Structural analysis of group V, VI, VII metal compounds by XAFS and DFT calculation

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Abstract. The characteristics of K, L1, and L3-edges XANES spectra of group IV, V, VI compounds, which have different coordination number, number of d-electrons and the symmetry of coordination sphere, have been classified. Two p → d transitions were observed in the second derivative spectra of L3-edge XANES spectra of all group IV, V, VI compounds. These two transitions can be assigned to split d orbitals. The splitting and area of the two resonances depend on the symmetry of coordination sphere because the splitting corresponds to ligand field splitting of d orbitals. The splitting of d orbitals has a correlation with the pre-edge peak area of K or L1-edge XANES spectra, which are attributed to the dipole forbidden transition of s → d occurred by mixing of p orbitals with d orbitals. This correlation is supported by DFT calculations of several group IV, V, VI structural models (four-, five- and six-coordinated). The clarification of the correlation between the splitting of the resonance and the structure of group IV, V, VI metal is important to provide structural information in unknown group IV, V, VI metal site.

1. Introduction
XANES is a powerful probe of the geometric and electronic structure within several angstroms around the central atom. The valence of central atom is often determined by the position of the K and/or L1-edges. The local symmetry is figured by pre-edge peak area of K or L1-edge XANES spectra, which show s → d transitions. The s → d transitions are dipole forbidden transition for regular octahedral site-symmetry, however, the dipole forbidden transition is partially allowed for distortion of octahedral environment, which brings about the absence of a center of inversion symmetry because p orbitals are mixed with d orbitals. Therefore, central atom with tetrahedral symmetry exhibits large pre-edge peak area in K and L1 edges XANES. Recently, Yamamoto reviewed the characteristics of pre-edge peaks in K-edge XANES spectra of 3d transition metals from the view points of the selection rule, coordination number, number of d-electrons, and symmetry of the coordination sphere [1]. The features of pre-edge peaks in K-edge XANES spectra for 4d elements and the L1-edge for 5d elements are analogous with those for 3d elements, but the pre-edge peak is broadened due to the wide natural width of core level.
The L$_3$-edge X-ray absorption resonance reflects electronic states of vacant $d$ orbitals of the absorbing atom. In the case of Mo(VI) L$_3$-edge X-ray absorption, two resonances are observed. The splitting and area of the two resonances depend on the symmetry of Mo site because the splitting corresponds to ligand field splitting of $d$ orbitals [2,3]. The spectrum of W L$_3$-edge XANES probes the 5$d$ orbitals character as well as the Mo L$_3$-edge XANES, since the prominent peak of W L$_3$-edge XANES spectrum is the resonance caused by $2p \rightarrow 5d$ transition. Although the features of L$_3$-edge XANES for 5$d$ elements such as Ta and Re are analogous with that for W, there is little information about a relationship between the splitting of the resonance and the structure of 5$d$ species because the resonance is not split distinctly as Mo L$_3$-edge resonance due to the wide natural width of core level. It appears that the resonance consists of an overlap of multiple (two or more) peaks. The multiple peaks of the resonance are very likely to correspond to the electron transition from 2$p$ orbitals to the split $d$ orbitals.

In this study, the characteristics of K, L$_1$ and L$_3$-edges XANES spectra of group IV, V, VI compounds (4$d$ (Nb, Mo) and 5$d$ (Ta, W, Re) transition metals) have been classified, in order to evaluate the influence of both period and group of element on the correlation between the split in the $d$ orbital and the area of pre-edge peak of K or L$_1$-edge XANES spectrum. The splitting of the L$_3$-edge resonance and the area of pre-edge peak of K or L$_1$-edge XANES spectrum were carefully evaluated. The energy gap of split $d$ orbitals of several models having 4-, 5- and 6-coordinated 4$d$ and 5$d$ transition metal center were calculated with density functional theory (DFT) and the relationship between the energy gap of $d$ orbitals and the structure of metal center was classified. Moreover, the mixing ratio of empty $p$ orbitals into $d$ orbitals of several models was also estimated and classified the correlation between the mixing ratio and the energy gap of split $d$ orbitals. It seems that the correlation between the split in the $d$ orbital and the area of pre-edge peak of the K or L$_1$-edge XANES spectra can provide the structural information in unknown group IV, V, VI metal sites.

2. Experimental

Nb and Mo L$_3$-edge XANES data were collected at a facility of the BL-1A station of the soft X-ray beam line at UVSOR, at the Institute for Molecular Science, Okazaki, Japan. The spectrum was recorded in a total electron yield mode at room temperature, using a InSb(111) two-crystal monochromator. The photon energy was calibrated by using of Nb and Mo L$_3$-edge of Nb and Mo metal samples, and this energy is set as the standard reference energy.

Nb and Mo K-edge and Ta, W and Re L$_3$ and L$_1$ edges XANES data were collected at a facility of the BL01B1 beam line at the SPring-8, of the Japan Synchrotron Radiation Research Institute, Japan in the transmission mode in an air at room temperature. Incident X-ray flux and transmitted flux were measured with ionization chambers. A Si (311) two crystal monochromator was used to obtain monochromatic X-ray beam. The photon energy was calibrated by metal samples.

DFT calculations were performed by B3LYP/LanL2DZ with Gaussian03 program package for the calculation of the splitting of empty $d$ orbitals corresponding to the ligand field. As the models of six-, five- and four-coordinated 4$d$ and 5$d$ transition metal site, (MH$_6$, [MH$_4$]$^{1+}$ and [MH$_4$]$^{2+}$ (M = Mo and W), [MH$_5$]$^{1+}$, MH$_5$ and [MH$_4$]$^{1+}$ (M = Nb and Ta), [MH$_6$]$^{1+}$, [MH$_3$]$^{2+}$ and [MH$_4$]$^{2+}$ (M = Re)) were used, respectively. Energy calculations were performed for structurally different models, and the splitting of $d$ orbitals by ligand field were estimated. Additionally, the contribution of $p$ orbitals to $d$ orbitals of the metal center were also determined from calculated molecular orbitals coefficients in order to estimate the pre-edge peak area of K or L$_1$-edge XANES, which corresponds to $s \rightarrow d$ dipole forbidden transition.

3. Results and discussion

Figure 1(A) shows the Mo L$_3$-edge XANES spectra of reference samples with Mo$^{6+}$ ion. Ba$_2$NiMoO$_6$, which has $Oh$ symmetry, give two peaks in the resonance. On the other hand, MoO$_3$ and (NH$_4$)$_3$MoO$_4$ samples, which have a distorted MoO$_6$ unit, and MgMoO$_4$ and NaMoO$_4$, which respectively have nearly $Td$ and $Td$ symmetry, exhibit only one peak. The second derivatives of the
Mo L₃-edge resonance makes it clear that the resonance consists of two peaks (MgMoO₄ and NaMoO₄ give a large peak with a shoulder peak at lower energy), as shown in Fig. 1(B). In general, 4d orbitals of octahedral (tetrahedral) MoO₆ (MoO₄) unit are split into e_g and t₂g (e and tₕ) orbitals by ligand field. The poorer the symmetry of MoO₆ (MoO₄) is from Oh (Td), the smaller (larger) the energy gap of the split 4d orbitals is. Additionally, the energy gap for MoO₄ unit is smaller than that for MoO₆ unit. Therefore, the energy gap of the two peaks in Fig. 1(B) would reflect the splitting of 4d orbitals by the ligand field. Additionally, we carried out the deconvolution of the Mo L₃-edge XANES spectra. All spectra could be fitted with two Lorentz functions, whose top positions were determined based on the values of the two peaks in Fig. 1(B), and an arctangent function. Figure 2 shows the results of the deconvolution of Ba₂NiMoO₆ and NaMoO₄, for examples. The ratio of the areas under the two peaks (peak 1: peak 2; The peak 1 appears at lower energy than the peak 2) for the samples having MoO₆ unit was about 3:2, whereas, that having MoO₄ unit was about 2:3. For the MoO₆ (MoO₄) unit, the t₂g (e) orbital appears at a lower energy than the e_g (tₕ) orbital and the X-ray absorption intensity is t₂g : e_g = 3 : 2 (e : tₕ = 2 : 3). Thus, the ratios of peak 1 to peak 2 reflect the absorption intensities of the split 4d states. From above results, we concluded that the resonance in the Mo L₃-edge XANES appears the electron transitions from 2p₃/2 orbital to the split 4d orbitals. Figure 1(C) shows the Mo K-edge XANES spectra of the reference samples. The pre-edge peak is mainly attributed to forbidden electron transition from 2s orbital to 4d orbitals. A less symmetric structure of Mo oxide species (distortion from Oh symmetry) provides a larger pre-edge peak because this forbidden electron transition is allowed by mixing p orbitals of tungsten and ligand into empty d orbitals. Therefore, MgMoO₄ and NaMoO₄ exhibit the large pre-edge peak. All group IV, V, VI oxides tested indicated a
similar tendency. We found that the combination of the area of pre-edge peak of the K or L1-edges XANES and the splitting of the L3-edge resonance provides more reliable information on the structure of the group IV, V, VI oxide species.

Figure 3 shows the area of pre-edge peak of the K or L1-edge XANES of group IV, V, VI compounds plotted against the energy gap of the split L3-edge resonance for the reference samples. Figure 3 reveals an interesting relationship, in that the area of pre-edge peak has a downward-sloping correlation with the energy gap of the split L3-edge resonance. We calculated the mixing ratio of emptied \( p \) orbitals into \( d \) orbitals for of the octahedral and tetrahedral group IV, V, VI structural models (MH\(_n\)) and investigated the relationship between the mixing ratio of \( p \) orbitals and the energy gap of \( d \) splitting with density functional theory calculations. The mixing ratio of \( p \) orbitals to \( d \) orbitals of the octahedral and tetrahedral group IV, V, VI structural models (MH\(_n\)) plotted against the split \( d \) orbitals by ligand field (Figure 4), which shows a downward-sloping correlation. Therefore, we concluded that the structure of the group IV, V, VI oxide species can be easily estimated by a combination of the pre-edge peak areas of the K or L1-edge XANES and the energy gap of the split L3-edge resonance.

4. Conclusion
The characteristics of K, L1, and L3-edges XANES spectra of group IV, V, VI compounds, which have a different coordination number, number of \( d \)-electrons and the symmetry of the coordination sphere, have been classified. The splitting of \( d \) orbitals has a downward-sloping correlation with the pre-edge peak area of K or L1-edge XANES spectra, which are attributed to the dipole forbidden transition of \( s \rightarrow d \) occurred by mixing of \( p \) orbitals with \( d \) orbitals. This correlation is supported by DFT calculations of several group IV, V, VI structural models. The clarification of the correlation between the splitting of the resonance and the structure of group IV, V, VI metal is important to provide structural information in unknown group IV, V, VI metal site.

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