Chlorine Occupancy Dependence of Crystal Structure of Pure β-Phase of Iron-Oxyhydroxide

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Crystal structure of β-phase of iron-oxyhydroxide (Akaganeite) with different chlorine occupancy was studied by X-ray diffraction with Rietveld analysis. The structure depends on chlorine occupancy, u in tunnel sites of the phase. The crystal system was assigned to monoclinic (I2/m) throughout u range whereas the lattice and structure parameters changed with u. The chemical formula was estimated to be Fe₄[O₄]Cl₂H₆Cl₂(C₂O₄)(H₂O)₃₋₄u. The X-ray diffraction analysis for each sample were soaked in NH₄OH solution or in distilled water to reduce the chlorine contents in the tunnel sites, and they were centrifuged again. After such washing processes, they were filtrated and dried at 60°C.

1. Introduction

Fine particles of β-phase of iron-oxyhydroxide, Akaganeite are known as one of the important components of stable rust formed on advanced weathering steel.

Study of rust formed on steel is indispensable since practical applications of steel to construction materials always concern this problem. There are at least three crystal phases of iron-oxyhydroxides, α-, β- and γ-phases. They have common double-units of oxygen-octahedron with 6 O²⁻ surrounding a Fe³⁺ ion, but linkages of them are different. In previous works, the fraction and volume distributions of rust particles formed on conventional and advanced weathering steel were estimated by analyzing temperature dependence of Mössbauer absorption spectra. It is known that the spin of Fe³⁺ ions in β-phase exhibits anti-ferromagnetic ordering with uniaxial anisotropy parallel to the crystalline b-axis. The magneto-crystalline uniaxial anisotropy constant, K_u, of pure β-phase with fine particles was estimated to be 2.1 × 10⁸ J/m³ by the Mössbauer method in our previous study. More accurate estimation of particle volume in rust became possible by using the value.

Crystal structure of β-phase has been studied by many investigators. One of structural characteristics of the phase is that it contains Cl⁻ ions. The oxygen-octahedron units share an oxygen atom with adjacent ones to form a framework surrounding a relatively large hole, an array of which along b-axis is called a “tunnel”. The tunnel sites are located at bcc-like positions in a unit cell. Cl⁻ ions statistically occupy some of the tunnel sites with a certain occupancy, u. A ball stacking model of β-phase is shown in Fig. 1.

Although several investigators have determined crystal system (tetragonal or monoclinic) and crystal parameters of β-phase, the chlorine occupancy dependence of them has not been known well yet. The purpose of this study is to understand dependence of structural characteristics of β-phase on chlorine occupancy.

2. Experimental

2.1 Sample preparation

Samples were synthesized by aging 0.1 M FeCl₃ solution with 1 M urea, (NH₄)₂CO at 60°C for 8 days. The synthesized samples were subjected to washing by following processes. The precipitates were separated from the supernatant liquid by centrifuging in distilled water. The samples were soaked in NH₄OH solution or in distilled water to reduce the chlorine contents in the tunnel sites, and they were centrifuged again. After such washing processes, they were filtrated and dried at 60°C.

Chlorine contents of the samples were determined by following potentiometric titration method with silver-silver chloride electrodes. The mixtures of each samples (0.25 g) and 1 M (COOH)₂-H₂O were dissolved at 80°C, and the solutions obtained were diluted with distilled water and were titrated with 0.1 M AgNO₃.

The washing conditions of samples and the chlorine contents determined by titration method are listed in Table 1. The sample N00 had the highest chlorine content. When the samples were soaked in NH₄OH solution (N02, N20, and N60), they showed the lowest chlorine content. The values of them were not much changed with soaking time in NH₄OH solution. To prepare a sample with intermediate chlorine content, another sample was prepared by soaking in distilled water for 15 days, and the sample...
Table 1  Washing conditions of samples and the chlorine contents determined by titration method. D.W.: distilled water, A.S.: NH₄OH solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Washing processes and their conditions</th>
<th>Chlorine content, Cl/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>N00</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>W15</td>
<td>5 times in D.W. in D.W. for 15 days</td>
<td>0.14</td>
</tr>
<tr>
<td>N20</td>
<td>in A.S. for 2hrs 5 times with D.W.</td>
<td>0.05</td>
</tr>
<tr>
<td>N20</td>
<td>in A.S. for 20hrs in A.S. for 60hrs</td>
<td>0.06</td>
</tr>
</tbody>
</table>

W15 with 0.11 of Cl/Fe was obtained. The samples of N00, W15 and N60 were subjected to XRD measurement and Rietveld analysis.

SEM (JEOL, JSM-5400) observations were performed to confirm the morphology of the particles. An image of the β-phase particles are shown in Fig. 2. The crystallites are fairly uniform, “mono-dispersed” with elongated shapes. The lengths of the longer and the shorter axis of the particles were approximately 400 and 50 nm, respectively. The particle sizes were again observed after washing treatment and they were not much changed before and after washing processes.

2.2 X-ray powder diffraction measurements

X-ray powder diffraction patterns were taken by using a monochromatized Fe Kα radiation source (Rigaku, RU300, Rotating Anode tube, 45 kV, 150 mA) and a 4-circle diffractometer (Huber, Model L440, 513, 414) with a scintillation counter. We chose fluorescent-free Fe Kα radiation as X-ray source since Cu Kα radiation generally used as X-ray source is absorbed by Fe atoms in β-phase, and they emit fluorescent radiation.

To reduce air scattering effects, helium gas was flowed through the incident and diffracted beam pass. A rectangular-type collimator with slit size of 1 × 10 × 150 mm was used at the incident pass. The zero point of 2θ axis was calibrated with a pattern of silicon pure powder (5N). The data were collected by conventional θ-2θ method in a 2θ range of 10–100° with a 0.02° step. An accumulation time was 8 s/step, for which back-ground noises were about 100 counts/step as will be shown in Fig. 4.

2.3 Rietveld analysis

XRD patterns obtained were analyzed by using Rietveld method15–17) with the program RITAN-FP.18) The Rietveld method devised by Rietveld in 1969 is a technique for refining crystal structure from the diffraction patterns.15) The calculated pattern, \( P_i(a) \) is fitted to the observed one, \( R_i \), for refining the lattice and structure parameters, \( a \) by minimizing the sum of weighted squares of residuals, \( S(a) \) as shown in eq. (1).

\[
S(a) = \sum_{i=1}^{N} W_i[R_i - P_i(a)]^2. \tag{1}
\]

\( (P_i(a)): \) calculated pattern, \( R_i: \) observed pattern, \( W_i = 1/R_i: \) the statistical weight, \( i: \) the step number

The \( P_i(a) \) is written as eq. (2). The symmetric profile function, \( G(\Delta 2\theta) \) used was the pseudo-Voigt function,19) and the background function, \( L(2\theta) \), the Legendre polynomials. Surface roughness, irradiation width and the preferred orientation factors were chosen to unity.

\[
P_i(a) = s \sum_k m_k F_k \left[ G(\Delta 2\theta_k) + L(2\theta_k) \right]. \tag{2}
\]

\( (F_k): \) structure factors, \( s: \) scale factor, \( m_k: \) multiplicity, \( \theta_k: \) Bragg angle, \( G(\Delta 2\theta_k) = G(2\theta_k - 2\theta_k) \)

The crystal structure factor, \( F_i \) is written as eq. (3). The summation is carried out over all the atoms in the unit cell. The lattice parameters \( (a, b, c, \beta) \) and the structure parameters on fractional coordinate for Fe and O sites \((x_j, y_j, z_j)\) and occupation factor for Cl site \((g_j)\) were calculated by refining the starting structural model for tetragonal (I4/m) from PDF No. 34-1266 and that for monoclinic (I2/m) from PDF No. 80-1770.9,11) Thermal vibrations were assumed to be isotropic. The Debye-Waller factors, \( T_j \) is written by eq. (4) in which the isotropic atomic displacement parameters, \( B_j \) were fixed to 0.5 for Fe, 0.8 for O and 2.0 for Cl sites.

\[
F_i = \sum_j g_j (f_j + \Delta f_j + i \Delta f'_j) T_j \exp[2\pi i(hx_j + ky_j + lz_j)].
\]

\( (g_j): \) occupation factor, \( x_j, y_j, z_j: \) fractional coordinate, \( f_j: \) atomic form factor \( \)

\[
T_j = \exp \left[ -B_j \left( \frac{\sin \theta_k}{\lambda} \right)^2 \right]. \tag{4}
\]

\( (B_j): \) isotropic atomic displacement parameter.

In this calculation, it is assumed that virtual Cl atoms with an effective atomic form factor, \( f_{eff} = g_i f_i \) exist at all the tunnel sites. Meanwhile, Cl occupancy of tunnel sites, \( \mu \) defines as statistical probability of chance to occupy a Cl– ion at a possible site in tunnels. Therefore, strictly speaking, \( g_i \) is not equal to the statistical occupancy \( (u) \) of atoms with

Fig. 2  A SEM image of the synthesized particles before washing.
Fig. 3 An example (sample: N00) of dependence of $S$ (goodness-of-fit) on $g$ (occupation factor). It has a minimum point at $g = 0.675$.

Table 2 Lattice parameters ($a$, $b$, $c$, $\beta$) of $\beta$-phase (monoclinic) with different Cl occupancy ($u$). The occupation factor ($g$), the values of $a/c$ and the unit cell volumes ($V_{\text{unit}}$) are also listed. The relationship between $u$ and $g$ will be discussed in section 4.1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Chlorine occupancy, $u$</td>
</tr>
<tr>
<td>N00</td>
<td>0.56</td>
</tr>
<tr>
<td>W15</td>
<td>0.44</td>
</tr>
<tr>
<td>N60</td>
<td>0.25</td>
</tr>
</tbody>
</table>

an atomic form factor ($f_j$). The values of $g_j$ were determined by minimizing the values of goodness-of-fit, $S$ as a criterion of fitting as shown in Fig. 3. The tunnel sites locate at (0,0,0) and (1/2,1/2,1/2), bcc-like position in a unit cell. Only even occupancy, $g$, is regarded as nearly equal to statistical factor, $u$, in the first approximation.

3. Results

3.1 Determination of crystal system

XRD patterns of the samples with different Cl occupancy, $u$ (N00, W15, N60) are shown in Fig. 4. It is clearly seen that the patterns change depending on $u$. Some weak peaks from $\alpha$-phase are mixed with those from $\beta$-one in W15 and N60 whereas $\alpha$-phase does not exist in N00 at all. The ratio of $\alpha$-phase to $\beta$-one in W15 and N60 are estimated to be $\sim 1$ and $\sim 4$ at%, respectively, by using the scale factor, $s$ in Rietveld analysis. Therefore, the $\alpha$-phase peaks were removed from the diffraction patterns of W15 and N60 by JADE (MDI), and only $\beta$-phase patterns were subjected to Rietveld analysis. As was shown in section 2.3, the patterns calculated by assuming tetragonal or monoclinic systems were fitted to the observed patterns.

The observed and calculated fitting patterns, and the difference between them, i.e. residuals of the fitting for N00 are shown in Fig. 5. Residuals of the fitting for W15 and N60 are also shown in Fig. 6. As shown in Fig. 5(a1) and (b1), the occupation factor ($g$) has a minimum point at $u = 0.56$. The unit cell parameters of $\beta$-phase for W15 and N60 are also assigned to monoclinic (I2/m) rather than tetragonal (I4/m) (Fig. 6). Therefore, it is clear that crystal system of $\beta$-phase throughout $u$ range can be assigned to monoclinic (I2/m).

3.2 Lattice and structure parameters

Lattice parameters ($a$, $b$, $c$, $\beta$) refined for monoclinic system, the values of $a/c$ and the unit cell volumes, $V_{\text{unit}}$ of $\beta$-phase are listed in Table 2 and their $u$-dependencies are plotted in Fig. 7. The lattice parameters change depending on Cl occupancy, $u$. The values of $a/c$ and $\beta$ have minimum and those of $a$, $b$, and $c$ and $V_{\text{unit}}$ have maximum at $u = 0.44$. It is interesting that the sample W15 with $u = 0.44$ show the highest crystalline symmetry throughout $u$ range, i.e. the $a/c$ is close to unity and the $\beta$, 90°. The unit cell parameters of W15 are close to tetragonal ($a = c$ and $\beta = 90^\circ$) which has higher symmetry than monoclinic ($a \neq c$ and $\beta \neq 90^\circ$).
Structure parameters calculated for monoclinic system are listed in Table 3. The fractional coordinates of \(x\) and \(z\) for Fe and O sites and occupation factor, \(g\) vary with \(u\).

Stahl et al. also prepared pure \(\beta\)-phase and analyzed crystal structure by Rietveld method. They claimed that the crystal system is monoclinic \((I2/m)\) and the lattice parameters, \(a = 1.05536(7)\) nm, \(b = 0.303449(8)\) nm, \(c = 1.05740(4)\) nm, \(\beta = 90.086(5)^\circ\), and occupation factor, \(g = 0.201(2)\). The lattice parameters are close to our results although \(g\) is smaller than ours.

4. Discussion

The following three points will be discussed to understand dependence of crystal structure of \(\beta\)-phase on Cl occupancy, \(u\).

1. Estimation of \(u\) in tunnel sites.
2. Consideration of a possible \(u\) range.
3. Origin of \(u\)-dependence of structure parameters.

4.1 Estimation of Cl occupancy, \(u\) from the Cl/Fe ratio, \(r\) determined by titration and consideration of relationship between \(u\) and the occupation factor, \(g\) obtained by Rietveld analysis

Occupancy of tunnel sites, \(u\) defined as statistical probability of chance to occupy a Cl\(^-\) ion at a possible site in tunnels. According to principle of charge neutrality, chemical formula of \(\beta\)-phase represented by all atoms in unit cell should be \(\text{Fe}^{3+}_{\frac{8}{10}}\text{O}^{2-}_{\frac{16}{18}}\text{H}^{+}_{\frac{8}{18}}\text{Cl}^{-}_{\frac{2u}{2u}}\). The relationship between \(u\)
and the value of Cl/Fe ratio, \( r \) determined by the titration method and that between \( u \) and the occupation factors, \( g \) by the Rietveld analysis are discussed in this section.

### 4.1.1 Estimation of \( u \) from \( r \)

The Cl/Fe ratio, \( r \) determined by titration as shown in Table 1 represents the atomic ratio of Cl atoms to all the Fe atoms in the sample. If the sample consist of only pure \( \beta \)-phase, \( r = 2u/8 = 0.25u \). It is assumed that amount of Cl existing in places other than tunnel sites is much smaller, and can be neglected since the samples were washed carefully. When a sample contains other phases in addition to \( \beta \)-one, \( u \) can be estimated by the formula \( r = u/(4(1+p)) \), where \( p \) is the atomic ratio of Fe in the other phases to that in \( \beta \)-one. In the present study as was shown in section 3.1, \( \alpha \)-phase coexisted with the \( \beta \)-one in the samples, W15 and N60. The ratio of \( \alpha \)-to \( \beta \)-phase for W15 and N60 were estimated to be 0.01 and 0.04, respectively, and they were adapted as \( p \) values. The values of \( u \) estimated by using those of \( r \) and \( p \) are listed in Table 4.

### 4.1.2 Estimation of fraction of water molecules, \( w \) and that of vacancies, \( v \) in tunnel sites by using \( u \) and \( g \)

As was shown in section 2.3, the occupation factors, \( g \) for Cl site by the Rietveld analysis should be regarded as nearly equal to \( u \) in the first approximation. In fact, as seen in

<table>
<thead>
<tr>
<th>Sample</th>
<th>( r )</th>
<th>( p )</th>
<th>( u )</th>
<th>( g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N00</td>
<td>0.14</td>
<td>0</td>
<td>0.56</td>
<td>0.68</td>
</tr>
<tr>
<td>W15</td>
<td>0.11</td>
<td>0.01</td>
<td>0.44</td>
<td>0.54</td>
</tr>
<tr>
<td>N60</td>
<td>0.06</td>
<td>0.04</td>
<td>0.25</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Table 4, the value of \( g \) is close to \( u \) in each sample, but \( g \) is always greater than \( u \). To solve an origin of such discrepancy, it is supposed that any other atoms or molecules having smaller scattering power than Cl\(^{-}\) ions in tunnel sites must exist. Among candidates of such atoms or molecules, \( \text{H}_2\text{O} \) will be most reasonable. Some previous investigations also suggested that \( \text{H}_2\text{O} \) molecules would occupy some of tunnel sites\(^{8,20} \), whereas Stahl et al. suggested that tunnel sites does not contain water molecules.\(^{13} \) In their analysis, they assumed that occupation factor, \( g = 2/3 \) (they regarded as \( g = u \)). As will be shown in next section, our estimated range of \( u \) is \( 0.25 \leq u \leq 0.56 \). Therefore, it is not clear whether their discussion can be applied to our range of \( u \).

If fraction of water molecules, \( w \) exist in tunnel sites, chemical formula of \( \beta \)-phase can be represented as \( \text{Fe}^{18}_2\text{Cl}_{10}^\text{eff.} \text{H}_2\text{O}_{2w} \text{Cl}_{2w}^\text{eff.}(\text{H}_2\text{O})_{2w}^\text{eff.} \). Meanwhile, effective atomic form factor for a tunnel site, \( f_{\text{Cl}}(k) \) can be a weighted average of the form factors of Cl\(^-\) ion, \( f_{\text{Cl}}(k) \) and that of \( \text{H}_2\text{O} \) molecule, \( f_{\text{H}_2\text{O}}(k) \) as shown in eq. (7).

\[
f_{\text{eff.}}(k) = u f_{\text{Cl}}(k) + w f_{\text{H}_2\text{O}}(k).
\]

In usually case, \( f_{\text{eff.}}(k) \) is nearly equal to \( f_{\text{eff.}}(0) \). As a simple approximation, if we assume that \( f_{\text{eff.}}(0) \) is proportional to the weighted mean of number of electrons, \( E \), i.e. \( E = 18 \) for Cl\(^-\) and \( E = 10 \) for \( \text{H}_2\text{O} \), eq. (7) can be written as follows,

\[
18g = 18u + 10w.
\]

If such assumption is correct, the value of \( w \) should exist between \( w = 0 \) and \( w = 1 - u \), i.e. between \( g = \frac{2}{3} \) and \( g = u \). As will be shown in Fig. 8, the values of \( g \) obtained by Rietveld analysis are in-between these two straight lines. Therefore, substituting the values of \( u \) and \( g \) (in Table 4) into eq. (8), the values of \( w \) can be estimated. Consequently, fraction of vacancies in tunnel sites, \( v \) are calculated as \( v = 1 - (u + w) \). The estimated values of \( u, g, w \) and \( v \) are listed in Table 5, and \( u \)-dependences of the \( g \), \( w \) and \( v \) are plotted in Fig. 8. The value of \( v \) increases with a decrease of \( u \), while \( g \) is almost proportional to \( u \). In addition, the value of \( w \) is nearly constant to about 0.2 regardless to \( u \).

### 4.2 Range of Cl occupancy, \( u \)

#### 4.2.1 Lower and upper limits of \( u \)

As shown in section 4.1, it was suggested that \( \beta \)-phase was stable only in the limited range of Cl occupancy, \( 0.25 \leq u \leq 0.56 \) with almost constant fraction of water molecules, \( w \approx 0.2 \).

The lower limit of \( u \) was 0.25 where the fraction of vacancy, \( v \) was 0.53. The results suggest that if \( v \) is bigger
4.3.1 Electrostatic considerations through H\(^+\) ions

The unit cell volumes, \(V_{\text{unit}}\) of N00, W15 and N60 were listed in Table 2 and their \(u\)-dependences were plotted in Fig. 7. The values of \(V_{\text{unit}}\) had maximum at \(u = 0.44\) (W15).

Table 5 Estimated values of Cl occupancy, \(u\), occupation factor, \(g\), fraction of water molecules, \(w\), and that of vacancies, \(v\) in tunnel sites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(u)</th>
<th>(g)</th>
<th>(w)</th>
<th>(v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N00</td>
<td>0.56</td>
<td>0.68</td>
<td>0.21</td>
<td>0.23</td>
</tr>
<tr>
<td>W15</td>
<td>0.44</td>
<td>0.54</td>
<td>0.17</td>
<td>0.39</td>
</tr>
<tr>
<td>N60</td>
<td>0.25</td>
<td>0.37</td>
<td>0.22</td>
<td>0.53</td>
</tr>
</tbody>
</table>

than half, the \(\beta\)-phase becomes unstable and transformed to \(\alpha\)-one. That means the proper Cl\(^-\) ions must be necessary to maintain the tunnel structure of \(\beta\)-phase.

On the other hand, the upper limit of \(u\) was 0.56 where \(v\) was 0.23. If the \(u\) exceeds a little over than \(1/2\), Cl\(^-\) ions are necessary to occupy at the consecutive adjacent sites between which distance is about 0.303 nm along the \(b\)-axis. Since the diameter of Cl\(^-\) ion is about 0.36 nm which is much bigger than the distance between the adjacent sites, this arrangement seems to be rather hard due to the Coulomb repulsion between the adjacent Cl\(^-\) ions. Therefore, some proper vacancies in tunnel sites must be necessary to relax the repulsion energy.

4.2.2 A phase having higher symmetry at intermediate \(u\)

It should be noted that the sample W15 of which \(u\) is 0.44 and \(v\) is 0.39 shows the highest crystalline symmetry, e.g. the unit cell parameters (\(a/c \cong 1\) and \(\beta \cong 90^\circ\)) were the closest to tetragonal (\(a = c\) and \(\beta = 90^\circ\)) among the samples shown in Table 2. A certain ordering of some vacancies and/or atoms in tunnel sites would be required to achieve such higher symmetry. However, it is not possible to analyze what kind of ordering exists from the present results.

4.3 Dependence of oxygen-octahedron volumes, \(V_{\text{Fe}}\) on \(u\)

4.3.1 Electrostatic considerations through H\(^+\) ions

The unit cell volumes, \(V_{\text{unit}}\) of N00, W15 and N60 were listed in Table 2 and their \(u\)-dependences were plotted in Fig. 7. The values of \(V_{\text{unit}}\) had maximum at \(u = 0.44\) (W15).

Table 6 Volumes of \(V_{\text{unit}}, V_{\text{Fe1}}, V_{\text{Fe2}}, V_{\text{C1}}\) (= \(V_{\text{Fe1}} + V_{\text{Fe2}}\), \(V_{\text{Cl}}\) and \(V_{\text{Rest}}\), \(V_{\text{Fe1}} = 1\) or 2) = 4 \times (volume of octahedron around Fe site), \(V_{\text{Cl}} = 2\times\) (volume of octadecahedron around tunnel site).

<table>
<thead>
<tr>
<th>Sample</th>
<th>chlorine occupancy, (u)</th>
<th>(V_{\text{unit}})</th>
<th>(V_{\text{Fe1}})</th>
<th>(V_{\text{Fe2}})</th>
<th>(V_{\text{C1}})</th>
<th>(V_{\text{Rest}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>N00</td>
<td>0.56</td>
<td>0.335</td>
<td>0.040</td>
<td>0.046</td>
<td>0.085</td>
<td>0.141</td>
</tr>
<tr>
<td>W15</td>
<td>0.44</td>
<td>0.337</td>
<td>0.045</td>
<td>0.043</td>
<td>0.088</td>
<td>0.144</td>
</tr>
<tr>
<td>N60</td>
<td>0.25</td>
<td>0.331</td>
<td>0.052</td>
<td>0.041</td>
<td>0.092</td>
<td>0.127</td>
</tr>
</tbody>
</table>

A unit cell is composed of tunnel sites at the bcc-like position and oxygen-octahedra as shown in Fig. 9. The octahedra are one of the most important elements in the unit cell. By connecting the center of oxygen ions, a unit cell can be divided into three elemental regions: I, octahedra around Fe (Fe1 and Fe2) site surrounded by 6 O\(^2-\) ions, II, octadecahedra around tunnel site surrounded by 12 O\(^2-\) ions, and III, the rest (Fig. 9). The volumes of I, \(V_{\text{Fe1}}\) or \(V_{\text{Fe2}}\), sum of \(V_{\text{Fe1}}\) and \(V_{\text{Fe2}}\), \(V_{\text{Fe}}\), those of II, \(V_{\text{C1}}\), and those of III, \(V_{\text{Rest}}\) are listed in Table 6 and their \(u\)-dependences are plotted in Fig. 10. The volumes of \(V_{\text{Fe1}}, V_{\text{Fe2}}\) and \(V_{\text{Fe}}\) monotonically increase or decrease depending on \(u\), while \(V_{\text{unit}}, V_{\text{C1}}\) and \(V_{\text{Rest}}\) have maximum or minimum at \(u = 0.44\).

To discuss the monotonical change of \(V_{\text{Fe}}\), let us consider about the electrostatic interactions of Cl\(^-\) ions and H\(^+\) ions since it is assumed that the existence of Cl\(^-\) ions in tunnel sites have an influence on the adjacent O\(^2-\) and Fe\(^{3+}\). If a tunnel site is empty or occupied by neutral water molecules, H\(^+\) ions will be attracted closer to O\(^2-\) ions since there are no...
other anions near-by. If a $\text{H}^+$ and an $\text{O}^{2-}$ ion approaches closer, the coulomb attraction between $\text{Fe}^{3+}$ and $\text{O}^{2-}$ ions will be reduced since $\text{Fe}^{3+}$ feel $\text{H}^+-\text{O}^{2-}$ as a mono-valent ($\text{H}^+\text{O}^{2-}$) ion. Then, the average distance between $\text{Fe}^{3+}$ and $\text{O}^{2-}$ ions become larger, and therefore, $V_{\text{Fe}}$ will increase with an increase of $u$ (with a decrease of $a$). A similar model based on the electrostatic consideration was also proposed by Post et al.\textsuperscript{8)} On the other hands, if a tunnel site is occupied by a $\text{Cl}^-$ ion, it attracts $\text{H}^+$ ion, and the $\text{O}^{2-}$ ions will be attracted by $\text{Fe}^{3+}$ a little closer. Then $V_{\text{Fe}}$ will decrease with an increase of $a$.

Although such electrostatic considerations were successful to understand $u$-dependence of $V_{\text{Cl}}$ qualitatively, $u$-dependence of $V_{\text{Cl}}$ and $V_{\text{Fe}^\text{II}}$ cannot be explained properly because they have maximum at $u = 0.44$ (sample W15). Such phenomena may have a relation to crystal symmetry which was discussed in section 4.2.2.

### 4.3.2 Analysis on displacements of ions depending on $u$

The $u$-dependence of $V_{\text{Fe}^\text{I}}$ and $V_{\text{Fe}^\text{II}}$ also can not be explained only by the electrostatic considerations discussed in the previous section since they are quite opposite: $V_{\text{Fe}^\text{I}}$ increases monotonically with a decrease of $u$ while $V_{\text{Fe}^\text{II}}$ decreases with that. To solve the origin of such $u$-dependence of $V_{\text{Fe}^\text{I}}$ and $V_{\text{Fe}^\text{II}}$, it is meaningful to examine the positions of Fe and O ions in detail. It is convenient that the positions of atoms in the oblique fractional coordinates in Table 3 are converted to those in rectangular real ones.

### Table 7 Relative positions of Fe and O sites in octahedra and the volume of octahedron around Fe1 and Fe2. Notation of O1f site is introduced to distinguish the difference of Fe-O1 distance in octahedra, and O1 and O1f sites are crystallographic equivalent with each other as is shown in Fig. 11(b).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative position</th>
<th>Volume of octahedron, (V/\text{nm}^3)</th>
<th>Relative position</th>
<th>Volume of octahedron, (V/\text{nm}^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X (\text{Fe}^\text{I})</td>
<td>Y (\text{Fe}^\text{I})</td>
<td>Z (\text{Fe}^\text{I})</td>
<td>X (\text{Fe}^\text{II})</td>
</tr>
<tr>
<td>N00</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>O2 0.0252</td>
<td>0.1515</td>
<td>−0.0934</td>
<td>O4 0.1254</td>
</tr>
<tr>
<td></td>
<td>O1 0.0098</td>
<td>0.1515</td>
<td>0.1469</td>
<td>O3 −0.1354</td>
</tr>
<tr>
<td></td>
<td>O1 0.0098</td>
<td>−0.1515</td>
<td>0.1469</td>
<td>O3 −0.1354</td>
</tr>
<tr>
<td></td>
<td>O4 −0.1923</td>
<td>0</td>
<td>0.0049</td>
<td>O2 −0.0077</td>
</tr>
<tr>
<td></td>
<td>O1f 0.2153</td>
<td>0</td>
<td>0.0478</td>
<td>O3f −0.0577</td>
</tr>
<tr>
<td>W15</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>O2 0.0098</td>
<td>0.1518</td>
<td>−0.1408</td>
<td>O4 0.1327</td>
</tr>
<tr>
<td></td>
<td>O2 0.0098</td>
<td>−0.1518</td>
<td>−0.1408</td>
<td>O4 0.1327</td>
</tr>
<tr>
<td></td>
<td>O1 −0.0005</td>
<td>0.1518</td>
<td>0.1328</td>
<td>O3 −0.1412</td>
</tr>
<tr>
<td></td>
<td>O1 −0.0005</td>
<td>−0.1518</td>
<td>0.1328</td>
<td>O3 −0.1412</td>
</tr>
<tr>
<td></td>
<td>O4 −0.1872</td>
<td>0</td>
<td>−0.0072</td>
<td>O2 −0.0012</td>
</tr>
<tr>
<td></td>
<td>O1f 0.2163</td>
<td>0</td>
<td>0.0486</td>
<td>O3f −0.0569</td>
</tr>
<tr>
<td>N60</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>O2 0.0332</td>
<td>0.1513</td>
<td>−0.1406</td>
<td>O4 0.1368</td>
</tr>
<tr>
<td></td>
<td>O2 0.0332</td>
<td>−0.1513</td>
<td>−0.1406</td>
<td>O4 0.1368</td>
</tr>
<tr>
<td></td>
<td>O1 −0.0033</td>
<td>0.1513</td>
<td>0.1690</td>
<td>O3 −0.1077</td>
</tr>
<tr>
<td></td>
<td>O1 −0.0033</td>
<td>−0.1513</td>
<td>0.1690</td>
<td>O3 −0.1077</td>
</tr>
<tr>
<td></td>
<td>O4 −0.1809</td>
<td>0</td>
<td>0.0178</td>
<td>O2 −0.0085</td>
</tr>
<tr>
<td></td>
<td>O1f 0.2331</td>
<td>0</td>
<td>0.0125</td>
<td>O3f −0.0775</td>
</tr>
</tbody>
</table>

### Table 8 Absolute values of displacement from W15 to N00 or N60. Large displacements occur at specific parts shown in gray.

<table>
<thead>
<tr>
<th>Displacement, (D/\text{nm})</th>
<th>Fe1</th>
<th>Fe2</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>O4</th>
</tr>
</thead>
<tbody>
<tr>
<td>N00-W15</td>
<td>0.009</td>
<td>0.009</td>
<td>0.010</td>
<td>0.041</td>
<td>0.008</td>
<td>0.011</td>
</tr>
<tr>
<td>N60-W15</td>
<td>0.008</td>
<td>0.012</td>
<td>0.040</td>
<td>0.017</td>
<td>0.034</td>
<td>0.027</td>
</tr>
</tbody>
</table>

Relative positions of Fe and O sites in the rectangular coordinates and the volumes of octahedron around Fe1 and Fe2 sites (1/4V_{Fe1} and 1/4V_{Fe2}) are listed in Table 7.

To show the positions visually, it is convenient that they are projected on a-c plane since a unit cell of $\beta$-phase was assigned to monoclinic symmetry of space group I2/m with miller-plane normal to b-axis. Schematic drawings of the atomic positions are shown in Fig. 11. The position shifts from W15 to N00 or N60, i.e. “displacement” of each site in an enlarged scale are also shown in Fig. 12. The absolute values of the displacements from W15 to N00 or N60 are also listed in Table 8. As is shown in Fig. 11(a) and Fig. 12, it is clear that the displacements of oxygen sites are much larger than those of Fe ones. As also shown in Table 8, when Cl occupancy changed, large displacements occur at some specific O sites, i.e. O2 sites for N00-W15 and O1, O3, O4 sites for N60-W15 while at other sites, they are much smaller (1/3-1/4).
Atomic positions of H sites were studied by Post et al. using neutron diffraction analysis. They found that H sites near tunnel sites (H1 and H2) lies near to a straight line connecting O and Cl (tunnel) sites. They pointed out that such alignments of O, H and Cl ions are due to hydrogen bonds formation between them, i.e. [O1–H1/Cl1/Cl1/Cl1] and [O3–H2/O1/Cl1/Cl1]. H⁺ ions will be attracted to Cl⁻ ions when a tunnel site is occupied by a Cl⁻ ion whereas O²⁻ ions attract H⁺ ions when a tunnel site is vacant. Therefore, the positions of O²⁻ ions close to tunnel sites (O1 and O3) likely shift toward H⁺ ions with decreasing u. Large displacements of O sites in Fig. 11 can be understood by not only charge neutrality discussed in section 4.3.1 but also formation of hydrogen bonding.

The Fe-O distances in octahedra and the difference of them between samples are listed in Table 9. There are large differences of Fe-O distances between N00-W15 at only Fe1-O2-Fe2 connections and those between N60-W15, at O1-Fe1-O1f and O3-Fe2-O3f while others are much smaller. As was shown in Fig. 11(b), the O2 site is connected to different Fe sites, Fe1 and Fe2 whereas O1 and O3 sites are connected to the same Fe sites, Fe1 and Fe2, respectively.

Table 9 Distances of Fe-O in octahedra and the differences of them between samples (N00-W15, N60-W15). They are large differences at specific parts shown in gray.

<table>
<thead>
<tr>
<th>O sites</th>
<th>O1–Fe1–O1f</th>
<th>Fe1–O2–Fe2</th>
<th>O3–Fe2–O3f</th>
<th>Fe1–O4–Fe2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance, d/\text{nm}</td>
<td>N00</td>
<td>0.211</td>
<td>0.221</td>
<td>0.180</td>
</tr>
<tr>
<td>W15</td>
<td>0.202</td>
<td>0.222</td>
<td>0.207</td>
<td>0.172</td>
</tr>
<tr>
<td>N60</td>
<td>0.227</td>
<td>0.233</td>
<td>0.209</td>
<td>0.177</td>
</tr>
</tbody>
</table>

| Difference, d/\text{nm} | N00–W15 | 0.009 | −0.001 | −0.027 | 0.048 | −0.006 | −0.002 | 0.005 | −0.005 |
| N60–W15 | 0.025 | 0.011 | 0.002 | 0.005 | −0.024 | 0.017 | −0.006 | 0.005 |
In N00, the Fe1-O2 distance become shorter ($d = 0.207 \rightarrow 0.180 \text{ nm}$, $\Delta d = -0.027$) and the Fe2-O2, larger ($d = 0.172 \rightarrow 0.220 \text{ nm}$, $\Delta d = 0.048$), then the O2 ions shift toward the direction from Fe2 to Fe1 sites. Therefore, as was shown in Fig. 10, $V_{\text{Fe1}}$ decreases and $V_{\text{Fe2}}$ increased when the Cl occupancy, $u$ increases from 0.44 (W15) to 0.56 (N00).

On the other hands, in N60, the O1-Fe1 distances become larger (O1-Fe1: $d = 0.202 \rightarrow 0.227 \text{ nm}$, $\Delta d = 0.025$) and O1-Fe1: $d = 0.222 \rightarrow 0.233 \text{ nm}$, $\Delta d = 0.011$), then the O1 ions move away from Fe1 site. Therefore, $V_{\text{Fe1}}$ increase, when $u$ decreases from 0.44 (W15) to 0.25 (N60). In addition, the O3-Fe2 distances become shorter ($d = 0.210 \rightarrow 0.186 \text{ nm}$, $\Delta d = -0.024$) and the O3-Fe2, larger ($d = 0.221 \rightarrow 0.238 \text{ nm}$, $\Delta d = 0.017$). Since the negative difference (−0.024) is larger than the positive one (0.017), $V_{\text{Fe2}}$ decreased slightly when $u$ decreases from 0.44 (W15) to 0.25 (N60).

### 4.3.3 Relationship between oxygen and tunnel sites

In the previous section, we showed that $u$-dependences of $V_{\text{Fe1}}$ and $V_{\text{Fe2}}$ originate from the displacement of the specific O sites by analysis of octahedra. However, why such displacement occur is not clear yet.

To clarify the origin of $u$-dependence of the oxygen displacements, local environment of $O^{2-}$ ions should be taken into account since the $\beta$-phase consists of not only Fe-O octahedra but also tunnel (T) sites. They are shown in Fig. 13. Every $O^{2-}$ ion is connected to three Fe$^{3+}$ ions. Two equidistant T sites exist near a O1 and O3 site while one T site exist near a O2 and O4 one (Fig. 13(a)). The distances between the O and the nearest T sites are also calculated and listed in Table 10. As shown in Fig. 13(b) and Table 10, it is clear that the O-T distance throughout $u$ range increases in the order of O1-T < O3-T < O4-T < O2-T.

Figure 14 is schematic drawings to show directions of the displacements. When $u$ increases from 0.44 (W15) to 0.56 (N00), i.e. Cl ions become to occupy more than 1/2 of T sites, displacement of O2 site locating at the farthest position from T site becomes dominant. In this case, oxygen ions in O2 site shift toward the direction in which the O2-T distance is not much changed (See also Table 10).

On the other hands, when $u$ decreases from 0.44 (W15) to 0.25 (N60), i.e. $v$ increases, large displacements occur at O1, O3 and O4 sites. The largest displacement among them is O1 site locating at the closest position from T site. Oxygen ions in O1 and O4 sites move toward T site whereas those in O3 site shift toward the direction in which the O3-T distance is not much changed (Table 10).

Therefore, it was suggested that the direction and absolute values of oxygen displacements were closely related to $u$ and the O-T distances, and the origin of such displacements would be electrostatic interactions through H$^+$ discussed in section 4.3.1.

### 5. Conclusions

Crystal structure of $\beta$-phase of iron-oxyhydroxide with different Cl occupancy ($u$) in tunnel sites was studied by using high-resolution X-ray diffraction with Rietveld analysis. The following structural characteristics were found:

1. The crystal system of $\beta$-phase was assigned to monoclinic (I2/m) rather than tetragonal (I4/m) throughout $u$ range.
2. The lattice and structure parameters systematically changed depending on $u$.
3. It was estimated that possible $u$ range would be $0.25 \leq u \leq 0.56$ and water molecules with constant fraction, $w \simeq 0.2$ would be also included in tunnel sites, i.e. Fe$^{3+}$O$_{16}$H$_{2w}$Cl$_{2w}$H$_2$O$_{2w}$ ($0.25 \leq u \leq 0.56$ and $w \simeq 0.2$).
4. A sample with $u = 0.44$ showed the highest crystal symmetry throughout the $u$ range.
5. The $u$-dependences of $V_{\text{Fe1}}$ and $V_{\text{Fe2}}$ originate from displacements of specific oxygen sites. The oxygen displacements were closely related to $u$ and the distance between O and tunnel sites.

### Acknowledgements

We are very grateful to Dr. M. Imafuku of Nippon Steel TechnoResearch Corp. and Dr. T. Itoh of AGC Seimichemical Co. for their technical supports on Rietveld analysis. Special thanks to Dr. Yasuo Takagi of Nippon Steel TechnoResearch Corp. for his instructive discussions.
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