Title:

The Electronic Structure of Heavy Fermions: Narrow
Temperature Independent Bands

Author(s):

A.J. Arko
J.J. Joyce
A.B. Andrews
J.L. Smith
E. Moshopoulou
Z. Fisk
M.B. Maple
A.A. Menovsky
P.C. Canfield

Submitted to:

Physica B
Proceedings of SCES'96
INVITED PAPER

RECEIVED

JUL 19 1996

OSTI

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The Electronic Structure of Heavy Fermions: Narrow Temperature Independent Bands^{†,††}

A.J. ARKO^a, J.J. JOYCE^a, A.B. ANDREWS^{a,*}, J. L. SMITH^a, E. MOSHOPOULOU^b, Z. FISK^b, M.B. MAPLE^c, A. A. MENOVSKY^d, AND P.C. CANFIELD^e

^a*Los Alamos National Lab., Los Alamos, NM 87545.*

^b*HFNML, Florida State Univ., Tallahassee, FL.*

^c*Dept. of Physics, University of California, San Diego, La Jolla, CA 92093.*

^d*Natuurkundig Laboratorium, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands.*

^e*Iowa State Univ./Ames Lab., Ames, Iowa.*

Abstract

The electronic structure of both Ce and U heavy fermions appears to consist of extremely narrow temperature independent bands. There is no evidence from photoemission for a collective phenomenon normally referred to as the Kondo resonance. In uranium compounds a small dispersion of the bands is easily measurable.

While U and Ce heavy fermions display nearly identical bulk properties¹, previous photoelectron spectroscopy (PES) on poly-crystalline specimens indicated possible fundamental differences since the 5f-density of states (DOS), as measured² from resonant PES, appeared to be much broader than the corresponding 4f DOS - indeed, much broader even than predicted by band calculations³. Further, while a typical Ce heavy fermion spectrum showed several features identified within a Kondo picture⁴ as (i) the "main" or f^0 peak at ≈ -2 eV, (ii) the KR, or $4f_{5/2}$, at E_F , and (iii) the Kondo sideband, or the $4f_{7/2}$, at ≈ -0.28 eV, a typical U spectrum measured at resonance in polycrystals showed² only a broad featureless triangular structure pinned at E_F . This led to the unsatisfactory situation whereby the single impurity model⁵ (SIM) is used to explain Ce compounds (but fails even there to explain photoemission as we have shown⁶⁻¹¹) while identical behavior in U compounds requires another, as yet undeveloped model. However, we show below that features entirely similar to the Ce- $4f_{5/2}$ are now found in uranium single crystal compounds as well, and that these features show measurable dispersion with momentum.

The fundamental assumption⁵ of SIM is that above the Kondo temperature (T_K) f-electrons are non-interacting impurities even in ordered compounds. Weak hybridization with ligand

conduction electrons leads to a collective singlet state below T_K which yields non-dispersive, strongly temperature dependent, narrow f-weight (i.e., the KR) at kT_K above E_F . Approximate solutions of SIM (i.e., GS¹² and NCA¹³) have formed the theoretical basis for heavy fermion PES. Their main predictions are: 1) The spectral weight of the KR scales with T_K ; 2) The KR is strongly renormalized with temperature, with only about half its $T = 0K$ spectral weight remaining at T_K ; 3) It is k-independent above the coherence temperature, $T_{coh} \ll T_K$. The model has been unsuccessful with U heavy fermions, but more importantly, the recent use of single crystals in Ce spectroscopy reveals⁶⁻¹¹ a temperature independent electronic structure, no scaling with T_K as required by SIM, and strong suggestions of band behavior even at elevated temperatures⁷, as described below.

ARPES measurements near the 4f or 5f resonance ($h\nu = 120$ or 110 eV) were done with resolution $\Delta E \approx 70$ meV at the Los Alamos beamline at the NSLS, or the AT&T Dragon beamline. High resolution spectra ($\Delta E < 45$ meV) at $h\nu < 40$ eV were done on the Argonne-Minnesota SEYA at SRC. Except where otherwise indicated, the measurements were done at $T = 20K$. Single crystal specimens were used in all cases except $CeAl_3$ and $CeSi_2$, while all measurements were done in the angle resolved mode (ARPES) with a $\pm 1^\circ$ aperture. All surfaces were prepared by cleaving crystals in-situ except for $CePt_{2+x}$ which was prepared⁷ by evaporating Ce onto Pt(111).

In Fig. 1 we show spectra at $h\nu = 120$ eV for several Ce heavy fermions with T_K 's ranging from ≈ 1 K to ≈ 400 K. One would be hard pressed to observe a pattern of scaling with T_K of the $4f_{5/2}$ - a necessary condition for a KR. Indeed the $4f_{5/2}$ intensity for $CeBe_{13}$ (100) ($T_K = 400K$) is smaller than it is for $CeAl_3$ ($T_K \approx 1$ K). $CeBe_{13}$ (110) and $CePt_{2+x}$ ($x \leq 1$) have similar intense $4f_{5/2}$ structure, but their T_K 's differ by more than a factor of 10. We have previously shown¹⁴ that invoking crystal field levels within GS theory does not destroy the scaling, nor does the inclusion of f^2 , i.e., the doubly occupied f-state. Further, there is no obvious difference in the PES spectra between non-magnetic, antiferromagnetic¹⁵ (e.g., $CeAl_2$) or ferromagnetic¹⁶ (e.g., $CeSb_2$) materials.

An essential prediction of NCA¹³ is the transfer of spectral weight from the KR to the f^0 peak with increasing temperature. Indeed, at $T = T_K$ the KR is predicted¹³ to be down to 50% of its $T = 0$ K intensity. In Fig. 2 we show the T-dependence of CeBe₁₃ (100) for a momentum near the [110] direction. Since $T_K = 400$ K there are no crystal field complications, thus within GS all the $4f_{5/2}$ intensity must be in the KR. In the figure the 20K spectrum was fit with a Lorentzian centered at 0.04 eV above E_F (simulating a KR) so that only its tail below E_F is occupied. Additionally, the $4f_{7/2}$ peak was simulated with a Gaussian, while a background was also included to produce the gray line through the 20K data. The dark lined curve superimposed on the 300K spectrum was then obtained from the 20K fit by decreasing the fitted KR amplitude by 50% and convoluting with a 300K Fermi function. It totally fails to reproduce the 300K spectrum. By contrast, a second fit of the 20K spectrum, using the same background and Gaussian for the $4f_{7/2}$, but now utilizing a fully occupied Lorentzian centered at -0.02 eV, exactly reproduced the 300K spectrum ("phonon fit" in Fig. 2) after simply broadening this 20K fit with 100 meV of simulated phonon broadening and convoluting with a 300K Fermi function. The KR fit *absolutely requires* a shift of the peak centroid toward E_F as the 300K Fermi function samples the intense KR above E_F , while the phonon fit results in a shift away from E_F , *as actually observed*. Thus there cannot be an intense feature just above E_F , nor is there any unconventional temperature dependence. Moreover, phonon broadening of a fully occupied state must be occurring.

There is also no unconventional temperature dependence in Yb compounds where NCA would place the KR on the occupied side of E_F . This is shown in Fig. 3 with ARPES data at the stated temperatures for YbAgCu₄ and YbCu₂Si₂ ($T_K \approx 35$ K for both). In the upper frame the spectra were normalized at the Cu-3d peak (not shown), while in the lower frame the YbCu₂Si₂ normalization was to the Si-2p states appearing at 100.5 eV kinetic energy due to second order light. We have previously shown¹⁷ that one never observes a T-dependence below 80 K. Some T-dependence exists¹⁸ in YbAl₃ which, however, is at most a 10% effect between 20K and 300K vs the predicted 50% effect, and is probably caused by a change in the mixed valence (hole occupancy $n_f \approx 0.65$, as determined¹⁸ from direct integration) due to lattice contraction. From the above one

can conclude that the near- E_F 4f features totally fail to reproduce the predicted behavior of the KR. Unlike a T-dependent KR situated above E_F , the features appear more like T-invariant fully occupied states whose spectral weight is independent of T_K .

Even more interestingly, the $4f_{5/2}$ displays amplitude modulations^{7,8} which are precisely periodic with the inverse lattice, as shown in Fig. 4 for CePt_{2+x} . This is highly suggestive of band states although actual dispersion, if any, is extremely small. Modulation due to photoelectron diffraction is ruled out because the $4f_{5/2}$ modulation occurs relative to the $4f_{7/2}$ feature whose ARPES cross section should have been identical. In the figure the spectra are labeled with letters which correspond to the indicated positions in the Brillouin zone where they were taken. A very important point to be made is that the spectra were taken at $T = 120 \text{ K} \approx 10T_K$. This further reinforces the temperature independent nature of the band-like $4f_{5/2}$ state.

Spectra very similar to those described above are found in U single crystal compounds as well. In Fig. 5 we show spectra taken at $h\nu = 110 \text{ eV}$ and 20 K for four heavy fermion compounds (UPt_3 , UBe_{13} , URu_2Si_2 and UPd_2Al_3) as well as antiferromagnetic USb_2 ($T_N \approx 200 \text{ K}$). Unless specifically shown in the figure, the k -direction is not known. A narrow feature exists in each material at E_F . From the data at anti-resonance ($h\nu = 92 \text{ eV}$, but not shown) and from the $h\nu$ -dependence of the peak intensity, we conclude that the near- E_F features are primarily of 5f character. Further, just as one finds 5d features in Ce compounds so also are there 6d features in U compounds as far as -3 eV binding energy (tic marks). These are unmistakable in UBe_{13} and USb_2 where there are no ligand d-electrons. Within 0.5 eV of E_F the 6d bands are likely strongly hybridized with 5f bands based on $h\nu$ -dependence, but space does not allow further elucidation.

In several U compounds (e.g., UPt_3 in Fig. 5) there occurs a strong 5f peak at $\approx -0.5 \text{ eV}$ at resonance (first pointed out¹⁹ by Grassman et al.). Oxygen dosing experiments suggest that it is primarily surface related. This may be the analogue of the famous -2 eV peak in Ce compounds which is likewise strongly surface related^{8,20}, although in weakly hybridized materials there may be an intensity component attributable to a bulk screening satellite²¹.

Just as in Ce compounds, the narrow near- E_F peaks display periodic amplitude modulation with momentum, but here an energy dispersion is also evident. For lack of space we will ignore the strongly dispersive 6d peaks. ARPES measurements were done at $h\nu < 40$ eV to maximize resolution ($\Delta E \approx 40$ meV, $\Delta k \approx 0.09 \text{ \AA}^{-1}$). In Fig. 6 we show UPt_3 (001) spectra taken at $h\nu = 30$ eV and 20 K for several analyzer settings relative to Γ or [001]. Note the large amplitude effect and about 20 meV of dispersion. Entirely similar spectra were also measured at $T = 80$ K, thus again demonstrating the lack of a temperature dependence. The intrinsic FWHM of the strong peak at Γ is ≈ 45 meV, or narrower than any $4f_{5/2}$ feature in Ce compounds.

Even stronger 5f dispersion and narrower FWHM's (< 30 meV) are observed in USb_2 as shown in Fig. 7 where spectra within 13° of Γ and within the first 100 meV of E_F are displayed. The amplitude normalization here is arbitrary (indeed, intensity at 3° is very weak), chosen primarily to make it easier to see dispersion (≈ 39 meV). The Fermi energy was determined from a reference Au specimen and was invariant for the analyzer settings in Figs. 6 and 7. A second band (probably 5f-6d hybridized, but not shown), disperses from E_F to ≈ -600 meV, while a satellite is not evident.

The data presented above strongly support a temperature invariant band nature of 5f states. Moreover, the similarity to 4f spectra suggests a similar 4f electronic structure, although actual dispersion of the $4f_{5/2}$ peak has not yet been observed, despite the observation of 100 meV of dispersion⁸ in the $4f_{7/2}$ peak in CeBe_{13} . One is forced to the conclusion that the single impurity model is inapplicable to ordered compounds at any temperature and we must use a form of the Anderson lattice which yields nearly the LDA bands but without a Kondo resonance. The conventional wisdom assumes²² that the Anderson lattice is only valid below the coherence temperature while at elevated temperatures it reverts to SIM. To the extent, then, that the above-formulated model results in a temperature dependent DOS, it too is inapplicable since we find no temperature effect. Moreover, it is simply not known whether it is extendible to uranium. A successful model will have to explain bulk property behavior in both 4f and 5f systems, while at the same time maintain temperature independent narrow bands in both, as seen in photoemission.

Whether the most common form of the Anderson lattice, renormalized band models^{23,24}, or related approaches²⁵ yield the necessary results remains to be seen. In the meantime the novel 2-electron band model of Sheng and Cooper²⁶, also based on the Anderson lattice but without the collective compensating electron cloud, in its early stages appears to contain all the necessary ingredients and certainly deserves consideration.

References

- † Work Supported by the US Department of Energy
- †† Part of work done at SRC which is supported by NSF under award #DMR-95-31009
- * Present address, Brookhaven National Lab., Upton NY, 11973.
- 1. G.R. Stewart, 1984, Rev. Mod. Phys. **56**, 755.
- 2. J.W. Allen, et al., Phys. Rev. Lett. **54**, 2635 (1985).
- 3. See, for example, R.C. Albers, et al., Phys. Rev. B **33**, 8116 (1986).
- 4. See, for example, F. Patthey, et al., Phys. Rev. B **35**, 5903 (1987).
- 5. See various articles in The Handbook on the Physics and Chemistry of the Rare-Earths, vol. 10, K.A. Gschneidner, Jr., L. Eyring and S. Hufner, editors (North Holland, Amsterdam, 1987).
- 6. J.J. Joyce, et al., Phys. Rev. Lett. **72**, 1774 (1994).
- 7. A.B. Andrews, et al., Phys. Rev. B **51**, Rapid Comm., 3277 (1995).
- 8. A.B. Andrews, et al., Phys. Rev. B **53**, 3317 (1996).
- 9. J.J. Joyce, et al., Phys. Rev. Lett. **68** 236 (1992).
- 10. A.J. Arko, et al., Phys. Rev. B **27**, 3955 (1983).
- 11. A.J. Arko, et al., Physica B **163**, 167 (1989).
- 12. O. Gunnarson and K. Schonhammer in Handbook on the Physics and Chemistry of Rare Earths, Vol. 10, edited by K.A. Gschneider, Jr. L. Eyring and S. Huffner, (Elsevier Publishers, Amsterdam), pp. 103-163, (1987).
- 13. N. E. Bickers, et al., Phys. Rev. B **36**, 2036 (1987).
- 14. J.J. Joyce and A.J. Arko, Phys. Rev. Lett. **70**, 1181 (1993).
- 15. F. Patthey, et al., Phys. Rev. B **35**, 5903 (1987).
- 16. A.B. Andrews, et al., Physica B **206-207**, 83 (1995).
- 18. A.B. Andrews, et al., Physica B **199&200**, 15 (1994).
- 17. R.I.R. Blyth, et al., Phys. Rev. B **48**, 9497 (1993).
- 19. A. Grassman, Physica B **163**, 547 (1990).
- 20. E. Weschke, et al., Phys. Rev. Lett. **69**, 1792 (1992).
- 21. M. R. Norman, et al., Phys. Rev. B **31**, 6251 (1985).
- 22. Z. Fisk, et al., Proc. Natl. Acad. Sci. USA, **92**, 6663 (1995).
- 23. Gertrud Zwicknagl, Advan. Phys. **41**, 203 (1992).
- 24. M.M. Steiner, et al., Phys. Rev. Lett. **72**, 2923 (1994).

25. S.H. Liu, in Handbook on the Physics and Chemistry of Rare Earths, Vol. 17, Ch. 111 (North Holland, Amsterdam, 1993) pp 87-148.
26. Q.G. Sheng, and B.R. Cooper, *Phil. Mag. Lett.* 72, 123 (1995).

Figure Captions

1. ARPES spectra at $h\nu = 120$ eV and $T = 20$ K (except for CePt_{2+x}) for 7 Ce heavy fermions. The intensity of the near- E_F features is relatively invariant with T_K , contrary to SIM.
2. CeBe_{13} (110) ARPES spectra at two temperatures. The fit at 20K was done with a Lorentzian above E_F simulating a Kondo resonance. The dark lined 300K fit was made by decreasing the KR intensity by 50% (see text). The phonon fit, described in Ref. 8, fits the data exactly, negating any NCA-derived temperature dependence.
3. PES spectra for YbAgCu_4 and YbCu_2Si_2 at the stated temperatures and photon energies. Any temperature effect is describable via conventional PES phenomena.
4. ARPES spectra at $h\nu = 120$ eV and $T = 120$ K for CePt_{2+x} at the indicated points in the Brillouin zone. Note the periodic intensity modulation of the $4f_{5/2}$ peak.
5. ARPES spectra at $T = 20$ K and $h\nu = 110$ eV for 5 uranium heavy fermions. Note the pervasive sharp peaks at E_F . Additional peaks (mostly 6d-bands) are marked by tic marks.
6. Expanded view of ARPES spectra at $h\nu = 30$ eV and $T = 20$ K for UPt_3 (001). The analyzer angle is relative to the Γ -point. Note the 20 meV of dispersion as well as the intense amplitude modulation.
7. Expanded view of ARPES spectra for USb_2 at $T = 20$ K and $h\nu = 35$ eV. About 39 meV of dispersion is evident. Amplitude normalization is arbitrary to facilitate viewing of dispersion.

Photoelectron Intensity (Arb. Units)

Photoelectron Intensity (Arb. Units)

$h\nu = 110 \text{ eV}$

$T = 20 \text{ K}$

URu₂Si₂

UPd₂Al₃

USb₂ (001)

UBe₁₃

UPt₃ (001)

-4

-3

-2

-1

0

Binding Energy (eV)