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Evidence for 6*d* valence states in α-U, UGa_2, and UGa_3 as revealed by resonant photoemission

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We have studied α-uranium, UGa_2, and UGa_3 with resonant photoemission. In agreement with Iwan, Koch, and Himpsel, we find for α-U a 2-eV photoemission feature in the off-resonance spectrum at $h\nu=94$ eV, which they have interpreted as a 5*f* shake-up satellite. In contrast, we show that this feature can be related to valence states of U because of (i) its sensitivity to O_2 exposure and (ii) its occurrence in UGa_2 and UGa_3 at ~ 1.4 eV, suggesting 6*d* valence-band emission as its origin.

Resonant photoemission has become increasingly the technique to identify and locate the *f*-derived photoemission features within the valence bands of rare-earth (RE) and actinide (*A*) systems.[1–8] It is particularly useful in cases where the *f* electrons are energetically degenerate or even hybridized with non-*f* electrons, e.g., the RE- or *A*-derived *d* electrons or, e.g, the transition-metal valence electrons in intermetallic compounds. However, since resonant photoemission is based on Fano-type interference effects[9] between direct photoionization of valence electrons and photoexcitation of a deep-core hole, the recent realization of the importance of screening effects[7,10–12] in normal photoemission from light-RE systems implies screening effects should be particularly important in resonant photoemission owing to the deep-core hole.

At present there exists no theoretical treatment of the $5d \rightarrow 5f$ resonance behavior and its various decay channels, which includes screening, except for uranium.[13] By analogy[14] with the $p \rightarrow d$ resonance of itinerant *d* states in Ni and the resonant enhancement of the Ni 6-eV valence-band satellite[15] which reflects localized excitations into different final-state multiplets, Johansson *et al.*[13] predicted a similar localized excitation channel for α-U producing a 2-eV shake-up satellite of the 5*f* itinerant valence states. Iwan, Koch, and Himpsel[4] actually observed a 2-eV photoemission feature emerging in the off-resonance spectra of the $5d \rightarrow 5f$ resonance, and ascribed it to the shake-up satellite predicted. It is the purpose of this paper to show that this 2-eV feature is not a satellite, but can be interpreted as photoemission from U-derived 6*d* valence states.

The occurrence of shake-up satellites is an indication that, owing to electronic correlation effects, the itinerant systems under investigation are close to the localized regime, at least in the final state probed by photoemission as, e.g., in Ni (Refs. 14 and 15) or Ce systems (Refs. 10–12). Hence, if the interpretation of the 2-eV feature as a satellite holds, it will imply that the 5*f* electrons in α-U are on the border line between itinerant and localized behavior. However, several facts and observations are at variance with "near-to-localized" 5*f* electrons in uranium.

(i) Band-structure calculations[16] describe U as a prototype *f*-band metal with a hybridized 5*f*, 6*d* valence band, cut by the Fermi level E_F, which agrees quite well with photoemission results at photon energies far above[17] or below[18] the resonance energies.

(ii) Effective electron masses owing to itinerant 5*f* electrons have been found in α-U by de Haas–van Alphen measurements.[19]

(iii) A possible valence-band satellite was not observed in resonant photoemission of itinerant 5*f*-electron systems with a larger U-U spacing than in α-U, e.g., UN,[20] UIr_3,[21] UNi_5,[22] and UBe_{13},[8] which are thus closer to the localized regime. Nor do clearly localized 5*f* compounds, e.g., USb, UTe, and UO_2,[5] exhibit such a satellite.

(iv) The analogy with Ni,[14] which led to the satellite interpretation,[4,13] is rather limited: First, increasing the Ni-Ni spacing in NiO (Ref. 23) or UNi_5 (Ref. 22) still allows the observation of the Ni satellite and its resonant enhancement at the $3p \rightarrow 3d$ resonance[22,23] as in Ni metal[15] in contrast to the U case [see (iii) above]. Second, the 6-eV satellite in Ni is also observed with x-ray photoemission spectroscopy [XPS, $h\nu=1486$ eV (Ref. 24)] while a 2-eV feature cannot be discerned in the high-resolution XPS spectrum of α-U.[17]

(v) The resonance behavior of the 2-eV feature in α-U, i.e., its intensity-versus-$h\nu$ curve, is rather unexpected, namely, the maxima (minima) of the 2-eV curve exactly coincide with the minima (maxima) in the resonance behavior of the main 5*f* valence-band emission.[4] Such a case does not exist in the theoretical treatment of resonance behaviors of main and satellite features,[25] which, however, gives good agreement for the Ni case.[23,25]

All arguments (i)—(v) cast strong doubts onto the interpretation of the 2-eV feature in α-U as a shake-up satellite. Furthermore, since several uranium oxides exhibit a chemically shifted 5*f* photoemission peak around 2 eV,[5,26] we decided to repeat the experiments on α-U as well as on UGa_2 for which a 7-eV valence-band satellite had been reported and also been taken as an indication for localized 5*f*-electron behavior.[27]

The resonant photoemission experiments were performed using synchrotron radiation 40 eV$\leq h\nu \leq$600 eV from the Berlin 775-MeV storage ring of the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY) in conjunction with the SX700 monochromator. Photoemission spectra were taken with a cylindrical-mirror analyzer with an overall resolution (electrons and photons) at $h\nu=100$ eV of $\Delta E \simeq 0.5$ eV. Polycrystalline samples of α-U, UGa_2, and UGa_3 characterized by x-ray diffraction to be single phase were filed in a vacuum of 1×10^{-10} Torr with a diamond file, until a minimum of the bulk-dissolved O-derived 2*p* signal around 6 eV was reached.

Photoemission energy-distribution curves of α-U taken near the off-resonance photon energy $h\nu=94$ eV are presented in Fig. 1. In contrast to our own expectation, the cleaner the uranium surface became, the more pronounced was the 2-eV feature [shaded in Figs. 1(a)—1(c)]. In Figs. 1(a) and 1(b), we compare our cleanest result with the finding of Iwan, Koch, and Himpsel[4] which confirms the 2-eV feature as an intrinsic property in the photoemission spectra of α-U near off-resonance. Absolutely opposite, exposure of the U surface to small amounts of oxygen reduces the spectral intensity of the 2-eV feature [see $\frac{1}{4}$ L O_2 exposure in Fig. 1(c); 1 L=1 langmuir $=10^{-6}$ Torr sec] while the O 2*p* intensity around 6 eV has markedly increased. The corresponding on-resonance spectrum in Fig. 2 shows that $\frac{1}{4}$ L O_2 does not yet produce the chemically shifted 5*f* emission peak (also at 2 eV), as higher exposures of O_2 clearly do. After the intrinsic 2-eV feature has disappeared at about $\frac{1}{2}$ L O_2 the spectral intensity again increases owing to oxide formation, as the corresponding on-resonance spectra monitor, which enhance the 5*f* emission only. Finally, at 100 L O_2, a UO_2 surface layer has been formed[26] as can be inferred from the filed UO_2 single-crystal spectrum in Fig. 1(g), and the corresponding on-resonance curve in Fig. 2.

The fact that the 2-eV feature is affected by the chemical processes happening during oxidation of the U surface [Figs. 1(a)—1(c)] suggests that it may be related to valence states of uranium, and is not a shake-up satellite. Furthermore, we believe that it reflects photoemission from

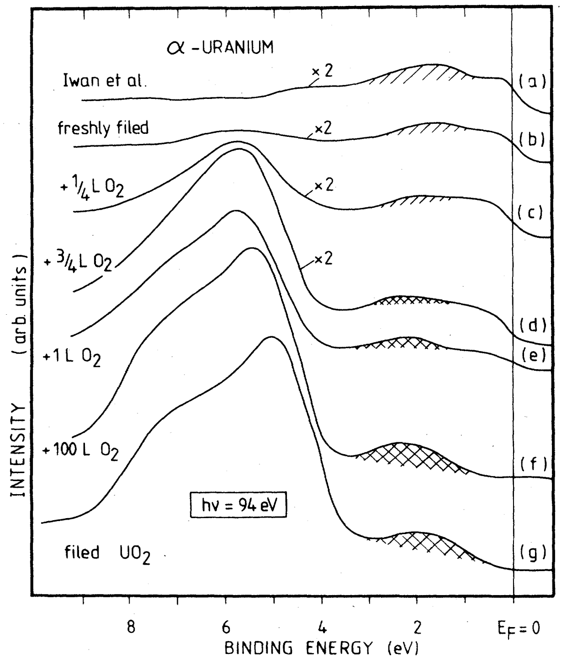

FIG. 1. Photoemission energy distribution curves taken near off-resonance at $h\nu=94$ eV of (a) (from Ref. 4) and (b) clean uranium, (c)—(f) as a function of oxygen exposure, and (g) solid UO_2. The shaded area in (a)—(c) denotes the 2-eV feature, the cross-hatched area in (d)—(g) denotes the oxygen-induced 5*f* emission. The apparent shift in the O 2*p* emission around 6 eV is caused by different oxide formation as a function of O coverage (see Ref. 26).

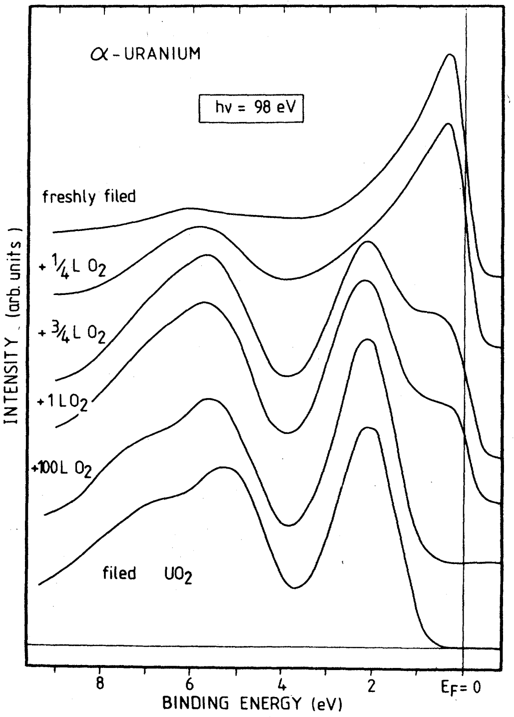

FIG. 2. Corresponding on-resonance ($h\nu=98$ eV) spectra to Fig. 1. Note the simultaneous existence of 5*f* valence-band emission near E_F and oxygen-induced 5*f* emission at 2 eV for $\frac{3}{4}$ L and 1 L oxygen exposure.

U-derived $6d$ valence-band states, because of the following.

(a) $6d$ electrons are involved in the covalent bonding of U with oxygen. So are the $7s$ electrons, but their photoemission cross section is too small at $h\nu \sim 100$ eV as compared to $6d$ electrons.[28]

(b) The $5d \rightarrow 6d$ resonance is much weaker than the $5d \rightarrow 5f$ resonance[5] because of different main quantum numbers.[9] This leaves the $6d$ emission almost unaffected, and explains quite naturally the observed[4] unusual relative resonance behaviors of the $5f$ main emission and the 2-eV feature [see (v) above]: The $6d$ emission (which corresponds to the 2-eV feature) is present for all $h\nu$, but only when the $5f$ emission disappears at off-resonance, does the 2-eV intensity appear to grow out of the background produced by the secondary-electron loss of the $5f$ peak. Apparently, the 2-eV intensity has its maximum when the $5f$ emission is completely quenched, and vice versa.

(c) Hence, the $6d$ emission is masked by the energetically degenerate emission from $5f$ states which have a bigger cross section for $h\nu > 60$ eV (Ref. 28) and contain ~ 3 times more electrons. This explains the absence of a $6d$ feature in the XPS spectrum[17] [see (iv) above].

(d) At low excitation energies ($h\nu < 30$ eV) the cross section is smaller for the $5f$ electrons than for the $6d$ electrons. In fact, $6d$ emission in α-U has been identified at 2 eV using a photon energy $h\nu = 21.2$ eV.[18]

Finally, in Fig. 3 we discuss two U alloys: UGa_2 with the hexagonal AlB_2 structure (U-U distance of 4.21 Å) and UGa_3 with the cubic Cu_3Au structure (U-U distance of 4.25 Å). We were motivated by the reported existence of a 7-eV valence-band satellite in UGa_2 (Ref. 27) which in view of our new interpretation of the 2-eV feature in U (see above) became rather doubtful, since at the same time other itinerant U alloys with bigger U-U spacings than in UGa_2 gave no indication of the 7-eV satellite, i.e., UIr_3,[21] UNi_5,[22] and UBe_{13}.[8] Our new measurements with excitation energies up to $h\nu = 600$ eV do in fact show [cf. Figs. 3(b) and 3(c)] that there is no evidence for a satellite around 7 eV in UGa_2 and UGa_3. Any spectral intensity in this energy region is caused by the residual bulk-dissolved O $2p$ signal. The 7-eV $4f$ core-level satellite,[27] however, was confirmed for both alloys (not shown).

The on-resonance spectra in Fig. 3 reveal the narrowing of the $5f$, $6d$ valence-band emission owing to the decreasing U-U wave-function overlap with increasing U-U spacing in going from α-U to UGa_2 and UGa_3. This band narrowing causes a shift of the $6d$ emission maximum towards E_F as shown by the off-resonance curves in Fig. 3. We take the shift of this feature from 2 eV in α-U to 1.4 eV in UGa_2 and UGa_3 as another indication of its $6d$ valence-state character. Its existence in UGa_2 and UGa_3 also shows that it is not a surface-related feature as its sensitivity to oxygen exposure might suggest (see Fig. 1), because for the UGa_2 and UGa_3 compounds we could not observe the same quenching of the 2-eV intensity as for α-U. In conclusion, we suggest that U $6d$ valence states are the origin of the off-resonance photoemission features at 2 eV in α-U, and at 1.4 eV in UGa_2 and UGa_3.

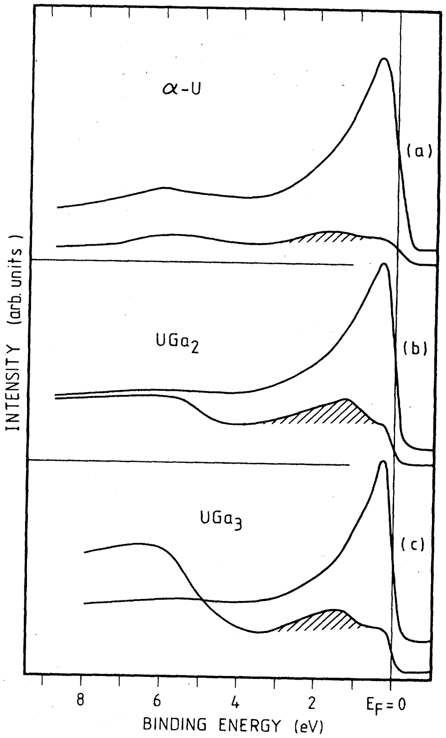

FIG. 3. Comparative photoemission energy distribution curves taken at on-resonance (upper curves, $h\nu = 98$ eV) and off-resonance [lower curves, (a) $h\nu = 94$ eV; (b), (c) $h\nu = 92$ eV] photon energies for (a) α-uranium, (b) UGa_2 (off-resonance curve times 7), and (c) UGa_3 (off-resonance curve times 12). The shaded area denotes the $6d$ valence-band emission.

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