Local structure of magnetite and maghemite and chemical shift in Fe K-edge XANES

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Local structures around Fe and chemical shifts in X-ray absorption fine structure (XAFS) spectra were investigated for synthetic Fe$_{1−δ}$O, Fe$_3$O$_4$ (magnetite), γ-Fe$_2$O$_3$ (maghemite), and SrFeO$_3−x$, as well as natural Fe$_3$O$_4$ and α-Fe$_2$O$_3$ (hematite) specimens. XAFS spectra near the Fe K-edge were measured at BL-9C and BL-12C of the Photon Factory, KEK, Japan. Similar measurements for Fe–N pairs in Fe nitrides (FeN, Fe$_2$N, Fe$_4$N) were obtained for comparison. The X-ray absorption near edge structure (XANES) spectra for various iron compounds, in particular Fe$_3$O$_4$ and γ-Fe$_2$O$_3$, and Fe–N specimens, showed clear chemical shifts of half-maximum positions with the changing oxidation states of the Fe ions in their structures. The energy at half maximum position should be used for the quantitative discussion of the oxidation and valence states of the Fe ion in Fe compounds rather than the threshold energy $E_0$ found using differentiating XAFS spectra. The δ values in Fe$_{1−δ}$O$_4$ (δ=0.333 for end-member γ-Fe$_2$O$_3$) for magnetite and maghemite were estimated by the extent of the chemical shifts. Decreases in the average Fe–O distances and extended X-ray absorption fine structure (EXAFS) Debye-Waller factor $σ^2$ values for spinel-type Fe$_{1−δ}$O$_4$ solid-solutions were consistent with the estimated δ values. The error in proving the Fe$^{3+}$/Fe$_{total}$ ratio in the system by the XAFS method would appear to be less than ±0.10, and higher reliability than this value would be acquired in the comparison of relative values at half-maximum positions.

**Keywords**: Local structure of γ-Fe$_2$O$_3$, Magnetite and defect spinel structure, XAFS, Chemical shift, Iron oxides and nitrides

INTRODUCTION

The structures of Fe oxides, Fe$_{1−δ}$O (wüstite), Fe$_3$O$_4$ (magnetite) and γ-Fe$_2$O$_3$ (maghemite), are closely related, having different numbers of cations in the cubic closest packing assembly of oxygen atoms. Fe$_{1−δ}$O has a NaCl-type structure. From an ionic-crystal point-of-view, Fe$_3$O$_4$ has an inverse spinel structure in which half of Fe$^{3+}$ ions occupy tetrahedral cation sites and equal numbers of Fe$^{2+}$ and Fe$^{3+}$ ions share octahedral cation sites. Fe$_{3−δ}$O$_4$ (Fe$_{3-0.333}$O$_4$=γ-Fe$_2$O$_3$), as a Berthollide compound, usually has a cation deficiency with no symmetry lowering. In γ-Fe$_2$O$_3$, selective formation of cation vacancies at octahedral cation sites and their ordering result in symmetry lowering from Fd-3m to P4$_3$2$_1$2 or P4$_4$2$_2$2 (Pecharromán et al., 1995). Site symmetry at the octahedral cation site is also decreased from .−3m in Fd-3m to .32 (at 4b) or .2 (at 12d) in P4$_3$2$_1$2. Careful oxidation of Fe$_3$O$_4$ yields γ-Fe$_2$O$_3$, and the reverse is also possible by heating in vacuo at ≈ 200 °C. Moreover, γ-Fe$_2$O$_3$ converts to α-Fe$_2$O$_3$ (hematite) on heating in air. Another Fe oxide, α-Fe$_2$O$_3$ has a corundum-type structure with a hexagonal closest packing assembly of oxygen atoms.

The X-ray absorption near-edge structure (XANES) is quite sensitive to the oxidation state of the absorbing
atoms and the three-dimensional atomic configurations around those atoms, and it offers information that diffraction experiments cannot yield. It is well known that the significant variation in Fe K-edge XANES spectra reflects the difference in first and higher-order neighboring environments (Waychunas and Apted, 1982). The XANES feature varies with oxidation state and coordination environment. The chemical shift of an absorption edge larger than 3 eV is found between Fe$^{2+}$ and Fe$^{3+}$ in various minerals (Calas and Petian, 1983; Waychunas and Apted, 1982). The chemical shift near the threshold energy in the XANES region is also dependent on the effect of covalent iron-anion bonding on the state of orbitals near the Fermi level. The covalent nature of sulfide bonds is stronger than for oxides, and the extent of shift in sulfides becomes smaller between Fe$^{2+}$ and Fe$^{3+}$. Therefore, general application of the XANES region for determining the oxidation state in any iron-based mineral is limited. Nevertheless, systematic trends in spectral features suggest that Fe$^{3+}$/Fe$^{\text{total}}$ values could be obtained from XANES spectra, with accuracy comparable to Mössbauer spectroscopy, by reference to empirical calibration curves from similar standards (Berry et al., 2003). XANES spectroscopy has the potential for the determination of oxidation states in minerals with similar structures and compositions. It was proposed that the quantitative determination of the Fe$^{3+}$/Fe$^{\text{total}}$ ratio is possible by XANES spectroscopy and uncertainty in the ratio is determined as $\sigma(\text{Fe}^{3+}/\text{Fe}^{\text{total}})$ = 0.02 (Berry et al., 2003) and = 0.03–0.10 (Dyar et al., 2002). Many methods have been proposed to estimate the extent of chemical shift and the quantitative reliability of Fe$^{3+}$/Fe$^{\text{total}}$ changes.

In this study, local structures around Fe and the extended X-ray absorption fine structure (EXAFS) Debye–Waller factor $\sigma^2$ (Å$^2$) for Fe-O bonds were investigated by the XAFS technique at the Fe K-edge for natural Fe$_3$O$_4$ magnetite-maghemite solid-solution, natural FeO$_2$ hematite and synthetic Fe$_{1-x}$O$_{y}$ Fe$_2$O$_4$, γ-Fe$_2$O$_3$, α-Fe$_2$O$_3$, and SrFeO$_2$. These structures are closely related. XAFS for Fe-N pairs in Fe nitrides (FeN, Fe$_3$N, Fe$_5$N) were also measured for comparison. The detailed features of XANES spectra, radial distribution around Fe, oxidation state of the Fe ion, and chemical shift were discussed.

**EXPERIMENTAL AND ANALYSIS**

Commercially available Fe$_{1-x}$O (99.9%) and Fe$_3$O$_4$ (99.9%: sp1) (Furu-uchi Chem. Co., Ltd.) and γ-Fe$_2$O$_3$ (99.9%: sp2) (CI Chem. Co., Ltd) were used. The samples of Fe$_5$N, Fe$_3$N, FeN and perovskite-type SrFeO$_2$ were the same specimens as published previously (Kikkawa et al., 2008a; Kikkawa et al., 2008b; Okube et al., 2008).

The crystals of Fe$_3$O$_4$ (sp2) and γ-Fe$_2$O$_3$ (sp1) were synthesized by oxidation of Fe$_3$O$_4$ in vacuo at 190 °C for 7 hours and 21 hours, respectively. The chemical compositions for synthesized specimens were determined using wet chemical methods and a Horiba EMGA620W oxygen/nitrogen combustion analyzer (Kikkawa et al., 2008a; Yamanaka et al., 2007). The estimated δ values in the Fe$_3$O$_4$ formula for Fe$_3$O$_4$ (sp2) and γ-Fe$_2$O$_3$ (sp1) were 0.060 and 0.245, respectively. A natural magnetite Fe$_3$O$_4$ (sp3) specimen from Bizan, Tokushima, Japan, and a natural hematite α-Fe$_2$O$_3$ specimen from Komezuka, Kumamoto, Japan, were also examined. The iron contents for natural Fe$_3$O$_4$ (sp3) and natural hematite specimens were estimated using a JCMA–733II electron microprobe analyzer. The iron contents in pure Fe$_3$O$_4$ and pure Fe$_2$O$_3$ are the ideal values of 72.34 wt% and 69.94 wt%, respectively. Because the difference between them is 2.4, it is possible to determine the Fe$_3$O$_4$ and FeO ratio by assuming that the total weight percentage of cation and oxygen should be 100%. The percentage of Fe$_3$O$_4$ and FeO for each natural specimen was re-calculated so that the total weight might be 100%, using the results assuming the ideal end-member compositions. The obtained δ values for Fe$_3$O$_4$ (sp3) and natural hematite were 0.02 and 0.33, respectively. All specimens were characterized by the X-ray diffraction technique.

Fine powdery specimens were mixed with BN powder and pressed into pellets of <0.2 mm in thickness and 10 mm in diameter. All samples showed edge jumps of 0.7 (Åμt) by adjusting the sample content, where μ is the linear absorption coefficient and t is the sample thickness. XAFS spectra near the Fe K-edge were measured in transmission mode at BL–9C and BL–12C of the Photon Factory in the National Laboratory for High Energy Physics (KEK), Tsukuba, Japan. A Si(111) double monochromator and focusing mirror were installed at the upstream side. The X-ray energy calibration was performed by setting the copper metal pre-edge absorption peak to 8.9788 keV.

The EXAFS interference function, $\chi(k)$, was extracted from the measured absorption spectrum using a standard procedure (Maeda, 1987; Yoshihisa et al., 1999a; Yoshihisa et al., 1999b). The radial structural function was obtained by Fourier transform over the k range of 2.5–11.5 Å$^{-1}$ (Fig. 1). In the quantitative analysis we employed a Fourier filtering technique and a nonlinear least-squares fitting method (Maeda, 1987; Yoshihisa et al., 2000). The XAFS93 program (Maeda, 1987) was employed for the data analysis. The mean free path, $\lambda$, of the photoelectron was assumed to depend on the wave number, $\lambda(k) = k/\eta$, where η is a constant. The local bonding distance differs in coordination number and valence state. Two or more kinds of distance parameters exist in iron compounds with
Local structure in Fe K-edge XANES

A spinel structure. Single-shell and double-shell fitting were carried out for the first-neighbor distances, where the number of neighboring atoms was fixed at crystallographic values. The structural model obtained by the diffraction method was used for the initial parameters in the double-shell model. In the single-shell model, obtained structure parameters were not dependent on initial values and converged to the same values. The single-shell model had little model dependence and was applicable to comparison with any compounds. The reliability index, \( R \), between the experimental and calculated EXAFS function was less than 0.057. Fe-O distances derived from least-squares fit to Fourier-filtered EXAFS spectra are listed in Tables 1 and 2.

Table 1. Local Fe-O distance by the double-shell and single-shell models

<table>
<thead>
<tr>
<th></th>
<th>Double-shell model</th>
<th>Single-shell model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe-O ((\text{Å}))</td>
<td>CN</td>
</tr>
<tr>
<td>(\alpha)-Fe(_2)O(_3)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(_{1-x})O</td>
<td>Fe(_{1-x})O</td>
<td>2.13(1)</td>
</tr>
<tr>
<td>Fe(_{1-x})O</td>
<td>Fe(_{1-x})O</td>
<td>1.953(8)</td>
</tr>
<tr>
<td>Fe(_{1-x})O ((\text{sp1}))</td>
<td>Fe(_{1-x})O</td>
<td>2.17(1)</td>
</tr>
<tr>
<td>Fe(_{1-x})O</td>
<td>Fe(_{1-x})O</td>
<td>1.97(1)</td>
</tr>
</tbody>
</table>

EXAFS Debye-Waller factor \(\sigma^2\) by the single-shell model was correlated to the bonding distance. The coordination number and occupancy ratio were fixed by crystallographic information.

Table 2. Local Fe-O distances for spinel-type Fe\(_{1-x}\)O\(_3\) solid-solutions by the single-shell model

<table>
<thead>
<tr>
<th></th>
<th>Fe-O ((\text{Å}))</th>
<th>(\sigma^2) ((\text{Å}^2))</th>
<th>(\eta) value</th>
<th>R value</th>
<th>(\delta_{\text{chem-shift}})</th>
<th>(\delta_{\text{chem-analysis}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(_{2})O(_4) (sp1)</td>
<td>2.035(5)</td>
<td>0.0188(12)</td>
<td>1.03(9)</td>
<td>0.006</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>Fe(_{2})O(_4) (sp2)</td>
<td>2.013(5)</td>
<td>0.0178(12)</td>
<td>1.05(8)</td>
<td>0.046</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Fe(_{2})O(_4) (sp3)</td>
<td>2.024(5)</td>
<td>0.0179(12)</td>
<td>1.00(8)</td>
<td>0.039</td>
<td>0.015</td>
<td>0.02</td>
</tr>
<tr>
<td>(\gamma)-Fe(_{2})O(_3) (sp1)</td>
<td>1.980(5)</td>
<td>0.0153(10)</td>
<td>0.94(9)</td>
<td>0.057</td>
<td>0.242</td>
<td>0.245</td>
</tr>
<tr>
<td>(\gamma)-Fe(_{2})O(_3) (sp2)</td>
<td>1.972(4)</td>
<td>0.0140(10)</td>
<td>1.06(7)</td>
<td>0.011</td>
<td>0.333</td>
<td>-</td>
</tr>
</tbody>
</table>

The estimated \(\delta_{\text{chem-shift}}\) values in Fe\(_{2}\)O\(_4\) for Fe\(_{2}\)O\(_4\) (sp2), Fe\(_{2}\)O\(_4\) (sp3) and \(\gamma\)-Fe\(_{2}\)O\(_3\) (sp1) by chemical shift are shown, where the \(\delta_{\text{chem-shift}}\) values for Fe\(_{2}\)O\(_4\) (sp1) and \(\gamma\)-Fe\(_{2}\)O\(_3\) (sp2) were assumed as the ideal end-member compositions. The \(\delta_{\text{chem-analysis}}\) values for Fe\(_{2}\)O\(_4\) (sp2), Fe\(_{2}\)O\(_4\) (sp3) and \(\gamma\)-Fe\(_{2}\)O\(_3\) (sp1) were determined by chemical analyses. The coordination number was fixed at 5.33 and \(\eta\) was the mean free path parameter.

Figure 1. Fourier transforms of the Fe K-edge EXAFS spectra for (a) \(\alpha\)- and \(\gamma\)-Fe\(_2\)O\(_3\), and (b) Fe\(_{1-x}\)O and Fe\(_{1-x}\)O. No phase shift correction was applied.
RESULTS AND DISCUSSION

XANES and dXANES for Fe oxides

The Fe K-edge XANES spectra for γ-FeO₂ and various kinds of Fe₃O₄, including natural specimens are shown in Figure 2a. Peak amplitudes were normalized to unity in this and the following diagrams. The XANES spectra were similar to each other because these phases have the same structure, except for the presence of cation vacancies, and FeO₆ octahedra in both phases were close to the regular one. Clear changes in pre-edge features were not observed among these compounds (Fig. 2). Both the main peak position and the energy at half-maximum for these oxides simply shifted to higher energy with increasing Fe³⁺ content: the difference in chemical shifts of the Fe K-edge was clearly visible in XANES spectra from Fe₃O₄ (sp1) and γ-Fe₂O₃ (sp2). The oxidation state can be estimated by the extent of chemical shifts, where we assume linearity in the chemical shift energy, and FeO₆ octahedra have the ideal end-member compositions. The δ values in Fe₃O₄ for Fe₃O₄ (sp2), FeO₆ (sp3) and γ-Fe₂O₃ (sp1) were 0.061, 0.015 and 0.242, respectively.

Details in XANES spectra can be examined more precisely by differentiating the XANES profile with photon energy (dXANES: Fig. 2b). Small changes in the oxidation state can also be examined utilizing dXANES. Figure 2b shows dXANES profiles for FeO₆ and γ-Fe₂O₃ with a small shift of the profile toward higher energy with increasing Fe³⁺ content. A certain kind of magnetite (sp2: oxidized magnetite) also showed a small shift of the profile toward higher energy with a small shift of the profile toward higher energy with increasing Fe³⁺ content. The features of the XANES spectra for the Fe nitrides were clearly different (Fig. 3b). Changes in the half-maximum positions with the Fe:N ratio were clearly visible in the nitrides, as in the Fe oxides. However, the threshold energy, E₀, of the target atom is usually defined at the maximum peak position in the dXANES profile. As seen in Figure 2b, dXANES profiles from FeO₆ and γ-Fe₂O₃, however, do not show a simple convex profile but rather, multiple peaks in the 7.115-7.13 keV range. For FeO₆ (sp3), the highest and the second-highest peaks at 7.122 keV and 7.126 keV, respectively, have basically the same height, and the normal procedure for defining E₀ does not apply. Even though FeO₆ and γ-Fe₂O₃ showed similar dXANES profiles with a chemical shift of entire profiles, the interpretation of dXANES spectra was complex.

Figure 3 shows the Fe K-edge XANES spectra for each of the Fe oxides and nitrides. The edge features were quite similar in Fe₃⁺O₆, FeO₆, and γ-Fe₂O₃, all of which had FeO₆ octahedra with little, if any, distortion (Fig. 3a). On the other hand, the XANES profiles from α- and γ-Fe₂O₃ were apparently different, despite having the same composition. Although they showed a similar extent of chemical shift, there was a shoulder on the lower energy side only on α-Fe₂O₃. This difference was due to the large distortion of FeO₆ octahedra in the α-Fe₂O₃ structure and thus, a splitting of the Fe³⁺ energy level at the site. Further, although the chemical shift of cubic perovskite-type SrFeO₃₋ₓ, in which Fe⁴⁺ locates at the center of a regular FeO₆ octahedron, at a half-maximum position was at higher energy than those of Fe₃⁺O₆, α-Fe₂O₃, and γ-Fe₂O₃ as expected from Fe⁴⁺ in SrFeO₃₋ₓ, its main peak position in the XANES spectrum was located at lower energy than those of Fe₃⁺O₆, α-Fe₂O₃, and γ-Fe₂O₃. This means that the main peak position did not directly reflect the oxidation state of the target atom in these structures.

The features of the XANES spectra for the Fe nitrides were clearly different (Fig. 3b). Changes in the half-maximum positions with the Fe:N ratio were clearly visible in the nitrides, as in the Fe oxides. However, the
main peak position showed an opposite trend, and determination of the valence state was difficult from the main peak positions in XANES and the maximum values in dXANES. In consequence, the energy at the half-maximum position in the XANES spectrum should be used for qualitative discussion of the oxidation and valence states of the Fe ion in Fe compounds rather than the threshold energy $E_0$ found by the differentiating XAFS spectrum.

Local Fe-O distances and EXAFS Debye-Waller factor $\sigma^2$ in Fe compounds

In Figure 1, the radial structural function for $\alpha$-Fe$_2$O$_3$ can be distinguished from $\gamma$-Fe$_2$O$_3$ according to the shape, with its shoulder and height, for the second nearest Fe-Fe peak, though a clear difference in shape was not seen in Fe$_{1-d}$O, Fe$_{3-\delta}$O$_4$, or $\gamma$-Fe$_2$O$_3$. The height for each peak depends on the coordination number, site symmetry, and amplitude of the Debye–Waller factor. Though the expected values were acquired by the double-shell model, the double-shell fitting was model dependent and had a disappointing calculation error due to correlation among parameters (Table 1). The single-shell model had little model dependence and was applicable for comparison with any compounds, including disordered and random phases. Table 1 shows the average Fe-O distances and EXAFS Debye–Waller factors $\sigma^2$ determined by the single-shell model. The average Fe-O distances for magnetite were longer than those for $\gamma$-Fe$_2$O$_3$ due to contributions from the longer Fe$^{2+}$-O distances in FeO$_6$ octahedra. The difference in the Fe-O distance between Fe$_3$O$_4$ (sp1) and $\gamma$-Fe$_2$O$_3$ (sp2) was 0.06 Å, which is significant in comparison to the analytical error ($\pm 0.005$). The relative comparison of results by precise EXAFS analyses has an accuracy that can determine the thermal expansion coefficient (Yoshiasa et al., 1999a). Decreases in the average distances and $\sigma^2$ values for spinel-type Fe$_{3-\delta}$O$_4$ solid-solutions were consistent with the estimated $\delta$ values. We conclude that the error in proving the Fe$^{3+}$/Fe$_{\text{total}}$ ratio in the system by the XAFS method would appear to be less than $\pm 0.10$, and higher reliability than this value would be acquired in the comparison of relative values at half-maximum positions.

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