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Ultramicroscopy 107 (2007) 1201–1206
ultramicroscopy
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Accurate labeling of the light-actinide $O_{4,5}$ edges

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Received 11 September 2006; received in revised form 24 January 2007; accepted 31 January 2007

Abstract

In this short article, the accurate labeling of the $O_{4,5}$ edges of the light actinides is addressed. The O_4 and O_5 edges are both contained in what is termed the 'giant resonance' and the smaller 'pre-peak' that is observed is a consequence of first-order perturbation by the 5d spin–orbit interaction on the 5d,5f exchange splitting. Thus, the small pre-peak in the actinide $5d \rightarrow 5f$ transition should not be labeled the O_5 peak, but rather the $\Delta S = 1$ peak.

PACS: 79.20.Uv; 71.10.−w; 71.70.Ej; 71.70.Gm

Keywords: EELS; TEM; Actinide; Absorption

1. Introduction

Actinide materials are of great interest presently to the physics and chemistry communities due to the intriguing and unique physical properties they exhibit as a result of the complicated electronic structure of the 5f states. In order to investigate these states, X-ray absorption spectroscopy (XAS) and electron energy-loss spectroscopy (EELS) are often employed, particularly transitions from d core states as this directly probes the f states. Since these transitions are of great importance to understanding actinide materials, it is imperative that we fully understand the $d \rightarrow f$ transitions and label them correctly. Here, the accurate labeling of the $O_{4,5}$ edges for the light actinides is addressed due to noticeable confusion in the literature and in private communications. The correct labeling of the edges will be presented along with analysis of calculated spectra.

2. Experimental

EELS spectra were collected in standard fashion using a Philips CM300 field-emission-gun transmission electron microscope and Gatan image filter with a $2k \times 2k$ CCD chip. For full details of sample preparation and experimental parameters see Refs. [1,2].

The $O_{4,5}$ EELS edges of Th, U, and Pu metal are shown in Fig. 1 as solid gray, where the background has been removed using an inverse power law extrapolation. First consider Th. There is a small peak at ~88 eV and a second larger peak at ~101 eV. Often, the small peak at 88 eV is labeled the O_5 edge and the large peak at 101 eV is labeled the O_4 edge. The same labeling scheme is frequently used for U, which again shows a smaller initial peak followed by a larger and broader peak. In each case, this is incorrect. In reality, the dipole allowed transitions in an *LS* coupled final state are both contained in the larger second peak, which is frequently referred to as the 'giant resonance'. The smaller peak at lower energy is a dipole-forbidden transition, produced by the finite spin–orbit interaction. The latter is small compared to the 5d,5f Coulomb and exchange interaction, which generates energy splittings around 20 eV. The origin of the pre-peak(s) has in fact been explained in detail for the rare earths [3–5] and the actinides [6].

Core-level photoemission data reported that the $5d_{3/2}$ and $5d_{5/2}$ sublevels are separated by 7.1, 8.6, and 12.4 eV, for Th, U, and Pu, respectively [7]. This agrees reasonably well with atomic Hartree–Fock calculations for the 5d

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doi:10.1016/j.ultramic.2007.01.014

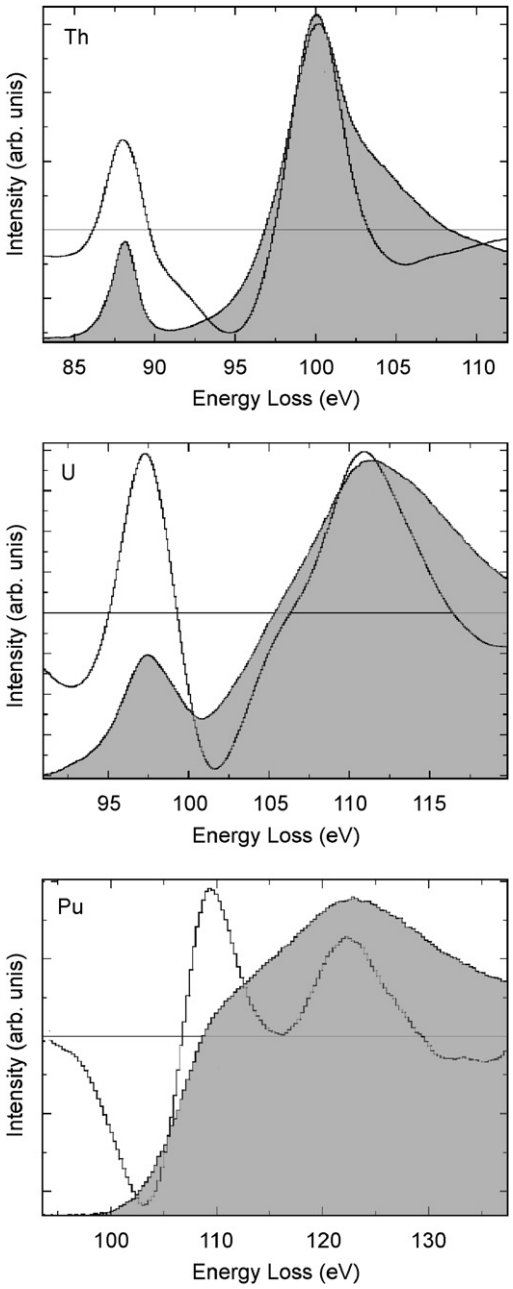

Fig. 1. The $O_{4,5}$ absorption edges for Th, U, and Pu metals collected in a TEM (solid gray). The second derivative is calculated for each spectra and overlayed as a black line.

spin–orbit interaction, which give splittings of 6.7, 7.9, and 9.3 eV for f^1, f^3, and f^5, respectively. In the case of Th and U, the separation between the pre-peak and the giant resonance is almost double the separation of the initial d states reported from photoemission [7]. To look at this in a more quantitative manner, the second derivative of each $O_{4,5}$ EELS edge can be calculated and compared to the edge itself. The second derivative of each edge is shown in Fig. 1 as an overlayed black line, and when this is done it seems that the O_4 and O_5 edges are indeed both contained in the giant resonance. For Th, there are two peaks in the second derivative, one for the small initial pre-peak and other for the giant resonance. In this case, the $5d_{3/2}$ and $5d_{5/2}$ initial states are close enough in energy that they are not resolved as separate in the giant resonance, partly due to the 2 eV lifetime broadening in actinide materials [8]. For U, the second derivative again shows two large peaks due to the pre-peak and the giant resonance. However, there is now a shoulder on the lower energy side of the giant resonance, which is located at approximately 105 eV. The difference between the inflection and the peak of the giant resonance is about 7 eV. This matches the 8.6 eV splitting between the initial $d_{3/2}$ and $d_{5/2}$ states of U reported by core-level photoemission quite well [7]. In the case of Pu, the second derivative shows two large peaks that both emanate from the giant resonance alone, one located at about 110 eV and the other located at about 122 eV. These are separated by 12 eV, which is very close to the 12.4 eV spin–orbit splitting of the $5d_{3/2}$ and $5d_{5/2}$ initial states of Pu reported by core-level photoemission [7].

The idea that the $5d_{3/2} \rightarrow 5f$ and $5d_{5/2} \rightarrow 5f$ dipole allowed transitions are both contained in the giant resonance can be further considered by comparison of the U and UO_2 EELS spectra. The $O_{4,5}$ EELS edge of UO_2 is shown in Fig. 2 as before with the spectra in gray and the second derivative overlayed as a black line. Notice that while the pre-peak is essentially unchanged from the metal, the inflection on the giant resonance has become more pronounced. This clearly shows that as the bonding environment changes, it is the inflection that changes and not the pre-peak. Thus, while it is tempting to ascribe the pre-peak and giant resonance as the O_5 and O_4 edges, respectively, this is incorrect. The electrostatic interactions are at least twice as large and these will completely mix the spin–orbit split peaks. The mixed spin–orbit split O_5 and O_4 peaks are both contained in the giant resonance and the small pre-peak is a consequence of first-order perturbation by the 5d spin–orbit interaction, as we will show below in the theoretical section.

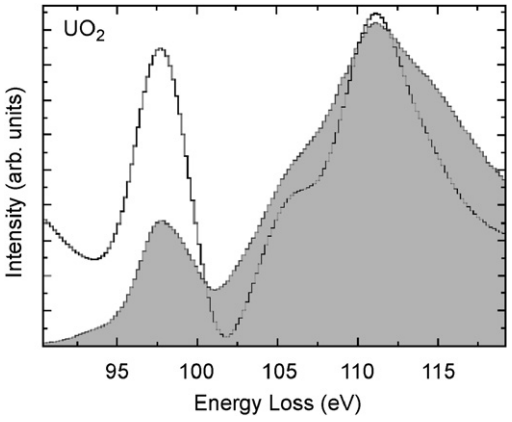

Fig. 2. The $O_{4,5}$ absorption edges for UO_2 collected in a TEM (solid gray). The second derivative is calculated for each spectra and overlayed as a black line.