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Inconsistencies with the single-impurity Anderson model in photoelectron spectra of cerium heavy fermion compounds

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Abstract

A series of cerium heavy fermion compounds have been studied in order to check for the systematics with T_K and the temperature dependence of the Kondo resonance predicted by the Kondo model. Neither the systematics nor the temperature dependence is found, the latter primarily determined from a detailed study in CeSi$_2$. The qualitative shapes of the features at E_F remain nearly constant irrespective of T_K, while all the temperature dependence can be explained as resulting from phonon broadening of core-like states as well as Fermi function broadening. In addition, if the d electron contribution to the spectra is subtracted, one obtains a symmetric, lorentzian line shape for the "main" 4f peak.

1. Introduction

Photoelectron spectroscopy (several excellent reviews exist; see *e.g.* ref. 1) has in the past yielded much of the impetus toward the development of heavy electron theory. This has been especially true in cerium-based heavy electron systems where, despite the occupancy of a single 4f electron, one observes in the photoelectron spectrum two, and more often three, features that can be identified as originating from 4f electrons. Several ideas have been used to explain these features: the single-electron band theory [2], multiple screening channels [2] and, most commonly, the concept of a Kondo resonance (KR) [3–5]. Within this latter concept, an extension of the single-impurity Anderson model, the peak usually observed at about -2 eV binding energy has been explained as being due to a localized d-screened 4f hole (the so-called "main peak" of the $4f^1 \rightarrow 4f^0 + e^-$ transition), while the feature contacting E_F and a second one at about -0.3 eV have been explained as resulting from the weak hybridization of the localized 4f state with the conduction bands [3, 4]. This pulls f weight to E_F and results in the narrow KR as well as the Kondo sideband (KS) at -0.3 eV (because of spin–orbit splitting). The width Γ of the KR is of order kT_K (where T_K is the Kondo temperature), while its centroid position in energy is actually about kT_K

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above E_F. Thus typically one should observe only the tail of the KR in a photoemission experiment and perhaps not even that if the KR is as narrow as predicted. The KS can be as much as five times broader than the KR depending on crystal field effects [3, 4]. The small Γ yields the heavy mass. The KR is predicted to be extremely temperature dependent in order to explain the cross-over from localized to itinerant behavior of the 4f electrons. Most theories [4, 5] would have the KR at nearly zero amplitude by about $5T_K$.

The Gunnarson–Schonhammer extension [3] of the Anderson model, as well as other theories, has at first glance been very successful in explaining the photoelectron spectra in cerium heavy fermions, particularly with the crucial observation [6] of the necessary temperature dependence in $CeSi_2$, but there have always been some unresolved questions. Uranium-based heavy fermions, for example, do not fit this picture at all. In uranium systems one observes [7] a 5f structure which, to be sure, is much broader than predicted from the single-electron picture but which can be synthesized by the addition of a band structure density of states (DOS) plus a feature at about -1 eV. The difficulty of the Gunnarson–Schonhammer theory in uranium heavy fermion systems has been explained as due to the multiple occupancy of the 5f levels. However, even for cerium compounds there exist problems. The persistent observation of a large 4f feature at E_F at room temperature in X-ray photoelectron spectroscopy (XPS) and resonance data in compounds with a very small T_K has been a cause for concern. In general it has been dismissed as being due to poor resolution, since in some theories [3] the KR does not actually go away as T increases, but only broadens out.

The very high resolution work of Patthey et al. [6] on $CeSi_2$ ($T_K \approx 35$ K) seemed to settle the question of the applicability of single-electron vs. many-body theory in heavy fermions with their observation of a temperature dependence of the Kondo peak which at first glance exactly fit Kondo predictions. (Incidentally, no other temperature dependence of the KR has ever been reported using photoemission data.) Their work consisted of spectra at helium (I) and helium (II) photon energies, with the subtracted spectra (the 4f intensity increases dramatically with energy) at various temperatures presumed to be representative of 4f emission. The temperature dependence reported there, however, is actually rather small after one accounts for Fermi function broadening. Only about 10% of the amplitude is unaccounted for. We were surprised at this small temperature dependence in view of the large effects predicted by other theories [4, 5]. Part of the explanation lies in the fact that Patthey et al. utilize the concept of crystal field splitting to yield a lower degeneracy level for the feature at E_F. However, even their own parametrization resulted in a larger temperature dependence than observed and, more importantly the width of their KR peak (actually the Kondo resonance for the crystal field state) was about 50 times broader than expected (3 meV). We saw similar effects in other heavy fermions. More importantly, however, we noticed that the observed temperature dependence was consistent with what might be expected from phonon broadening [8], which must be

present in all systems. We felt that the best way to settle our doubts regarding phonon broadening was to re-measure the temperature dependence of the KR in $CeSi_2$ and at the same time measure the phonon broadening of the Si 2p core levels in the same specimen to see if it is sufficient to account for the observed temperature dependence of the 4f features at E_F. Any temperature dependence due to the Kondo model must exist over and above these other necessary effects. Preliminary data on a large number of cerium and ytterbium systems at resonance showed that there is a serious question about the temperature dependence of the feature defined as the KR, or any feature for that matter. Indeed, in $CeBe_{13}$ the temperature dependence is small and opposite to predictions. In this paper we will concentrate on $CeSi_2$ and show that any temperature dependence of the KR can be completely accounted for by phonon broadening together with Fermi function broadening. In addition we will show that the 4f line shape near E_F is nearly independent of T_K as well as T and that the line shape of the -2 eV peak is substantially different from the single-particle Anderson model predictions [4].

2. Experimental details

We have improved the resolution of our ERG monochromator at the Los Alamos beam line at NSLS (presently our overall instrumental resolution $E/\Delta E \approx 1500$ at 120 eV) to the point where we are no longer resolution limited in our measurements of the cerium valence bands. (Some additional work was done at the Synchrotron Radiation Center in Wisconsin.) Well-annealed, arc-melted polycrystalline samples of $CeAl_3$ and $CeSi_2$, ($T_K \approx 3$ and 35 K [9]) as well as single crystals of $CeBe_{13}$ and $CeSb_2$ ($T_K \approx 300$ and <10 K [9]) were used in our measurements and were fractured *in situ* to expose a clean surface. The base pressure was maintained at about 8×10^{-11} Torr. The low temperature was provided by a continuous flow cryostat mounted on a VG wide bore manipulator for sample positioning. The cryogen was either liquid helium (yielding $T \approx 10$–20 K) or liquid nitrogen (yielding $T \approx 80$ K). The temperature was measured with a thermocouple in contact with the cryostat but not with the sample; hence the uncertainity in T, particularly at low temperatures. A typical high resolution spectrum was collected in about 60 min. The electronics were stable to better than 1 mV for several days, although the monochromator drifted by a few millielectronvolts with temperature, requiring frequent checks of the reference Fermi level. The usual difficulty of normalizing spectra at resonance was circumvented by normalizing the spectra to the Si 2p or the Al 2p core levels, which were measured simultaneously at the same energy and resolution as the valence bands. This method allows us to estimate the amount of 4d intensity contained in the 120 eV spectrum by measuring the d spectrum and the core levels in isostructural lanthanum compounds where no 4f intensity is expected. We were surprised to discover that the d resonance can be as much as 50% of the f resonance. We will see below that this dramatically modifies the line shape of the -2 eV peak.

3. Results and discussion

In Fig. 1 we show photoelectron spectra within the first 600 meV of the Fermi energy for the four compounds mentioned above. The temperature for all spectra is in the 10–20 K range, while the resolution is of the order of 90 meV. The spectra were taken at the 4f resonance energy, $h\nu = 120$ eV, so that the bulk of the intensity is due to 4f electrons. We have mentioned the large d contribution, but it tends to predominate in the -1 to -2 eV range and is small at E_F. (We do not display the full 4 eV wide valence band since the -2 eV peak is seen in all samples and adds little to the discussion.) We notice immediately that all spectra display the typical [10] double-peaked structure near E_F, irrespective of the T_Ks, which vary by two orders of magnitude. Moreover, the crystal structures for the four compounds differ dramatically so that the various crystal field splittings would be expected to be substantially different. Instead we find qualitatively and to some extent even quantitatively the same two features. Only CeAl$_3$ shows a slight decrease in the amplitude of the feature at E_F relative to the -0.3 eV peak, but it is clear that the feature is present at E_F and has a width nearly identical to that seen in other compounds. The width will be more thoroughly discussed in connection with Fig. 2, but suffice it to say that in all compounds it is of the order of 150 meV for the feature at E_F, and of the order of 220 meV for the sideband. This is nearly twice our stated resolution, so that the crutch of resolution can no longer be applied for the existence of the so-called KR at room temperature. In the paper of Patthey *et al.* [6] it is noticed that the widths are too large, but they dismiss this as resulting from lifetime broadening. We submit, however, that lifetime broadening should then affect the bulk properties as well.

An important spectrum in Fig. 1 is that of CeSb$_2$, a non-Kondo ferromagnetic compound [11] whose susceptibility displays good local moment
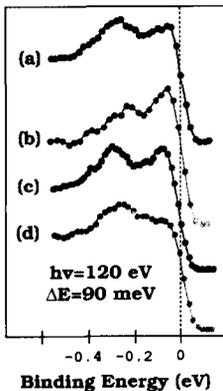
Fig. 1. High-resolution spectra in the near-E_F region for (a) CeSb$_2$, (b) CeBe$_{13}$, (c) CeSi$_2$ and (d) CeAl$_3$. Note that the double-peaked structure is a general feature of Ce 4f emission unrelated to T_K and crystal structure.

behavior down to the ferromagnetic transition of 10 K. On the basis of the Kondo model we would assume that T_K is vanishingly small with minimal hybridization with the conduction bands, and hence minimal 4f intensity is expected at E_F. Yet we see that the double-peaked structure is identical to that of other materials. It would appear that we are dealing with core-level-like structures in all materials. This of course raises questions regarding the accepted electronic structure, which we will not answer in this paper except to point out that the data can more easily be explained by assuming different screening channels for the photoelectrons rather than the Kondo model.

In Fig. 2 we take a more careful look at the temperature dependence of the $CeSi_2$ spectrum shown in Fig. 1. In this material, which was used by Patthey et al. [6] to prove the applicability of the single-impurity Anderson model to the cerium heavy fermions, we first fit the 10 K data of Patthey et al. with two lorentzians (at −20 meV and −0.28 eV FWHM (full width at half-maximum) as stated above). It was possible to obtain a nearly perfect fit to their data, which suggests that the features are lorentzian in line shape. The stated resolution of Patthey et al. was 18 meV. We then broadened the two lorentzians by 90 meV to correspond to our resolution, cut them off by a 10 K Fermi function and superimposed the resulting line shape on our 10 K data in the top spectrum of Fig. 2. The fit to our data is almost exact,
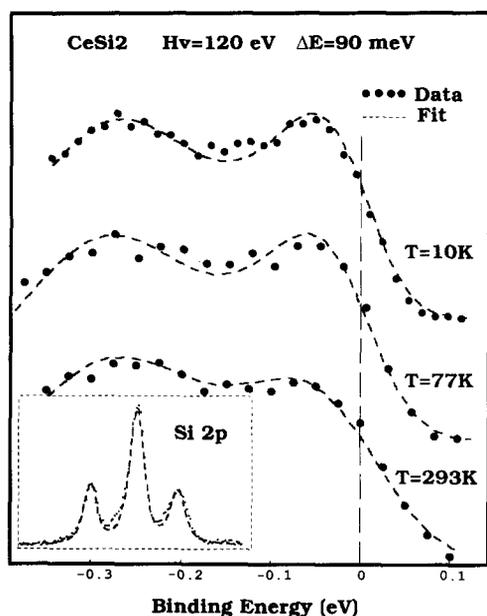
Fig. 2. Phonon model fits at various temperatures to the $CeSi_2$ spectra in the near-E_F region. All fitting parameters are the same in the three spectra except for the Fermi function and phonon broadening. The topmost spectrum (at a temperature of 10–20 K) and fit are the same as the $CeSi_2$ spectrum in Fig. 1. The phonon broadening for the other temperatures was obtained from a fit to the Si 2p core levels (typical fit shown in inset).

suggesting that our data and the data of Patthey *et al.* are entirely self-consistent. It also shows beyond doubt that the natural linewidths are at least an order of magnitude broader than expected from the Kondo model.

In addition to the low temperature spectrum, we measured the same spectrum also at about 80 and 300 K. At the same time, however, we also measured the Si 2p core levels with the same 90 meV resolution at all three temperatures. The phonon broadening of the core levels was determined from fitting the core levels with standard fitting techniques [12] using Voigt functions, which are a mix of lorentzians convoluted with gaussians. It assumed that at 10–20 K there is no phonon broadening in the line shape, so that all the gaussian broadening is due to the instrument response. At higher temperatures the contribution from the phonons to the gaussian broadening is included in an r.m.s. fashion and was found to be as large as 90 meV at 300 K and about 20 meV at 80 K. A typical fit is shown in the inset of Fig. 2.

Having determined the amount by which the 2p core levels broaden with temperature, we now apply the same broadening parameter to the 4f states. We simply take the fitted curve at 10 K, broaden it by the above-determined phonon-broadening parameter which was convoluted with the instrument response through an r.m.s. technique, convolute it again with the appropriate Fermi functions for 80 and 300 K and obtain the fits shown in the second and third spectra of Fig. 2. These fits are overlayed on the actual data at 80 and 300 K and it can be seen that the results agree almost exactly. All the temperature dependence is completely accounted for by the phonon and Fermi function broadening, thus leaving no room for any additional temperature dependence from the Kondo interaction. It must be concluded then that the near-E_F features in $CeSi_2$ are in fact temperature independent. A cursory fit to other materials shows that the temperature independence probably applies in each case. We have, moreover, fitted the data of Patthey *et al.* using our broadening parameters and have obtained an exact fit to their spectra at higher temperatures.

A necessary consequence of the single-impurity Anderson model is that the line shape of the "main" peak usually found near -2 eV relative to E_F is actually highly asymmetric [4] owing to the pulling of the f weight toward the Fermi energy via the hybridization interaction. Indeed, in most cerium compounds this peak is apparently highly asymmetric. However, we have repeatedly found that a third distinct feature at about -1.5 eV also resonates strongly at the 4d threshold, which we believe corresponds to the Ce 5d states and which could account for the apparent asymmetry. To check this out, we measured the corresponding isostructural lanthanum compounds and determined the strength of the resonance by measuring the 5d intensity relative to a non-resonating ligand core level (*e.g.* Al 2p, Si 2p, Be 1s, etc.). For consistency we also measured the 5d photocurrent relative to the photon mesh current. We were surprised to discover that the La 5d intensity at resonance is usually about 50% of the intensity of the corresponding Ce 4f "main" peak at resonance. In Fig. 3 we show the $CeBe_{13}$ and $LaBe_{13}$ spectra
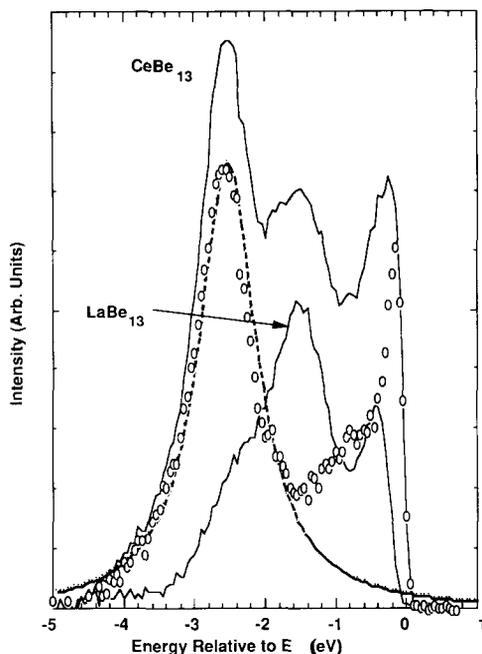
Fig. 3. Full valence band spectra for CeBe$_{13}$ and LaBe$_{13}$ (thin solid lines) taken at $h\nu = 120$ and 117 eV respectively and the 4f spectrum (data points) obtained by subtracting the LaBe$_{13}$ spectrum from the CeBe$_{13}$ spectrum. Data were normalized to core levels and mesh current. The LaBe$_{13}$ spectrum has been shifted by 200 meV to correspond to the maximum d intensity in CeBe$_{13}$. The subtracted curve is fitted with a lorentzian line shape (dashed line).

taken at their resonance energies ($h\nu = 120$ and 117 eV respectively). We chose this material because the data were taken on single crystals with no grain boundary complications and also because the "main" peak is actually found at -2.4 eV, well separated from the d peak which is clearly resolved in the figure. The maximum of the LaBe$_{13}$ d intensity unfortunately occurs about 200 meV lower in binding energy than the corresponding CeBe$_{13}$ d intensity, so that if one wishes to subtract out the d component, it becomes necessary to shift the LaBe$_{13}$ spectrum by 200 meV. This has been done in Fig. 3. The subtraction results in errors at the Fermi cut-off but is quite reliable below about 0.5 eV. Superimposed on the subtracted curve in Fig. 3 is a lorentzian line shape to demonstrate the lorentzian shape of the "main" peak. Note then that the "main" peak is much narrower and more symmetric than predictions [4]. This has also been observed by others [13].

We are thus left with many inconsistencies if we persist in regarding the photoelectron features in cerium heavy fermions as arising from the Kondo interaction. These inconsistencies are: (i) the temperature dependence of the intensity and width of the near-E_F features is totally accounted for by simple phonon broadening and Fermi function broadening; (ii) the width of the feature at E_F, normally called the Kondo resonance, is about two

orders of magnitude broader than expected from the Kondo model even at the lowest temperatures and its line shape can be adequately fitted with lorentzians; (iii) the "main" peak is symmetric and lorentzian in shape once the d contribution is subtracted out; (iv) the spectral weight of the near-E_F features shows no systematics with T_K (the spectral weight should be a linear function of T_K) or crystal structure (vastly different crystal field states should produce large variations in intensity); (v) a double-peaked structure near E_F, entirely similar to that seen in heavy fermion compounds, is also found in $CeSb_2$, a material whose bulk properties show no Kondo-like behavior down to the ferromagnetic transition temperature of 10 K. Similar results have also been obtained in corresponding ytterbium compounds [14], where the presumed Kondo resonance is on the occupied side of the Fermi energy. The lack of temperature dependence in those materials will be reported in a later publication [14].

Where does all this leave us? We must first of all point out that our data do not in any way negate the idea of a Kondo-like interaction in heavy fermions. Bulk property data [9] have been very adequately explained using the single parameter T_K, so that there is undoubtedly validity to the model. The question is, rather, can the features seen in photoemission be identified in terms of the presently accepted model? Our response to this question is probably not. The second question that we pose is whether the single-impurity Anderson model can be justifiably extended to include the Kondo lattice. We would leave the answer to this question to others, but it would seem that some basic assumptions may have to be modified. It is entirely possible that the actual Kondo resonance exists as predicted, is indeed as narrow as predicted and is indeed above E_F, but cannot be observed by photoelectron or BIS spectroscopy. What is observed is much more consistent with the idea of different screening channels [2, 16] of photoemission. We may wish to look again at some of the ideas of Norman *et al.* [2].

Acknowledgment

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