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4f Heavy Fermion Photoelectron Spectra Do Not exhibit the Kondo Scale[†]

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It has been our contention for some time that the Single Impurity Anderson Model (SIAM), as extended by Gunnarsson and Schonhammer¹ (GS), or the non-crossing approximation² (NCA), does not correctly describe the 4f photoelectron spectra of heavy fermions. Recently we have concentrated on Yb heavy fermions³ since in these materials the Kondo resonance (KR) is fully occupied and thus accessible via photoemission. In particular, we have repeatedly pointed out that the width, position, spectral weight, lineshape, and temperature dependence of the features assumed to be the KR and its sidebands, are nearly independent of the Kondo temperature, T_K , while at the same time bearing a striking resemblance to the simple 4f core level spectra of pure Yb metal, or of Lu in isostructural Lu compounds. It is important to resolve these issues in view of the fundamental nature of the problem.

However, considerable discrepancy exists between the reports of various research groups. In particular, Malterre et al.⁴ and Tjeng et al.⁵ claim to find nearly perfect agreement with GS in their measurements on polycrystalline samples of YbAgCu₄ and YbAl₃ respectively, while our own measurements³ on the same materials (single crystal in the case of YbAl₃), as usual, indicate very poor agreement. To be sure, Malterre et al. do finally concede that the width and position of their KR is wrong (actually, identical to our findings) but they invoke final state effects for the discrepancy. Tjeng et al., on the other hand, find agreement with GS in all aspects in their YbAl₃ results, a finding most likely related to their judicious choice of a high- T_K material so that the width and position of the KR are fortuitously nearly correct to start with, while the remaining discrepancies are alleviated by an unphysical choice of background in a spectrum which contained up to 80% surface features.

To complicate matters further, in a recent paper⁶ on the L_{III} edge XAS in Yb heavy fermions, Lawrence et al. find reasonable systematics between T_K and the hole occupancy, n_f , defined as $W_{13}/(W_{13}+(13/14)W_{14})$, where W_{13} and W_{14} are the integrated spectral weights of

the trivalent and divalent portions of the 4f signal. Indeed, our own XAS experiments in Ce compounds⁷ using total yield photoelectron spectroscopy, indicate that the n_f obtained in that fashion (assuming that the features can be thusly interpreted) bears some resemblance to values expected from GS and NCA, except that the expected temperature dependence is non-existent. By contrast, the n_f values obtained by direct integration of the photoelectron spectrum, to obtain W_{13} and W_{14} , yield very small n_f 's with W_{14} values up to an order of magnitude too large.

Ignoring the lack of temperature dependence in our XAS data for now, it was natural to conclude by GS proponents that the deeper probing XAS experiments are measuring the true bulk, while the surface sensitive ultraviolet photoelectron spectra (UPS) are probing a surface or subsurface layer whose n_f and T_K differ substantially from the bulk. This, of course does not address the question of how it is, if the above is true, that the even more surface sensitive scraped poly-crystal measurements of Refs. [4,5] managed to obtain any agreement with GS at all, particularly the measurements of [4] which were done at the extremely surface sensitive photon energy of 40 eV. We, of course, believe that indeed most of what [4] and [5] measured was strongly influenced by the surface, and any agreement with GS is purely fortuitous, coming about from the many degrees of freedom allowed in the GS and NCA codes.

Nonetheless we chose to test the bulk vs. surface hypothesis by performing measurements on YbCu_2Si_2 and YbAl_3 single crystals at $h\nu \approx 120$ eV (UPS) and $h\nu \approx 1500$ eV (XPS) to see if the n_f values increase markedly at XPS energies as the electron escape depth increases by about a factor of 3-5. Measurements were performed at both 300K and 20K using single crystals cleaved in-situ, with photoelectrons collected in normal emission for maximum bulk sensitivity. UPS measurements were performed at NSLS and the Univ. of Wisconsin SRC at a resolution $\Delta E \approx 100$ meV, while XPS measurements were done at the Univ. of Minnesota with $\Delta E \approx 400$ meV.

Fig. 1 shows rather typical UPS spectra at 20K and 300K for YbCu_2Si_2 ($T_K \approx 35$ K) and YbAl_3 ($T_K \approx 300$ K). The raw YbCu_2Si_2 data in the top frame have been normalized to the photon flux, with the Si-2p states from higher order light just above the valence bands used as confirmation of the normalization. The middle frame shows the same data but with the secondary

background, surface states, and Cu-3d states subtracted off for clarity. The bottom frame shows similarly subtracted data, but now for YbAl₃. Note that in each case the temperature dependence of the divalent signal is somewhere between 10% and 15%, substantially lower than the 50% expected for both materials in this temperature range. Actually, the sample to sample variations in the temperature dependence are enormous, being as low as 0% but very rarely higher than 15%. Such temperature changes are often seen even in non-4f spectra and we thus cannot assign it to the Kondo effect without corroborating agreements with predictions. Direct integration of the divalent and trivalent spectral weights yields n_f values between 0.6 and 0.65 for both materials, values consistent with previous reports of the data of Oh et al.⁸ for YbAl₃, but totally inconsistent with the 0.77 of Tjeng et al. in Ref. x, and Lawrence et al. The discrepancy is even greater in YbCu₂Si₂ where Lawrence et al. obtain $n_f=0.85$, which translates into a ratio, $R=(W_{13}/W_{14})$, of the divalent to trivalent spectral weights of 6 versus our value of less than 2.

Since it is clear that UPS and L_{III} edge measurements are in fundamental disagreement, we measured the valence band spectra of the two materials at the much deeper probing XPS photon energies to determine if a sub-surface layer (the surface itself yields the obvious surface states) with a significantly larger T_K is responsible for the UPS results. The data are shown in Fig. 2 for YbCu₂Si₂ at 20K. The bottom frame shows a superposition of UPS and XPS spectra to emphasize the similarities. Note, however, that the surface states in the XPS spectrum form a very small percentage of the total signal ($\approx 10\%$) so that we are indeed probing much deeper (see decomposition of spectrum in upper frame). Integration of the 4f signal to determine W_{13} and W_{14} again results in values of n_f somewhere between 0.6 and 0.65, depending on the exact method used to subtract the background. Temperature dependences up to about 15% are also observed although the results are somewhat obscured by the point-to-point variation on the sample surface when using the 150 micron photon beam. Thus it is demonstrated that a factor of 3 to 5 in penetration depth does not yield results different from UPS, and we are measuring bulk.

At the present time we do not have an explanation for the discrepancy between L_{III} edge X-ray absorption and photoemission, although we can say unequivocally that photoemission

does not measure the low temperature scale, and that the escape depth is not an issue. We are looking into three possibilities: 1) The LIII edge studies are correct and photoemission suffers from a shake-down satellite which obscures the W_{13}/W_{14} ratio, R; or 2) Photoemission measures the true bulk 4f intensity and it is the edge studies which suffer from satellite problems (In this case there is a fundamental problem with the GS model); or 3) Both measurements are obscured by satellites. Since the GS model makes numerous approximations it is not surprising if an interaction (e.g., U_{fd}) that was ignored could yet prove to be important. However, shake-down satellites, while possible, are a much less frequent occurrence in photoelectron spectra, since their existence requires that the final state is the lower energy state. Thus if the divalent state is preferred in the final state, why doesn't it exist in the ground state to begin with? For this reason it is easier to postulate the existence of shake-up satellites, but it will require a complete calculation to settle this point.

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Figure Captions

Fig.1 UPS data for CeCu_2Si_2 ($T_K=35\text{K}$) and YbAl_3 ($T_K=400\text{K}$) taken at 80 K and 300 . a) Raw CeCu_2Si_2 data normalized to photon flux. The Si-2p feature above the Fermi energy is from 2nd order light. b) Same data as in (a) but with background, Si-2p, and Cu-3d subtracted. Note the mere 10% change in divalent 4f intensity with T. c) YbAl_3 data with same subtractions as in (b). The Al-2p feature is due to 3d order light.

Fig. 2 **Top Frame:** XPS valence band data for CeCu_2Si_2 , decomposed into various components. Note that surface states comprise only 10% of near- E_F intensity. **Bottom Frame:** Same XPS spectrum as above, but now superimposed on a UPS spectrum of CeCu_2Si_2 . Note the larger surface to bulk ratio in UPS data, but otherwise all 4f features are identical to XPS.

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