

## Double-Electron Excitations in $L$ -edges X-ray-Absorption Spectra of W, Ir and Cs Oxide Compounds

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Very strong double-electron excitations have been observed for the first time in the W, Ir  $L_3$ -edge and Cs  $L_{1,2,3}$ -edges X-ray-absorption spectra of tungsten and iridium oxide thin films and cesium oxide containing glasses. They are expressed as peaks with a width of several electron-volts located at the absorption background above the edge. The positions of these features are in good agreement with atomic calculations in the  $Z+1$  approximation. They can be attributed to the transitions  $2p4d \rightarrow 5d5d$  for the  $L_{2,3}$ -edges and  $2s4d \rightarrow 6p5d$  for the  $L_1$ -edge with the dipole selection rules for the angular and total angular momentum  $\Delta L = \pm 1$ ,  $\Delta J = 0, \pm 1$ .

**KEYWORDS:** multielectron transitions, X-ray-absorption spectra

### §1. Introduction

Multielectron excitations have been studied for the first time in the  $K$ -edge absorption spectra of noble gases.<sup>1-4</sup> In the last years a number of works devoted to such effects in solids has appeared.<sup>5-9</sup> Usually, the multielectron transitions are very weak and cannot be practically observed on the background of the EXAFS-oscillations as in the case of 3d elements.<sup>9</sup> Only a special precise analysis has allowed to extract the contribution of multielectron processes in some systems.<sup>5,7,8</sup> In the case of the La, Ce and Ba  $L_3$ -edges good observed signals have been reported earlier,<sup>6</sup> but their qualitative interpretation as a  $2p4d \rightarrow \epsilon d4, \epsilon f$  two-electron transitions with atomic character does not satisfy the dipole selection rule  $\Delta L = \pm 1$ .

In this work we present the experimental data on  $L$ -edges of 5d elements (Ir, W and Cs), where the strong double-electron transitions have been detected, and their interpretation in the  $Z+1$  approximation.

### §2. Experimental

The experimental X-ray-absorption spectra of the Ir, W  $L_3$ -edge and the Cs  $L_{1,2,3}$ -edges have been measured in transmission mode at the ADONE storage ring (INFN LNF, Frascati) using the EXAFS station on the "PWA" BX-1 wiggler beam line. The storage ring ADONE has

operated at 10-20 mA and 1.2 GeV with a wiggler current of 4200 A. The synchrotron radiation has been monochromatized using the Si(111) channel-cut crystal monochromator, and its intensity has been measured by two ionization chambers filled with a krypton gas. The energy resolution has been estimated equal to  $\sim 1$  eV.

The amorphous  $WO_{3-x}$  thin films have been prepared by thermal evaporation in medium vacuum on a polyimide substrate at three different temperatures  $T_s = 320, 370$  and  $460$  K. The polycrystalline  $IrO_2$  thin film has been prepared by reactive magnetron sputtering of metallic Ir in mixed oxygen and argon atmosphere on a polyimide substrate at room temperature. The cesium-phosphate glasses have contained about 30 % of cesium oxide.

### §3. Results and Discussion

The X-ray-absorption coefficient  $\mu(E)$  was calculated from the intensities of synchrotron radiation before  $I_0$  and after  $I$  passing through the sample. Then, the background contribution  $\mu_b(E)$  was approximated by the Victoreen rule ( $\mu_b = A/E^3 + B/E^4$ ) and subtracted from the experimental spectrum  $\mu(E)$ . The atomiclike term  $\mu_0(E)$  was found by a cubic-spline approximation, and the EXAFS signal  $\chi(E)$  was determined as  $\chi(E) = (\mu - \mu_b - \mu_0) / \mu_0$ . The experimental  $I$  and  $I_0$  signals for the Ir  $L_3$ -edge are presented in Fig. 1, and the EXAFS spectra for all edges are shown in Figs. 2, 3

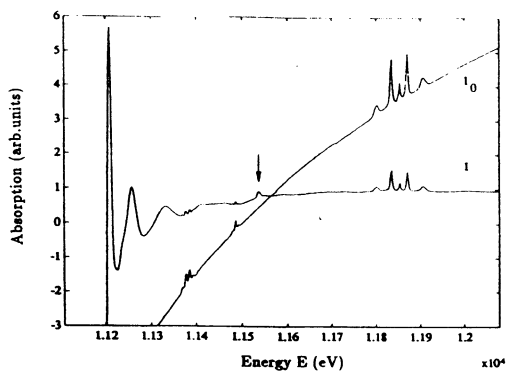


Fig. 1. Experimental  $I$  and  $I_0$  signals of the Ir  $L_3$ -edge in  $\text{IrO}_2$  thin film. The arrow indicates the position of the double excitation.

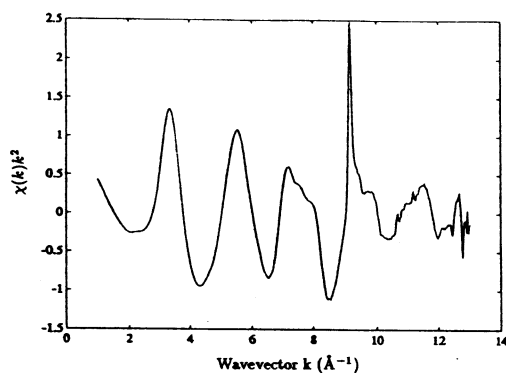


Fig. 2. EXAFS  $\chi(k)k^2$  of the Ir  $L_3$ -edge in  $\text{IrO}_2$  thin film. The strong narrow peak corresponds to the double excitation.

and 4. The positions of double excitations are marked by the arrows.

The most intensive signal is observed in the Ir  $L_3$ -edge spectrum as very strong resonance at  $\sim 326$  eV above the white line. It is well visible even in the absorption coefficient and, in opposite to several features, which are located at lower and higher energies and are the glitches, has a "real" origin of some transition with a step-like edge (see, Fig. 1). In the EXAFS-signal it contributes at  $\sim 9.2 \text{ \AA}^{-1}$  (Fig. 2) and leads to significant modification of the fine structure. In the case of the W  $L_3$ -edge the resonance is less resolved (see, Fig. 3) and appears at  $\sim 270$  eV above the white line. In Fig. 4 the EXAFS-signals from the Cs  $L_{1,2,3}$ -edges in cesium-phosphate glasses are presented. In all three cases the contribution from double excitations are well observed at  $\sim 96 - 99$  eV above the white line (the signal from the  $L_1$ -edge was aligned using the first derivative maximum).

Note that one of the reasons, for which it is usually difficult to detect multielectron transitions in crystalline compounds, is the presence of high frequency signals from the outer coordination shells. Therefore, amorphous and glass materials are perfect objects for such study.

The calculations, performed in the  $Z+1$  approxima-

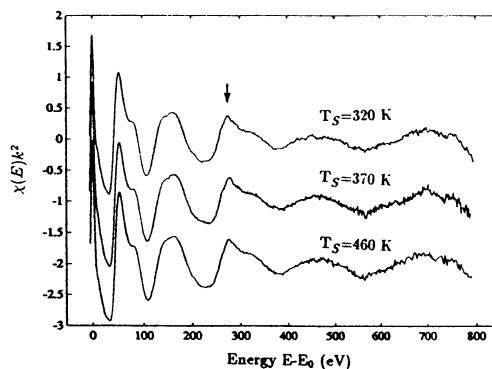


Fig. 3. EXAFS  $\chi(E)k^2$  of the W  $L_3$ -edge in  $\text{WO}_{3-x}$  amorphous thin films preparing at different substrate temperatures. The arrow indicates the position of the double excitation.

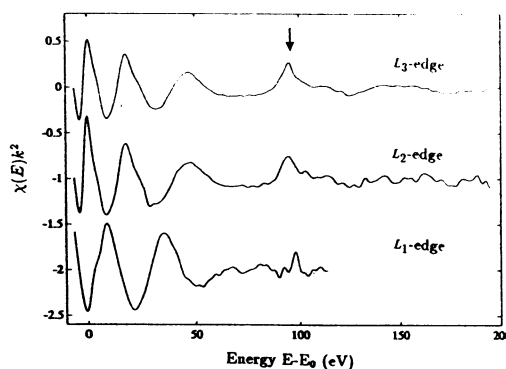


Fig. 4. EXAFS  $\chi(E)k^2$  of the Cs  $L_{1,2,3}$ -edges in cesium oxide containing glasses. The arrow indicates the position of the double excitation.

tion, show that the observed resonances can be attributed to double excitations of the electron in the main channel ( $2s \rightarrow 6p$  for the  $L_1$ -edge and  $2p \rightarrow 5d$  for the  $L_{2,3}$ -edges) and the second electron from the  $4d$  level into the  $5d$  final state. Such transition satisfies the dipole selection rules for the angular and total angular momentum  $\Delta L = \pm 1$ ,  $\Delta J = 0, \pm 1$ . The values of the energy difference  $\Delta E$  between one- and double-excited states, calculated in the  $Z+1$  approximation and derived from experimental spectra, are shown in Table I. Note that the bonds in studied compounds have different degree of covalency and, as the result, the true charge of the metal atom can differ from the formal valence defined by the chemical formula due to the different overlap of the electron shells with oxygen atoms. To take into account the last effect, the calculations for each element were performed for several various configurations of the ground and excited states. It is known that the cesium atoms have the ionic type of the bond, therefore the configuration of the  $\text{Cs}^{1+}$  ion gives the best agreement with experimental data. The iridium oxide is less ionic compound that leads to the necessity of a small modification of the absorbing ion charge to have better agreement with the experiment. In the case of the tungsten oxide thin films

Table I. The energy difference  $\Delta E$  between one- and double-excited states.

Element	Edge	Ion charge	Ground state	Double-excited state	calculated	experimental
Cs	$L_1$	0	$6s^1$	$2s^{-1}4d^{-1}5d^16s^16p^1$	94	$\sim 96 - 99$
		1+	$6s^0$	$2s^{-1}4d^{-1}5d^16s^06p^1$	98	
	$L_2$	0	$6s^1$	$2p^{-1}4d^{-1}5d^26s^1$	93	
		1+	$6s^0$	$2p^{-1}4d^{-1}5d^26s^0$	96	
	$L_3$	0	$6s^1$	$2p^{-1}4d^{-1}5d^26s^1$	93	
		1+	$6s^0$	$2p^{-1}4d^{-1}5d^26s^0$	96	
Ir	$L_3$	4+	$5d^56s^0$	$2p^{-1}4d^{-1}5d^76s^0$	305	$\sim 326$
		5+	$5d^46s^0$	$2p^{-1}4d^{-1}5d^66s^0$	340	
W	$L_3$	4+	$5d^26s^0$	$2p^{-1}4d^{-1}5d^46s^0$	272	$\sim 270$
		5+	$5d^16s^0$	$2p^{-1}4d^{-1}5d^36s^0$	291	
		6+	$5d^06s^0$	$2p^{-1}4d^{-1}5d^26s^0$	300	

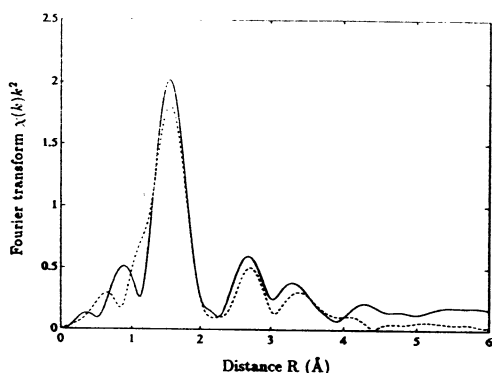


Fig. 5. Fourier transforms of the Ir  $L_3$ -edge EXAFS  $\chi(k)k^2$  before (solid line) and after (dashed line) eliminating of the double excitation contribution.

the high distortion of the first (oxygen) coordination shell around the tungsten atoms<sup>10</sup>) and the presence of the d electrons, which take active part in the bonding, are the reason of the significant overlap and mixing of the tungsten (5d) and oxygen (2p) electron shells which leads to the need of an essential correction of the ion charge.

As it was mentioned above, the presence of the double-excitation contribution modifies significantly the fine structure past the absorption edge. This leads automatically to the distortion of the EXAFS-signal (and its Fourier transform) and, accordingly, increases the error in the determination of structural parameters. The influence of such effects in the Fourier transform is analogous to the effect of the step-like function, i.e. it produces additional contribution in all range that increases the background and distorts the shape and positions of structural peaks (see, Fig. 5). Note that non-compensated intensive glitches lead to the same result.

#### §4. Summary and Conclusions

We presented the experimental data on the double-

electron excitations in the W, Ir  $L_3$ -edge and Cs  $L_{1,2,3}$ -edges X-ray-absorption spectra of tungsten and iridium oxide thin films and cesium oxide containing glasses. Their interpretation in the Z+1 approximation as the transitions  $2p4d \rightarrow 5d5d$  for the  $L_{2,3}$ -edges and  $2s4d \rightarrow 6p5d$  for the  $L_1$ -edge is in good agreement with the experiment. It was shown that such contributions must be eliminated before the EXAFS data analysis otherwise the significant distortion of the EXAFS-signal will lead to the inaccuracies of the extracted parameters.

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