**Ab-Initio** Multiplet Calculations of Fe-\(L_{2,3}\) X-ray Absorption Spectra in LiFePO\(_4\) and FePO\(_4\)**

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Soft X-ray absorption near-edge structures (XANES) at the \(L_{2,3}\)-edges of transition metal has been widely used for investigating the chemical reactions during charge-discharge cycles in the cathode materials of lithium-ion batteries. In order to extract the information about the electronic structures from the experimental results, however, a theoretical tool that can deal with the strong electronic correlations between 2\(p\) and 3\(d\) electrons is necessary. In this study, the ab-initio multiplet method based on the relativistic configuration interaction (CI) method has been applied to the calculations of Fe-\(L_{2,3}\) XANES of LiFePO\(_4\) and FePO\(_4\). Experimental XANES spectra were quantitatively reproduced by this method. The effects of local symmetries around Fe ions to the spectral shapes were also discussed.

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1. Introduction

Lithium transition metal oxides and lithium transition metal phosphates, such as LiCoO\(_2\) and LiFePO\(_4\), have been extensively studied as cathode materials of lithium-ion batteries.\(^1\)-\(^4\) X-ray absorption spectroscopy (XAS) becomes a popular tool for investigating the redox behavior of cathode materials during the charge/discharge cycles in microscopic viewpoint. Hard X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) at the transition metal (TM) \(K\)-edge are commonly used because it enable us to perform in-situ observation of electrochemical reactions inside cathode materials.\(^5\),\(^6\) TM \(K\)-edge mainly ascribed to the electronic transition from the TM-1s core states into the spatially delocalized 4\(p\) unoccupied states. Therefore, the TM-\(K\) XANES and EXAFS are sensitive to the changes of local atomic structures, such as inter-atomic distances and symmetries. However, we cannot directly obtain the information of TM 3\(d\) states, which are directly related to the chemical reactions inside cathode materials, by using the TM \(K\)-edges.

Recently, soft X-ray absorption spectroscopy observing TM \(L_{2,3}\)-edges re-attract attentions. As TM-\(L_{2,3}\) XANES is dominated by the TM 2\(p\) \(\rightarrow\) 3\(d\) electronic transitions, it is sensitive to the changes of chemical states of TM ions. The same electronic excitation process can be observed by the TM-\(L_{2,3}\) electron energy-loss near-edge structure (ELNES). The spectral shapes of XANES and ELNES are nearly the same when ELNES is measured with transmission geometry, thereby providing identical information. Experimental results of TM-\(L_{2,3}\) XANES/ELNES of cathode materials, including the lithium transition metal oxides and phosphates, have been reported by many groups.\(^7\)-\(^11\) Despite its potential usefulness, TM-\(L_{2,3}\) XANES/ELNES was not fully utilized due to the lack of appropriate theoretical tools having the quantitatively reproduce and predict spectra.

Because of the strong interactions among spatially localized 2\(p\) and 3\(d\) electrons, the shapes of TM-\(L_{2,3}\) XANES are strongly modified from the empty 3\(d\) partial density of states: this is known as multiplet effects. In order to treat the electronic transition from core levels, relativistic effects should also be considered. Therefore, the conventional program packages based on the non-relativistic density functional theory cannot be used for the analysis of these edges.

Theoretical approaches commonly used for the analysis of TM-\(L_{2,3}\) XANES are the crystal field multiplet (CFM) and charge transfer multiplet (CTM) methods,\(^12\) in which the crystal-field effects are taken into account as adjustable parameters. Although the CFM and CTM methods have succeeded to simulate many TM-\(L_{2,3}\) XANES, they cannot predict the multiplet structures a priori. The development of a parameter-free ab-initio approach for simulating TM-\(L_{2,3}\) XANES has long been an issue with great interest.

For this purpose, the present author have developed the ab-initio multiplet method for TM-\(L_{2,3}\) XANES, which is based on configuration interaction (CI) theory. This method can describe the full multiplet structures among 2\(p\) and 3\(d\) electrons. The spin-orbit coupling at core 2\(p\) levels are automatically taken into account by solving Dirac equation instead of Schrödinger equation. Experimental spectra from many compounds having different \(d\)-electron numbers and coordination numbers have been successfully reproduced without any empirical parameters.\(^13\)-\(^15\) This ab-initio multiplet method has been applied for the chemical state analysis of LiNiO\(_2\) and Li\(_2\)MnO\(_3\) with layered structures, during the intercalation/de-intercalation of Li ions.\(^16\),\(^17\) The systematic calculations of TM-\(L_{2,3}\) XANES have also been made and reported as the theoretical fingerprints that can be directly compared to the experimental results.\(^18\)

In this work, the ab-initio multiplet method is applied to the Fe-\(L_{2,3}\) XANES of LiFePO\(_4\) with olivine structure and Li-deintercalated FePO\(_4\). The usefulness of the method to the lithium transition metal phosphates is demonstrated. The effects of local symmetries on Fe sites on the shapes of Fe-\(L_{2,3}\) XANES are also discussed.

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2. Computational Procedure

The Fe-L$_{2,3}$ XANES of LiFePO$_4$ and FePO$_4$ have been calculated using the \textit{ab-initio} multiplet method for XANES which is based on the relativistic configuration interaction theory. The details of the theoretical method have been described in Ref. 13). In this section, we briefly recall the theoretical method and detailed procedures for the present calculations.

As mentioned above, the spectral shape of TM-L$_{2,3}$ XANES is dominated by the strong electronic correlation between spatially localized 2$p$ and 3$d$ electron. In order to deal with these strong correlations, we start with ‘no-pair’ Hamiltonian, which is given in the second quantized form

\[ H = \sum_{i,j=1}^{L} (\hat{h}_{ij} a_i^+ a_j + \frac{1}{2} \sum_{i,j,k,l=1}^{L} (ij|kl) a_i^+ a_j^+ a_k a_l) \]  

(1)

where $i, j, k, l$ indicate the MOs, $N$ is the number of electron in the system, $L > N$ is the number of given orbitals. $a_i^+$ and $a_i$ are the creation and annihilation operators for an electron in $i$-th orbital, respectively. $(\hat{h}_{ij})$ and $(ij|kl)$ are the one- and two-electron integrals over four-component MOs, where $\hat{h}$ is the single-particle Dirac operator

\[ \hat{h} = c \alpha \cdot \sigma + mc^2 \beta + v_{\text{self}}(r) \]  

(2)

with $v_{\text{self}}$ the electrostatic potential from nuclei.

The molecular orbitals (MOs) were obtained by the relativistic density functional calculations using the FeO$_6$ cluster models. The atomic positions of the clusters were taken from experimental crystalline structures. To take into account by evaluating these integrals over all possible configurations for describing the wavefunctions of the initial and final states, respectively. The MOs mainly composed of Fe 1$s$-3$p$ and O 1$s$, 2$s$ states were set to be fully occupied.

Once the eigenstates of Hamiltonian matrix are obtained, the oscillator strength of the electric dipole transition is evaluated by the following formula,

\[ I_d = \frac{2m}{\hbar^2} (E_f - E_i) \left| \sum_{i=1}^{N} \mathbf{e} \cdot \mathbf{r}_k \left| \Psi_i \right| \right|^2, \]

where $\Psi_i$ and $\Psi_f$ are the many-electron wavefunctions corresponding to the initial and final states, while $E_i$ and $E_f$ are their energies, respectively. Theoretical spectra are obtained by broadening the oscillator strength using Lorentz functions. In the present work, the full width at half maximum (FWHM) of Lorentz functions were set to 0.5 eV over the whose energy region of Fe L$_{2,3}$-edges.

This CI method is known to systematically overestimate the absolute transition energies. This can be ascribed to the incompleteness of our basis MOs and the limitation of the number of Slater determinants. In this study, the present study, the transition energy was corrected by taking the energy difference between MOs for the Slater’s transition state (as a Ref. 24).

3. Results and Discussions

The Fe-L$_{2,3}$ XANES of LiFePO$_4$ (Fe$^{2+}$) and FePO$_4$ (Fe$^{3+}$) were calculated by the \textit{ab-initio} multiplet method described in Sec. 2. Relativistic density functional calculations were made using cluster models composed of Fe and the neighboring O atoms, namely (FeO$_6$)$_0$. The FeO$_6$ octahedra are strongly distorted: the point group symmetry around a Fe ion is $C_{4v}$ symmetry for both compounds. The neighboring Fe-O bond lengths in LiFePO$_4$ are 208, 212, 220, 223 pm, while those in FePO$_4$ are 215, 204, 190, 191 pm. Total number of electrons in the cluster models, $m$, was obtained from formal charges, thus $m = 10$ and 9 for LiFePO$_4$ and FePO$_4$, respectively.

Many-electron wavefunctions were expressed as linear combinations of Slater determinants. As described in Sec. 2, we only considered the electronic configurations corresponding to the $2p \rightarrow 3d$ transitions for the initial and final states. The total number of Slater determinants considered in LiFePO$_4$ (FePO$_4$) was $\varepsilon(C_6 \times \varepsilon(C_6) = 210$ ($\varepsilon(C_6 \times \varepsilon(C_6) = 252$) and $\varepsilon(C_5 \times \varepsilon(C_5) = 720$ ($\varepsilon(C_5 \times \varepsilon(C_5) = 1260$) for the initial and final states, respectively. The oscillator strengths of the electric dipole transitions were calculated between these numbers of multiplet levels, and theoretical spectra were obtained by broadening them by the Lorentz functions.

Figures 1 and 2 show the theoretical Fe-L$_{2,3}$ XANES spectra of LiFePO$_4$ and FePO$_4$, respectively. In order to investigate the dependence of spectral shapes on the spin-states of Fe ions, two theoretical spectra from high-spin (HS) and low-spin (LS) initial states were drawn. A number of features can be found in the theoretical spectra both from HS and LS initial states. The presence of such fine structures can be ascribed to the strong electronic correlation between Fe-2$p$ and 3$d$ electrons, and the crystal field splitting on Fe-3$d$ levels. It can also be clearly seen that the spectral shapes drastically change by choosing the different spin states as the initial state. The results clearly show that the spin states of Fe ions can unambiguously be determined using these theoretical spectra as fingerprints.
The experimental spectra reported in the literature\textsuperscript{25} are also shown for comparison. Similar experimental results were also reported by several groups.\textsuperscript{26,27} Many features can be observed in the experimental spectra: they are labeled by a−i for LiFePO\textsubscript{4} and a−j for FePO\textsubscript{4} in Figs. 1, 2. Good agreements between experiment and theory can be found if we choose the HS state as the initial state both in LiFePO\textsubscript{4} and FePO\textsubscript{4}. All the spectral features found in experimental spectra were reproduced well. The results clearly show that a Fe ion in LiFePO\textsubscript{4} is divalent with high-spin state, while a Fe ion in FePO\textsubscript{4} is trivalent with high-spin states. The results also demonstrate the power of the \textit{ab-initio} multiplet method for quantitatively reproduce and predict the TM-L\textsubscript{2,3} XANES spectra from the sites with low point group symmetries, such as C\textsubscript{4v}, without any empirical parameters.

In order to investigate the effects of local symmetries on the Fe L\textsubscript{2,3}-edges, theoretical spectra of LiFePO\textsubscript{4} and FePO\textsubscript{4} are compared with those of FeO and cubic LaFeO\textsubscript{3} in which Fe\textsuperscript{2+} and Fe\textsuperscript{3+} ions are located at the sites with octahedral (O\textsubscript{h}) symmetry, respectively. Note that the most stable phases of LaFeO\textsubscript{3} are orthorhombic and rhombohedral system, in which the point group symmetry around Fe\textsuperscript{3+} are C\textsubscript{2} and C\textsubscript{3\texttt{h}}, respectively. In this work, however, the calculations were made for the cubic phase in order to clarify the effects of the local distortion on the spectral shapes. Figure 3(a) shows the theoretical spectra of Fe\textsuperscript{2+,3+-L\textsubscript{2,3}} XANES in FeO and LiFePO\textsubscript{4}. Surprisingly, the spectral shapes of Fe\textsuperscript{2+} in FeO and LiFePO\textsubscript{4} are quite similar, despite the large distortion of FeO\textsubscript{6} octahedra in LiFePO\textsubscript{4}. By carefully comparing the spectra, however, we can recognize the splitting of peak c at L\textsubscript{2}-edge and the peak h at L\textsubscript{2}-edge in LiFePO\textsubscript{4}, as indicated by the vertical lines in Fig. 3(a). The result indicate that shapes of Fe\textsuperscript{2+,3+-L\textsubscript{2,3}} XANES are dominated by the multiplet effects, while the effects of local symmetry are small. Thus, measurements with high-energy resolution is necessary to identify the effects of local distortion of atomic structures around Fe\textsuperscript{2+} from the Fe-L\textsubscript{2,3} XANES.

The effects of local symmetries on the spectra become much more significant in the case of Fe\textsuperscript{3+-L\textsubscript{2,3}-edges as shown in Fig. 3(b). The clear difference of spectral shapes between LaFeO\textsubscript{3} and FePO\textsubscript{4} can be found. Especially, the L\textsubscript{3} main peak in LaFeO\textsubscript{3} labeled d in the upper panel is split into three peaks in FePO\textsubscript{4} (labeled c, d and e in the lower panel). The larger symmetry dependence of the theoretical spectra of Fe\textsuperscript{3+} than that of Fe\textsuperscript{2+} can be explained by inspecting the character of Fe-\textit{φ}\textsubscript{3d}, the MOs mainly composed of Fe-3\textit{d} states. In fact, the O-2\textit{p} composition averaged over all Fe-\textit{φ}\textsubscript{3d} in LiFePO\textsubscript{4} is 33\%, while that in FePO\textsubscript{4} is 10.9\%, by the Mulliken’s population analysis. The larger fraction of O-2\textit{p} in Fe-\textit{φ}\textsubscript{3d} in Fe\textsuperscript{3+} compounds than in Fe\textsuperscript{2+} compounds should be the origin of the greater sensitivity to the local symmetries around Fe ions as shown in Fig. 3(b).

4. Conclusion

The Fe-L\textsubscript{2,3} XANES of LiFePO\textsubscript{4} and FePO\textsubscript{4} with olivine structures have been calculated using the \textit{ab-initio} multiplet method. In each compound, both HS and LS states were chosen as initial states. The spin states of Fe ions can unambiguously be determined by comparing theoretical spectra to the experimental ones directly: the Fe ions in LiFePO\textsubscript{4} are divalent with HS states, while those in FePO\textsubscript{4}...
are trivalent with HS states. The effects the difference of symmetries around Fe sites were also investigated by comparing the theoretical spectra of LiFePO4 and FePO4 to those of FeO and cubic LaFeO3 in which Fe ions are located in the sites with octahedral ($O_h$) symmetry. The dependence of the spectral shapes of Fe $L_{2,3}$-edges was small in the case of Fe$^{2+}$ compounds. The much stronger symmetry dependence can be found in the case of Fe$^{3+}$ compounds, which originated from the stronger covalent bonding between Fe-3$d$ and O-2$p$ levels.

The present results clearly demonstrate the power of the ab-initio multiplet method to quantitatively reproduce and predict the experimental spectra of TM-$L_{2,3}$ XANES. The combinations of the high-quality measurements and the ab-initio multiplet method would be unique and very powerful technique for the characterization of TM ions cathode materials.

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