Dispersion of 5f electron states: Angle-resolved photoemission on ordered films of U metal

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Ordered overlayers of U metal characterized by a hexagonal low-energy electron diffraction pattern were grown *in situ* by deposition of U metal onto a W(110) substrate and subsequent annealing. Angle-resolved photoemission reveals clearly dispersion of U $5f$-derived states. The experimental data are in excellent agreement with results of relativistic local density approximation band-structure calculations. The bandlike properties of the U $5f$ states stem from direct f-f interaction rather than from f-d hybridization as might be expected for $4f$-derived bands in Ce systems. [S0163-1829(98)02420-5]

The question as to whether the f states are localized or itinerant in character is of high importance for an understanding of the electronic properties of light rare earths and actinides. In contrast to heavy rare-earth systems, where the $4f$ states are fully localized and responsible for the magnetic properties of the materials, the f states in light rare earths reveal hybridization with valence-band states. Particularly in Ce compounds, this kind of hybridization leads to exotic properties like the Kondo effect and heavy-fermion behavior.[1] In electron spectroscopies these interactions are usually reflected by the appearance of satellite structures in the core-level spectra.[2] Photoemission (PE) spectra of the $4f$ states of Ce are characterized by a double-peaked structure, where a first peak at about 2 eV binding energy (BE) represents the usual $4f^{n-1}$ PE final state and a second feature near the Fermi energy (E_F) corresponds to a $4f$ configuration close to the ground state. Although this latter feature, the so-called Kondo peak, may become dominant in α-like Ce compounds, the spectra can still be described within a localized picture of the $4f$ states,[3] and in only a few cases might an itinerant model be more favorable.[4,5]

For the $5f$ states of the actinides the situation is different, since due to a node in the radial wave function these states are spatially more extended than the $4f$ states in lanthanides and are, therefore, subject to much stronger hybridization. As a consequence the $5f$ states are believed to be bandlike in light actinide metals, and only beginning with Am a transition from bandlike to localized behavior is expected.[6] PE spectra of the $5f$ states of uranium metal are characterized by a huge peak at E_F with a weak shoulder at about 1.5 eV BE.[7] Since these spectra look similar to the $4f$ spectra of α-like Ce systems,[2–4] the question arises as to whether they really reflect emissions from a $5f$ band that should be described in the framework of single-particle band-structure calculations, or a localized description is more appropriate.[8] Direct observation of energy dispersion, as obtained from angle-resolved PE, could be a proof of a bandlike behavior of the $5f$ states. In fact, dispersion of $5f$-related states has been reported for UIr_3, UPt_3, and recently for USb_2.[9] In these compounds, however, the interatomic U-U distances are too large for a direct f-f overlap, and $5f$-admixed hybrid bands merely reflect the dispersive properties of the valence states. Pure f bands, which are dominated by direct f-f hybridization, may only be found in systems with small interatomic U-U spacings as, e.g., in U metal. In such systems,

however, the U concentration is large, and the preparation of clean and structurally ordered surfaces, as necessary for PE experiments, is difficult due to the chemical reactivity and the radioactivity of the actinide.

In the present paper we report on the first experimental observation of pure $5f$ dispersion in actinides by means of angle-resolved PE. Structurally ordered films of uranium metal were prepared by thermal deposition of the pure metal onto a W(110) substrate and subsequent annealing. The films reveal sharp hexagonal low-energy electron diffraction (LEED) patterns corresponding to a new close-packed phase of uranium that is characterized by interatomic U-U spacings of 3.2 ± 0.1 Å. The observed dispersion of the $5f$ states is in excellent agreement with relativistic local-density approximation–linear combination of atomic orbitals calculations. A detailed theoretical analysis shows that the band-like character of the $5f$ states arises primarily from a direct overlap between $5f$ orbitals of neighboring uranium atoms rather than from f-d hybridization, as may be expected for $4f$-derived bands in Ce systems.[2]

Ordered films of U were prepared by *in situ* deposition of the actinide metal onto a cooled W(110) substrate (liquid-nitrogen temperature) followed by annealing. Uranium metal was thermally evaporated from a dismantled tungsten crucible with a pin hole, which was heated by electron bombardment up to temperatures of about 2300 K. The evaporator was tightly shielded by a water-cooled screen with a small hole in the front plate in order to get a well-collimated atomar beam of the radioactive material. The evaporation rate (4 Å/min) and the thickness of the deposited films were calibrated with quartz microbalances. To keep radioactive contaminations of the equipment as low as possible the whole space around the evaporator, sample, and microbalances was additionally protected by a movable screen that was pulled out during the PE experiment.

Deposition of uranium onto the cooled W(110) substrate led to the formation of a nonordered overlayer. Ordering of the U film was achieved by step-by-step annealing of the ''as-deposited'' layer (80 Å thick) up to a temperature of 1400 K. After that, a sharp hexagonal LEED pattern was observed that is not compatible with any of the known bulk phases of uranium metal (orthorhombic α, tetragonal β, and bcc γ phases).[10] Instead, the LEED data suggest the formation of a close-packed structure with an interatomic U-U distance $a = 3.2 \pm 0.1$ Å. The formation of this new phase is ascribed to interactions with the tungsten substrate. Similar substrate-induced deviations from the bulk-phase diagram are by now well-known phenomena in thin-film physics. Even recently, for thin Eu overlayers on Mo(110) the formation of a close-packed phase instead of the expected bcc structure has been reported.[11] Since for U metal growth of bcc γ-U was also expected from the preparation conditions (annealing to high temperatures) and the bulk-phase diagram, the observed formation of a close-packed structure constitutes a close parallelism to the Eu case. The LEED data, however, do not allow us to decide definitively whether the close-packed pattern relates to a cubic structure like α-Th and γ-Ce, or to a hexagonal arrangement, as for most rare-earth metals. From the energy-dependent variations of the LEED pattern in our experiments, which revealed almost identical intensity profiles of all six first-order LEED spots, a

hexagonal symmetry might be concluded. On the other hand, a fcc phase with different domains rotated by 60° relative to each other would lead to similar results. In both cases, the interatomic U-U spacing corresponds to an atomic volume that agrees well with the related values of the bulk phases.

Angle-resolved photoemission experiments were performed at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) exploiting radiation from the plane-grating monochromator beamline SX700/II. Photon energies were tuned in the range 50–98 eV to measure band dispersion in the direction normal to the sample surface and to take advantage of resonant excitations ($5d \rightarrow 5f$ resonance at 98 eV). PE spectra were taken with a rotatable hemispherical electron-energy analyzer (AR65 from VSW, Inc.) with an angle resolution of 1°. The overall-system energy resolution was $\cong 100$ meV (full width at half-maximum). All measurements were performed at the temperature of liquid nitrogen. The base pressure in the experimental setup was in the range of 1×10^{-10} mbar.

Band-structure calculations both for fcc- and hcp-like structures were performed in the framework of the local-density approximation with the standard Hedin-Lundqvist exchange-correlation potential[12] exploiting an optimized method of linear combination of atomic orbitals[13] in its fully relativistic version.[14] Uranium was considered to be a conventional metal with itinerant $5f$ states. The used valence basis includes $7s$, $6p$, $6d$, and $5f$ states. Using the linear tetrahedron method the **k** sums were performed over a mesh containing 509 **k** points in the irreducible part of the Brillouin zone. The ordered U films were treated as ideal crystals without accounting for surface and real structure effects.

In the inset of Fig. 1 we compare our PE data to those for polycrystalline U metal. Spectra taken at $h\nu = 98$ eV for a freshly filed bulk uranium sample[7] (solid line) and the ordered U film (solid line through the experimental points) look similar to each other. Notwithstanding, the spectrum of the ordered film reveals much sharper structures within the first 2 eV below E_F, where emissions from the $5f$ states are expected. Particularly shoulder A, which according to Ref. 7 points to a good quality of U samples, is by far more pronounced for the film than for the polycrystalline sample. A broad structure observed in both spectra at about 5–6 eV BE lies in the region of the $7s$ states of uranium. The PE cross section of $7s$ states, however, is small at the photon energy used: In our case, this structure might also originate from possible slight oxygen (rest gas) or carbon (from substrate) contaminations caused by annealing of the exceedingly reactive uranium overlayer. An interpretation in terms of many-body effects can also not be excluded.[15]

A series of valence-band PE spectra taken at different photon energies in normal-emission geometry is shown in Fig. 1. The spectra were normalized to photon flux. Intensity modulations are mainly due to the presence of $5d \rightarrow 5f$ Fano resonance at 98 eV photon energy. Three main spectral features A, B, and C are observed revealing different degrees of dispersion: The highest-BE feature A shifts within a range of almost 0.6 eV exhibiting zigzag behavior when going from one spectrum to another. Structure B reveals weaker dispersion: In the photon-energy range from 98 to 70 eV it moves slightly away from E_F and shifts back to lower BE in the 60-eV spectrum. At 50 eV photon energy, this feature again
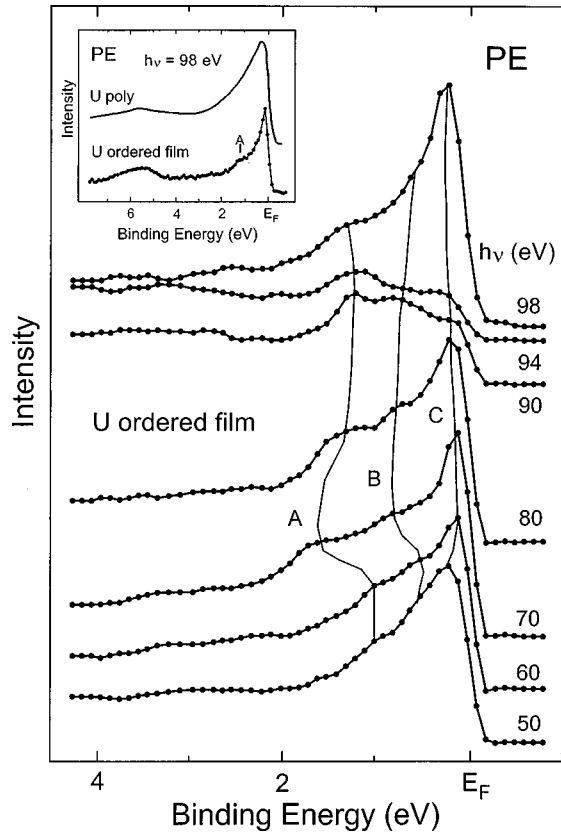
FIG. 1. A series of normal-emission spectra from an ordered film of U metal taken in the energy region of the U $5f$ PE signal. The spectra were taken at various photon energies including the region of the $5d \rightarrow 5f$ Fano resonance (off resonance, $h\nu = 94$ eV; on resonance, $h\nu = 98$ eV). In the inset a PE spectrum of the ordered film (solid line through experimental points) is compared to the one of a polycrystalline bulk sample (solid line, Ref. 7).

FIG. 2. Calculated total DOS (solid line) together with the partial $5f$ (broken line) and $6d$ (dash-dotted line) contributions for the hcp phase of U metal. The lattice constant in the direction perpendicular to the surface (c) was assumed to be 5.2 Å according to the ideal close-packed c/a ratio. The inset shows the band dispersion along the Γ-A direction.

shifts away from the Fermi energy. In contrast to structures A and B, feature C reveals no clear dispersion. It is located at about 0.2 eV BE, and only at $h\nu = 60$ eV is a weak shift to lower BE observed. At the $5d \rightarrow 5f$ Fano resonance all three features A, B, and C reveal resonant enhancements as can be seen from comparison of the two topmost spectra in Fig. 1. The on-resonance intensity of feature C at $h\nu = 98$ eV is approximately five times higher than the off-resonance signal at $h\nu = 94$ eV. The resonant enhancement of features A and B is weaker. Structures that reveal larger dispersion resonate to a lesser extent and vice versa.

The experimental data were compared with results of band-structure calculations for hcp and fcc phases of U metal. An excellent agreement between theoretical bands and PE data has been obtained for the hypothetic hcp structure. The agreement with the fcc calculations is less perfect. While the total width of the bands are correctly predicted, the fcc calculations fail in the description of details of the band dispersion.

In Fig. 2 and Fig. 2 (inset) the calculated electron density of states (DOS) and the band dispersion in the Γ-A direction are shown for the hcp phase, respectively. The total DOS (solid line) is presented together with a plot of the $5f$ and $6d$ contributions (broken and dash-dotted lines, respectively). The main part of the DOS is located above the Fermi level. In this energy range, it consists of a series of rather narrow
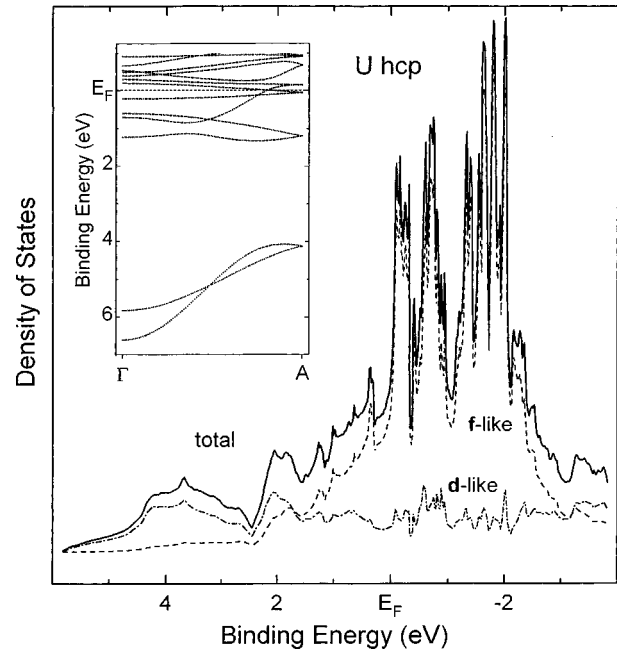
peaks, which have almost pure f character. In the region of the occupied states the relative contribution of d character to the DOS is higher as compared to that of the unoccupied states. Note that the relative amount of $6d$ derived contributions to the DOS varies with binding energy: While for the broad structure at highest BE (between 2.5 and 4.5 eV BE) the contribution of d character is predominant, the next, more narrow feature at about 2 eV BE contains already almost 50% of f character. For the following features the $5f$ admixture increases drastically reaching as much as 90% for the sharp structure at about 0.2 eV BE. The inset in Fig. 2 shows the calculated dispersion of valence bands along the Γ-A direction. This direction was sampled by angle-resolved PE in the present study. Our eigenvector analysis reveals that each subband plotted in the inset above 1.5 eV BE has more than 75% of f character.

The large $5f$ contribution to the electron states results in the observed strong intensity variations at the $5d \rightarrow 5f$ Fano resonance. It is important to note, however, that the degree of resonant enhancement is not proportional to the amount of $5f$ admixture as might be expected in a naive consideration. This fact has severe consequences to the evaluation of PE data: Usually, $4f$ or $5f$ contributions into PE spectra are experimentally determined by taking the difference of on- and off-resonance PE spectra.[2,7] Applied to uranium metal, this method leads to serious mistakes since only the peak at E_F would appear in the difference spectrum, while the contributions from the bands at higher BE's become suppressed. In fact, a 2-eV feature in the valence-band PE spectra of α-U, that originally had been attributed to a $5f$ shakeup satellite by Iwan et al.,[16] was later on identified with a d-band emission due to its different resonant behavior in respect to

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the main $5f$ PE signal.[7] According to the present results on hexagonal U metal it is rather probable that both interpretations are wrong and the 2-eV feature represents emission from a part of the $5f$ band.

The reason for the different resonant behavior of the individual branches is not easy to understand. In a recent paper[17] we have shown for valence-band $5d$ electrons that the spectral on-resonance intensity reflects the local character of the wave functions. This explanation cannot be applied to the present case of nearly pure $5f$ wave functions, which are almost equally localized. A distinct difference between the highest occupied f band (feature C) and the other occupied f bands is, however, that the former reveals almost pure $5f_{5/2,|mj|=3/2}$ character (with only 10% admixture of $5f_{7/2,|mj|=3/2}$). In a spherical harmonics representation, this character predominantly corresponds to $z(x \pm iy)^2$ with nodes both in the z direction and in the xy plane. The other bands, which exhibit much weaker resonant enhancements, are $5f_{5/2}$-$5f_{7/2}$ hybrids with $|m_j| \neq 3/2$ and up to 40% admixture of $5f_{7/2}$. We suppose that these symmetry properties are responsible for the different resonant behavior of the individual branches. A strong dependence of the resonant PE cross sections from the total angular momentum j has also been observed previously for $4f$ multiplets of rare-earth systems.[18] A proof of this conjecture, however, demands extensive cross-section calculations including a proper consideration of multiplet effects in the intermediate $5d^9 5f^{n+1}$ state that are beyond the scope of the present study.

Excellent agreement between the experimental and the calculated bands is shown in Fig. 3(a). In particular, the 0.25-eV hybridization gap between the two lowest f bands is clearly seen in the experimental data (features A and B). Furthermore, the calculated total occupied $5f$ bandwidth amounts to 1.25 eV in nice agreement with 1.4 eV obtained in the experiment. Here, the question arises whether the observed dispersions are caused by f-d hybridization and reflect, therefore, mainly the behavior of the $6d$ bands, or f-f interaction itself is responsible for the observed itinerant character.

This point has been examined theoretically by performing model band-structure calculations with artificially excluded f-d hybridization. As demonstrated in Fig. 3(b) neglecting f-d hybridization causes a slight shift of the occupied bands towards E_F and a disappearance of the above mentioned hybridization gap. However, it does not change significantly the width of the $5f$ bands. In contrast to this, a suppression of f-f hybridization changes drastically the calculated valence-band structure [Fig. 3(c)] and leads to a reduction of the occupied $5f$ bandwidth to 0.3 eV.

Our model study clearly shows that in contrast to lanthanide systems, where f-d hybridization is expected to play the premier role in delocalization of the $4f$ states, the direct f-f overlap leads to the dispersion and hybridization repelling of the $5f$ states in uranium metal.

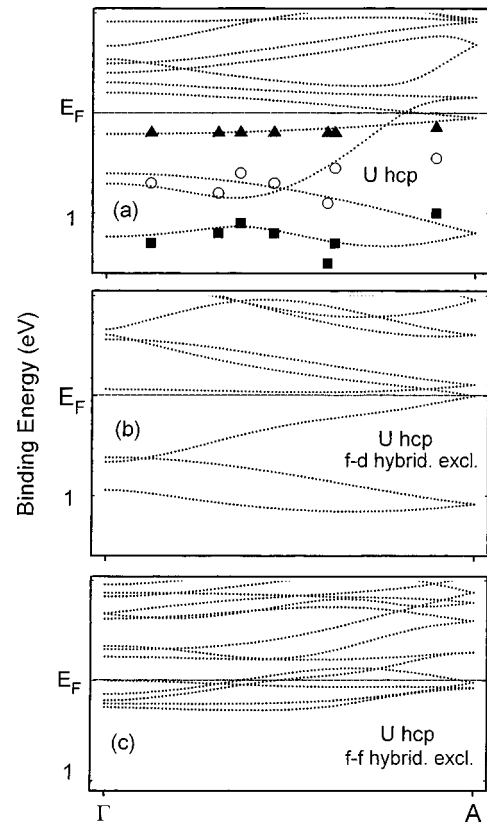In summary, for the first time, to our knowledge, single-

FIG. 3. (a) Calculated bands along the Γ-A direction for hcp U metal. (b) and (c) Results of model calculations with excluded f-d and f-f hybridization, respectively. In (a) the theoretical results are compared with the experimental data. Squares, circles, and triangles denote data related to features A, B, and C, respectively.

crystalline overlayers of U metal were grown *in situ* by direct deposition of the actinide metal onto an oriented substrate. Angle-resolved PE study on these films reveals clear dispersive behavior of the $5f$ states, which is in excellent agreement with band-structure calculations. The dispersion of the U $5f$ states is caused by direct f-f interaction, rather than by hybridization between f and valence orbitals as expected for U compounds with large interatomic U-U spacings or $4f$ systems.

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