First Principles Calculation of Fe $L_{2,3}$-edge X-ray Absorption
Near Edge Structures of Iron Oxides

Hidekazu Ikeno$^{1,*1}$, Isao Tanaka$^1$, Toru Miyamae$^{1,*1}$, Takahiro Mishima$^{1,*2}$, Hirohiko Adachi$^1$ and Kazuyoshi Ogasawara$^2$

$^1$Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan
$^2$School of Science and Technology, Kwansei Gakuen University, Sanda 669-1337, Japan

X-ray absorption near edge structure (XANES) at $L_{2,3}$-edge of 3d transition elements is dominated by strong correlation effects among 2p core hole and 3d electrons. In the present study, we have performed systematic configuration interaction (CI) calculations in order to reproduce and interpret Fe-$L_{2,3}$ XANES of FeO, LaFeO$_3$ and SrFeO$_3$. Relativistic four components wave functions were obtained by solving Dirac equations with density functional theory. CI calculations were made using the relativistic molecular orbitals instead of atomic orbitals, which enables inclusion of the O-2p orbital contributions through covalency. The oscillator strength of the electric dipole transition was then computed. Experimental XANES spectra of three compounds were satisfactorily reproduced by the theoretical spectra obtained for (FeO)$_{\text{m+n}}$ clusters in octahedral symmetry. Chemical shifts between compounds were quantitatively reproduced as well. Component analysis of CI was systematically made in order to analyze the origin of differences in spectral shapes.

(Received November 25, 2003; Accepted January 6, 2004)

Keywords: X-ray absorption, electron energy-loss near edge structures (ELNES), relativistic effects, configuration interactions, iron oxides

1. Introduction

Many oxides of 3d transition elements have been widely used in modern technology. Since 3d electrons play central roles in them, experimental characterization of the 3d electrons is very important. X-ray absorption near edge structures (XANES) as well as electron energy loss near edge structures (ELNES) provides detailed information on electronic states near the Fermi energy. It monitors electronic transitions from a core orbital to unoccupied states that are allowed by electric dipole transition rule. The 3d states can therefore be analyzed directly using either $L_{2,3}$-edge or $M_{2,3}$ edge XANES and ELNES. 3d elements have $L_{2,3}$-edge in a few 100 eV region, which is desirable for soft X-ray experiments as well as for ELNES. As a matter of facts, there have been a number of experimental $L_{2,3}$ XANES are available for major 3d-metal compounds. Their chemical shifts, spectral shape as well as the ratio between $L_2$ and $L_3$ spectra, i.e., branching ratio have been systematically investigated. The most primitive way to analyze the spectra is a so-called finger printing technique. A measured spectrum is identified by comparison with reference spectra obtained for standard materials. However, the finger printing technique is obviously not useful for new systems in which atomic/electronic structures are not analogous to preexisting compounds. A good theoretical tool to analyze the experimental spectra is therefore mandatory. If one can obtain reliable theoretical spectrum for a given atomic arrangements and electronic states, the theoretical spectrum can be used as a new finger print.

A popular method to compute theoretical $L_{2,3}$-edge XANES is the crystal field multiplet calculation in which crystal field effects are incorporated into an atomic multiplet program using group theoretical formalism. Crystal field effects are included with parameters and they are determined so as to best fit to experimental spectra. A number of compounds have been investigated through this approach, and the parameters have been determined for many ions with different valence states and coordination environment. Although this method has been successful for reproducing many experimental spectra, the major drawback can be found in the method that uses empirical parameters. With the decrease of the symmetry of ligand field, the number of empirical parameters increases, thereby giving rise to the ambiguity of the computational results. Entirely first principles method is therefore strongly required.

In 2001, a novel method to perform such a non-empirical calculation has been reported by the present authors’ group. Totally relativistic first principles molecular orbital calculations were made. Electronic correlations among $2p_{1/2}$, $2p_{3/2}$ and 3d electrons were rigorously calculated by taking Slater determinants of all electronic configurations made by these molecular orbitals. In other words, configuration interactions (CI) among these molecular orbitals were computed. They have succeeded in reproducing experimental spectra from three compounds having different d-electron numbers and coordination numbers, i.e., SrTiO$_3$, NiO and CaF$_2$. In the present study, we have extended this method to three kinds of iron oxides with different formal charges, i.e., FeO (Fe(II)), LaFeO$_3$ (Fe(III)), and SrFeO$_3$ (Fe(IV)). The usefulness of the method for the iron compounds with different formal d-electron numbers is confirmed. Components analysis of CI has been made to analyze the origin of peaks that appear in the spectra.

2. Computational Procedure

For the calculation of theoretical Fe $L_{2,3}$-edge XANES, model clusters of (FeO)$_{\text{m+n}}$ that are composed of an Fe ion and six nearest neighbor O ions were used. The total number of electrons in the cluster was obtained from formal charges,
Thus $m = 10, 9, 8$ for FeO (Fe(II)), LaFeO$_3$ (Fe(III)), and SrFeO$_3$ (Fe(IV)) respectively. All cluster models were made to show octahedral ($O_h$) symmetry for simplicity even when real crystals exhibit slight distortion from the cubic symmetry. The Fe-O bond lengths were 216.0, 195.0 and 192.5 pm for FeO, LaFeO$_3$, and SrFeO$_3$, respectively. In order to take account effective Madelung potential, point charges were put at the external atomic sites.

Fully relativistic molecular orbital (MO) calculations were carried out by solving Dirac equations with density functional theory using relativistic SCAT code. In this code, four-component relativistic molecular orbitals are expressed as linear combination of atomic orbitals (LCAO). The numerically generated four-component relativistic atomic orbitals (1$s$ to 4$p$ for Fe and 1$s$ to 2$p$ for O) were used as basis functions.

After one electron calculations of relativistic MO, configuration interaction (CI) calculations were performed. In present calculation, only Fe 2$p$ orbitals and MO mainly composed of Fe 3$d$ orbitals were considered explicitly, since the CI calculation for all $N$ electrons in the cluster requires prohibitive computational time and resources. An effective many-electron Hamiltonian is expressed as,

$$H = \sum_{i=1}^{n} h(r_i) + \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{1}{|r_i - r_j|},$$

where $n$ is the number of electrons in the selected MO. The one-electron operator $h(r_i)$ is described as,

$$h(r_i) = -\frac{1}{2}\nabla^2 + \frac{\alpha}{r_i} + \beta c^2 - \sum_{s} \frac{Z_s}{|r_i - R_s|} + V_0(r_i),$$

where $\alpha$, $\beta$ are Dirac matrices, $c$ is the velocity of light, $p_i$ is the momentum operator, $Z_s$ is the charge of $s$th nucleus, and $V_0(r)$ is the potential from other $N$-n electrons. In this approach, the Coulomb interaction and exchange-correlation interaction among the selected $n$ electrons are considered explicitly, while those interactions between the selected $n$ electrons and other $N$-n electrons are included in $V_0(r)$. The explicit form of $V_0(r)$ was derived by Watanabe and Kamimura.

As basis functions to diagonalize the many-electron Hamiltonians described in eq. (2.1), all the possible Slater determinants corresponding to the ground state (GS) configuration and the excited state (ES) configuration including a core hole were constructed. The many-electron wave functions are then expressed as linear combination of those Slater determinants

$$\Psi_i = \sum_{\lambda=1}^{M} C_{\lambda i} \Phi_{\lambda},$$

where $M$ is the number of Slater determinants.

In the case of FeO (Fe(II)), the GS configuration is $(2p)^6(\phi_{3d})^5$, and the ES configuration is $(2p)^7(\phi_{3d})^5$ where $\phi_{3d}$ denotes the MO mainly composed of Fe 3$d$ orbitals. The possible electronic configurations for GS are 210 (= $sC_6 \times 10C_4$) and those of ES are 720 (= $sC_5 \times 10C_4$). Thus 930 of Slater determinants were used as basis functions. For LaFeO$_3$ (Fe(III)), the GS configuration is $(2p)^6(\phi_{3d})^5$, and the ES configuration is $(2p)^7(\phi_{3d})^5$. The possible electronic configurations for GS are 252 (= $sC_6 \times 10C_5$) and those of ES are 1260 (= $sC_5 \times 10C_6$). 1512 of Slater determinants were therefore used as basis functions. Regarding SrFeO$_3$ (Fe(IV)), the GS configuration is $(2p)^8(\phi_{3d})^4$, and the ES configuration is $(2p)^9(\phi_{3d})^5$. The possible electronic configurations for GS are 210 (= $sC_6 \times 10C_4$) and those of ES are 1512 (= $sC_5 \times 10C_5$). The number of Slater determinants used as basis functions was 1722.

The matrix elements of $H$ between two Slater determinants, $\Phi_p$ and $\Phi_q$, can be generally expressed as,

$$H_{pq} = \langle \Phi_p | H | \Phi_q \rangle = \sum_{i=1}^{L} \sum_{j=1}^{L} A_{ij}^{pq} (|i| |j|) + \sum_{i=1}^{L} \sum_{j=1}^{L} \sum_{k=1}^{L} \sum_{l=1}^{L} B_{ijkl}^{pq} (|ij| |kl|),$$

where $L$ is the number of selected MO and,

$$\langle ij | hj \rangle = \sum_{\lambda=1}^{M} \sum_{\mu=1}^{M} \int \phi_{\lambda i}^*(r)h_{\mu j}(r)\phi_{\mu j}(r)dr,$$

$$\langle ij | kl \rangle = \sum_{\lambda=1}^{M} \sum_{\mu=1}^{M} \int \phi_{\lambda i}^*(r)\phi_{\mu j}^*(r)dr \times \frac{1}{|r_i - r_j|} \phi_{\mu k}(r)\phi_{\lambda l}(r)dr_1 dr_2.$$

Here $h_{\lambda i}(r)$ is the $\lambda$th component of the $i$th relativistic MO and $h_{\mu j}(r)$ is the $\mu$th component of the $j$th relativistic MO. The coefficients $A_{ij}^{pq}$ and $B_{ijkl}^{pq}$ can be obtained by expanding the Slater determinants.

The oscillator strength of the electric dipole transition averaged over all directions is given by

$$I_{ij} = \frac{2}{3} (E_j - E_i) \left| \Phi_i \sum_{k=1}^{n} \sum_{k=1}^{n} |r_k| \Phi_j \right|^2,$$

where $\Phi_i$ and $\Phi_j$ are many-electron wave functions for the initial state and the final state, while $E_i$ and $E_j$ are their energies. Using eq. (2.3), eq. (2.7) can be expanded as

$$\langle \Phi_i | \sum_{k=1}^{n} \sum_{k=1}^{n} |r_k| \Phi_j \rangle = \sum_{\lambda=1}^{M} \sum_{\mu=1}^{M} C_{\lambda i}^* C_{\mu j} \left\langle \Phi_i \sum_{\lambda=1}^{M} \sum_{\mu=1}^{M} C_{\lambda i}^* C_{\mu j} \right\rangle \Phi_j \sum_{\lambda=1}^{M} \sum_{\mu=1}^{M} A_{ij}^{pq} (k|l|),$$

where

$$\langle k | l \rangle = \sum_{\lambda=1}^{4} \int \phi_{\lambda i}^*(r)\phi_{\lambda j}(r)dr.$$

3. Results and Discussion

Calculations were made for FeO (Fe(II)), LaFeO$_3$ (Fe(III)), and SrFeO$_3$ (Fe(IV)). With the increase of the formal charge of transition elements, the covalent bonding between Fe-3$d$ and O-2$p$ is known to increase in general. Figure 1 shows contour maps of $t_{2g}$ molecular orbitals in three clusters obtained by non-spin polarized and non-relativistic calculations. The O-2$p$ component in $t_{2g}$ is found
to increase with the increase of the formal charge of Fe. As a matter of fact, atomic orbital population of O-$2p$ is 2%, 7% and 18% in $t_{2g}$ for FeO, LaFeO$_3$, and SrFeO$_3$, respectively. The atomic orbital population of O-$2p$ is greater for $e_g$ orbital. They are 9%, 16% and 23% for FeO, LaFeO$_3$, and SrFeO$_3$, respectively. CI calculations using the molecular orbitals instead of atomic orbitals enable inclusion of the O-$2p$ orbital contributions through the covalency. Using relativistic molecular orbitals, CI calculations were thoroughly made. Computed oscillator strengths given by eq. (2.7) were shown with bars in Fig. 2. They were broadened by Gaussian functions of FWHM = 1.0 eV to make theoretical $L_{2,3}$-edge XANES. They are compared with experimental spectra in Fig. 2. Best fitting with experimental spectra can be found when absolute transition energy of the theoretical spectra is shifted by $-6.4$ eV. The error may be ascribed to underestimation of correlation effects in the present theoretical method as discussed by Ogasawara et al. 6,7 When all theoretical spectra are shifted for the same amount, they can reproduce three experimental spectra to the details. Chemical shifts of each compound as defined by the relative position of the most prominent peak are also well reproduced. As compared with FeO, it is $+2.2$ eV for both LaFeO$_3$ and SrFeO$_3$. Figure 3 shows contributions of four configurations to many electron eigenvalues. Although only a part of these components significantly contribute for the oscillator strength, the diagram is quite useful. The $L_3$ absorption can be divided into two parts with different number of electrons in $t_{2g}$ and $e_g$ orbitals. Therefore, the width of the $L_3$

![Fig. 1 Contour map of $t_{2g}$ molecular orbital in $(\text{FeO}_6)^{n-}$ cluster obtained by non-relativistic and non-spin polarized calculation. Solid and dotted curved are for positive and negative values, respectively.](image1)

![Fig. 2 Theoretical Fe $L_{2,3}$-edge XANES in (a) FeO, (b) LaFeO$_3$ and (c) SrFeO$_3$ (upper panel), and corresponding experimental XANES spectra taken from Refs. 10) and 11) (lower panel). Bars in the upper panel show oscillator strength with many-electron eigenvalues before the Gaussian broadening.](image2)
absorption is primarily determined by the difference in the averaged energy of two configurations, which is given by the excitation energy from \( L_2 \) to \( L_3 \). The energy is called 10Dq or \( \Delta_0 \) when a metal ion is octahedrally coordinated. Theoretical \( \Delta_0 \) for three clusters as estimated by the difference in one-electron eigenvalues was 1.1, 1.8 and 1.8 eV for FeO, LaFeO\(_3\), and SrFeO\(_3\), respectively. The larger \( \Delta_0 \) by 39% explains why the \( L_3 \) of LaFeO\(_3\), and SrFeO\(_3\) show a tail toward high energy in the region at around 714 eV. FeO does not show such a tail.

No overlap between \( L_3 \) and \( L_2 \) can be found for FeO. A small overlap can be found for both LaFeO\(_3\) and SrFeO\(_3\). The magnitude of the overlap can be primarily determined by the magnitude of the splitting between \( 2p_{1/2} \) and \( 2p_{3/2} \). However, the magnitude of splitting is not dependent on valence state of ions. As a matter of fact, the splitting for Fe-2p levels in three clusters is the same as 12.5 eV by the present relativistic calculation. The origin of the overlap between \( L_3 \) and \( L_2 \) in LaFeO\(_3\) and SrFeO\(_3\) cannot be explained by the difference in the splitting of Fe-2p levels. The overlap can be explained by the difference in \( \Delta_0 \), which is the same origin as the tail in the \( L_3 \) spectrum toward high energy in LaFeO\(_3\) and SrFeO\(_3\).

Measurement and interpretation of Fe-L\(_{2,3}\) spectra of LaFeO\(_3\) and SrFeO\(_3\) have been made by Abbate, de Groot and coworkers in 1992.\(^{10}\) They have concluded that the presence of a ligand hole as denoted by \( L \) play a major role in determining the spectrum of SrFeO\(_3\). Using the crystal field multiplet method, they claimed that the calculation taking 3d\(^4\) as a ground state cannot reproduce the experimental spectrum. They have proposed that the use of 3d\(^2\)L as a ground state configuration of SrFeO\(_3\) is essential. In the present calculation, however, the experimental spectrum can be satisfactorily reproduced by the calculation by taking \( \phi_{3d} \) as a ground state, where \( \phi_{3d} \) is the molecular orbital mainly composed of Fe-3d. It is true that significant admixture of O-2p and Fe-3d takes place especially for Fe(IV). There should be non-negligible contribution of the ligand hole to the Fe-L\(_{2,3}\) spectrum. However, the major part of the contribution can be included by the CI calculations using the molecular orbitals instead of atomic orbitals. Using the computational method in this study, the major part of the ligand hole effect on the L\(_{2,3}\) spectrum can be included without information on the covalency \textit{a priori}. Thus the present method should be more useful for analysis of new kind of materials in which little information is available.

4. Summary

First principles calculation of Fe-L\(_{2,3}\) XANES of FeO, LaFeO\(_3\) and SrFeO\(_3\) have been made by CI calculations using fully relativistic four components wave functions. Relativistic MO calculations were carried out by solving Dirac equations with density functional theory. CI calculations were made using the molecular orbitals instead of atomic orbitals, which enables inclusion of the O-2p orbital contributions through covalency. Then the oscillator strength of the electric dipole transition was computed. Experimental XANES spectra of three compounds were satisfactorily reproduced by the theoretical spectra obtained for (FeO\(_6\))\(^{m-}\) clusters in octahedral symmetry. Chemical shifts between compounds were quantitatively reproduced as well. Component analysis of CI was systematically made in order to analyze the origin of differences in spectral shapes.
Acknowledgements

This work was supported by three programs from Ministry of Education, Science, Sports and Culture of Japan, i.e., 1) Grant-in-aid for Scientific Research on Priority Areas (No. 751), 2) Computational materials science unit in Kyoto University, and 3) 21st century COE program.

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