

**5*f*-band width and resonant photoemission of uranium intermetallic compounds**

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New experimental results and theoretical arguments are used in conjunction with previously published data to demonstrate that resonant photoemission (RPS) does not provide a reliable measure of the occupied 5*f* density of states in uranium intermetallic compounds. We implicate a resonant Auger process in this phenomenon and argue that RPS measurements (in conjunction with x-ray photoemission spectroscopy data) in this context are more useful as a qualitative guide to U 5*f*-ligand hybridization.

The unique thermodynamic and transport properties of so-called "heavy-fermion" systems<sup>1</sup> have directed widespread attention to a number of uranium-bearing intermetallic compounds: UBe<sub>13</sub>, UPt<sub>3</sub>, UAl<sub>2</sub>, UCu<sub>5</sub>, etc. Most theoretical analyses of these materials intimately involve the 5*f*-electron spectral density—either as input or output.<sup>2</sup> As a result, experiments designed to measure this quantity have been plentiful.<sup>3-7</sup> All these measurements utilize electron spectroscopy.<sup>8</sup> One can probe the occupied states below the Fermi level with either x-ray (XPS) or ultraviolet (UPS) photoelectron spectroscopy, both of which provide the spectra of these states weighted by their respective cross sections. However, to measure the 5*f* part of the spectral weight, most experiments to date employ resonant photoemission spectroscopy (RPS),<sup>8,9</sup> whereby electron emission from valence levels is greatly enhanced as the photon energy sweeps through the threshold of a near core level (5*d* in this case). These measurements are predicated upon the belief<sup>10</sup> that photoemission in this context preferentially ejects 5*f* electrons and hence reveals the 5*f* partial density of states. The purpose of this Rapid Communication is to point out that resonant photoemission does *not* image the occupied 5*f* density of states in numerous uranium intermetallic compounds although (in conjunction with XPS) it can be a useful tool to estimate the amount of ligand hybridization in these materials.

Our analysis of resonant photoemission in uranium intermetallic compounds is based on new experimental results (for UB<sub>4</sub> and USi<sub>3</sub>), measurements already present in the literature, and theoretical estimates of the relative decay rate of the photoabsorption intermediate state to various photoemission final states. A survey of the data reveals that, for a given system, the occupied 5*f*-band width extracted from an RPS experiment systematically exceeds the value obtained from high-resolution XPS measurements. The latter often provides a good measure of the 5*f* spectral density because the cross section for direct photoemission from 5*f* states in uranium is greater (by at least an order of magnitude) than the cross section from most other valence states at x-ray photon energies.<sup>11</sup>

By contrast, we argue that a resonant Auger decay mode can (almost uniquely in light actinides) broaden the RPS signal to a width almost twice that of the 5*f* density of states.

The samples of UB<sub>4</sub> and USi<sub>3</sub> were made by melting the constituents in an inductively heated levitation crucible under an Ar atmosphere and were found to be homogeneous single-phase specimens by x-ray diffraction and metallography. The XPS measurements are identical to those of an earlier report.<sup>12,13</sup> The new RPS data for UB<sub>4</sub> and USi<sub>3</sub> were recorded using synchrotron radiation from the BESSY (Berlin) and National Synchrotron Light Source (Brookhaven) storage rings, respectively. Figure 1(a) shows the measured spectra of UB<sub>4</sub> at photon energies  $h\nu = 102, 110, \text{ and } 1486.6 \text{ eV}$ . The RPS spectra correspond to off and on resonance as determined from the total absorption curves around the 5*d* threshold.<sup>14</sup> The corresponding spectra for USi<sub>3</sub> are shown in Fig. 1(b).

We take the full widths at half maximum of the experimental XPS spectra (1.3 eV for both UB<sub>4</sub> and USi<sub>3</sub>) as indicative of the true width of the occupied portion of the 5*f* spectral density in these materials. Such measurements presumably expose all intrinsic *f*-*f* correlation effects—which may be considerable. By contrast, the RPS spectra at  $h\nu = 110 \text{ eV}$  are considerably broader than the curves obtained at x-ray photon energies. In order to isolate the 5*f* component, it is conventional<sup>4-7</sup> to subtract the off-resonance spectrum from the on-resonance spectrum. These are labeled "difference" in Fig. 1. The widths of the difference spectra are 2.4 eV (UB<sub>4</sub>) and 2.1 eV (USi<sub>3</sub>). Clearly, these values still are much larger than the width observed at  $h\nu = 1486.6 \text{ eV}$ . It is evident that the RPS curves cannot be representative of the 5*f* density of states; the spectra cannot exhibit a width greater than that revealed by x-ray photons which (at worst) represents a mixture of 5*f* states with other valence states.

The anomalous broadening of resonant photoemission spectra compared to XPS spectra for UB<sub>4</sub> and USi<sub>3</sub> is not confined to these particular materials. It is, in fact, a quite general phenomenon for many uranium intermetal-

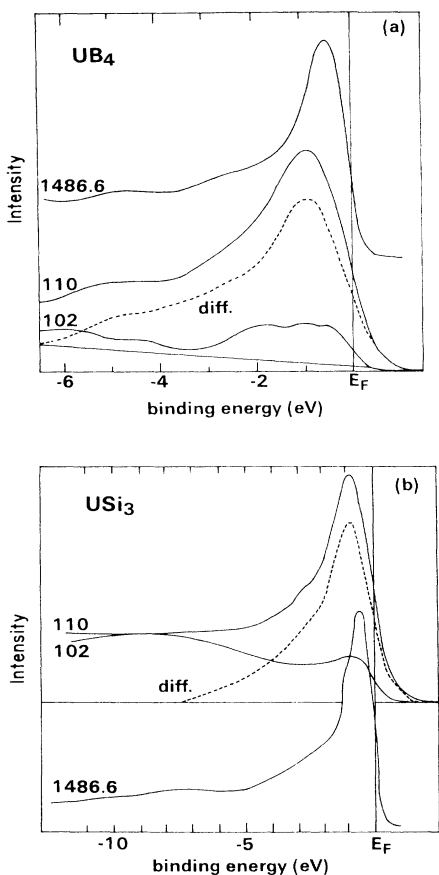


FIG. 1. Photoelectron spectra of (a)  $UB_4$  and (b)  $USi_3$  at photon energies  $h\nu = 1486.6$  (XPS), 110.0 (on-resonance), and 102.0 eV (off-resonance). The difference spectra between the on- and off-resonance spectra are also shown (dashed curve) in each case.

lic compounds. This can be seen from a compilation of spectral widths at different photon energies taken from the recent literature (Table I). Notice that the widths at high (1486.6) and low (40–60 eV) photon energies are comparable for  $\alpha$ -U,  $UBe_{13}$ ,  $USi_3$ , and  $UB_4$ , while the on-resonance widths are much greater. The discrepancy disappears for  $UGl_3$ ,  $UAl_2$ ,  $UIn_3$ , and  $USn_3$ . The results in Table I reveal two systematics. First, if one qualitatively orders the compounds in Table I according to the extent of hybridization between U 5f states and ligand states,<sup>20</sup> the systems with greater hybridization exhibit greater spectral broadening. Second, greater broadening occurs for resonant excitation at the  $5d_{3/2}$  threshold (110 eV) than at the  $5d_{5/2}$  threshold (98 eV).

Our problem is to discover a *differential* broadening mechanism, i.e., one which operates at RPS photon energies but not at XPS photon energies. Since we cannot account for the observed widths merely by adding the resonant contribution<sup>9</sup> from overlapping 6d states, we propose instead an explanation based on an analysis of the resonant photoemission process. We presume (as usual) that the initial excitation step is quasiatomic: a 5d electron makes an optical transition from the ground state

TABLE I. Full width at half maximum (eV) of the valence-band spectra of uranium and its intermetallic compounds as determined by photoelectron spectroscopy at different incident photon energies. The photon energies (eV) are indicated in parentheses.

Compound	XPS (1486.6)	On resonance	Below resonance
$U$ -metal	1.1 <sup>a</sup>	1.9 (99) <sup>b</sup> 2.1 (108) <sup>b</sup>	1.1 (60) <sup>b</sup>
$UBe_{13}$	1.3 <sup>c</sup>	2.1 (98) <sup>d,e</sup> 2.3 (109) <sup>f,e</sup>	1.5 (40) <sup>g</sup>
$USi_3$	1.3	2.3 (110)	1.5 (40) <sup>h</sup>
$UGe_3$	1.9 <sup>h</sup>	1.9 (98) <sup>h</sup>	1.5 (50) <sup>h</sup>
$UB_4$	1.3	2.5 (110)	
$UAl_2$	1.3 <sup>h</sup>	1.1 (98) <sup>i,j</sup>	
$UIn_3$	1.9 <sup>h</sup>	1.6 (98) <sup>k</sup>	
$USn_3$	1.9 <sup>h</sup>	1.6 (98) <sup>k</sup>	

<sup>a</sup>Reference 15.

<sup>b</sup>Reference 16.

<sup>c</sup>Reference 3.

<sup>d</sup>Reference 4.

<sup>e</sup>These widths correspond to the difference spectra between the photon energy shown in the bracket and 92-eV excitation energy.

<sup>f</sup>Reference 5.

<sup>g</sup>Reference 17.

<sup>h</sup>Reference 18.

<sup>i</sup>Reference 6.

<sup>j</sup>Width of the background subtracted spectrum.

<sup>k</sup>Reference 19.

( $5d^{10}5f^36d^26s$ ) into a virtual bound state (“5f”) in the continuum (one of the terms of the  $5d^95f^46d^26s$  multiplet) trapped near the atom by an angular momentum barrier.<sup>21</sup> This intermediate state decays to one of a number of different final ionic states. The three channels most relevant to the present discussion are shown in Fig. 2. These are (a) direct 5d photoemission which can be viewed as a tunneling of the excited “5f” state into the  $\epsilon_f$  continuum, (b) resonant 5f photoemission wherein a super-Coster-Kronig (SCK) Auger transition fills the 5d hole and ejects a 5f electron from the valence band, and (c) resonant Auger decay<sup>22–25</sup> wherein a “5f”  $\rightarrow E_F$  transition accompanies a SCK Auger event which fills the 5d hole from the 5f band.

The key observation is that the line shape of the resonant Auger signal is given by a self-convolution of the 5f band if the intra-atomic Coulomb interaction  $U_{vv}$  is not too large. This produces a signal near  $E_F$  which is considerably broader than the spectral weight of the 5f band; for  $\alpha$ -U metal this procedure leads to a broad peak with a full width at half maximum of 3 eV. Moreover, the “5f”  $\rightarrow E_F$  transition guarantees that this feature appears in the observed spectrum at constant binding energy<sup>26</sup> rather than constant kinetic energy as in the case of a conventional Auger process. Consequently, the experimentally observed broadening can result if the resonant Auger decay channel steals sufficient strength from the “usual”

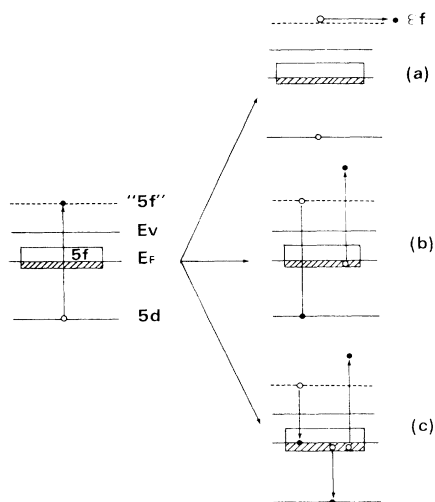


FIG. 2. Schematic representation of different decay channels of intermediate excited state ( $5d^9 5f^4$ ) following the resonant absorption ( $5d \rightarrow 5f$ ): (a) direct  $5d$  emission, (b) autoionization leading to resonant photoemission from  $5f$ , and (c) resonant Auger decay.

decay modes [Figs. 2(a) and 2(b)]. In the following, we argue that this is indeed the case for uranium-bearing materials—and almost uniquely so.

The resonant Auger process envisioned above will reproduce the experimental results only for a particular ordering of the important energies in the problem. The “ $5f$ ”  $\rightarrow E_F$  transition is an essential ingredient. For this to occur, there must exist a non-negligible  $5d$ - $5f$  direct Coulomb interaction  $U_{cv}$ .<sup>26</sup> On the other hand, there must be substantial oscillator strength into the initial  $5d \rightarrow “5f”$  transition well above the Fermi level. This means that we require the  $5d$ - $5f$  exchange interaction  $U_{ex}$  to exceed  $U_{cv}$ .<sup>21</sup> In practice, this is no problem since metals always screen the direct interaction more efficiently than the exchange interaction.<sup>27</sup> However,  $U_{cv}$  also must be comparable to (or exceed) the  $5f$  band width  $W$  to ensure that “ $5f$ ” actually has quasiatomic character and that a resonant optical transition occurs in the first place. Finally, as noted above, the intraband Coulomb interaction  $U_{vv}$  must be small enough so that a bandlike Auger line shape obtains. Putting all this together, the required sequence is  $U_{ex} > U_{cv} > W > U_{vv}$ .

Table II demonstrates that an Auger process can cloak the valence band in an RPS experiment only for a very restricted range of materials. For lanthanides,  $U_{vv} \gg W$  and the spectrum is essentially atomiclike.<sup>9</sup> In nickel metal,  $U_{vv}$  is comparable to  $W$ , but still large enough to split the resonant Auger satellite 6 eV below the valence band.<sup>31</sup> The ratio  $U_{vv}/W$  is well below unity for all the other transition metals, but  $d$ -band screening generally drives  $U_{cv} < W$ .<sup>33</sup> Hence, one is left with only the early actinides and their intermetallic compounds. Of course, this does not prove that the process in Fig. 2(c) actually occurs in these systems to any significant degree. Unfortunately, the relevant rate calculations are extremely difficult to perform in the condensed state. Nonetheless, we can build a strong circumstantial case using intuitive argu-

TABLE II. Estimates of various energies (eV) relevant to the discussion of resonant Auger emission. See text.

	$U_{vv}$	$W$	$U_{cv}$	$U_{ex}$
Light actinides	2.5 <sup>a,b</sup>	3 <sup>c</sup>	5.5 <sup>d</sup>	10 <sup>e</sup>
Rare-earth metals	5 <sup>a</sup>	0.1 <sup>a</sup>	10 <sup>f</sup>	10 <sup>e</sup>
Light $3d$ transition metals	1 <sup>g</sup>	5 <sup>g</sup>	3 <sup>h</sup>	10 <sup>e</sup>

<sup>a</sup>Reference 28.

<sup>b</sup>Reference 12.

<sup>c</sup>Estimated from many XPS and BIS spectra.

<sup>d</sup>Reference 29.

<sup>e</sup>Atomic theoretical estimate.

<sup>f</sup>Reference 30.

<sup>g</sup>Reference 31.

<sup>h</sup>Reference 32.

ments and quantitative atomic calculations.

We have performed relativistic time-dependent local-density-approximation (RTDLDA) calculations<sup>34</sup> for the relative photoemission cross sections corresponding to processes (a) and (b) of Fig. 2 for a uranium atom near the  $5d$  threshold. These results (which do not include the resonant Auger channel) reveal that  $\sigma_a(\omega)/\sigma_b(\omega) \sim 5$ . Moreover, the Auger matrix element in channel (b) and the excited “ $5f$ ”  $\rightarrow 5f(E_F)$  transition amplitude is similar to the  $5f \rightarrow \epsilon f$  amplitude in channel (a). Thus, even though it is a higher-order process, resonant Auger decay (c) will be comparable in strength to direct resonant photoemission (b) even if only 20% of channel (a) is transferred to the Auger channel. As indicated earlier, there are two factors which promote this transfer for the case of uranium intermetallic compounds. First, the relatively large value of  $U_{cv}$  enhances the effective  $5f$  density of states at  $E_F$ .<sup>26</sup> Second, any hybridization with delocalized ligand orbitals increases the efficiency of overlap-driven transfer of the localized “ $5f$ ” orbital to a delocalized  $5f$  band state. This last observation accounts for the correlation noted in Table I and explains the fact that the magnetic (e.g.,  $UIn_3$ ) and near-magnetic (e.g.,  $USn_3$  and  $UAl_2$ ) compounds do not exhibit any broadening of their spectral features in RPS as compared to that in XPS excitation.

In summary, this Communication presents new experimental data to show that resonant photoemission does not image the occupied  $5f$  density of states in uranium intermetallic compounds. We marshal experimental results and theoretical arguments to show that a resonant Auger process obscures the valence band in UPS measurements of these materials. This conclusion seriously questions the conventional practice of extracting  $5f$  spectral weight from resonant photoemission spectroscopy of these compounds. RPS remains useful (when employed in conjunction with XPS) as a qualitative indicator of ligand hybridization.

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