Title
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Journal
Solid State Communications, 83(8)

ISSN
0038-1098

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Publication Date
1992-08-01

DOI
10.1016/0038-1098(92)90649-t

Solid State Communications, Vol. 83, No. 8, pp. 551-554, 1992.
Printed in Great Britain.

0038-1098/92$5.00+.00
Pergamon Press Ltd

CRYSTAL FIELDS, LINEWIDTHS AND TEMPERATURE DEPENDENCE IN THE PHOTOELECTRON SPECTRA OF HEAVY FERMION Ce AND Yb COMPOUNDS*

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(Revised manuscript received 10 June 1992 by A. A. Maradudin)

We report high-resolution photoemission results for the 4f levels in $YbCu_2Si_2$ and $CeSi_2$. The data are compared to the predictions of the Anderson impurity model for valence band photoemission. These predicted spectra are obtained both in an approximate fashion by broadening crystal field (CF) states whose parameters are determined from existing neutron scattering data, as well as from a Gunnarson-Schonhammer calculation. Inclusion of crystal fields does not affect our two fundamental conclusions: that there is a natural linewidth in the problem (≈130meV) which is much greater than predicted by the Anderson model, and that the expected temperature dependence of the Kondo resonance is absent. Due to the large natural linewidth, experimental resolution (60-95meV) is not a limiting factor.

The prevailing model used to explain the photoemission spectra (PES) of heavy fermion compounds is the Anderson impurity model [1,2,3]. A key prediction of the model is the existence of the so-called Kondo Resonance (KR). This is predicted to be of width kT_K (where T_K is the Kondo temperature), to be of integrated weight kT_K/Γ (where Γ is the hybridization width), and to lie a distance kT_K above (below) the Fermi energy E_F in cerium (ytterbium) compounds. For Ce compounds the KR can be viewed in inverse photoemission (BIS) since only the tail of the KR lies below E_F; for Yb compounds, however, the KR should be directly observed in photoemission spectra (PES). The KR is expected to renormalize to zero (i.e. vanish) at $T \gg T_K$. In the presence of spin orbit and crystal field splitting the predicted spectra are considerably more complicated[4]. In addition to the KR of the ground state multiplet, crystal field and spin orbit sidebands are predicted above and below E_F, with characteristic temperature scales for renormalization of the spectral weight which can be substantially different than T_K.

In recent work[5] we have examined the PES for a series of Ce compounds with T_K's varying from 0-300K. We demonstrated that the spectral weight of the feature which lies near E_F does not scale with T_K (i.e. as T_K/Γ, or the associated sidebands) but rather appears to have similar weight independent of T_K; that the feature near E_F has a natural linewidth which is much larger than kT_K or kT_{KCF}; and that there is no observable temperature dependence beyond that expected on the basis of Fermi function broadening and a small amount of phonon broadening.

In this paper we present new data for $YbCu_2Si_2$ and re analyze existing data [5,6] for $CeSi_2$ to show that the latter two conclusions hold even in the presence of spin orbit (SO) and crystal field (CF) effects. We make use of existing inelastic neutron scattering data for both compounds to determine the crystal field splittings and linewidths to be used in a simple determination of the expected spectra for the case where crystal fields and the Kondo effect coexist. Given that the KR should be readily observed in PES in ytterbium, our analysis for $YbCu_2Si_2$ directly establishes that the linewidth is larger than predicted and that the temperature dependent renormalization is much smaller than expected. For $CeSi_2$, where only the "tail" of the KR is occupied (along with the KR sidebands), we have performed (in addition to the above simple lineshape analysis of broadened neutron states) a full Gunnarson-Schonhammer (GS) calculation containing the CF states, but not including the effects of the finite f-f correlation U, which we find has minimal effect on the spectrum, provided that T_K remains invariant with U. The fits from the GS calculation are substantially narrower than measured.

Experiments were carried out at the Los Alamos U3C beamline at NSLS and at the University of Wisconsin's SRC. The $YbCu_2Si_2$ samples were flux-grown single crystals cleaved along the basal plane in ultra high vacuum (UHV); the $CeSi_2$ samples were arc-melted polycrystals fractured in UHV. The chamber base pressure was $5x10^{-11}$ torr. Temperature was controlled by placing the sample in direct contact with a cryostat cooled either by liquid helium (T≈20K) or by liquid nitrogen (T≈80K) or held at room temperature. The total experimental resolution was determined to be 60 or 80meV for $YbCu_2Si_2$ at hv=60eV and 95meV for $CeSi_2$ at the 4d resonance of hv=120eV. Although the characteristic Kondo and crystal field widths are expected to be smaller than this, we will show subsequently, that the natural linewidth is of order 130 meV; for this reason our experimental resolution is adequate. To further establish this point we will analyze data for $CeSi_2$ reported by Patthey et al[6] taken at 18meV resolution using He_I and He_{II} discharge radiation, and

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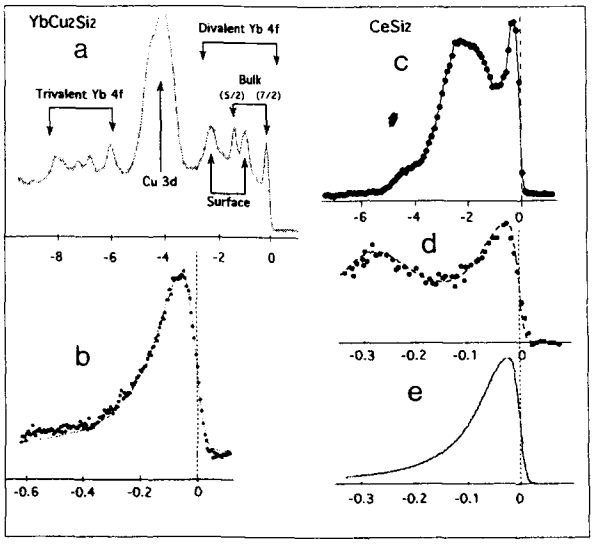

Fig. 1 (a) Photoemission spectrum of $YbCu_2Si_2$ at hν=60eV with resolution ΔE=60meV (b) The bulk J=7/2 peak of part A isolated as discussed in the text. (c) The spectrum of $CeSi_2$ at hν=120eV (d) Data from Ref. 6 for the region near the Fermi level in $CeSi_2$; the resolution is 18meV. The peak at 280meV is the J=7/2 spin orbit sideband. (e) The J=7/2 feature of part D isolated by fitting the data to a two peak Voigt fit (see text).

show that there is no essential change in our conclusions.

The compound $YbCu_2Si_2$ is a nearly trivalent Yb compound with a Kondo temperature of order 50K as determined from the specific heat[7] or inelastic neutron quasielastic linewidth[8]. In Fig. 1a we show the spectra of $YbCu_2Si_2$ taken at hν=60eV. As is generally true for heavy fermion compounds with Kondo temperatures of order 100K, the valence is non-integral. A series of peaks with binding energies in the range 6-12eV represent $f^{13} \rightarrow f^{12}$ transitions from the trivalent component of the ground state. The peaks within 3eV of E_F represent $f^{14} \rightarrow f^{13}$ transitions from the divalent component. Based on similar spectra taken at several photon energies we estimate the valence from the ratio of the weights of these two sets of features to be 2.9, i.e. the number of holes in the 4f shell is $n_f = 0.9$.

In the language of the Anderson model[4] the $f^{14} \rightarrow f^{13}$ transitions are the Kondo resonances. The peak labeled J=5/2 represents an "excited state" resonance from the divalent component of the ground state to the J=5/2 spin orbit excited state of the f^{13} final state. The peak labeled J=7/2, representing transitions into the lower spin-orbit manifold of the final state, should be further split due to crystal field splitting. The measured J=7/2 spectrum should consist of four doublets. The lowest (the ground state KR) should lie a distance kT_K below E_F and should have a width kT_K: the other three should lie at energies below E_F corresponding to the crystal field splittings. Theory further predicts that the divalent f^{14} component of the ground state, which arises from hybridization, should vanish as the temperature is raised through T_K. For Yb this would result in a suppression of *all* the resonances discussed above (i.e. ground state, CF and SO excited state resonances) since they all represent transitions out of the f^{14} component of the ground state. This can be seen in Fig. 13 and 34 of Bickers et al[4] (in the latter figure positive energies represent binding energies below E_F in PES for Yb). For the case of $n_f = 0.9$ theory predicts at the very least, a factor of two decrease in the spectral weight of both the KR and the sidebands as T increases from T = 0 to $3T_K$.

To test these predictions we first normalize the spectra at different temperatures to the Cu 3d peak (at 4eV binding energy). We then isolate the bulk J=7/2 peak (Fig. 1b) by subtracting off the surface peaks. To determine the predicted spectrum we use neutron scattering results[10] for the CF splittings; peaks are observed at 12 and 30meV in the neutron experiment, and an additional peak at 80meV is inferred from fits to the susceptibility. We approximate the predicted spectrum by first including three Lorentzians of equal weight at 12, 30 and 80meV; we make the assumption that the linewidths of the excited doublets in PES are equal to the measured neutron linewidths (≈8meV). An additional Lorentzian representing the ground state doublet KR lies a distance kT_K≈4meV below E_F and also has width 4meV. The spectrum is multiplied by the Fermi function at 20K and convoluted with instrumental resolution (60meV). The resulting curve is shown as the broad line in the bottom of Fig. 2 (and the dashed line in the top frame) and is compared to the experimental spectrum in the top of Fig. 2. It can be seen that the data is substantially broader than predicted. This reflects the existence of a natural linewidth which is substantially larger than kT_K. To estimate this natural linewidth we generate a Voigt function fit to the data, using a 60meV Gaussian to account for instrumental resolution, a 20K Fermi function cutoff, and a Lorentzian peak,

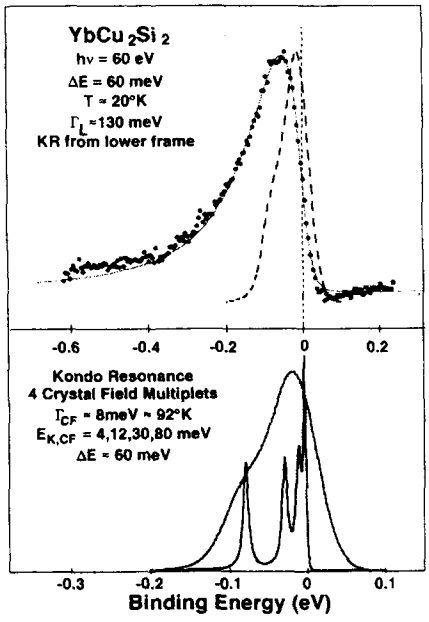

Fig. 2 The bulk J=7/2 peak for $YbCu_2Si_2$ from Fig. 1 B (points) compared to the spectrum predicted from Anderson single impurity model. In the bottom frame, the four crystal field levels, determined from neutron scattering, are shown together with the Gaussian broadened composite. This predicted line is shown again as the dashed line in the top frame. The solid line is the Voigt function fit discussed in the text. The data is substantially broader than the Anderson Model prediction; it is dominated by a natural linewidth ≈130meV.

which was allowed to vary in width and position to fit the PES data. The resulting Lorentzian parameters are Γ_L=130 meV (FWHM) and E≈60meV below E_F. This is shown as the solid line at the top of Fig. 2. The Voigt function fits the data very well; the data has a smooth symmetrical character as opposed to the asymmetric lineshape expected from the composite crystal field prediction.

The temperature dependence of the J=7/2 peak is shown in the top frame of Fig. 3. Apart from Fermi function broadening (0.1eV at 300K) there is no discernible temperature dependence. (The J=5/2 peak, not shown here, shows *no* temperature dependence.) As already discussed, for Yb the CF and SO resonances should vanish on the same scale as the ground state KR; here the scale is 50K so that by 300K the peaks should be reduced in intensity at the very least by a factor of two. The data distinctly violate the impurity theory as extended to PES.

For $CeSi_2$ we perform not only a similar analysis as above, but also a full GS T=0 calculation including CF states with infinite U (since finite U changes no widths at E_F). We constrained T_K to the thermodynamic value of ≈35K as determined from the specific heat[11]. Neutron scattering[12] shows two excitations, at 25 and 48 meV, with widths 13-14meV, due to crystal field splitting of the J=5/2 manifold. In addition the spin-orbit splitting is expected to be 0.2-0.3eV. The Anderson Model expectations for the spectra for Ce compounds are more complicated than for the Yb case. Due to hybridization the excited CF and SO multiplets acquire some $4f^0$ character. Photoemission causes excitations from the dominant (n_f ~1) $4f^1$ component of the hybridized ground state to the $4f^0$ component of the excited state. Hence sidebands below E_F are expected at the CF and SO excitation energies. The widths of these excitations (kT_{KCF} and kT_{KSO}) can be substantially larger than the width of the ground state KR doublet, which lies above E_F and has width kT_K. In our simple analysis we will assume that kT_{KCF} is equal to the linewidths of the CF excitations measured in neutron scattering. (The crystal field splittings would in any case set an upper limit on kT_{KCF}.) In the GS T=0 calculation these widths as well as weights are determined by the input parameters of the calculation.

The experimental spectrum for $CeSi_2$ at hν=120eV, shown in Fig. 1c, consists of the main $4f^1 \rightarrow 4f^0$ excitation at ≈ 2eV binding energy and a second feature near E_F. This feature consists of two peaks, one at E_F and the other at 0.28eV. This can be seen either in the 21.2 eV data (ΔE=18meV) of Patthey et al [6] (Fig. 1d) or in our 4d resonance data taken at 120 eV with ΔE=95meV (Fig. 3). The peak at 280meV is assumed to represent the J=7/2 SO manifold, the peak near E_F the J=5/2 manifold.

To isolate the J=5/2 peak for lineshape analysis we proceed as follows. As shown in Joyce et al[5], both Patthey's 18meV resolution data and our 95meV resolution data can be fit with nearly identical Voigt functions, both having two Lorentzians (E_1=280meV, Γ_1= 220meV; E_2=20meV, Γ_2=145meV) cut off by a T=20K Fermi function, but with appropriately different experimental widths (18 or 95meV). The 20meV feature obtained after subtracting out the 280meV component from Patthey's data is shown in Fig. 1e. To determine the curve expected from CF states found in neutron scattering, we proceed as for $YbCu_2Si_2$. Lorentzians at 25 and 48meV represent the CF sidebands; the widths are set equal to the neutron linewidth (13-14meV). A Lorentzian situated 4meV *above* E_F with width 4meV represents the ground state KR. These are cut off by a T=20K Fermi function; an 18meV Gaussian represents instrumental resolution. The spectrum thus ob-

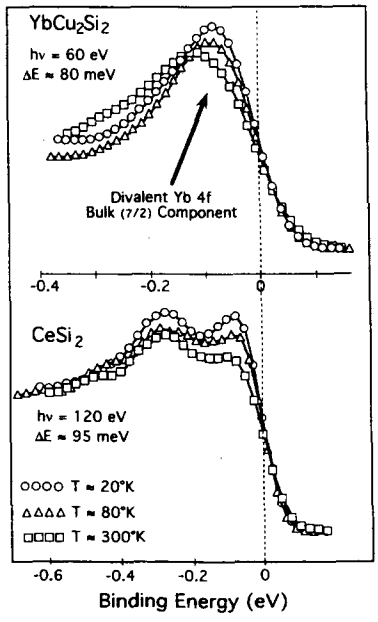

Fig. 3 The photoemission spectra for $YbCu_2Si_2$ and $CeSi_2$ in the near E_F region at three temperatures. (For $CeSi_2$, hν=120eV and ΔE=95meV; for $YbCu_2Si_2$, hν=60eV and ΔE=80meV). The strong temperature dependence predicted by the Anderson Model is not observed.

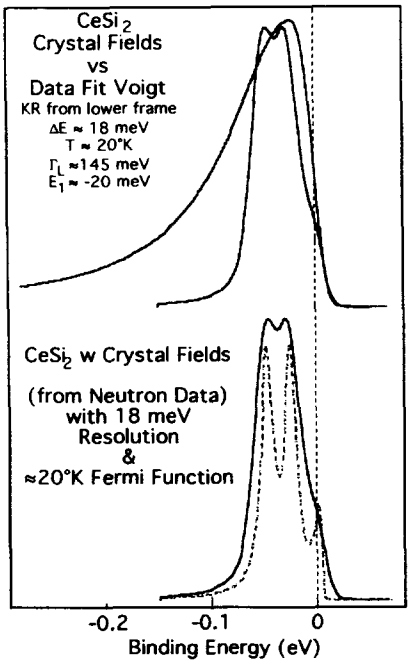

Fig. 4 The J=5/2 spectrum near E_F for $CeSi_2$ from Fig. 1E compared to lineshape from broadened crystal field states. In the bottom frame the three crystal field doublets determined from neutron scattering are shown, together with the Gaussian broadened composite. The latter is replicated in the top frame and directly compared to the data. Again, the data is substantially broader (≈145meV). The parameters of the Voigt fit are given in the top frame.

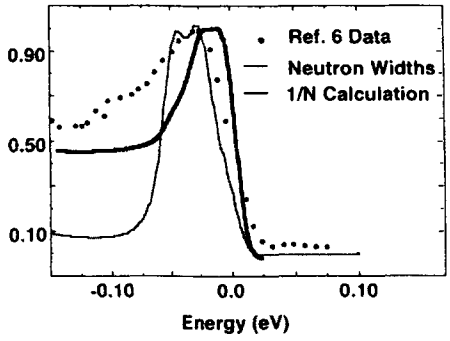

Fig. 5 Comparison of lineshapes obtained from the PES experiment of Ref. 6 (dots) vs lineshapes calculated from the GS model (heavy solid line) and broadened neutron linewidths (light solid line). All fits are poor, but the extra weight for the KR in the GS calculation yields a substantially worse fit than the simplistic neutron linewidth spectrum.

tained is shown at the bottom of Fig. 4 while in the top it is compared to the experimentally determined J=5/2 spectrum. Again the observed linewidth is substantially broader than predicted. With the stated resolution of Ref. 6 the CF levels should be resolvable, as demonstrated in the lower frame. Instead the data is much broader and symmetrical; it is dominated by the large natural linewidth (145meV). We will explore the sensitivity of the measured linewidth to assumptions about the non-f background in a future publication.

Since the above lineshape analysis may appear somewhat ad-hoc (although the only serious question is one of relative weights for the various CF's), we also include the full GS calculation in Fig. 5 with parameters as in ref. 6, but including the correct CF's with infinite U. Due to the added strength of the KR relative to the CF's, one can see that the fit becomes substantially worse than our approximate fits which give equal weight to all levels. Thus, surprisingly, our approximate representation (using Lorentzians at the neutron CF levels) of the GS excitation spectrum is actually a best case scenario. In Fig. 3 we show the temperature dependence of the J=5/2 and J=7/2 peaks for $CeSi_2$. The data have been normalized to the incident photon flux. No dramatic temperature dependence is observed; rather the small decrease with temperature can be explained primarily by Fermi function broadening and secondarily by inclusion of a small but reasonable amount of phonon broadening[5]. Fig.34 of Ref. 4 states that depletion of CF(SO) sidebands occurs with characteristic temperature equal to the CF(CO) splitting. It thus predicts a weak T dependence which may be difficult to distinguish from that due to ordinary mechanisms. Despite earlier claims[6], PES for Ce heavy fermions is not the optimum experiment to test for thermal renormalization of the excitation spectrum resulting from the Kondo model.

We thus have seen, both for a Yb and a Ce compound, that inclusion of excited multiplets, both crystal field and spin orbit, in the analysis of the photoemission spectrum does not alter the fundamental conclusions that the feature in PES near E_F has a linewidth (≈130meV) much larger than predicted by Anderson impurity theory, and that for $YbCu_2Si_2$ the predicted renormalization of the spectra with increasing temperature is absent. Due to the large natural linewidth these conclusions are not altered by the fact that our experimental resolution (60-95meV) is larger than the Kondo energies. Although the Anderson impurity model has proven highly successful in explaining the thermodynamic behavior of heavy fermion compounds, the extensions of the model to PES cannot explain these valence band photoemission results.

Acknowledgment - We wish to thank the referee for encouraging us to perform the full GS calculation.

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