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A. Kuzmin, J. Purans, Ph. Parent, H. Dexpert. Low and High-Temperature In Situ X-Ray Absorption Study of the Local Order in Orthorhombic α -MoO₃ Upon Hydrogen Reduction. Journal de Physique IV Proceedings, 1997, 7 (C2), pp.C2-891-C2-892. 10.1051/jp4:1997267 . jpa-00255350

HAL Id: jpa-00255350

<https://hal.science/jpa-00255350>

Submitted on 1 Jan 1997

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Low and High-Temperature *In Situ* X-Ray Absorption Study of the Local Order in Orthorhombic α -MoO₃ Upon Hydrogen Reduction

A. Kuzmin, J. Purans, Ph. Parent* and H. Dexpert*

Institute of Solid State Physics, Kengaraga 8, LV-1063 Riga, Latvia

** LURE, Université Paris-Sud, Bât. 209D, 91405 Orsay cedex, France*

Abstract. *In-situ* x-ray absorption spectroscopy has been applied to the study of the modifications of the short range order in orthorhombic α -MoO₃ under low and high-temperature hydrogen reduction. It was observed that at low-temperature ($T \approx 110^\circ\text{C}$) reduction, a formation of molybdenum bronzes H_xMoO_3 ($x \leq 2$) occurs while at high-temperature ($T \geq 400^\circ\text{C}$) reduction, α -MoO₃ transforms into MoO₂. Both processes have great applied importance since they are related to electrochromic and catalytic properties of α -MoO₃. The information on the local atomic and electronic structure, obtained from the Mo K-edge XAFS and XANES analyses, allowed us to follow all steps of the reduction process and to formulate a mechanism of hydrogen interaction with the layered-type structure of α -MoO₃.

Molybdenum trioxide (α -MoO₃) has a layer structure built up of distorted MoO₆ octahedra which are connected in the *c*-axis direction by corners and edges so as to form zig-zag rows and in the perpendicular *a*-direction only by corners [1]. It is known that the reduction process of α -MoO₃ proceeds, depending on the temperature (T) of the reaction, by the following two ways. At low temperature ($T \approx 20\div 100^\circ\text{C}$) in the presence of Pt or Pd catalyst, α -MoO₃ transfers successively to a series of molybdenum bronzes H_xMoO_3 ($x \leq 2$) whose topology is close to α -MoO₃ with hydrogen atoms being placed at intralayer positions for $x < 0.85$ and at intralayer and interlayer positions for $x > 0.85$ [2]. This low- T reaction has technological applications such as secondary battery electrodes, reversible hydrogen storage cells, electrochromic devices and electrocatalyzers [2]. At high-temperature ($T \geq 400^\circ\text{C}$), α -MoO₃ reduces to MoO₂ and further reduction is used to obtain metallic molybdenum of high purity [3]. Note also that high- T reduction of α -MoO₃ is of interest because molybdenum (6+) oxide is an important catalyst [3].

In this work, the *in-situ* x-ray absorption spectra of α -MoO₃, reduced by hydrogen, were measured in transmission mode at the Mo K-edge using a setup of the LURE DCI EXAFS-3 beam line. The synchrotron radiation was monochromatized by the Si(311) double-crystal monochromator and its intensity was measured by two ionization chambers containing argon gas. The low- T measurements were performed at $T = 110^\circ\text{C}$, while high- T measurements in the temperature range from RT to 400°C . The details of the experiments and of the data analysis will be published in the forthcoming paper [4].

Upon reduction, the formal valence state of Mo ions decreases from 6+ to 4+ leading to the partial filling of the initially empty $4d(\text{Mo})-2p(\text{O})$ band and to the significant lowering of the MoO₆ octahedra distortion. This conclusion is supported by the decrease of the pre-edge peak in the Mo K-edge XANES (Figure 1) and by the quantitative analysis of the first shell XAFS signal [4]. The symmetrization of the MoO₆ octahedra is qualitatively seen in Figure 2 as a decrease of the 1st shell distortion in Fourier transforms of the XAFS signals. Nevertheless, although a tendency of the short-range order modifications is similar, the accurate analysis shows that at high- T , α -MoO₃ transforms gradually to rutile-type MoO₂ while at low- T , a set of phase transitions occurs resulting in α -H₂MoO₃ having the structure close to that of the parent oxide. Comparing the FT's of the final products (Figure 2), one can see that the second shell peak at 3.2 Å is higher in α -H₂MoO₃ than in MoO₂; this is due to the multiple-scattering effects within 4 nearly linear Mo-O-Mo chains in α -H₂MoO₃ (the largest Mo-O-Mo angles in MoO₂ are only about 144°).

Recently it was suggested that the reduction of α -MoO₃ to MoO₂ is a double-step process: α -MoO₃ $\rightarrow$ Mo₄O₁₁ $\rightarrow$ MoO₂ [3]. Our results show (Figure 3) that the Mo₄O₁₁ phase was not present during the experiment that agree also with the results of [5]. Moreover, the high- T reduction of α -MoO₃ leads to progressive transition from α -MoO₃ to MoO₂ without presence of any intermediate phase [4]. On the contrary, at low- T , α -MoO₃ transforms successively to the series of bronzes H_xMoO_3 accumulating hydrogen ions as OH⁻ ($x < 0.85$) and/or OH₂⁺ ($x > 0.85$) groups [6] and maintaining general topology of the α -MoO₃ lattice. Note also that while in α -MoO₃, the peak at 2.3 Å (Figure 2) corresponds mainly to the Mo $\rightarrow$ O $\rightarrow$ O $\rightarrow$ Mo double-scattering (DS) signal, which is generated within the 1st shell and contains the shortest Mo-O bond (1.66 Å), the same peak in α -H₂MoO₃ and MoO₂ is related to the short (~ 2.6 Å) Mo-Mo bond (Figure 4) [4]. In the latter case the same DS signal contributes at about 0.4 Å longer distances than in α -MoO₃, i.e. at ~ 2.7 Å in FT shown in Figure 2.

Figure 1: Change of the Mo K-edge XANES upon low- T (α - $\text{MoO}_3 \rightarrow \alpha\text{-H}_2\text{MoO}_3$) and high- T ($\alpha\text{-MoO}_3 \rightarrow \text{MoO}_2$) reduction. The pre-edge shoulder is marked by arrow.

Figure 2: Variation of the experimental XAFS spectra and their FT's upon hydrogen reduction. Only several signals are shown for clarity. The ranges of the FT and the 1st shell back-FT are indicated by dashed lines.

Acknowledgments

A.K. and J.P. are grateful to the staff of the LURE DCI EXAFS-3 beam line for the support of the experiments. This work was also supported in part by the International Science Foundation, Grants LF8000 and LJ8100 (A.K. and J.P.).

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Figure 3: FT's of experimental (dotted line) and calculated (solid and dashed lines) XAFS spectra.

Figure 4: Experimental (dashed lines) and calculated (solid lines) XAFS signals corresponding to the peak at 2.3 Å (see Figure 2).