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Actinide—noble-metal systems: An x-ray-photoelectron-spectroscopy study of thorium-platinum, uranium-platinum, and uranium-gold intermetallics

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A systematic study of the valence bands and selected core levels of polycrystalline samples of the intermetallic compounds ThPt, $ThPt_2$, $ThPt_3$, UPt, UPt_2, UPt_3, UPt_5, UAu_3, and U_2Au_3 has been performed by x-ray-photoelectron spectroscopy using Al $K\alpha$ radiation. The $5f$-electron states are found to be pinned to the Fermi energy in all uranium compounds suggesting a band description for these states. From the measured binding energies together with experimentally determined work functions a charge transfer from Th and U to the noble metals is concluded to take place. The highly asymmetric line shape of the U $4f$ core level is discussed and is found to be due to the high density of occupied and empty states near the Fermi energy. In the uranium-gold system the presence of a Kotani-Toyozawa satellite indicates the onset of a more localized $5f$-electron behavior. Magnetization measurements give support to the itinerant nature of the $5f$ electrons in the uranium-platinum compounds.

I. INTRODUCTION

The electronic structure of the light actinides is characterized by strongly hybridized $5f$ and $6d$ electrons.[1] Recent bremsstrahlung isochromat spectroscopic (BIS) studies performed by Baer and Lang[2] on α-uranium metal showed the existence of an unoccupied $5f$ band above the Fermi energy in agreement with the theoretical predictions of Freeman *et al.*[3]

Actinide atoms in intermetallic compounds are generally further apart than in the pure metals. Thus overlap between $5f$ wave functions on neighboring actinide atoms is reduced and the $6d$-$5f$ bandwidth can be smaller than that associated with the pure metals. Hill's[4] correlation between the occurrence of magnetic ordering and the interatomic spacing lends further support for a more localized behavior of the $5f$ electrons in the compounds.

Experiments on intermetallic compounds with transition elements are of interest for two reasons. First, the degree of $5f$-electron localization can be studied as a function of the interatomic actinide spacing. Second, changes in the electronic structure of the d bands of the transition metals can be examined.

Uranium and thorium form stable diatomic molecules with platinum metals which is an indication for the existence of covalent bonds. X-ray-photoelectron spectroscopy (XPS) measurements on UPt and ThPt (Ref. 5) suggested a covalent mixing of the d bands in agreement with the theoretical considerations of Gingerich and Gupta.[6]

In general uranium compounds show a larger crystal volume than is expected from a mechanical mixture of their component atoms.[7] This behavior is in contrast to thorium compounds and $3d$ compounds indicating the influence of the uranium's $5f$ electrons. The interatomic spacing is large in the uranium—transition-metal compounds, allowing a placing in the "magnetic" region of the Hill plot.

Especially the uranium—$5d$-transition-metal compounds show low-temperature magnetic ordering and high-temperature paramagnetic behavior. The compound UPt was found to be a weak ferromagnet below 30 K with a magnetic moment of about $0.2\mu_B$/atom which vanishes under pressure.[8] This behavior was interpreted in terms of itinerant ferromagnetism. Recent photoemission spectra of the valence band of UPt (Ref. 5) gave further support to the itinerant nature of the $5f$ electrons. In order to extend systematically the investigation on $5f$ and $5d$ (transition-metal) behavior as a function of the interatomic U—U spacing and the number of d electrons of the transition metal, respectively, we report here on magnetization and photoemission experiments on polycrystalline samples of the compounds ThPt, $ThPt_2$, $ThPt_3$, UPt, UPt_2, UPt_3, UPt_5, UAu_3, and U_2Au_3.

II. EXPERIMENTAL DETAILS

All samples were prepared by arc melting of high-purity constituents under reduced argon atmosphere. The uranium-platinum and the thorium-platinum compounds are formed in a strong exothermic reaction. This behavior is in contrast to the uranium-gold compounds where several remelt processes were necessary to stabilize the compounds. All samples had the color of platinum metal and were harder than their constituents. The compound UPt_3 showed hexagonal crystallites on the sample surface. The uranium-platinum and thorium-platinum kept their metallic appearance in air whereas the uranium-gold samples became dark colored in a few minutes indicating their sensitivity to oxygen.

The U-Pt, Th-Pt, and U-Au samples were annealed for one week in sealed Mo crucibles at temperatures of 1000 and 800 °C, respectively. X-ray-diffraction measurements indicated the correct phases for the known compounds. The relevant structure parameters are given in Table I. The magnetization measurements were performed in a sample vibrating magnetometer between 2.5 and 210 K.

The XPS measurements were carried out in a vacuum generator ESCA III photoelectron spectrometer having an inherent resolution of 1.1 eV mainly due to the Al $K\alpha$ linewidth. The samples were mechanically cleaned in the sample preparation chamber under UHV conditions (10^{-9} Torr) and then introduced into the spectrometer (4×10^{-10} Torr). The work functions of the samples have been determined by the onset of the secondary emitted electrons on the low-kinetic-energy side of the photoelectron spectra. In this way contact potential differences of the samples relative to the spectrometer are measured. For further details see Ref. 9.

We note the extreme sensitivity of the uranium-gold sample as compared to the uranium-platinum samples with respect to the oxidation. From the measured O 1s intensities during identical measuring intervals we deduced a factor of 10 higher oxidation rate of the uranium-gold samples as compared to the U-Pt system indicating weaker bonding between the noble metal and uranium. As an example the oxidation effect on the U 4f core levels in UAu_3 is shown in Fig. 1. We add that at liquid-nitrogen temperature

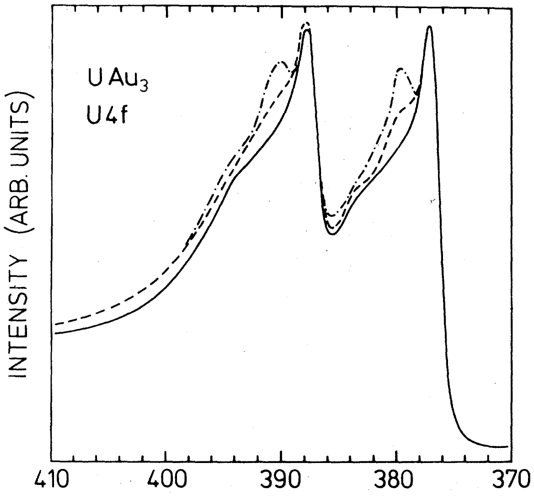

FIG. 1. Experimental XPS spectra of the U 4f core-level region in the compound UAu_3 excited with Al $K\alpha$ radiation. The influence of oxide contamination is indicated. The dashed-dotted line represents measuring intervals of 6 min, the dashed line of 4 min, and the full curve of 2 min, respectively. After each interval the sample was transferred back to the preparation chamber, scraped again and then repositioned in the spectrometer.

TABLE I. Crystal structures, lattice parameters, and mean atomic volumes of uranium-platinum compounds and their constituents.

	Crystal structure	$V(\text{Å})^3$	$V_{\text{theor}}\ (\text{Å})^3$	U–U (Å)	U–Pt (Å)	Pt–Pt (Å)
α-U	orthorhombic	20.75	20.75	2a 2.75	. . .	. . .
				4a 2.85		
UPt	orthorhombic	22.10	17.91	4a 3.61	2a 2.86	2a 2.53
(ThPt)	CrB		(23.92)	(2a 3.66)		
UPt_2	orthorhombic	18.61	16.96	4a 3.81	1a 2.81	4a 2.75
				2a 4.12	2a 2.84	2a 2.80
	$InNi_2$				4a 2.99	
UPt_3	hexagonal	17.62	16.48	2a 4.12	6a 2.88	4a 2.88
	$MgCd_3$			2a 4.89	6a 2.96	4a 2.96
UPt_5	cubic	17.03	16.01	12a 5.25	12a 3.08	6a 2.62
	$AuBe_5$				4a 3.21	12a 3.08
Pt	cubic	15.06	15.06	. . .	. . .	12a 2.77
	fcc					

the oxidation rate is reduced to a value comparable to that of the U-Pt compounds.

III. RESULTS AND DISCUSSION

A. Valence-band spectra

The experimental results for the uranium- and thorium-platinum compounds and their constituents are shown in Figs. 2 and 3. The spectra of the pure metals are in good agreement with the literature.[10,11] Thorium compounds provide a measure for the non-f electronic density of states because in Th metal the $5f$ states are not occupied. By comparing the spectra of Th metal with U metal the favorable $5f/6d$ photoionization cross-section ratio becomes apparent. The two sets of spectra differ only by extra structure in the uranium-platinum spectra near the Fermi ener-

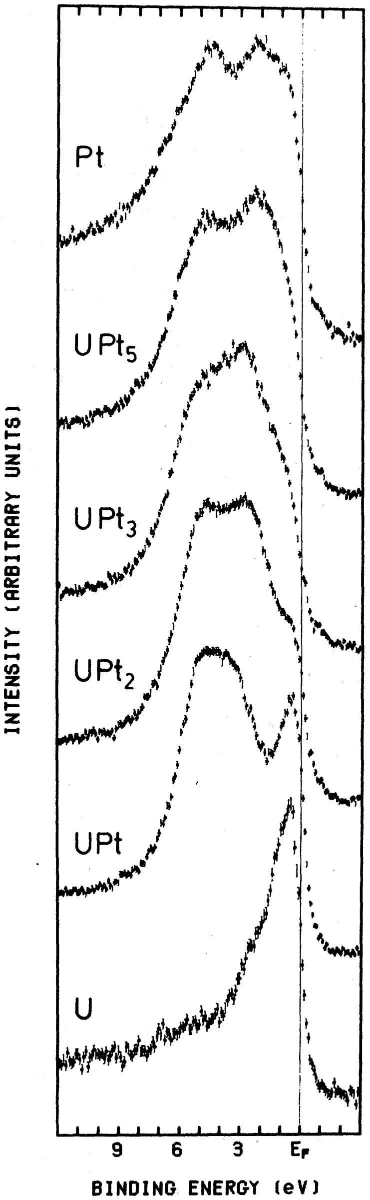

FIG. 2. Experimental XPS spectra of the valence bands of α-U, Pt, and their compounds excited with Al $K\alpha$ radiation. The total instrumental resolution in Figs. 1–4 and 6 is 1.1 eV.

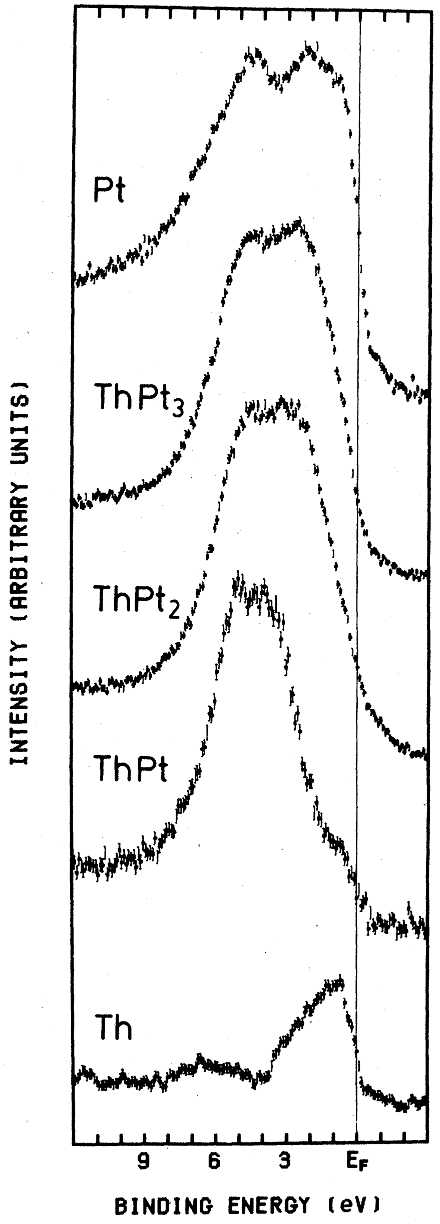

FIG. 3. Experimental XPS spectra of the valence bands of Th, ThPt, $ThPt_2$, $ThPt_3$, and Pt excited with Al $K\alpha$ radiation. The structure at about 6 eV in the Th spectrum is due to the $K\alpha_{3,4}$ satellite of the $6p_{3/2}$ core level.

gy. This structure is a peak in UPt, a shoulder in UPt_2, a weak shoulder in UPt_3 and only a slight distortion on the low-binding-energy side of the Pt 5*d* band in UPt_5. We attribute this structure to the presence of 5*f* electrons. A similar observation is made in the uranium-gold compounds, the valence bands of which are shown in Fig. 4. The contribution of the 5*f* electrons is easily identified through the increased emission intensity near the Fermi level as compared to the pure Au-metal spectrum. In order to determine the positions and intensities of the 5*f*-electron states in the data the valence-band spectra were normalized to their respective 4*f* core-level intensities and then the valence-band spectra of the Th-Pt compounds were subtracted from the respective U-Pt compounds. In all uranium compounds the position and relative intensities of the 5*f*-electron spectra are not altered as compared to pure α-uranium. This behavior indicates that no additional hybridization or occupation number variation of the 5*f* electrons occurs. This similarity suggests a similar behavior of the 5*f* electrons in these compounds. Band-structure calculations for α-U of Freeman *et al.*[3] yield good agreement with XPS, APS,[12] and (to some extent) BIS (Ref. 2) measurements, indicating that the shape of the XPS spectra has to be interpreted as a cutoff of a partially filled band similar to the 3*d* bands of transition metals. Consequently, we interpret the 5*f* electrons in the uranium-platinum as well as in the uranium-gold compounds as band electrons.

For the 5*d* bands of Au and Pt we observe a strong bandwidth narrowing as a function of concentration due to the reduced overlap of the 5*d* orbitals.[13] The Pt 5*d*-band intensities correspond in all but two cases to the ones expected from a superposition of the constituents. These exceptions are UPt and ThPt where hybridization effects due to covalent mixing have been suggested.[5] The observed energy shift of the centroid of the 5*d* bands will be discussed in connection with the core-level shifts below.

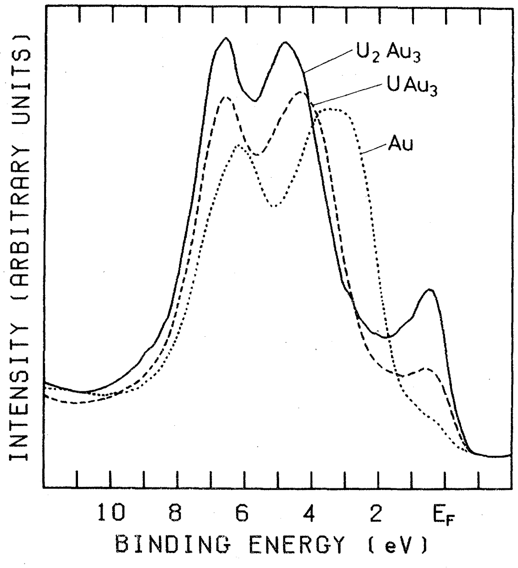

FIG. 4. Experimental XPS spectra of the valence bands of Au, UAu_3, and U_2Au_3 excited with Al $K\alpha$ radiation.

B. Core-level spectra: Binding-energy shifts

The measured core-level binding energies relative to the Fermi energy together with the measured work functions of the compounds are shown in Table II. For the actinides as well as for the noble metals the core-level binding-energy shifts are of the order of at most 1 eV towards higher binding energy. In order to draw conclusions from the relative energy shift one has to refer to a common zero of binding energy, which is the vacuum level of the sample. The kinetic energies of the electrons are always measured with respect to the work function of the spectrometer rather than that of the sample. In order to compare binding energies one has to consider therefore work-function changes of the constituents upon alloy formation. Unfortunately the measured work function includes the surface dipole barrier which leads to a difference between the crystal zero and the vacuum zero.[14] We use the approximation of employing experimentally determined work functions being representative for Fermi-energy shifts. The results are illustrated in Fig. 5 in the form of a schematic level diagram of the uranium-platinum system including the corresponding work functions. On this absolute binding-energy scale we observe increasing binding energy for the uranium levels with increasing platinum concentration whereas the platinum levels show weaker shifts in the reverse direction. This behavior indicates charge transfer from uranium to platinum consistent with the electronegativity of the elements. The thorium-platinum and uranium-gold compounds show qualitative agreement with these observations (see Table II). Grohs *et al.*[15] found only small charge transfer in the compounds UNi_5 and UCu_5. This finding is compatible with our results because the electronegativities and work functions of Ni and Cu are lower than those of Pt and Au.

A correct treatment of the binding-energy shift requires the consideration of volume and relaxation effects. The mean atomic volume in the uranium-platinum compounds is always larger than expected from the mechanical mixture of their component atoms (see Table I). From this observation a decrease in binding energy is generally expected. In order to discuss the effect for the constituents one has to consider the interatomic spacings. For the urani-

TABLE II. Electron binding energies of selected core levels and work functions in thorium-platinum, uranium-platinum, and uranium-gold compounds and their constituents.

	wf[a] (eV)	$A\,5d_{5/2}$ (eV)[b]	$A\,4f_{7/2}$ (eV)[b]	$A\,4d_{5/2}$ (eV)[b]	$N\,4f_{7/2}$ (eV)[c]	$N\,4d_{5/2}$ (eV)[c]
Au	5.0 ± 0.1	. . .	. . .	. . .	84.0 ± 0.05	335.1 ± 0.2
UAu_3	4.2 ± 0.1	. . .	377.8 ± 0.1	737.3 ± 0.2	84.55 ± 0.05	335.7 ± 0.2
U_2Au_3	3.8 ± 0.1	. . .	377.7 ± 0.1	736.9 ± 0.2	84.7 ± 0.05	335.8 ± 0.2
U	3.5 ± 0.1	94.0 ± 0.2	377.4 ± 0.1	736.4 ± 0.2	. . .	. . .
UPt	3.9 ± 0.1	94.4 ± 0.2	377.6 ± 0.1	737.2 ± 0.2	71.9 ± 0.05	315.1 ± 0.2
UPt_2	4.5 ± 0.1	95.0 ± 0.2	378.2 ± 0.2	737.6 ± 0.2	71.65 ± 0.05	315.2 ± 0.2
UPt_3	4.6 ± 0.1	94.8 ± 0.2	378.6 ± 0.2	737.7 ± 0.2	71.65 ± 0.05	315.0 ± 0.2
UPt_5	4.9 ± 0.1	94.6 ± 0.2	378.4 ± 0.1	737.1 ± 0.2	71.5 ± 0.05	314.7 ± 0.2
Pt	5.3 ± 0.1	. . .	. . .	. . .	71.2 ± 0.05	314.7 ± 0.2
$ThPt_3$	4.3 ± 0.2	85.5 ± 0.2	333.1 ± 0.2	674.9 ± 0.2	71.4 ± 0.05	314.7 ± 0.2
$ThPt_2$	4.0 ± 0.2	85.5 ± 0.2	333.3 ± 0.2	675.2 ± 0.2	71.4 ± 0.05	314.7 ± 0.2
ThPt	3.3 ± 0.2	86.2 ± 0.2	333.7 ± 0.1		72.0 ± 0.05	315.2 ± 0.2
Th	3.3 ± 0.2	85.4 ± 0.2	333.1 ± 0.1	675.2 ± 0.2	. . .	. . .

[a] wf is work function.

[b] *A* is actinide metal: Th, U.

[c] *N* is noble metal: Pt, Au.

um atoms these spacings are always larger than in the pure metal and this should result in smaller binding energies which is in contrast to the measurements. For the platinum atoms the situation is more complicated due to their anisotropic arrangement in the lattice.

Considering relaxation effects, *d* metals with relatively broad bands should better relax than the 5*f* metals. This would lead to a decrease in relaxation with increasing uranium concentration causing an effective negative shift for the noble-metal core levels and an effective negative shift for the uranium levels. Again our observations show that this effect cannot compensate charge transfer.

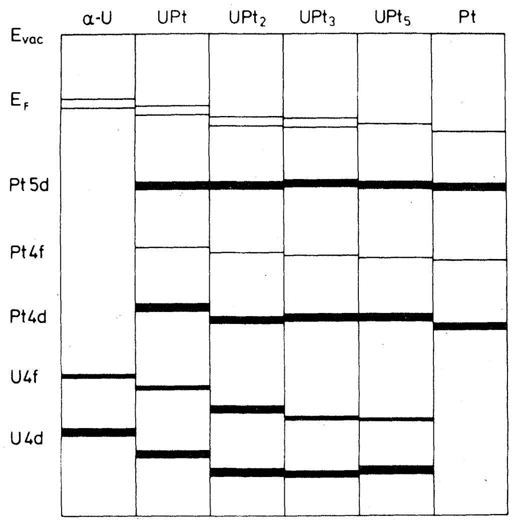

FIG. 5. Schematic representation of the electronic levels in uranium-platinum compounds and their constituents on an absolute binding-energy scale. The width of the levels includes the estimated experimental error.

The stability of the 5*f* states with respect to the Fermi energy is well understood assuming a band picture for these electrons. Any lowering of the Fermi level would result in a lowering of unoccupied 5*f* states below this energy. This would lead to charge flow within each atomic cell or from the transition metal to uranium. This is in contrast to our observations.

We note that on the absolute binding-energy scale shown in Fig. 5 the Pt 5*d* band exhibits no shift indicating effective screening by conduction electrons.

C. Core-level spectra: Line-shape analysis

The line shape of core levels recorded by XPS allows an indirect insight into the local electronic structure near the Fermi energy.[16] This is due to a many-body effect: The electron-hole interaction in the photoemission process. The simplest formulation of the theory is in terms of the analytical expression of Doniach-Sunjić[17] (DS) where the asymmetry of the line is described by the singularity index α, which is a function of angular-dependent partial screening charges. This DS line shape is strictly applicable only to simple metals with broad conduction bands.

Therefore the DS line-shape analysis is expected to be a crude approximation for the actinides and the transition metals due to the high density of states at the Fermi level. Nevertheless the core-level line shapes of most transition metals could be described well by this theory. The singularity index α is found to be 0.04 ± 0.02 in Au metal whereas in Pt metal this value amounts to 0.19 ± 0.02.[18] In the latter case the line shape is fitted less satisfactorily due to the end of the d band just above the Fermi energy. We analyzed the data for the transition-metal core levels in the compounds with the DS line shape taking into account an integral background due to the inelastic scattering of the electrons on their way through the sample.[19] The spectrometer resolution function was convoluted with the DS function and the Al $K\alpha_{3,4}$ satellites have been subtracted in a first step of the analysis. Our line-shape analysis for the $4f$ noble-metal core levels gave very good agreement with the quoted values for α and the linewidth γ.

In all but one compound studied here the noble-metal $4f$ core-level asymmetries have a value of $\alpha = 0.07 \pm 0.01$. This value corresponds to the one of pure Au metal indicating that the local density of states at the Pt sites is similar to that of Au. This effect is visualized as a shift in the Pt bands relative to E_F indicating a filled d band. In UPt_5 the Fermi level is crossed by the d band. Here the analysis yields a value of 0.11 for α which lies between the values of Au and Pt metal. From the equality of the α values in the thorium-platinum and the uranium-platinum compounds it follows that the $5f$ electrons have little influence on the local density of states at the Pt sites.

For the U $4f$ core lines we expect a different behavior due to the characteristic f-electron density of states above the Fermi level. During photoemission, simultaneous transitions between occupied and empty levels at the Fermi energy become possible leading to line broadening and shake-up-like satellites. Furthermore, in the final state of the photoemission, the unoccupied levels are lowered due to the core hole left behind. If they are positioned just above the Fermi energy, shake-up processes will become even more pronounced. (In Th metal a satellite structure on the high-binding-energy side of the Th $4f$ core-level spectra has been observed and has been recently ascribed to be due to the Kotani effect.[20]) If one of these levels is positioned below E_F the final state will be a one- or two-hole system. In the photoemission spectrum this will correspond to two lines being separated by the self-energy of the lowered state. According to Kotani and Toyazawa[21] the line shape corresponding to the one-hole state is described by the DS expression whereas the second line has a Lorentz profile due to the short hole lifetime at the Fermi energy. We analyzed the data with this combination of line shapes.

As typical example, the U $4f$ core levels of UPt_5 are shown in Fig. 6. The result of the fit procedure is indicated by the full curve.

In α-uranium we get a value for the singularity index $\alpha = 0.45$ which is difficult to interpret in the DS theory. This value would correspond to ideal s screening which is certainly not the case. In the compounds the fit curve is always slightly higher than the data at the high-binding-energy side of the line (see Fig. 6). The singularity index is larger (0.5 to 0.7) and the lifetime width increases considerably as compared to pure U metal (from 0.17 to 0.29 eV, with a maximum in UPt_2). As a characteristic feature in the fit process of the compounds we note that the integral background is nearly neglected. Let us try to interpret these results.

According to Kotani and Toyozawa the singularity index is a function of the density of states and the squared density of states at E_F. Any narrowing of the f states due to reduced overlap therefore increases the local density leading to a higher value of α. Furthermore an increased density of states at the Fermi level increases the probability of simultaneous excitations leading to increased shoulders on the high-binding-energy side of the core-level spectra. Due to the proximity of the initial states to the Fermi level the transition rates become amplified and the final-state structures get smeared out. This simulates an enlarged asymmetry and linewidth causing the observed deviation of the fit in the low-kinetic-energy region of the line.

Another source of additional broadening is multiplet splitting due to the "magnetic" electrons in the final state.[22] There exist no observations of multiplet

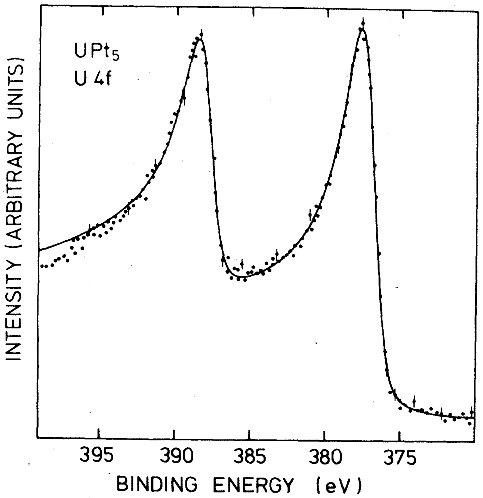

FIG. 6. U $4f$ core-level spectrum in UPt_5. The full curve represents the result of a combination of a Lorentzian and a DS line-shape analysis. The relevant parameters for the DS line shape are $\alpha = 0.56$ and $\gamma = 0.26$ eV (see text).

splittings in the 4*f* spectra of U compounds in the literature. Even in the cases of the oxides and halogenides, in spite of large effective paramagnetic moments ($\mu_{\rm eff}3.2-3.7\mu_B$/atom), no multiplet splitting was reported.[23] In the compounds studied here the paramagnetic moments are smaller (see Sec. III D) and consequently we exclude this broadening mechanism. Underlying initial-state multiplet structure can contribute as well as to the linewidth and asymmetry. A broadening mechanism which was proposed by the authors of Ref. 24 for UN is a mixed-valence behavior. Grohs *et al.*[15] attributed U 4*f* core-level and valence-band features present in their spectra of UCu_5 to be due to the same phenomenon. We observe similar features in the spectra of UAu_3. In our case we believe that these structures are due to oxygen contamination (see Fig. 1, dashed and dashed-dotted lines).

Considering now the Lorentzian, our analysis yields for its intensity in all cases a value of less than 10% of the main line. The line positions relative to the main line vary between 1.5 eV in UPt_5 and 3.8 eV in α U. In U_2Au_3 the Lorentzian is found at 5.1 eV, in UAu_3 at 5.9 eV higher binding energy than the main line.

In α-U this extra line is due to slight oxygen contamination. If we exclude an UO_2 surface layer we are faced with a quasiternary system in the uranium-platinum compounds. The measured work functions of these compounds increase with increasing platinum concentration. This would lead to a concentration-dependent shift of the oxygen-induced line to lower binding energy relative to E_F. Therefore we cannot exclude the possibility of slight oxygen contamination being the origin of the Lorentzian line in the uranium-platinum compounds.

In the uranium-gold system however the position of this line is not compatible with an oxide line. Furthermore its intensity is too high for being ascribed to an oxygen-induced shake-up process. Plasmon excitation can be excluded also, since no losses have been found near the Au 4*f* core lines. A valence fluctuation seems also unlikely because one would have to assume a fluctuation of the uranium atom between a valence found in the metal (near U^{3+}) and a valence larger than that for tetravalent UO_2.

Satellites have been also observed in UAl_2,[25] UAs,[26] UGa_2,[27] and (not explicitly) in UCu_5,[15] whereas in α-U metal, in the uranium-platinum system studied here and in UNi_5(Ref. 15) these satellites are absent. We interpret the satellite structure in the compounds mentioned above as being due to the Kotani-Toyozawa effect. The intensity and lifetime width of the Kotani-Toyozawa satellites are given by the strength of the 5*f*-conduction-electron interaction. Consequently the presence of these satellites indicates a decreased 5*f*-conduction electron mixing in the *sp*- and closed *d*-shell compounds as compared to the compounds with an open *d*-shell configuration, where a stronger 5*f*-6*d*-5*d* hybridization is observed. Any decrease of this interaction indicates an increase in the localization of the 5*f* states. Therefore the presence of the Kotani-Toyozawa satellites in the uranium-gold compounds points to a more localized behavior of the 5*f* states.

D. Magnetic properties

The magnetic properties of the uranium-platinum compounds are summarized in Table III. The compound UPt has been reported to be a weak ferromagnet with a Curie temperature of 30 K and a saturation moment which is 5 to 10 times smaller than that expected from a possible 5*f* electronic shell configuration of U ions.[28] Magnetization measurements under pressure (up to 20 kbar) yield a continuous decrease of the moment at constant Curie temperature. This behavior is in sharp contrast to the weak ferromagnetic system $ZrZn_2$.[8] Luengo and Maple[29] determined the entropy change associated with the formation of the ferromagnetic state. They found that the values are 10 and 4 times smaller, respec-

TABLE III. Magnetic properties of uranium-platinum compounds.

	Magnetism	U–U spacing (Å)	$\mu_{\rm eff}$ (μ_B/f.u.)[a]	$\delta_{\rm CW}$ (K)	Ordering temperature (K)	Ordered moment (μ_B/f.u.)
UPt	F[b]	3.61	2.61	0	30	0.2–0.5
UPt_2	F[b]	3.81	2.0 ± 1	−85	15	0.05–0.2
UPt_3	AF[c]	4.12	2.61 ± 0.5	−95	15	· · ·
UPt_5	P[d]	5.25	2.73 ± 1	−310	· · ·	· · ·

[a] f.u. is formula unit.
[b] F is ferromagnet.
[c] AF is antiferromagnet.
[d] P is paramagnet.

tively, than those expected from a Hund's-rule calculation for the $5f^2$ or $5f^3$ configuration but 10 times larger than for typical itinerant ferromagnets. The effective paramagnetic moment was found to be $2.61\mu_B$/atom.[30] This value is between a localized $5f^1$ ($2.54\mu_B$/atom) and a quenched $5f^2$ ($2.83\mu_B$/atom) configuration. In summary, the experimental evidence points to a behavior between localization and itineracy of the $5f$ electrons in the UPt compound.

The results of the susceptibility measurements of the compounds UPt_2, UPt_3, and UPt_5 are shown in Fig. 7.

Recently it has been reported that the compound UPt_2 is a weak ferromagnet below 15 K with a saturation moment of the same order of magnitude of UPt.[31] This behavior is similar to the one in $NpOs_2$ and $PuPt_2$ (cubic $MgCu_2$ structure), which are supposed to show itinerant magnetism.[32] The effective moment is between $5f^1$ and $5f^2$ quenched configurations which would support a band view of these electrons.

The compound UPt_3 shows a weak maximum in the susceptibility curve at 15 K. The $MgCd_3$ structure of UPt_3 is a hexagonal stacked polytype of the cubic $AuCu_3$ structure. Materials crystallizing in the $AuCu_3$ structures, like $NpPd_3$, $NpPu_3$, and $PuPt_3$ show a similar behavior which is ascribed to an antiferromagnetic transition.[32] The paramagnetic region is described by a Curie-Weiss behavior with $\mu_{\text{eff}} = 2.85\mu_B$/atom between 23 and 110 K and with $\mu_{\text{eff}} = 2.61\mu_B$/atom between 110 and 210 K. This value is close to the one corresponding to a quenched $5f^2$ configuration. The compound UPt_5 shows no ordering down to 2.5 K. The paramagnetic region is determined by Curie-Weiss behavior with a $\mu_{\text{eff}} = 1.76\mu_B$/atom below 75 K and a $\mu_{\text{eff}} = 2.73$ above 75 K. UPt_5 is therefore similar to UPt_3 in the high-temperature region.

In spite of large interatomic U—U spacings no localized magnetic moments, such as exist for the lanthanides, are observed. The charge density of the $5f$ wave functions in the free atom approaches zero at about 2-Å units in the light actinides. In UPt_3 and in UPt_5 therefore no direct $5f$ overlap is expected. From the absence of localized paramagnetic moments a strong hybridization of the $5f$ with the conduction electrons is concluded to occur.

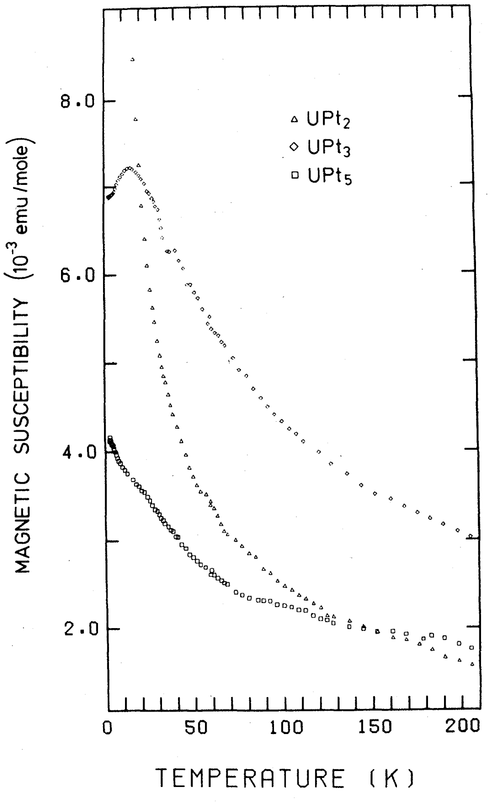

FIG. 7. Magnetic susceptibility of uranium-platinum compounds.

IV. SUMMARY

X-ray-photoemission measurements have shown that the U $5f$ states do not change position and intensity in the compounds as compared to pure α-uranium metal. Taking into account the band character of the $5f$ electrons in α-U and the results of the magnetization measurements, where no effective moments corresponding to localized configurations have been found, a band description of the $5f$ electrons in the uranium compounds studied here seems to be appropriate. We note that our line-shape analysis suggests the onset of a more localized behavior of the $5f$ electrons in the uranium-gold compounds.

In the compounds the reduced overlap of the outer orbitals (as in the case for the concentration-dependent narrowing of the Pt $5d$ band) leads to band narrowing and causes an increase in the density of states above the Fermi level. The increased core-line asymmetry and linewidth in the compounds as compared to uranium metal are therefore interpreted to be a consequence of increased final-state conduction-electron excitations.

The observed decrease of the Pt $5d$-emission intensity for UPt and ThPt is an indication for hybridization.[33] These two compounds form stable molecules in the gas phase indicating the existence of $5d$-$6d$ covalent mixing.

The Au valence bands in the compounds show no indication of hybridization effects, indicating a weaker covalency in these compounds. This finding is supported by their sensitivity to oxidation.

The analysis of the core-level binding energies in the compounds, correcting for the measured work functions, indicates a charge transfer from the actinide to the noble metals. The line-shape analysis for the core levels yields equal values of the singularity index α for Au and Pt in the compounds. This similar behavior of Pt and Au is due to the filling of the Pt *5d* band in the uranium compounds.

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