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# Dispersion of f states in U-metal and CeRh$_3$

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## Abstract

Photoemission (PE) experiments on ordered films of U-metal and RE-Rh surface compounds (RE=Ce, La) are reported. For U-metal, formation of a new close-packed phase is observed. PE spectra of the ordered U-film reveal a clear dispersion of the U 5f-derived states. The experimental data are in excellent agreement with the results of relativistic LDA band-structure calculations. The bandlike properties of the U 5f states stem from f–f interaction rather than from f–d hybridization as might be expected for 4f-derived bands of Ce-compounds. In CeRh$_3$, resonant angle-resolved PE spectra reveal a weak energy shift of the Fermi-level peak, which may be ascribed to a dispersive behaviour of the Ce 4f states. Data on LaRh$_3$ were used for discrimination of 5d- and 4f-related effects in the PE spectra of CeRh$_3$.

*Keywords:* Photoemission; Electron bands; Actinide; Rare-earth systems

## 1. Introduction

The question as to whether f states in a solid should be treated within a localized or a bandlike picture is of high importance for the understanding of the electronic properties of rare-earth's (REs) and actinides. In contrast to heavy REs, where the f states are usually fully localized and responsible for the magnetic properties of the materials, f states in light REs are subject to larger hybridization with valence states. Together with small interconfigurational energies this may lead to exotic many-body phenomena like the Kondo-effect and heavy-fermion behaviour [1,2]. In photoemission (PE), hybridization effects are usually reflected by satellite structures that appear in addition to the final states expected for the localized systems [3]. For Ce-systems, that reveal the strongest hybridization effects among RE materials, the 4f PE spectra consist of a characteristic double-peaked structure: A peak at about 2-eV binding energy (BE) relates to the 4f$^0$ final state expected for a nonhybridized 4f$^1$ ground state, while a second feature at the Fermi-energy ($E_F$), the so-called Kondo-peak, reflects a final state close to the ground-state configuration. The appearance of the Kondo-peak is usually explained by configuration interaction within the framework of a localized Anderson single-impurity model [4]. The relative intensity of this peak with respect to the 4f$^0$ emission increases with increasing f–d hybridization, and in strongly hybridized Ce-systems, the double-peaked structure of the PE spectra degenerates almost to a huge single peak at $E_F$ [5]. Here the question arises as to whether the spectra should still be described within the localized Anderson picture or whether a band approach is more adequate, which assigns the peak at $E_F$ to emissions from a narrow band and explains the residual intensity of the 4f$^0$ state as a correlation satellite in analogy to the famous 6-eV satellite in Ni metal [6].

For the 5f states of the actinides, the situation is different. 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 stronger f–f and f–d hybridizations. 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 behaviour is expected [7,8]. 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 [9]. Thus, they look very similar to the 4f spectra of strongly hybridized Ce-systems, and the argumentation given above for Ce-systems may be reversed asking whether the spectra really

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reflect emissions from a 5f band or a localized description is also possible [10].

Direct observation of energy dispersion, as obtained by angle-resolved PE, could be taken as a proof of a bandlike behaviour of f states. In fact, observation of f dispersion has been reported for some Ce- and U-systems [11–13]. The given experimental evidence for bandlike properties, however, is not very convincing. For Ce-systems, binding-energy shifts of the Fermi-level peak of the order of 50 meV have been reported that might be assigned to a band dispersion of the 4f states. On the other hand, the PE and bremsstrahlung-isochromat spectra (BIS) reveal strong $4f^0$ and $4f^2$ satellites, respectively, that cannot be explained within a single-particle theory, whereas they are consistently described within the framework of the Anderson single-impurity model. For U-compounds, f dispersions have been reported for systems, where the U 5f emission is superimposed by intense valence-band signals, and the question arises as to whether the observed effects really reveal a property of the 5f states.

In the present contribution, we report on an angle-resolved PE study on ordered films of pure uranium metal and a Ce-Rh surface compound grown onto a W(110) substrate. For U-metal, formation of a new close-packed phase is observed. The valence-band PE spectra are dominated by 5f emissions that reveal a clear dispersive behaviour in agreement with the results of our LDA–LCAO (local density approximation–linear combination of atomic orbitals) band-structure calculations. The prepared Ce-Rh system reveals a crystalline structure and stoichiometry equivalent to $CeRh_3$ with (111) orientation of the surface. $CeRh_3$ is a compound, for which BIS and PE spectra cannot be described within a single-impurity Anderson model by the same set of parameters [14–17]. Particularly, the f-emission in the BIS spectra consists almost completely of a huge $4f^1$ peak that coincides in energy with the calculated position of the f-band in this compound [14]. Therefore, $CeRh_3$ represents a possible candidate for bandlike behaviour of the 4f states. For the surface compound, a 50-meV shift of the Fermi-level peak in 4d→4f resonant PE spectra is observed as a function of emission angle, that in fact may be taken as an indication for bandlike properties of the 4f states. Resonant PE data of the isoelectronic $LaRh_3$ compound were used to exclude possible contributions from resonantly enhanced Ce 5d states.

## 2. Preparation

The films were prepared in situ by deposition of the pure metals onto a liquid-nitrogen cooled W(110) substrate. Subsequent annealing leads to ordered films, which reveal in all cases sharp hexagonal LEED (low energy electron diffraction) patterns. The Ce-Rh (La-Rh) system was prepared by codeposition of Ce (La) and Rh onto W(110) with an atomic deposition ratio of 1 to 3, and subsequent annealing [18]. For Ce-Rh, the resulting LEED pattern is equal to a (2×2) overstructure of Rh(111) pointing to a morphology equivalent to the (111) face of the cubic $CeRh_3$ phase ($AuCu_3$-type). In the case of the uranium film, the obtained hexagonal LEED pattern was not compatible with any of the known bulk phases of uranium metal (orthorhombic $\alpha$-, tetragonal $\beta$-, and bcc $\gamma$-phase). Instead, the LEED data suggest the formation of a close-packed structure with an interatomic U–U distance of $3.2\pm0.1$ Å stabilized by interactions with the tungsten substrate.

The measurements were performed using synchrotron radiation from the plane grating monochromator SX700/II at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). Photon energies were tuned within the range of 50 eV to 121 eV covering both the U 5d→5f and the Ce (La) 4d→4f Fano-resonances. PE spectra were taken with a rotatable hemispherical electron-energy analyzer (AR65 from VSW) with an angle resolution of 1°. The overall-system energy resolution was tuned to about 100 meV (full width at half maximum) (FWHM). All experiments were performed at a temperature of liquid nitrogen. The base pressure in the experimental set-up was in the range of $1\times10^{-10}$ mbar. Oxygen contamination was checked by monitoring the O 2p signal and was found to be negligible.

For band-structure calculations, a relativistic optimized LDA–LCAO approach together with the standard Hedin–Lundqvist exchange-correlation potential was used [19,20]. The scalar relativistic approximation was employed in the case of the RERh-compounds, whereas spin-orbit coupling was taken into account for U-metal.

## 3. Results

PE data from the ordered uranium film are in good agreement with those of polycrystalline uranium samples as shown in the inset in Fig. 1. Notwithstanding, the spectrum of the ordered film is characterized by much sharper structures within the first 2 eV below $E_F$, where emissions from the 5f states are expected. A broad structure observed in both spectra at about 5 to 6 eV BE may originate from weak oxygen or carbon contaminations. An interpretation in terms of many-body effects can also not be excluded [21].

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 the 5d→5f Fano-resonance at 98 eV photon energy[1]. Three

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[1] Note that the presence of a Fano-resonance reflects a certain degree of localization of the intermediate $5d^9 5f^{n+1}$-state, but should not be taken as an indication of a 5f-localization in the ground state.

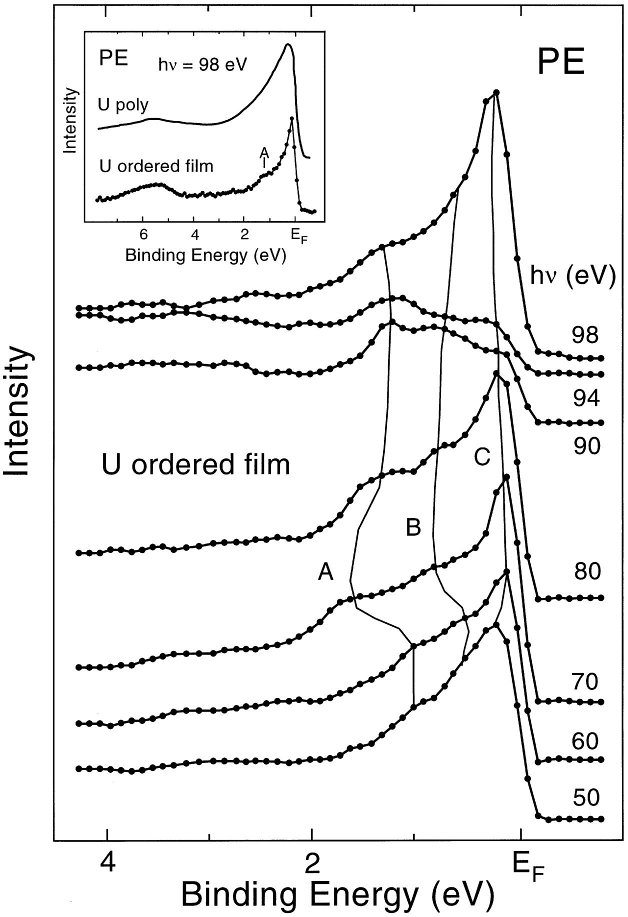

Fig. 1. Normal-emission PE spectra from an ordered film of U-metal taken in the binding energy region of the U 5f signal. The spectra were taken at various photon energies including the region of the 5d→5f Fano-resonance (off-resonance, $h\nu=94$ eV; on-resonance, $h\nu=98$ eV). In the inset, a PE spectrum of the ordered film (solid line through experimental points) is compared to the one of a polycrystalline bulk sample (solid line) [9].

main spectral features A, B, and C are observed that reveal different dispersions and resonant enhancements. Particularly, structures, which show larger dispersion, resonate to a less extent and vice versa [22]. In Fig. 2(a), the experimentally observed dispersions are compared to results of band-structure calculations for a hypothetic hcp-phase of U-metal. An excellent agreement between the calculated bands and PE data is obtained indicating the validity of the bandlike description of the 5f states.

Analysis of the angular-momentum character of the electron states along the $\Gamma$-A direction shows that in the four branches within the first 2 eV below $E_F$, the f admixture is always larger than 75%. This indicates that the different resonant enhancements of the individual branches do not reflect variations of 5f character as might be assumed in a naive picture of resonant PE.

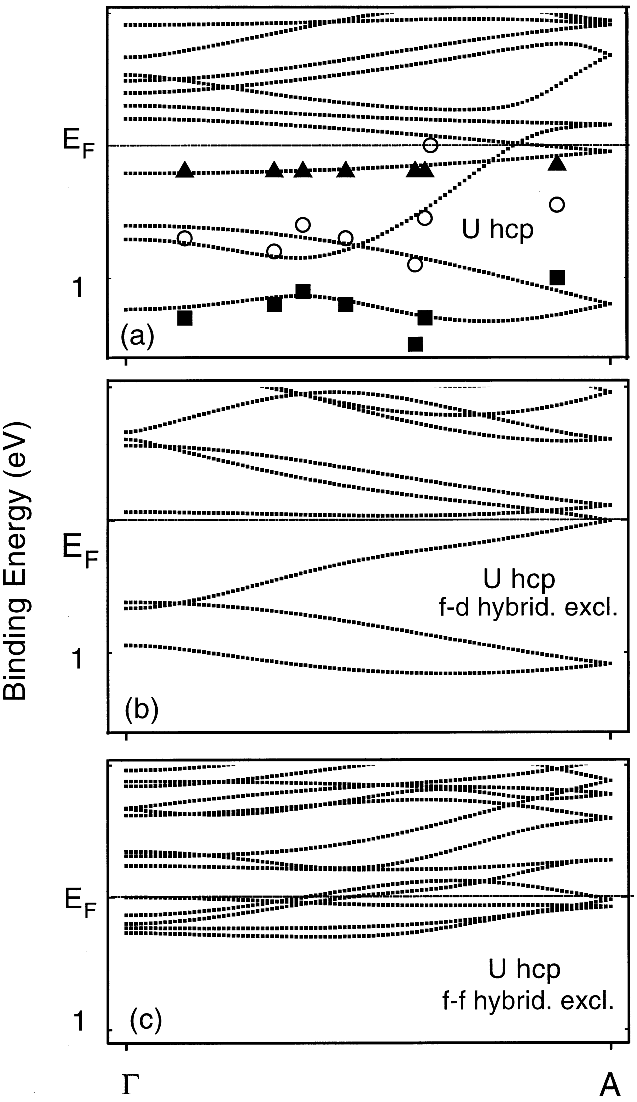

Fig. 2. (a): Calculated bands along the $\Gamma$-A direction for hcp U-metal. (b) and (c): Results of model calculations with excluded f–d and f–f hybridization, respectively. In (a), the theoretical results are compared with the experimental data. Squares, circles, and triangles denote data related to features A, B, and C, respectively, which are shown in Fig. 1.

This fact has severe consequences to the evaluation of resonant PE data: Usually, 4f or 5f contributions to PE spectra are experimentally determined by taking the difference between on- and off-resonance spectra. Applied to uranium metal, this method leads to serious mistakes since the difference spectrum is dominated by the Fermi-level peak, while the contribution from the bands at higher BEs becomes suppressed. We suppose that symmetry properties like different admixtures of $5f_{7/2}$ and $5f_{5/2}$ configurations, are responsible for the observed differences in the resonant behaviour of the U 5f states.

To test whether the observed dispersive behaviour is caused by direct f–f-overlap or by f–d hybridization, model band-structure calculations with artificially excluded f–d or f–f hybridization were performed. As shown in Fig. 2(b), the neglect of f–d hybridization leads only to a slight shift of the occupied 5f bands toward $E_F$, without significant change of their dispersive character. In contrast, suppression of f–f hybridization changes drastically the calculated valence band structure [Fig. 2(c)] and leads to a reduction of the occupied 5f bandwidth to 0.3 eV. The results show that direct f–f-overlap and not f–d hybridization are the main reason for the band-like properties of the U 5f states.

For the Ce-Rh system, analysis of PE data are complicated by a strong superposition of Ce 4f- and Rh 4d-derived features. Resonant PE can be used to discriminate between the different contributions. Fig. 3(a) shows on- and off-resonance spectra taken at the Ce 4d→4f Fano-resonance. The spectra were normalized to photon flux. The on-resonance spectrum ($h\nu=121$ eV) is dominated by 4f emissions revealing the characteristic double-peaked structure of strongly hybridized Ce-systems. The off-resonance spectrum ($h\nu=112$ eV) reflects valence-band contributions, that are characterized by much weaker intensities as compared to the resonantly enhanced 4f signal. The difference between on- and off-resonance PE spectra was taken as the pure 4f contribution to the on-resonance data. As we have seen in the case of uranium, however, f-derived features may reveal distinct resonant behaviour [23]. Furthermore, valence-band states may also become resonantly enhanced and may contribute more strongly to the on-resonance spectra than expected from the off-resonance data [24].

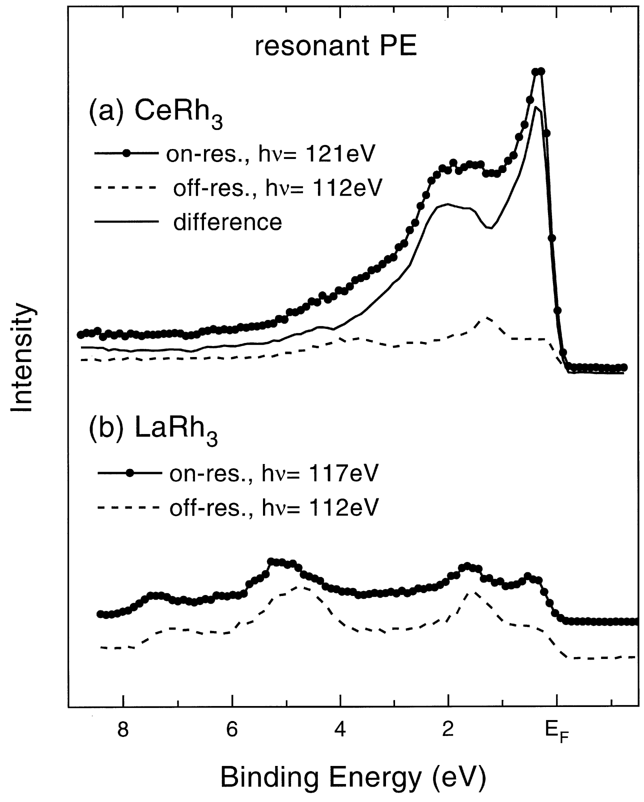

Fig. 3. (a) Comparison of on-resonance (dots) and off-resonance (dashed line) PE spectra of $CeRh_3$. The difference spectrum is shown by a solid line. (b) Comparison of the on-resonance (dots) and off-resonance (dashed line) PE spectra of $LaRh_3$.

In order to account for the latter restriction, angle-resolved PE data from an ordered $LaRh_3$ film were taken on and off 4d→4f resonance at 117-eV and 112-eV photon energy, respectively [Fig. 3(b)]. As for the Ce-Rh system, the data were taken in normal emission geometry and normalized to photon flux. Apart from the occupied 4f states, the system is isoelectronic to the Ce compound. Shape and intensity of both spectra in Fig. 3(b) are very similar to the off-resonance spectrum of $CeRh_3$. In contrast to La metal, where strong resonant cross-section variations have been observed [24], the presence of the 4d→4f Fano-resonance has almost no consequences on the valence-band emission of the La-compound indicating that the valence-band charge density is mainly localized at the Rh sites. On the basis of this result one may conclude, that in the case of $CeRh_3$, the difference between the on- and off-resonance spectra represents in fact the pure 4f contribution. Since dehybridization occurs for Ce atoms in the outermost atomic surface layer, the peak at 2 eV is predominantly due to a surface emission [5,14]. The bulk spectrum consists, thus, basically of only one peak at the Fermi-level. Within a band picture, this peak reflects the f-admixtures to the valence band and should reveal dispersive properties. Fig. 4 shows angle-resolved PE spectra in the Fermi-energy region taken on-resonance at different polar angles. Vertical solid lines serve as guides-to-the-eye to identify limits of energy shifts of the Fermi-level peak. In fact, weak energy shifts in the order of 50 meV are observed, that might be assigned to 4f dispersion. The inset shows a comparison of the experimentally observed dispersion of the Fermi-level peak with energy bands calculated along a straight line through the k-space parallel to the high-symmetry line $\overline{\Gamma R}$ but shifted with respect to the latter by a fixed amount of $k_\perp$ in $\overline{\Gamma M}$ direction. The actual value of $k_\perp$ was estimated assuming a nearly-free electron final state characterized by a parabolic dispersion curve, that was fitted to the s-like band forming the bottom of the valence band. In the figure, several weakly dispersive bands can be seen, from which only the two branches at lowest binding energy reveal f-admixtures of 10–15%, while the f-character of the bands at higher binding energy amounts to less than 5%. Since the resonant PE intensity will be related to the square of the f-admixture [22], a single peak close to $E_F$ is expected from the band-structure calculation, that is shifted by about 0.3 eV to higher binding energy with respect to the experimentally observed feature. This energy shift, however, should not be taken too seriously, since this shift may simply be due to an error in the determination of $k_\perp$ introduced by a possible energy dependence of the electron effective mass and, therefore, by variations of the curvature of the assumed nearly free electron parabola. More important is that the expected

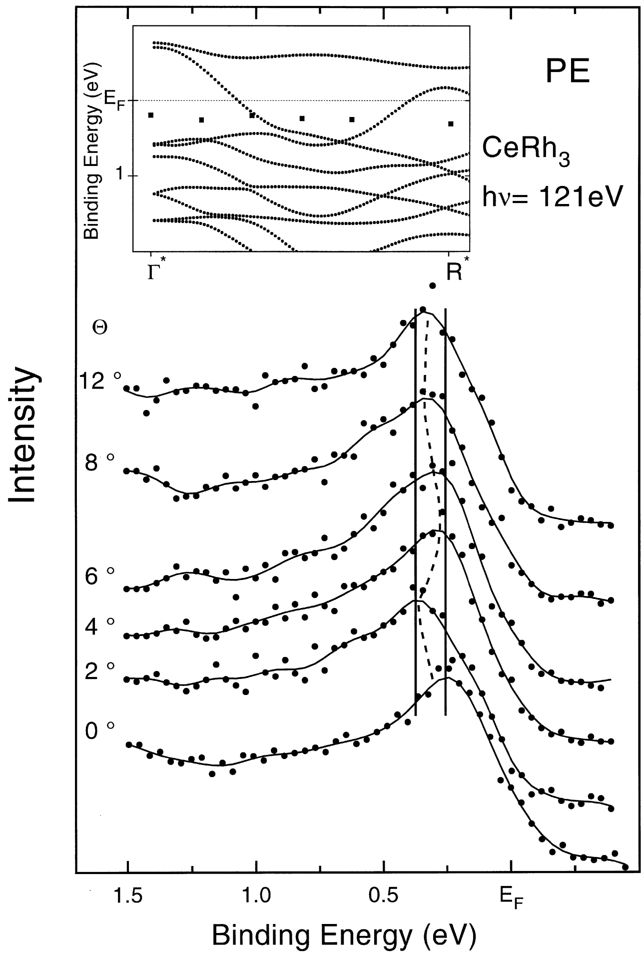

Fig. 4. Angle-resolved resonant PE spectra in the Fermi-energy region of $CeRh_3$ taken at different emission angles. The dotted line connecting the spectra serves as a guide-to-the-eye to indicate dispersion effects. The inset compares the experimental data (solid squares) with results of a band-structure calculation along a circle between *Γ*R** and points within the *ΓR* plane, where *Γ** lies at 40% of the *Γ-R* direction and *R** is the projection of the high-symmetry point *R* onto a circle through the *Γ** point (in the *Γ*-X direction). This circle corresponds to the Brillouin zone area sampled in the present PE experiment assuming free-electron final states.

dispersion of the peak is of the same order as the one observed in the experiment, a fact that supports an interpretation of the spectra in terms of LDA.

In summary, we have shown that the f states of uranium metal reveal a dispersive behaviour, 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 d orbitals as expected for the Ce 4f states in $CeRh_3$, where experimentally observed energy shifts of the order of 50 meV might also be attributed to f dispersion.

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