Double electron transitions [*MN*] or [*MO*] above $_{74}$W M_{III} edge in X-ray absorption spectra

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The x-ray absorption spectra in metallic W (Tungsten) have been measured above M_{III} edge using the third generation synchrotron radiation, ALS, Berkeley. Several features caused by multi-electron transitions were detected on M_{III} in solid phase. [3p4f], [3p5s], and [3p5p] double electron transitions were identified by the Z+1 approximation.

1.INTRODUCTION

Photo-absorption in atoms has generally been treated as a single-electron excitation process. However, the existence of the simultaneous excitations of several electrons in the atom, where the removal of a core electron by photo-absorption causes excitation of additional electrons in the same atom, has been known in x-ray absorption spectra for a long time (Wuilleumier, 1971).

In x-ray absorption spectra, experimental investigations of the shake processes in inner-shell ionization phenomena have been performed by detecting discontinuities. The multi-electron photo-excitations can be observed directly only in spectra of monatomic gases and vapors, so the shake-process has been studied extensively in noble gases (Armen *et al.*, 1985; Ito *et al.*, 1992; Schaphorst *et al.*, 1993; Deslattes *et al.*, 1983; Bernieri & Byrattini, 1987; Kuetgens & Hormes, 1991; Ito *et al.*, 1998).

It was pointed out by Kodre and co-workers (Kodre *et al.*, 1992) that for solid targets it is difficult to identify weak transitions corresponding [*KL*] to multi-electron excitation in x-ray absorption spectra, that is, the oscillation due to the x-ray absorption fine structure masks small signals in the energy region where multiple electron excitation occurs (Ito, 1998). The occurrence of the double-electron excitations in condensed systems was first observed in Si *K*-edge spectra, where a simultaneous excitations of 1s and 2p electrons gives rise to the [*KL*] edge feature (Filipponi *et al.*, 1988). The presence of these excitations was later found to be a common characteristic of third-period atoms (Filipponi *et al.*, 1993a; Di Cicco *et al.*, 1992). [*KM*] and [*KN*] double-electron transitions are reported in Br compounds (D'Angelo *et al.*, 1993; Burattini *et al.*, 1993; Ito *et al.*, 1995; Gomilsek *et al.*, 1999). Li *et al.* (1992) presented other threshold related with [*LN*] transitions above the Pb L_{III} edge in PbO_2. They assigned this transition to4f electron shakeup excitations by the Z+1 approximation. Moreover, Filipponi *et al.* (1993*b*), and Di Cicco and Filipponi (1994) reported [*LN*] double- and [LN^2] triple- hole configurations in atom-like Hg and Liquid Pb and Bi as well as in PbO, $Pb(CH_3CO_2)_2$, and Bi_2O_3 compounds. Therefore, the understanding of the transition processes involved in multielectron excitations is very important for the analysis in XAFS (Ito *et al.*, 1998; Kodre *et al.*, 1992; Filipponi *et al.*, 1988; Filipponi *et al.*, 1993a; Di Cicco *et al.*, 1992; D'Angelo *et al.*, 1993; Burattini *et al.*, 1993; Ito *et al.*, 1995; Gomilsek *et al.*, 1999; Li *et al.*, 1992; Filipponi *et al.*, 1993*b*; Di Cicco & Filipponi, 1994; Chaboy & Tyson, 1994; Stern, 1982; D'Angelo *et al.*, 1996). These processes have therefore received a special attention in XAFS analysis.

In the present study, the x-ray-absorption experiment was executed for W M_{II}I edge in order to the contribution of the simultaneous excitations of [$M_{III}N$] or [$M_{III}O$] to the background effect in the x-ray-absorption fine structure.

2.EXPERIMENTAL

The x-ray absorption spectra for $_{74}$W were measured using the beam line 9.3.2 at the Advanced Light Source at a circular current of 200 ~ 400 mA for 8 hours. The harmonic content of the incoming beam was minimized by using a focusing mirror and detuning the Si(111) double-crystal reflection. The calculated energy resolution (combined intrinsic crystal resolution and vertical angular divergence of the beam) was less than 1 eV at the energy of $_{74}$W *M*-edge. A high purity metal foil of $_{74}$W of 18 μm was used for monitoring the absorption by measuring the partial electron yield (PEY) emitted from the surface of the sample as a function of exciting energy. The photoelectrons were collected by a circular copper ring (ϕ=0.3 mm, 24 mm diameter) situated at 5 mm from the sample and applying an accelerating potential of 400 V. The incident intensity (Io) of the x-ray beam was recorded as the current from a 95% transparent aluminum mesh in the beam-path. Spectra were obtained at room temperature over a 110 eV range with a step size of 0.5 eV as shown in Fig.1.

3.RESULTS & DISCUSSION

As seen in Fig.1, there is almost no oscillation in XAFS. This fact may be attributed to the setup in the experiment. The situation such as strongly suppressed spectra is well explained by Emura formula (Emura et al., 1993*a*,*b*, 1995), that mainly takes care of optical luminescence detection method for XAFS measurements. However, it is applicable to almost all methods detecting the secondary processes as a probe, for example, a photo-conductivity measurement etc. (Ishii *et al.*, 1999). There, the key physical quantities are an effective sample thickness and individual efficiencies for the events. For the photo-electron detecting, the effective thickness could be given with a penetration depth of the incident x-rays or an extended escape depth of the photo-electron. The penetration depth is about 0.25 μm at 2 KeV, which is not so thin but also not too thick. The energy 2 KeV of the incident x-rays

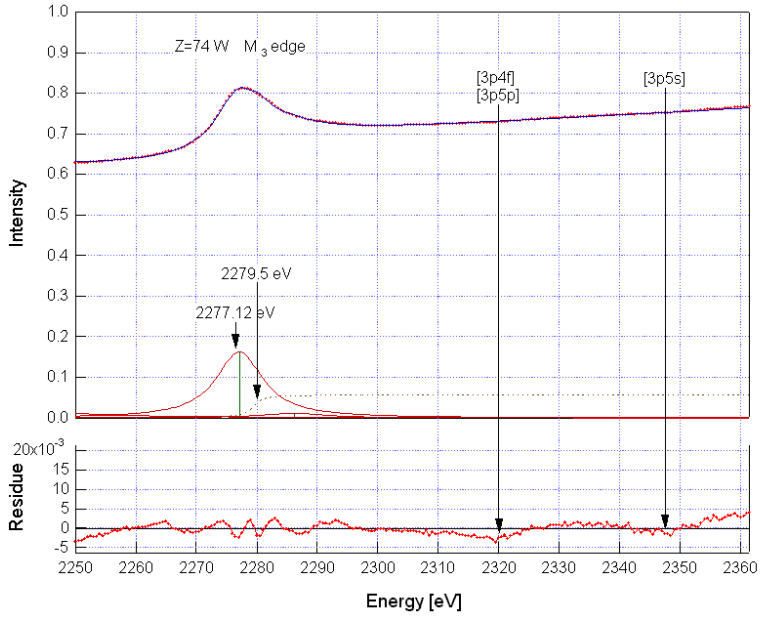

Figure 1. The x-ray absorption spectra above $_{74}$W-M_{III} edge. The arrows indicate the energy position predicted by the Z+1 approximation.

excites the electrons of *M* shell and *N* shell. The excited electrons of *N* shell are more energetic than those of *M* shell excited. It suggests that the yield of the *N* shell excitation is larger than one of the *M* shell excitation. This situation corresponds to the curve (1) in Fig.4 of Emura *et al.* (1993*a*). From the curve, we could expect a very suppressed spectrum. Broad structures above the $_{74}$W M_{III} edge can be found in Fig.1. The threshold onsets occur at 40 eV and 80 eV. The possible explanation is to assign the structures to the double-electron transition of [3p4f], [3p5s], and [3p5p] shown in Table 1. In this Table, the position of thresholds is compared with those predicted by the Z+1 approximation model. This model gives 40 eV and 70 eV for the *N*- and *O*-levels, respectively, using the x-ray atomic energy level (Bearden & Burr, 1967) of $_{74}$W to calculate the energy of the second core hole. It is found that these values are consistent with [3p4f], [3p5s], and [3p5p] double electron transitions. These are in good agreement with the predictions of the Z+1 model as listed in Table 1. This is a rough approximation which makes use of the Z+1 wave functions for the excited atom and does not take account of the crystal structure of the photoabsorber. Nevertheless, this approach is successful in approximating the energy difference. As Di Cicco et al. (1994) suggested this, the Z+1 approach represents a correct guideline in this case.

Table 1. Electron configuration and energies of two-electron transitions for $_{74}$W atom. The energies (ΔE) are given relative to the *M* edge(M_{III}) of $_{74}$W atom.

Configuration	ΔE (eV)	
	Z+1	measured
[3p4f]	40.6	40
[3p5p]	45.6, 34.6	40
[3p5s]	82.8	68

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