



XAFS study of short range order in the heavily disordered $\text{Mo}_x\text{W}_{1-x}\text{O}_3$ oxides

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Abstract

We have done comparative XAFS analysis on the Mo K and W L₃ edges of polycrystalline $\text{Mo}_x\text{W}_{1-x}\text{O}_3$ solid solutions. It was found that their structures are closely related to corner-shared WO_3 -type for $x < 0.9$ while $\alpha\text{-MoO}_3$ -type structure is present for $x \geq 0.9$. The obtained structural parameters for the first shell around metal ions allow to distinguish several structural phase transitions due to the change of composition. A set of subshells within the first shell was found, and they are in good agreement with Raman data.

The $\text{Mo}_x\text{W}_{1-x}\text{O}_3$ system presents great applied interest as a material for the construction of electrochromic devices, e.g. smart windows [1]. Depending on the preparation procedure, the phases formed by these mixed oxides can be divided into several groups relative to their structure: the single crystals have structures similar to WO_3 modifications of ReO_3 -type except for $x > 0.95$ when layered $\alpha\text{-MoO}_3$ -type structures appears [2], while the solid solutions prepared by dehydration of the corresponding hydrates using the *chimie douce* approach have structure of hexagonal WO_3 -type for $x < 0.6$ and ReO_3 -type for $x > 0.6$ [3]. Until now only X-ray diffraction (XRD) has been used as direct structural probe to characterize the $\text{Mo}_x\text{W}_{1-x}\text{O}_3$ system [2,3]. Since it is mainly sensitive to the long range order, the application of X-ray absorption spectroscopy (XAS) gives a new sight on the local structure. Moreover, the XAS allows to look separately on the local environment around Mo and W ions by studying the Mo K and W L₃ edges.

Polycrystalline $\text{Mo}_x\text{W}_{1-x}\text{O}_3$ ($x = 0.1, 0.2, 0.3, 0.5, 0.7$ and 0.9) solid solutions were obtained by high

temperature synthesis. The X-ray absorption fine structure (XAFS) spectra at the Mo K and W L₃ edges in solid solutions, monoclinic WO_3 and $\alpha\text{-MoO}_3$ were measured in transmission mode at room temperature in the energy range 1000 eV above the absorption edge using a standard setup of the DCI D13 (EXAFS-3) beam line at LURE. The synchrotron radiation was monochromatized using the Si(3 1 1) double-crystal monochromator, and its intensity was measured by two ionization chambers containing argon gas. The samples were previously characterized by XRD and Raman spectroscopy. The analysis of the EXAFS data was performed by the EDA package [4,5].

The Fourier transforms (FT) of the experimental XAFS spectra are shown in Fig. 1. There four ranges (0.5–2.2, 2.2–2.8/3.0, 2.8/3.0–4.0 and > 4.0 Å) can be separated and attributed [4] respectively to: (1) the single-scattering (SS) contribution from the 1st coordination shell; (2) the MS contribution from the 1st shell plus some contribution from W(Mo) ions located in the second shell; (3) the SS and MS contributions from the 2nd shell composed by W(Mo) ions (there is a strong focusing effect within the Me–O–Me chains when the $\widehat{\text{MeO}}\text{Me}$

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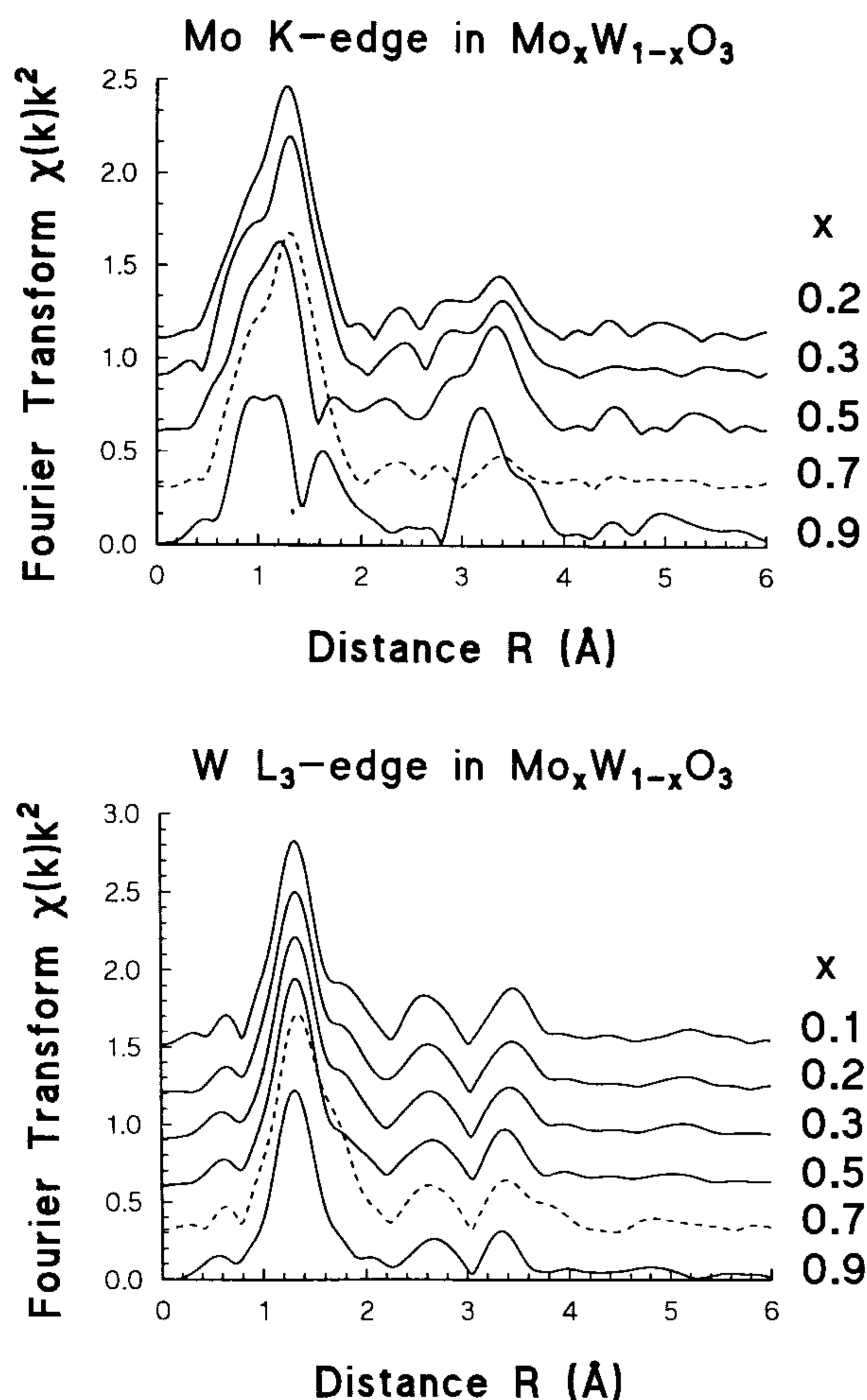


Fig. 1. Fourier transforms (FT) of the experimental XAFS spectra measured at the Mo K and W L_3 edges in $\text{Mo}_x\text{W}_{1-x}\text{O}_3$ solid solutions. The FT of the solid solution having β - MoO_3 -like structure is shown by dashed line.

angle is close to 180°) plus the SS contribution from the 3rd shell formed by oxygens; (4) outer shell contributions containing mainly W(Mo) ions. The analysis of the first shell allows to distinguish four groups of distances within it: 1.65–1.70, 1.75–1.85, 1.95–2.16 and 2.3–2.4 Å from which the first three give the main contribution to XAFS (Fig. 2). In agreement with Raman results, the 1st group was found only for $x \geq 0.9$, and it corresponds to the short Me = O bond. Since a set of distances is very wide, the distortion of $[\text{MeO}_6]$ octahedron, calculated as $\Delta = (1/6) \sum_{i=1}^6 [(R_i - \bar{R})/\bar{R}]^2$, is useful characteristic of the system (Fig. 2). It is the lowest for

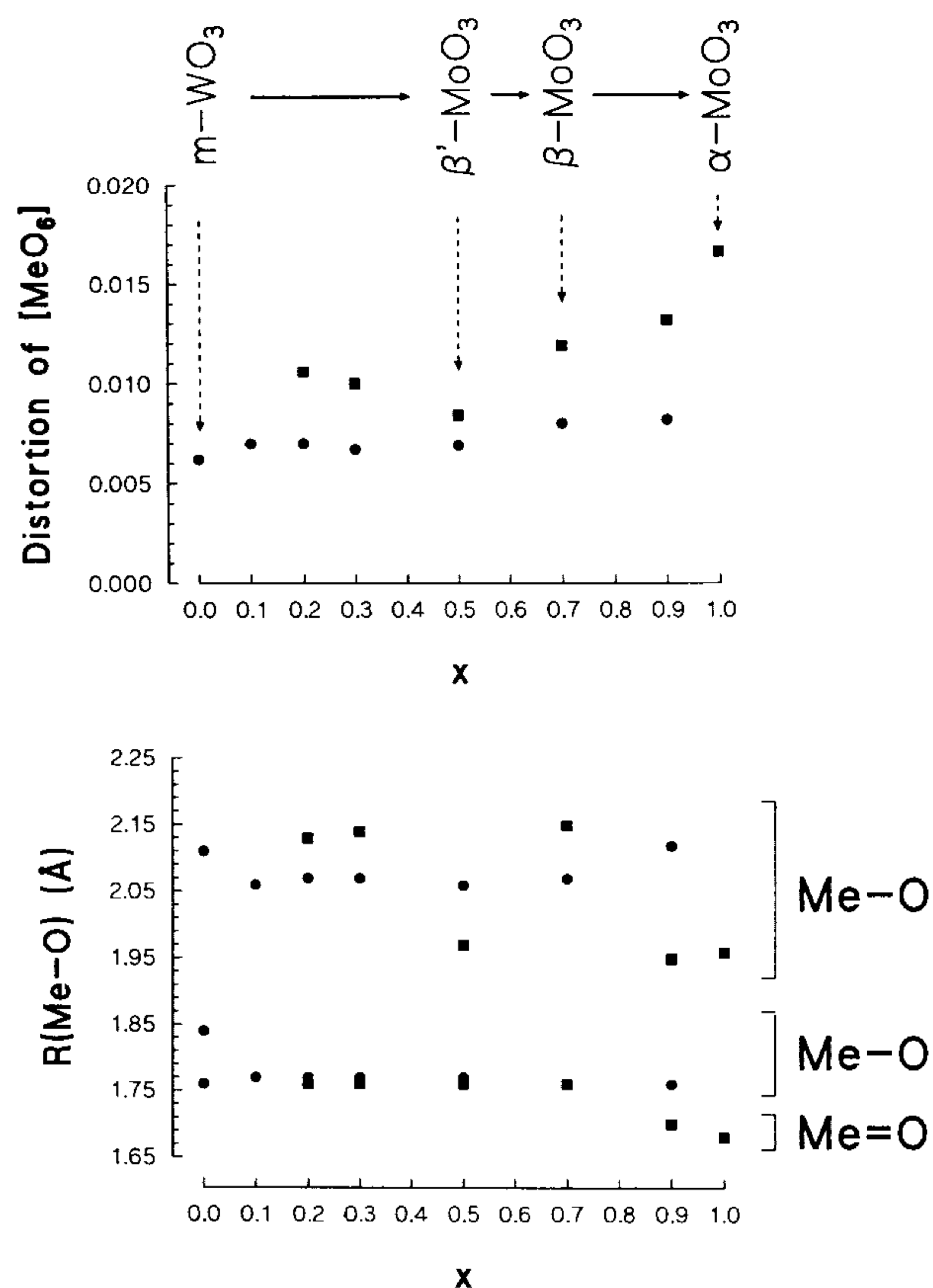


Fig. 2. Variations with composition of the $[\text{MeO}_6]$ octahedron distortion and the Me–O bond lengths giving the main contribution to XAFS at the Mo K (squares) and W L_3 (circles) edges in $\text{Mo}_x\text{W}_{1-x}\text{O}_3$ solid solutions.

$x = 0$ in $m\text{-WO}_3$ and increases with x becoming the highest in $\alpha\text{-MoO}_3$.

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