

X-Ray Absorption Study of the Short Range Order of Tungsten and Molybdenum Ions in BaO-P₂O₅-WO₃ and CaO-P₂O₅-MoO₃ Glasses

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Abstract. The analysis of XANES and EXAFS in BaO-P₂O₅-WO₃ and CaO-P₂O₅-MoO₃ glasses at the W L_{1,3} and Mo K edges was performed in comparison with a number of crystalline WO₃, CaWO₄, Na_{0.66}WO₃, α -MoO₃, β -MoO₃ and amorphous a-WO₃, a-MoO₃ compounds. The results of the EXAFS modelling by two different methods ((1) multi-shell single-scattering model within harmonic approximation and (2) model-independent radial distribution function (RDF) approach) allowed us to extract detailed structural information on the first coordination shell of metal (W or Mo) ion. Using the obtained data together with the information given by other experimental techniques, we propose a structural model of the local environment distortion around tungsten and molybdenum ions in phosphate glasses.

Tungsten-phosphate and molybdenum-phosphate glasses belong to a group of glasses which incorporate distorted octahedral structural units [MeO₆] (Me=W, Mo) within the glass network and whose structure is still not well understood [1-3]. Besides they exhibit interesting electrochromic properties and high ionic conductivity that makes them potential materials for electro-optical applications [3,4]. Recent use of the x-ray absorption spectroscopy to study tungsten-phosphate glasses showed possibility to obtain original and complementary to other experimental techniques information on the local environment around tungsten ions [3,4]. In this work we present an accurate EXAFS study of the short range order of tungsten and molybdenum ions in phosphate glasses using conventional multi-shell harmonic approximation and model-independent radial distribution function (RDF) approach, developed recently by one of us [5].

The tungsten-phosphate and molybdenum-phosphate glasses had the following compositions (in mol.%): 40 BaO-40 P₂O₅-20 WO₃ (20%WO₃), 30 BaO-30 P₂O₅-40 WO₃ (40%WO₃), 20 BaO-20 P₂O₅-60 WO₃ (60%WO₃), 34 P₂O₅-66 WO₃ (66%WO₃), 45 CaO-45 P₂O₅-10 MoO₃ (10%MoO₃), 40 CaO-40 P₂O₅-20 MoO₃ (20%MoO₃), 30 CaO-30 P₂O₅-40 MoO₃ (40%MoO₃) and 20 CaO-20 P₂O₅-60 MoO₃ (60%MoO₃). A set of reference compounds was also used: polycrystalline powders of WO₃, Na_{0.66}WO₃, CaWO₄ and α -MoO₃, polycrystalline β -MoO₃ and amorphous a-WO₃ and a-MoO₃ thin films.

X-ray absorption spectra (XAS) (Figure 1) of glasses and reference compounds were measured in transmission mode at the W L_{1,3} and Mo K edges using a standard setup of the ADONE PWA-BX1 wiggler beam line, equipped with the Si(220) channel-cut crystal monochromator and two ion chambers containing krypton gas, and the LURE DCI EXAFS-3 beam line, equipped with the Si(311) double-crystal monochromator and two ion chambers containing argon gas, respectively. All measurements were performed at room temperature. The details of the experiments can be found in [4,6].

The XAS were treated by the "EDA" software package [5]. The EXAFS signals were extracted following standard procedure and the contributions from the first shell were singled out by the Fourier filtering (see Figures 2 and 3). Thus obtained 1st-shell EXAFS signals were utilised in the best-fit procedure using two different methods: (1) multi-shell single-scattering model within harmonic approximation and (2) model-independent RDF approach [5]. To compare the results of two methods, the model-independent RDF's were decomposed into a set of Gaussian lines whose parameters were found in good agreement with the ones obtained by the first method. Note that the total number of obtained parameters satisfies to the Nyquist criterion and to the Fisher's $F_{0.95\%}$ -test. The details of the data analysis can be found in [5,6].

The XANES signals at the W L₃-edge contain a strong resonance - the so-called "white line" (WL), located just below the continuum threshold E_0 (Figure 1): it corresponds to the dipole-allowed transition from the $2p_{3/2}(W)$ level into a quasi-bound $5d(W)+2p(O)$ mixed-state. The same final state is probed by the excitation of the $2s(W)$ electron at the L₁-edge, however, in this case the intensity of the transition depends strongly on the local symmetry and the degree of the pd -mixing. The transition is dipole-forbidden in regular octahedron, having an inversion center, but becomes allowed in distorted octahedron (WO₃) and in tetrahedron (CaWO₄). Thus, the intensity of the peak (shoulder) below the continuum threshold at the K or L₁ edge allows to estimate roughly the coordination and the degree of distortion in the 1st shell. A comparison of the XANES signals suggests that in glasses, both W and Mo ions are located in strongly distorted octahedral-like coordination.

The qualitative results of the XANES analysis agree well with the quantitative data obtained by EXAFS. The simulation of the first-shell EXAFS signals in BaO-P₂O₅-WO₃ glasses by two methods, mentioned above, suggests that the RDF's around tungsten are composed of two groups of 3 oxygen ions each located at ~ 1.73 and ~ 2.02 Å. Note that in 60%WO₃-glass, there

are octahedra of two types, distorted as 3:3 (~70%) and 4:2 (~30%): the latter distortion is similar to the one in crystalline WO_3 . Close RDF's were found in $\text{CaO-P}_2\text{O}_5\text{-MoO}_3$ glasses, however, here the RDF peak of the distant group of oxygen ions is strongly asymmetric with a tail at long distances. As a result, the local surrounding of molybdenum can be approximated by three groups of oxygens consisting of 3, 2 and 1 atoms at ~ 1.68 , ~ 1.98 and ~ 2.11 Å, respectively. Note that in the 66% WO_3 -glass without BaO, the 1st-shell is splitted into two groups of 2 and 4 oxygen ions at ~ 1.72 and ~ 1.95 Å. Thus the type of the first-shell distortion in phosphate glasses differs from the one in the reference crystals and amorphous thin films (see Table 1) and can be attributed to the *off-centre* displacement of W or Mo ions in the $\langle 111 \rangle$ directions. Note that in pure crystalline and amorphous MeO_3 compounds, W or Mo ions are displaced *off-centre* in the $\langle 110 \rangle$ directions (Table 1).

The degree of the $[\text{MeO}_6]$ distortion Δ was estimated using the formula $\Delta = \langle |R - \langle R \rangle| \rangle$ [6,7] from the RDF's, determined by the method 2. The error of Δ is about ± 0.001 Å: it is related to the uncertainty of the shape of the RDF. Note that in the glasses, Δ decreases with increasing MeO_3 content (Figure 4(a)) that is attributed to a decrease of the number of long Me-OPO_3 bonds, and, besides, Δ is larger in the molybdenum glasses and oxides (Figure 4(a) and Table 1). In tungsten containing reference compounds, the values of Δ agree with the ones from diffraction studies [7] and correlate with the valence state of tungsten ions: this dependence allows to estimate the valency of W in glasses (Figure 4(b)). The obtained results suggest that in spite of a signal from the $\text{W}^{5+} d^1$ - ions has been detected by electron paramagnetic resonance (EPR) spectroscopy [8] in these glasses, the total amount of W^{5+} ions is too small to be detectable in the EXAFS signal.

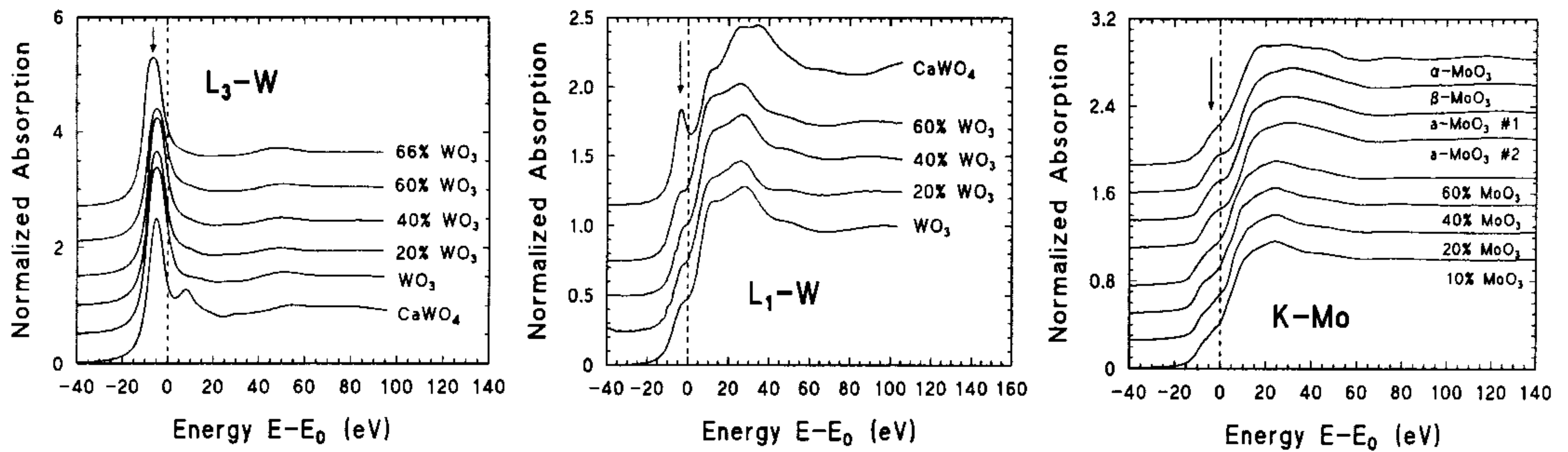


Figure 1: XANES signals at the W $L_{1,3}$ and Mo K edges in glasses and reference compounds. The positions of the WL's are indicated by arrows. Note the increase of the shoulder intensity at the L_1 and K edges with increasing $[\text{MeO}_6]$ distortion.

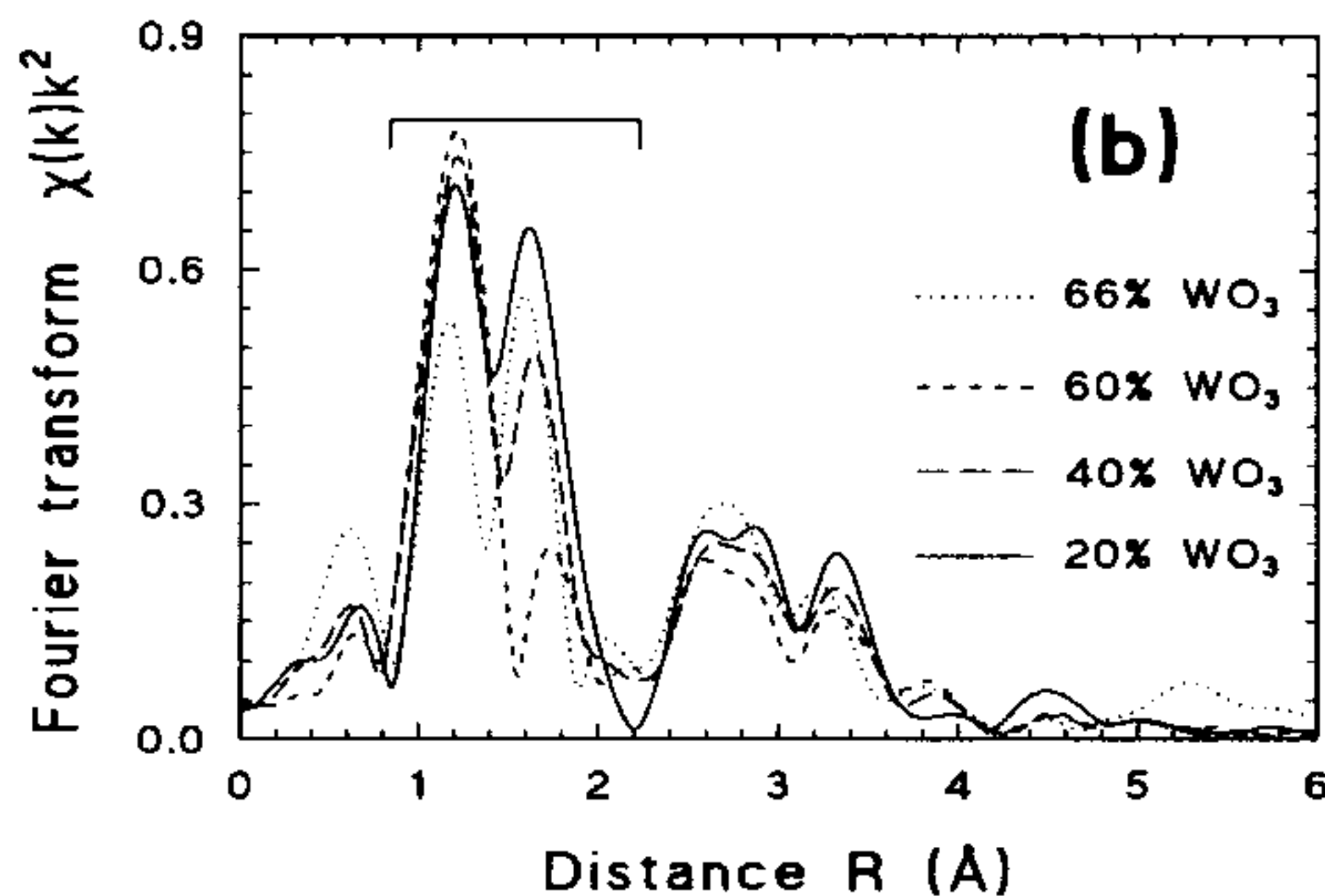
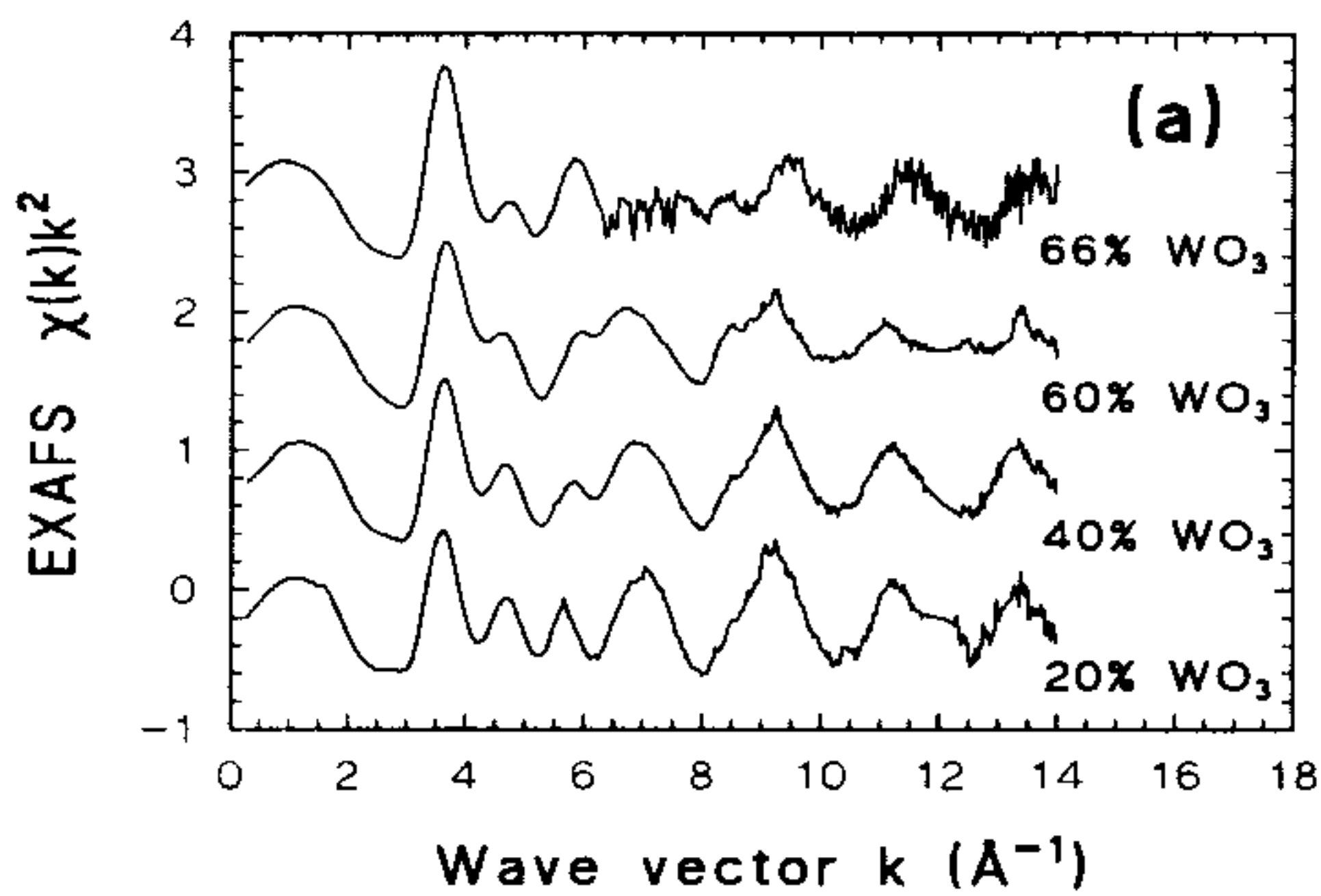


Figure 2: EXAFS signals and their FT's at the W L_3 -edge. The region of the first shell is indicated by solid bracket.

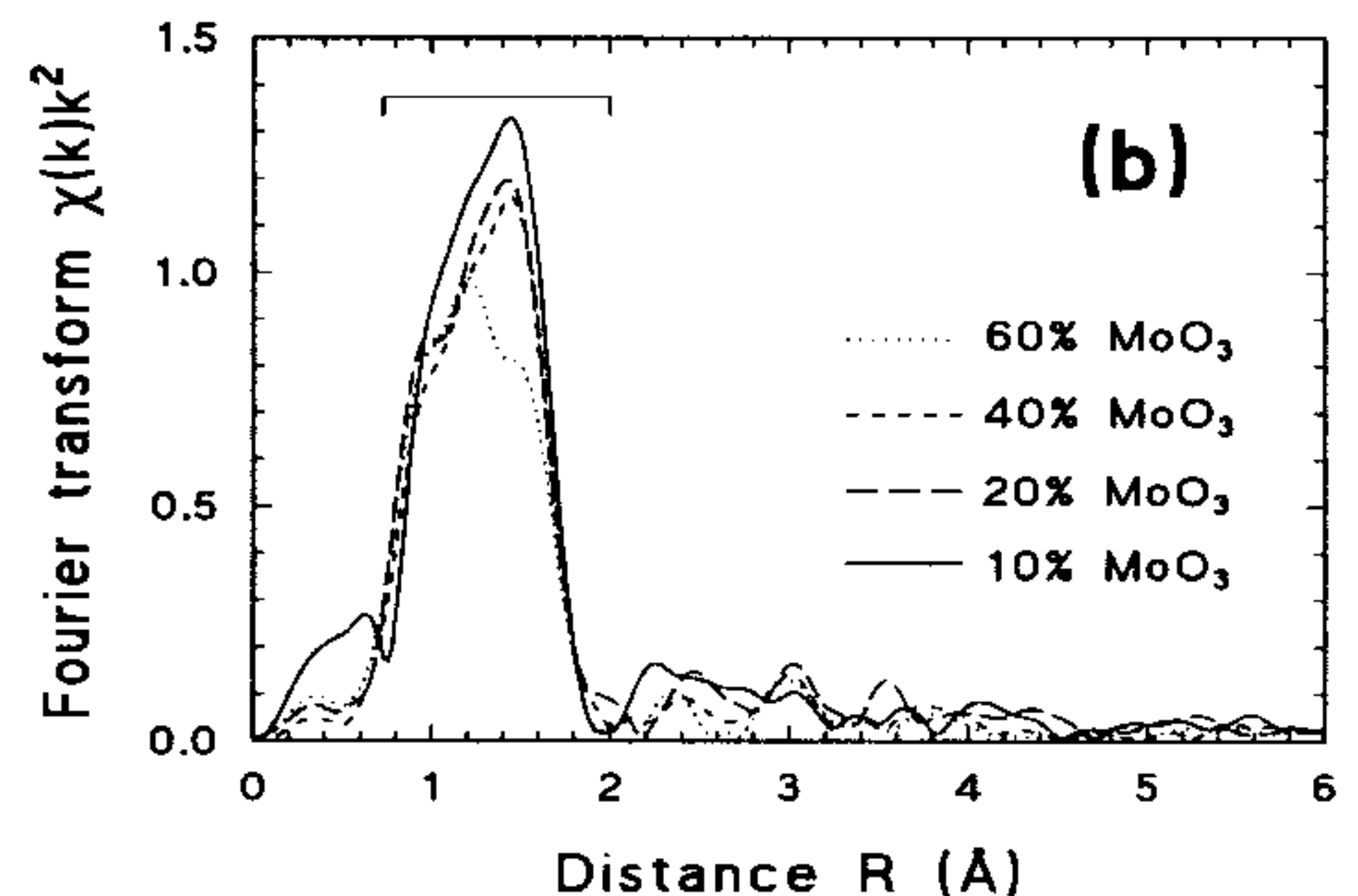
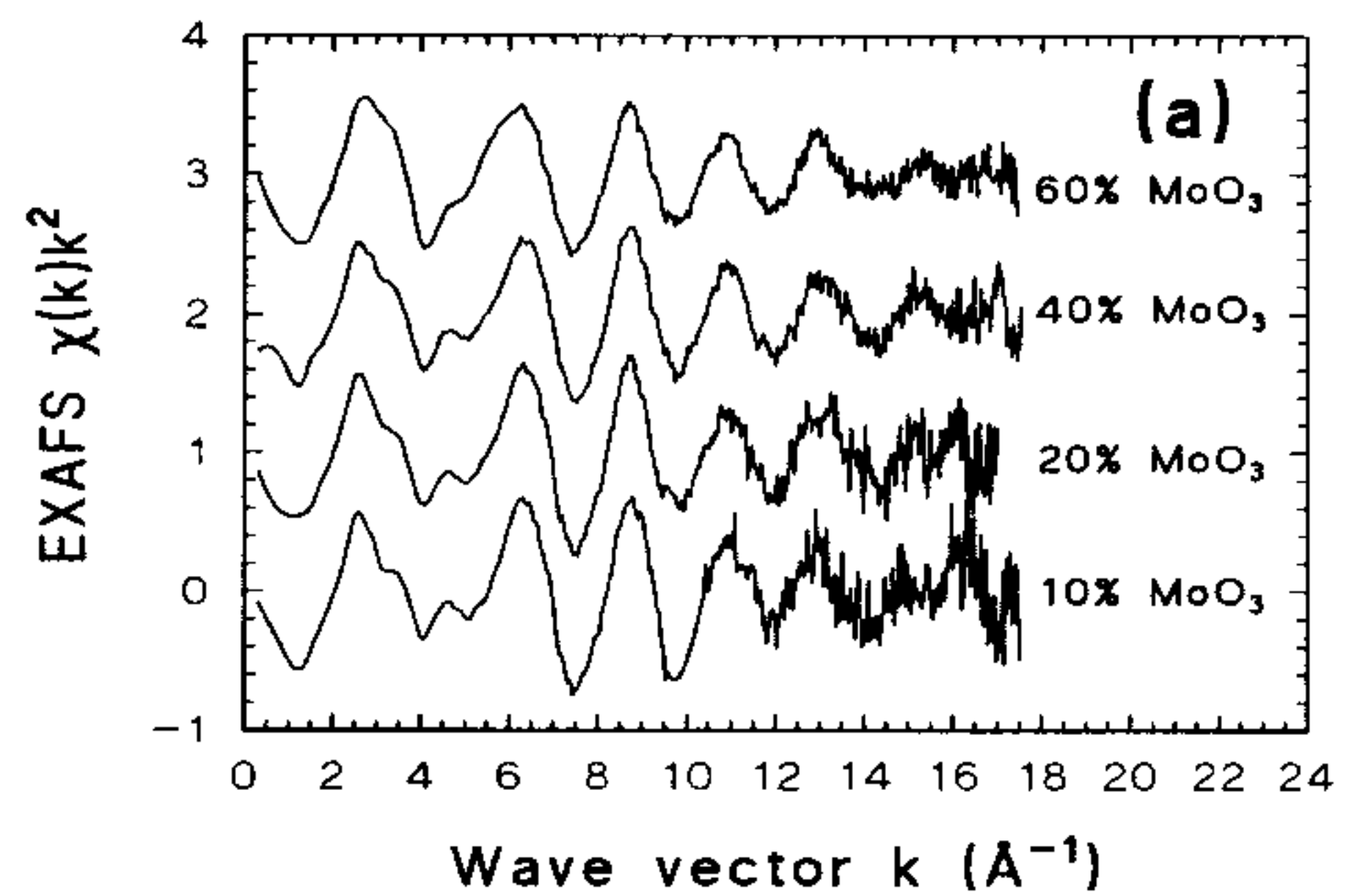


Figure 3: EXAFS signals and their FT's at the Mo K-edge. The region of the first shell is indicated by solid bracket.

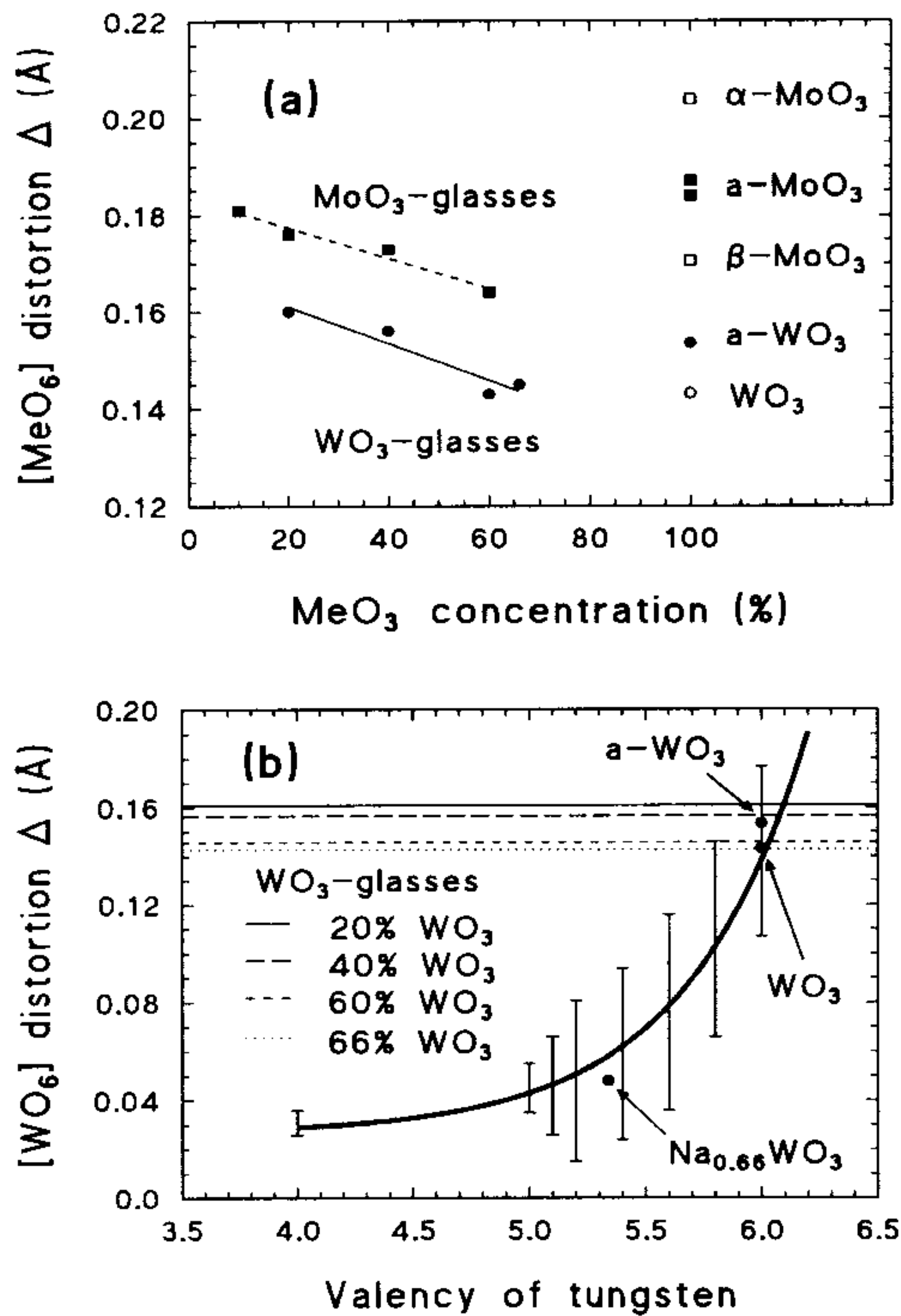


Figure 4: (a) Distortion Δ of the $[\text{MeO}_6]$ octahedron vs. MeO_3 concentration. (b) Dependence of the WO_6 distortion Δ from the valence state of tungsten. Solid line represents results from [7].

Table 1: Distortion Δ (± 0.001) of the first shell and its type in glasses and reference compounds from the EXAFS data. The attributed direction of the *off-centre* displacement is also given.

Compound	Type of distortion	Direction of displacement	Δ (Å)
CaWO_4	4		0.045
$\text{Na}_{0.66}\text{WO}_3$	6		0.048
WO_3	4 : 2	$\langle 110 \rangle$	0.143
a- WO_3	4 : 1 : 1	$\langle 110 \rangle$	0.154
20% WO_3	3 : 3	$\langle 111 \rangle$	0.160
40% WO_3	3 : 3	$\langle 111 \rangle$	0.156
60% WO_3	3 : 3 (~70%) 4 : 2 (~30%)	$\langle 111 \rangle$	0.143
66% WO_3	2 : 4		0.145
$\alpha\text{-MoO}_3$	2 : 2 : 2	$\langle 110 \rangle$	0.204
$\beta\text{-MoO}_3$	4 : 2	$\langle 110 \rangle$	0.171
a- MoO_3 #1	4 : 1 : 1	$\langle 110 \rangle$	0.187
a- MoO_3 #2	4 : 1 : 1	$\langle 110 \rangle$	0.184
10% MoO_3	3 : 2 : 1	$\langle 111 \rangle$	0.181
20% MoO_3	3 : 2 : 1	$\langle 111 \rangle$	0.176
40% MoO_3	3 : 2 : 1	$\langle 111 \rangle$	0.172
60% MoO_3	3 : 2 : 1	$\langle 111 \rangle$	0.164

In spite of the changes occurring within the first shell of metal ions in glasses, the peaks in FT's beyond the first one remain similar (see Figures 2(b) and 3(b)): they are attributed mainly to the multiple-scattering (MS) effects within the first shell octahedron [4,6]. It is known that the MS contribution from an octahedron is less sensitive to its distortion than the single-scattering one [9]. At the same time, the MS contribution depends strongly on the photoelectron angular momentum (the absorption edge type), especially, in the case of the double-scattering paths $\text{Me}_0 \rightarrow \text{O}_1 \rightarrow \text{O}_2 \rightarrow \text{Me}_0$ ($\angle \text{O}_1\text{Me}_0\text{O}_2 \approx 90^\circ$) within the first coordination shell whose contribution is smaller in the K, L_1 -EXAFS than in $\text{L}_{2,3}$ -EXAFS [9,10]. These peculiarities of the MS signals explain the similarity of the peaks at 2.2 - 3.8 Å in the same series of glasses and the difference between the peaks in FT's of tungsten and molybdenum glasses.

Acknowledgments

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