An Abnormally Large EXAFS Debye-Waller Factor for a Mo-O Bond in Hexamolybdate

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Abstract. Temperature dependence of EXAFS was analyzed for Mo₆O₁₉²⁻ and W₆O₁₉²⁻ compounds. The Fourier transform peak for bridging Mo-O bond is quite smaller than that for other Mo-O bonds in Mo₆O₁₉²⁻. Such a phenomenon was not observed in W₆O₁₉²⁻. That reason of small peak is abnormally large Debye-Waller factor for this bond, which comes from the large static fluctuation of the bridging Mo-O bonds.

Keywords: EXAFS; Debye-Waller Factor; Mo₆O₁₉²⁻
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INTRODUCTION

Hexamolybdate (Mo₆O₁₉²⁻) has six octahedral units of MoO₆, which share their edges and apexes with each other, as shown in Fig.1. There are three different types of Mo-O bonds; terminal Mo-O(O1), bridging Mo-O(O2) and central Mo-O(O3) bonds. It was surprising that the peaks pertaining to the bridging Mo-O bonds are almost not present in the Fourier transform of the Mo K-edge EXAFS for the Mo₆O₁₉²⁻ compound [1]. On the other hand, the peaks for the bridging M-O2 bonds appear in other hexametalate (M₆O₁₉ⁿ⁻, M=W, Ta, Nb) data [1,2], which have quite similar structures to that of hexamolybdate. It has been shown by Evans et al. [2] that the disappearance of the Mo-O peaks is due to a very large Debye-Waller factor for the bridging Mo-O bonds. They analyzed only the terminal and bridging Mo-O bonds (the contribution from the central Mo-O was neglected) using data obtained at room temperature. In this paper, we analyze the EXAFS for Mo-O bonds with 3 shells including the central Mo-O bond. Furthermore the temperature dependencies (20 K-523 K) of the Debye-Waller factors in Mo₆O₁₉²⁻ and W₆O₁₉²⁻ are discussed in detail.

EXPERIMENT AND ANALYSES

Tetrabutyl ammonium (TBA) hexamolybdate was prepared according to the following procedure [1]: HCl was added to a Na₂MoO₄·2H₂O solution. Cyclohexanone in equal proportions to this solution was added and the mixture shaken for 20 minute. After that time tetrabutyl ammonium hexamolybdate was obtained as precipitate by the addition of (C₄H₉)₄NBr to the extracted phase. Tetrabutyl ammonium
hexatungstate was also prepared according to the above procedure.

The X-ray absorption spectra for the powder samples of \([\text{C}_4\text{H}_9\text{N}]_2\text{Mo}_6\text{O}_{19}\) and \([\text{C}_4\text{H}_9\text{N}]_2\text{W}_6\text{O}_{19}\) were measured in transmission mode at BL 10B (Si(311) channel-cut crystal monochromator) and BL12C (Si(111) double crystal monochromator) of Photon Factory (KEK). The measurement temperature for \([\text{C}_4\text{H}_9\text{N}]_2\text{Mo}_6\text{O}_{19}\) was 20 K-523 K, and that for \([\text{C}_4\text{H}_9\text{N}]_2\text{W}_6\text{O}_{19}\) was 20 K-300 K. To analyze the EXAFS data, we used the XANADU code [3].

Theoretical EXAFS for the curve fitting is described as

\[
\chi(k) = \sum_j N_j S_0^2 f_j(k_j) \exp\left(-2\sigma_j^2 k_j^2\right) \exp\left(-\frac{2r_j}{\lambda(k_j)}\right) \times \sin\left[2k_j r_j + \phi_j(k_j) - \frac{4}{3} C_3 k_j^3\right]
\]

where \(r\) is interatomic distance, \(N\) is coordination number, \(\sigma\) is Debye-Waller factor and \(C_3\) is third order cumulant, which is assumed to be zero. \(\lambda(k)\) is electron mean free path, \(f(k)\) is backscattering amplitude and \(\phi(k)\) is phase shift, which are obtained from FEFF8.10 code [4].

**RESULTS AND DISCUSSION**

Figure 2 shows Mo \(K\)-edge EXAFS \(\chi_{corr}(k)\) spectra (phase and amplitude corrected by oxygen atom) for \(\text{Mo}_6\text{O}_{19}^2-\) (solid line) and W \(L_{III}\)-edge data for \(\text{W}_6\text{O}_{19}^2-\) (dashed line). Figure 3 shows their Fourier transforms. The peaks of the Mo-O and W-O appear at 1.67-2.3 Å, and that of Mo-Mo and W-W appear at 3.3 and 3.5 Å, respectively. It is noted that the Mo-O peak intensity is quite small for \(\text{Mo}_6\text{O}_{19}^2-\) in comparison with \(\text{W}_6\text{O}_{19}^2-\). The Fourier transform pattern of \(\text{W}_6\text{O}_{19}^2-\) is normally expected from the structure shown in Fig.1 but that in \(\text{Mo}_6\text{O}_{19}^2-\) is abnormal.

The interatomic distances and Debye-Waller factors for Mo-O, W-O, Mo-Mo, W-W bonds obtained from the curve-fitting method at room temperature are listed in Table 1. Additionally, those parameters obtained by the X-ray diffraction (XRD) method are also shown [5-8]. In this Table we show \(\sigma\) values for XRD as the standard deviation of the interatomic distances.

**TABLE 1.** The interatomic distance \(r\) and Debye-Waller factor \(\sigma\) of the EXAFS and XRD [5-8] for \(\text{Mo}_6\text{O}_{19}^2-\) and \(\text{W}_6\text{O}_{19}^2-\) at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>(\text{Mo}<em>6\text{O}</em>{19}^2-)</th>
<th></th>
<th>(\text{W}<em>6\text{O}</em>{19}^2-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r/Å)</td>
<td>(\sigma/Å)</td>
<td>(r/Å)</td>
<td>(\sigma/Å)</td>
</tr>
<tr>
<td>EXAFS</td>
<td>XRD°</td>
<td>EXAFS</td>
<td>XRD°</td>
</tr>
<tr>
<td>O1</td>
<td>1.67</td>
<td>1.68</td>
<td>0.037</td>
</tr>
<tr>
<td>O2</td>
<td>1.87</td>
<td>1.93</td>
<td>0.111</td>
</tr>
<tr>
<td>O3</td>
<td>2.33</td>
<td>2.32</td>
<td>0.067</td>
</tr>
<tr>
<td>Mo/W</td>
<td>3.28</td>
<td>3.28</td>
<td>0.058</td>
</tr>
</tbody>
</table>
The interatomic distance \( r \) of Mo-O2 obtained from EXAFS (=1.87 Å) is shorter than that of the XRD (=1.93 Å). Other bonding parameters are similar between EXAFS and XRD for Mo\(_6\)O\(_{19}\)\(^{2-}\).

To analyze the EXAFS Debye-Waller factor for Mo\(_6\)O\(_{19}\)\(^{2-}\) and W\(_6\)O\(_{19}\)\(^{2-}\) in detail, the temperature dependences of \( \sigma^2 \) is presented in Fig. 4 and 5. EXAFS for Mo\(_6\)O\(_{19}\)\(^{2-}\) is measured at 20-523 K (Fig. 4) and that for W\(_6\)O\(_{19}\)\(^{2-}\) is at 20-300 K (Fig. 5).

\[
\sigma^2 = \sigma_T^2 + \sigma_S^2 .
\]

(2)

Within the Einstein approximation the thermal vibration factor is written by

\[
\sigma_T^2 = \frac{2\mu \omega_E}{h} \coth \left( \frac{h \omega_E}{2k_B T} \right)
\]

(3)

where \( \mu \) is reduced mass for the concerning atomic pair, \( \omega_E \) is the Einstein frequency and \( k_B \) is the Boltzmann constant. We fitted the Debye-Waller factor for Mo-O2 and Mo-Mo by equation (3) and shown as solid line in Fig. 4. From the fitting \( \omega_E \) for Mo-O2 and Mo-Mo is estimated as 6.80×10\(^{13}\) s\(^{-1}\) and 3.93×10\(^{13}\) s\(^{-1}\), respectively. The value of the static disorder factor \( \sigma_S^2 \) for Mo-O2 is obtained to be quite large (= 0.0074 Å\(^2\)), though one for Mo-Mo and also other Mo-O bonds are almost zero. For W\(_6\)O\(_{19}\)\(^{2-}\), \( \sigma_S^2 \) is not so large, either. We conclude that the abnormally large Debye-Waller factor for the only Mo-O2 bond in Mo\(_6\)O\(_{19}\)\(^{2-}\) is originated from the large static disorder or fluctuation of the bridging Mo-O2 bond.

**CONCLUSION**

We analyzed three shell model (Mo-O1, O2, and O3) for the temperature dependent EXAFS of Mo\(_6\)O\(_{19}\)\(^{2-}\) and W\(_6\)O\(_{19}\)\(^{2-}\). The Debye-Waller factor of Mo-O2 bonds is abnormally large because of the contribution from the static disorder factor. Mo\(_6\)O\(_{19}\)\(^{2-}\) is known as to show high reactivity as the oxidant. And the active point is located on bridging oxygen atoms. We think that this reactivity associated with the large fluctuation of the position of the bridging oxygen atom.

**REFERENCES**