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Evidence for possible 4f bands at $T \gg T_K$ in the heavy-fermion single crystal CePt$_{2+x}$

A. B. Andrews, J. J. Joyce, A. J. Arko, and J. D. Thompson
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

J. Tang, J. M. Lawrence, and J. C. Hemminger
Institute for Surface and Interface Science, The University of California, Irvine, California 92717

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We report the observation of strong amplitude variations with **k** in the $4f$ photoelectron spectra of a nearly trivalent heavy-fermion compound (CePt$_{2+x}$). The amplitude of the $4f$ feature, previously identified as the Kondo resonance, displays the full symmetry of the lattice, suggesting some band character already at $T \approx 10T_K$. Kondo lattice-derived bands are expected to exist only at $T \ll T_K$, so that this would seem to favor conventional bands at high T. The single-impurity model by contrast demands purely localized behavior at these temperatures.

Photoelectron spectroscopy (PES) in Ce heavy-fermion compounds has been controversial for a number of years. The most comprehensive attempts at a description of the excitation spectrum are the approximate solutions of the single-impurity Anderson model (SIAM). These solutions, namely, the Gunnarsson-Schonhammer (GS) approximation,[1] and the noncrossing (NCA) approximation[2] both yield similar predictions for the excitation spectrum. At the heart of the theory is the postulate that the $4f$ electrons in heavy-fermion Ce compounds are essentially localized (trivalent Ce) and that it is only the small hybridization with the ligand conduction electrons which result in $4f$ spectral weight near the Fermi energy, E_F. In Ce compounds the theory predicts that the centroid of this weight, the so-called Kondo resonance (KR), is at k_BT_K above the Fermi energy E_F and it is only the remanent tail below E_F which yields the occupied weight. Additionally, there may exist occupied crystal field and spin-orbit (SO) sidebands. The magnitude of the KR spectral weight should be directly proportional to the hybridization, or, equivalently, to the degree to which Ce deviates from trivalence; indeed, it should be directly proportional to the thermodynamic quantity T_K, the Kondo temperature, and is thus a *bulk property* of the material. Within the impurity model, the KR has no **k** dependence by construction, since, to calculate the spectral weight requires integration over all conduction electrons. Several papers[3–5] claim to observe directly this correlation of spectral weight with T_K, and find it in close agreement with the predictions of GS and NCA. By contrast, our own work on many Ce compounds[6] (generally cleaved single crystals) fails to show such correlation.

The observation of the de Haas–van Alphen (dHvA) effect in many Ce heavy fermions[7] clearly indicates that at very low temperatures the KR must be a narrow band whose Fermi surface closely resembles one derived from conventional band theory [e.g., the local density approximation (LDA)]. This has led to the concept of a Kondo lattice[8] whose effects will be observable only below the characteristic coherence temperature, $T^{\text{coh}} \ll T_K$. Below T^{coh} we obtain Kondo bands, while above T^{coh} the $4f$'s are localized so that the GS and NCA solutions are presumed to correctly represent the photoemission spectrum. The $4f$ energy dispersion with **k** due to the Kondo lattice is of the order k_BT_K since the bandwidth is associated with the thermodynamic quantity T_K. The observation of strong **k**-dependent effects at $T \gg T_K$, then, would call into question the very applicability of the NCA or GS.

No attempts have been made up to now to look for **k**-dependent effects in the KR, although several papers[9,10] have argued that the $4f$'s in strongly hybridized materials (e.g., CeRh$_3$ where T_K is of the order 1000 K) should be treated within the band model rather than the SIAM. They maintained, however, that weakly hybridized or low-T_K heavy fermions could still be described by GS, based on apparently good fits to PES spectra.[11] However, while reasonable fits can usually be obtained for a single spectrum after adjusting parameters and smoothing, systematic efforts to verify the model are less convincing. For example, the T_K needed to fit PES data rarely approximates the value measured in bulk properties.

In this paper we report the first PES observation of **k**-dependent effects at $T \gg T_K$ in Ce-$4f$ features which would normally be identified as the KR and SO sideband. We emphasize that this observation is made in a nearly trivalent very low-T_K material (CePt$_{2+x}$, $T_K < 20$ K) in which the KR from all expectations should have been of negligible intensity at the measurement temperature $T^{\text{meas}} = 120$ K (based[3]

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on NCA). Moreover, while $T^{\rm meas} \approx 6T_K$ to $12T_K$, it is perhaps as much as $100T^{\rm coh}$, i.e., a temperature where the SIAM assumes only localized states. Assuming that the range of validity for Kondo lattice bands does not extend to $10T_K$, our results are then suggestive of more conventional (possibly renormalized) band effects.

The compounds $\rm CePt_{2+x}$ grow in the $\rm C_{15}MgCu_2$ Laves phase for the series $0 \leqslant x \leqslant 1$. Lattice parameters obtained from a series of arc-melted polycrystals confirm that a_0 varies linearly with x from $a_0(x=0) = 7.75$ Å to $a_0(x=1) = 7.67$ Å. The susceptibility χ is almost independent of x (except for minor differences below 100 K), indicating that T_K for $0 \leqslant x \leqslant 1$ is comparable to that of antiferromagnetic $\rm CePt_2$ ($T_N = 1.7$ K) and hence < 20 K. The present sample was prepared *in situ*, following the method of Tang, Lawrence, and Hemminger,[12] who showed that by vapor depositing Ce onto a well-polished and cleaned single crystal of Pt(111) with a subsequent 800 °C anneal, the Ce diffuses into the bulk to produce an approximately 5–10 mL thick (111)-oriented ordered compound as evidenced by a good low-energy electron diffraction pattern with 2×2 hexagonal symmetry, characteristic of $\rm CePt_{2.2}$. A further check on the film stoichiometry was obtained from the ratio of the x-ray photoemission spectroscopy spectral weights of Pt and Ce core levels, calibrated for the given instrument.

In the present experiment the stoichiometry of the crystal film was independently determined from a measurement of the ratio of the (Pt $4f$)/(Ce $5p$) spectral weights. These were compared to ratios obtained from PES data on arc-melted samples where the ratios varied linearly for $x = 0.2$, 0.5, and 1.0. A value of $x = 0.9$ was obtained for the film, but this determination is skewed towards higher Pt values since the top layer of the crystalline film is Pt rich, as shown by Tang.[12] Correcting for this we obtain $x \approx 0.7$, but the precise value of x is less important than the evidence that the crystalline film grows as $\rm CePt_{2+x}$, since all materials are nearly trivalent, with $T_K < 20$ K, for all $x \leqslant 1$. Indeed, PES valence band spectra of polycrystals are nearly identical for all $x \leqslant 1$ at $h\nu = 120$ eV. In what follows, we compare the film data to polycrystalline $\rm CePt_3$, with the understanding that the latter represents $\rm CePt_{2+x}$ for $0 \leqslant x \leqslant 1$. We further measured the x-ray absorption spectra (using the total electron yield at the Ce $3d$ absorption edge) of the film and the polycrystalline samples, to estimate the $4f$ occupation n_f from the amplitude of the f^0 satellite. No f^0 peak was observed in any $\rm CePt_{2+x}$, thus confirming the nearly trivalent nature of the crystalline film and arc-melted samples.

Measurements were carried out at the Los Alamos U3C beamline at NSLS, using an angle resolved VSW spectrometer with a ±1° annular aperture. Spectra were taken at the $4f$ resonance ($h\nu = 120$ eV) and antiresonance ($h\nu = 112$ eV), with total resolution $\Delta E \approx 90$–110 meV. The sample temperature was ≈ 120 K (or $\approx 10T_K$), determined from a fit to the Fermi edge at $h\nu = 21$ eV and 20 MeV resolution. Significant $\mathbf{k}_\perp$ conservation, as evidenced by band dispersion with photon energy at normal emission, confirmed a true bulk crystal.

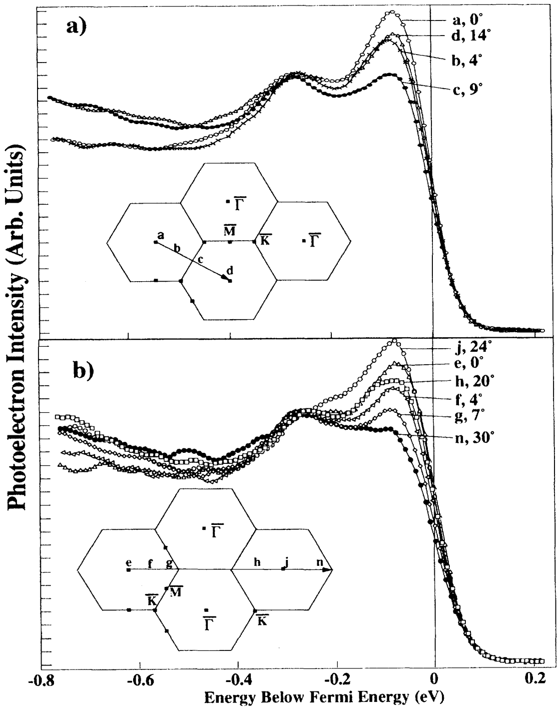

FIG. 1. Valence band spectra of $\rm CePt_{2+x}$ crystal film within the first 0.8 eV of E_F for several orientations. The data have been normalized at the SO peak at -280 meV and smoothed by a 40 meV full width at half maximum Gaussian (corresponding to four data points) to aid the eye. The zero of energy is placed at the midpoint of the Fermi edge since reference spectra were not taken at each angle. The insets represent the extended surface Brillouin zone for the (111) plane of the crystal. (a) Data along the $\bar\Gamma$-$\bar M$ direction, at 0, 4, 9, and 14° from normal. (b) Data along the $\bar\Gamma$-$\bar K$ direction, at 0, 4, 7, 10, 24, and 30° from normal.

PES angular scans are presented in Fig. 1 for Ce $4f$ states near E_F. The insets in Figs. 1(a) and 1(b) are extended surface Brillouin zones (BZ's) for the (111) plane. The arrows mark the direction of $\mathbf{k}_\parallel$ for each set of measurements, while individual spectra are identified at the appropriate location in the zone with lower case letters. The near-E_F peak is of greatest interest since it is this peak which is identified as the KR in the GS or NCA calculations. We varied the takeoff angle such that $\mathbf{k}_\parallel$ was varied either along $\bar\Gamma$-$\bar M$ [Fig. 1(a)] or along $\bar\Gamma$-$\bar K$ [Fig. 1(b)] in the surface Bz. In Fig. 1(a) the $\bar M$ point is obtained at 7° from normal (near curve c, at 9°), while the next $\bar\Gamma$ point is at 14° from normal (curve d). The $\bar K$ point in Fig. 1(b) occurs at 8° from normal. One can see from Fig. 1 that the symmetry of the lattice is closely reproduced by the angular amplitude variation. The intensity near E_F is strongest at all $\bar\Gamma$ points (data were taken as far as the third zone), while it is much weaker near the zone boundaries. Along the $\bar K$-$\bar K$ zone edge the KR intensity remains more or less constant and weak. [See curves g, and n, in Fig. 1(b). Also, several additional undisplayed curves along $\bar K$-$\bar K$ overlay with g]. Intensity increases again for curve h at 20° where $\mathbf{k}_\parallel$ is now within 4° of the next high intensity $\bar\Gamma$ point (curve j). A slight (2°) downward misorientation of the crystal precluded an exact reproduction of the signal from zone to zone.

Except for photoelectron diffraction, it is difficult to devise a mechanism whereby nondispersive features display

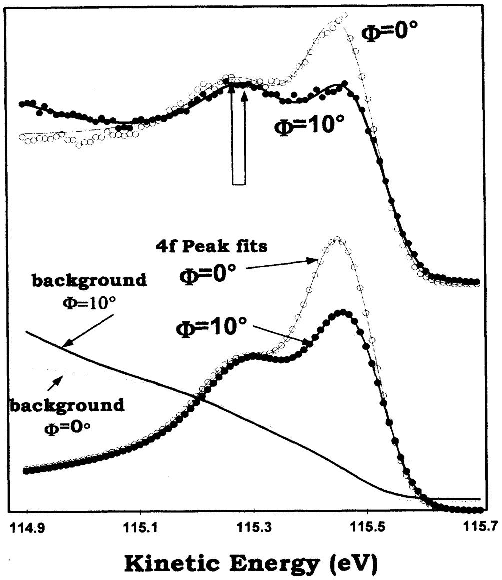

FIG. 2. PES spectra (normalized at the SO peak) for CePt_{2+x} at 0° (open circles and thin lines) and 10° (dark circles and lines) from normal, with lines through data for each angle representing fits composed of two peaks with Doniach-Sunjuic line shapes plus the featureless backgrounds shown. The data and composite fits through them have been shifted upward for clarity. The Fermi energy is fixed at 115.51 eV. The small dispersion is actually seen in the raw data. The fits only help to quantify it. The reduction in amplitude results primarily from a convolution with the Fermi function.

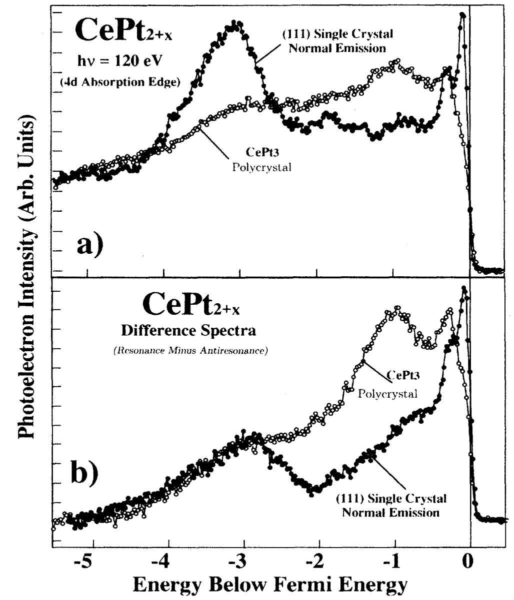

FIG. 3. Comparison of single crystal film CePt_{2+x} spectrum at normal emission with polycrystal CePt_3 spectrum. Both are taken at the resonant photon energy of 120 eV. (a) Raw spectra normalized at the -280 meV peak. (b) Difference curves obtained by subtracting the PES spectra at antiresonance ($h\nu = 112$ eV) from the spectra in Fig. 2(a) and normalized at -3 eV.

periodic amplitude variations at a kinetic energy of 120 eV where the final states likely form a continuum. We have determined that we are not observing diffraction effects based on the *relative* amplitude changes in the $4f^1$ features separated by a mere 280 meV. The same relative amplitude changes also rule out the unlikely case of periodic cross-section effects. Thus we consider the possibility of dispersion in bandlike states. While in Fig. 1 the features appear nondispersive, this may be entirely due to uncertainty in the exact location of the Fermi energy. However, several sets of spectra were taken consecutively at different angles (e.g., 0° and 10°, within 30 min of each other) with no change in settings except detector angle, specifically to look for dispersion. These consistently indicate an energy shift in the SO peak positions up to 30 MeV (actually seen unaided with some effort), while reference spectra show negligible Fermi energy shifts in this angular range. One such set is shown in Fig. 2 with spectra at normal emission (open circles and thin lines) and 10° (dark circles and lines). To better quantify the dispersion they were fit with two Gaussian-broadened Doniach-Sunjuic line shapes plus featureless backgrounds approximated from data at antiresonance. The Fermi energy was held fixed at a kinetic energy of 115.51 eV. Nothing was done to the raw data except normalization at the SO peak. While no multiparameter fit can be considered unique (although it should be constrained to adhere to the physics of PES), the fits are entirely consistent with the KR moving by ≈ 35 meV toward E_F between 0° and 10° as shown, while the SO shifts by about 25 meV. The reduction in peak amplitude at E_F comes primarily from convolution with the Fermi function, although the unconvoluted fitted peak wants to decrease by $\approx 10\%$. Thus even minuscule dispersion near E_F can easily explain the experimental results. The fitted energy dispersion is about an order of magnitude larger than that expected from the Kondo lattice. On the other hand, the KR dispersion obtained from fitting is actually consistent with LDA-derived bands[13] for CePt_2. Similar effects have now also been observed[14] in several other simple crystal heavy fermions, most notably CeBe_{13}. In the latter compound the beryllium s-p density of states (DOS) is of negligible intensity so that the large amplitude variations are unambiguously due to Ce DOS alone. While dispersion seems to be the most likely source of the amplitude modulation, whatever it may prove to be, it complicates any interpretation within the GS or NCA models since this is now a function of momentum even at $T \gg T_K$.

We now turn our attention to a second, possibly related, phenomenon. In Fig. 3 we compare the single crystal film data at normal emission to a polycrystalline CePt_3 spectrum. The raw spectra are displayed in Fig. 3(a), while the difference curves (spectrum at $h\nu = 120$ eV minus the spectrum at $h\nu = 112$ eV), which are often assumed as representative of $4f$ emission only,[4,5] are shown in Fig. 3(b). The latter are normalized to each other at -3 eV. Remarkable and unexpected differences are evident in the f-derived features. Indeed, from the polycrystal spectra one might conclude that there is agreement with GS or NCA in that the absence of the near-E_F peak agrees[3] with the small T_K. The normal emission single crystal data, by contrast, clearly shows that the emission at E_F is much stronger than can possibly be explained by the GS and NCA, particularly if one factors in the measuring temperature of $\approx 10T_K$. Interestingly, the SO peak in Fig. 3(b) appears stronger in the polycrystal. Additionally we note that the polycrystal spectra might suggest that the -1 eV peak (the strongest) is the "main" f^1-f^0 peak. By contrast, the single crystal data clearly show that it is the small -3 eV feature which corresponds to the main f^1-f^0 transition. The -1 eV peak was observed at various angles to be highly dispersive and at some angles stronger than the near-E_F peak. It is to be identified with Ce $5d$ emission which is known to resonate[15] at the $4d$ absorption edge. (As an aside, the SO plus KR spectral weights should constitute about 10% of the "main peak" spectral weight.[15] Instead they constitute about 70% even after subtracting the d weight, indicative of a nearly divalent material. This is a serious additional disagreement with GS and NCA.)

One possible explanation for the discrepancy between single and polycrystal samples is that the polycrystal data represent an average over the whole BZ, so that if the band disperses above E_F for a significant fraction of the zone, a weak intensity would be observed at E_F. However, we always found a nonzero intensity at E_F along the two high symmetry directions studied, thus leading to speculation that the discrepancy lies in the nature of polycrystal samples themselves. Cleaving (and certainly scraping) can result in significant strains and high surface step densities. The resulting disorder can destroy the phase coherence of the narrow electronic states. Further, impurities accumulate in the grain boundaries of arc-melted polycrystals, and are preferentially exposed on cleaving or scraping, resulting in a disordered surface. All of these emphasize the limitations of working with polycrystal heavy fermions for PES studies.

A number of conclusions follow from all this. (1) The $4f$ electronic structure of nearly trivalent, low-T_K heavy fermions suggests bandlike properties (persisting at least up to $\approx 10T_K$) since it displays the full symmetry of the BZ. The intensity of the near-E_F peak has no obvious relation to T_K since, among other things, it varies with momentum and is far too large. This supports our earlier observation that no such correlation exists. Because of the bandlike nature at $T \gg T_K$, we assume that these features represent conventional bands as opposed to Kondo lattice bands (although the latter are not ruled out). (2) Dispersion appears to be the most likely source of the amplitude effect. Better resolution and intensity with a future undulator light source should unambiguously settle this issue. (3) Final state effects likewise can be ruled out since no mechanism known to us yields itinerant final states from localized initial states. Thus the observation of $\mathbf{k}$-dependent behavior at $T \gg T^{\mathrm{coh}}$ is to be associated with itinerant initial states. This makes it far easier, for example, to explain the dHvA effect in heavy fermions. (4) The absence of the near-E_F peak in polycrystals does not preclude its existence in the bulk or in a high quality single crystal. Any correlation between this intensity and T_K reported from polycrystals in the past[3–5] should now be reexamined. (5) Strong, dispersive d-band features exist near -1 to -2 eV in resonance spectra previously thought[4,5] to be purely $4f$. They must be accounted for in any fits to various models.

Given all this, we assert that there is as yet no comprehensive theory of heavy-fermion photoemission since the $4f$ states do not behave as single impurities, but are strongly influenced by the crystal lattice.

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[1] O. Gunnarsson and K. Schonhammer, Phys. Rev. B **28**, 4315 (1983).

[2] N. E. Bickers, D. L. Cox, and J. W. Wilkins, Phys. Rev. B **36**, 2036 (1987).

[3] D. Malterre, M. Grioni, P. Weibel, B. Dardel, and Y. Baer, Phys. Rev. B **48**, 10 599 (1994).

[4] J. W. Allen, S. J. Oh, O. Gunnarsson, K. Schonhammer, M. B. Maple, M. S. Torikachlivi, and I. Lindau, Adv. Phys. **35**, 275 (1986).

[5] F. Patthey, J.-M. Imer, W.-D. Schneider, H. Beck, Y. Baer, and B. Delley, Phys. Rev. B **42**, 8864 (1990).

[6] J. J. Joyce, A. J. Arko, J. M. Lawrence, P. C. Canfield, Z. Fisk, R. J. Bartlett, and J. D. Thompson, Phys. Rev. Lett. **68**, 236 (1992); J. J. Joyce and A. J. Arko, *ibid.* **70**, 1181 (1993).

[7] P. H. P. Reinders, M. Springford, P. T. Coleridge, R. Boulet, and D. Ravot, Phys. Rev. Lett. **57**, 1631 (1986).

[8] N. D'Ambrumenil and P. Fulde, J. Magn. Magn. Mater. **47&48**, 1 (1985).

[9] C. Laubschat, E. Weschke, M. Domke, C. T. Simmons, and G. Kaindl, Surf. Sci. **269/270**, 605 (1992).

[10] E. Weschke, C. Laubschat, R. Ecker, A. Hohr, M. Domke, and G. Kaindl, Phys. Rev. Lett. **69**, 1792 (1992).

[11] J.-S. Kang, J. W. Allen, O. Gunnarsson, N. E. Christensen, O. K. Andersen, Y. Lassailly, M. B. Maple, and M. S. Torikachlivi, Phys. Rev. B **41**, 6610 (1990).

[12] J. Tang, J. M. Lawrence, and J. C. Hemminger, Phys. Rev. B **48**, 15 342 (1993).

[13] D. D. Koelling (private communication).

[14] A. B. Andrews, J. J. Joyce, A. J. Arko, P. C. Canfield, and Z. Fisk (unpublished).

[15] J. M. Lawrence, J. J. Joyce, A. J. Arko, R. J. Bartlett, P. C. Canfield, and Z. Fisk, Phys. Rev. B **47**, 1546 (1993).