures 3—5 show the linear relationships between $\log \sigma$ at dc and θ for γ-, α-, and β-FeOOH. The linear relationships break at an inherent coverage for each FeOOH, which can be ascribed to the change in E_i. The coverage at which the line breaks relates to the number of the particular adsorption sites on the crystal surface.

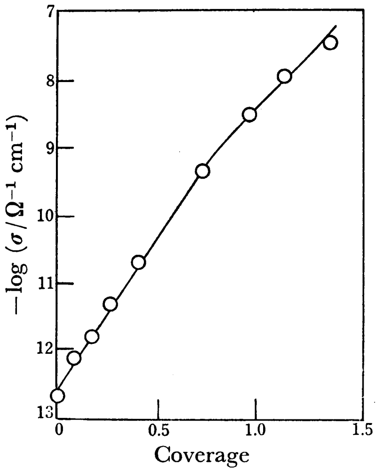

Fig. 3. Relationship between dc electrical conductivity and the coverage of adsorbed water at 30 °C for γ-FeOOH.

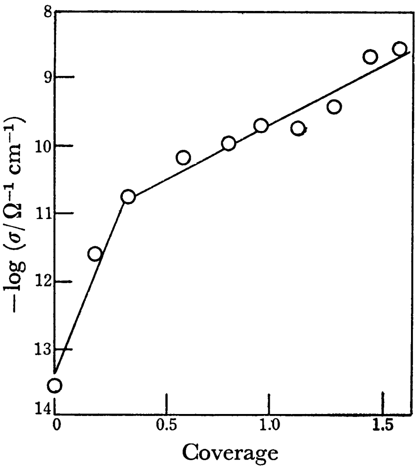

Fig. 4. Relationship between dc electrical conductivity and the coverage of adsorbed water at 30 °C for α-FeOOH.

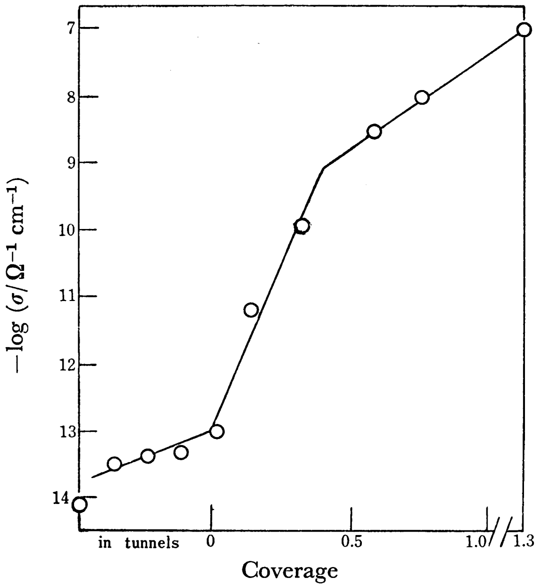

Fig. 5. Relationship between dc electrical conductivity and the coverage of adsorbed water at 30 °C for β-FeOOH.

Ewing[3)] postulated that the crystal structure of γ-FeOOH is built up of layers parallel to the (010) plane, each layer being made up of octahedra embracing iron atoms at centers of octahedra and linked together by sharing corners (Fig. 6(A)); the layers are joined to each other by hydrogen bonds. The linear relationship for γ-FeOOH (Fig. 3) in a wide range of coverage up to 0.8 is in line with the fact that the predominant (010) plane of γ-FeOOH has only one kind of OH as the water-adsorption site. However, the linearity breaks at the coverage of 0.8, since the protonic conduction through the bilayer of adsorbed water prevails over the electronic conduction.

The surface structure of α-FeOOH is shown in Fig. 6 (B).[4)] Water molecules up to a coverage of 0.3 are

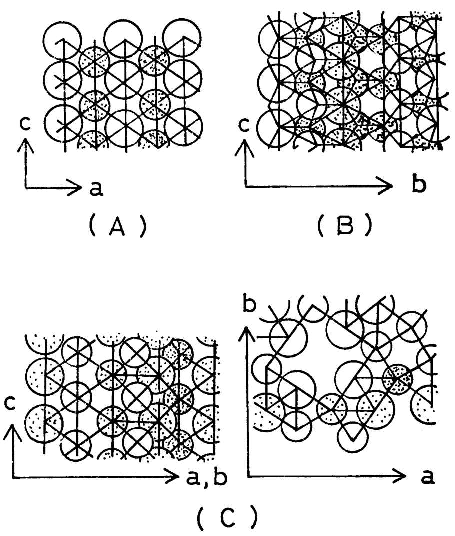

Fig. 6. Structure of the predominant surface of γ-FeOOH (A), α-FeOOH (B), and β-FeOOH (C). Large circle denotes OH^- and small circle O^{2-}.

adsorbed on the hydroxyls in the groove of the (100) plane of α-FeOOH; the line in Fig. 4 breaks at 0.3.

Mackay[5] showed that β-FeOOH has a hollandite structure having tunnels parallel to the c-axis, in which Cl^- and H_2O can be occluded (Fig. 6(C)). The vacant part in the tunnel, produced by the removal of Cl^-, is the most active site for water adsorption, and the number of the adsorption site can be determined by the Cl^- content in the tunnel. The adsorption begins when water molecules enter the tunnels. The abscissa in Fig. 5 represents the coverage of the sites in tunnels and that of the outer surface (coverage: 0—1.3). We see that the conductivity-increase of β-FeOOH due to the adsorption in the tunnel is less conspicuous than that due to the adsorption on the outer surface. The linear relationship between $\log\sigma$ and θ in the coverage range from 0 to *ca.* 0.5 is ascribed to the transformation of physisorbed water molecules with bifurcated hydrogen bonding to chemisorption.

When water is desorbed from each FeOOH sample at 30 °C under a pressure of 10^{-5} Torr for several hours, the conductivity is reduced to the order of the original value for the sample without adsorbed water; the chemisorption of water appears to be reversible. It seems that the chemisorbed water molecules are connected to the FeOOH surface by both hydrogen bonds and weak charge-transfer bonds.

Physisorption

Clusters of the Physisorbed Water Molecules. The protonic conduction through the physisorbed water layer seems to predominate over the d-electron conduction in a restricted coverage range. In the coverage range 0.7—2, $\log\sigma$ is proportional to the logarithm of relative pressure, $\log(P/P_0)$, at 30 °C, where P and P_0 are the vapor pressure and the saturated one, respectively. Figure 7 shows the relationship between $\log\sigma$ at dc and $\log(P/P_0)$ for β- and γ-FeOOH. The lines on the right side of the bending point (indicated by an arrow, Fig. 7) correspond to the region of protonic conduction. When the linear relationship is expressed by

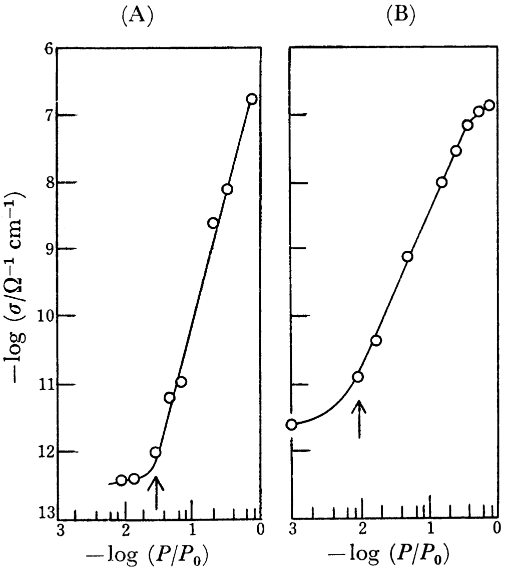

Fig. 7. Proportionality between $\log\sigma$ at dc and $\log(P/P_0)$ for β-FeOOH (A) and γ-FeOOH (B).

$$\sigma \propto (P/P_0)^s, \tag{9}$$

s values obtained from the slope of each line are: α-FeOOH, 1.1; β-FeOOH, 4.1; and γ-FeOOH, 2.2.

The adsorbed water layer is supposed to consist of solid-like two-dimensional clusters of water molecules. The relation given by Eq. 9 is interpreted by the presence of the clusters of adsorbed water molecules. The protonic conduction in the adsorbed water layer requires the production of protons by the ionic dissociation of water molecules. The dissociation of H_2O is determined by two bonding states, *i.e.*, the bonding between an adsorbed molecule and the surface, and that between adsorbed molecules. The proton formation from associated water molecules should differ from that of a single molecule. The association of m molecules on the FeOOH surface can be expressed by

$$m\mathrm{H_2O(g)} = m\mathrm{H_2O(ads)};\quad K_{\mathrm{ads}}, \tag{10}$$

$$m\mathrm{H_2O(g)} = (\mathrm{H_2O(ads)})_m;\quad K_{\mathrm{ass}}. \tag{11}$$

The number of association, m, is determined by the field strength of the surface. The dissociation equilibrium of a proton can be written as

$$(\mathrm{H_2O(ads)})_m = \mathrm{H^+} + (\mathrm{H_2O(ads)})_{m-1}\mathrm{OH^-};\quad K_{\mathrm{dis}}, \tag{12}$$

where (g) and (ads) denote gaseous water molecule and adsorbed one, respectively. The equilibrium constants for Eqs. 10, 11, and 12 are denoted by K_{ads}, K_{ass}, and K_{dis}, respectively. From Eqs. 10—12 the concentration of protons, p, is given by

$$p = \sqrt{K_{\mathrm{ads}}K_{\mathrm{ass}}K_{\mathrm{dis}}}P^{m/2}. \tag{13}$$

We see that σ_{p} is proportional to $P^{m/2}$, the mobility changing slightly with the adsorption of water. m is found to be $2s$ from a comparison of Eqs. 13 and 9.

The number of association m suggests a model of the cluster on the surface of each FeOOH, as shown in Fig. 8. For α-FeOOH (Fig. 8(A)), two molecules in the b-axis direction (dark circles) tend to form a dimer ($m=2$). When all grooves exposed on the β-FeOOH surface are filled with H_2O at a coverage of 0.3, H_2O molecules can come into contact with the six nearest neighbors; in this case *m* equals 7 (Fig. 8(C)). The adsorbed water molecules on γ-FeOOH surfaces (Fig. 8(B)) are connected to each other by tetrahedral hydrogen bonding (Fig. 11), the *m* value approaching 5.

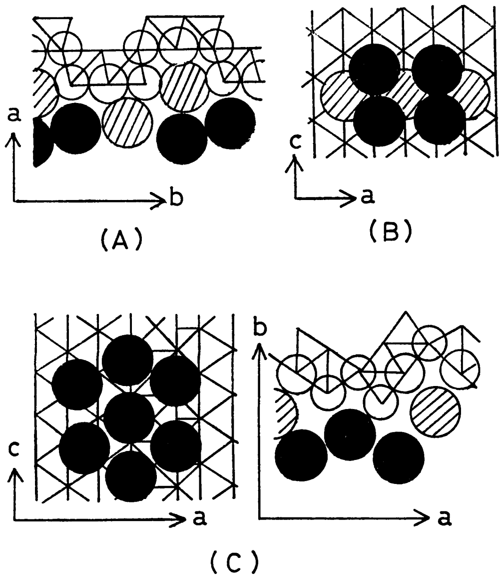

Fig. 8. Associated structures of water molecules physisorbed on α-FeOOH (A), γ-FeOOH (B), and β-FeOOH (C). Large and small circles denote OH^- and O^{2-}, respectively. Hatched circle and dark one denote the adsorbed water molecule contributing to the electronic conduction and to the protonic conduction, respectively.

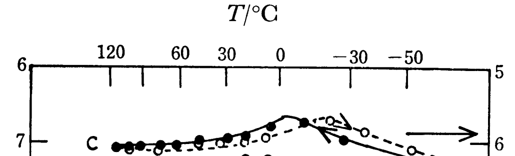

Fig. 9. Temperature dependence of electrical conductivity of γ-FeOOH with adsorbed water of various coverages.
dc: $\theta=0$ (□), $\theta=0.3$ (◇), $\theta=0.5$ (△), $\theta=0.7$ (▽), $\theta=1$ (●,○), and $\theta=1.5$ (☆). $\theta=1$ (●,○): 1 kHz (a), 100 kHz (b), and 7 MHz (c).

Phase Transition of Adsorbed Water Layer. The proton conduction through the adsorbed layer shows characteristic temperature dependence. Figure 9 shows the temperature dependence of the dc electrical conductivity of γ-FeOOH with adsorbed water of different coverages (θ=0—1.5 at 30 °C). The coverage determined at 30 °C increases with a lowering in temperature due to the condensation of vapor on the samples below 30 °C. It decreases with rise in temperature due to the desorption above 30 °C. The linear log σ *vs.* $1/T$ relationships for the coverage above 0.5 become nearly vertical in the range from −40 to −5 °C. The higher the coverage, the lower the temperature at which conductivity jumps. The log σ *vs.* $1/T$ relationships of water-adsorbed samples ($\theta=1$ and 1.5) have maxima at 10 °C. The log σ *vs.* $1/T$ relationships of γ-FeOOH ($\theta=1$ at 30 °C) at different frequencies are also shown in Fig. 9. The higher the frequency, the smaller the change in conductivity with temperature. The conductivities at 1 and 10 kHz reach maxima at 10 °C with rise in temperature. On the other hand, the conductivity at 7 MHz has no maximum at 10 °C, but at -7 ± 3 °C, where dc and lower frequency conductivities increase vertically with rise in temperature. The hysteresis of conductivity-temperature change was observed at all frequencies.

The steep change in conductivity in the temperature range from −40 to −5 °C may be due to a phase transition of the adsorbed water layer. All the phenomena observed appear to be similar to a solid-liquid transition of water in porous solids, which shows freezing-point depression.[23–25] However, the phase transition does not seem to be the solid-liquid transition for two reasons: (1) The adsorbed water layer of

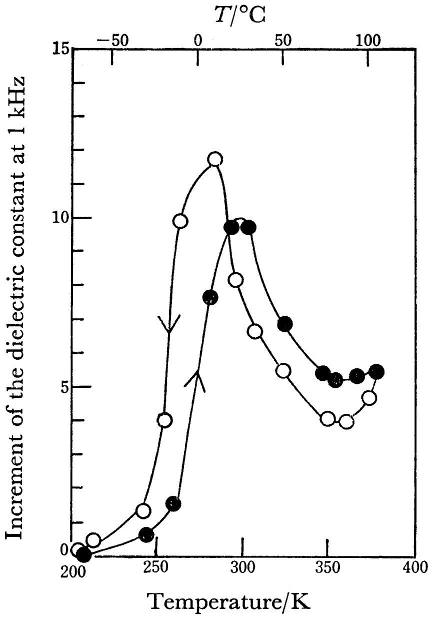

Fig. 10. Temperature dependence of the increment of the dielectric constant at 1 kHz of γ-FeOOH covered with adsorbed water ($\theta=1$ at 30 °C).

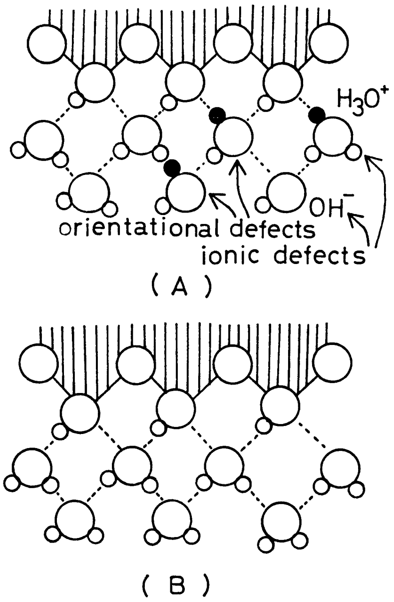

Fig. 11. Hydrogen-disordered (A) and hydrogen-ordered (B) structures of bilayer of water adsorbed on γ-FeOOH. Small, open circle denotes a hydrogen atom. Small, black circle denotes the misplaced hydrogen atom (or ion). Large circle denotes an oxygen atom (or ion).

thickness less than three molecular layers can not be regarded as a liquid phase. (2) The phase transition between ice I and liquid water causes no significant conductivity changes, since the electrical conductivity of ice I at -20 °C is 10^{-8}—10^{-10} Ω^{-1} cm^{-1} [26] and that of liquid water 10^{-9} Ω^{-1} cm^{-1}.[27] The variations of dielectric constant with temperature should also be taken into consideration. Figure 10 shows the temperature dependence of the dielectric constant for γ-FeOOH at 1 kHz ($\theta=1$ at 30 °C). The results are referred to the dielectric studies on polymorphs of ice by Whalley *et al.*,[28,29] who argued that an order-disorder transition of the position of hydrogen atoms affects the dielectric constant. It seems that the phase transition of the adsorbed water layer on the FeOOH surface is not a solid-liquid transition but an order-disorder transition of hydrogen atoms. A model of the order-disorder transition of hydrogen atoms in the adsorbed water layer on γ-FeOOH is shown in Fig. 11. The disordered adsorbed-water layer containing many orientational and ionic defects would result in high dielectric constant and high conductivity. The electrical conduction at dc and that at frequencies higher than 100 kHz arise from the migration of ionic (protonic) defects and the formation of orientational defects, respectively.[30] Most orientational defects appear at the temperature of order-disorder transition; the conductivity at 7 MHz reaches maximum at the transition temperature. The fact that H_2O-adsorbed FeOOH ($\theta=1$ or 1.5) has the highest protonic conductivity at 10 °C might be related to the maximum of the adsorbed water in the disordered state at the temperature. The hysteresis observed can be attributed to a strong interaction between the adsorbed water and the FeOOH surface. The strong interaction also promotes the dissociation of water. Gallagher and Phillips[31,32] observed the hydrogen-exchange between hydroxyls of FeOOH and water.

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