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EXAFS studies of MeO_{3-x} (Me = W, Mo, Re, Ir) crystalline and amorphous oxides

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The structure of the first coordination sphere of transition metals in such compounds as c-ReO_3, c-IrO_2, c-WO_3, a-WO_3, c-MoO_3 and a-MoO_3 has been studied by the EXAFS method in the "ADONE" synchrotron source. Different approximations are discussed and the sets of the most suitable parameters are presented. It has been found that different methods of preparing amorphous tungsten oxide thin films lead to differences in their structure.

1. Introduction

The high intensity of synchrotron radiation allows EXAFS spectra to be obtained in a wide energy range with a good signal/noise ratio and high resolution. Such EXAFS spectra allow, firstly, to determine the sets of close-lying distances in the first and the next coordination spheres of the excited atom with a high accuracy and a decrease correlation between the fitting parameters N_i, R_i, σ_i^2, Γ_i and E_0.

Earlier, we investigated by the EXAFS method [1,2] the nonstoichiometric tungsten oxides WO_{3-x} and water-containing tungsten compounds at the L_3-edge of tungsten. For these compounds a continuous set of distances W–O (from 1.7 to 2.3 Å) in the first coordination sphere is usual, and their structure consists of strongly distorted WO_6 octahedra linked by the corners with different W–O–W angles. In the interval from 2 to 3 Å of the Fourier transform (FT) a well resolved peak from a multiple scattering signal is found. Moreover, for heavy elements, the signal from the second coordination sphere is observed in the EXAFS spectra and in some compounds (e.g., $WO_{2.90}$, $WO_{2.96}$) a focusing effect is also present in the W–O–W chains.

The obtained results for crystalline compounds are the basis for the investigation of electrochromic amorphous WO_3 thin films prepared by different methods – thermal evaporation, high-frequency sputtering, chemical deposition, etc. Earlier, we studied by the EXAFS method a-WO_3 films prepared by fast thermal evaporation at low vacuum [2].

In this work crystalline oxides such as ReO_3, IrO_2 and MoO_3 have been studied in comparison with WO_3. The structural unit of all these compounds is a distorted oxygen octahedron of the metallic atom. We have also studied chemically stable amorphous thin films of a-WO_3 prepared by slow thermal evaporation and amorphous films of a-MoO_3 prepared by fast evaporation.

2. Experimental

Transmission EXAFS spectra were taken on W, Ir and Re L_3-edges and the Mo K-edge using the EXAFS station (Si[220] and Si[111] channel-cut crystal monochromators) on the BX-1 wiggler beam line ("PWA" "ADONE" LNF INFN). The storage ring "ADONE" operated at 20–50 mA and 1.5 GeV with a wiggler current of 4000 A.

The thin films of a-WO_3, a-MoO_3 (amorphous) and c-IrO_2 (polycrystalline) were prepared at the Institute of Solid State Physics in Riga. The thin films of a-WO_3 were obtained by slow thermal evaporation in medium vacuum on a polyimide substrate at $T_s = 200\,^\circ$C. These films are chemically stable and were used in electrochromic devices with a liquid electrolyte. The thin a-MoO_3 films were obtained by high thermal evaporation in low vacuum on a polyimide substrate at $T_s = 150\,^\circ$C and were chemically not as stable. These films were used in solid-state (Deb-structure) electrochromic devices. The polycrystalline thin films of c-IrO_2 were prepared by reactive magnetron sputtering of metallic Ir in an O_2 and Ar atmosphere on a polyimide substrate at room temperature and were also used in electrochromic devices. The powders c-WO_3 (monoclinic), c-MoO_3, c-ReO_3 and c-$CaWO_4$ were taken as reference compounds.

3. Experimental results and discussion

The Fourier transform (FT) of EXAFS spectra $\chi(k)k^2$ with a Gaussian window in the k-space intervals of 2–16 $Å^{-1}$ for the Re, Ir and W, and 2–14 $Å^{-1}$ for the Mo oxides (figs. 1–7), and the inverse FT in different R-space intervals allowed us to separate contributions in the EXAFS spectra from different shells: 0.8–2.2 Å: the first coordination shell (Re–O, W–O, Ir–O, Mo–O); 2.2–3.2 Å: multiple scattering in the first coordination shell (ReO_6, WO_6, IrO_6, MoO_6); 3.2–4.5 Å: the second coordination shell (Re–O–Re, W–O–W, Ir–O–Ir, Mo–O–Mo) with a focusing effect in ReO_3 crystals [3] and significant contributions from multiple scattering in all these materials with heavy metals. The

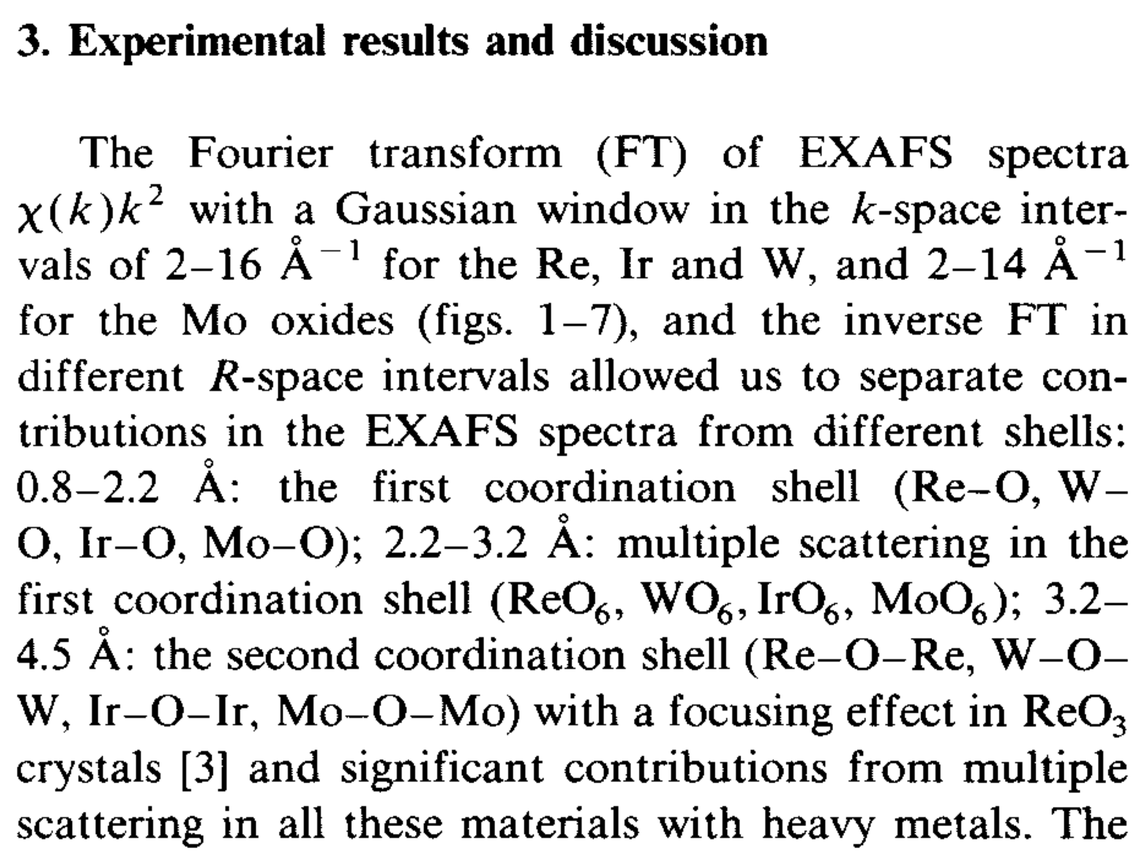


Fig. 1. ReO_3: (A) the Fourier transform of EXAFS (without phase correction); (B) experimental ($R = 0.7$–2.0 Å) (circles) and calculated (solid line) curves $\chi(k)k^2$ for the first coordination sphere.

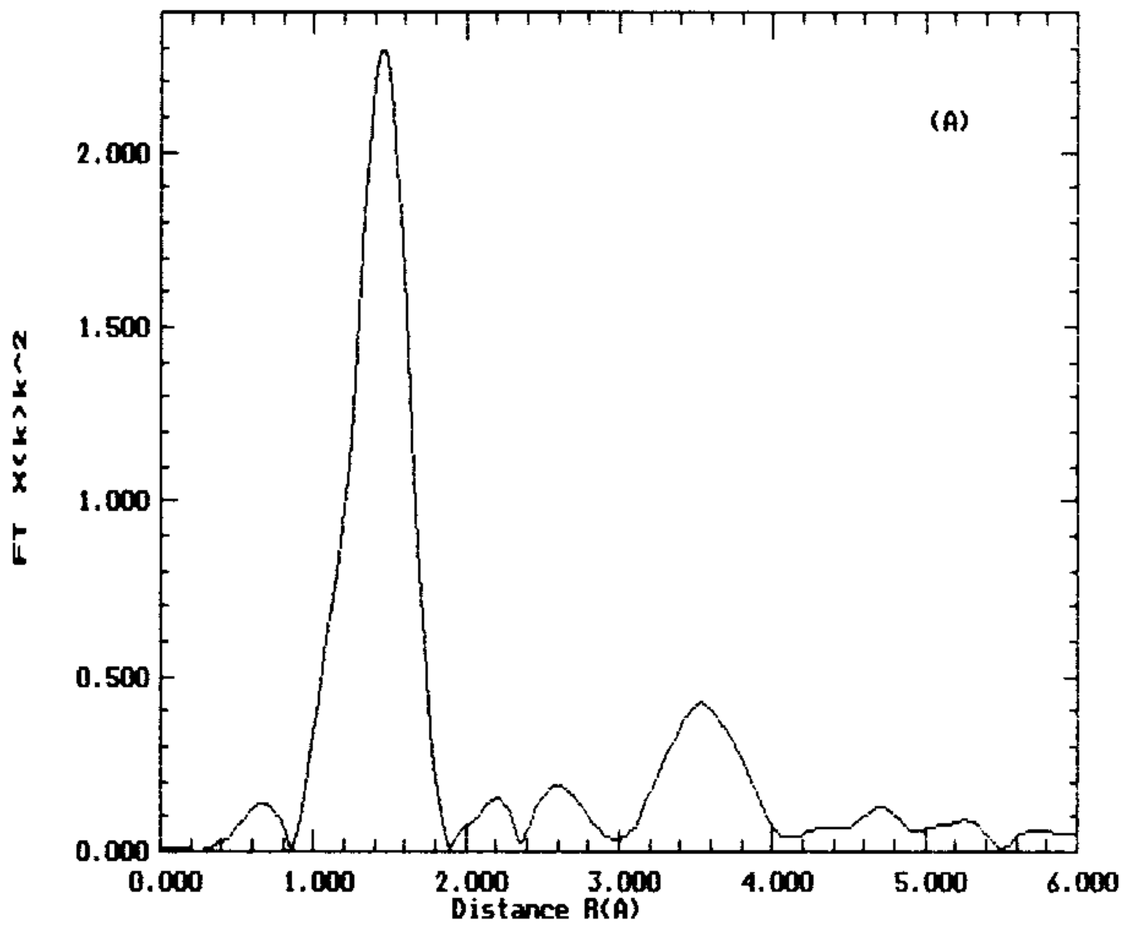


Fig. 2. $CaWO_4$: (A) the Fourier transform of EXAFS (without phase correction), (B) experimental ($R = 0.85$–1.9 Å) (circles) and calculated (solid line) curves $\chi(k)k^2$ for the first coordination sphere.

analysis of the first coordination sphere was performed by inverse FT and by fitting of its results in the single scattering approximation with the amplitude $f(\pi, k)$ and phase $\phi(k)$ calculated in curved wave approximation [4]:

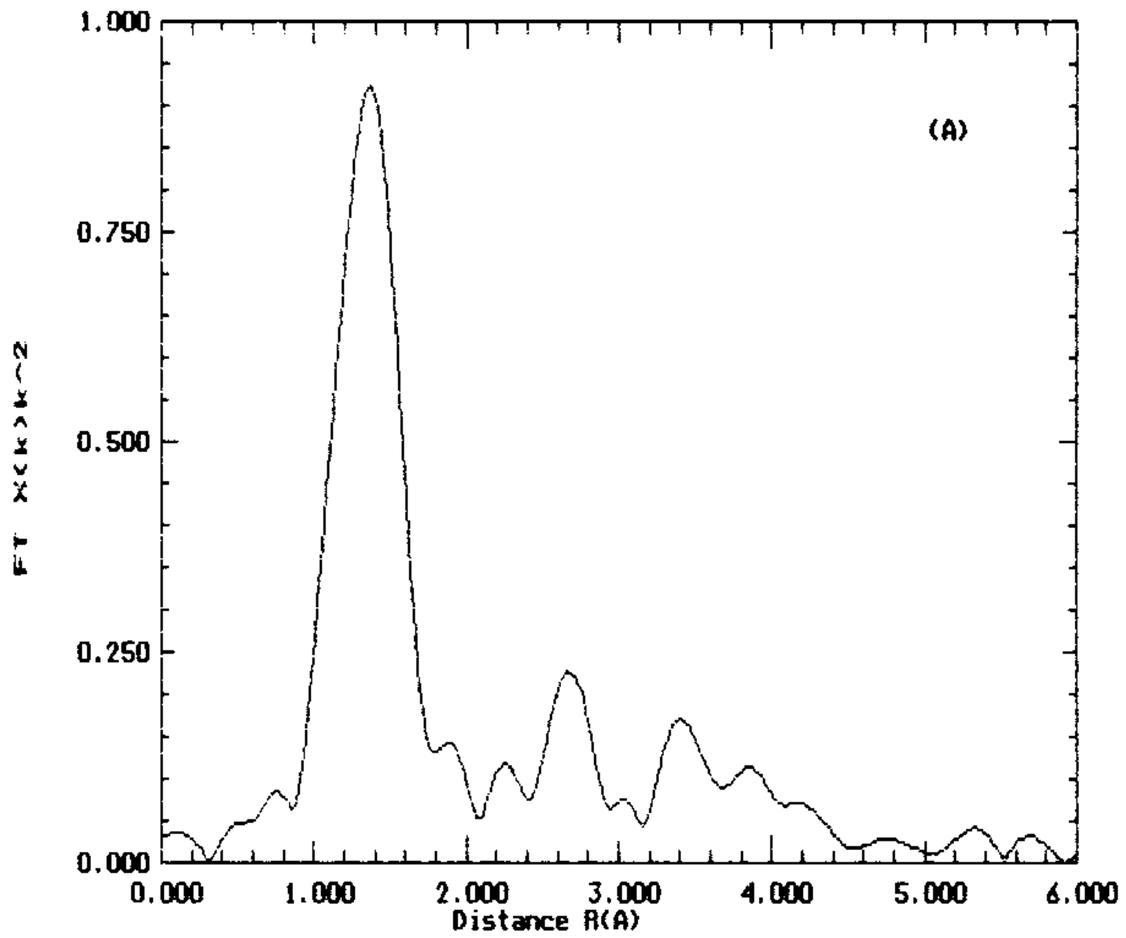
$$\chi(k) = \sum_i \frac{N_i S_{0i}^2}{R_i^2 k} f_i(\pi, k)\, e^{-2\sigma_i^2 k^2}\, e^{-2R_i\Gamma/k} \times \sin\bigl(2kR_i + \phi_i(k)\bigr).$$

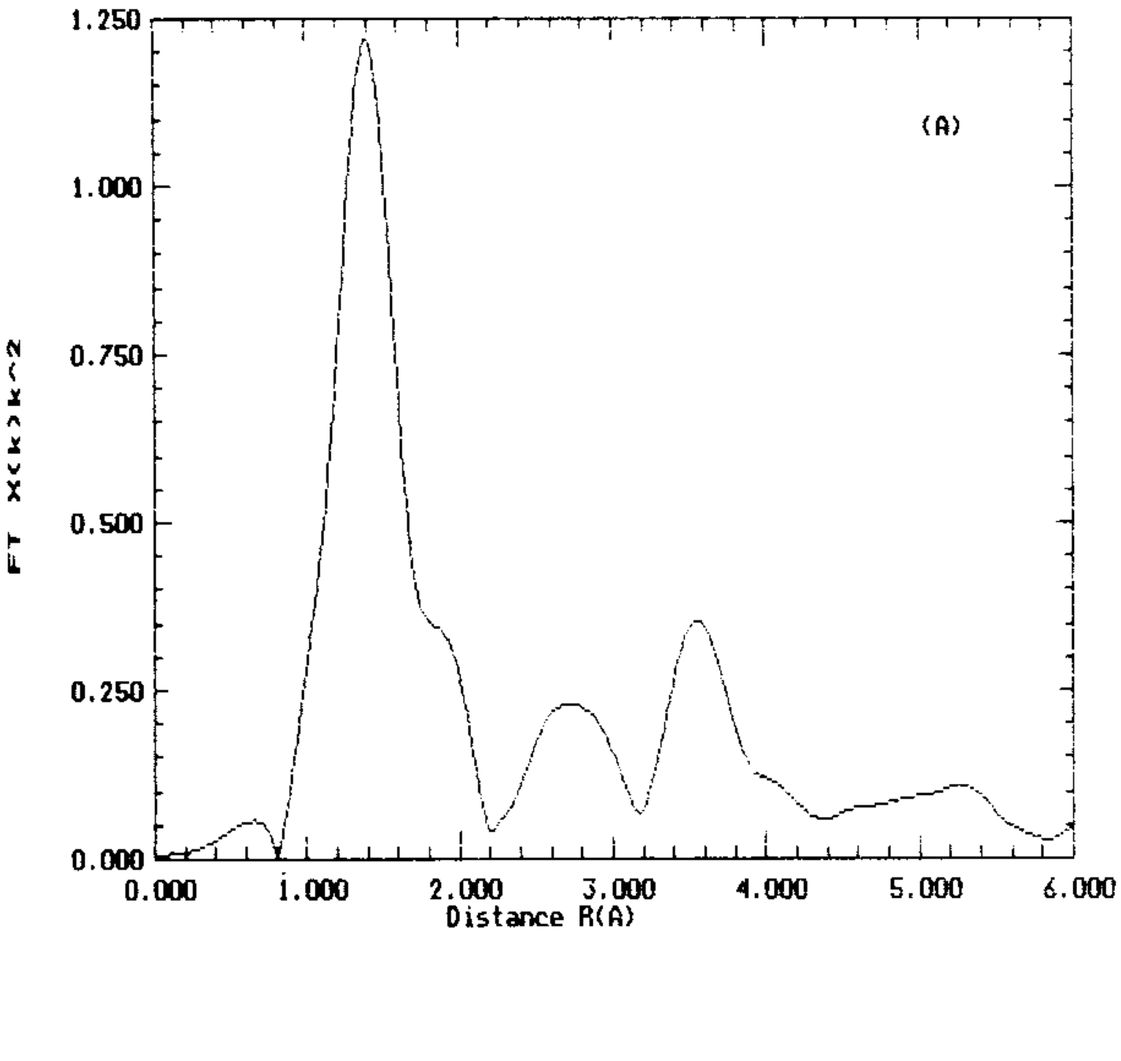
A least-squares procedure by the modified Levenberg–Marquardt method [5,6] was used to obtain a set of the most suitable parameters, $N_i S_0^2$, R_i, σ_i^2 and Γ. The obtained results are presented in table 1. The fitting was performed in $\chi(k)k^2$ space and E_0 was used as a fixed

input parameter from the reference crystals. The results are shown in figs. 1–7. All the computer programs for the data analysis were prepared at the Institute of Solid State Physics in Riga.

The EXAFS spectrum of the ReO_3 crystal with perfect octahedral ReO_6 structural units connected by corners and $CaWO_4$ with perfect tetrahedral WO_4 units and their FT (figs. 1 and 2) are in good agreement with previous results [3,7], and the one-shell fitting is in good agreement with crystallographic data for Re–O and W–O distances.

The first coordination sphere in ReO_3 and $CaWO_4$ is well described by one distance (Re–O and W–O), and the obtained parameters S_0^2, Γ and σ_i^2 are in good agreement with each other. For IrO_2 with the rutile type





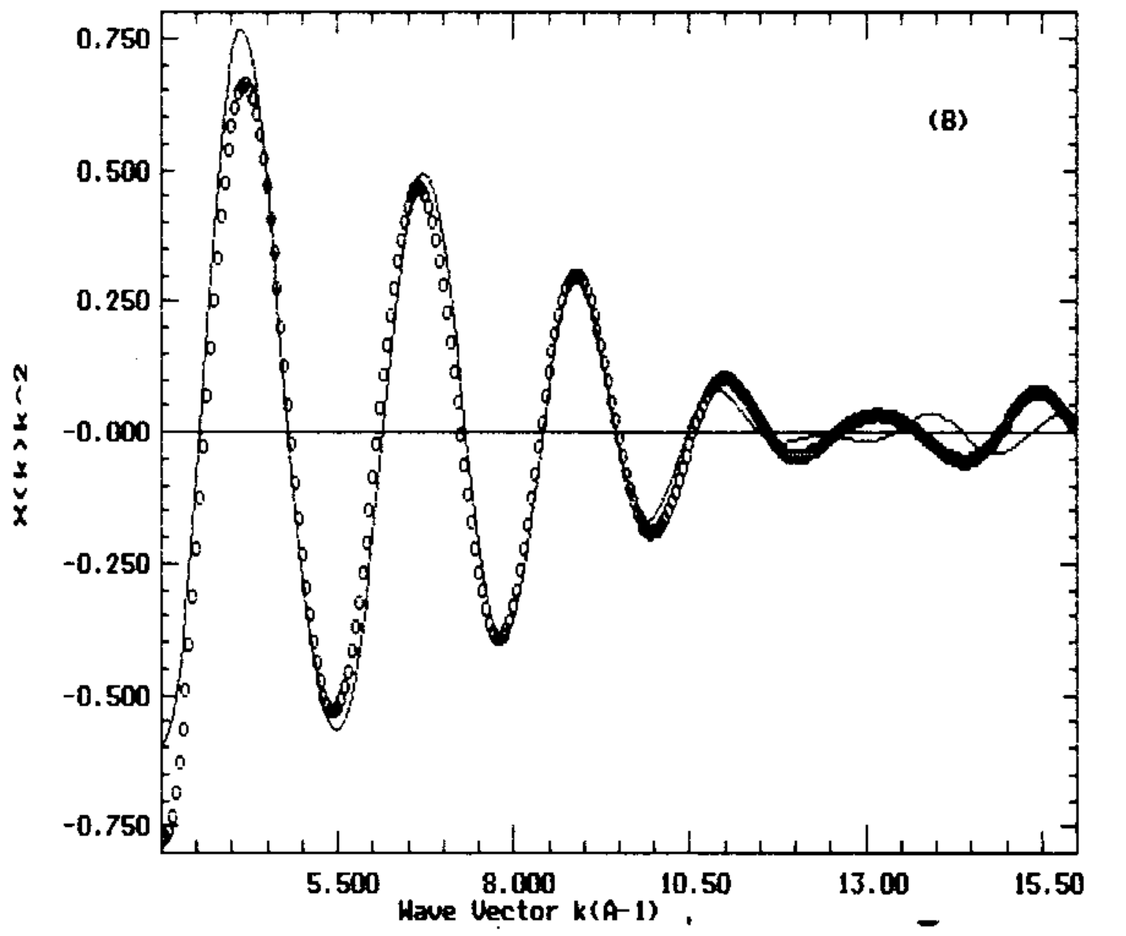


Fig. 4. a-WO_3: (A) the Fourier transform of EXAFS (without phase correction); (B) experimental ($R = 0.85$–2.1 Å) (circles) and calculated (solid line) curves $\chi(k)k^2$ for the first coordination sphere.

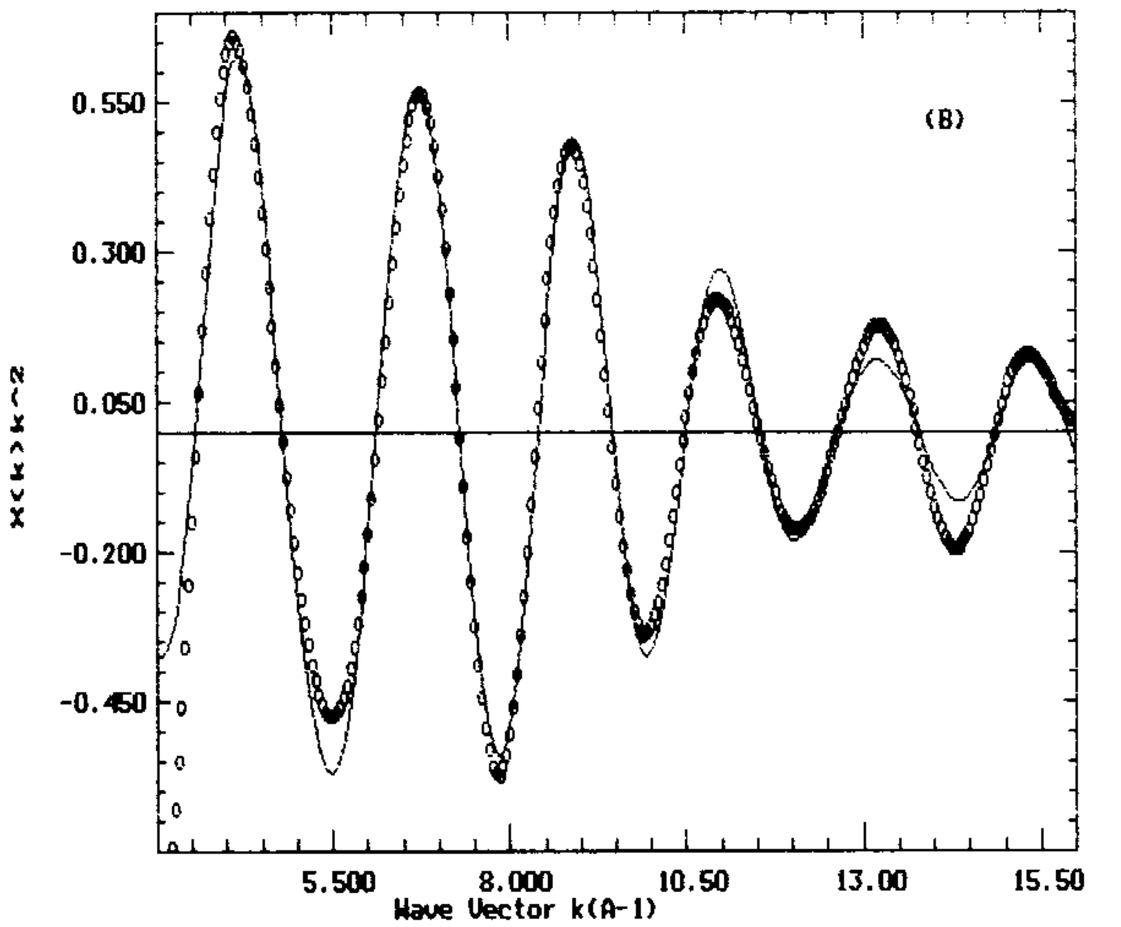


Fig. 3. c-WO_3: (A) the Fourier transform of EXAFS (without phase correction); (B) experimental ($R = 0.8$–2.2 Å) (circles) and calculated (solid line) curves $\chi(k)k^2$ for the first coordination sphere.

structure, we use the two-shell approximation which is in accordance with the crystallographic data. The distances Ir–O_1 and Ir–O_2 and coordination numbers in thin films are similar to those in crystalline IrO_2. In monoclinic WO_3 the wide set of distances between tungsten and oxygen (from 1.73 to 2.20 Å) leads to a complicated beating of the EXAFS amplitude in all the k-space from 2 to 17 $Å^{-1}$.

In the small and medium values of the wave vector (2–10 $Å^{-1}$) all the distances (the short, 1.75 Å, the medium, 1.85 Å, and the long, 2.1 Å) give a comparable contribution to the EXAFS spectrum, but in the large values of the wave vector ($\geqslant 10$ $Å^{-1}$), only oscillations from the short distances are important. Moreover, the EXAFS from the short distances has essentially smaller

values of σ^2. On the average, the EXAFS spectrum of the monoclinic WO_3 is produced by a short distance, equal to 1.78 Å. The shoulder near 1.8 Å in the FT is due to the distances 1.9 and 2.1 Å [7]. Thus, more exactly, the EXAFS spectrum can be described by the set of three distances 1.77, 1.90 and 2.1 Å.

In a four-shell approximation, we obtain a better agreement with crystallographic data, which we divide into six groups of W–O distances (see table 1). The obtained Debye–Waller parameters most probably reflect the dispersion of distances, rather than amplitudes of oscillations of the W–O bond.

The EXAFS spectra and their FT for amorphous films of a-WO_3 depend essentially on the method of preparation. The chemically stable films, obtained by slow thermal evaporation at a substrate temperature of about 200 °C, differ in structure from those obtained by fast evaporation. Results for the latter have been published earlier [2]. The differences are in the form of FT peaks for the first coordination sphere (0.8–2.2 Å), the multiple scattering peak (2.2–3.2 Å) and the second coordination sphere (3.2–4.5 Å). The main difference for the first coordination sphere is a faster reduction of the EXAFS amplitude after 10 $Å^{-1}$, leading to the reduction of the FT peak. The results in table 1 for a-WO_3 show that this effect is due to the large value of the Debye–Waller factor (0.005 $Å^2$) for a short distance (1.754 Å). Moreover, we observe the absence of the shoulder in the FT at 1.8 Å, due to the high value of the Debye–Waller factor for long distances (2.1 Å).

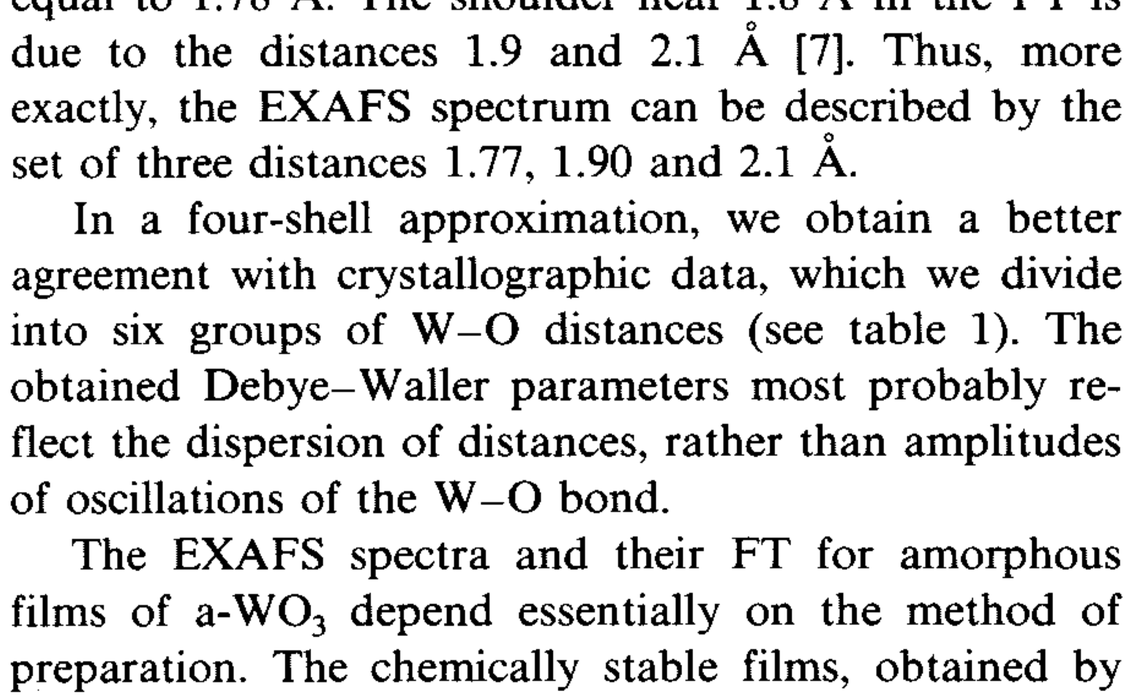
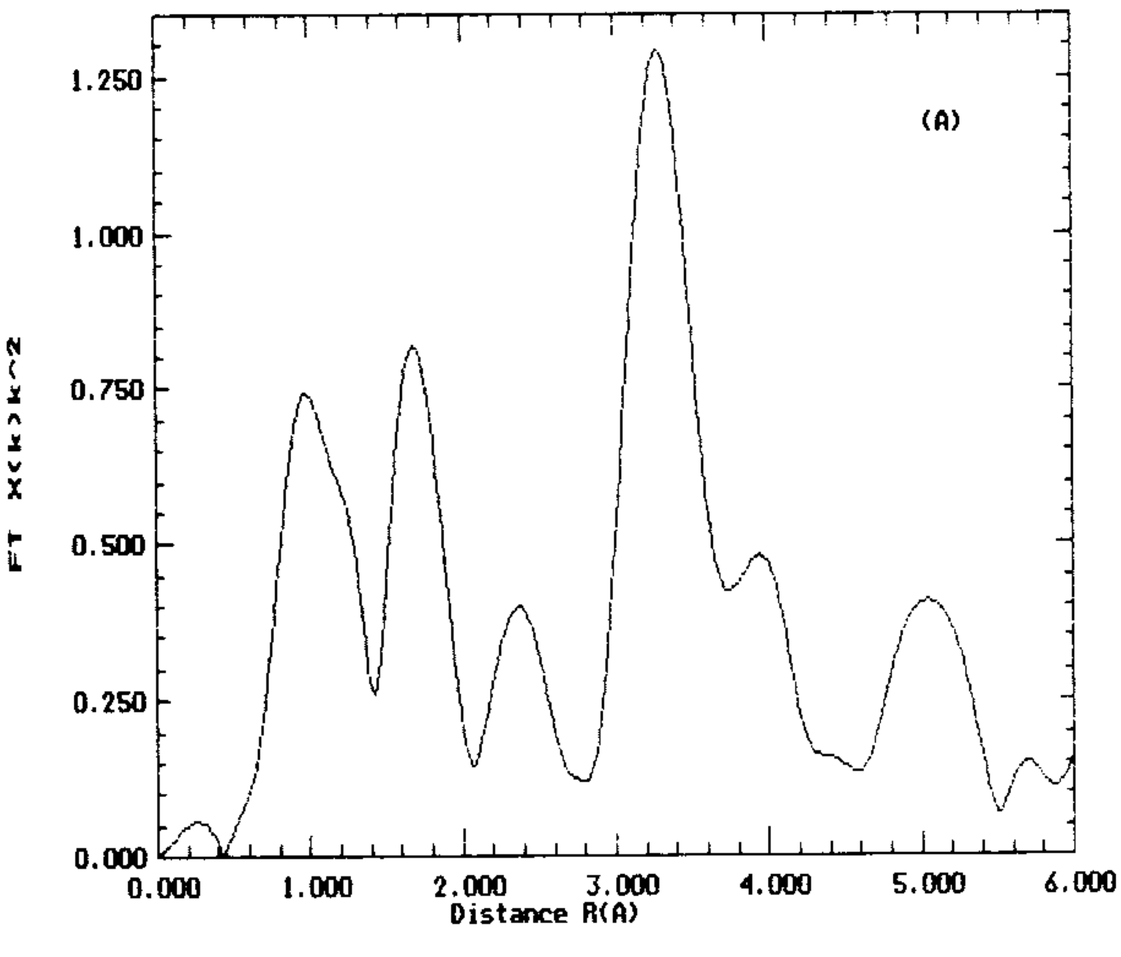


Fig. 5. a-IrO_2: (A) the Fourier transform of EXAFS (without phase correction); (B) experimental ($R = 1.1$–2.1 Å) (circles) and calculated (solid line) curves $\chi(k)k^2$ for the first coordination sphere.



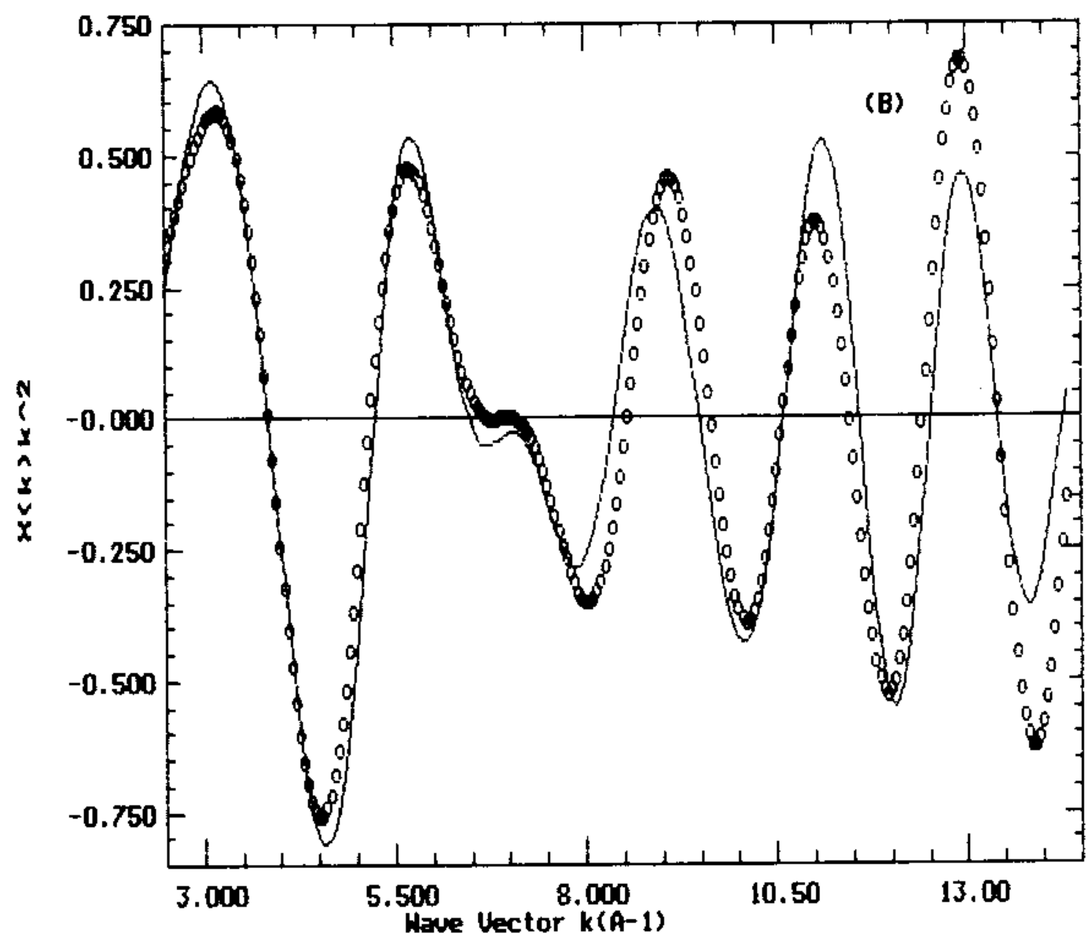


Fig. 6. c-MoO_3: (A) the Fourier transform of EXAFS (without phase correction); (B) experimental ($R = 0.5$–2.05 Å) (circles) and calculated (solid line) curves $\chi(k)k^2$ for the first coordination sphere.

Table 1
The best fit EXAFS parameters and X-ray diffraction data (N: coordination number, S_0^2: scaling factor, R: distance between atoms, σ^2: Debye–Waller factor, Γ: constant for mean free path approximation, $\lambda = k/\Gamma$)

Compound	Bond	EXAFS					X-ray diffraction	
		N	S_0^2	R [Å]	σ^2 [Å]	Γ [Å^{-2}]	N	R [Å]
c-ReO_3	Re–O	6	0.51	1.884	0.0023	0.50	6	1.87
c-$CaWO_4$	W–O	4	0.52	1.789	0.001	0.40	4	1.78
c-WO_3	W–O	2	0.50	1.747	0.001	0.87	1.0	1.74
	W–O	2	0.50	1.799	0.001	0.87	0.5	1.80
							1.0	1.86
	W–O	1	0.50	1.904	0.002	0.87	1.5	1.90
							0.5	2.01
	W–O	2	0.50	2.120	0.003	0.87	1.5	2.14
a-WO_3	W–O	4.1	0.47	1.743	0.005	0.54		
	W–O	1.5	0.47	1.866	0.002	0.54		
	W–O	2.5	0.47	2.132	0.007	0.54		
a-IrO_2	Ir–O	2.5	0.68	1.934	0.002	0.50	2	1.90
	Ir–O	3.5	0.68	2.017	0.002	0.50	4	2.02
c-MoO_3	Mo–O	1.0	0.95	1.681	0.0001	0.60	1	1.67
	Mo–O	1.0	0.95	1.785	0.0001	0.60	1	1.73
	Mo–O	1.8	0.95	1.980	0.0001	0.60	2	1.95
	Mo–O	1.1	0.95	2.256	0.0010	0.60	1	2.25
	Mo–O	1.1	0.95	2.461	0.0010	0.60	1	2.33
a-MoO_3	Mo–O	1.1	0.90	1.645	0.0001	0.63		
	Mo–O	2.6	0.90	1.797	0.0011	0.63		
	Mo–O	1.2	0.90	1.991	0.0045	0.63		
	Mo–O	1.1	0.90	2.045	0.0050	0.63		

The EXAFS spectrum and its FT for crystalline MoO_3 differs very strongly from tungsten oxides, linking with another type of the crystal lattice with bonds through the ribs and wider set of distances Mo–O from 1.65 to 2.35 Å (fig. 6). The FT for the first coordination sphere consists of two peaks, and its EXAFS is described by the set of parameters from table 1. The obtained distances are in good agreement with crystallo-

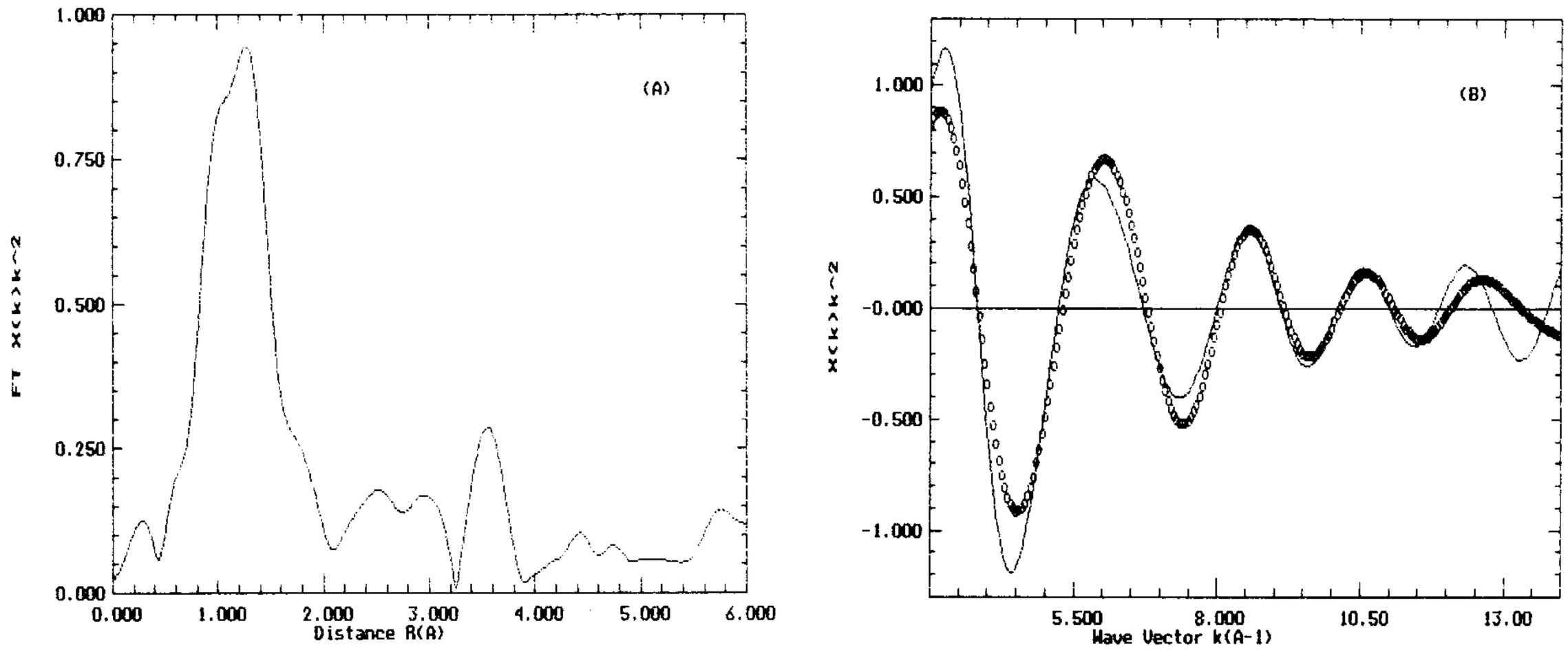


Fig. 7. a-MoO_3: (A) the Fourier transform of EXAFS (without phase correction); (B) experimental ($R = 0.5$–2.05 Å) (circles) and calculated (solid line) curves $\chi(k)k^2$ for the first coordination sphere.

graphic data, and the increase of the Debye–Waller factor value correlates with the increase of Mo–O distances.

On the other hand, in amorphous films of molybdenum oxide the EXAFS and its FT (fig. 7) are in good agreement with c-WO_3 and a-WO_3, which testifies to their similar structure. Thus we can conclude that in a-MoO_3 films oxygen polyhedra are connected by corners.

The analysis of the multiple scattering effects in the first and the second coordination spheres is in progress.

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