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December 13, 2007

Understanding the $O_{4,5}$ edge structure of actinide metals

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Using electron energy-loss spectroscopy (EELS) and many-electron atomic spectral calculations, we examine the $O_{4,5}$ ($5d \rightarrow 5f$) edge structure of the ground-state α phase of Th, U, Np, Pu, Am, and Cm metal. Results show that the dipole-allowed transitions are contained within the giant resonance and that the small pre-peak in the actinide $5d \rightarrow 5f$ transition should not be labeled the O_5 peak, but rather the ΔS=1 peak. Lastly, we present for the first time the $O_{4,5}$ EELS spectra for Np, Am, and Cm metal.

The actinides are of great interest 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. Actinide materials are also rapidly growing in importance for energy and industry, particularly given expanding interest in next-generation nuclear reactors [1]. Yet, despite this rising awareness, there remains a discernable lack of knowledge of the fundamental physics and materials science of the actinide elements, even for the elemental metals [2]. A better understanding of the electronic structure of actinide metals, alloys, and compounds is required for accurate modeling of the behavior of these materials. In order to begin providing this, we have undertaken a continuing investigation of the 5f states of actinide metals though experiment and theory [3-10].

To investigate the 5f states of actinide elements using electron energy-loss spectroscopy (EELS) or x-ray absorption spectroscopy (XAS), transitions from d core states are utilized because they directly probe the f states due to the electric-dipole transitions $\Delta l = \pm 1$. The selection rules for these transitions strongly limit the final states that can be reached from the initial 5f^n state, which means that the spectrum becomes a fingerprint of the initial state. These transitions to the 5f states can be excited using either a 3d, 4d, or 5d core level, giving different spectral behaviors [2]. Here, we examine the $O_{4,5}$ (5$d \rightarrow$ 5f) EELS edge of Th, U, Np, Pu, Am, and Cm metal as acquired in a 300 keV field-emission-gun transmission electron microscope. Experimental $O_{4,5}$ EELS spectra of the ground-state α phase of each metal are presented along with analysis of many-electron atomic spectral calculations, to discern fundamental aspects of the electronic structure of the 5f states. While the Th, U, and Pu spectra have been presented before [4],

the Np, Am, and Cm spectra are shown for the first time, extending the known $5d \rightarrow 5f$

transitions for actinide metals into the middle of the $5f$ series.

The $O_{4,5}$ edges of Th, U, Np, Pu, Am, and Cm metal are shown in Fig. 1, where all

the edges are normalized to the same peak intensity. It is immediately noticeable that the

spectra for each of the elemental metals are distinctly different but that they all contain a

broad edge, often referred to as the giant resonance [11,12]. This edge is preceded by a

narrow structure in Th, U, and Np, usually referred to as pre-peak. The giant resonance is

ill-defined for the actinide $O_{4,5}$ ($5d \rightarrow 5f$) transition because the core $5d$ spin-orbit

interaction is smaller than the core-valence electrostatic interactions [13-16]. This

effectively smears out the transitions, encapsulating both the O_4 ($5d_{3/2}$) and O_5 ($5d_{5/2}$)

peaks within the giant resonance, and making distinction between them difficult or even

impossible. The dipole-allowed transitions are contained within the giant resonance,

whereas the pre-peak is a result of the finite spin-orbit interaction [8, 13].

Multiplet theory can be used to calculate core-level spectra for EELS and XAS of

the $M_{4,5}$, $N_{4,5}$, and $O_{4,5}$ edges given by the transitions $f^n \rightarrow d^9 f^{n+1}$. These calculations are

performed in the same way as for the rare earths $M_{4,5}$ and $N_{4,5}$ absorption edges [17,18],

only the parameters are different. Contrary to band-structure calculations, the multiplet

structure is calculated in intermediate coupling, which treats spin-orbit, Coulomb, and

exchange interactions on equal footing [19]. The calculated actinide $O_{4,5}$ spectra in Fig. 2

are convoluted using a Fano line shape broadening of $\Gamma = 2$ eV for the giant resonance

and a Lorentzian line shape of $\Gamma = 0.5$ eV for the pre-peak structure, where we assume

the cross-over between these two regions to be at a relative excitation energy of 5 eV.

Calculated actinide $O_{4,5}$ absorption spectra for the ground state configurations f^0 to f^9

reproduce the general trends in the data very well. First, the pre-peaks in the Th and U $O_{4,5}$ EELS edge are produced in agreement with the experimental EELS [4,5] and XAS [20] spectra. Second, the width of the calculated $O_{4,5}$ edge reduces by about half when going from $n = 5$ to 6, which is exactly what we observe between Pu and Am in the $O_{4,5}$ EELS in Fig. 1.

To better understand the actinide $O_{4,5}$ edges, it is instructive to consider the shape of the $4f$ rare earth $N_{4,5}$ ($4d$) edges [21-23] and the $3d$ transition metal $M_{2,3}$ ($3p$) edges [24], which also exhibit a giant resonance similar to the actinide $O_{4,5}$ edge. In all three of these cases, the core-valence electrostatic interactions dominate the core spin-orbit interaction. The $4f$ metals show a pre-peak structure that is similar to the light actinides and is largely insensitive to the local environment [21-23], meaning the pre-peak structure changes little with bonding environment. The $3d$ metals show a pre-peak structure that is strongly dependent on the crystal field and hybridization [24]. Since the $5f$ localization is between those of $4f$ and $3d$, the $O_{4,5}$ pre-peak behavior for the actinides is expected to show only a mild dependence on the environment. Indeed, examining the $O_{4,5}$ edge of α-U and UO_2 in Ref. 8 shows there is only a slight change in the pre-peak structure where a small shoulder appears on the high energy side of the peak at about 98 eV in UO_2.

Examining the electric-dipole transitions $5d\,^{10}5f^n \rightarrow 5d\,^95f^{n+1}$ with and without $5d$ core level spin-orbit interaction by means of atomic multiplet calculations reveals further insight. The calculated actinide $O_{4,5}$ absorption spectra in the presence (thick black line) and absence (thin red line) of $5d$ spin-orbit interaction for the ground state configurations f^0 to f^9 are shown in Fig. 3. The decay channels that give rise to the broadening are not

taken into account, instead all spectral lines are broadened with the same Lorentzian line shape of $\Gamma = 0.5$ eV. This is narrower than the experimental line width of the giant resonance and better shows the shifts in the line intensities. The pre-peak region and giant resonance are expected to be below and above ~5 eV, respectively. The results for the calculated $O_{4,5}$ EELS edges of $n = 1$ (~Th), $n = 3$ (~U), and $n = 5$ (~Pu) show that when the $5d$ spin-orbit interaction is switched off, the pre-peak structure vanishes, meaning the pre-peaks are a consequence of the perturbation by the $5d$ spin-orbit interaction, which allows transitions with $\Delta S = 1$. For instance, in the transition $f^0 \rightarrow d^9 f^1$, dipole transitions from the initial state $^1S_0$ are allowed only to the final state $^1P_1$ and would result in a single resonance peak. Spin-orbit interaction mixes this state with the $^3D_1$ and $^3P_1$ final states. These spin triplet states that are causing the pre-peaks are at lower energy compared to the singlet state, due to the strong core-valence exchange interaction [16]. While this result is clear for $5f^0$, it becomes rapidly more complicated for increasing values of the $5f$ count. For less than half-filled shell, with a ground-state of maximum spin S, there are always final states with spin $S+1$, however, this is no longer the case for more than half-filled shell [25]. Final states of spin $S+1$ can not be reached in pure LS coupling, since dipole-transitions do not change the spin, i.e., only $\Delta S = 0$ transitions are allowed. Spin-orbit interaction mixes states with $\Delta S = \pm 1$, and in first-order perturbation theory the relative intensity of the pre-peaks will be proportional to $(\Delta E_{\text{spin-orbit}})^2/(2\Delta E_{\text{electrostatic}})^2$, where $\Delta E_{\text{spin-orbit}}$ and $\Delta E_{\text{electrostatic}}$ are the effective splitting due to the spin-orbit and electrostatic interaction, respectively. This means the relative intensity of the pre-peak structure is a sensitive measure for the strength of the $5d$ core spin-orbit interaction relative to the $5d,5f$ electrostatic interaction. We find a good agreement between this

simple perturbation model and the experimental data. Since the spin-orbit parameter is normally close to the calculated value [26], it means that in the metal the electrostatic core-valence interaction is not much reduced in size compared to the atomic case. It gives further evidence that the intermediate coupling of the atomic model still holds in the metallic case. For instance, the intermediate coupling in Pu with $5f^5$ is close to jj coupling, meaning that almost all electrons occupy the $j = 5/2$ level.

As mentioned, for $n \geq 7$ the final state has the same spin multiplicity as the ground state and there are no forbidden spin transitions. States of the same spin are mixed by the $5d$ spin-orbit interaction, which increases in size over the series (from $\zeta_{5d} = 2.70$ eV for Th to 4.31 eV for Cm). Despite their complicated nature, examining the calculated $O_{4,5}$ edges for $5f$ counts from 0 to 9 show that in all cases the pre-peak intensity increases with the size of the $5d$ spin-orbit interaction relative to the electrostatic interactions, while the angular quantum number for the $5f$ states ($j = 7/2$ or $5/2$) strongly influences the precise spectral shape of the pre-peak structure and the position of the giant resonance. Therefore, the pre-peak intensity and structure is dependent on the spin-orbit interaction of both the $5d$ and $5f$ states.

In summary, we have presented EELS spectra and many-electron atomic spectral calculations of the $O_{4,5}$ edge of Th, U, Np, Pu, Am, and Cm metal, where the Np, Am, and Cm edges are the first reported experimental $O_{4,5}$ spectra for metals (the $O_{4,5}$ edge for CmO_2 is reported in Ref. 27). An assignment of the actinide $O_{4,5}$ edge can be made on the basis of final state LS coupling, and in doing so it can be shown that the dipole allowed transitions are contained within the giant resonance. The giant resonance splits into three transitions that are dipole allowed: $\Delta S = 0$ and $\Delta L = -1, 0, 1$ ($\Delta L = 1$ for ^1S ground state),

where S and L are the spin and orbital quantum numbers of the ground state. The $5d$ spin-orbit interaction acts as a perturbation giving rise to pre-peaks containing $\Delta S = 1$ states. These states have a lower energy than the $\Delta S = 0$ states with a separation determined by the strong $5d,5f$ exchange interaction. Although this simple picture begins to break down for $n > 1$ because the ground state and final states are strongly mixed, a global assignment can still be made on the basis of the spin states. Although atomic calculations are a simplification in the case of solids, they explain the trend along the series in the actinides rather well and show that the pre-peak observed in the $O_{4,5}$ edge is a dipole "forbidden" transition. The relative intensity of the pre-peak is a measure for the ratio between the spin-orbit interaction and electrostatic interaction, and shows that the intermediate coupling of the atomic model also applies to the metals.

References

1   D. Clery, *Science* **309**, 1172 (2005).

2   K. T. Moore, G. van der Laan, *Rev. Mod. Phys.,* in review.

3   G. van der Laan and B. T. Thole, *Phys. Rev. B* **53**, 14458 (1996).

4   K. T. Moore, M .A. Wall, A. J. Schwartz, B. W. Chung, D. K. Shuh, R. K. Schulze, and J.G. Tobin., *Phys. Rev. Lett.* **90**, 196404 (2003).

5   K. T. Moore, M. A. Wall, A. J. Schwartz, B. W. Chung, S. A. Morton, J. G. Tobin, S. Lazar, F. D. Tichelaar, H. W. Zandbergen, P. Söderlind, and G. van der Laan, *Philos. Mag.* **84**, 1039 (2004).

6   G. van der Laan, K. T. Moore, J. G. Tobin, B. W. Chung, M.A. Wall, and A. J. Schwartz, *Phys. Rev. Lett.* **93,** 097401 (2004).

7   K. T. Moore, G. van der Laan, R. G. Haire, M. A Wall, and A .J. Schwartz, *Phys. Rev. B* **73**, 033109 (2006).

8   K. T. Moore and G. van der Laan, *Ultramicroscopy* **107**, 1201 (2007).

9   K. T. Moore, G. van der Laan, M. A. Wall, A. J. Schwartz, and R. G. Haire, *Phys. Rev. B* **76**, 073105 (2007).

10   K. T. Moore, G. van der Laan, R. G. Haire, M. A. Wall, A. J. Schwartz, and P. Söderlind, *Phys. Rev. Lett.* **98**, 236402 (2007).

11   G. Wendin, *Phys. Rev. Lett.* **53**, 724 (1984).

12   *Giant resonances in atoms, molecules, and solids, NATO Advances in study Institute, Series B:Physics,* Vol. 151, J. P. Connerade, J. M. Esteva, and R. C. Karnatak, Eds. (Plenum, New York, 1987).

13   H. Ogasawara, A. Kotani, and B. T. Thole, *Phys. Rev. B* **44**, 2169 (1991).

14   H. Ogasawara and A. Kotani, *J. Phys. Soc. Jpn*. **64**, 1394 (1995).

15   H. Ogasawara and A. Kotani, *J. Synchrotron Rad.* **8**, 220 (2001).

16   For the transition Th $5f^0$ -> $5d^9 5f^1$, the parameters for the multiplet calculation are $\zeta(5d)$ = 2.70 and $\zeta(5f)$ = 0.21 eV for the spin-orbit interaction and F^2 = 7.76, F^4 = 4.94, G^1 = 9.01, G^3 = 5.56, G^5 = 3.96 eV for the 80% reduced 5d,5f electrostatic interactions. These values increase gradually along the actinide series.

17   B. T. Thole, G. van der Laan, J. C. Fuggle, G. A. Sawatzky, R. C. Karnatak, and J. M. Esteva, *Phys. Rev. B* **32**, 5107 (1985).

18   K. Starke, E. Navas, E. Arenholz, Z. Hu, L. Baumgarten, G. van der Laan, C. T. Chen, and G. Kaindl, *Phys. Rev. B* **55**, 2672 (1997).

19   G. van der Laan, *Lect. Notes Phys.* **697**, 143 (2006).

20   G. Kalkowski, G. Kaindl, W. D. Brewer, and W. Krone, Phys. Rev. B **35**, 2667 (1987).

21   J. L. Dehmer, A. F. Starace, U. Fano, J. Sugar, and J. W. Cooper, *Phys. Rev. Lett.* **26**, 1521 (1971).

22   A. F. Starace, *Phys. Rev. B* **5**, 1773 (1972).

23   J. Sugar, *Phys. Rev. B* **5**, 1785 (1972).

24   G. van der Laan, *J. Phys.: Condens. Matter* **3**, 7443 (1991).

25   B. T. Thole and G. van der Laan, *Phys. Rev. B* **38**, 3158 (1988).

26   R. E. Watson and M. Blume, *Phys. Rev.* **139**, A 1209 (1965).

27   K. O. Kvashnina, S. M. Butorin, D. K. Shuh, J.-H. Guo, L. Werme, and J. Nordgren, *Phys. Rev. B* **75**, 115107 (2007).

Figure Captions

FIG. 1: The $O_{4,5}$ EELS edges for the α-phases of Th, U, Np, Pu, Am, and Cm metal. Electron diffraction and imaging of the Am sample in the TEM showed that it contained heavy amounts of stacking faults, which can be argued produces a combination of α and β phases as it is simply a change in the 111 plane stacking. However, spectra taken from areas with varying amounts of stacking faults showed no detectable difference in structure.

FIG. 2: Calculated actinide $O_{4,5}$ absorption spectra for the ground state configurations f^0 to f^9. The spectra have been convoluted using a Fano line shape broadening with $\Gamma = 2$ eV for the giant resonance and a Lorentzian line shape of $\Gamma = 0.5$ eV for the pre-peak region.

FIG. 3: (Color online) Calculated actinide $O_{4,5}$ absorption spectra with (black thick line) and without (red thin line) $5d$ core spin-orbit interaction for the ground state configurations f^0 to f^9. Atomic values of the Hartree-Fock Slater parameters were used as tabulated in Ref. [13]. The relative energy refers to the zero energy of the average of the total final-state configuration. The decay channels that give rise to the broadening were not taken into account. All spectral lines were broadened with the same Lorentzian line shape of $\Gamma = 0.5$ eV. The pre-peak region and giant resonance are expected to be below and above ~5 eV, respectively.
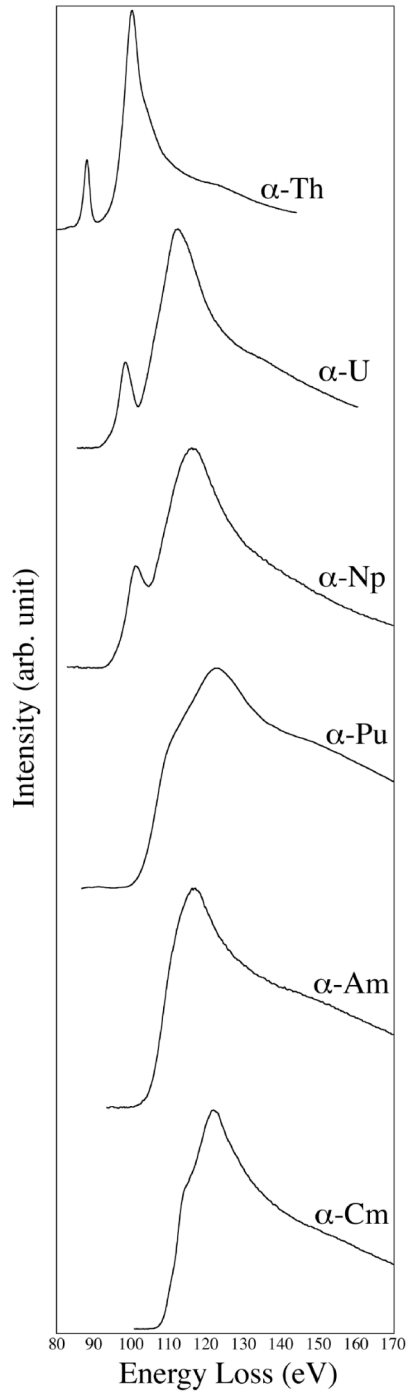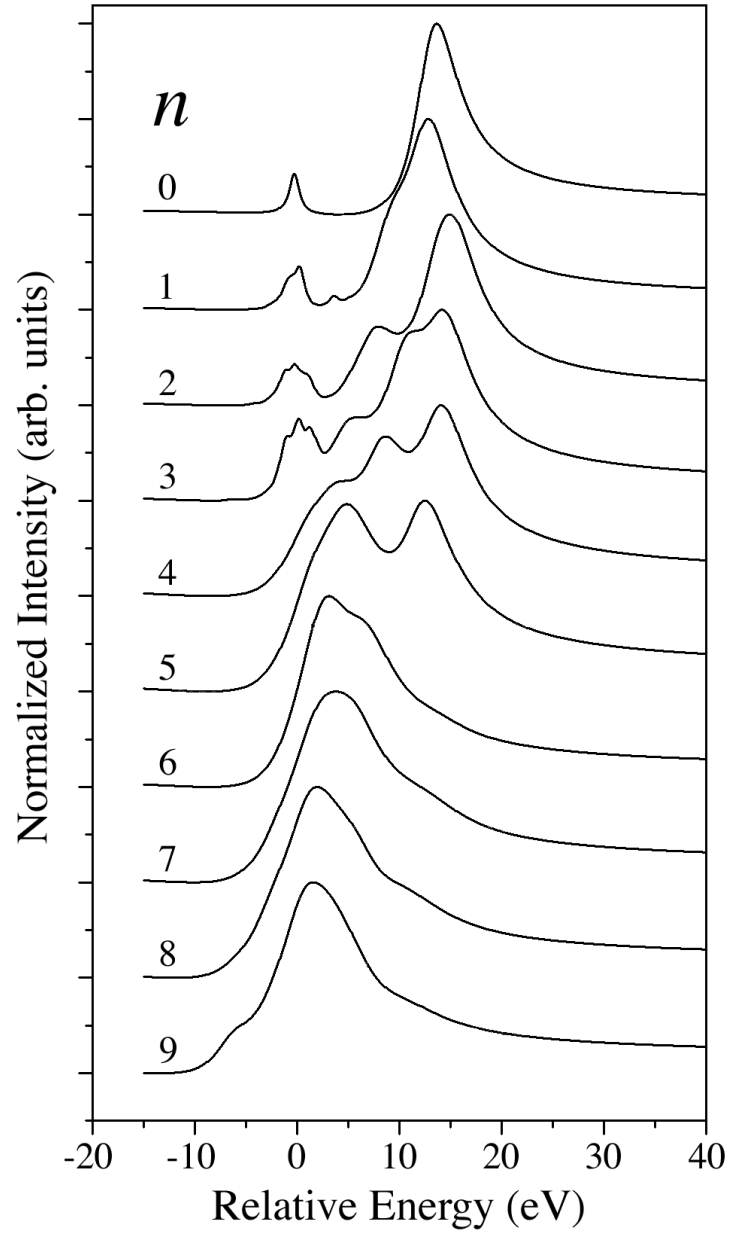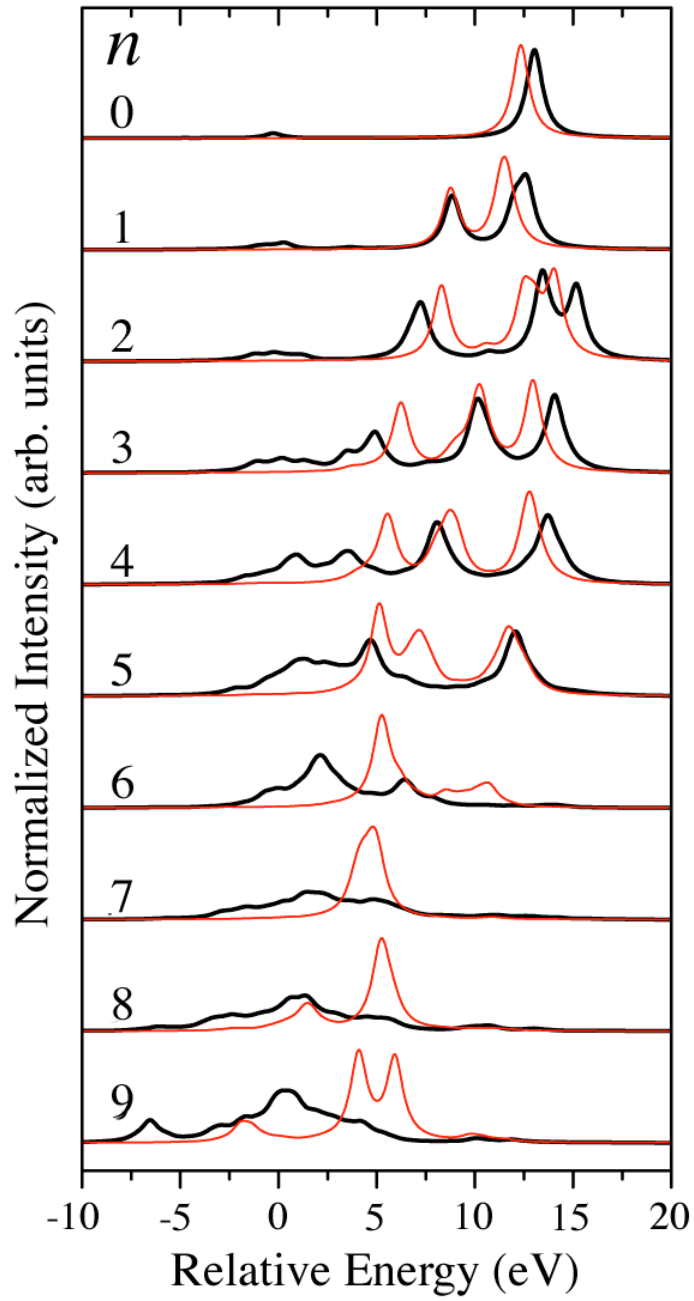
Figure 1

Figure 2

Figure 3