Decay channels of the $5d \rightarrow 5f$ excitation in thorium

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The valence bands and Auger emission of thorium have been studied in the $5d \rightarrow 5f$ excitation region using synchrotron radiation. Three decay channels of the $5d$ hole have been identified: ordinary Auger deexcitation, resonant Auger deexcitation, and direct recombination. The latter two originating from strongly exchange-coupled $5d^9 5f^1$ virtually excited states. A kinetic energy shift of the O_5VV Auger line is observed around a $5d \rightarrow 5f$ resonant absorption peak at $h\nu = 89$ eV and is attributed to overlap of the above two Auger features. The relative importance of these decay channels is discussed in terms of the discrete $5d^9 5f^1 \rightarrow$ continuum $5d^9 \epsilon f$ transition probability and the $5d \rightarrow 5f$ dipole oscillator strength of the $5d^9 5f^1$ multiplet state.

In the $np \rightarrow nd$, $4d \rightarrow 4f$, and $5d \rightarrow 5f$ core-excitation regions of transition metals,[1] rare earths,[2] and actinides,[3] respectively, photoemission intensities exhibit resonance-like enhancement. This phenomenon has been interpreted as due to interference effects between direct photoionization and the core-involving excitations,[4] whereby the core-excited state decays into a photoelectron and a hole via direct recombination channel. The excited state can also decay via Auger deexcitation and thus gives rise to enhancement of Auger emission. So far, studies on these decay channels have been limited,[5] and mechanisms governing their relative importance have not been well elucidated.

In this paper, we present results of synchrotron radiation photoemission studies on Th metal in the $5d \rightarrow 5f$ core-excitation region ($80 \leq h\nu \leq 130$ eV). An anomalous shift of the O_5VV (or $5d_{5/2}VV$) Auger kinetic energy is observed, as in previous studies on the O_5P_3V (or $5d_{5/2}6p_{3/2}V$) Auger emission,[6] and is interpreted as due to two-electron-excited final states produced by a resonant OVV Auger transition from an exchange-coupled $5d^9 5f^1$ state. The relative importance of three deexcitation channels, direct recombination, ordinary Auger transitions, and resonant Auger transitions, is explained by two factors, namely the discrete $5d^9 5f^1 \rightarrow$ continuum $5d^9 \epsilon f$ transition probability within the core-excited states and the $5d \rightarrow 5f$ dipole oscillator strength of the $5d^9 5f^1$ multiplet state.

The Th(111) surface was cleaned by repeated argon-ion sputtering and annealing cycles. Photoemission and partial yield spectra were measured with a two-dimensional electron spectrometer using photons from the Tantalus storage ring at the Synchrotron Radiation Center, University of Wisconsin—Madison. The spectra were taken with a working pressure of $\sim 5 \times 10^{-11}$ Torr. The total resolution of the monochromater plus analyzer was ~ 0.5 eV. Spectral intensities were normalized to photon flux to obtain intensity profiles.

Thorium has no localized $5f$ electrons but has a small itinerant $5f$ character (~ 0.5 electron per atom).[7,8] Figure 1 shows energy distribution curves (EDC's) taken at various photon energies in the $5d \rightarrow 5f$ excitation region. The two prominent features at 0—1 and ~ 2 eV below E_F correspond well to the calculated density of states[9] (DOS) shown at the bottom of Fig. 1. At resonance ($h\nu \sim 90$—100 eV), enhancement of the valence band occurs via a direct recombination of the virtually excited state,

$$5d^{10}V^n + h\nu \rightarrow 5d^9 5f^1 V^n \rightarrow 5d^{10}V^{n-1} + e \ , \qquad (1)$$

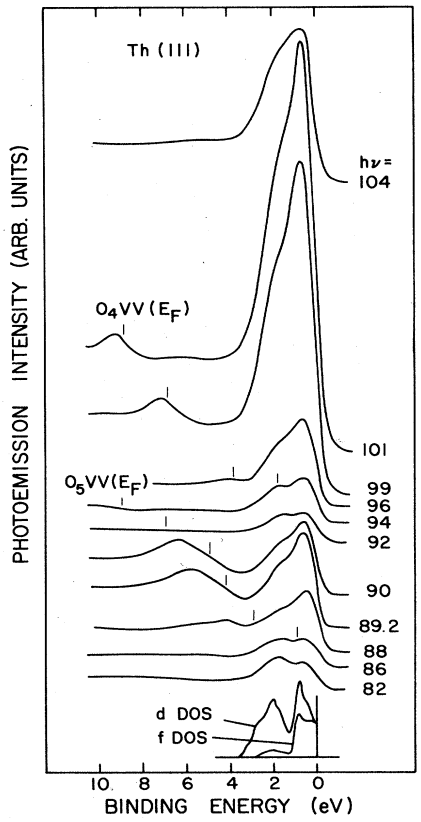

FIG. 1. Energy distribution curves for Th. The vertical bars indicate constant kinetic energies of O_4VV and O_5VV Auger emission with two valence electrons at E_F. The d and f partial DOS's obtained by the band calculation (Ref. 8) are shown.

where V denotes a valence electron which is $6d,7s$ or $5f$ like. This process enhances the $5f$ component of the valence band (within ~ 1 eV of E_F) more effectively than that due to $6d,7s$ states (super—Coster-Kronig process).[9] The $h\nu$ dependence of the O_4VV and O_5VV Auger emission is shown in Figs. 1 and 2. The OVV emission is also expected to sample preferentially the $5f$ part of the valence band. As the on-site Coulomb energy between two $5f$ electrons is sufficiently small [$U \sim 1.5$ eV (Ref. 10)] as compared to the $5f$ band width ($W \sim 5$ eV),[8] the OVV Auger spectra are expected to give self-convolutions of the $5f$ DOS.[11,12]

Intensity profiles of the valence band and Auger emission features are plotted in Fig. 3 together with a partial-yield spectrum representing the photoabsorption profile. Three absorption features are labeled by A, B, and C. The absorption profile is qualitatively similar to that of the La $4d \rightarrow 4f$ absorption[5] given in the inset of Fig. 3, where A, B, and C correspond to $^1P_1$, $^3D_1$, and $^3P_1$ components of the $4d^9 4f^1$ multiplet, respectively. Only the $^1P_1$ state is dipole allowed in the LS-coupling limit, and the $^3D_1$ and $^3P_1$ lines gain finite oscillator strengths through mixing with the $^1P_1$ state in the intermediate coupling scheme. In the case of Th, peaks B and C are stronger than in La because the above LS-coupling terms mix more strongly due to the larger spin-orbit splitting of the Th $5d$ core level than the La $4d$ core level.[13] Note that peak B is above the $5d_{5/2}$ threshold in Th whereas it is below the $4d_{5/2}$ threshold in La. One can see from Fig. 3 that the OVV Auger decay channel is more important around peak B than around peak A. In the case of La only the Auger decay channel has been observed for peak B.[5] Around peak A, both the direct recombination and Auger deexcitation channels are equally important in Th and LaB_6.

In order to explain the Auger versus direct-recombination decay behavior in each $5d \rightarrow 5f$ absorption-peak region, we distinguish between ordinary

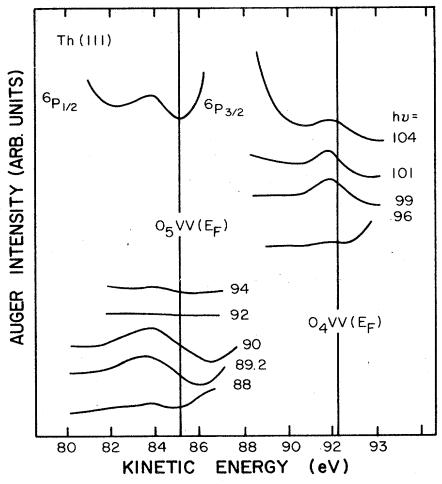

FIG. 2. Energy distribution curves for Th in the O_4VV and O_5VV Auger emission regions as a function of electron kinetic energy relative to E_F. For $96 \leq h\nu \leq 101$ eV, the intense $6p_{3/2}$ core level overlaps the O_5VV Auger emission.

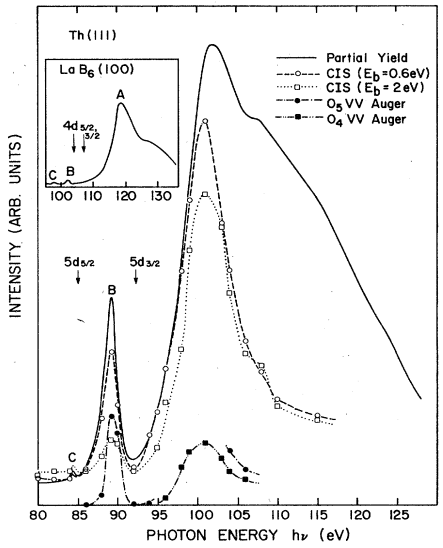

FIG. 3. Constant initial state (CIS) curves for two valence-band photoemission features at 0.6 and 2 eV below E_F, a partial yield spectrum taken at a constant final-state energy of 4 eV, and intensity profiles of the O_4VV and O_5VV Auger emission. The CIS's represent the peak height in the EDC's, while the Auger intensities have been obtained by integrating peak areas by assuming smooth backgrounds. The 2-eV CIS for $h\nu = 86$ eV is not shown because of an overlap of the O_5VV Auger emission. The binding energies of the $5d_{5/2}$ and $5d_{3/2}$ core levels (Ref. 15) are indicated by arrows. In the inset, a partial-yield spectrum for LaB_6 in the $4d \rightarrow 4f$ region (Ref. 5) is shown for comparison.

Auger transitions, where an electron excited from the core level does not interact strongly with the $5d$ ($4d$) core hole in the Auger initial state, and resonant Auger transitions, where the excited electron interacts with the core hole through exchange interactions. For photon energies above the core-level threshold, the excited electron has a probability of leaving the core-hole site and entering a continuum.[14] Then the core hole decays via an ordinary OVV Auger transition:

$$5d^{10}V^n + h\nu \rightarrow 5d^9 5f^1 V^n \rightarrow 5d^9 V_s V^n \epsilon f \rightarrow 5d^{10}V^{n-2}\epsilon f + e \ , \tag{2}$$

where ϵf denotes an electron in a spatially extended state outside the potential barrier of the core-hole site, and the relaxed core hole in the third stage is screened by an electron V_s which is predominantly $5f$-like.[15] If the excited electron stays at the core-hole site during the OVV Auger decay, the following process may be considered:

$$5d^{10}V^n + h\nu \rightarrow 5d^9 5f^1 V^n \rightarrow 5d^{10}V^{n-2}5f^* + e \ , \tag{3}$$

where $5f^*$ denotes an electron which is released from the strong exchange interactions with the $5d$ core hole in the $5d^9 5f^1$ excited state and enters a $5f$ state above E_F.[5,6] This process is analogous to the Auger resonant Raman effect with core holes in the final state,[16] and should be considered as a one-step process with the $5d^9 5f^1$ virtually

excited state. Alternatively this process may be viewed as a two-electron excitation ($V \rightarrow \epsilon f$ and $V \rightarrow 5f^*$) enchanced resonantly by the $5d \rightarrow 5f$ virtual excitation. We refer to this process as a resonant Auger electron emission. An electron emitted by Eq. (3) reflects the unoccupied $5f$ DOS through $5f^*$ in the final state and therefore would have a constant binding energy rather than a constant kinetic energy as the empty $5f$ DOS has a peak $\lesssim 4$ eV above E_F.[8,17,18] Thus if resonant [Eq. (3)] and ordinary [Eq. (2)] Auger emission lines overlap and are not resolved into separate features, then one would expect an apparent kinetic energy shift of the Auger emission to lower energies as the photon energy is lowered.

The kinetic energy of an electron emitted by the resonant Auger emission (3) is given by $E_K^{A'} \sim h\nu - E(V^{-2}) - E(5f^*)$, while the ordinary Auger electron kinetic energy is given by $E_K^A = E(5d_{5/2}^{-1}) - E(V^{-2})$, where $E(V^{-2})$, $E(5d_{5/2}^{-1})$, and $E(5f^*)$ represent, respectively, the energies of the two-V-hole, $5d_{5/2}$-hole, and $5f^*$-electron states relative to the ground state. For photon energies around peak B, the two kinetic energies E_K^A and $E_K^{A'}$ are close to each other because $h\nu \sim E(5d_{5/2}^{-1}) + 4$ eV and $E(5f^*) \lesssim 4$ eV (Refs. 8 and 17) for these photon energies. Therefore, the observed O_5VV feature for photon energies around peak B may be assigned to overlapping ordinary [Eq. (2)] and resonant [Eq. (3)] Auger emission. A similar kinetic energy shift has been observed for the O_5P_3VV Auger emission of Th in the same photon energy region B and has been interpreted as due to overlapping ordinary Auger and a two-electron excitation $5d^{10}6p^6V^n \rightarrow 5d^{10}6p^5V^{n-1}5f^*$ enhanced by the resonant Auger process of the type of Eq. (3).[6,17]

Now we are in a position to discuss the relative importance of the above three competing decay channels (1)—(3). First, we consider the region of peak B. In LaB_6, the ordinary Auger decay channel is closed at peak B since it is below the La $4d$ threshold and the $4f \rightarrow \epsilon f$ step [the second step in Eq. (2)] is not open. Thus the excited state $4d^9 4f^1 V^n$ must decay either via direct recombination [Eq. (1)] or a resonant Auger transition [Eq. (3)]. The relative importance of the latter two channels can be determined by the dipole oscillator strength for the nd^9nf^1 multiplet line: Strong dipole moment favors $nf \rightarrow nd$ direct recombination which simultaneously excites emission of a photoelectron. This would explain the observation that direct recombination for the peak B is appreciable in Th but not in LaB_6 (Ref. 5), as the absorption peak B is much stronger for Th than for La (see Fig. 3).

In the region of peak A, the virtually excited discrete state nd^9nf^1 partly makes a transition to a continuum state $nd^9V_s\epsilon f$ and then decays via an ordinary Auger transition [Eq. (2)], and partly decays via direct recombination [Eq. (1)] or resonant Auger emission [Eq. (3)]. However, direct recombination dominates resonant Auger emission because of the very large nf-nd oscillator strength. This would explain the observation that both the direct recombination and ordinary Auger recombination channels are equally important but that the resonant Auger deexcitation channel (3) is negligibly small in the region of peak A for Th and LaB_6.

In conclusion, decay processes in the $5d \rightarrow 5f$ excitation region of Th metal have been studied. Following photoabsorption $5d^{10}V^n + h\nu \rightarrow 5d^9 5f^1 V_n$, the excited state decays either via an ordinary Auger transition after escape of the $5f$ electron out of the potential barrier and relaxation of the core hole, or decays (as a virtually excited state) via one of the two channels, direct recombination or resonant Auger deexcitation. The relative importance of the latter two channels is determined by the $5d \rightarrow 5f$ oscillator strength of the multiplet term of the virtually excited $5d^9 5f^1$ state. Photoemission and Auger intensity profiles of metallic LaB_6 are also well explained in terms of these processes. In heavier actinides and rare earths with more f-electron transitions between multiplet states, the appearance of satellites and their different resonance behaviors would complicate deexcitation processes.[3,19,20]

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lower for O_5VV than for O_4VV by ~ 0.7 eV. We attribute this to the different spin-orbit symmetry of the core levels leading to different sampling probabilities for the $5f_{7/2}$ and $5f_{5/2}$ components of the valence band. The spin-orbit splitting of Th $5f$ is estimated to be ~ 0.3 eV [F. Gerken and J. Schmidt-May, J. Phys. F **13**, 1571 (1983)], so that a difference of $\lesssim 0.6$ eV is expected between the O_4VV and O_5VV Auger spectra, representing self-convolutions of the $5f$ DOS, consistent with the experiment.

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