

# XANES studies of $\text{MeO}_{3-x}$ (Me = W, Re, Ir) crystalline and amorphous oxides

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X-ray absorption near-edge spectroscopy (XANES) of the  $L_1$ - and  $L_3$ -edges of transition metals (W, Re, Ir) oxides has been studied in the “ADONE” synchrotron source. The distortion of oxygen polyhedra and the metal valence state correlate with the amplitude of the pre-edge peak in  $L_1$ -spectra and the “white line” in  $L_3$ -spectra.

## 1. Introduction

X-ray absorption near-edge spectroscopy has recently found increasing application [1] in the probing of the local structure and electronic properties of a large variety of materials through both experimental and theoretical advances. In this paper a systematic study of the L-edge absorption of the transition metal (W, Re, Ir) oxides is presented. The applicability of  $L_1$ - and  $L_3$ -edge spectra for probing the local distortion of oxygen polyhedra and the metal valence state in these systems is discussed.

The feature in which we are interested for the  $L_3$ -edge is the “white line” (WL), whose amplitude should reflect the local density of the d-state and the number of unoccupied 5d states. For the  $L_1$ -edge we are interested in the pre-edge feature arising from the  $2s \rightarrow 5d(\text{Me}) + 2p(\text{O})$  transition determined by the site symmetry of the transition metal.

The obtained results for crystalline compounds are the basis for an investigation of electrochromic amorphous  $a\text{-WO}_3$  thin films prepared by different methods – thermal evaporation, high frequency sputtering, chemical deposition, etc.

## 2. Experimental

Transmission XANES spectra were taken on W, Re, Ir  $L_1$ - and  $L_3$ -edges using the EXAFS station (for  $L_1$  – Si[220] and for  $L_3$  – Si[111] channel-cut crystal monochromators) of one of the wiggler beam lines (BX-1, “PWA” ADONE LNF INFN). The “ADONE” storage ring was operated at 20–50 mA and 1.5 GeV with a

wiggler current of 4000 A. The amplitudes of the lines were normalized to the absorption jump. The thickness effects were estimated by different measurements for some samples [2].

The thin films were obtained by slow  $a\text{-WO}_3$  (no. 1) and fast (no. 2) rate thermal evaporation in middle and low vacuum on a polyimide substrate at  $T_s = 200^\circ\text{C}$ . The amorphous  $a\text{-WO}_3$  (no. 3) and polycrystalline  $c\text{-IrO}_2$  thin films were prepared by reactive radio frequency (rf) and magnetron sputtering of metals in  $\text{O}_2$  and Ar atmospheres on a polyimide substrate at room temperature. The powders  $c\text{-WO}_{3-x}$  [3],  $c\text{-ReO}_3$  and  $c\text{-CaWO}_4$  were taken as reference compounds.

## 3. Experimental results and discussion

Fig. 1 shows the  $L_3$ -edge region in the crystalline compounds  $\text{ReO}_3$ ,  $\text{WO}_3$ ,  $\text{IrO}_2$  and  $\text{CaWO}_4$ . The most striking difference between the XANES spectra for these compounds is in the amplitude and the width of the WL and that a post-edge peak is seen only in the spectrum of  $\text{CaWO}_4$ , at about 12 eV higher energy than the WL. The structures of the first three compounds consist of oxygen octahedra connected by corners ( $\text{ReO}_3$ ,  $\text{WO}_3$ ) or by the edge ( $\text{IrO}_2$  – the rutile type), but the structure of the last compound ( $\text{CaWO}_4$ ) consists of oxygen tetrahedra, and this is why the post-edge peak exists.

In tungsten compounds  $\text{WO}_{3-x}$  with a different valence state of tungsten (from  $\text{W}^{4+}$  to  $\text{W}^{6+}$ ), we have observed a drastic change of the WL amplitude but in general the shape of the spectra is practically close to the  $\text{WO}_3$  spectrum. The amplitudes of the WL are presented in table 1 (column C). In these compounds

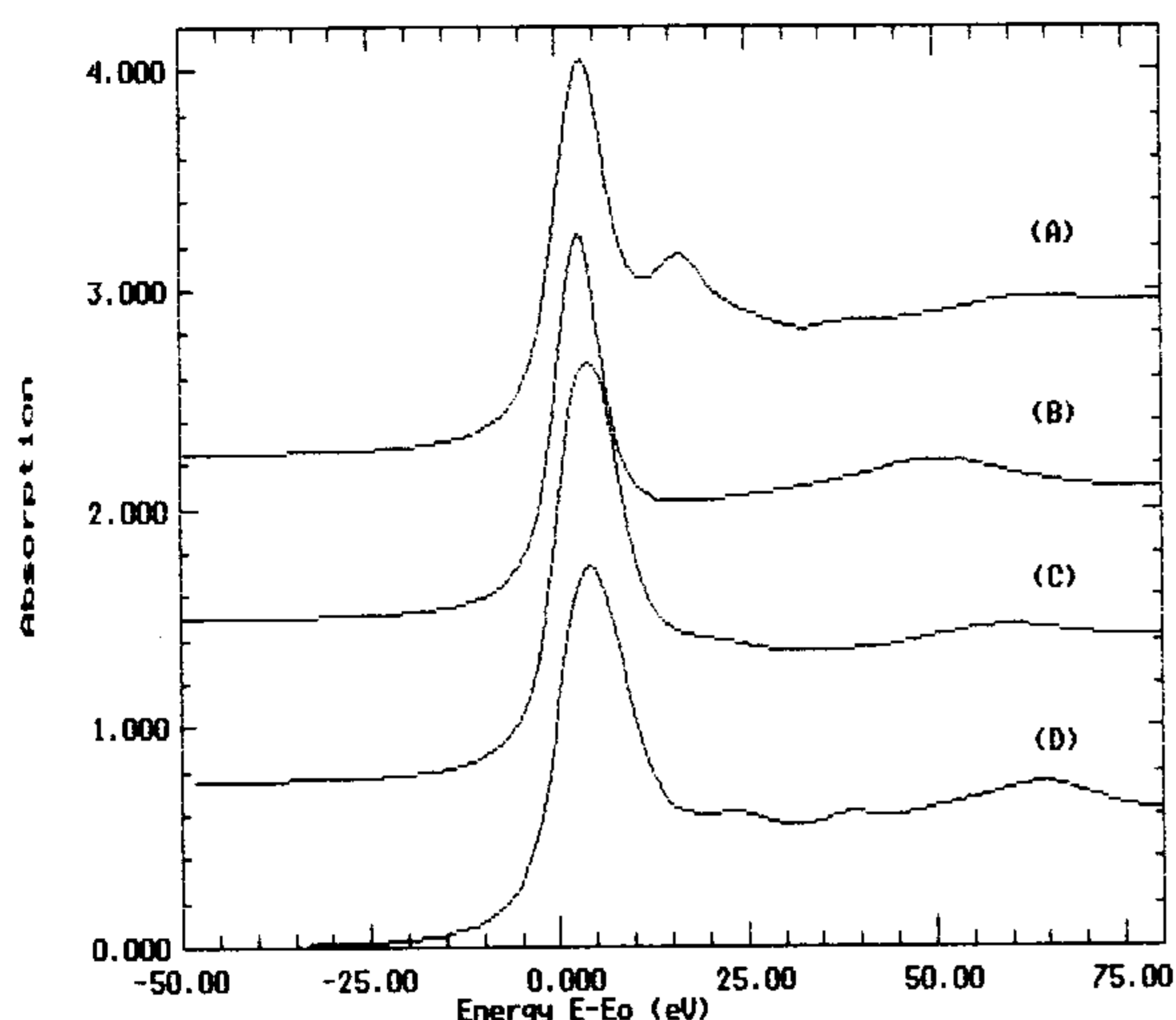


Fig. 1. The  $L_3$ -edge of W in  $CaWO_4$  (A) and  $WO_3$  (C), Ir in  $IrO_2$  (B), and Re in  $ReO_3$  (D).

the average W–O distance increases monotonically with a reduction of tungsten from  $W^{6+}$  ( $WO_3$ ) to  $W^{4+}$  ( $WO_2$ ), and also with decreasing distortion of the  $WO_6$  octahedra [4]. In the EXAFS spectra we have also observed a drastic change of the average W–O distance calculated in a one-sphere approximation (fig. 2). We believe that the increase of WL intensity in the compounds  $WO_3$ ,  $WO_{2.96}$ ,  $WO_{2.90}$  and  $WO_{2.72}$  is due to the increase of distortion of  $WO_6$  octahedra, and the decrease of the WL amplitude in the last compound  $WO_2$  originates from the filling of an unoccupied 5d level.

The WL amplitudes (fig. 3) in water-containing layered compounds  $WO_3 \cdot nH_2O$  are much higher than in c- $WO_3$ , which is due to the presence of a very short

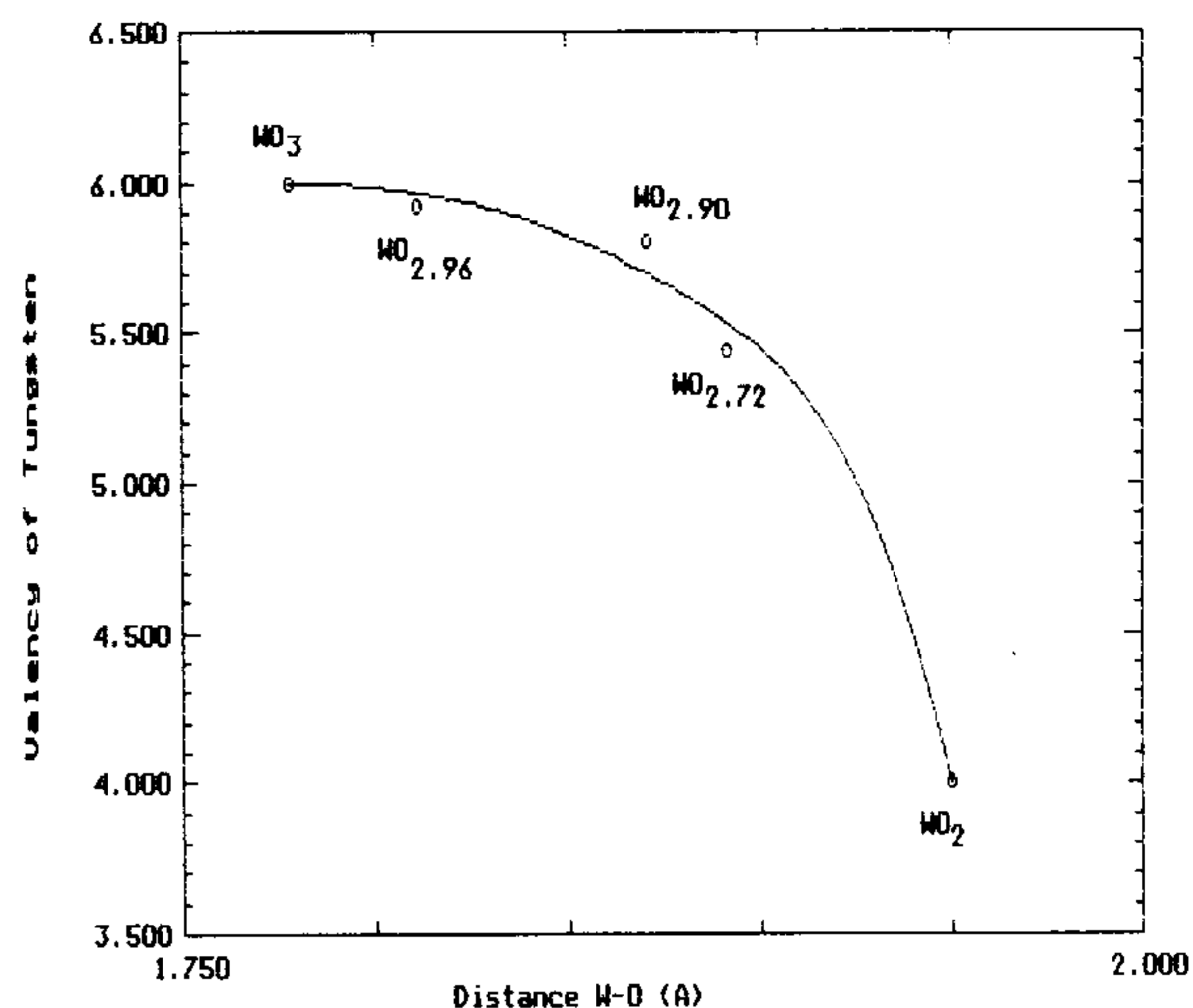


Fig. 2. The dependence of the tungsten valency on the W–O distance calculated in the one-sphere approximation.

terminal W=O bond opposite to the water molecule site. From the EXAFS spectra in practically all crystalline compounds and amorphous thin films with a 6+ tungsten valence state, we have obtained by the one-sphere approximation an average distance equal to 1.78–1.80 Å.

In amorphous chemically stable thin films of a- $WO_3$  (no. 1) the WL amplitude is smaller than in a- $WO_3$  (no. 2) films, which are chemically not as stable. The WL amplitude in rf prepared film (no. 3) is close to that in a- $WO_3$  (no. 1).

Figs. 4, 5 and 6 show the  $L_1$ -edge region in crystals and a- $WO_3$  thin films. The intensity of the pre-edge peak corresponds to the  $2s \rightarrow 5d(W) + 2p(O)$  transition and can be used to determine the distortion of an

Table 1  
The relative amplitudes of the XANES features in  $L_1$  and  $L_3$  absorption spectra

Compound	$L_1$ -XAS		$L_3$ -XAS
	A	B	C
c- $ReO_3$	$0.22 \pm 0.02$	$1.07 \pm 0.15$	$2.6 \pm 0.1$
c- $CaWO_4$	0.71	1.00	2.2
c- $WO_3$	0.42	1.21	2.5
c- $WO_{2.96}$	0.31	1.11	2.8
c- $WO_{2.90}$	0.25	1.18	2.9
c- $WO_{2.72}$	0.22	1.24	3.0
c- $WO_{2.00}$	0.25	1.24	2.7
c- $WO_3 \cdot \frac{1}{3}H_2O$	–	–	3.1
c- $WO_3 \cdot H_2O$	0.50	1.23	3.0
c- $WO_3 \cdot 2H_2O$	–	–	3.2
a- $WO_3$ no. 1	0.51	1.26	2.9
a- $WO_2$ no. 2	–	–	3.7
$WO_3$ rf no. 3	0.46	1.37	3.1
$IrO_2$	–	–	2.4

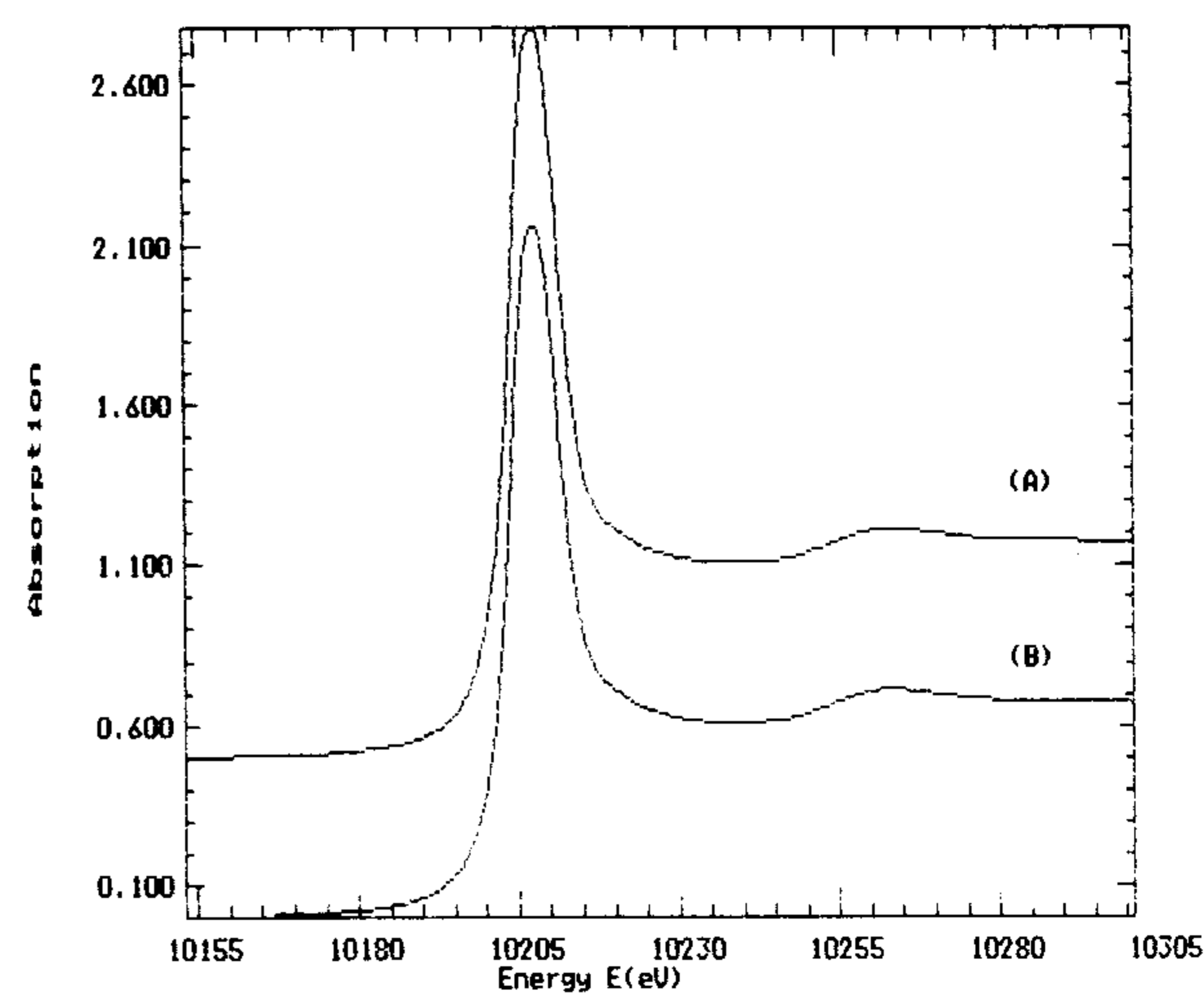


Fig. 3. The  $L_3$ -edge of tungsten in a- $WO_3$  (A) and c- $WO_3 \cdot H_2O$  (B).

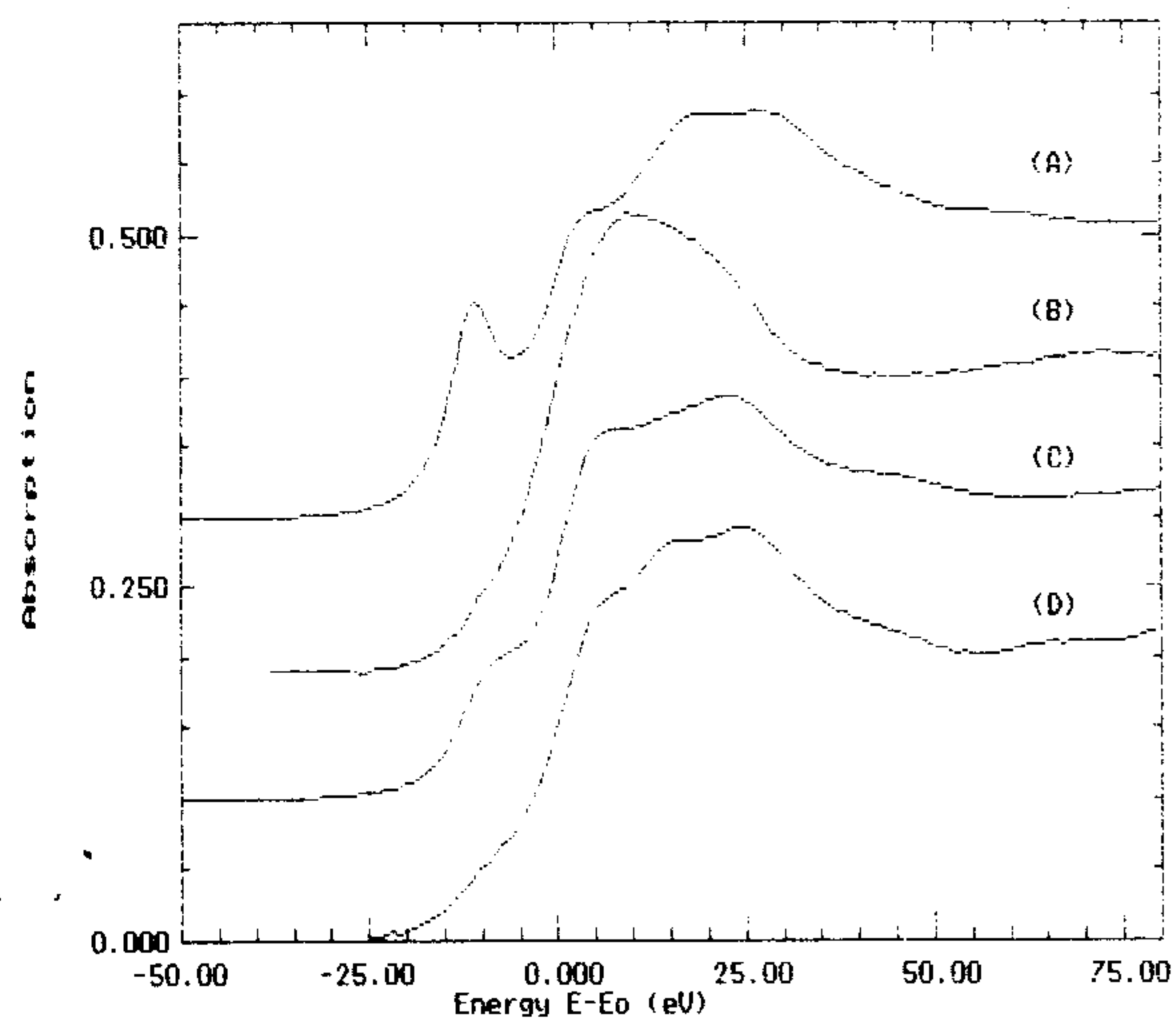


Fig. 4. The  $L_1$ -edge of W in  $CaWO_4$  (A) and  $WO_3$  (C), Ir in  $IrO_2$  (B), and Re in  $ReO_3$  (D).

octahedral complex [5]. Its amplitude (column A in table 1) is too small for perfect ( $ReO_3$ ) or near-perfect ( $WO_2$ ,  $IrO_2$ )  $WO_6$  octahedra, but it is too large for highly distorted octahedra ( $WO_3$ ,  $WO_3 \cdot nH_2O$ ) and it is highest for  $WO_4$  tetrahedra ( $CaWO_4$ ). The distortion of the octahedra facilitates d-p orbital mixing, thereby enhancing the pre-edge peak amplitude [6]. There is a

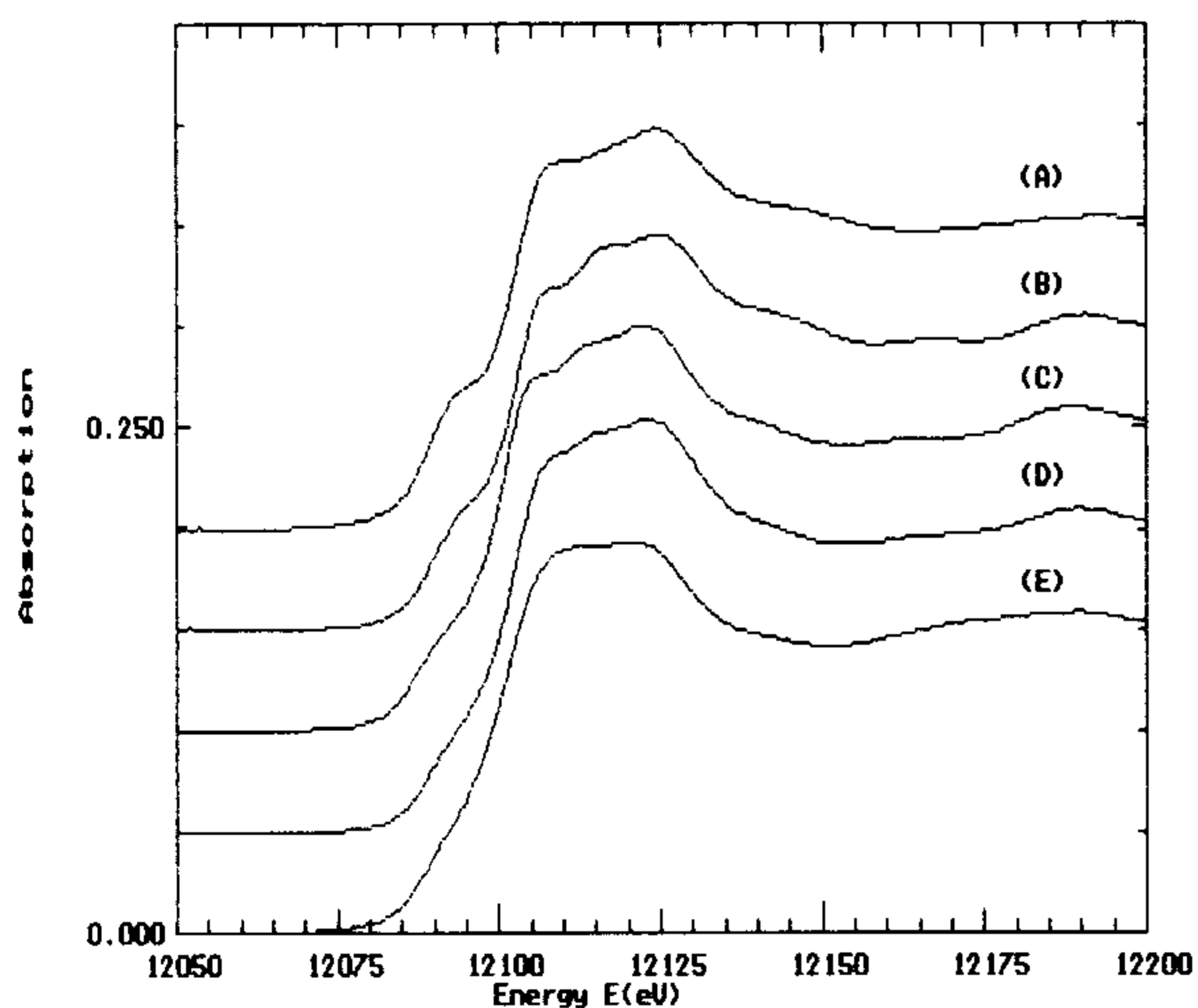


Fig. 5. The  $L_1$ -edge of tungsten in crystalline tungsten oxides:  $WO_3$  (A),  $WO_{2.96}$  (B),  $WO_{2.90}$  (C),  $WO_{2.72}$  (D) and  $WO_{2.0}$  (E).

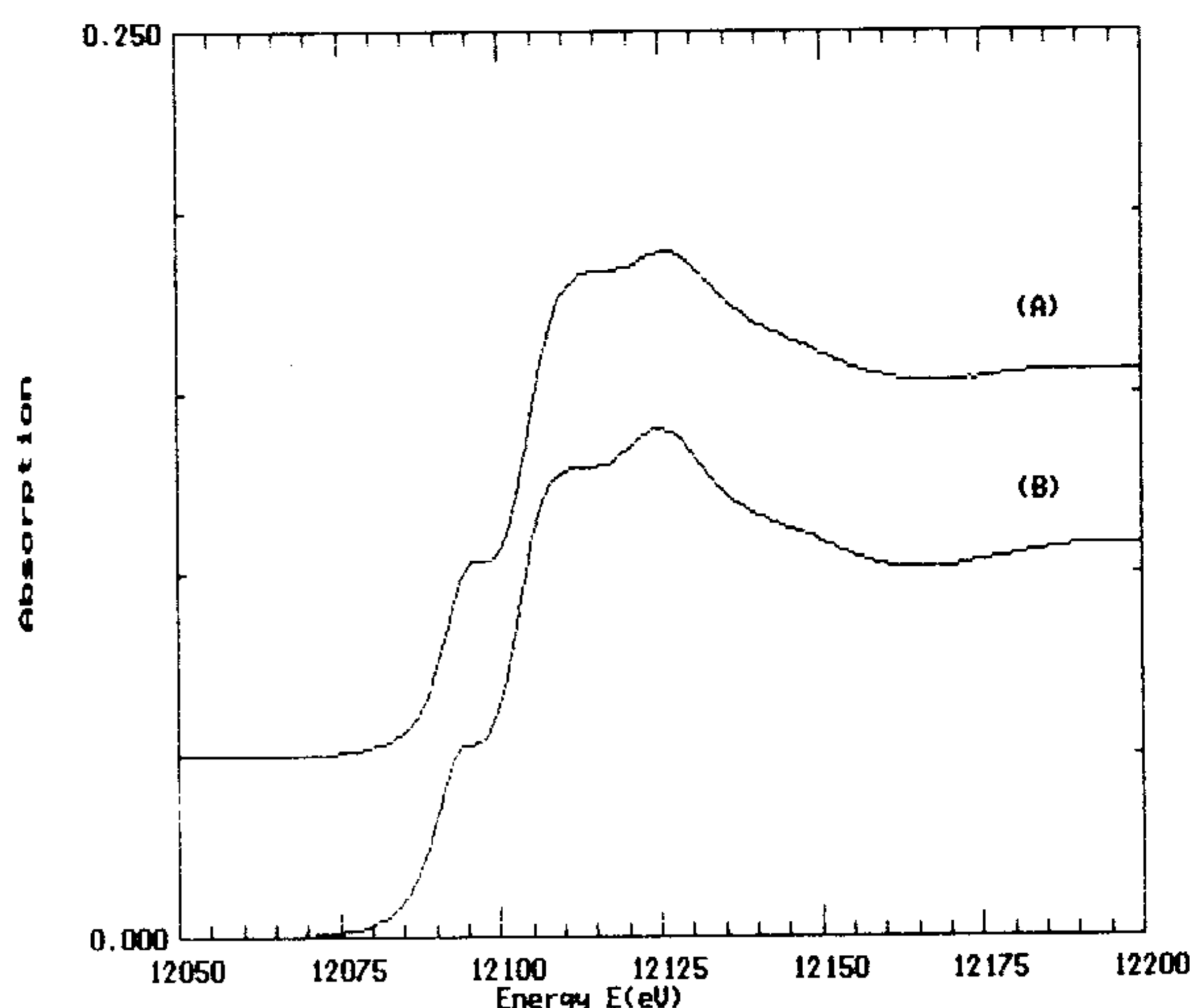


Fig. 6. The  $L_1$ -edge of tungsten in a- $WO_3$  (A) and  $WO_3 \cdot H_2O$  (B).

very good anticorrelation between the amplitude of the pre-edge peak and the WL (table 1).

The amplitudes of the pre-edge peak and the WL in amorphous thin films (no. 1, no. 3) are close to those of water-containing crystals of  $WO_3 \cdot H_2O$  with  $W=O$  terminal bonds.

The amplitude of the first main peak (column B in table 1) in the  $L_1$ -edge is assigned to the  $2s \rightarrow 6p(W) + 2p(O)$  transition and the next peaks are also visible in the main absorption ramp.

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