First Principles Study of Core-hole Effect on Fluorine K-edge X-ray Absorption Spectra of MgF$_2$ and ZnF$_2$

Tomoyuki Yamamoto$^{1,*}$, Teruyasu Mizoguchi$^{2}$, Kazuyoshi Tatsumi$^{3}$, Isao Tanaka$^{4}$, Hirohiko Adachi$^{1}$, Yasuji Muramatsu$^{5}$, Eric M. Gullikson$^{6}$ and Rupert C. C. Perera$^{6}$

$^{1}$Fukui institute for fundamental chemistry, Kyoto University, Kyoto 606-8103, Japan
$^{2}$Institute of Engineering Innovation, The University of Tokyo, Tokyo 113-8656, Japan
$^{3}$Department of Nuclear Engineering, Nagoya University, Nagoya 464-8603, Japan
$^{4}$Department of materials science and engineering, Kyoto University, Kyoto 606-8501, Japan
$^{5}$Japan atomic energy research institute (JAERI), Kansai Research Establishment, Mikazuki-cho, Hyogo 679-5148, Japan
$^{6}$Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA

First principles calculations have been carried out to investigate the core-hole effects on the theoretical fine structures of the X-ray absorption spectra of MgF$_2$ and ZnF$_2$ at F K-edge. Significant differences are found between the calculated spectral fine structures with and without core-holes. Experimental profiles of the near-edge X-ray absorption fine structures are well reproduced by the theoretical ones when the core-hole effect is introduced. The dependence of supercell size on the theoretical fine structures is also examined.

(Received February 3, 2004; Accepted March 31, 2004)

Keywords: near-edge X-ray absorption fine structure, first principles calculation, core-hole effect, zinc difluoride, magnesium difluoride

1. Introduction

Near-edge X-ray absorption fine structure (NEXAFS) is sensitive to changes in local electronic environment of the materials and has been widely used for the characterization of the electronic structures. A number of theoretical calculations to interpret the fine structures of NEXAFS spectra have been performed by using the molecular orbital calculations and the multiple scattering methods.$^{1}$ Most of the theoretical works have not been successful in systematic and quantitative reproduction of NEXAFS spectra. Recently, the first principles periodic calculations based on the density functional theory (DFT) that uses the orthogonalized linear combination of atomic orbital (OLCAO) method$^{2}$ has been successful in quantitatively reproducing the fine structures of many kinds of solid state materials.$^{2-7}$

The NEXAFS spectra at F K-edge were extensively studied both experimentally and theoretically for alkali fluorides,$^{8-11}$ and alkaline-earth difluorides.$^{12,13}$ Those of the 3d transition metal difluorides with the rutile type of structure have been also investigated.$^{14-17}$ However their theoretical calculations have provided only qualitative reproductions of the experimental data. Therefore, in the present study, the first principles calculations using the Density Functional Theory (DFT) have been carried out for MgF$_2$ and ZnF$_2$ and compared with the experimental NEXAFS spectra of MgF$_2$ and ZnF$_2$ at F K-edge. In our calculations the full-potential linearized augmented plane wave (FP-LAPW) method was employed, which is one of the most accurate DFT methods. However, there are large discrepancies between experimental and theoretical line shapes of the F K-edge X-ray absorption spectra of MgF$_2$ and ZnF$_2$ for ground state calculations, i.e., without core-hole effects. We also performed calculations with core-hole effects. In this case we assumed the excited state with one electron vacancy on 1s orbital of F of interest and one additional electron in the system, which corresponds to the final state of the F K-edge X-ray absorption. The theoretical spectra obtained showed better agreement with the experimental F K-edge NEXAFS spectra of MgF$_2$ and ZnF$_2$ than results from the ground state calculations.

Our band structure calculations require three-dimensional periodic boundary conditions. When we create a core-hole at F 1s orbital, other core-holes will appear in the neighboring cells, which yield the interactions between these core-holes. We have examined the dependence of the cell size on the theoretical line shapes of the NEXAFS spectra by changing the calculated supercell size.

2. Calculation and Experimental Procedures

First principles calculations have been carried out for MgF$_2$ and ZnF$_2$ with the rutile type of structure using the FP-LAPW package, WIEN2k.$^{18}$ The effective exchange-correlation functional, GGA-PBE,$^{19}$ was employed. All electrons up to 3p were treated as core electrons in the case of Zn, while only 1s electrons were treated as core electrons for Mg and F. The muffin-tin radius, $R_{MT}$, was set to be 1.8 Bohr and the product of the muffin-tin radius and the maximum reciprocal space vector $K_{max}$, i.e., the plane-wave cutoff, $R_{MT}K_{max}$ was fixed at 7.0 for all calculations.

High-resolution X-ray absorption spectra at F K-edge were also measured at beamlines 6.3.1 & 6.3.2 in the Advanced Light Source (ALS). The X-ray absorption spectra were obtained by collecting by drain current, the total electron yield (TEY) method. The incident photon beam was monochromatized using a 600 lines/mm grating and was irradiated perpendicularly onto the sample surface. Commercially available high purity powder with the rutile type of structure prepared in the SOEKAWA CHEMICAL Co., Ltd., was put on the Indium sheet.
3. Results and Discussion

Observed F K-edge NEXAFS spectra of MgF$_2$ and ZnF$_2$ are shown in Fig. 1(a). These observed spectra showed similar spectral profiles as earlier experiments. The most intense peak, peak E, appeared at the threshold, 687.8 eV, in the case of ZnF$_2$, while only weak peak, peak A, was shown there and second peak, peak B, was the most intense one in the spectrum of MgF$_2$. In order to interpret these differences in observed NEXAFS spectra between MgF$_2$ and ZnF$_2$, we performed the first principles DFT calculations. At first, the projected partial density of states (p-PDOS) of F $p$-component in the unoccupied levels of the unit cell of MgF$_2$ and ZnF$_2$ and the radial transition probability (RTP) from F $1s$ to unoccupied levels within the electronic-dipole selection rule were carried out at the ground states. Resultant theoretical NEXAFS spectra obtained by a product of the above two, i.e., p-PDOS and RTP, were compared with the measured spectra and are presented in Fig. 1(b). The calculated spectra could qualitatively reproduce the difference between observed spectra, but both of the calculated spectral profiles shifted to higher energy side than the experimental spectra. The agreements of spectral fine structures between experiments and calculations were not satisfactory, even when using the most accurate DFT methods, i.e., FP-LAPW method.

The core-hole effects were introduced in our present calculations where one electron on the F 1$s$ orbital of interest was removed and one additional electron was added in the system. This state approximately corresponds to the final state of the F K-edge X-ray absorption. Here the 2 $\times$ 2 $\times$ 3 supercells consisting of 72 atoms were employed, which were expanded twice and three times along a and b, and c directions of the unit-cell, respectively. When the core-hole is introduced, geometrical symmetry decreases from the space group of $P4_2/mmm$ for rutile structure to $Amn2$. Resulting theoretical NEXAFS spectra of MgF$_2$ and ZnF$_2$ at F K-edge are shown in Fig. 1(c) together with the experimental and ground state calculations. As shown in Fig. 1(c), the calculated spectra with the core-hole effects showed better agreements in spectral profiles with the experiments than those at ground state. The core-hole effect on the theoretical analysis of NEXAFS spectra have been investigated by a number of researchers for various materials. As illustrated in Fig. 1, the core-hole plays an important role in the analysis of the spectral fine structure of F K-edge NEXAFS. In these calculations, transition energies were estimated by the difference between the total electronic energy at ground and core-hole states. As shown in Fig. 1(c), calculated energies were slightly higher ($\Delta E/E = +2\%$). However, differences in threshold energies between MgF$_2$ and ZnF$_2$ were well reproduced by the present calculations using 72 atoms supercells.

The cell-size dependence on the fine structures of the theoretical NEXAFS spectra was also examined by changing the supercell sizes. Here we employed 1 $\times$ 1 $\times$ 1, 1 $\times$ 1 $\times$ 2, 2 $\times$ 2 $\times$ 2 and 2 $\times$ 2 $\times$ 3 supercells. The corresponding k-point sampling meshes were 5 $\times$ 3 $\times$ 3, 2 $\times$ 3 $\times$ 3, 3 $\times$ 2 $\times$ 2 and 2 $\times$ 2 $\times$ 2 in the brillouin zone for 1 $\times$ 1 $\times$ 1, 1 $\times$ 1 $\times$ 2, 2 $\times$ 2 $\times$ 2 and 2 $\times$ 2 $\times$ 3 supercells, respectively, to obtain an almost same spacing in the whole reciprocal space in all models. Resultant theoretical spectra by using above supercells are shown in Fig. 2. As shown in Fig. 2, the theoretical profiles of MgF$_2$ shifted towards the lower energy sides as the supercell sizes were increased. Same effect was also observed in the case of ZnF$_2$, in which intensity of the second peak, corresponding to the peak F in the experimental spectrum, decreased as increment of the cell size. However, there still remain small discrepancies between experiments and calculations, i.e., peak A was missing in MgF$_2$ and intensity of peak F was slightly overestimated in ZnF$_2$, although these theoretical spectra reproduced the experimental ones better than those at ground state. For better reproduction of the experimental fine structure of these difluorides, larger distance between core-holes might be necessary to avoid the interactions between core-holes, since the wave functions of F $p$-components are delocalized.

In conclusion, the first principles DFT calculations were carried out to investigate the core-hole effect on the
theoretical fine structures of the F NEXAFS spectra of MgF\textsubscript{2} and ZnF\textsubscript{2}. Our present calculations using the supercells consisting of 72 atoms reproduced the experimental fine structures very well, when core-hole effects were taken into consideration. Supercell size dependence on the theoretical fine structures was also examined. The smaller supercells could provide only qualitative reproductions of the experimental NEXAFS profiles even when core-hole effects were fully introduced. This type of first principles calculations has an implication to carry out the systematic and quantitative interpretations of the spectral fine structures of NEXAFS spectra.

Acknowledgements

This work was supported by three projects by Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT). They are the computational materials science unit in Kyoto University, the Grant-in-Aid for Scientific Research on Priority Areas (No. 751), and the 21st century COE program. This work was also supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Science of the U.S. DOE under Contract No. DE-AC03-76SF00098.

REFERENCES