

## Low and High-Temperature *In Situ* X-Ray Absorption Study of the Local Order in Orthorhombic $\alpha$ -MoO<sub>3</sub> Upon Hydrogen Reduction

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**Abstract.** *In-situ* x-ray absorption spectroscopy has been applied to the study of the modifications of the short range order in orthorhombic  $\alpha$ -MoO<sub>3</sub> 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  $\text{H}_x\text{MoO}_3$  ( $x \leq 2$ ) occurs while at high-temperature ( $T \geq 400^\circ\text{C}$ ) reduction,  $\alpha$ -MoO<sub>3</sub> transforms into MoO<sub>2</sub>. Both processes have great applied importance since they are related to electrochromic and catalytic properties of  $\alpha$ -MoO<sub>3</sub>. 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  $\alpha$ -MoO<sub>3</sub>.

Molybdenum trioxide ( $\alpha$ -MoO<sub>3</sub>) has a layer structure built up of distorted MoO<sub>6</sub> 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  $\alpha$ -MoO<sub>3</sub> 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,  $\alpha$ -MoO<sub>3</sub> transfers successively to a series of molybdenum bronzes  $\text{H}_x\text{MoO}_3$  ( $x \leq 2$ ) whose topology is close to  $\alpha$ -MoO<sub>3</sub> 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 ( $T \geq 400^\circ\text{C}$ ),  $\alpha$ -MoO<sub>3</sub> reduces to MoO<sub>2</sub> and further reduction is used to obtain metallic molybdenum of high purity [3]. Note also that high- $T$  reduction of  $\alpha$ -MoO<sub>3</sub> is of interest because molybdenum (6+) oxide is an important catalyst [3].

In this work, the *in-situ* x-ray absorption spectra of  $\alpha$ -MoO<sub>3</sub>, 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  $400^\circ\text{C}$ . 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 MoO<sub>6</sub> 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 MoO<sub>6</sub> 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- $T$ ,  $\alpha$ -MoO<sub>3</sub> transforms gradually to rutile-type MoO<sub>2</sub> while at low- $T$ , a set of phase transitions occurs resulting in  $\alpha$ -H<sub>2</sub>MoO<sub>3</sub> 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  $\alpha$ -H<sub>2</sub>MoO<sub>3</sub> than in MoO<sub>2</sub>: this is due to the multiple-scattering effects within 4 nearly linear Mo-O-Mo chains in  $\alpha$ -H<sub>2</sub>MoO<sub>3</sub> (the largest Mo-O-Mo angles in MoO<sub>2</sub> are only about  $144^\circ$ ).

Recently it was suggested that the reduction of  $\alpha$ -MoO<sub>3</sub> to MoO<sub>2</sub> is a double-step process:  $\alpha$ -MoO<sub>3</sub>  $\rightarrow$  Mo<sub>4</sub>O<sub>11</sub>  $\rightarrow$  MoO<sub>2</sub> [3]. Our results show (Figure 3) that the Mo<sub>4</sub>O<sub>11</sub> phase was not present during the experiment that agree also with the results of [5]. Moreover, the high- $T$  reduction of  $\alpha$ -MoO<sub>3</sub> leads to progressive transition from  $\alpha$ -MoO<sub>3</sub> to MoO<sub>2</sub> without presence of any intermediate phase [4]. On the contrary, at low- $T$ ,  $\alpha$ -MoO<sub>3</sub> transforms successively to the series of bronzes  $\text{H}_x\text{MoO}_3$  accumulating hydrogen ions as OH<sup>-</sup> ( $x < 0.85$ ) and/or OH<sub>2</sub> ( $x > 0.85$ ) groups [6] and maintaining general topology of the  $\alpha$ -MoO<sub>3</sub> lattice. Note also that while in  $\alpha$ -MoO<sub>3</sub>, 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  $\alpha$ -H<sub>2</sub>MoO<sub>3</sub> and MoO<sub>2</sub> is related to the short ( $\sim 2.6$  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  $\alpha$ -MoO<sub>3</sub>, i.e. at  $\sim 2.7$  Å in FT shown in Figure 2.

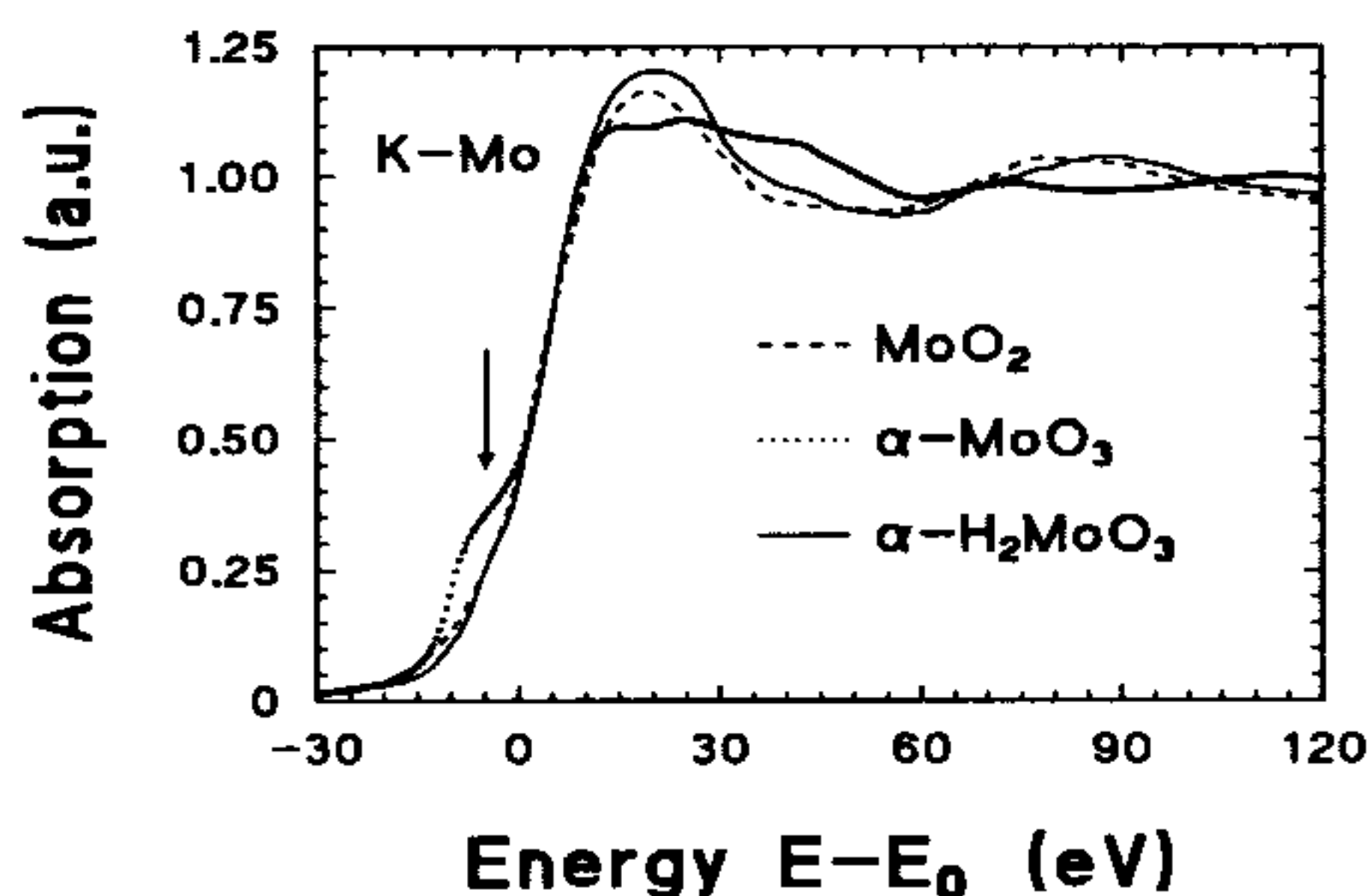


Figure 1: Change of the Mo K-edge XANES upon low- $T$  ( $\alpha$ - $\text{MoO}_3 \rightarrow \alpha\text{-H}_2\text{MoO}_3$ ) and high- $T$  ( $\alpha$ - $\text{MoO}_3 \rightarrow \text{MoO}_2$ ) reduction. The pre-edge shoulder is marked by arrow.

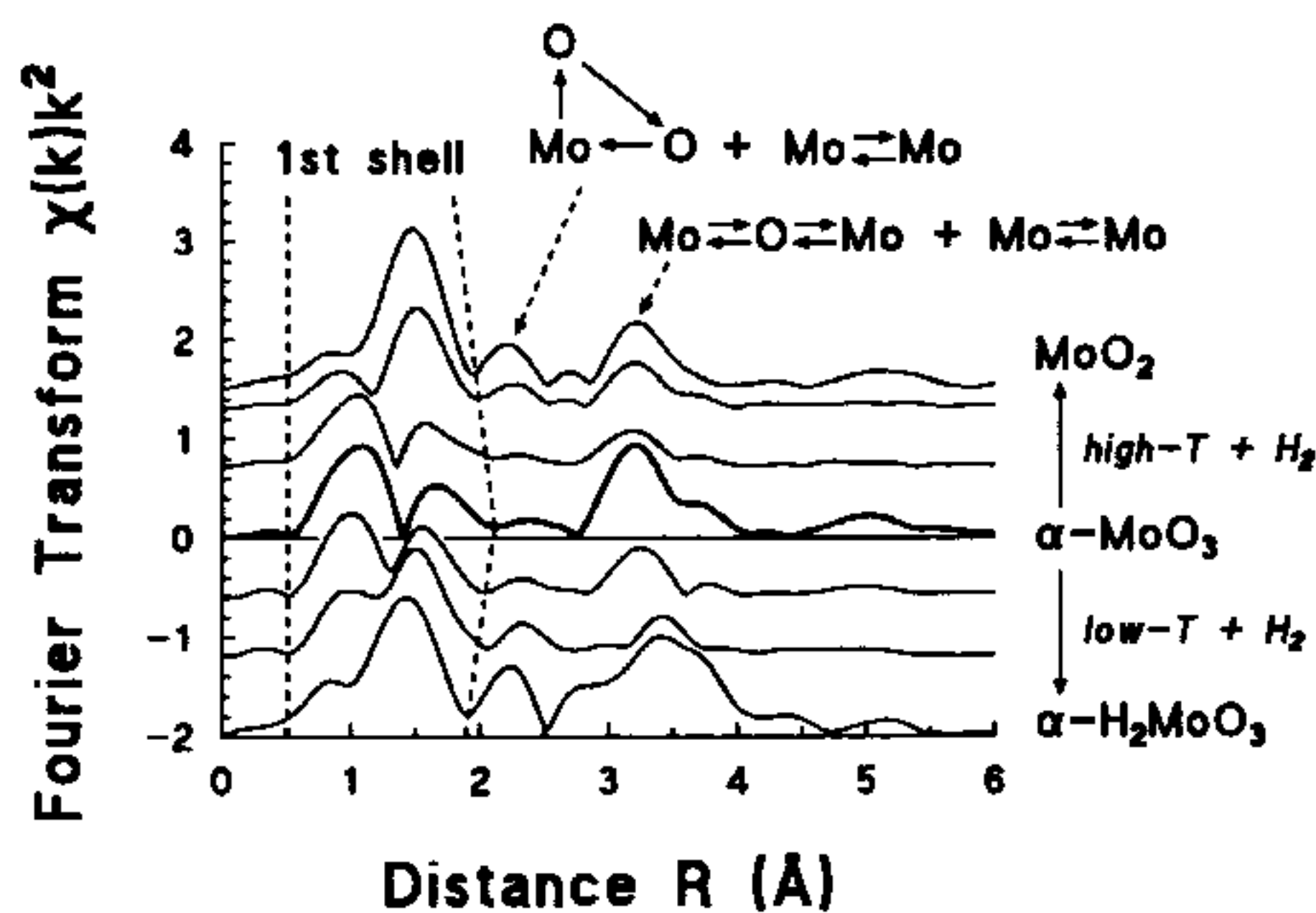
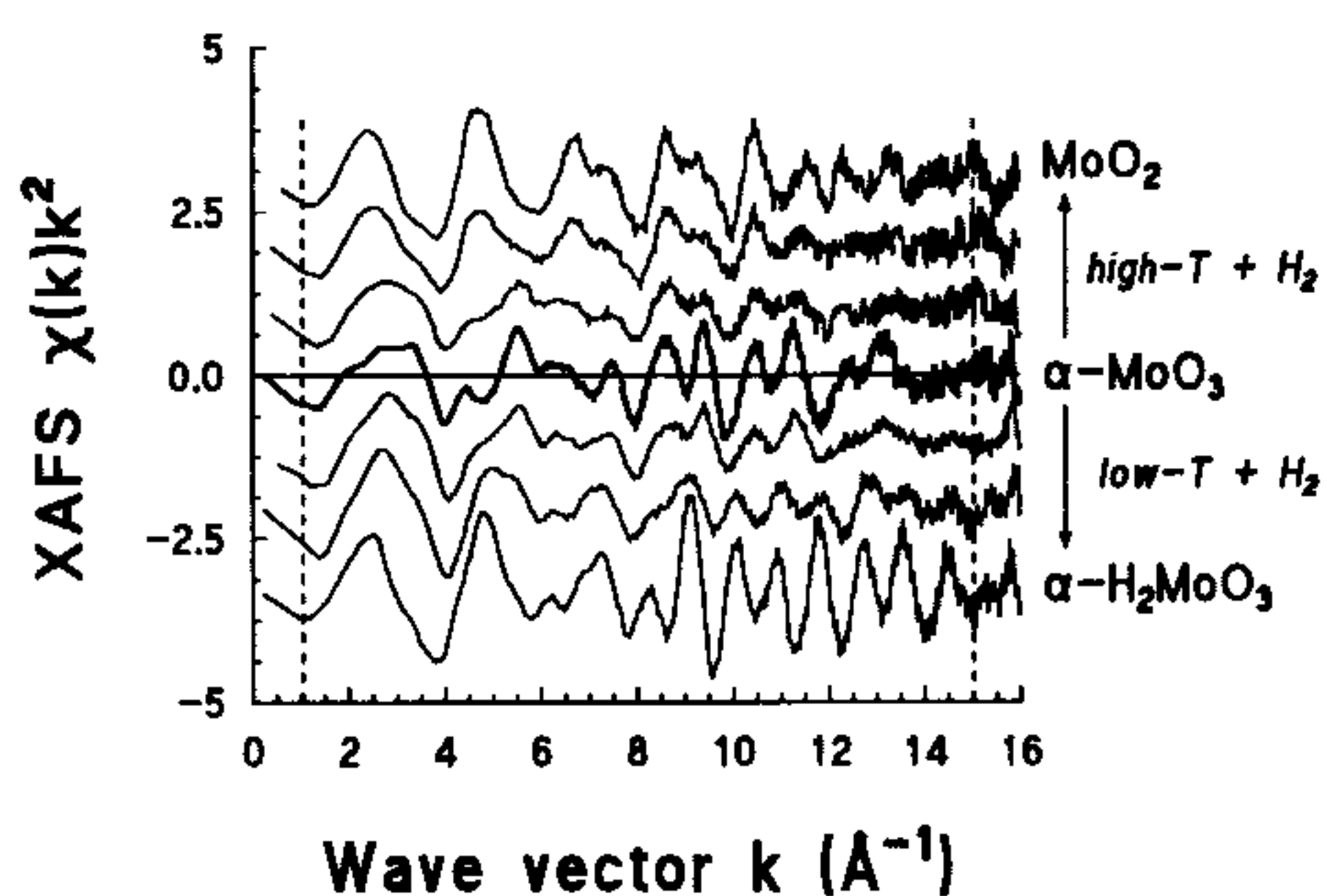


Figure 2: Variation of the experimental XAFS spectra and their FT's upon hydrogen reduction. Only several signals are shown for clarity. The ranges of the FT and the 1st shell back-FT are indicated by dashed lines.

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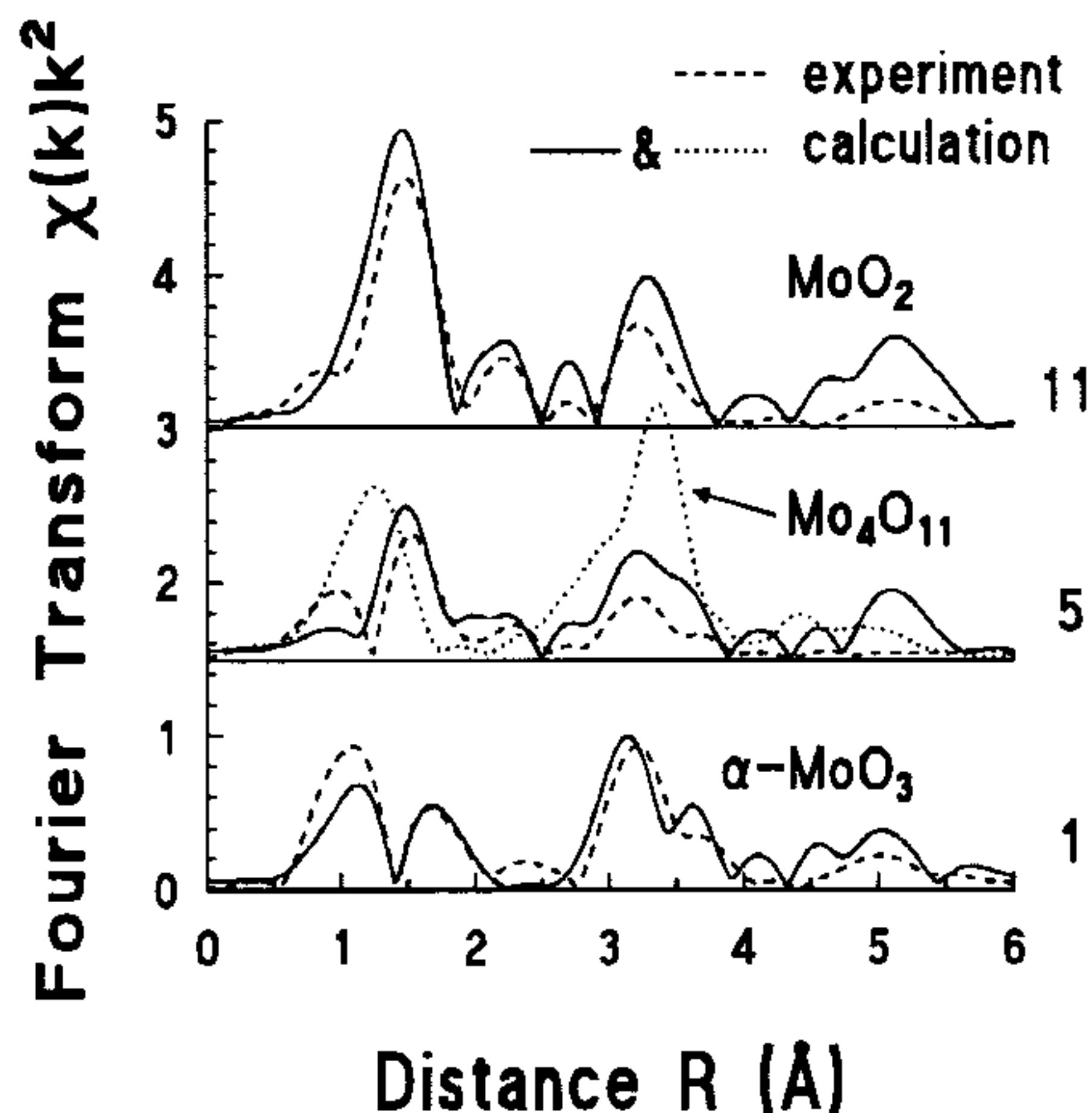


Figure 3: FT's of experimental (dotted line) and calculated (solid and dashed lines) XAFS spectra.

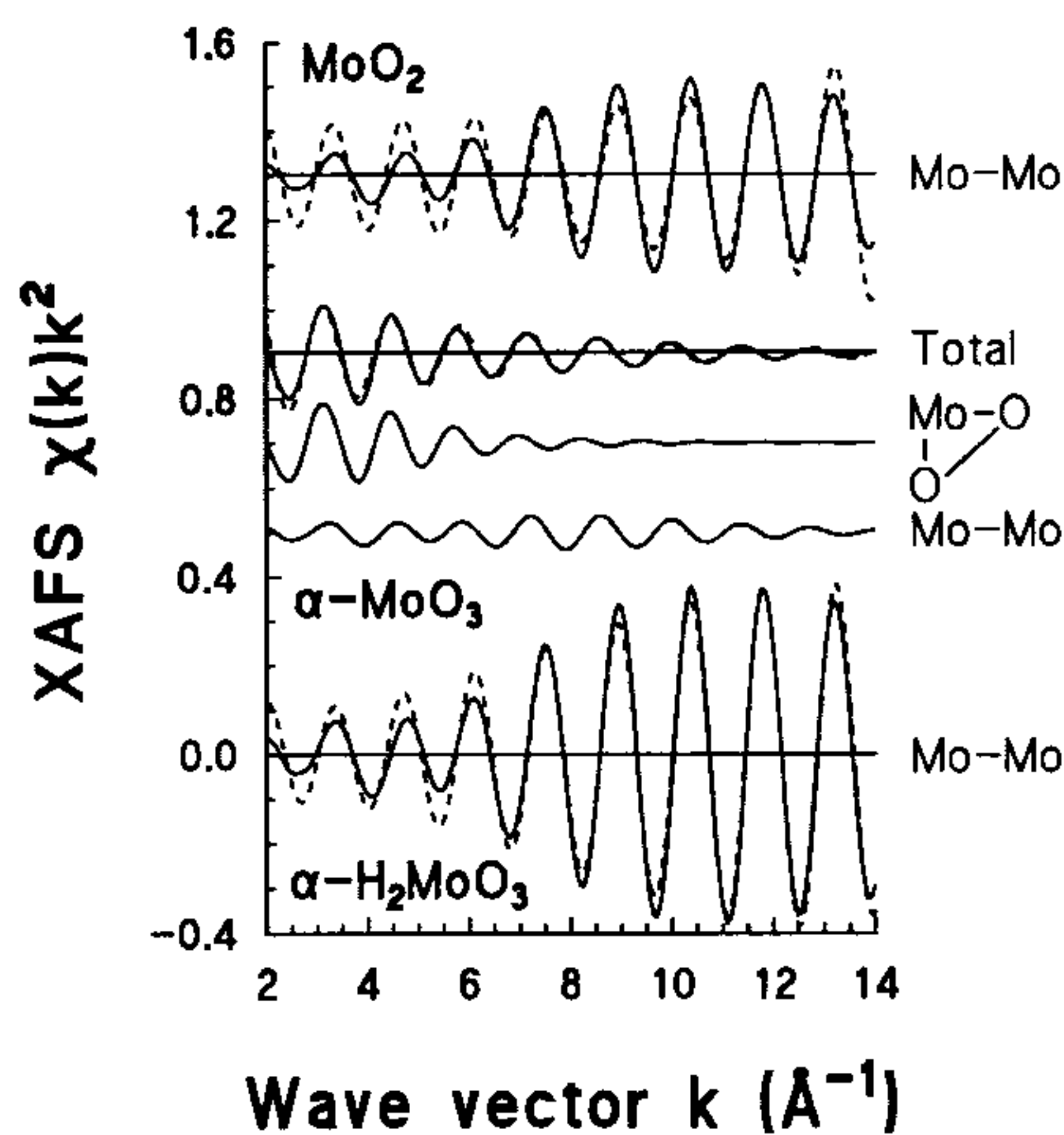


Figure 4: Experimental (dashed lines) and calculated (solid lines) XAFS signals corresponding to the peak at 2.3 Å (see Figure 2).