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Resonant photoemission as a tool to study f and d electrons in actinide compounds

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Using synchrotron radiation in the energy range $60 \leq h\nu \leq 130$ eV, we have measured $h\nu$-dependent photoemission energy distribution curves and constant-initial-state spectra from single crystals of $U_xTh_{1-x}Sb$, UTe, UO_2, and UPd_3. The U $5f$ and U and Th $6d$ conduction bands, as well as the Sb and Te $5p$ valence-band emission, all exhibit Fano-type resonance behavior at the $5d$ core ionization thresholds. The $5f$ emission shows the strongest intensity variation, which can be explained by the super-Coster-Kronig character of the decay of the autoionizing core excited state. Thus f and d emission features in the photoemission spectra are unambiguously identified by their different resonance behavior. It is concluded that the spectra are dominated by localized $5f$ states in all of these compounds.

I. INTRODUCTION

The coupling between different ionization channels changes the spectral features in the valence-band emission when the photon energy is tuned through a core absorption edge. Such a Fano-type resonance[1] behavior has been found, e.g., for the $3p$ edges in Ni (Ref. 2) and Cu,[3] for the $4d$ absorption edges in rare-earth compounds,[4–6] and recently for the $5d$ thresholds in USb (Ref. 7) and α-U.[8] To date, this so-called "resonant photoemission" has been used to study the core-hole photoexcitation process itself, e.g., the many-electron processes involved and the various decay channels of the excited state.[9] The resonance enhancement of the Ce $4f$ emission has also been used to locate the $4f$ level in Ce compounds.[10–12] Here we want to use the $5d$ core-hole excitation to assign $5f$ and/or $6d$ character to emission features in the valence bands of various uranium and thorium compounds. We have studied semiconducting UO_2 (Ref. 13) and metallic UPd_3 (Ref. 14) which are considered to have a localized $5f^2$ configuration as well as $U_xTh_{1-x}Sb$ (Ref. 15) and UTe (Ref. 16) which have recently been shown to have a quasilocalized[17] $5f^3$ configuration which is hybridized with itinerant $6d$ states. Since the resonance behavior can be understood[6,9] within an atomic picture,[18] it does not *a priori* tell us anything about the localized-versus-itinerant character of the $5f$ electrons. However, we can give an unambiguous assignment of the $5f$ emission in energy, and we find that these energy positions favor a localized description of the $5f$ electrons in the presently investigated compounds. Furthermore, by studying the intensity variations in the valence bands it is possible to derive to what extent the $5f$ electrons are hybridized with valence p or d electrons.

II. THEORETICAL CONSIDERATIONS

A Fano-type resonance behavior of the photoemission intensity is generally viewed as being due to autoionization of some (virtual) intermediate excited state.[6,9] As an example, we discuss the valence electron emission of an uranium atom having a trivalent (U $5f^3$) configuration. The main photoabsorption above the $5d$ ionization threshold corresponds to processes of the type

$$5d^{10}5f^36d\,7s^2+h\nu\rightarrow[5d^95f^46d\,7s^2]^*\ , \qquad (1)$$

where the asterisk denotes an excited state within this configuration. For clarification in the present discussion of decay processes, we adopt a purely atomic picture and do not explicitly denote the nature of the screening electrons. After the photoabsorption, the intermediate state in Eq. (1) can decay via various channels. For the $5f$ and $6d$ valence electron emission we have, in particular, to consider the following Auger decay processes

$$[5d^95f^46d\,7s^2]^* \begin{array}{ll} \xrightarrow{\text{SCK}} 5d^{10}5f^26d\,7s^2+e^- & \text{(2a)} \\ \xrightarrow{\text{CK}} 5d^{10}5f^36d^07s^2+e^- , & \text{(2b)} \end{array}$$

where CK and SCK denote Coster-Kronig and super-Coster-Kronig transitions, respectively. The final states in Eq. (2a) correspond to a $5f$ ionized state while Eq. (2b) describes a U $6d$ photoionization. The name CK is used for an Auger process in which one of the final-state holes has the same main quantum number as the initial vacancy. In a SCK process all three participating electrons belong to the same main shell. From studies of core-hole decay processes we know that generally CK processes are more rapid than ordinary Auger processes (all three electrons in different shells) and that SCK processes often are found to be particularly important.[19] Since the coupling of the $5f$ emission to the $5d$ absorption in Eq. (2a) is of the SCK-type while for the $6d$ emission [Eq. (2b)] it corresponds to a CK process, we anticipate the strongest resonance behavior for the $5f$ electrons. Equations (2a) and (2b) thus demonstrate that different final single-hole states can couple differently to the $5d$ photoabsorption.

Experimentally, the resonance behavior manifests itself as a minimum in the photoemission intensity-versus-$h\nu$ curve, which is followed by an enhancement when $h\nu$ is tuned through the $5d$ core absorption edge. The minimum reflects Fano-type interference effects[1] which occur between two channels: direct photoionization and excitations into an intermediate state (1) only, while the enhancement is owing to the subsequent processes of Eq. (2).

Except for the very Th-rich compounds, the photoemission density of states (PDOS's) of $U_xTh_{1-x}Sb$ and UTe were thought[20,21] to consist of a "$5f$-$6d$" hybridized conduction band (CB) with a high DOS of $5f$ electrons at E_F and an anion-derived p valence band (VB) several eV below E_F. With our present resolution ($\Delta E \sim 0.15$ eV) we are able to resolve several spectral features in the conduction band and to follow their spectral behavior through the $5d$ core-hole threshold. The different resonant behavior of the various spectral features and a comparison of ThSb and USb allows a delineation of $5f$ and $6d$ contributions to the conduction bands and the identification of f-p hybridized parts in the valence bands.

A comparative x-ray photoelectron spectroscopy (XPS) study[14] of UPd_3 and $ThPd_3$ (Ref. 22) has found the $5f$ main peak -0.86 eV below $E_F=0$ assigning Pd d character to all the other notable valence-band features. In semiconducting UO_2 the $5f$ emission is located at -1.36 eV and clearly separated from the O $2p$ emission. Thus, it could serve as a base line for all other $5f$ resonance studies. There is, however, some uncertainty[23,13] about a weak spectral feature around -9 eV. Though, in principle, it could be part of the O $2p$ band, Schneider and Laubschat[24] have recently suggested that it is a $5f$ satellite due to a two-hole-bound final state, whose existence they claim to be indicative of localized $5f$ electrons in uranium compounds.

The unifying characteristic in all the above compounds is the localized or quasilocalized nature of the $5f$ state, while the electronic properties scan the entire range from metallic (UPd_3), through semimetallic (USb,UTe), to semiconducting (UO_2). Future studies will examine itinerant $5f$ bands.

III. EXPERIMENTAL

Measurements were performed with a two-dimensional display-type spectrometer[25] using synchrotron radiation $60 \le h\nu \le 130$ eV at the Synchrotron Radiation Center of the University of Wisconsin-Madison. It combines an ellipsoidal reflection mirror low-pass filter with a retarding grid high-pass filter to achieve a band pass energy analyzer (energy resolution of 0.15 eV) and accepting a full 86° cone of emission angles. Data were obtained from single crystals of $U_xTh_{1-x}Sb$ ($x=0.0$, 0.34, and 1.0) and UTe of dimensions $\sim 3\times3\times5$ mm^3 which were cleaved along the (100) planes in a 1×10^{-10}-Torr vacuum. A single crystal of UO_2 could be cleaved and exhibited a (111)-(1×1) surface in low-energy electron diffraction. The UPd_3(0001) surface was cleaned by repeated cycles of 600 V Ne^+ ion bombardment and annealing at $\sim 700\,^\circ$C. Angle integrated energy distribution curves (EDC's) of photoelectrons were measured in a vacuum of 10^{-11} Torr in which a sample stayed clean for several hours as monitored by Auger spectroscopy and the oxygen $2p$ signal in photoemission.

IV. RESULTS AND DISCUSSION

A. $U_xTh_{1-x}Sb$ and UTe

In Fig. 1 we compare the photoelectron spectra from ThSb, $U_{0.34}Th_{0.66}Sb$, USb, and UTe recorded at two different photon energies, $h\nu=60$ and 92 eV. Looking first at the 60-eV spectra we observe, for all the compounds, a similar structure of the photoemission DOS. At the Fermi level E_F there is a narrow ($1-2$ eV wide) conduction band followed at higher binding energies by a several eV broad, fully occupied Sb- or Te-derived p valence band. There is, however, a clear distinction between the ThSb spectrum and the spectra from the uranium containing compounds. In ThSb the VB emission dominates the spectrum recorded at $h\nu=60$ eV, while for all the other compounds the main intensity originates from the CB features. This difference can be directly related to the presence of $5f$ electrons in the uranium compounds. The VB contains, in all cases, six electrons which correspond to a fully occupied p band. Starting with the antimonides, we note that the Sb atom has a $5p^3$ atomic configuration. Thus, there is a formal charge transfer of three electrons from the U (hexavalent) and Th (tetravalent) atoms to the Sb derived p bands. In UTe only two U electrons can enter the VB due to the $5p^4$ atomic configuration of tellurium. We have previously concluded[15,16] that the uranium atoms in the presently investigated compounds have a configuration close to $5f^3$. We can, therefore, connect the following approximate configurations to the various CB spectra. In ThSb the CB contains one $6d$ electron while in USb there are three $5f$ electrons. In the mixed $U_xTh_{1-x}Sb$ compounds the situation is intermediate between the pure cases. Finally, in UTe the CB configuration is essentially of the type $5f^36d^1$. It is immediately clear from the much higher CB intensity in the uranium compounds compared to the ThSb CB spectrum that at $h\nu=60$ eV the photoemission of the $5f$ electrons gives the dominant contribution to the spectrum. The $6d$ photoionization cross section is considerably smaller than that of the $5f$'s even after taking into account that there are three U $5f$ electrons in the pure uranium compounds, while there is only one Th $6d$ electron in the corresponding thorium compound.

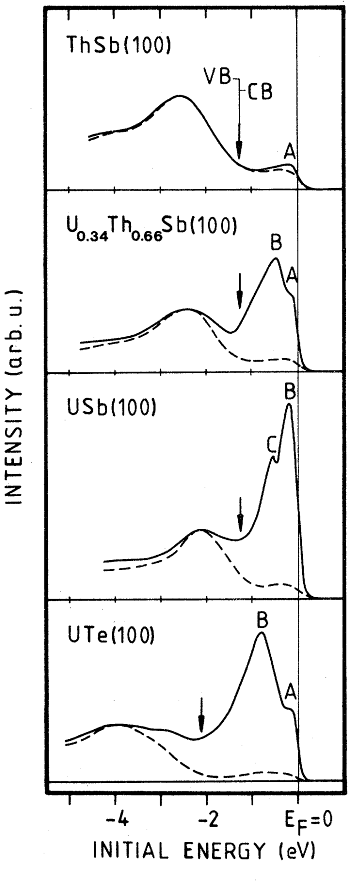

FIG. 1. Energy distribution curves for ThSb, $U_{0.34}Th_{0.66}Sb$, USb, and UTe at $h\nu=60$ eV (solid line) and $h\nu=92$ eV (dashed line). For each sample the curves are normalized to equal p valence-band heights. The arrows indicate the separation between the conduction (CB) and valence (VB) bands as used for the integrated CB and VB intensities to obtain the CIS curves in Figs. 2 and 3. Spectral features $A-C$ are discussed in the text.

Turning next to the 92-eV spectra in Fig. 1 we find that, for the uranium compounds, the spectral shapes are completely different from what was obtained using the lower photon energy. The CB intensities have decreased drastically and only a very weak, featureless CB structure can be seen. Only in ThSb is the same spectrum obtained at both excitation energies. If we further compare the 92-eV CB spectra from the different samples, we find that all the characteristic differences which were seen at $h\nu=60$ eV have disappeared. Since the observed differences at the lower photon energy were attributed to the U $5f$ electrons, this result shows that at $h\nu=92$ eV the $5f$ emission is almost vanishing.

We will now investigate this drastic photon energy dependence of the VB and CB photoemission intensities in a more quantitative way. In Fig. 2 we present constant-initial-state (CIS) spectra from the ThSb, USb, and UTe CB regions. These curves were obtained from EDC's (measured in 2 eV photon energy steps around the 5*d* core-hole thresholds and normalized to the incident photon flux) by integrating the intensity over the whole CB width. The energy positions which we have used to divide the CB and VB energy regions are shown by the arrows in Fig. 1. At first we consider the USb CB CIS curve in Fig. 2. Previously we have concluded[15] that the USb CB emission spectrum is dominated by the 5*f* electrons with the spectral features *B* and *C* being due to f^2 final-state multiplet levels.[27,28] From Fig. 2 we can thus make the following conclusions concerning the photon energy dependence of the U 5*f* photoionization cross section: Firstly, this cross section has a maximum at photon energies in the range 30–40 eV (not shown in Fig. 2). The 5*f* intensity then decreases gradually with increasing photon energy until for $h\nu=92$ eV a minimum is reached. This energy position corresponds to the U $5d_{5/2}$ core ionization threshold. Within the next 6 eV of photon energy, the intensity increases by a factor of about 70 and the 5*f* emission has a sharp maximum at $h\nu=98$ eV. At $h\nu=100$ eV a new but less pronounced minimum is found which is correlated with the position of the $5d_{3/2}$ threshold. At higher photon energies the 5*f* emission is again increasing. These results are in good qualitative agreement with previous results for USb by Baptist *et al.*[7] and for α-U by Iwan *et al.*[8]

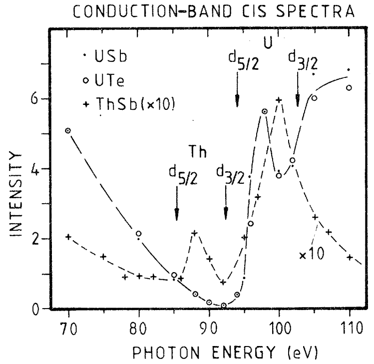

FIG. 2. Constant-initial-state (CIS) spectra for the conduction bands of USb, UTe, and ThSb (×10). The curves are obtained from integrated (up to the arrows in Fig. 1) EDC's which have been normalized to the incident photon flux. The normalization of the three CIS curves is done for USb and UTe to equal conduction-band intensity at $h\nu=98$ eV (dominant 5*f* emission) and for ThSb and USb to equal valence-band emission at $h\nu=92$ eV. Also shown are the Th and U 5*d* core absorption edges (from Ref. 26).

In Fig. 2 we also show the CB CIS spectrum of UTe. The USb and UTe curves have been normalized to each other by assuming that the intensities at $h\nu=98$ eV are the same. Although the CB configurations of these two compounds are different, we expect that at this resonance maximum both spectra are dominated by the emission from the uranium 5*f* 's (in both cases $5f^3$, see Ref. 16) and therefore that the two CB spectra, to a good approximation, are equally intense. The spectral feature *A* has been shown[15,16] to contain considerable 6*d* character and is less affected by the resonance (to be discussed below). With this normalization we note that the USb and UTe intensity variations fall on a common curve within our experimental accuracy. This similarity is consistent with our previous conclusion[16] that USb and UTe have the same $5f^3$ configuration.

The ThSb CB photoemission intensity also shows a photon energy dependence in the vicinity of the 5*d* core ionization thresholds. The shape of the CIS curve in Fig. 2 is, however, quite different from the USb and UTe curves. As in the uranium compounds, we find Fano resonance edges at the 5*d* ionization energies which for ThSb are at 85 and 92 eV.[26] The maxima are, however, much less pronounced and especially the feature following the $5d_{5/2}$ threshold is very weak. Comparing the U- and Th-derived CB CIS curves we find that at 92 eV both curves go through a minimum. This is caused by the coincidence of the U $5d_{5/2}$ and the Th $5d_{3/2}$ core ionization energies which are both close to 92 eV. For the different antimonides we have used the existence of this simultaneous minimum to normalize the resonance curves to each other via the intensities of the Sb-derived valence-band spectra. Since at 92 eV both the Th and U emission is at a minimum, any uranium or thorium contribution to the VB emission should be very small. At this photon energy we expect therefore the VB spectra to be entirely determined by the Sb 5*p* ionization cross section. Based on this assumption we have normalized all the antimonide spectra according to the integrated VB intensity at $h\nu=92$ eV.

As was demonstrated in Fig. 2 the U and Th emission each exhibit a very characteristic resonance behavior. We will now investigate what type of photon energy dependence is obtained for the solid solutions $U_xTh_{1-x}Sb$. In Fig. 3 we compare the USb and ThSb CB CIS spectra from Fig. 2 with the corresponding curve for $U_{0.34}Th_{0.66}Sb$. The normalization of the CIS curves relative to each other has been made via the VB intensities, as described above. The solid solution produces a curve which shows both the typical USb and ThSb resonance features. To further demonstrate this observation we have, in Fig. 3, included a CIS spectrum which is obtained as a linear combination of the USb and ThSb curves, according to the stoichiometric composition of the solid solution. As can be seen from Fig. 3 this curve follows the measured CIS spectrum very closely.

So far we have only investigated the photon energy dependence of the total integrated CB intensity and found that the Th and U resonance behavior contribute according to the stoichiometric composition of the solid solution. Is it further possible to detect different photon energy dependencies of different parts of the CB spectrum? The CB EDC of $U_{0.34}Th_{0.66}Sb$ reveals two spectral features (see Fig. 1), a shoulder *A* close to E_F and a peak *B* at -0.5 eV. One possible way to investigate whether these features have different orbital character, in terms of U 5*f* and Th 6*d* contributions, is to compare the EDC's recorded at two different photon energies. In Fig. 3 we note that a comparison of the spectra at 86 and 88 eV should have the potential to reveal if there are characteristic differences between the orbital compositions of peaks *A* and *B*. When the photon energy is tuned from $h\nu=86$ to 88 eV the U 5*f* emission decreases while at the same time the Th 6*d* emission becomes stronger. Looking at the relative photoionization cross sections, taking also into account the [U]/[Th] concentration ratio, we find that at $h\nu=86$ eV the U contribution is 4 times more intense than the Th contribution while at $h\nu=88$ eV the U and Th intensities are comparable. Since the difference in photon energy is only 2 eV we expect all other differences, i.e., changes in the electron loss functions, changes in the spectrometer transmission function, etc., to be of minor importance. In Fig. 4 we present the EDC's of $U_{0.34}Th_{0.66}Sb$ at these two photon energies. There are significant differences. Along with increasing U 5*f* emission intensity we find that peak *B* is enhanced while peak *A* becomes more pronounced as the Th 6*d* emission is emphasized. From this comparison we can thus conclude that peak *B* has to be associated with the main U 5*f* emission. It is also clear that the Th 6*d* character in the shoulder *A* is significant. These findings indicate that the 5*f* emission is below E_F and not pinned at E_F, favoring a localized description of the 5*f* electron states.

Next we will consider the resonance behavior of the VB features. A good measure of the total VB emission is more difficult to obtain than for the CB intensity. First of all the VB is much wider than the CB, which makes the result quite dependent on the background subtraction procedure. The background contribution is also considerably stronger in this part of the spectrum because of the CB loss intensity. As a further problem, the shape of the VB spectrum might also change as a func-

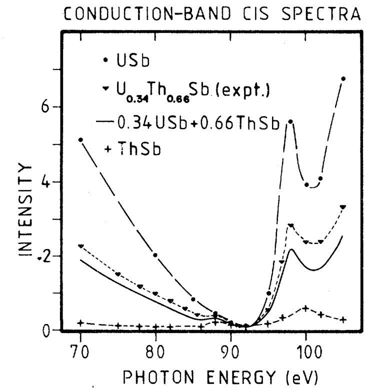

FIG. 3. CIS spectra for USb, $U_{0.34}Th_{0.66}Sb$, and ThSb as in Fig. 2. Also shown is a superposition of the USb and ThSb CIS curves multiplied by 0.66 and 0.34, respectively, which gives good agreement with the experimental CIS curve for $U_{0.34}Th_{0.66}Sb$.

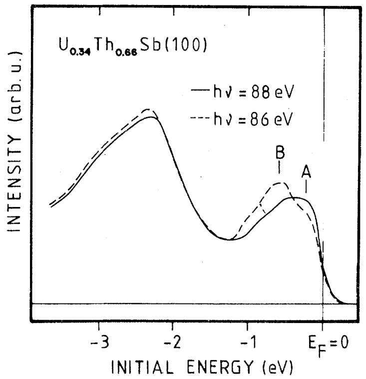

FIG. 4. EDC's for $U_{0.34}Th_{0.66}Sb$ for $h\nu=88$ and 86 eV normalized to the incident photon flux. The 88-eV spectrum shows stronger 6*d* emission (feature *A*), the 86-eV spectrum reveals more 5*f* character (feature *B*). See text also.

tion of photon energy, which makes accurate comparisons of the VB intensities for different photon energies difficult. These changes will be further discussed below. Because of these inherent problems we have not investigated the VB intensity variations in the same quantitative way as was done above for the CB. We will only point out a few observations. For ThSb the background is not as problematic as for the uranium compounds, since the CB intensity is relatively low. We find for the ThSb VB emission a photon energy dependence which is almost identical to the CB CIS curve shown in Fig. 2. The main difference is the remaining intensity at the resonance minima, which is much larger for the VB (see, e.g., the 92-eV spectra in Fig. 1). With respect to the amplitudes of the variations we find, in fact, that the Th resonance behavior is about twice as strong for the VB as for the CB. The orbital composition of the fully occupied VB could provide an explanation. The neutral Sb atom has a $5p^3$ configuration. If we use one electron as a reasonable charge transfer from the Th to the Sb sites we end up with essentially two VB electrons which still have Th d character. Since there is one Th electron in the CB, the Th character in the VB is about twice as large as in the CB, which is consistent with the observed stronger resonance behavior of the VB. In the uranium compounds the VB spectra also show a significant resonance behavior. In this case, however, the CB intensity variations are clearly dominant.

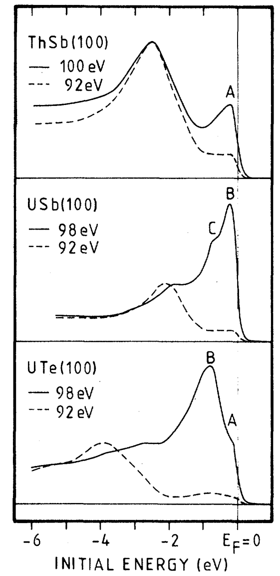

FIG. 5. EDC's for ThSb, USb, and UTe on- and off-resonance. The curves are normalized to equal p peak heights. Note the enhanced emission at $h\nu=98$ eV at the top of the valence bands in USb and UTe indicating a strong f-p hybridization.

Another aspect of the photon energy dependence of the VB spectra is demonstrated in Fig. 5. Here the spectra at the resonance minima (off-resonance) and maxima (on-resonance) of ThSb, USb, and UTe are compared. For each compound the intensities of the spectra have been normalized to equal heights of the VB maxima. We note a marked difference between the thorium and the uranium compounds. For ThSb there is no significant difference in the VB spectral shape between the spectra recorded at different photon energies. However, for the uranium compounds we note a considerable shift of the VB maximum towards E_F when the $5f$ resonance maximum is reached. For USb the shift is about 0.5 eV while for UTe it is as large as 1.5 eV. At 92 eV the U $5f$ emission is at a minimum so in these spectra the Sb $5p$ and Te $5p$ contributions will dominate the VB spectra. Therefore, from the 92-eV spectra we can locate the p-band peaks to 2.1 eV for USb and to 3.9 eV for UTe. At $h\nu=98$ eV, when the $5f$ emission dominates the spectrum, the main VB emission is instead found at an energy which corresponds to the top of the VB. We interpret these changes as due to a substantial f-p hybridization, as originally suggested by neutron scattering experiments[29] and supported by band-structure calculations.[30] (Note, however, that it is questionable if it is relevant to treat the ground state of the uranium pnictides and chalcogenides within a band picture.[15,16]) At $h\nu=98$ eV the $5f$ hybridized parts of the VB are very much enhanced. The change in the spectral shapes thus shows that it is only at the top of the VB that the $5f$ hybridization is of any importance. This interpretation of the shifts is given further support by the comparison with the ThSb spectrum. In this case, there are no $5f$ electrons involved and consequently no shift is observed. In the ThSb VB spectrum there is only an intensity variation of the whole VB structure along with the Th $6d$ cross-section variations. This indicates that the Th d contribution to the VB is evenly distributed over the whole VB.

B. UO_2 and UPd_3

It is quite established that the $5f$ electrons in semiconducting UO_2 and metallic UPd_3 are localized and have a $5f^2$ ground-state configuration (see Refs. 13 and 31). In Fig. 6 we present their VB spectra recorded at $h\nu=60$ and 80 eV, respectively. Semiconducting UO_2 exhibits no emission intensity at E_F, a dominant $5f$ emission peak at -1.37 eV, and oxygen-derived p emission with broad structures p_1 at ~ -4.8 eV and p_2 at ~ -7.0 eV. All emission features agree very well with recent XPS studies by Baer and Schoenes.[23] The only exception is p_3 which we find at -10.3 eV while Baer and Schoenes locate it at -9.4 eV. The origin of p_3 is unclear.[13,23] Though it could originate from a p valence-band structure, Schneider and Laubschat[24] have recently suggested that it represents a $5f$ satellite due to a two-hole final state. Similar $5f$ and/or $4f$ satellites have been observed in XPS spectra of several other uranium compounds[14,23,24,32] at 7 ± 1 eV below the f main line. Schneider and Laubschat have shown that the occurrence of this satellite is an indication for $5f$ localization and a weakening of the f-d (and f-p) hybridization. If our p_3 feature represented a $5f$ satellite we would expect it to show a resonance behavior correlated to the $5f$ resonance, in analogy with the 6-eV satellite in Ni[2] or the 2-eV satellite in α-U.[8]

An initial-state $5f^2$ configuration leads to a $5f^1$ final state in photoemission with two spin-orbit components ($^2F_{5/2}$ and $^2F_{3/2}$) split by 0.9 eV (Ref. 33) and an intensity ratio of 6:1 (Ref. 28) in Russel-Saunders coupling. Such a double structure is not seen in the $5f$ emission spectrum of UO_2 in Fig. 6, due in part to the large width of the $5f$ peak. This width is too large to be due to lifetime effects alone [compare, e.g., with the $5f$ widths found in UTe (Ref. 16)], so we conclude that vibrational effects play a major role in this compound. Another possible reason[23] that we cannot resolve the $5f$ spin-orbit components is that only in the $\vec{L}$-$\vec{S}$ limit does one expect a 6:1 intensity ratio. In the pure $\vec{j}$-$\vec{j}$ limit the intensity ratio is instead 37:1.[28]

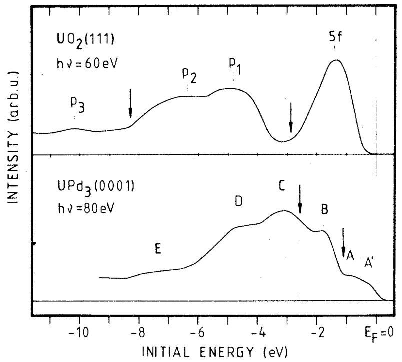

FIG. 6. EDC's for UO_2 at $h\nu=60$ eV and UPd_3 at 80 eV. The curves are not normalized. Similar as in Fig. 1 the arrows distinguish different spectral features for the integrated intensities to obtain the CIS curves in Fig. 7.

For UPd_3 we observe in Fig. 6 several emission features which we have labeled $A-D$ according to the notation of Baer *et al.*[14] Their XPS peak positions agree very well with our values. Peaks A' and E have not been observed in XPS (partly due to limited resolution), but are readily visible in angle-resolved photoemission for $h\nu\leq41$ eV.[34] By comparing the XPS spectra of UPd_3 and $ThPd_3$ it was concluded[14] that peak A contained all the occupied $5f$ DOS, while $B-D$ probably represented palladium-derived d states. The fact that A was found at -0.9 eV and not at E_F confirmed the localized $5f$ character in UPd_3, as originally derived from inelastic neutron scattering experiments.[31]

As described above (cf. Sec. IV A) for $U_xTh_{1-x}Sb$ and UTe we have obtained CIS spectra for distinct emission features in UO_2 and UPd_3 by integrating the intensity within the arrows in Fig. 6. EDC's have been measured in 2-eV steps and have been normalized to the incident photon flux. The CIS spectra for the UO_2 $5f$ emission and the spectral features A and B of UPd_3 are shown in Fig. 7. Again we recognize the typical $5f$ Fano resonance profile with two intensity minima at $h\nu=92$ and 102 eV due to the $5d_{5/2}$ and $5d_{3/2}$ core absorption edges. The UO_2 $5f$ CIS spectra shows the strongest intensity variation which is consistent with its pure f character.[13] The UPd_3 CIS curves A and B also show strong intensity variations. The less pronounced minima as compared to UO_2 reflect the amount of Pd or U d character and/or background intensity. This is also the reason for the generally higher intensity of curve B as compared to A in Fig. 7. Otherwise curves A and B are very similar and, in fact, should not be distinguished at all. They both contain the $5f$ electron emission and the earlier spectral assignment A or B of Ref. 14 is most probably governed by the underlying Pd d emission features, since they are also observed in rare-earth Pd_3 compounds.[35] This conclusion is emphasized in Fig. 8 where EDC's at $h\nu=92$ eV (off-resonance) and 98 eV (on-resonance) are compared. The UO_2 spectra have been normalized to equal p_1 peak heights, the UPd_3 spectra to equal heights of peak C which is

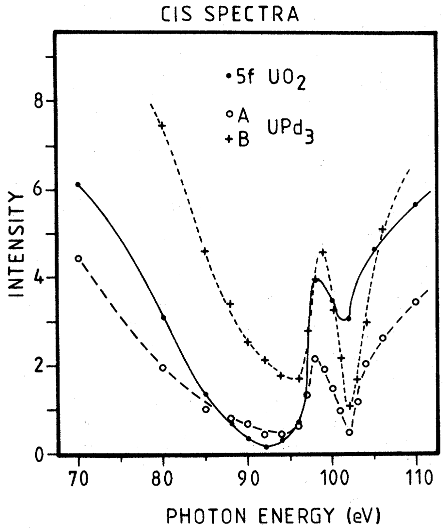

FIG. 7. CIS spectra for the UO_2 5*f* emission and the spectral features $A + A'$ and *B* of UPd_3. The higher intensity of *B* as compared with *A* is due to a higher amount of Pd *d* emission in *B*.

believed to be pure Pd 3*d* emission.[14] At $h\nu = 92$ eV the 5*f* emission in UO_2 vanishes almost completely, while in UPd_3 features *A* and *B* are still clearly visible proving considerable residual *d* character. A difference curve of the 98- and 92-eV EDC's reveals a broad emission peak with a maximum at -1.2 eV. We believe that this broad peak (encompassing the spectral features *A'*, *A*, and *B*) represents the emission from the localized $5f^2$ ground state. Again, we do not resolve a f^1 final-state splitting[28] in UPd_3 due to the large width of the 5*f* emission. In addition, there are two inequivalent uranium sites[36] in the double-hexagonal structure of UPd_3, which could smear out sharp features. Angle resolved photoemission[34] shows small but measurable band dispersion $E(\vec{k})$ for all emission features except peak *A*. No dispersion is expected for localized levels. The observed little dispersion might arise from the underlying Pd *d* emission. Features $C - E$ all exhibit[34] a stronger $E(\vec{k})$ dispersion and a very small Fano resonance behavior (not shown here). Peak *E* is most likely due to *s,p* hybridized parts of the Pd *d* bands, since it is not observed in XPS (Ref. 14) where the *s,p* photo-cross-section is very low.

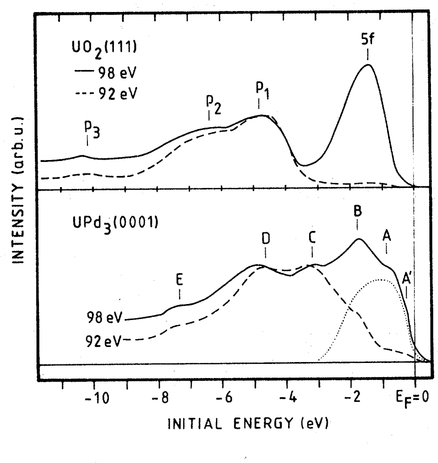

FIG. 8. EDC's for UO_2 and UPd_3 on- and off-resonance. The curves are normalized to equal p_1 and *C* peak heights, respectively. In UO_2 the 5*f* emission vanishes nearly completely at $h\nu = 92$ eV while the features p_1, p_2, and p_3 are still visible. In UPd_3 all peaks $A - E$ remain to be seen in the 92-eV spectrum. A difference spectrum shows the pure 5*f* contribution (dotted line).

For UO_2 the CIS spectrum of p_1 and p_2 exhibits very little resonance behavior (not shown). In contrast to USb or UTe (see Fig. 5) we observe in Fig. 8 hardly any *f*-*p* hybridization, i.e., any enhancement of emission states in the gap or near the top of the *p* valence band as discussed in Sec. IV A above. However, Gubanov *et al.*[37] have calculated that 0.6 *f* electrons contribute to the oxygen 2*p* band. In view of our findings it means that these 0.6 *f* electrons are distributed uniformly over the whole *p* band and cannot be detected out of ~ 12 *p* electrons per formula unit.

Finally, we note that the resonance of the p_3 feature is also very weak and can be understood by the change of the loss intensity due to the resonating 5*f* emission. The fact that it appears at a different initial energy as in XPS suggests that in our photon energy range $h\nu < 130$ eV p_3 most likely reflects a valence-band *p* feature, while in XPS ($h\nu \simeq 1.4$ keV) it could be superimposed by the 7-eV satellite.[24] It is not clear why a satellite should be too weak to be discernible in our photon energy range but show up in XPS. One reason could be a change from the adiabatic to the sudden regime as observed in photoemission from zinc.[38]

V. SUMMARY

We have studied the photon energy dependence of the valence electron photoemission (CIS spectra) for several uranium and thorium compounds; USb, ThSb, mixed $U_{0.34}Th_{0.66}Sb$, UTe, UO_2, and UPd_3. For all these compounds a strong Fano-type resonance behavior is observed at the 5*d*-core level thresholds. A comparison between the ThSb and USb resonance curves shows that the amplitude of the U 5*f* intensity variations (per 5*f* electrons) in the photon energy range 70 – 150 eV is at least a factor of 3 stronger than the variations of the Th 6*d* intensity. The U 5*f* and Th 6*d* emission show unique resonance curves. For the mixed $U_{0.34}Th_{0.66}Sb$ system a photon energy dependence of the integrated CB intensity is found, which is a weighted average of the curves for the pure uranium and thorium compounds. The characteristic Th and U resonance behavior also enables a delineation of the U 5*f* and Th 6*d* emission in the mixed compounds. In $U_{0.34}Th_{0.66}Sb$ the main 5*f* emission is found 0.5 eV below the Fermi level, indicating a localized *f* character. It is also shown that the PDOS contains significant 6*d* character at the Fermi level. Comparing USb and UTe we find identical CB CIS curves for the two compounds, which implies that they have a common $5f^3$ configuration. For each sample the CIS spectra of the anion derived *p*-band features show a similar $h\nu$ dependence as the U- and Th-derived conduction-band peaks, though a closer investigation of the photon energy dependence of the VB structures reveals significant differences between the various compounds. In ThSb we find that the VB shape is independent of photon energy. However, in the uranium compounds the main VB peak is shifted towards E_F as the 5*f* emission is enhanced. This demonstrates a considerable *f*-*p* hybridization in the topmost part of the valence band.

For UO_2 and UPd_3 we find a similar 5*f* resonance behavior with a 5*f* emission peak in UPd_3, which has an energetic position and half-width as in UO_2 in agreement with the localized $5f^2$ ground-state configuration in both of these compounds. Structures in the EDC's of UPd_3 are mainly Pd *d* derived. In UO_2 there is no evidence for a *f*-*p* hybridization in the oxygen-derived part of the valence band.

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