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Temperature-invariant valence-band $4f$ photoemission features in the heavy-fermion compound YbAl_3

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A high-resolution photoemission (PES) study of the heavy-fermion compound YbAl_3 has been undertaken to test the qualitative and quantitative predictions of the single-impurity model. Corroborating data on YbAgCu_4 and YbCu_2Si_2 are also presented. For Yb-based heavy fermions the model predicts a fully occupied Kondo resonance so that its width, intensity, and temperature dependence should be directly accessible by PES. Due to the existence of temperature- and/or contamination-dependent surface features, which are not dealt with by the model, a rigorous normalization and curve-fitting procedure was required to extract the bulk $4f$ line shape. For the particular temperature cycling method employed by us, we do not observe any temperature dependence in the peak that had been previously identified as the Kondo resonance. We find that both the binding energy and width of this peak are significantly larger than theory predicts. It is also found that the trends in $4f$ line shape and surface shift between YbAl_3 and LuAl_3 are consistent with the trends seen between the $4f$ core levels of elemental Yb and Lu. Similar results are also found in YbCu_2Si_2 and YbAgCu_4 for similar cycling methods. Recent observations of temperature dependence in these systems are most easily understood in terms of surface phenomena.

I. INTRODUCTION

The single-impurity Anderson model for the behavior of heavy-fermion systems has proven very successful in describing the bulk, low-energy properties of these materials. Extensions to photoemission spectroscopy (PES), notably the Gunnarsson-Schonhammer (GS) calculation of spectral weights from the Anderson model¹⁻³ and the similar noncrossing approximation⁴ (NCA) have, until recently, been thought equally successful in reproducing heavy-fermion spectra.^{5,6} Although the qualitative agreement between Kondo theory and the experimental results might be considered by some as reasonable, we have lately shown that there are serious discrepancies between the specific quantitative, and some of the qualitative, predictions of the theory, and high-resolution photoemission data.⁷⁻¹⁰ In particular, the trends and functional dependences on the Kondo temperature (T_K) are generally not realized, even though fitting a single spectrum from any one material at one temperature might be successfully accomplished by allowing parameters, such as T_K , to vary.

Central to the Anderson model is the existence of the Kondo resonance (KR), a feature whose intensity and line shape in photoemission spectra are dictated by the T_K of the particular material. The particle excitation spectrum is predicted to consist of a deeper lying, d -screened f^0 state, together with the KR and its sidebands near the Fermi level (E_F). The Kondo interpretation of

the near- E_F region of a Yb heavy-fermion PES spectrum is shown schematically in Fig. 1. The basic component is the KR, of width $k_B T_K$, located an energy $k_B T_K$ below E_F . Spin-orbit (SO) splitting gives rise to a sideband which has its own Kondo temperature, $T_{K_{SO}}$. There will, in addition, be smaller crystal-field (CF) splittings of the KR giving rise to further sidebands, again with their own Kondo temperatures, $T_{K_{cf}}$. If these crystal-field splitting are small (say 10–30 meV, as is usually the case), their main effect on the unbroadened calculated spectrum is to

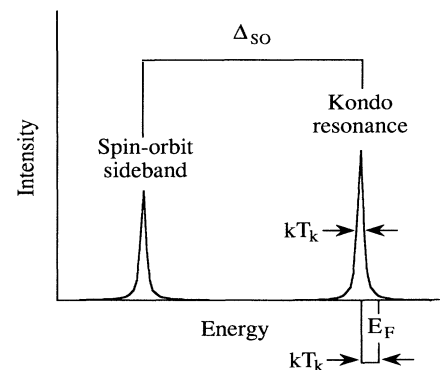


FIG. 1. Schematic diagram of the Kondo model interpretation of Yb heavy-fermion f^{14} photoemission spectra.

cause the KR to have an apparent width greater than kT_K . They have thus far not been resolved in a PES spectrum despite more than adequate resolution. The spectral weight of the KR is dependent on the T_K of the material, and the temperature at which the measurement is performed. Thus at constant temperature, systematic variation of the KR spectral weight should be seen between compounds with differing T_K , and for any given compound the KR spectral weights (and to a large degree the weights of the various sidebands as well) should decrease as temperature increases. For $T \gg T_K$ (or $T_{K_{SO}}$, $T_{K_{cf}}$) the KR (or the sidebands) should renormalize to zero; i.e., the KR should disappear.

In recent work^{7,9,10} it has been shown that for Ce compounds the spectral weight of the features previously regarded as KR related do not scale with T_K . In addition, the total peak width (i.e., including instrument and thermal broadening) is essentially constant (100–150 meV, depending somewhat on resolution) irrespective of T_K , and its intensity shows no temperature dependence above that accounted for by thermal and Fermi function broadenings. Ce heavy fermions are perhaps not ideally suited to such investigations, since the KR in Ce heavy fermions lies above E_F , and thus what should be observed in PES is only the tail of the KR, plus the SO and CF sidebands. While difficult to calculate explicitly, $T_{K_{SO}}$ and $T_{K_{cf}}$ are expected to be about a factor of 5 greater than T_K , and so the SO and CF sidebands should display appropriate temperature dependencies. It has nevertheless been argued that the lack of observed temperature dependence in Ce compounds, as well as the constant spectral weight, can be attributed to the SO and CF states. We have shown recently, however,¹¹ that effects of crystal-field states as well as double f occupancy due to a finite Coulomb correlation (U_{ff}) cannot explain this lack of dependence on T_K . The low-temperature scale has simply not been demonstrated in Ce systems.

Direct observation of the temperature dependence of the KR in CePd₃ and CeSi₂ using inverse photoemission [Bremmstrahlung isochromat spectroscopy (BIS)] has been claimed.^{12,13} The problem here is that the resolution attainable in BIS is inherently poor—of order 600 meV. This is one to two orders of magnitude larger than the energy scale involved. With such a disparity, quantitative analysis is impossible, and even qualitative analysis is not unique since, for example, an f band 500 meV wide and a KR 50 meV wide will be indistinguishable. The problems with the temperature-dependent BIS measurements thus are twofold. First, because of the poor resolution they cannot unambiguously determine that they are dealing with a Kondo resonance. Thus they cannot demonstrate that the observed temperature dependence is due to the impurity Hamiltonian, since several phenomena can result in a temperature dependence. Second, the inability to normalize on a temperature independent non- $4f$ feature in CeSi₂ precludes a direct comparison to the impurity model. In CePd₃ such a feature exists for normalization.¹² However, when normalized to the Pd $4d$ peak, most of the temperature dependence is found in

the f^2 peak at 4 eV and not in the KR. Indeed there is a net increase in the $4f$ spectral weight, not unlike what one might get with a buildup of CeO₂ on the surface at higher temperatures. The point here is that the mere observation of a temperature dependence is insufficient as proof of the model. Failure to observe any temperature dependence, however, brings the model into serious question.

From the above it should be clear that there is a considerable advantage to be gained by the study of Yb rather than Ce-based heavy fermions: The presence of the KR below E_F means that it is directly accessible to high-resolution PES experiments. (Needless to say, the same rule holds as above regarding the observation of any temperature dependence and proof of the impurity model.) Working with a material where the KR is fully occupied, and well separated from the SO sideband, we avoid the ambiguities associated with Ce compounds. In this paper we report a study of YbAl₃, a material for which observation of a KR has been claimed some time ago.^{14,15} A recent paper¹⁶ also claims to observe a temperature dependence in YbAl₃ which, according to their analysis, agrees with the impurity-model predictions.

The definition of a heavy fermion is rather loose, being generally regarded as a material in which the electronic contribution to the specific heat γ is 2–3 orders of magnitude greater than that of Cu ($\sim 1 \text{ mJ K}^{-2} \text{ mol}^{-1}$). In this respect YbAl₃, for which $\gamma = 45 \text{ mJ K}^{-2} \text{ mol}^{-1}$,¹⁷ is not a particularly heavy fermion, although it certainly falls into the regime for which Kondo theory is considered to be valid. YbAl₃ has a T_K of around 400 K,¹⁸ thus $k_B T_K = 36 \text{ meV}$. The existence of the CF levels is uncertain from inelastic neutron scattering,¹⁹ but if they exist, they fall within 10 meV of the quasielastic peak. Thus by the Kondo model, YbAl₃ should exhibit a KR $\sim 40 \text{ meV}$ below E_F , with a total width $< 50 \text{ meV}$.

In the early work on YbAl₃ the authors were unable to test the above predictions: In one case¹⁴ the experimental resolution was 260 meV and the authors were unable to accurately determine the Fermi energy or the natural linewidth, while in the other,¹⁵ it has recently been shown²⁰ that the sample used contained large fraction of the YbAl₂ phase. In neither case were temperature-dependent data presented. For YbAl₃ it is crucial to measure the temperature dependence (predicted to be large between 20 and 300 K) because the large theoretical width of the KR is only a factor of 2 smaller than the natural (deconvoluted) $4f$ linewidths usually observed in Yb heavy fermions. Thus width alone, while significant, is an inconclusive determinant of the Kondo model for this system. There have previously been no published calculations of temperature dependence explicitly for Yb heavy Fermions. GS theory is strictly valid only at $T=0$, and NCA calculations, valid at all temperatures, have only been performed for Ce systems. Recently, however, two as yet unpublished papers,²¹ claim to see a $4f$ temperature dependence in scraped polycrystalline YbAl₃ and YbAgCu₄. We will discuss these at length below, since our results, obtained in a slightly different fashion, appear at first glance to be in fundamental disagreement.

Some NCA calculations are presented in these recent papers.^{16,21} It turns out that a close approximation to the NCA predictions is to calculate the $T=0$ spectrum of a Yb material with $T_K=400$ K using GS theory, and then scale the resulting spectrum with temperature according to NCA results for a Ce system (see Fig. 34 in Ref. 4). For the GS calculation we used values for ground-state f energy (-0.75 eV) and spin-orbit splitting (1.29 eV) from Ref. 15. The hybridization width (0.0146 eV) was chosen to give the correct Kondo temperature. A flat band 10 eV wide was used, rather than an explicit (but still arbitrarily scaled) calculation, as this gives essentially the same result. Crystal-field effects were not included, as the CF states should be within the main resonance. The effect of the temperature scaling of the GS spectrum is shown in Fig. 2. (The spectra have been broadened by a Gaussian of width 60 meV, to simulate our experimental resolution, and cut off by an appropriate Fermi function.) This should not be regarded as a direct calculation of the theoretical temperature dependence, although it compares favorably with actual NCA calculations.¹⁶ From this estimate we suggest that it is reasonable to expect about a 10% intensity drop between liquid-helium (20 K) and liquid-nitrogen (80 K) temperatures, and a 50% drop between 80 K and room temperature (300 K). Indeed, the recent work^{16,21} for polycrystalline YbAl_3 and YbAgCu_4 shows apparent intensity decreases between 20 and 100 K similar to Fig. 2. The precise values are in any case not crucial, since we plan to demonstrate that no temperature dependence is observed when the sample surface is stabilized against temperature and/or contamination effects.

We also performed measurements on the non-heavy-fermion compound LuAl_3 , which adopts the same Cu_3Au crystal structure as YbAl_3 , with a very similar lattice parameter [at 20 K, $\text{LuAl}_3=4.178$ Å, $\text{YbAl}_3=4.191$ Å (Ref. 22)]. Since Lu metal has an f^{14} configuration the $4f$ levels in LuAl_3 are fully occupied core levels lying several eV below the Fermi level. Measurements on this compound thus allow a comparison to be made between spectral features in the KR region of YbAl_3 and $4f$ core levels. In addition, since the valence-band region in LuAl_3 is not obscured by $4f$ emission, some idea of the

valence-band line shape of YbAl_3 can be gained from that of LuAl_3 .

The bulk of the measurements in this paper deal with YbAl_3 . Only the final two figures (13 and 14) show YbCu_2Si_2 and YbAgCu_4 , respectively, as corroborating evidence for the temperature independence of the $4f$ features when samples are cleaved and measured at $T < \approx 100$ K.

II. EXPERIMENT

The YbAl_3 and YbCu_2Si_2 samples used were single crystals grown from fluxes.²² This is the only method that is known to produce YbAl_3 crystals without contamination from the YbAl_2 phase. Susceptibility measurements for the YbAl_3 samples were in good agreement with published results.²² The YbAgCu_4 sample was a polycrystalline rod cleaved *in situ*.

Photoemission experiments were performed using Los Alamos beamline U3C (Ref. 23) at the National Synchrotron Light Source at Brookhaven National Laboratory. The beamline endstation was a Vacuum Science Workshop (VSW) UHV chamber, with a base pressure of $\sim 10^{-10}$ mbar (in the absence of sample cooling). A goniometer mounted VSW HA50 hemispherical analyzer, fitted with a multichannel detection system, was used to acquire the photoelectron spectra. The overall energy resolution was determined by measuring the Fermi level of a gold film at liquid-helium temperature. This film was in electrical contact with the sample, enabling an accurate determination of the Fermi energy to be made. Spectra from YbAl_3 and LuAl_3 were taken at two different photon energies: 60 eV, with an overall energy resolution ≈ 60 meV, and 120 eV with a resolution of ≈ 95 meV. Temperature was controlled by placing the samples in direct thermal contact with a cryostat cooled by either liquid nitrogen or liquid helium. Clean surfaces were obtained by cleaving the single crystals *in situ*. The single phase nature of the resulting surface was confirmed by measuring the photoemission spectra of the Al $2p$ core levels: The presence of a significant amount of the YbAl_2 phase causes a chemical shift which tends to obscure the spin-orbit splitting.²⁴

III. RESULTS AND DISCUSSION

Photoemission spectra of the $4f$ and valence-band regions of YbAl_3 and LuAl_3 are shown in Fig. 3. The YbAl_3 spectrum clearly shows the presence of two groups of $4f$ features, which may be regarded as due to f^{13} - f^{12} transitions at binding energies > 5 eV, as well as the presumed KR related features close to E_F , which, for a mixed-valence material, may be regarded as due to f^{14} - f^{13} transitions. For convenience we will refer to these two groups as f^{13} and f^{14} peaks, respectively. The origin of the f^{13} peaks is uncontroversial: They are well explained in terms of f^{12} final-state multiplets calculated by the coefficients of fractional parentage.²⁵ Note that the f^{14} group consists of two well-resolved doublets, corresponding to bulk and surface Yb atoms, whereas only bulk f^{13} emission is observed. This indicates that, while

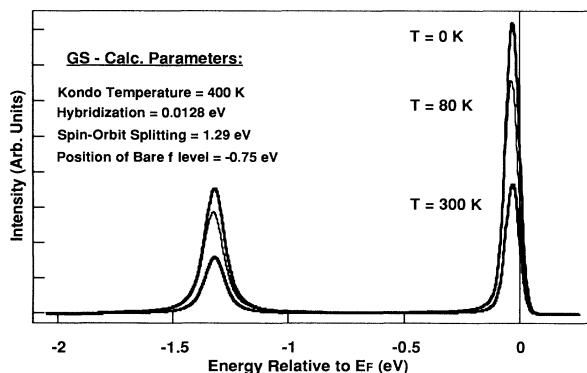


FIG. 2. Estimated theoretical temperature dependence of the features in Fig. 1. For details see text.

bulk YbAl_3 is a heavy fermion, its surface is predominantly divalent. Note also that the valence-band region of LuAl_3 is relatively featureless, which would suggest that the line shape of the f^{14} peaks in YbAl_3 is unlikely to be significantly affected by the underlying valence-band features. It is these f^{14} peaks, especially the bulk doublet, which are primarily of interest. In the other^{14–16} PES studies of YbAl_3 , the bulk f^{14} doublet was identified as the KR and its spin-orbit sideband. In LuAl_3 only an f_{14} group is seen, again consisting of well-resolved bulk and surface doublets.

In both compounds, but particularly for YbAl_3 , it can be seen that the bulk f^{14} doublet lies on a background consisting largely of the surface peaks. It follows that any perceived intensity change in the bulk peaks is likely to be a function not only of any *real* changes in bulk $4f$ intensity but also of any change in intensity and line shape of the underlying surface peaks. These peaks are likely to be significantly affected by contamination or surface reconstruction. Thus the bulk states can only be understood after a rigorous treatment of the surface states: In the following we describe the behavior of the surface peaks, and our fitting procedure. Such fitting is crucial in any determination of the temperature dependence (or lack thereof).

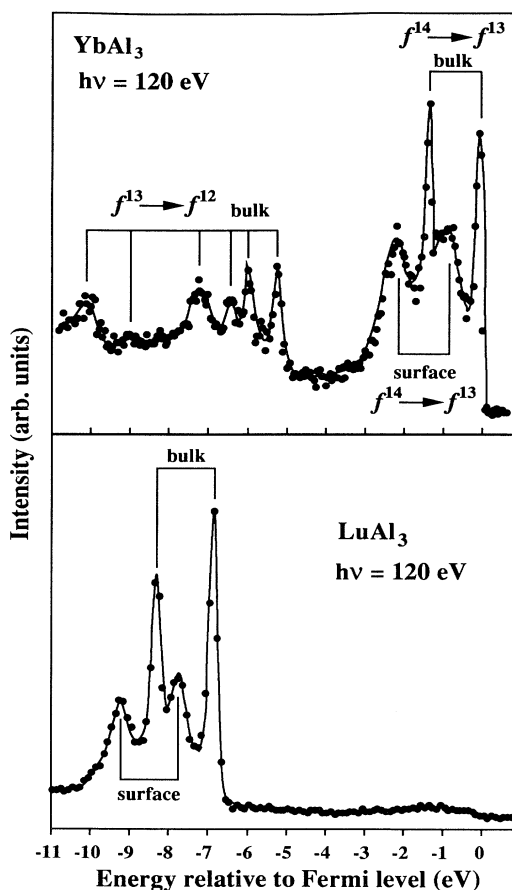


FIG. 3. Spectra of YbAl_3 and LuAl_3 . The solid line is intended only as a guide to the eye.

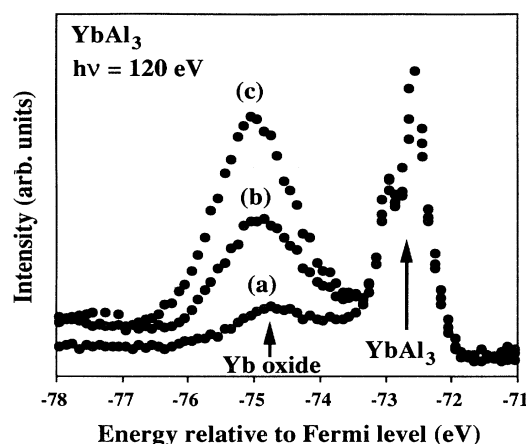


FIG. 4. Spectra of the Al $2p$ core levels in a YbAl_3 sample cleaved at room temperature in a vacuum of $\sim 10^{-10}$ Torr. Time after cleave: (a) 5 min, (b) 1 min, (c) 15 min.

We have found that at low temperatures the contamination rate is greatly slowed, but at room temperature contamination can be extremely rapid: Fig. 4 shows the growth of oxide on a YbAl_3 sample cleaved at room temperature. The effects of contamination on the f^{14} line shape are illustrated in Fig. 5. Note in particular how the initial effects are largely confined to the surface peaks, but significant contamination levels will tend to wipe out the bulk peaks. Given this tendency of contamination to reduce the intensity of the bulk f^{14} peaks, and the rapidity with which this can occur at room temperature, it follows that one way that an apparent temperature dependence of these peaks could occur would be as an artifact of contamination as the temperature is changed. We further note that the bulk/surface ratio is inevitably a function of the surface sensitivity of the measurement. Figure 6 shows the effect of changing the emission angle on the apparent bulk $4f$ intensity. As there is no guarantee that any two cleaves will occur parallel to each other, the effective emission angle is unlikely to be constant between

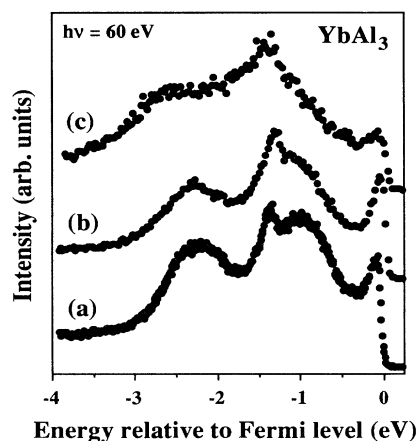


FIG. 5. Spectra of YbAl_3 , showing the effects of contamination on the $4f$ line shape. (a) as cleaved, $T=80$ K, (b) after 120 min in vacuum, (c) after warming to room temperature.

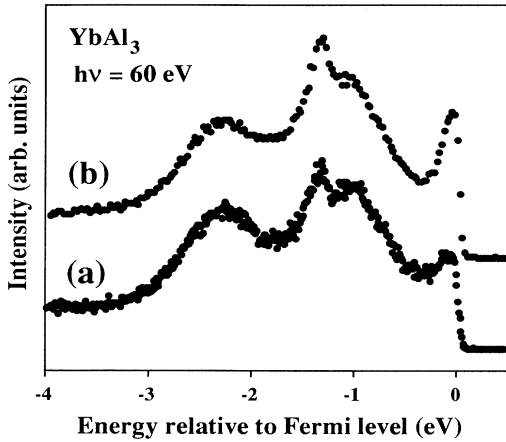


FIG. 6. Spectra of YbAl_3 taken at different emission angles. $T = 20$ K. (a) $\sim 45^\circ$ off normal, (b) \sim normal emission.

cleaves. Thus in any comparison of spectra taken at different temperatures, the spectra must be taken from the same cleave. The line shape of the surface-related peak is also likely to be affected by the surface structure. Although there has been no systematic study of heavy-fermion surface structure it is known that the surface peak line shape and binding energy in Yb is a function of the surface structure,²⁶ and several other rare-earth metals show temperature-dependent surface reconstructions.²⁷ It seems reasonable to suggest that the possibility of temperature-dependent surface structure on rare-earth compounds such as heavy fermions cannot be discounted.

In order to make meaningful quantitative comparisons between experiment and theory, it is necessary to employ curve fitting to extract the bulk linewidth and intensity, since the surface $4f$ line shape cannot be regarded as stable. It should be noted that this fitting procedure should not be regarded as an alternative to the Kondo model, as it does not presuppose the origin of the features, but is necessary, since the model takes no account of the surface. We employed standard photoemission line shapes²⁸ and a least-squares minimization procedure: The results for the f^{14} regions of both YbAl_3 and LuAl_3 are shown in Fig. 7. The bulk and surface doublets were each represented by a Doniach-Sunjić line shape convoluted with a Gaussian line shape. The surface-related peaks were constrained to have the same spin-orbit splitting and branching ratios as the bulk peaks. The Doniach-Sunjić line shape represents the intrinsic width of the photoemission peak, while the Gaussian component includes the instrumental, thermal, or, in the case of the surface peaks, disorder broadening. The fits also included an integral type background (measurements of LuAl_3 indicate almost zero intensity from the Al density of states near E_F), and for YbAl_3 a Fermi function cutoff, fixed at the position determined from the Au-film measurement. For the $f^{7/2}$ peak in YbAl_3 we find a binding energy of 65 meV and a Lorentzian width of 73 meV. Interestingly enough, nearly identical values were obtained in the recent study²¹ of YbAgCu_4 , a material whose $T_K \approx 100$ K, with no apparent crystal-field levels.

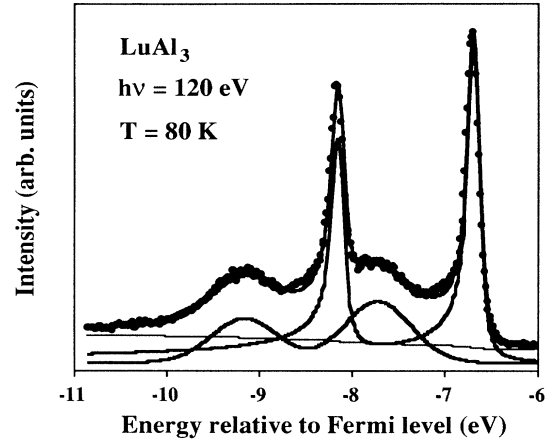
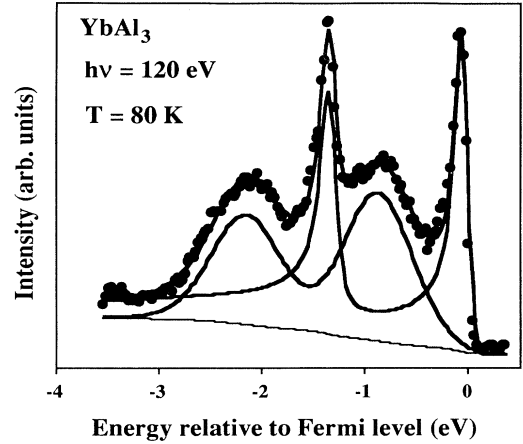


FIG. 7. Spectra of the f^{14} regions of YbAl_3 and LuAl_3 , taken at liquid-nitrogen temperature. The data are shown as points, the results of our fitting procedure, showing the bulk and surface doublets and the background, are shown as solid lines.

In both materials these values are higher than those predicted by Kondo theory (see Sec. I). The width of the KR in YbAgCu_4 is thus nearly an order of magnitude larger than predictions. This is a fact that should not be glossed over, since the width and position of the KR are the fundamental determinants of the low-temperature scale. In any case, in YbAl_3 this same width is no more than a factor of 2 larger than the predicted Kondo width due to the larger T_K . Thus for YbAl_3 additional insight is sought from a temperature-dependent study, since a single spectrum for YbAl_3 might possibly be interpreted as confirming the Kondo model if one is satisfied with factors of 2–4 disagreements. Clearly, additional self-consistency tests of the model are also desirable, such as the above measurements of YbCu_2Si_2 ($T_K \approx 35$ K) and YbAgCu_4 ($T_K \approx 100$ K) to see if the $4f$ linewidths are appropriately narrower if T_K is smaller. In addition to Ref. 21 above, we have also made these measurements and found the linewidths in all materials to be experimentally indistinguishable,^{8,9} irrespective of T_K . In Table I we show the Lorentzian widths for YbAl_3 and LuAl_3 . We did not force the fit to give equal widths for the main and

TABLE I. Results of the curve fits shown in Fig. 6 with results for elemental Yb and Lu (from Ref. 23) as well as YbAl_3 and LuAl_3 . Doniach-Sunjic line shapes were used in all cases. Also tabulated are the binding-energy differences Δ_{SB} between the bulk and surface f^{14} components.

	FWHM (meV)		Δ_{SB} (eV)
	$f^{7/2}$	$f^{5/2}$	
YbAl_3	73	89	0.819
LuAl_3	83	92	1.035
Yb		100	0.60
Lu		120	0.77

spin-orbit peaks, and so for each material two widths are given. Table I also shows the widths found for the $4f$ core levels of elemental Yb and Lu in a previous study.²⁹ Here again Doniach-Sunjic line shapes were used, but the $f^{5/2}$ and $f^{7/2}$ widths were set to be equal, making this a slightly different fitting procedure. With those stipulations we note the following trends in width: (a) The $f^{5/2}$ width is larger than the $f^{7/2}$ width in both LuAl_3 and YbAl_3 , (b) the width of the $f^{7/2}$ peak in LuAl_3 is slightly larger than in YbAl_3 , and the width in Lu is slightly larger than in Yb. In Table I we also show the binding-energy difference between the bulk and surface doublets Δ_{SB} . Here we note that Δ_{SB} is slightly greater in LuAl_3 than in YbAl_3 , and Δ_{SB} is slightly greater in Lu than in Yb. Thus in comparison to the core levels of LuAl_3 , the f^{14} peaks in YbAl_3 show the same trends in peak width and Δ_{SB} as is found for the core levels of elemental Yb and Lu. We further note that the increase in width of the $f^{5/2}$ peak relative to the $f^{7/2}$ peak is also characteristic of a core level, since the lifetime of the lower-lying state will be shorter. The trend in Δ_{SB} in the compounds is similar to that in the metals. It is not immediately clear from the Kondo model that the energy of a divalent Yb surface core level should be related to the energy of the KR and its sidebands. And yet the surface binding energy is shifted relative to the bulk f^{14} peaks by an amount entirely consistent with the behavior of core levels.

We now turn to a search for the predicted temperature dependence in the f^{14} peaks. In order to compare spectra taken at different temperatures they must first be normalized. Since it is the bulk peaks for which the Kondo model predicts temperature dependence, it might at first seem reasonable to normalize the spectra to the intensity of the surface peaks. But, as we have shown, it is very likely that these peaks will themselves have some form of temperature dependence. The effect of normalizing to the surface peaks is shown in Fig. 8(a), where it appears that the bulk peaks are significantly affected by the temperature increase. A more appropriate procedure is to use a temperature-independent parameter as the normalization quotient. For YbAl_3 a suitable parameter is the integrated intensity of the bulk Al $2p$ levels, using second order light of $h\nu=120$ eV, while taking valence-band data at $h\nu=60$ eV (thus all data can be taken without moving the monochromator, ensuring constant energy referencing). The samples were cleaved at low temperature

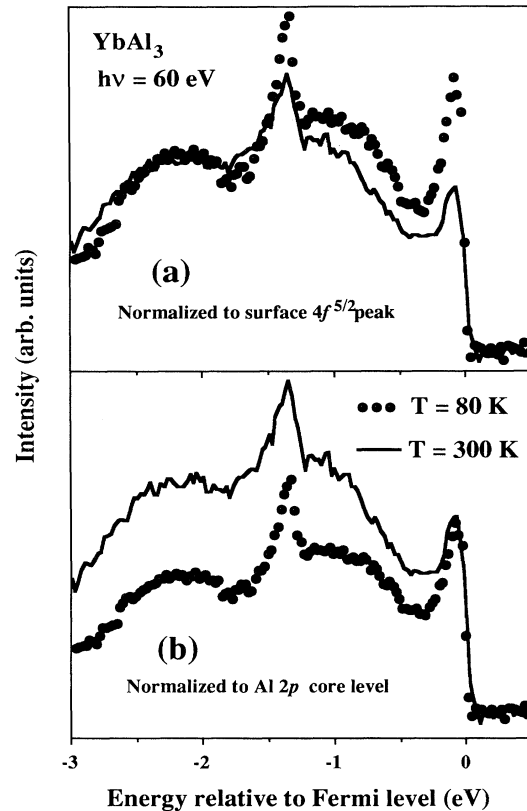


FIG. 8. The effects of two different normalization procedures on the relative intensities of spectra taken at liquid-nitrogen and room temperature from the same cleaved surface. (a) Normalized to the surface peak intensity, (b) normalized to the Al $2p$ intensity.

(~ 80 K) in a vacuum $< 5 \times 10^{-11}$ mbar, valence band and Al $2p$ spectra recorded, then warmed slowly to 300 K, where the second set of valence band and Al $2p$ spectra were recorded. We found that cleaving at low temperature and then warming produced lower contamination rates than in the sample cleaved at room temperature (see Fig. 4), although this was heavily cleave dependent. In the best cases, spectra were recorded for as long as 30 min after warming before contamination became appreciable. The considerably retarded contamination rates at low temperature allowed longer data acquisition times, of typically an hour or more, hence the slightly better statistics in the 80 K data of Figs. 8 and 9. Essentially, the idea in the normalization procedure is that, while normalization to mesh current alone should be sufficient all other effects remaining unchanged, it rarely works in practice due to the above discussed surface and/or position changes. After mesh current normalization, the spectra were renormalized to the integrated area shown in Fig. 9. Note that the intensity increase on the high binding-energy side of the $2p$ peaks at 300 K, due to Al oxide (see Fig. 5) is left out of the integration. The renormalization factor was then applied to the valence-band spectra (after they had been normalized to mesh current). This procedure has been used to normalize the

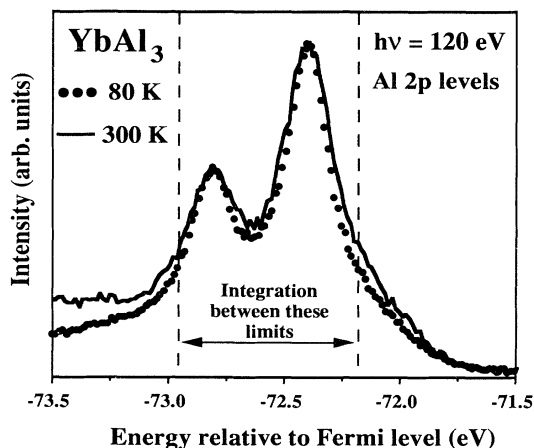


FIG. 9. Spectra of the Al $2p$ levels of YbAl_3 , showing the integrated areas used in the normalization procedure of Fig. 8(b).

spectra of Fig. 8(b). Note that it is now much less clear how the bulk peaks are affected, but it is obvious that there are significant changes in the surface peaks.

In addition to illustrating that an apparent temperature dependence can be an artifact due to an invalid normalization procedure, this also reinforces the advantage of employing curve fitting to extract the bulk $4f$ line shape when the surface peak line shape is not constant. The results of such a procedure for the data of Fig. 8(b) are shown in Fig. 10. Note that in stark contrast to the result implied by Fig. 8(a), our rigorous procedure in fact shows that there is almost no temperature dependence in the bulk f^{14} peaks of YbAl_3 (compare these data with the theoretical estimates shown in Fig. 2). We note in passing that the Lorentzian widths, and $f^{7/2}$ binding energy, determined from this high-resolution data agree within 2 meV to those found for the 120-eV data of Fig. 6. It should be noted that the changes in surface line shape imply that contamination levels increased in going from

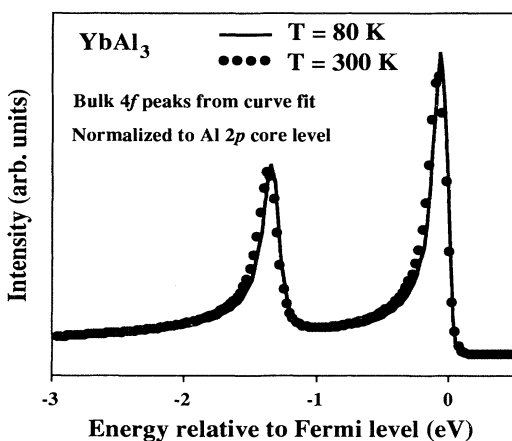


FIG. 10. The bulk $4f$ line shapes extracted from a curve fit to the data of Fig. 7(b). The results at two temperatures are nearly identical.

liquid-nitrogen to room temperatures. However, this is unlikely to have had a significant effect on the bulk line shape. If it did, then its most likely effect would be to reduce the intensity in going from 80 to 300 K. Clearly this does not occur.

It is fair to ask whether this normalization procedure also yields zero temperature dependence for the bulk f^{13} features. To answer this question it was necessary to perform a second experiment on a different sample, since time constraints due to surface contamination did not allow us to take data out to high binding energies at high resolution. Figure 11 shows the trivalent (i.e., f^{13}) $4f$ features of YbAl_3 taken at 120 eV photon energy in second order, with the Al $2p$ levels appearing at 102.5 eV kinetic energy from third-order light. Data were taken at room temperature and at 80 K. Note that the curves almost overlay each other, with any small differences well within the noise level. Our noise level only allows us to put an upper limit of 5% on any spectral weight changes in the f^{13} signal, but even this number is already a factor of 2 smaller than the quoted 11% of Tjeng *et al.*¹⁶ obtained from x-ray absorption, while the expected decrease between 300 and 80 K, based on the quoted¹⁶ values of n_f (the hole occupancy, =0.75), should be about 17%. Here n_f is the weight of f^{14} peaks and $(1 - n_f)$ is the weight of f^{13} peaks, so that a 50% loss in $(1 - n_f)$ yields a 17% gain in n_f .

It is always a more convincing proof if the lack of temperature dependence is directly seen in the raw data without the need for analysis. However, this can only be so if the surface peaks are also temperature independent. Fortunately this occurs below about 100 K. It has been found experimentally that temperature-dependent surface changes no longer manifest themselves below this temperature if the sample was also cleaved at low temperature. We saw in the introduction that according to NCA we should observe about a 10% reduction in spectral weight

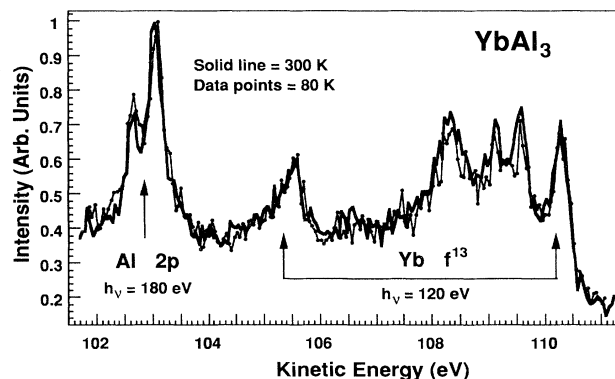


FIG. 11. The trivalent f^{13} features for YbAl_3 obtained with second-order light at $h\nu = 120$ at $T = 300$ K (thick solid line) and 80 K (thin line with data points). The two spectra are normalized using the Al $2p$ core level, which appears in the same spectrum from third-order light, $h\nu = 180$ eV. Temperature dependence, if any, is less than 5%. NCA theory predicts a near 20% effect.

of the bulk $4f$'s corresponding to the f^{14} features, between 20 and 80 K. This is well within our noise level and is easily discernible, since at low temperatures we can get good statistics due to the slow contamination rates. Thus, by controlling the flow of liquid helium through the cryostat to vary the temperature, and cleaving at ~ 80 K, we were better able to prevent surface changes over the range 20–80 K. In this case we find that the surface line shape remains constant. As Fig. 12 shows, the bulk line shape has also remained unchanged, as the two spectra overlay almost perfectly (the spectra were normalized at the valence-band maximum, although, because they were taken within minutes of each other, they displayed almost identical intensities without normalization). Thus we find no temperature dependence in the bulk f^{14} peaks over the range 20–300 K.

To convince ourselves that this is a general effect, we performed the same measurement over the same temperature range on a freshly cleaved (at 80 K) single crystal YbCu_2Si_2 as well as polycrystalline YbAgCu_4 . The results are shown in Figs. 13 and 14, respectively. The T_K 's for these materials are ≈ 35 and ≈ 100 K, respectively, so that an appropriately larger temperature effect is expected vs YbAl_3 . Moreover, as we have seen, a large temperature dependence was indeed recently reported for a scraped, polycrystalline YbAgCu_4 (Ref. 21) and YbAl_3 (Ref. 16) in the 20–80 K range. By contrast, our data show no temperature dependence except for a minor effect in the $f^{5/2}$ peak of YbAgCu_4 due to changes in the surface states even at these temperatures (see Fig. 14). This differs dramatically from the impurity-model predictions, and from measurements on polycrystalline scraped samples in this temperature range.

We do not yet fully understand our differences with other research groups although there are several clues as to what is going on. We strongly suspect that the differences lie in our use of single crystals and the apparent ability to stabilize the surface by cleaving at low temperature.

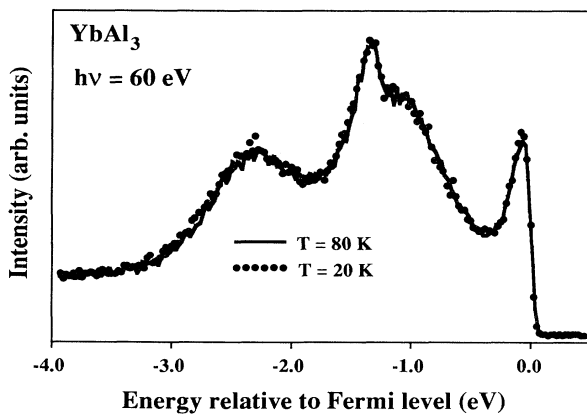


FIG. 12. PES spectra of YbAl_3 , taken at liquid-helium and liquid-nitrogen temperatures from the same cleaved surface, using throttled helium for temperature control. Note the lack of temperature dependence.

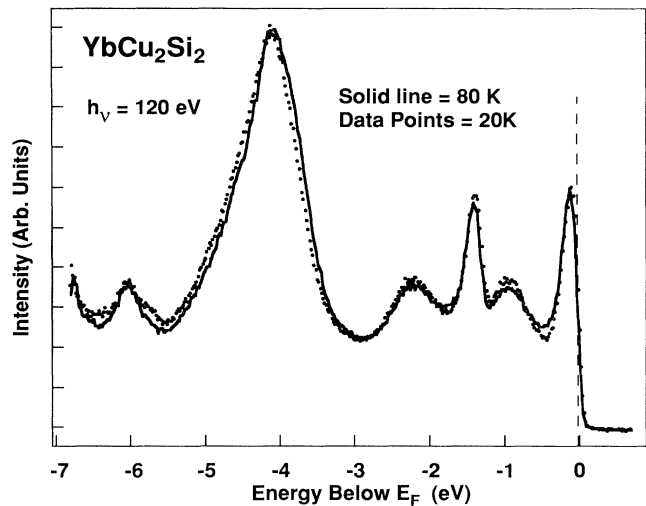


FIG. 13. Valence-band PES data for YbCu_2Si_2 between 20 and 80 K with sample cleaved at 80 K and temperature controlled with throttled helium. No temperature dependence is observed despite a Kondo temperature of 35 K.

Spectra from scraped polycrystalline samples are very sensitive to any surface effects owing to the more glancing takeoff angle (on the average, due to surface roughness) of emitted electrons. In those measurements the bulk-to-surface ratio in the spectra is found¹⁶ to be only about 0.1, so that small changes in the surface can greatly affect the apparent bulk amplitude. By contrast in our measurements, where the electron takeoff angle from a smooth cleaved single crystal is near normal emission, the bulk-to-surface ratio was as high as 50% at $h\nu = 120$ eV. This convinces us that we are probing the bulk more

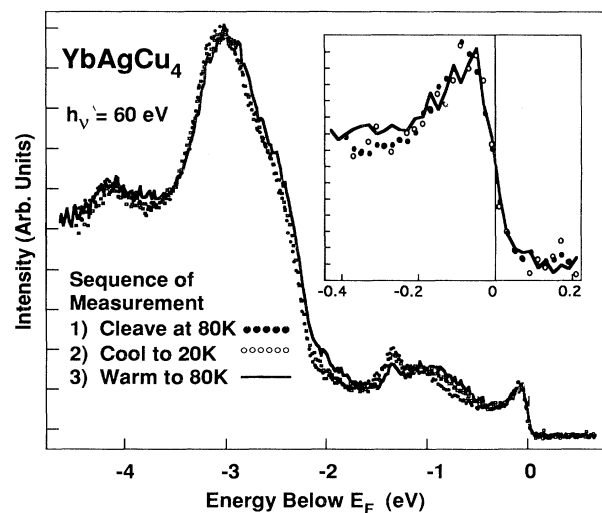


FIG. 14. Valence-band PES data for polycrystalline YbAgCu_4 ($T_K = 100$ K) between 20 and 80 K, with sample cleaved at 80 K. Inset shows a blowup of the near-Fermi region. Again, no temperature dependence is evident.

deeply with single crystals, and certainly increases the confidence level of our fits. At least part of the source of the temperature dependence can be attributed to phonon broadening, which would be more pronounced with the better resolution of other experiments, although we concede that the effects reported in Refs. 16 and 21 are far too large to be entirely explained by phonons.

The data are more easily understood if we assume that there is a large surface component to the temperature-dependent (Refs. 16 and 21) f^{14} for the following reasons: By cleaving at low temperatures and making measurements below ≈ 80 K, any surface reconstructions are inhibited and the data should be most representative of the bulk. By contrast, the polycrystals are scraped at room temperature, allowed to anneal, and are then finally cooled. This argument is also consistent with the notion that a slight oxygen contamination on the surface likewise inhibits surface reconstruction and thus explains the temperature independent results observed in YbAl_3 all the way to room temperature (a slight contamination is evident in Fig. 8). This would also be consistent with our previous report⁸ of temperature independence of the $4f$ features in YbCu_2Si_2 , which also had a slight oxygen contamination on the surface. Thus it can be argued that whatever is causing the temperature dependence of the $4f$ features as reported from polycrystalline data can rather easily be turned off with slight strains or contamination of the surface. Hence we suggest that the bulk of the temperature dependence observed by others may not be entirely an intrinsic effect but rather an artifact of the surface. Moreover, none of these other researches report a temperature dependence for the f^{13} peaks, which according to theory, must occur.

One may argue that a slightly oxidized surface is not representative of the material we are trying to measure. To this we respond that it is certainly more representative than scraped polycrystalline samples as evidenced by our vastly more intense bulk $4f$ signal. However, our low-temperature results are surely representative of the bulk. Moreover, the f^{14} and f^{13} features we observe are unaltered in width and position relative to the polycrystalline results. We appear to be, in fact, observing the same features. If, on the other hand, we allow, for the sake of argument, the possibility that for our surfaces we are not observing the Kondo resonance but rather some other entirely similar feature, which for these slightly strained or contaminated surfaces is temperature independent, then we open the door to the possibility that at least one other mechanism can in fact yield results similar to the Kondo model. This is in fact our point, since the features identified as the Kondo peaks are experimentally indistinguishable from ordinary core levels, and we question the need to call them anything else.

We have also considered the possibility that the low-temperature cleave causes a strain which (possibly slight oxidation as well) somehow results in a subsurface layer that is more divalent and thus has a substantially higher T_K . Within the Kondo picture this could lead to temperature independence in this temperature range. However, we would require a T_K of at least 1000 K in order to eliminate all temperature dependence below 80 K, and as

much as 5000 K to eliminate it up to room temperature. While this would alleviate the disagreement with the deeper probing x-ray-absorption experiments¹⁶ which claim to see an 11% temperature effect, the PES data do not support this interpretation. Recall that a higher T_K within the Kondo impurity model implies an increase in the f^{14} amplitude, as well as an increase in the $f^{7/2}$ width and a shift to higher binding energies. However, no changes in width and position are observed experimentally, while the PES f^{14} intensity may actually decrease slightly relative to the f^{13} intensity upon slight oxidation. Thus we are again led to the conclusion that for PES measurements, the concept of some form of surface effects most consistently explains the conflicting data. We cannot totally rule out the possibility that phonon broadening is responsible for much of the observed^{16,21} effects, since a large temperature dependence is seen in Yb metal where the $4f^{7/2}$ is situated at ≈ 1.5 eV. Phonon effects, especially surface phonons, may furthermore be easily suppressed by strains and/or oxidation.

Thus, even if a demonstrable temperature dependence occurs, it does not unambiguously follow that the temperature dependence prediction of the Kondo model has been shown to be correct, since, as we have demonstrated, there are a number of other factors which may change the PES line shape and f^{14} intensity, such as surface reconstruction, phonon broadening, lattice parameter changes, surface oxidation, etc. In short, in observations of temperature dependence one must rule out these factors before attributing the effect to that predicted by Kondo theory. On the other hand, a total lack of temperature dependence, as reported here and previously,^{8,10} raises serious questions regarding the validity of the Kondo model as applied to photoelectron spectroscopy.

IV. CONCLUSIONS

Our results do not support the Kondo interpretation of heavy-fermion photoemission. For a material with $T_K \approx 400$ K the reduction in f^{14} amplitude at 300 K relative to 20 K should have been more than a factor of 2. Samples cleaved and measured below 80 K, on the other hand, show no temperature dependence irrespective of T_K . We further fail to observe any temperature dependence up to 300 K in YbAl_3 for the cycling technique employed by us. Previously, a similar lack of temperature dependence to 300 K was observed in YbCu_2Si_2 in which $T_K \approx 35$ K, and where room temperature represents $\approx 8T_K$. Furthermore, the widths of the f^{14} peaks were nearly identical to YbAl_2 (natural asymmetric linewidth of about 80 meV). It is possible that a surface reconstruction explains the discrepancies with other researchers,^{16,21} implying that much of their temperature dependence may be surface related. Our cold cleaves prevent such reconstruction. The quantitative discrepancies between our results and the theory for YbAl_3 are substantial though of themselves not overwhelming due to the large T_K . Thus we maintain that there is still no conclusive evidence for a Kondo related temperature dependence in PES or BIS from *any* heavy-fermion material:

Our results, both in this and previous work show no such effect; the CeSi₂ PES results of Patthey *et al.*³⁰ can be reproduced using only Fermi function and thermal broadenings,⁷ and the CePd₃ and CeSi₂ BIS results of Malterre *et al.*^{12,13} appear to be an artifact of their normalization procedure.³¹ The work of Tjeng *et al.*¹⁶ does show an effect similar to that seen in Fig. 8(a), but we suspect a temperature-dependent surface reconstruction as the most consistent explanation for all the conflicting data. Similarly, a clear temperature dependence is also observed²¹ (even below 80 K) in scraped polycrystalline YbAgCu₄. Their analysis of peak width and position is identical to our results (natural linewidth again about 80 meV) and thus nearly an order of magnitude larger than Kondo predictions. The discrepancies between their and our temperature data cannot be reconciled within the Kondo impurity model, but it may be possible to reconcile it within a picture employing surface reconstruction and/or phonon broadening. We can put an upper limit of 5% on any weight change in the f^{13} peaks between 300 and 80 K even for clean, annealed surfaces. In addition to the failure of the Kondo model to explain our results, it appears that a simple core-level interpretation would be able to predict the peak widths, and also the binding energy of the surface peaks, which the Kondo model ignores.

These results raise some questions concerning the validity of the Kondo model, but only with respect to photoelectron spectroscopy. The underlying Kondo theory of the heavy-fermion behavior has been extremely successful and it is highly unlikely that it is a failing of this theory that is responsible. Thus there remain at least two further possibilities: either there is some hitherto overlooked problem with the $1/N$ approximation³² so that it does not correctly represent the Anderson model, or heavy-fermion photoemission spectra are not characteristic of the presumed final state, particularly in view of the possible agreement of deeper probing x-ray-absorption measurements with the Kondo picture. If either of these possibilities is correct, the interpretation of photoemission data from heavy fermions within the single-impurity model remains a highly questionable exercise, as even the previous claims of KR observation may not bear close inspection.³³ The possibility of an entirely different approach²⁹ to heavy-fermion photoemission cannot be ruled out.

ACKNOWLEDGMENT

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