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Understanding the $O_{4,5}$ edge structure of actinide metals: Electron energy-loss spectroscopy and atomic spectral calculations of Th, U, Np, Pu, Am, and Cm

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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 metals. Results show that (i) atomic calculations explain the trend in $O_{4,5}$ structure along the actinide series and (ii) the dipole-allowed transitions are contained within the giant resonance. Therefore, the small prepeak in the $5d \rightarrow 5f$ transition of Th, U, and Np should not be labeled the O_5 peak, but rather the $\Delta S = 1$ peak. In presenting the $O_{4,5}$ EELS spectra for Np, Am, and Cm, we extend the known $d \rightarrow f$ transitions for actinide metals.

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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 discernible lack of knowledge of the fundamental physics and materials science of the actinides, 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 through 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, each yielding different spectral behaviors.[2] Here, we examine the $O_{4,5}$ ($5d \rightarrow 5f$) EELS edge of Th, U, Np, Pu, Am, and Cm metals as acquired in a 300 keV field-emission-gun transmission electron microscope (TEM). Experimental $O_{4,5}$ EELS spectra of the ground-state α phase of each metal are presented along with the analysis of many-electron atomic spectral calculations to discern fundamental aspects of the electronic structure of the $5f$ states. By presenting the $O_{4,5}$ spectra of Th, U, Pu, Np, Am, and Cm, the recorded $5d \rightarrow 5f$ transitions for actinide metals is extended into the middle of the $5f$ series, past the localized-itinerant transition of the $5f$ states that occurs near Pu.

The $O_{4,5}$ edges of Th, U, Np, Pu, Am, and Cm metals are shown in Fig. 1, where all the edges are normalized to the same peak intensity. It is immediately noticeable that the spectrum for each of the elemental metal is distinctly different, but that they all contain a broad edge that is often referred to as the giant resonance.[11,12] This edge is preceded by a narrow structure in Th, U, and Np that is typically referred to as a prepeak. 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 the distinction between them difficult or even impossible. The dipole-allowed transitions are contained within the giant resonance, whereas the prepeak is a result of the finite spin-orbit interaction.[8,13]

Multiplet theory can be used to calculate the 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 the $M_{4,5}$ and $N_{4,5}$ absorption edges for the rare earths,[17,18] except that 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 prepeak structure, where we assume the crossover between these two regions to be at a relative excitation energy of 5 eV. The 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 prepeaks in the Th and U $O_{4,5}$ EELS edges 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 $n=6$, 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 these cases, the core-valence electrostatic interactions dominate the core spin-orbit interaction. The $4f$

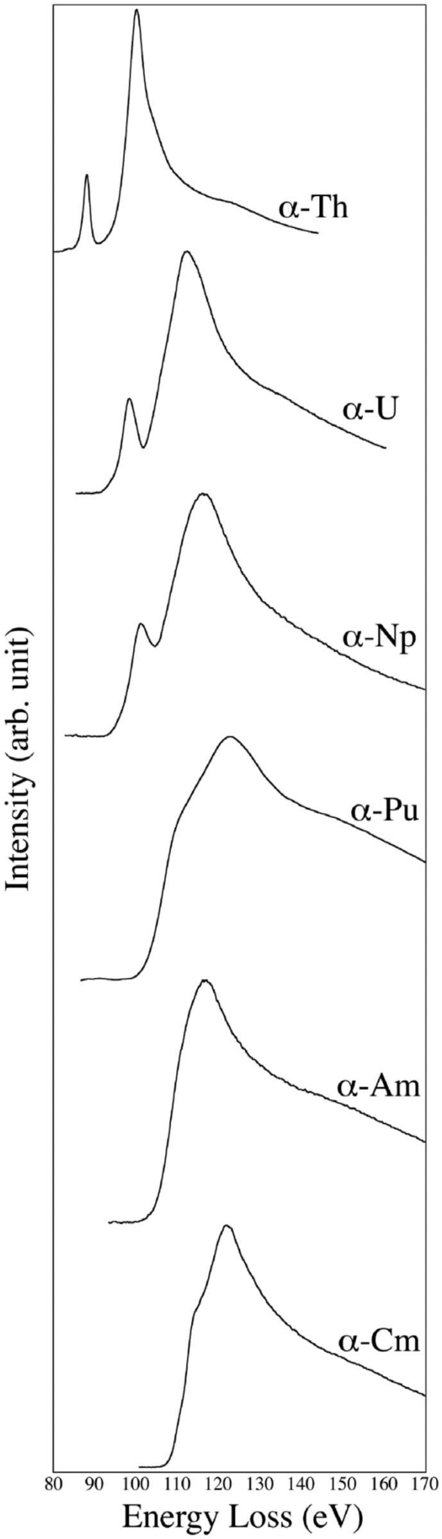

FIG. 1. The $O_{4,5}$ EELS edges for the α phases of Th, U, Np, Pu, Am, and Cm metals. Electron diffraction and imaging of the Am sample in the TEM showed that it contained heavy amounts of stacking faults, which can be argued produces a combination of α and β phases as it is simply a change in the 111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

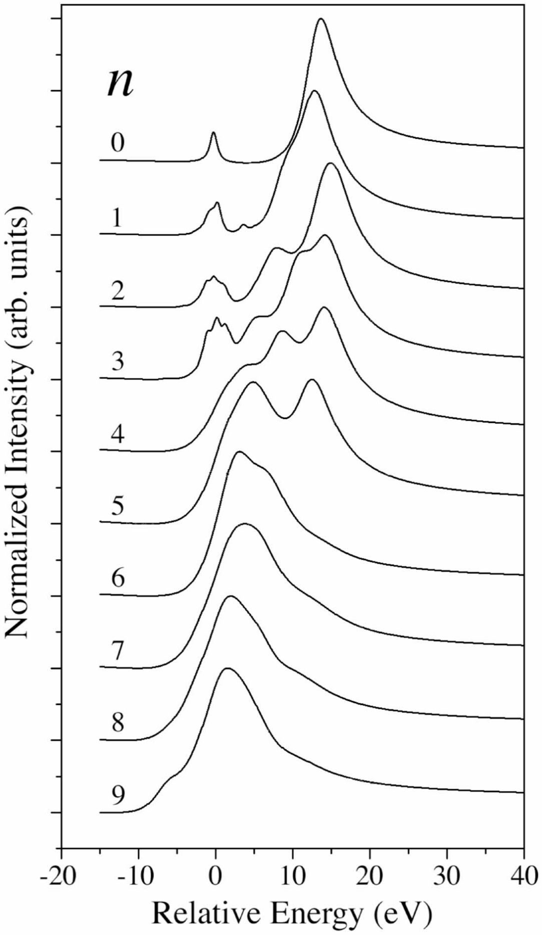

FIG. 2. Calculated actinide $O_{4,5}$ absorption spectra for the ground-state configurations f^0–f^9. The spectra have been convoluted using a Fano line shape broadening with $\Gamma=2$ eV for the giant resonance and a Lorentzian line shape of $\Gamma=0.5$ eV for the prepeak region.

metals show a prepeak structure that is similar to the light actinides and is largely insensitive to the local environment,[21–23] meaning the prepeak structure changes little with bonding environment. The 3*d* metals show a prepeak structure that is strongly dependent on the crystal field and hybridization.[24] Since the 5*f* localization is between those of 4*f* and 3*d*, the $O_{4,5}$ prepeak 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 that there is only a slight change in the prepeak 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 $5d^{10}5f^n \rightarrow 5d^9 5f^{n+1}$ with and without 5*d* 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 5*d* 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

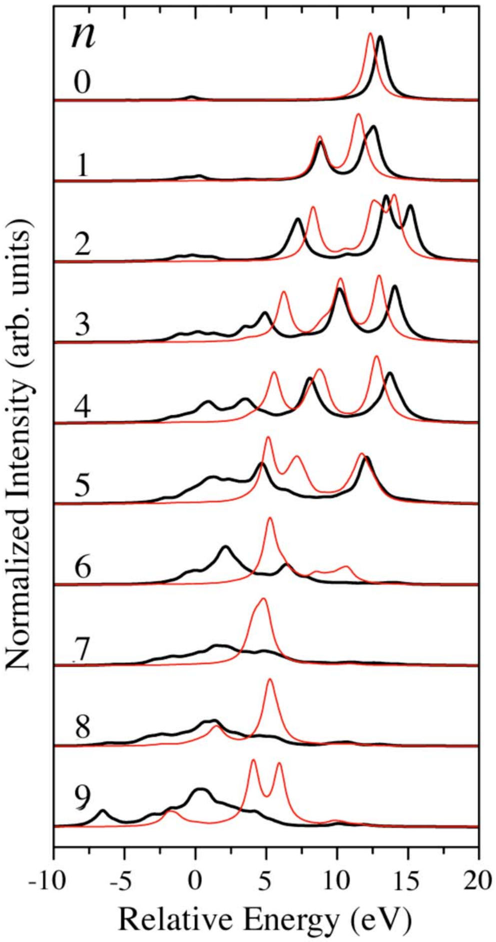

FIG. 3. (Color online) Calculated actinide $O_{4,5}$ absorption spectra with (black thick line) and without (red–thin line) 5*d* core spin-orbit interaction for the ground-state configurations f^0 to f^9. Atomic values of the Hartree–Fock Slater parameters were used as tabulated in Ref. 13. The relative 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 prepeak region and giant resonance are expected to be below and above ~5 eV, respectively.

shape of $\Gamma=0.5$ eV. This is narrower than the experimental linewidth of the giant resonance and better shows the shifts in the line intensities. The prepeak 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 5*d* spin-orbit interaction is switched off, the prepeak structure vanishes, meaning the prepeaks are a consequence of the perturbation by the 5*d* spin-orbit interaction, which allows transitions with $\Delta S=1$. For instance, in the transition $f^0 \rightarrow d^9f^1$, 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 prepeaks are at a 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 5*f* 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 $S+1$ cannot 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 in states with $\Delta S=\pm 1$, and in first-order perturbation theory, the relative intensity of the prepeaks 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 interactions, respectively. This means that the relative intensity of the prepeak structure is a sensitive measure of the strength of the 5*d* core spin-orbit interaction relative to the 5*d*,5*f* electrostatic interaction. We find 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 $n \geqslant 7$, the final state permits the same spin multiplicity as the ground state and there are no forbidden spin transitions. States of the same spin are mixed by the 5*d* 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 5*f* counts from 0 to 9 shows that in all cases the prepeak intensity increases with the size of the 5*d* spin-orbit interaction relative to the electrostatic interactions, while the angular quantum number for the 5*f* states ($j=7/2$ or $5/2$) strongly influences the precise spectral shape of the prepeak structure and the position of the giant resonance. Therefore, the prepeak intensity and structure are dependent on the spin-orbit interaction of both the 5*d* and 5*f* 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 metals (the $O_{4,5}$ edge for Cm oxide was recently 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 5*d* spin-orbit interaction acts as a perturbation giving rise to prepeaks containing $\Delta S=1$ states. These states have a lower energy than the $\Delta S=0$ states, with a separation determined by the strong 5*d*,5*f* 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 prepeak observed in the $O_{4,5}$ edge is a dipole "forbidden" transition. The relative intensity of the prepeak is a measure of 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.

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