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UNDERSTANDING PHOTOEMISSION SPECTRA IN URANIUM BASED
HEAVY FERMION SYSTEMS*

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INTRODUCTION

For some time now spectroscopists have been puzzled by the lack of correspondence between Ce-based and U-based heavy fermion (HF) photoemission spectroscopy (PES). In 4f systems (most 4f compounds, not just HF) one generally observes a "two-peaked" structure¹ associated with 4f PES, while most (again not just HF) 5f compounds yield a single broad triangular-shaped 5f intensity.^{2,3} Since there is substantial correspondence in bulk property data (such as specific heat) between 4f and 5f HF systems,⁴ it was a cause of some concern that PES failed to show this correspondence. Indeed it was difficult to understand how the very large overall widths of 5f spectra can be reconciled with features expected to be at least an order of magnitude narrower.

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Cerium spectra are generally interpreted in terms the Kondo model.⁵ Gunnarsson and Schönhammer⁶ have used the ideas employed in the Anderson⁷ single magnetic impurity model and calculated the expected particle-hole excitation spectrum. Their results (and subsequent refinements)⁸⁻¹³, indicate that the 4f-electron PES should yield a peak at ~ -2 eV due to the $4f^{1+}4f^0$ transition screened by conduction d-electrons (sometimes referred to as the "main peak"), a sharp Kondo resonance at (or just above) E_F , and a sideband split off from the Kondo resonance by Δ_{SO} , the spin orbit energy. Spectra consistent with the above description have been observed in α - and γ -cerium,¹⁴ while in HF systems supposedly only the sideband is seen since the Kondo resonance itself^{1,9,10} is unobservable for $T_K \sim 10$ K.

In U-based HF's, the situation is more complex. While sharp features superimposed on a generally broad background have actually been observed¹⁵ precisely at E_F , their FWHM's (~ 150 meV) are much too large, and the intensity much too high, to be associated with a Kondo resonance that has a $T_K \sim 10$ K. The sideband interpretation for the sharp peak is also ruled out owing to its position precisely at E_F . Ignoring for the moment the broad overall width of 5f spectra, the most plausible explanation of the PES data of ref. 15 is that the sharp features at E_F represent the band structure ground state. Indeed the recent observation¹⁶ of the dHvA effect in HF systems, in agreement with band structure calculations, supports the notion that the band model cannot be ignored. A modified band structure approach¹⁷ can, of course, also explain the Ce data. Here the "main peak" has the same interpretation as in the Kondo model while the peak at E_F is attributed to f-screening which may reproduce the original ground state.¹⁸

Previous work in well-hybridized 5f systems (URh_3 , UIr_3 , UGe_3) has demonstrated¹⁹ that both the dHvA data and PES are in complete agreement with the calculated band structure. Fig. 1a shows the 5f spectrum obtained at resonance²⁰ (see below) in UIr_3 superimposed on a calculated spectrum obtained by appropriately broadening the 5f DOS (all spectra normalized at E_F). The measured 5f intensity at energies below E_F is substantially smaller than the predicted intensity owing to the 5f transition cross-

Fig. 1 Comparison of calculated and experimentally derived 5f PES intensities in a) UIr_3 and b) UBe_{13} . Note that the calculated intensity is underestimated in b) and over estimates in a).

section which is decreasing monotonically below E_F (Boring²¹ et al.) By convoluting the theoretical spectrum with this energy-dependent cross-section $\sigma(E)$, one reproduces the experimental PES spectrum almost exactly.

By contrast, in HF systems, a simple broadened 5f DOS from a band calculation utterly fails to reproduce the experimental spectra. This is amply demonstrated in Fig. 1b where the measured 5f PES intensity below E_F is now substantially larger than the calculated value. Convolution with $\sigma(E)$ will still further exaggerated the disagreement. This extra intensity was first pointed out by Allen et al.² who attributed it to Coulomb correlation. It has been used as proof of the failure of band theory in HF systems.

In this paper, however, we will provide evidence from a series of systematic measurements on ternary alloys to show that at least part of the extra 5f intensity is due to the hitherto missing "main peak" (or d-screened f-hole peak) just as in the 4f systems. We will choose to call this peak a 5f satellite. We will show that the remaining intensity is consistent with a band structure DOS. The failure to recognize the satellite previously is due to its broad nature and proximity to E_F . Thus the fundamental difference between 4f and 5f spectra is eliminated.

EXPERIMENTAL DETAILS

Most of the measurements reported here were done on the newly commissioned U2 beamline at NSLS in Brookhaven National Laboratory using an ERG monochromator. The overall instrument resolution at $h\nu \sim 100\text{eV}$ was $\sim 250\text{meV}$. Samples were made by arc-melting the constituent materials several times and heat-treating the buttons at 1000°C under argon atmosphere for ~ 3 days. X-ray powder patterns confirmed the single-phase nature of each sample. Electropolished parallelepipeds ($\sim 3\text{ mm} \times 3\text{ mm} \times 8\text{mm}$) were fractured in vacuum (base pressure $\sim 3 \times 10^{-11}$ torr) to expose a clean surface. All spectra were taken at photon energies of $h\nu=92\text{eV}$ (anti-resonance), 94eV , 99eV (first resonance) and 108eV (second resonance). Each sample surface was checked for oxygen contamination by also taking a spectrum at $h\nu=40\text{eV}$ where the oxygen 2p cross-section is substantially larger. No contamination was evident.

A spectrum representative of only 5f emission can in principle be obtained by subtracting the spectrum obtained at the anti-resonance ($h\nu=92\text{eV}$) where 5f emission is nearly zero,²² from a spectrum at the 5d to 5f Fano resonance ($h\nu=99\text{eV}$ or 108eV) where two separate channels contribute to a strong 5f intensity. The assumption is made that the cross-sections for the remaining features are not changing dramatically in this range, so that the spectrum for $h\nu=92\text{eV}$ is normalized to be equal to, or lower in intensity than the spectrum for $h\nu=99\text{eV}$ at all electron energies. In this paper the 5f intensities in the figures were obtained from such a subtraction.

It should be remembered that at the Fano resonance (99eV or 108eV) the U-6d intensity is enhanced along with the 5f intensity, but to a much lesser degree since the Auger process is merely Koster-Kronig type rather than super Koster-Kronig (all 3 electrons in the same principle quantum shell). It may occur then that the subtracted spectrum contains U-6d intensity as well. This is particularly important if the ligand atom has no d-electrons, as we will see below.

RESULTS AND DISCUSSION

The development of the final state satellite can be clearly seen in Figs. 2a and 2b. In Fig. 2a we show 5f spectra obtained at resonance for

Fig. 2 a) 5f intensity obtained at resonance for URh_3B_x , with UIr_3 substituted for the case $x=0$. Note the intensifying shoulder at ≈ -1 eV. b) 5f intensity for $\text{UPd}_x\text{Rh}_{3-x}$. The difference curve is a subtraction of the UPdRh_2 spectrum from the UPd_2Rh spectrum. Note the double 5f peak in the inset for $\text{UPd}_{1.5}\text{Pt}_{1.5}$.

the system URh_3B_x where x ranges from 0.4 to 1. (Data for $x=0$ was obtained on a system with substantially poorer resolution. Instead we show the spectrum for isoelectronic UIr_3 which has a 5f DOS similar to URh_3 .) Note that for UIr_3 (and URh_3) there exist two strong 5f peaks in the spectrum, both of which are completely understood within a band structure picture¹⁹ (see introduction). The peak at -2.5 eV which can only be understood within a hybridized band picture represents the f-d bonding band. We will hence call this the bonding peak. Boron added to URh_3 (boron sits in the center of the AuCu_3 lattice) has the effect of decreasing f-d hybridization first by expanding the lattice and second by competing with uranium for the filling of the Rh d-band.²³ Experimentally this is evidenced in Fig. 2a by a decrease in the bonding peak intensity as x increases. Band structure calculations²³ are totally consistent with this picture. We wish to point out that the URh_3B_x system does not obtain the heavy fermion type renormalizations which result in a temperature-dependent electronic specific heat term.²⁴ It remains a narrow band system even for $x=1$ albeit with a DOS increasing with x . However, one can see in Fig. 2a that even as the bonding peak is decreasing in accordance with band calculations, the structure at E_F is broadening and developing a shoulder at -1 eV. This latter feature is not expected from the calculated DOS nor is it indicated from bulk property measurements which instead point to a continuous narrowing of the 5f band with x . We believe that this shoulder represents a developing final state photoemission satellite at ≈ -1 eV which increases in intensity as the 5f band becomes narrower. We suggest that the satellite is a result of the localization on the uranium site due to the perturbation caused by the removal of an f-electron and the subsequent incomplete d-screening. A repopulation of the f-hole, on the other hand, on a time scale consistent with photoemission may closely approximate the ground state. The peak at E_F may represent this f-screened state. This is similar to the interpretation of the Ni data.²⁵

Similar behavior is observed in Fig. 2b in the system $\text{UPd}_x\text{Rh}_{3-x}$. Substitution of Pd (with a filled 4d band) for Rh again results in a decrease of f-d hybridization and hence the bonding peak at -2.5eV . For $x=1$ we already see a clear development of the shoulder at -1eV while the bonding peak still has substantial intensity. For $x=2$ (a heavy fermion system based on bulk property measurements)²⁶ the 5f spectrum gains considerable width over that of $x=1$. By subtracting the two spectra (approximately normalized at E_F) we see that the difference between them (dotted curve) very much resembles the 5f spectrum of UPd_3 . In this latter case, where the 5f electrons are known to be completely localized,²⁷ only a single, broad, Lorentzian-shaped peak is observed, centered at $\approx 1.2\text{eV}$ below E_F , and presumably representing a d-screened f-hole. It would appear then that in the general case of itinerant 5f electrons the photoemission spectrum consists of a superposition of a d-screened satellite plus a spectrum entirely consistent with the band structure ground state.

The inset of Fig. 2b leaves no doubt that two peaks are indeed observed in some uranium systems. In $\text{UPd}_{1.5}\text{Pt}_{1.5}$ (x-ray data show that the material is single phase) the d-screened peak is of equal intensity with the f-screened peak and separated by almost 2eV thus making it easily observable and unambiguous. Furthermore, our overall resolution is sufficient to see that in this material the f-screened peak has its maximum slightly below E_F . This may yet prove illuminating in the understanding of localization vs. itinerancy.

A re-examination of those heavy fermion 5f photoemission spectra where band calculations are available reveals that in general these too can be described as a superposition of a band structure ground state plus a satellite. This is especially true for UPt_3 whose 5f intensity resembles that of URh_3B and UPd_2Rh . We will however focus our attention on UBe_{13} (see Fig. 1b) which appears to have a 5f spectrum that is broader than all other 5f systems (extending out to $\sim -6\text{eV}$). It appears to have intensity at higher binding energies that is not entirely accounted for by band structure and a satellite.

The problem in UBe_{13} (and U_2Zn_{17} , which shows similar behavior) is that uranium 6d electrons also resonate (to a lesser extent) with the 5f's. This is, of course, a general problem of f-electron resonant photoemission but one which is minimized in compounds where the ligand atom (Rh, Ir, Pd, Pt) has primarily d-electrons available for bonding. In these latter compounds the uranium 6d-electrons are strongly hybridized with the ligand d's so that the 6d DOS almost exactly mimics the ligand d-DOS. Since the 92 eV and 99 eV spectra are normalized on a d-like peak before subtracting, the 6d contribution (if any) gets normalized out for the most part. In addition, because of the strong hybridization, the 6d-resonance cross section is probably substantially diminished. Resonance is after all an atomic process. In UBe_{13} , however, the ligand DOS bears no resemblance to the 6d DOS. Hence the d-intensity is not normalized out in a subtraction and is the most likely cause of the long "5f" tail.

To test the above ideas we looked at isostructural ThBe_{13} where one enhances only 6d emission at resonance. Fig. 3 shows the resonance, anti-resonance and difference curves for ThBe_{13} . We make the reasonable assumption that the difference curve is representative of Th-6d emission only, and that a similar 6d spectrum is obtained for UBe_{13} . We further assume that at a binding energy of 5 eV, only d-intensity remains in the UBe_{13} difference spectrum. By normalizing the two subtracted spectra at -5eV , we can determine and eliminate the 6d contribution to the UBe_{13} difference spectrum (Fig. 4a) and finally obtain the intensity associated with 5f emission only. The result (in Fig. 4a) shows a remarkable

Fig. 3 EDC's obtained at resonance ($h\nu=102.5 \text{ eV}$) and anti-resonance ($h\nu=110 \text{ eV}$) for ThBe_{13} . The difference curve should represent 6d emission.

Fig. 4 a) Subtraction of the ThBe_{13} 6d spectrum (Fig. 3) from the UBe_{13} difference curve (containing 5f and 6d intensity) should result in 5f intensity only (dotted curve). b) Comparison of the above derived 5f intensity (solid curve) with a calculated 5f DOS (dashed curve). Dotted curve represents the difference between them.

resemblance to the 5f spectrum of UPt_3 including the small peak at -2.5 eV. If, in addition, we now subtract out the contribution expected from the band structure²¹ DOS (Fig. 4b), we find that the excess intensity is again a Lorentzian peak centered at ~ -0.8 eV, strongly resembling our satellite and the UPd_3 5f spectrum. Thus again it would appear that 5f PES in UBe_{13} can be described as a superposition of a band structure DOS plus a d-screened final state satellite.

It would appear that we finally have the long-sought correspondence (second peak and more) between 4f and 5f HF spectra. The problem now becomes one of interpretation. We have presented above an interpretation of 5f PES spectra. We suggest that the interpretation can be extended to 4f systems as well, meaning that 4f PES likewise represents d-screened and f-screened features. This does not extend, however, to a negation of the Kondo model in HF systems, but rather only to a proper interpretation of PES spectra. What we have shown is that band structure is important in 5f based HF's and that 5f intensity is found at E_F in the ground state even at room temperature. Any renormalization that occurs within this band structure on a temperature scale of 10K is unobservable with the presently available resolution. It may yet become possible to transform from one model to the other. We leave it to theorists to provide the link between the band picture and the Kondo picture.

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