

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 $\text{Mo}_6\text{O}_{19}^{2-}$ and $\text{W}_6\text{O}_{19}^{2-}$ compounds. The Fourier transform peak for bridging Mo-O bond is quite smaller than that for other Mo-O bonds in $\text{Mo}_6\text{O}_{19}^{2-}$. Such a phenomenon was not observed in $\text{W}_6\text{O}_{19}^{2-}$. 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; $\text{Mo}_6\text{O}_{19}^{2-}$

PACS: 61.10.Ht

INTRODUCTION

Hexamolybdate ($\text{Mo}_6\text{O}_{19}^{2-}$) has six octahedral units of MoO_6 , 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 $\text{Mo}_6\text{O}_{19}^{2-}$ compound [1]. On the other hand, the peaks for the bridging Mo-O bonds appear in other hexametalate ($\text{M}_6\text{O}_{19}^{\text{n}-}$, 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 $\text{Mo}_6\text{O}_{19}^{2-}$ and $\text{W}_6\text{O}_{19}^{2-}$ are discussed in detail.

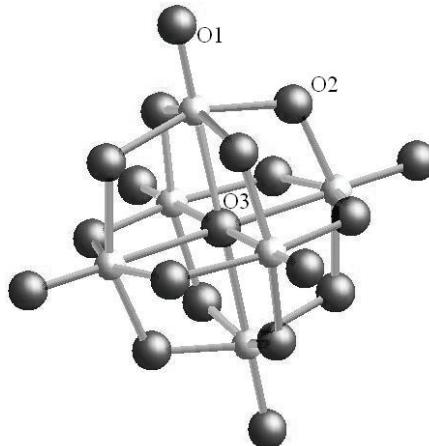


FIGURE 1. Schematic structures of $\text{M}_6\text{O}_{19}^{\text{n}-}$: ● M = Molybdenum or Tungsten atom and ● Oxygen.

EXPERIMENT AND ANALYSES

Tetrabutyl ammonium (TBA) hexamolybdate was prepared according to the following procedure [1]: HCl was added to a $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ 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 $(\text{C}_4\text{H}_9)_4\text{NBr}$ 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 $[(C_4H_9)_4N]_2Mo_6O_{19}$ and $[(C_4H_9)_4N]_2W_6O_{19}$ 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 $[(C_4H_9)_4N]_2Mo_6O_{19}$ was 20 K-523 K, and that for $[(C_4H_9)_4N]_2W_6O_{19}$ 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

$$\chi(k) = \sum_j \frac{N_j S_0^2}{k_j r_j^2} f_j(k_j) \exp(-2\sigma_j^2 k_j^2) \exp\left(\frac{-2r_j}{\lambda_j(k_j)}\right) \times \sin\left[2k_j r_j + \varphi_j(k_j) - \frac{4}{3} C_{3j} k_j^3\right] \quad (1)$$

where r is interatomic distance, N is coordination number, σ 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 $\varphi(k)$ is phase shift, which are obtained from FEFF8.10 code [4].

RESULTS AND DISCUSSION

Figure 2 shows Mo K -edge EXAFS $\chi_{\text{corr}}(k)$ spectra (phase and amplitude corrected by oxygen atom) for $Mo_6O_{19}^{2-}$ (solid line) and W L_{III} -edge data for $W_6O_{19}^{2-}$ (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 $Mo_6O_{19}^{2-}$ in comparison with $W_6O_{19}^{2-}$. The Fourier transform pattern of $W_6O_{19}^{2-}$ is normally expected from the structure shown in Fig.1 but that in $Mo_6O_{19}^{2-}$ 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 σ values for XRD as the standard deviation of the interatomic distances.

TABLE 1. The interatomic distance r and Debye-Waller factor σ of the EXAFS and XRD [5-8] for $Mo_6O_{19}^{2-}$ and $W_6O_{19}^{2-}$ at room temperature.

	$Mo_6O_{19}^{2-}$				$W_6O_{19}^{2-}$			
	$r / \text{\AA}$		$\sigma / \text{\AA}$		$r / \text{\AA}$		$\sigma / \text{\AA}$	
	EXAFS	XRD ⁵	EXAFS	XRD ⁶	EXAFS	XRD ⁷	EXAFS	XRD ⁷
O1	1.67	1.68	0.037	0.023	1.70	1.72	0.027	0.040
O2	1.87	1.93	0.111	0.040	1.92	1.92	0.060	0.040
O3	2.33	2.32	0.067	0.021	2.31	2.33	0.062	0.006
Mo / W	3.28	3.28	0.058		3.31	3.29	0.053	

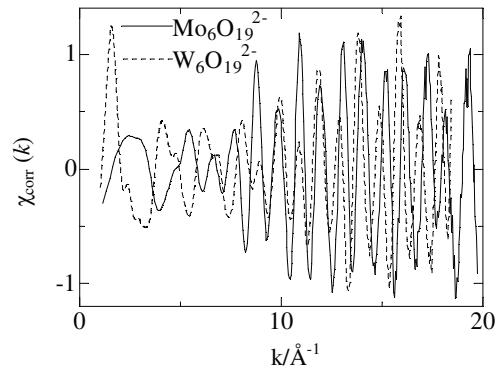


FIGURE 2. Mo K -edge EXAFS $\chi_{\text{corr}}(k)$ spectra of $Mo_6O_{19}^{2-}$ (solid line) and W L_{III} -edge of $W_6O_{19}^{2-}$ (dashed line) measured at room temperature [1].

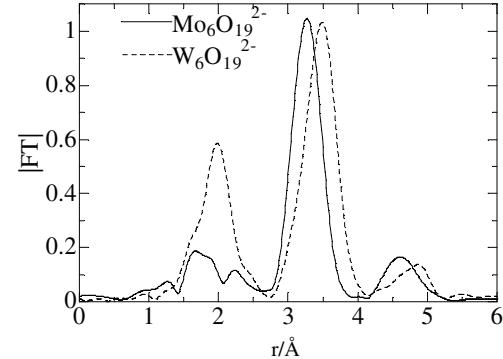


FIGURE 3. Mo K -edge EXAFS Fourier transform of $Mo_6O_{19}^{2-}$ (solid line) and W L_{III} -edge of $W_6O_{19}^{2-}$ (dashed line) measured at room temperature [1].

First we found as characteristic feature that the Debye-Waller factor σ for Mo-O2 is quite large ($=0.111 \text{\AA}$) compared to W-O2 ($=0.060 \text{\AA}$) and other bonds as Mo-O1 ($=0.037 \text{\AA}$) and Mo-O3 ($=0.067 \text{\AA}$). The σ value of Mo-O2 for XRD is almost same as that for O1 and O3. Only the EXAFS σ value for Mo-O2 is abnormal.

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 $\text{Mo}_6\text{O}_{19}^{2-}$.

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

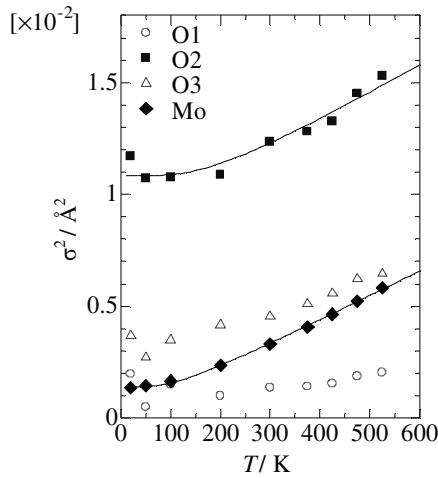


FIGURE 4. The temperature dependence of Debye-Waller factor for three different types of Mo-O bonds and Mo-Mo bonds in $\text{Mo}_6\text{O}_{19}^{2-}$.

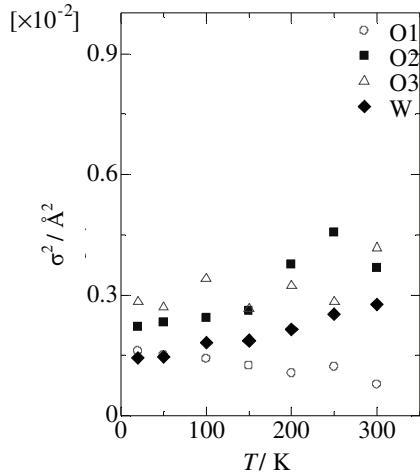


FIGURE 5. The temperature dependence of Debye-Waller factor for three different types of W-O bonds and W-W bonds in $\text{W}_6\text{O}_{19}^{2-}$.

In general, the Debye-Waller factor for EXAFS consists of two parts: a thermal vibration σ_T^2 and a static disorder σ_S^2 as,

$$\sigma^2 = \sigma_T^2 + \sigma_S^2 .$$

(2)

Within the Einstein approximation the thermal vibration factor is written by

$$\sigma_T^2 = \frac{\hbar}{2\mu\omega_E} \coth\left(\frac{\hbar\omega_E}{2k_B T}\right) \quad (3)$$

where μ is reduced mass for the concerning atomic pair, ω_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 ω_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 σ_S^2 for Mo-O2 is obtained to be quite large ($= 0.0074$ Å²), though one for Mo-Mo and also other Mo-O bonds are almost zero. For $\text{W}_6\text{O}_{19}^{2-}$, σ^2 is not so large, either. We conclude that the abnormally large Debye-Waller factor for the only Mo-O2 bond in $\text{Mo}_6\text{O}_{19}^{2-}$ is originated from the large static disorder or fluctuation of the bridging Mo-O2 bond.

CONCLUSION

We analyzed three shell model (M-O1, O2, and O3) for the temperature dependent EXAFS of $\text{Mo}_6\text{O}_{19}^{2-}$ and $\text{W}_6\text{O}_{19}^{2-}$. The Debye-Waller factor of Mo-O2 bonds is abnormally large because of the contribution from the static disorder factor. $\text{Mo}_6\text{O}_{19}^{2-}$ 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.

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