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In situ XAFS study of phase transitions and hydrogen intercalation in $\text{WO}_3\text{--MoO}_3$ system

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Abstract

The $\text{WO}_3\text{--MoO}_3$ system has several reconstructive and displacive phase transitions which can be induced by temperature and/or by change of stoichiometry or valence state of metal ions under hydrogen intercalation. We have studied in situ the local electronic and structural changes arising in $\text{WO}_3\text{--MoO}_3$ system with hydrogen intercalation and temperature. In situ XAFS measurements at the Mo K and W L_3 edges in $\text{H}_y\text{Mo}_x\text{W}_{1-x}\text{O}_3$ compounds, performed at different hydrogen intercalation level and temperatures (from RT to 500°C), allowed us to determine the rearrangement in the first and second coordination shells of Mo and W cations during phase transitions. It was found that hydrogen insertion leads, depending on W/Mo ratio, to the appearance of localized (mixed valence) or delocalized electronic states with different Mo and W surrounding.

The $\text{Mo}_x\text{W}_{1-x}\text{O}_3$ system exhibits 'displacive' or 'reconstructive' phase transitions induced respectively by hydrogen intercalation or temperature and leading to a rearrangement in the local electronic and atomic structures [1, 2].

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 of the Mo K and W L_3 edges in orthorhombic MoO_3 (ortho- MoO_3) and $\text{Mo}_x\text{W}_{1-x}\text{O}_3$ were measured in transmission mode using standard setup of the DCI EXAFS-3 beam line at LURE with the Si(3 1 1) double-crystal monochromator. The in situ measurements were done in the temperature range from RT to 500°C in H_2 or N_2 atmospheres.

First, we consider the effect of hydrogen intercalation on pure MoO_3 oxide (Fig. 1). The ortho- MoO_3 has layered structure composed of highly distorted $[\text{MoO}_6]$

octahedra with Mo ions in off-center position ($R(\text{Mo--O}) = 1.67, 1.74, 2 \times 1.95, 2.25$ and 2.33 Å) joined by corners ($R(\text{Mo--Mo}) = 2 \times 3.70$ and 2×3.96 Å) and edges ($R(\text{Mo--Mo}) = 2 \times 3.44$ Å). Its XAFS was interpreted previously [3]. The insertion of hydrogen at 400°C leads to a symmetrization of $[\text{MoO}_6]$ octahedra ($R(\text{Mo--O}) = 1.70, 4 \times 1.97$ and 2.04 Å) (the peak at 1.5 Å in Fig. 1) and some rearrangement of outer coordination shells. Thus ortho- MoO_3 transforms into the stable molybdenum bronze [4] which remains after cooling to RT.

The intercalation of hydrogen into the $\text{WO}_3\text{--MoO}_3$ system leads to the formation of $\text{H}_y\text{Mo}_x\text{W}_{1-x}\text{O}_3$ hydrogen bronzes [2] and to the appearance of Mo and W ions in a mixed valence state ($5+$ and $6+$). Depending on the W/Mo ratio and the amount of inserted hydrogen, the electronic state can be localized or delocalized. The intercalation process is accompanied by the local deformations around metal ions leading to the symmetrization of $[\text{MeO}_6]$ octahedra. This transformation is clearly seen in Figs. 1 and 2: the surroundings of Mo and W ions

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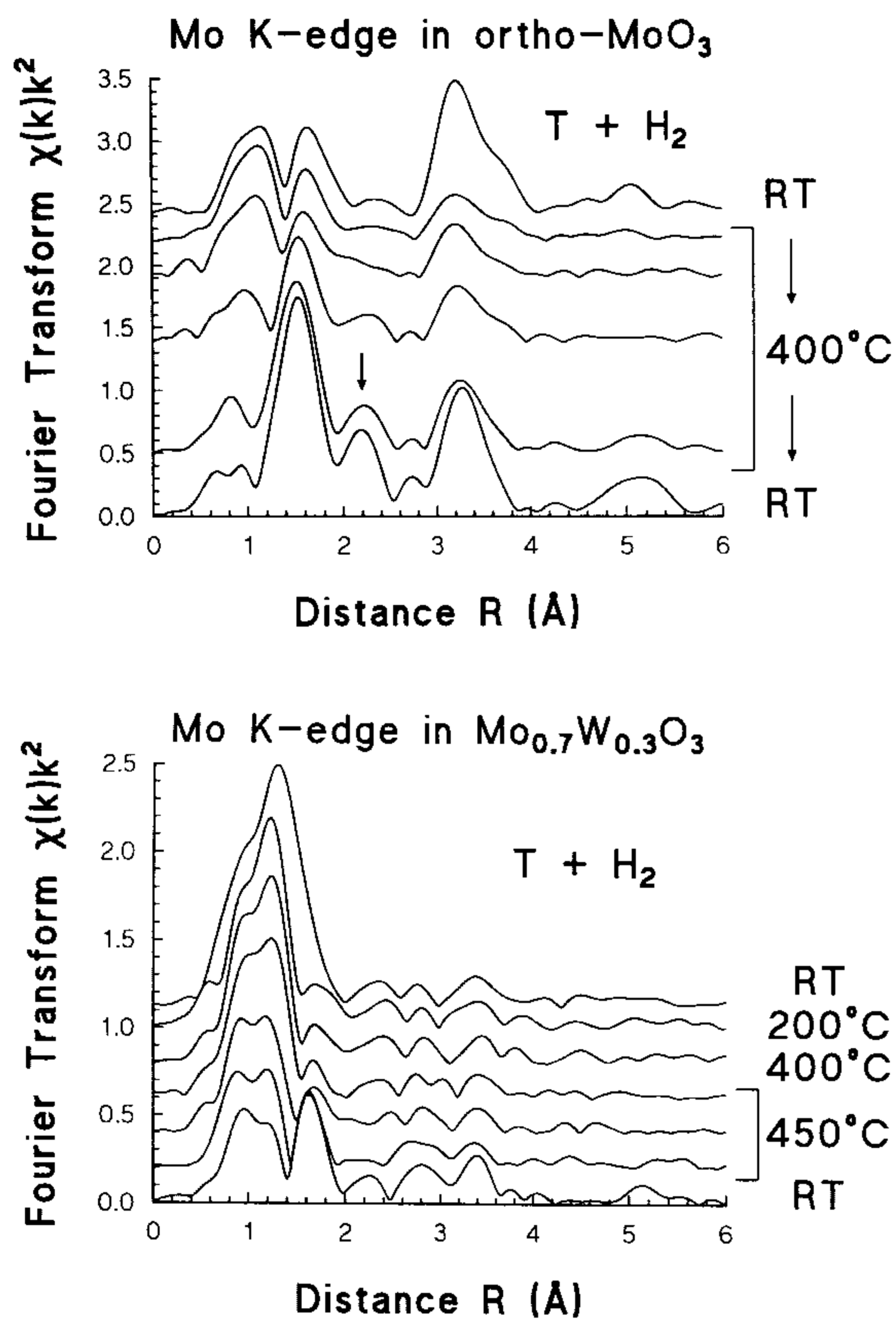


Fig. 1. Successive changes with hydrogen intercalation and temperature in the FTs of the experimental XAFS spectra measured at the Mo K-edge in ortho-MoO₃ and Mo_{0.7}W_{0.3}O₃. Note large contribution of the oscillating part of the atomic background absorption at the Mo K-edge giving rise to the peak at ~ 0.6 – 1 Å.

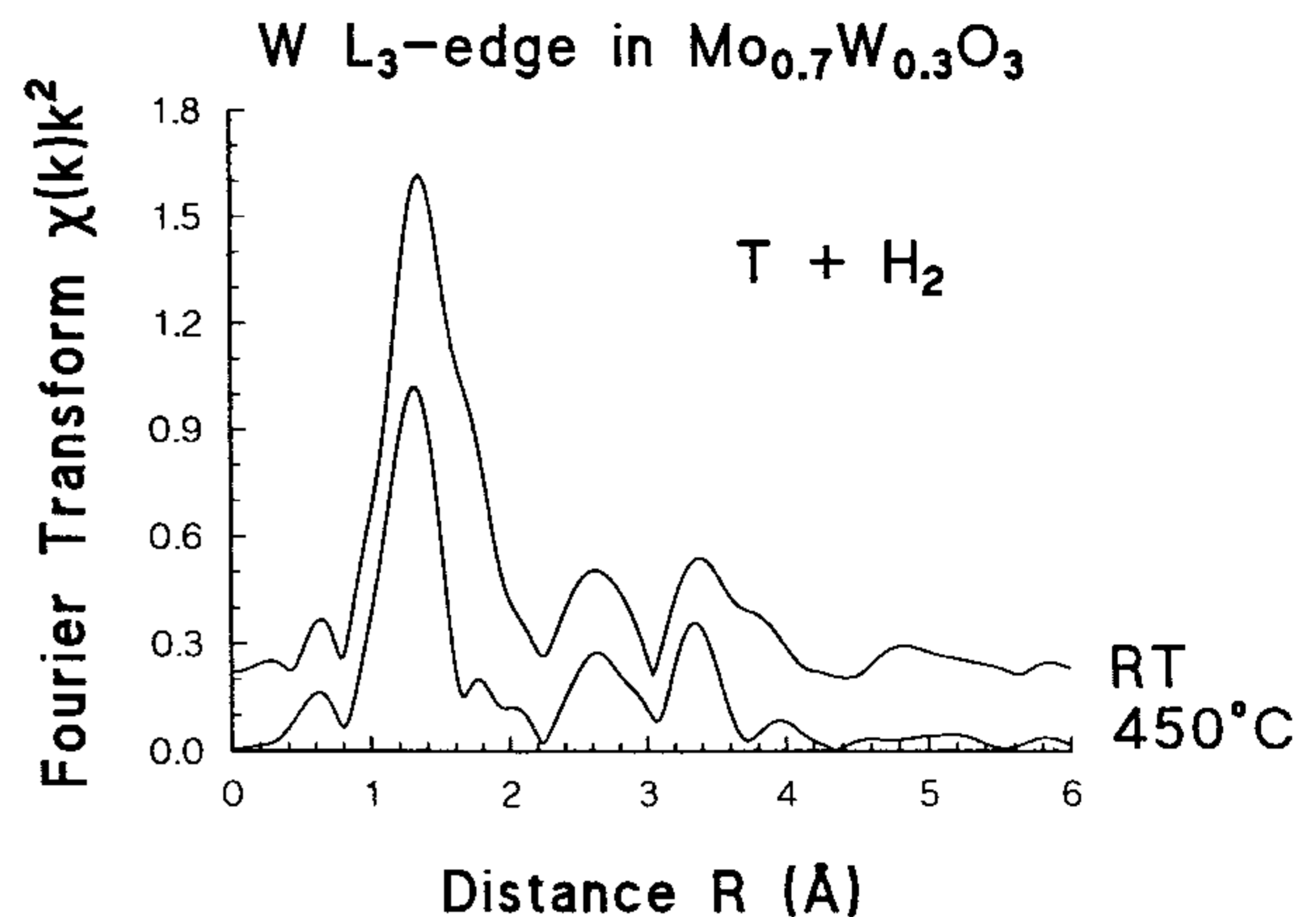


Fig. 2. Successive changes with hydrogen intercalation and temperature in the FTs of the experimental XAFS spectra measured at the W L₃-edge in Mo_{0.7}W_{0.3}O₃.

become less distorted both in the first (0.5–2.0 Å) and second (3–4 Å) shells with hydrogen insertion. Moreover, one can see that the surrounding of Mo ions is affected first and more strongly.

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