Resonant 5*f* valence-band satellite at the 5*d* threshold in uranium metal

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Photoelectron energy distribution curves for polycrystalline α-uranium show a giant Fano-type resonance for the intensity of the 5*f* valence-band features at the Fermi energy E_F, when the photon energy is tuned through the 5*d* core absorption edge at around $h\nu \approx 94$ to 103 eV. Further, a sharp (full width at half maximum = 2.2 eV) 5*f* satellite excitation at an initial energy $E_i = -2.3$ eV below E_F has been observed, which has a close analogy to the "6 eV satellite" in Ni. This shakeup satellite shows also a strong resonant enhancement (≥ 6 times) at the 5*d* core-level threshold, but a distinctly different cross-section dependence. The origin of the resonances of the 5*f* main line and the 2.3-eV satellite is discussed in an atomic framework taking 5*f* and 6*d* screening into account.

I. INTRODUCTION

As a prototype actinide metal, uranium has been the subject of many studies in order to elucidate its electronic structure (see, e.g., Refs. 1–5 and references therein). On the theoretical side, most of the efforts have up to now been directed towards the valence-band electronic structure[2–5] and the existence of a valence-band satellite has been considered.[1] On the experimental side, optical,[6] photoelectron-emission,[7–12] and bremsstrahlung isochromat spectroscopy[9] have been employed to study the valence bands and inner-shell electronic structure. Despite this extensive work, until recently there has been no agreement about basic concepts such as the occupancy of the 5*f* level and its itinerant character (see, e.g., Ref. 1).

In the present paper we present and discuss results from photoemission experiments using synchrotron radiation in the photon energy range from 20 to 130 eV. In particular, we have observed for the first time a distinct valence-band satellite peak at an initial energy − 2.3 eV below the Fermi energy E_F which shows a pronounced resonance effect when the photon energy is close to the 5*d* core-level binding energies ($h\nu = 94.2$ and 102.8 eV). We discuss the origin of this resonance satellite, which has a close analogy to the "6-eV satellite" in Ni and the satellite structure observed recently in other 3*d* metals (e.g., Refs. 13–15) in a simplified atomic framework taking solid-state screening effects into account. Our discussion of the satellite follows ideas put forward by Johansson *et al.*,[1] who suggested that the valence-band spectrum of uranium might contain satellites originating from excitations to localized 5*f*-electron configurations and discussed different kinds of core-hole screening for the actinide metals. Similar concepts have been used by Sham and Wendin[16] for the interpretation of the x-ray photoelectron (XPS) 5*p* spectrum of Th metal. For the 5*f* main band close to E_F we observe a resonance behavior and cross-section dependence, which closely follows the total-absorption cross section in the 5*d* core-absorption range.

II. EXPERIMENT

The experiments were performed with a two-dimensional display-type spectrometer[17] combined with a toroidal-grating monochromator using synchrotron radiation from the storage ring Tantalus I in Stoughton, Wisc. The count rates were about

10^5/s for the uranium $5f$ bands with an overall resolution of 0.3 eV.

As sample a thin uranium foil was used. It was mechanically polished to a mirror finish. In an UHV preparation chamber with a base pressure of 5×10^{-11} Torr, the sample was sputter-annealed by Ar^+ bombardment and direct heating for more than 24 h. The cleanliness was checked by Auger and photoelectron spectroscopy. After repeating the cleaning procedures several times it was possible to suppress the main surface contaminants C, O, and S below 2% of a monolayer.

In Fig. 1 the photoelectron energy distribution curve (EDC) for the valence-band region excited with photons of $h\nu = 60$ eV is displayed. It shows the dominant $5f$ peak at the Fermi energy E_F. Despite the high surface sensitivity for these photon energies this spectrum closely resembles published XPS data for "clean" samples (e.g., Refs. 7 and 9). For U we have determined a work function of $e\Phi = 3.2 \pm 0.2$ eV.

III. RESULTS

In Fig. 2 angle-integrated photoelectron spectra of uranium are shown at photon energies around the $5d$ one-electron excitation threshold [$5d_{5/2}$ at $h\nu = 94.2$ eV and $5d_{3/2}$ at $h\nu = 102.8$ eV (Ref. 7)]. The spectra are normalized to the incident photon flux. For photon energies corresponding to the one-electron $5d_{5/2}$ threshold ($h\nu \simeq 92-94$ eV) the $5f$ valence-band feature at the Fermi edge is strongly suppressed to nearly zero intensity. Beyond threshold the $5f$ intensity at E_F is resonantly enhanced with a cross-section dependence which closely follows the shape of the total absorption coefficient (see Fig. 3 and Refs. 6 and 18). A similar cross-section dependence has been reported for the $5f$ levels of uranium in USb.[19]

In addition to the $5f$ resonance at E_F a new structure is observed in the EDC's 2.3 eV below E_F which shows a resonance enhancement right at the one-electron $5d$ threshold. This is clearly seen in the EDC for $h\nu = 94$ eV (Fig. 2). The weaker structures around 6 and 10 eV initial energy E_i are probably due to contamination as suggested by Verbist *et al.*[10] These features can be detected at the $5d$ threshold because the $5f$ intensity is suppressed by more than a factor of 30 while the $2p$ cross section of probable contaminants carbon, sulfur, or oxygen, is rather constant in that photon energy region. At present, we cannot rule out completely the

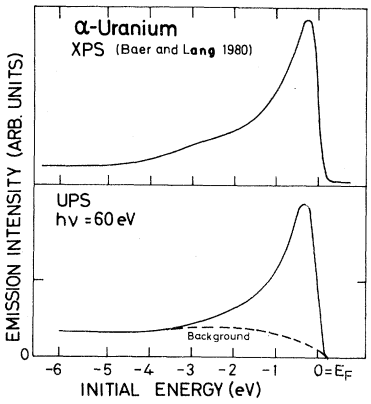

FIG. 1. Comparison of a photoelectron energy distribution curve of polycrystalline uranium at $h\nu = 60$ eV with the XPS spectrum reported by Baer and Lang (Ref. 9). Although the surface sensitivity is high at $h\nu = 60$ eV the 60-eV spectrum does not show a detectable contribution due to contamination.

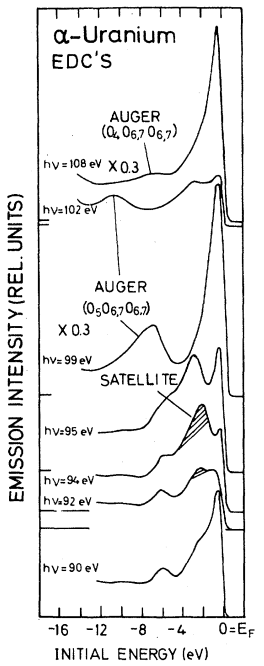

FIG. 2. Angle-integrated photoelectron energy distribution curves for uranium in the region of the giant $5d \rightarrow 5f$ resonance (90 eV $\leq h\nu \leq$ 108 eV). The $5f$ intensity at E_F is suppressed by more than a factor of 30 at the $5d_{5/2}$ threshold (see the spectra for $h\nu = 92$ and 94 eV) and resonantly enhanced above threshold (see, e.g., the spectrum for $h\nu = 99$ eV). At an initial energy 2.3 eV below E_F a new satellite structure is observed which is resonantly enhanced at the $5d_{5/2}$ and $5d_{3/2}$ onsets. At threshold the satellite coincides with the Auger electron spectrum, which moves to apparently larger initial energies with increasing photon energy.

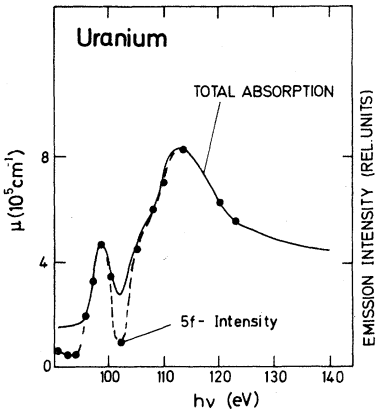

FIG. 3. Partial cross section (dots) of the uranium $5f$ valence band (area under the EDC's between E_F and $E_i = -2$ eV with a smooth background subtracted as shown in Fig. 1). The solid line gives the total absorption cross section of uranium (Refs. 6 and 17). The partial cross-section data have been normalized to the absorption cross section at $h\nu = 100$ eV.

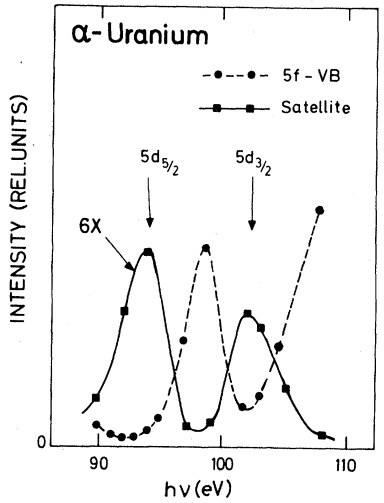

FIG. 4. Partial cross section of the 2.3-eV satellite (squares) compared to the partial cross section of the $5f$ main line at E_F (dots). The separation of the main line and the satellite is indicated in Fig. 5. The 2.3-eV satellite intensity shows maxima at the $5d$ one-electron thresholds indicated by the arrows (Ref. 7) [i.e., at $h\nu = E_i(5d) - E_F$], where the $5f$ valence-band intensity is suppressed.

existence of further valence-band satellites at these initial energies. We note, however, that these structures do not show a resonant enhancement at the $5d$ threshold.

The 2.3-eV peak is an intrinsic feature of uranium metal and not due to an oxygen-induced chemical shift of the $5f$ level. Such a chemical shift would be of the order of ≈ 2 eV.[7] There are three arguments in favor of the intrinsic nature of the 2.3-eV peak in uranium:

(i) A possible oxygen $2p$ contribution in the EDC's was not observed. It would result in a broad (≈ 4 eV) band centered at $E_i \approx -6$ eV in the EDC's.[10]

(ii) For oxidized uranium we have found an oxygen-induced $5f$ band ≈ 2 eV below E_F with a width (full width at half maximum) of ≈ 1.2 eV, while the new resonant structure at $E_i = -2.3$ eV has a width of 2.2 eV.

(iii) The oxygen-induced $5f$ peak shows the same resonance behavior as the uranium-metal $5f$ peak at E_F while the satellite structure at $E_i = -2.3$ eV has its intensity maxima where the $5f$ intensity is nearly zero (Fig. 4).

IV. DISCUSSION

The resonance behavior of the feature 2.3 eV below E_F is similar to that observed for the resonant two-hole bound states of the $3d$-metals Ni, Cu, and Zn.[13–15] In analogy we interpret this feature as a quasi-bound-state which is highly localized.[20–22]

The question arises whether this shakeup satellite structure is also excited off-resonance as for instance the 6 eV peak in Ni, or whether it is hidden because of its weakness by the one-hole valence band structure. Recent XPS measurements[9] show evidence for the existence of the shakeup satellite off-resonance.

Next we consider the resonance behavior of the $5f$ maximum at E_F and of the 2.3-eV satellite. Despite the itinerant character of the $5f$ electrons in uranium[9] we discuss the valence-band spectra in an atomic framework. This seems to be a good approximation for highly correlated metals for the explanation of valence-band features in the presence of a photoexcited hole.[23–25] We assume, neglecting other inner shells, a $5d^{10}5f^n(6d\ 7s)^{6-n}$ ground-state configuration. Johansson *et al.*[1] have determined $n = 2.5$ as the approximate $5f$ occupation number. Thus $5f$ valence-band photoemission can be described by the following expression:

$$5d^{10}5f^n(6d\ 7s)^{6-n} + h\nu \rightarrow 5d^{10}5f^{n-1}(6d\ 7s)^{6-n} + e^- \quad . \quad (1)$$

Metallic screening mechanisms[25–27] in correlated metals with empty nl levels lead to a modification of Eq. (1). The screening charge in the presence of a hole has highly localized character and can be treated as an atomiclike screening orbital. In urani-

um, empty $5f$ and $6d$ levels are available for screening, resulting in two different screening mechanisms. This situation is similar to the case of the rare-earth metals.[27]

For uranium the main screening will be performed by a $5f$ electron.[1] In the presence of a hole at a given site the empty $5f$ levels are pulled below E_F and can be filled by $5f$ electrons from the neighbors. That implies that the quasiparticle, consisting of a $5f$ hole plus a $5f$ screening electron, is hopping from site to site with a long lifetime at a particular site compared to the photoemission process (see, e.g., Ref. 20). Then Eq. (1) is modified in the following way:

$$5d^{10}5f^{n-1}(6d\ 7s)^{6-n} \xrightarrow{\text{screening}} 5d^{10}(5f^{n-1}5f)(6d\ 7s)^{6-n}. \quad (2)$$

$(5f^{n-1}5f)$ describes the quasiparticle configuration (hole plus screening electron) and has to some extent atomic character. It is different from the itinerant ground state $5f^n$. According to our interpretation the final-state configuration in Eq. (2) describes the main $5f$ line at E_F (Fig. 1) (see also the discussion in Refs. 1, 16, and 25).

The competing screening mechanism is $6d$ screening; i.e., the $5f$ hole is dressed by a localized $6d$-screening electron:

$$5d^{10}5f^{n-1}(6d\ 7s)^{6-n} \xrightarrow{\text{screening}} 5d^{10}(5f^{n-1}6d)(6d\ 7s)^{6-n}. \quad (3)$$

$(5f^{n-1}6d)$ denotes the $5f$ hole dressed with a $6d$ screening electron while the $5f$ screening orbital is left empty. The final-state configuration in Eq. (3) represents the satellite 2.3 eV below E_F.

Next we consider the resonant photoemission at the $5d$ one-electron threshold. At threshold direct excitation into the empty $5f$ screening orbitals is possible:

$$5d^{10}5f^n(6d\ 7s)^{6-n} + h\nu \rightarrow 5d^9 5f^{n+1}(6d\ 7s)^{6-n}. \quad (4)$$

This direct excitation into the $5f$ orbital implies that the $5f$ screening orbital is filled and only $6d$ screening is active. We exclude further $5f$ screening since, due to the effective Coulomb interaction other empty $5f$ levels are kept above E_F. This $6d$ screening mechanism [Eq. (4)] and the Super-Coster-Kronig (SCK) decay of the $5d$ hole ($5d\,5f\,5f$,$O_{4,5}O_{6,7}O_{6,7}$) leads to the following final state:

$$5d^{10}(5f^{n-1}6d)(6d\ 7s)^{6-n} + \text{Auger electron}. \quad (5)$$

When compared to Eq. (3), Eq. (5) explains the resonant enhancement of the $(5f^{n-1}6d)$ satellite structure, which is located 2.3 eV below E_F.

According to this interpretation of the valence-band spectra of uranium, one should also expect shakeup satellites in the core-level spectra similar to the case of Ni.[28] We note, however, that in the presence of a core hole the $5f$ electrons become highly localized leading to a multiplet splitting in the final state which, e.g., exceeds that for the $3d^9$ configuration in Ni core spectra. Thus the satellite intensity can be spread out over a manifold of final ^{2S+1}L states, preventing a clear identification of a core satellite.

Further interesting information regarding the screening mechanisms can be obtained from an analysis of the photon-excited Auger-electron emission. In an Auger process the following final states can be reached if we consider $5f$ or $6d$ screening:

$$5d^{10}5f^n(6d\ 7s)^{6-n} + h\nu \rightarrow 5d^9 5f^n(6d\ 7s)^{6-n} + e^-$$

$$\underset{\text{(Auger)}}{\xrightarrow{\text{SCK}}} 5d^{10}5f^{n-2}(6d\ 7s)^{6-n} + 2e^- \xrightarrow{\text{screening}}$$

$$\xrightarrow{5f} 5d^{10}(5f^{n-2}5f)(6d\ 7s)^{6-n} + 2e^- \quad (6a)$$

$$\xrightarrow{6d} 5d^{10}(5f^{n-2}6d)(6d\ 7s)^{6-n} + 2e^- \quad . \quad (6b)$$

Equation (6a) resembles a local $5f^{n-1}$ configuration, which will show almost the same multiplet splitting and hence the same line shape as the final state for the 2.3-eV satellite [Eq. (3)] assuming that the spatial extent of the $6d$ orbital in the $(5f^{n-1}6d)$ configuration prevents the $6d$ electron from coupling to the $5f$ multiplet.

In order to check these ideas we can compare the line shape of the resonant satellite to the line shape of the Auger peak. First we have determined the line shape of the satellite (Fig. 5) by comparing EDC's at resonance (94 eV) and far off-resonance (60 eV). The spectra are normalized at the $5f$ peak at E_F. The difference curve is shown in Fig. 5(b). Subtraction of a smooth background due to scattered electrons results in the satellite line shape [Fig. 5(c)]. Tentatively we have assumed two different curves representing the background (curves *a* and *b*). We argue that only curve *a* in panel 5(c) represents the satellite, since only this structure exhibits a resonant enhancement at the $5d$ threshold.

Next we compare the lineshape of the satellite with the line shape of the Auger-electron spectrum ($O_5O_{6,7}O_{6,7}$) [panel (d) in Fig. 5]. Owing to the large spin-orbit splitting of the $5d$ shell we observe for photon energies $h\nu \leq 102$ eV only the $O_5O_{6,7}O_{6,7}$ Auger spectrum (see also Fig. 2) not obliterated by the $O_4O_{6,7}O_{6,7}$ spectrum. The Auger spectrum is considerably broader and asymmetric

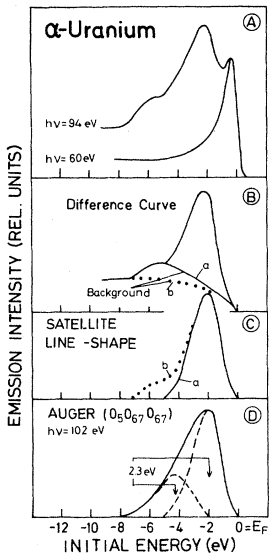

FIG. 5. Determination of the line shape of the 2.3-eV satellite derived from the difference EDC obtained from an EDC at resonance ($h\nu = 94$ eV) and off-resonance ($h\nu = 60$ eV) [panel (a)]. From the difference curve smooth background curves due to scattered electrons have been subtracted in order to obtain the line shape [panel (b)]. In panel (c) two different satellite line shapes are shown according to different assumptions for the background [curves *a* and *b* in panel (b)]. The resonance behavior suggests that curve *a* in panel (c) is the true contribution from the 2.3-eV shakeup satellite. In panel (d) the line shape of the optically excited Auger spectrum ($O_5O_{6,7}O_{6,7}$ at $h\nu = 102$ eV) is shown, which can be decomposed into two symmetric peaks separated by 2.3 eV.

compared to the satellite line shape [curve *a* panel (c)]. This observation lends strong support to our discussion of the screening mechanisms since we interpret the Auger spectrum according to Eqs. (6a) and (6b) as a superposition of two differently screened Auger bands with a screening-induced separation of ≈ 2.3 eV [dashed curves in panel (d), Fig. 5]. As shown in Fig. 5, panel (d), a screening-induced separation of approximately 2.3 eV results, close to the energy difference of the $5f$ valence band and satellite. This seems to be an accidental coincidence, since we expect a stronger screening for the two-hole Auger state compared to the satellite. We note that a different background subtraction for the satellite resulting in curve *b* in panel 5(c) does also not result in the line shape of the Auger peak as one might have expected on first glance.

Finally we turn to the discussion of the resonance behavior of the $5f$ valence-band feature at E_F (Fig. 3). We have already noted above that the partial cross section for this valence-band feature closely follows the absorption cross section[6,18] (Fig. 3). The giant resonance of the $5f$ levels above the $5d$ one-electron threshold at $h\nu = 99$ and 117 eV is due to $5d \rightarrow 5f$ transitions and is directly comparable to the giant $4d \rightarrow 4f$ resonance in the rare-earth metals (e.g., Refs. 29 and 30 and the theoretical treatment in Ref. 31). The different resonance behavior of the $5f$ valence-band one-hole final state compared to the shakeup satellite may be due to different matrix elements and different thresholds for the final-state multiplets. Additionally, $5f \leftrightarrow \epsilon f$ interaction far above threshold has to be taken into account[32]: $5d \rightarrow \epsilon f$ excitations far above threshold lead to resonance effects if the outgoing ϵf wave function matches the $5f$ wave function quite well at the site of excitation.

In summary, we have observed a resonant valence-band shakeup satellite at initial energies -2.3 eV below E_F in the EDC's of uranium at the $5d$ threshold which is similar to the satellite observed for $3d$ transition metals.[13–15,23]

This satellite can be well understood in an atomic picture taking $5f$ and $6d$ screening into account. We have compared the line shape of the $5f$ satellite with the line shape of the corresponding $O_5O_{6,7}O_{6,7}$ Auger spectrum having a similar final-state configuration.

The differences in the line shapes are attributed to different screening mechanisms for the primary electron excited into an $5f$ empty level (satellite at threshold) or to a continuum state above threshold (Auger peak). We have also observed a giant resonance behavior of the $5f$ main band at initial energies close to E_F. The partial cross section for this band closely follows the total absorption cross section in the range of the $5d$ absorption.

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