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4f bands in Ce heavy fermions and mixed valent compounds at $T \gg T_K$

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Abstract

We report evidence of 4f band character in Ce 4f states at $T \gg T_K$ using high-resolution angle-resolved resonant photoemission. The Ce intermetallic compound $CePt_{2+x}$ was grown and studied in situ by the method of MBE and was characterized by LEED, XPS and XAS. These new findings suggest a need for a re-examination of 4f photoemission in Ce compounds.

The Gunnarsson–Schonhammer (GS) model of the electronic properties of Ce heavy fermions [1] has lent insight into the final state transition probabilities observed in XPS and XAS spectroscopies. For the 4f 'valence' excitations probed by UPS spectroscopy, however, the measure of success is less certain. In the GS model the near E_F features are due to a many-body excitation known as the Kondo resonance (KR), located at $\sim k_B T_K$ above E_F (so that only the remnant tail below E_F is visible in the PES), where T_K is the Kondo temperature. A key prediction is that the spectral weight of the KR should scale with the hybridization or alternatively the f-occupancy n_f. Although the magnitude of the scaling may be somewhat reduced due to the existence of crystal field states (at higher T_K values), and double f-occupancy (finite U_{ff}), calculations incorporating these refinements [2] show that strong correlations do persist between the weight of the KR and T_K. Recently Joyce et al. [2] noted that the Ce 4f spectral weights and line shapes are virtually identical in both trivalent and mixed-valent compounds, despite widely varying compositions and crystal structures. They concluded that the intensity of the near E_F states does not exhibit the expected scaling behavior.

Efforts to explain the lack of scaling have partly focused on the nature and role of the surface contribution, a problem mainly for the experimentalist. Until recently, the majority of UPS experiments [3] on these materials have employed arc-melted polycrystalline samples which are either cleaved or scraped in situ. Flux-grown single crystals cleaved in situ afford improved surface to bulk signal ratios, minimal contamination and reduced inhomogeneous broadening. Nonetheless, even in these one often obtains atomically rough surfaces with high step densities. In this paper, we report the results of an alternative approach which solves these problems, namely in situ growth via MBE. To the best of our knowledge this is the first ARRPES study of Ce inter-metallic prepared and studied in situ.

The compound $CePt_{2+x}$ $(0 \leq x \leq 1)$ grows in the C_{15}

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$MgCu_2$ Laves phase with a lattice parameter $a_0 \approx 7.7$ Å as determined from LEED. The sample was grown following the method of Tang et al. [4] and we refer the reader to this work and to a related publication [6] for further details. The mixed-valent character of the film was established by measurement of the 3d core level spectra using XPS [4]. The susceptibility χ (as determined from arc-melted samples), indicates that T_K is comparable to that of antiferromagnetic $CePt_2$ ($T_N = 1.7$ K) and hence <20 K.

EDCs were collected at the 4f resonance ($h\nu = 120$ eV) and anti-resonance ($h\nu = 112$ eV) with $\Delta E \approx 90$ meV. Our position in $k_{||}$ was ascertained by LEED, however we were unable to determine the precise value of $k_\perp$ because of the narrowness of the 4d absorption edge. Scans along the high symmetry directions Γ–M and Γ–K reveal amplitude variations which match the lattice periodicity [5], i.e. the intensity near E_F is strongest at the Γ points (as far as the third zone), and decreases toward the zone boundaries. Fig. 1 shows fits at Γ and M using a Doniach–Sunjuic line shape with an integral background and a Fermi level cutoff. The reduction in amplitude between 0° to 10° can be explained by the apparent dispersion of the features towards E_F (≈30 meV) so that the Fermi level cutoff produces the modulation. Thus in Fig. 1, the fit at 10° may be derived from the fit at 0° by decreasing the binding energy of both peaks, while holding the line shape fixed and allowing the background to relax. This fit may be regarded as somewhat arbitrary since it is not unique, but the dispersion is visible in the raw data.

We have also observed similar phenomena in flux grown single crystals. For reasons of space we limit ourselves to $CeSb_2$ and $CeBe_{13}$. $CeSb_2$ has 2-D Sb sheets separating Ce/Sb planes (and thus likely to yield a smooth cleave). The compound orders ferromagnetically at $T \sim 15$ K and has a Ce–Ce distance ~3.22 Å, somewhat less than metallic Ce. T_K is unknown, but is certainly <15 K, so that the measurement temperature 20 K > T_K. Fig. 2(a) shows the near E_F spectrum of $CeSb_2$, normalized to photon flux and adjusted for takeoff angle ($\sim\cos\theta$). The drop in intensity of the peak at E_F is even larger than that seen in $CePt_{2+x}$. $CeBe_{13}$ has a cubic $NaZn_{13}$ structure with a Ce–Ce distance of 5.1 Å and $T_K \sim 300$ K. Fig. 2(b) shows two different cleaves of a single crystal

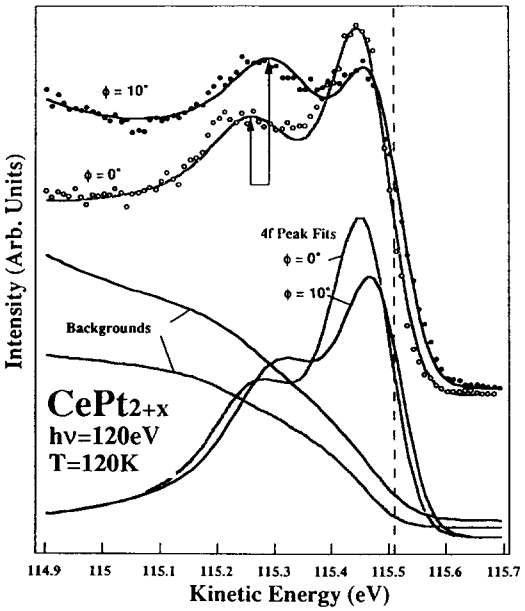

Fig. 1. Fits to the data at 0° or Γ (circles = data, grey lines = fit) and 10° or M (circles = data, black lines = fit) as described in the text.

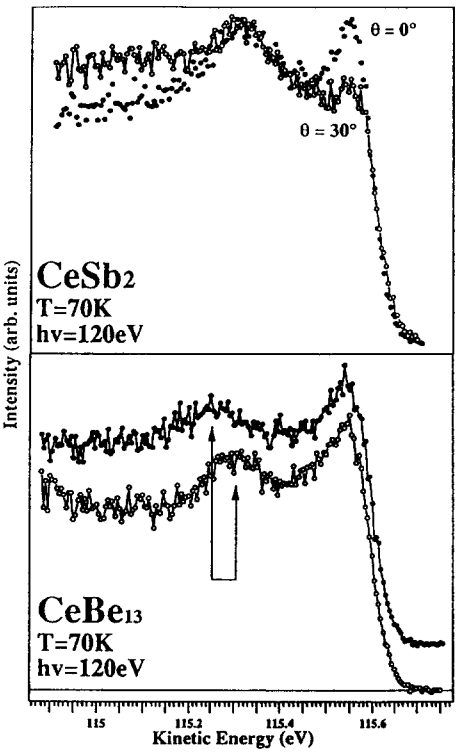

Fig. 2. (a) Flux normalized spectra for $CeSb_2$ filled (open) circles are 0° and (30°), respectively. (b) Comparison of two different cleaves on flux grown single crystals of $CeBe_{13}$.

$CeBe_{13}$ sample, which yield a difference in binding energy for the spin–orbit side band of ~50 meV, at least twice what we would expect for a T_K of 300 K in a renormalized band scheme.

We have verified that this behavior is not observed in polycrystalline samples of $CeAl_3$ and $CeSi_2$, so it cannot be due to an artifact of our experimental method. We are also convinced that the periodic amplitude variation is not a consequence of the existence of d-states at E_F, since these constitute <20% of the spectral weight at E_F with only broad (>0.4 eV) features present which would not selectively affect the Fermi level peak. In any case, analyses using the GS or NCA model [3] have always neglected the d-band contribution entirely. The surface is known to be more trivalent than the bulk (since reduced coordination leads to smaller hybridization and increased localization of the f electrons), so we can also rule out a surface related effect.

A more serious problem occurs when we try to understand the data for $CePt_{2+x}$ within the framework of a renormalized band scheme [6]. Renormalized quasiparticle bands exist only below a characteristic coherence temperature $T^{coh} \ll T_K$; above T_K the phase coherence is lost and localization is restored. Hence, the observation of $\boldsymbol{k}$-dependence at ~10 times the coherence temperature in the f-derived features is difficult to rationalize. The magnitude of the estimated energy dispersion is roughly a factor of ~10 greater than what is expected from the Kondo lattice in a renormalized band description. Since $CePt_{2+x}$ is a low-T_K material ($T_K < 20$ K), the KR should be of negligible intensity at the measurement temperature $T^{meas} = 120$ K. Thus, we must consider whether a possible reconciliation is offered within a conventional band interpretation, since it is known from de Haas–van Alphen (dHvA) measurements that the f electrons reside in a narrow band (for $T \ll T_K$) with a Fermi surface resembling that calculated in the LDA. In summary, our results indicate that in situ preparation will benefit any UPS study of Ce intermetallics and call for further high-resolution angle-resolved work. They also show that the width of the 4f 'bands' is larger than that expected for a periodic lattice of impurities.

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