Title
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Journal
Journal of Superconductivity and Novel Magnetism, 12(1)

ISSN
1557-1939

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Publication Date
1999-02-01

DOI
10.1023/a:1007723114818

Journal of Superconductivity, Vol. 12, No. 1, 1999

Strongly Correlated ϕ-Electron Systems: A PES Study

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1. INTRODUCTION

The term "heavy fermions" refers to materials (thus far only compounds with elements having unfilled $4f$ or $5f$ shells) whose large specific heat γ-values suggest that the conduction electrons at low temperatures have a very heavy effective mass [1]. Magnetic susceptibility measurements, χ, generally yield a Curie–Weiss behavior at high temperatures with a well-developed moment, which would be consistent with localized behavior of the f-electrons. Thus, the f-electrons appear to behave as noninteracting single impurities at elevated temperature. Below a characteristic Kondo temperature, T_K, the susceptibility levels off or even decreases [2]. This is interpreted as a compensation of the f-moment by the ligand conduction electrons that are believed to align antiparallel to form a singlet state and has led to the widespread use of the Anderson Impurity Hamiltonian and the Single Impurity Model (SIM). Weak hybridization with these conduction electrons yields a narrow, highly temperature dependent, DOS at the Fermi energy, often referred to as the Kondo resonance (KR). At still lower temperatures, it is generally agreed that in stoichiometric compounds a lattice of these singlet states finally results in extremely narrow bands at the Fermi energy, whose bandwidth is of the order $k_B T_K$. Clearly coherent bands cannot form above T_K owing to the narrow width.

Conventional band theory is unable to explain the high-temperature properties as well as the very heavy mass. The evolution of theoretical models has been driven by experiment. To date, the f component of the one electron addition/removal spectra of alloys containing Ce ions, as well as ordered Ce compounds, are qualitatively similar. Due to the difficulty of separating out the f component of the spectrum, the only concentration dependence that has been identified is the linear dependence of the overall intensity. This unsatisfactory state of affairs has caused theorists to focus their attention primarily on single impurity models that have the same qualitative features as observed in experiments. Thereby, effects that are present in ordered compounds have been, hitherto, largely ignored. Thus the SIM and its approximate solutions, i.e., the Gunnarsson–Schonhammer [3] (or GS) and the noncrossing approximation [4] (or NCA), has been the theoretical mainstay of interpreting heavy fermion photoemission data. There is, however, another school of thought that claims that the f-electrons nevertheless form well-defined Bloch states and very narrow bands at all temperatures [5–7]. Renormalized band theories [8] may yet prove useful, especially those that incorporate physics similar to the Kondo effect and its temperature dependence, perturbatively. However, the apparent success of the Single Impurity Model (SIM) in explaining macroscopic bulk phenomena suggests a correctness, at least at some level, though recent results (C. Booth, private communication) indicate that attempts to extract bandwidths from bulk data yield totally unphysical results. This suggests a need to re-evaluate the SIM even in connection with bulk data.

There are other considerations as well. Nozieres [9] has pointed out that the formation of the spin-compensating polarization clouds may be expected to only involve the conduction electrons within $k_B T_k$ of the fermi-energy. Thus, the number of electrons forming the compensating polarization cloud may be expected to be of the order of $k_B T_k \rho(\mu)$, where $\rho(\mu)$ is the conduction band density of states evaluated at the fermi level. Since $k_B T_k$ is much less than the depth of the occupied portion of the conduction band density of states, this yields an estimate of much less than

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0896-1107/99/0200-0175$16.00/0

one conduction electron per f ion. Thus, the estimated number of electrons in the polarization cloud is less than the number of f moments to be screened so an alternative description, other than the single impurity description, may have to be utilized for concentrated compounds. While it has not been determined which periodic approach is best, the periodic Anderson Model (PAM) appears to fit this description since in this picture the compensating conduction electrons are allowed to hop from f-site to f-site thus effectively screening in spite of insufficient numbers, and forming a narrow hybridized f–d band—*a magnetic polaron*. We consider this picture in more detail.

The PAM Hamiltonian [10,11] is actually an extension of the SIM, with the addition of a hopping term, Tahvildar-Zadeh *et al.* [10,11] show that it can be written as

$$H = H_f + H_d + H_{fd} + H_{\text{hop}}$$

where the first three terms are nearly identical to the SIM, while the hopping term is

$$H_{\text{hop}} = (-t^*/2\sqrt{D}) \sum_{(i,j)\sigma} (d^\dagger_{i\sigma} d_{j\sigma} + \text{h.c.})$$

In the above equation, $d(d^\dagger)_{i\sigma}$ destroys (creates) a d-electron with spin σ on site i. The hopping is restricted to the nearest neighbors and scaled as $(-t^*/2\sqrt{D})$. Here $t^* = 1$, the width of the Gaussian density of states, as the energy scale. The unhybridized d-bandwidth is $2\sqrt{D}$, and this broadens further with hybridization. This model, then retains the screening and moment formation of the impurity problem, but is further complicated by the lattice effects and the interaction between the moments.

Though at present the PAM cannot yet be applied to real systems due to computational difficulties, the predicted trends for model periodic systems fit the data substantially better than SIM, as we will see. Among the major differences between PAM and SIM is a much slower temperature dependence of the KR. Further, in a photoemission spectrum much more spectral weight is expected in the KR vs. the localized f-state, the so-called f^0 feature in Ce, thus yielding an apparently smaller localized f-occupancy, or n_f. Most importantly the PAM predicts the formation of f–d hybridized bands already at temperatures as high as 10 T_K whose width exceeds $k_B T_K$ by a substantial amount. The quasiparticle peaks do not lose spectral weight with temperature, but only broaden (except for Fermi function truncation), as actually observed in our experiments.

2. EXPERIMENTAL RESULTS

Photoemission spectra from single crystal heavy fermions [12] (data from many different compounds) yield overwhelming proof that the SIM is inapplicable to periodic crystalline systems. Among our findings are: (1) The intensity of the feature identified with the KR is for the most part temperature independent, except for broadening and fermi function truncation; (2) The KR can be as much as an order of magnitude broader than SIM predictions; (3) the f-level occupancy, n_f, is unrelated to the T_K and in general far too small; (4) The spectral weight of the KR is unrelated to T_K and in general far too large; (5) In Ce compounds the KR, or the $4f_{5/2}$, shows clear evidence of dispersion at $T \gg T_K$, with a bandwidth $W \gg k_B T_K$. Dispersion has not been clearly observed in Yb heavy fermions, but points 1–4 apply, with point 5 still under investigation.

Though we can choose from dozens of data sets to present our case, a truly unique test of the single impurity model can be made with the compound $YbInCu_4$, a heavy fermion with an isostructural phase transition at $T_V = 40$ K, accompanied by a 0.5% volume change, as well as a change in T_K from a value of $\approx$400 K below T_V to a value of 27 K above T_V. While it was initially thought that this represents the Yb counterpart of the Ce Kondo volume collapse, it soon became apparent that the phase transition is due to a density of states (DOS) effect driven by a low carrier density [13]. Nevertheless, the change in T_K with no change in the electronic structure except for increased hybridization, allows one to test the predictions of the SIM, without the complications deriving from different DOS effects in different compounds.

In Fig. 1, we show a series of spectra taken at temperatures above and below T_V. Only the divalent near-E_F region is shown, including both the bulk $4f_{5/2}$ (the spin-orbit component) and the bulk $4f_{7/2}$, or the KR. From direct integration of the bulk divalent and trivalent (not shown) portions of the spectrum, the n_f at 20 K is of the order of 0.5, far below the value of about 0.85 determined [13] from L_{III} edge studies and χ. While we do not yet understand the nature of this disagreement with L_{III}, it is clear from Fig. 1 that we are indeed observing a true bulk transition in the data. In particular, the intensity of the $4f_{5/2}$ is nearly constant from 200 K down to about 70 K and then shows a rapid increase near and below T_V. Our thermometry does not allow a more detailed comparison. By contrast, the $4f_{7/2}$ appears

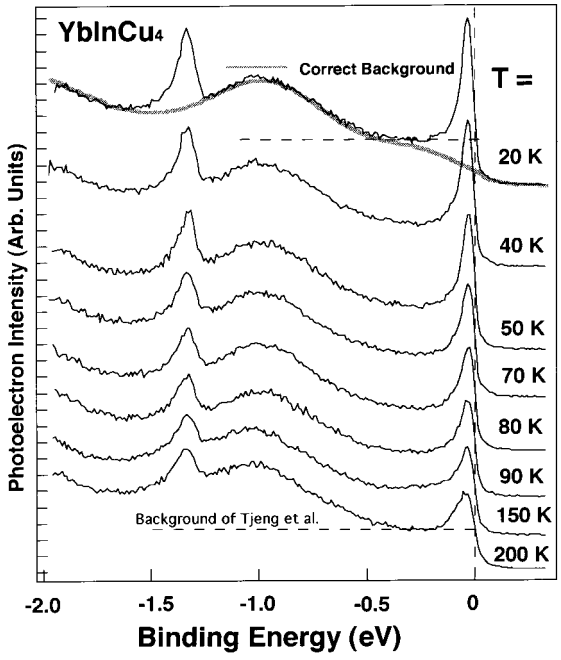

Fig. 1. Normal emission spectra at stated temperatures for $YnInCu_4$ at $h_n = 40$ eV. Note that the spin-orbit component at −1.3 eV binding energy is T-independent above 70 K. Thus, we clearly see the bulk phase transition.

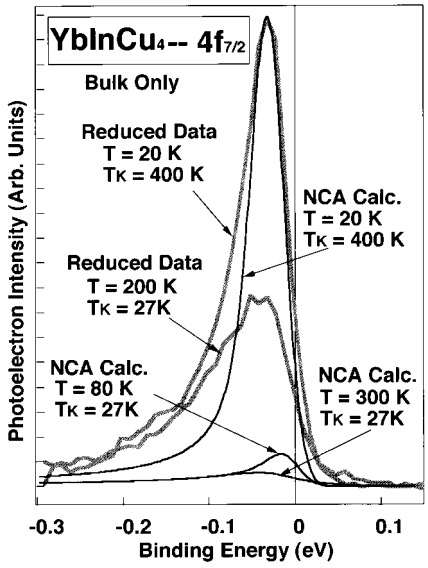

Fig. 2. Reduced bulk $4f_{7/2}$ peaks at 20 K and 200 K, with NCA calculations (thin solid lines) superimposed for comparison. The 200 K data have an order of magnitude too much weight relative to NCA predictions.

to continually decrease with temperature all the way to 200 K, but this is primarily due to a broadening of the feature, combined with the Fermi function truncation. When these are taken into account, the $4f_{7/2}$ is likewise nearly T-independent above 70 K. Hence, all temperature dependence is a consequence of the bulk transition at T_V.

Comparison to NCA calculations (code provided by D. Cox) is made in Fig. 2. The bulk components were separated from the spectra by subtracting a background a shown in Fig. 1. Using the incorrect straight line background shown in Fig. 1, first used by Tjeng *et al.* [14], the $4f_{7/2}$ intensity is underestimated by a factor of 2.5. Only the bulk $4f_{7/2}$ at 20 K and 200 K is shown in Fig. 2, with the thin-lined spectra representing NCA calculations at 20 K, 80 K, and 300 K, and normalized to the data at the peak of the 20 K spectrum. NCA spectrum were Gaussian broadened by 40 meV to simulate instrument resolution. Though the 20 K data peak in Fig. 2 is the narrowest $4f_{7/2}$ ever observed by us in Yb compounds, its intrinsic width (after deconvolving instrument resolution) FWHM = 65 meV is still nearly a factor of two larger than NCA predictions of FWHM ≈ 40 meV for a material with $T_K = 400$ K. More importantly, above T_V where T_K drops to 27 K, the 200 K data peak is about an order of magnitude more intense than the NCA predictions. Further, NCA predicts that this peak should narrow in intrinsic width from ≈40 meV to < 10 meV and shift toward E_F by 30 meV. No shift is observed, while the 200 K data peak actually broadens to FWHM ≈ 100 meV. These are qualitative differences which seriously call into question the applicability of the SIM.

The band nature of Ce–4f states at $T \gg T_K$ is demonstrated in Fig. 3. Though evidence for dispersion is seen to some degree in nearly every single crystal Ce heavy fermion investigated, best results are obtained in samples with a mirrorlike cleaved surface. The intensity of the Ce–$4f_{5/2}$ correlates more strongly with crystalline perfection than with T_K, with the most perfect single crystals yielding the most intense KRs. Indeed, an intense Ce–$4f_{5/2}$ peak is observed in $CeSb_2$, a layered material with a ferromagnetic transition at 10 K which implies that $T_K < 10$ K. Measurements [15] at 20 K from a (001) cleaved surface reveal about 25 meV of dispersion with angle relative to Γ, behavior amazingly similar to that predicted by PAM. The left panel of Fig. 3 shows ARPES data at 45 eV photon energy, and we see that as the peak disperses away from E_F it rapidly loses intensity as the f-character is diminished and replaced by d-character (consistent with PAM). On the other hand,

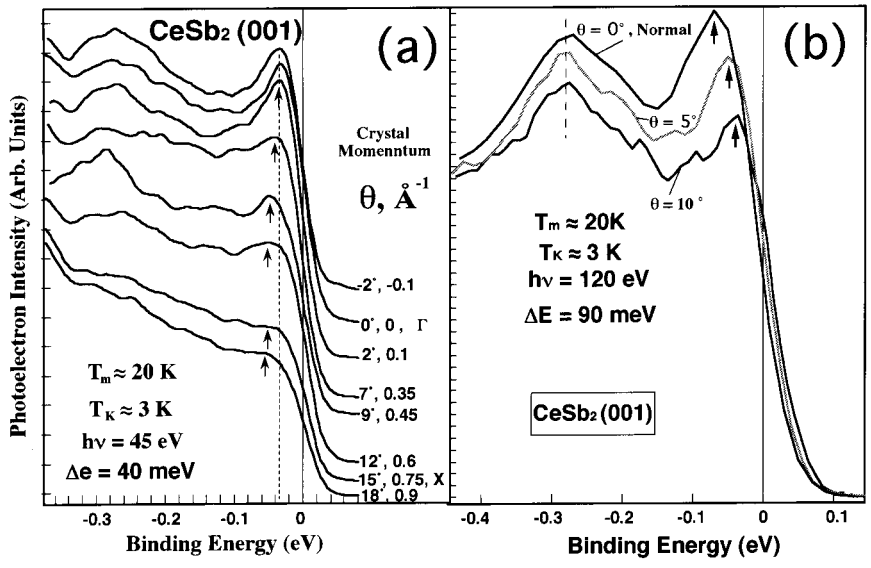

Fig. 3. Angle resolved photoemission spectra from $CeSb_2$ at 20 K and $h\nu =$ 40 eV (left frame) and $h\nu = 120$ eV (right frame), along two different directions in the Brillouin zone, but both starting at Γ. About 20 meV of dispersion is evident.

if in a different direction the dispersion is toward E_F (Fig. 3b), the $4f_{5/2}$ intensity is only slightly diminished as the $4f$ band disperses just above E_F and flattens out, leaving the tail on the occupied side. This flattened region can be identified with the KR as in the SIM, though it persists far above T_K. Similar dispersion has been observed now in several Ce compounds.

$5f$-electron heavy fermions display an amazingly similar electronic structure, i.e., narrow $5f$ bands. We have already shown this [15] to be the case in UPt_3 and USb_2, but in Fig. 4 we show perhaps the best data set ever taken on a uranium system. Here we present data for UAsSe, a tetragonal, ferromagnetic material, with $T_c \approx 113$ K, whose resistivity [16] has an upturn at low temperatures suggestive of Kondo-like behavior even below T_c. Angle resolved data at 20 K and 40 eV photon energy are shown within the first 14° from Γ. Again the surface is a mirrorlike cleaved surface. The peak near Γ is intense and clearly of $5f$ character, based on photon energy dependence and resonance results. As it disperses away from E_F it diminishes in intensity since, according to PAM, it acquires d-character. The Fermi energy as measured on a Au reference is as shown, indicating that even at Γ this feature is below E_F and never crosses E_F for the directions measured. This may be a hint as to the nature of the electronic structure.

3. CONCLUSIONS

A model for periodic Kondo systems will inevitably have to include the lattice. Preliminary PAM calculations [10,11] indicate that this inclusion yields results differing qualitatively, rather than just quantitatively, from the SIM predictions. The photoemission data on single crystal heavy fermions [12] are consistent with the following PAM predictions: (1) the temperature dependence of the KR is much slower than expected from the SIM: indeed, it is primarily due to broadening and Fermi function truncation; (2) the spectral weight of the KR relative to

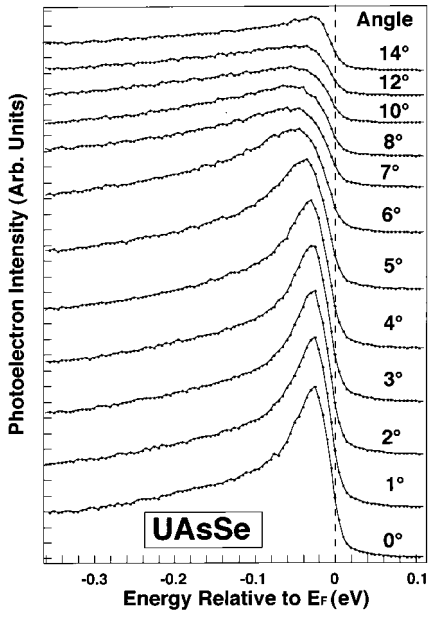

Fig. 4. Angle resolved spectra at 20 K for UAsSe with angles measured from the sample normal, i.e., Γ. Note that the intense f-feature diminishes rapidly as it disperses away from the Fermi energy, consistent with the PAM. About 30 meV of dispersion are evident.

the localized $4f$ feature (not discussed here) is much larger than the SIM expectations (equivalently, n_f values are far too small); (3) the KR and its sidebands does not lose spectral weight with T, but rather only broadens; (4) f-electrons in both Ce and U systems form narrow bands already far above T_K (the jury is still out for Yb systems); (5) the width of these bands is much larger than $k_B T_K$; (6) f-character is obtained in only some regions of the Brillouin zone, i.e., momentum dependence of the KR above T_K.

While the PAM seems to predict the correct trends, we have no reason yet to rule out other models, such as those of Liu [6,7] and Sheng and Cooper [5]. Such discrimination may occur when the models develop sufficiently to allow real system calculations.

ACKNOWLEDGMENTS

Work supported by the U.S. Department of Energy. Experiments performed at the Synchrotron Radiation Center of the University of Wisconsin which is operated under the auspices of the NSF under award no. DMR-95-31009.

REFERENCES

1. K. A. Gschneidner, Jr., L. Eyring, and S. Hufner, eds., *Handbook on the Physics and Chemistry of the Rare-Earths*, Vol. 10 (Elsevier Publishers, Amsterdam, 1987), and references therein.
2. G. R. Stewart, *Rev. Mod. Phys.* **56**, 755 (1984).
3. O. Gunnarsson and K. Schonhammer in K. A. Gschneider, Jr, L. Eyring, and S. Huffner, eds., *Handbook on the Physics and Chemistry of Rare Earths*. Vol. 10, (Elsevier Publishers, Amsterdam, 1987), pp. 103–163.
4. N. E. Bickers *et al.*, *Phys. Rev. B* **36**, 2036 (1987).
5. Q. G. Sheng and B. R. Cooper, *Phil. Mag. Lett.* **72**, 123 (1995).
6. S. H. Liu, in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 17 (North Holland, Amsterdam, 1993), Chap. 111, pp. 87–148.
7. S. H. Liu, *Physica B* **240**, 49 (1997).
8. Gertrud Zwicknagl, *Adv. Phys.* **41**, 203 (1992).
9. P. Nozieres, *Ann. de Phys.* **10**, 19 (1985).
10. A. N. Tahvildar-Zadeh, M. Jarrell, and J. K. Freericks, *Phys. Rev. B* **55**, R3332 (1997).
11. A. N. Tahvildar-Zadeh, M. Jarrell, and J. K. Freericks, *Phys. Rev. Lett.* (accepted).
12. A complete review of single crystal data and various theories will appear as: A. J. Arko, P. S. Riseborough, A. B. Andrews, J. J. Joyce, M. Jarrell, and A. Tahvildar-Zadeh, in K. A. Gschneider and L. Eyring, eds., *Handbook of the Physics and Chemistry of Rare Earths*, (1998).
13. A. L. Cornelius *et al.*, *Phys. Rev. B* **56**, 7993 (1997).
14. L. H. Tjeng *et al.*, *Phys. Rev. Lett.* **71**, 1419 (1993).
15. A. J. Arko *et al.*, *Phys. Rev. B* **56**, Rapid Commun. **R7041** (1996).
16. Z. Henkie *et al.*, *J. Phys. Chem. Solids* (1998).