Momentum-resolved photoemission of the Kondo peak in an ordered Ce-containing alloy

M. Garnier, D. Purdie, K. Breuer, M. Hengsberger, and Y. Baer

Institut de Physique, Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland

A comparison of uv-photoemission spectra recorded from the surface alloys $Pt(111)(\sqrt{3} \times \sqrt{3})R30°Ce$ and $Pt(111)(2 \times 2)La$ allows the contribution from the $4f$ electrons to be seen easily. The valence-band structure of these two surfaces is very similar, and the most obvious $4f$ contribution in high-resolution photoemission spectra of the Ce-containing alloy is the tail of the Kondo peak cut at E_F. Within the limits of our measurement, no dispersion of this feature in the occupied regime is detected. The Kondo peak displays a marked intensity dependence on the emission angle, suggesting that hybridization is present in only a limited part of reciprocal space. The temperature dependence of this near-E_F feature supports this interpretation. [S0163-1829(97)50942-8]

The general picture of the Ce $4f$ electrons in the solid state is one where the population of these levels is almost unity, the shortfall being due to a finite hybridization with the conduction band. This situation, coupled with a strong Coulombic interaction making an f^2 configuration extremely unfavorable, is at the heart of the heavily renormalized low-temperature properties of Ce-based materials.[1] Photoemission has played a prominent role in early work on polycrystalline Ce compounds, the goal here being the observation of the low-energy excitations associated with the extraordinary thermodynamic properties of these Ce-based materials.[2,3] Although the aim is basically achieved,[4,5] this goal suffers from the conceptual problem that one is using a surface-sensitive technique in an attempt to make contact with bulk properties. From an experimental point of view, therefore, understanding the behavior of the Ce $4f$ electrons in the solid state using photoemission can only be advanced through the study of systems with a high degree of surface characterization, under the most stringent experimental conditions.

Several studies examining the growth of Ce thin films and initial alloy formation have been published in recent years.[6–13] In the present paper we follow on from work by Tang *et al.*,[8] using high-resolution photoemission to examine a thin well-ordered Ce/Pt(111) alloy. A report of medium-energy resolution (100 meV) resonant photoemission measurements from such an alloy has already been published, in which dispersion of the $4f$ feature was considered to be the origin of amplitude modulations observed for this peak.[14] As recognized by the authors, however, these measurements, which involve the use of monochromatized synchrotron radiation, suffer from an uncertainty in the position of the Fermi level, E_F.[14] We will demonstrate that precise knowledge of the Fermi-level position is important if one wants to extract the maximum amount of information from photoemission spectra. In addition to our examination of this Ce/Pt(111) alloy we study a comparative La/Pt(111) alloy, allowing us to see the contribution to the spectra due to the f-electron population.

Photoemission measurements were performed using a hemispherical electron analyzer and a high-intensity unmonochromatized He uv source. The base pressure in the system was in the low 10^{-11} Torr range, rising to 1×10^{-10} Torr during operation of the He lamp. Unless otherwise stated, all spectra reported here were recorded at 10 K, with an instrumental resolution of 5 meV.

Connected to our measurement chamber is a surface preparation facility, in which the Pt(111) substrate was cleaned by standard cycles of ion bombardment and annealing. Surface cleanliness and order were checked by Auger electron spectroscopy and low-energy electron diffraction (LEED), respectively. Photoemission data from the clean substrate are in accord with previously published results.[15] Evaporation of Ce and La onto the room temperature sample was carried out using a well degassed commercial evaporator in a vacuum of 1×10^{-10} Torr, with an evaporation rate of approximately 1 Å/min regulated using a quartz microbalance.

We have concentrated our efforts on relatively thick coverages of the two evaporants studied, resulting in well-ordered surface alloys. An initial Ce evaporation of ~ 10 Å onto Pt(111) results in the extinction of all LEED spots, in agreement with the earlier study.[8] Subsequent annealing of this surface (600 °C, 10 min) restores order as determined by LEED, producing, in the first approximation, a symmetry corresponding to $Pt(111)(\sqrt{3} \times \sqrt{3})R30°Ce$. Although this designation is not strictly correct, it will be used throughout this paper to refer to our surface. Without wanting to discuss in depth the LEED pattern, details of which are given elsewhere,[16] we note that the LEED symmetry observed in this work does not figure in the phase diagram proposed by Tang *et al.* for the annealed Ce/Pt(111) system.[8] For the La/Pt(111) system, a similar treatment with similar results was performed. The final LEED symmetry observed in this case was $Pt(111)(2 \times 2)La$.[16] Angle-resolved HeI photoemission data, presented elsewhere, show that these two surfaces have a remarkably similar electronic structure.[16]

The two principal lines produced by our discharge lamp have energies of 21.2 eV (HeI) and 40.8 eV (HeII). In order to observe the $4f$ spectral contribution with our system, photoemission must be performed using the latter of these, as the Ce $4f$ photoionisation cross section at HeI is very low. Figure 1 shows the comparison between an angle-integrated HeII photoemission spectrum of $Pt(111)(\sqrt{3} \times \sqrt{3})R30°Ce$ and that of $Pt(111)(2 \times 2)La$. The spectrum from Pt(111)
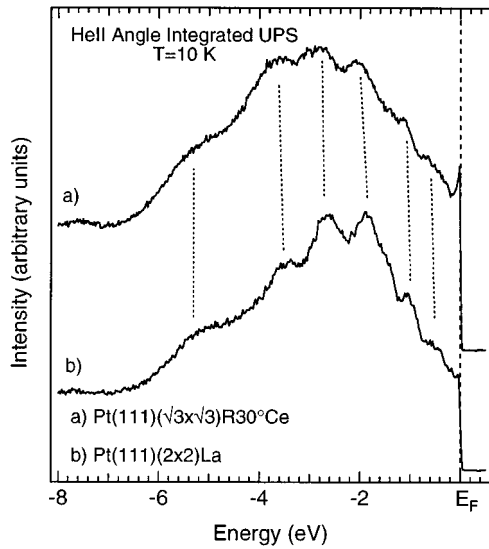
FIG. 1. Angle integrated HeII UPS data from Pt(111)$(\sqrt{3} \times \sqrt{3})R30°$Ce and Pt(111)$(2 \times 2)$La (nominal designations, see text). The feature appearing at E_F in the Ce/Pt(111) alloy spectrum is associated with the presence of $4f$ electrons. The spectra were recorded with an instrumental resolution of 5 meV.

$(\sqrt{3} \times \sqrt{3})R30°$Ce shows good agreement with previously published HeII ultraviolet photoemission spectroscopy (UPS) data from Pt(111)(1.96×1.96)Ce[8] [which we will refer to hereafter as Pt(111)(2×2)Ce]. Furthermore, an equivalent for each feature present in the valence band of Pt(111)$(\sqrt{3} \times \sqrt{3})R30°$Ce, bar one, is readily found in the spectrum of Pt(111)(2×2)La. The one striking difference between the two spectra in Fig. 1 is the existence of a sharp feature lying just below E_F in the surface containing Ce. This feature is clearly due to the presence of the Ce f electron. It is strongly reminiscent of the occupied tail of the Kondo resonance observed in high-resolution photoemission data from polycrystalline Ce-based heavy fermions[5] and, for the sake of the discussion, will be referred to as the Kondo peak.

In agreement with results for Pt(111)(2×2)Ce,[8] Pt(111)$(\sqrt{3} \times \sqrt{3})R30°$Ce was found to be extremely stable against contamination arising from the residual vacuum. The most sensitive probe of the surface quality was found to be the Kondo peak, which becomes steadily weaker under illumination from our uv source. The surface degradation could easily be healed, however, by annealing the sample to 500 °C for ∼10 minutes. The combination of an essentially stable sample, whose surface exhibits well-defined crystallinity, and a high-resolution angle-resolving spectrometer allows us to examine the momentum dependence of the Kondo peak. This measurement constitutes a major step forward in photoemission studies from Ce and Ce-based compounds. The vast majority of previous photoemission studies have been carried out on polycrystalline samples,[4] where all measurements are necessarily k integrated. Although momentum-resolved photoemission measurements of the $4f$ states have already been performed on cleaved single crystals,[17,18] and on a well-ordered Ce/Pt surface alloy,[14] these were measurements carried out with an energy resolution significantly inferior to that employed in the present
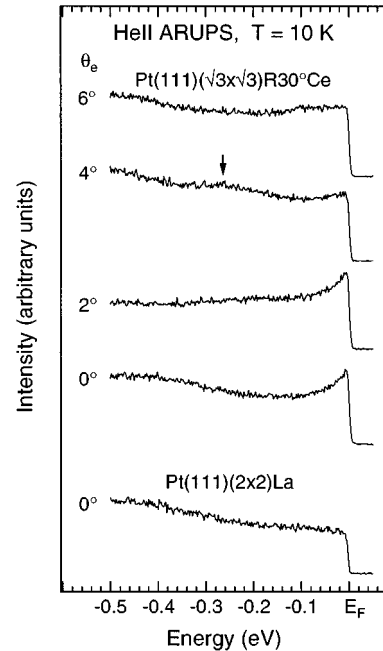

FIG. 2. A selection of angle-resolved HeII UPS data from Pt(111)$(\sqrt{3} \times \sqrt{3})R30°$Ce, and the normal-emission angle-resolved HeII spectrum of Pt(111)(2×2)La. The arrow indicates a possible signature for the spin-orbit peak (see text). $k_\parallel$ is along the $\overline{\Sigma}$ direction of Pt(111).

work. Furthermore, absolute calibration of the energy scale for work performed at the Ce $4f$ resonance using monochromatized synchrotron radiation is not trivial.[14,17]

Figure 2 shows a selection of HeII angle-resolved photoemission spectra in the near E_F region from Pt(111)$(\sqrt{3} \times \sqrt{3})R30°$Ce, together with the normal emission ($\theta_e = 0°$) HeII spectrum from Pt(111)(2×2)La. All off-normal angle-resolved data shown were recorded with $k_\parallel$ along the $\overline{\Sigma}$ direction of Pt(111).[15] Within 150 meV of E_F, the spectral form for the Ce surface alloy at normal emission is the same as that observed from many polycrystalline Ce compounds: as E_F is approached from below, the intensity of the spectrum rises resulting in a sharp feature peaking ∼4 meV below the Fermi level.[5] The degree to which the peak position approaches E_F is limited simply by the resolution of our spectrometer. Away from normal emission, the Kondo peak is quickly suppressed. For all spectra where the Kondo peak is present, the position of the intensity maximum does not move, ruling out, within the limits of our measurement, dispersion of a feature below E_F. For the effect to be explained by a conventional broad band above the Fermi level, this band would have to come within ∼2 meV of E_F for it to be significantly (thermally) populated in the initial state. It is difficult to see how such a band could explain photoemission intensity down to −50 meV (Fig. 2). Spectra have been measured up to $\theta_e = 30°$ in the direction shown, an angle putting $k_\parallel$ past the second $\overline{\Gamma}$ for states at E_F, and only around normal emission is a clear Kondo peak observed. However, in agreement with the resonant photoemission study of Pt(111)$(2 \times 2)R30°$Ce,[14] our measurements indicate the reappearance of the Kondo peak at the second $\overline{\Gamma}$ point, suggesting the presence of surface umklapp scattering. The same peak at-
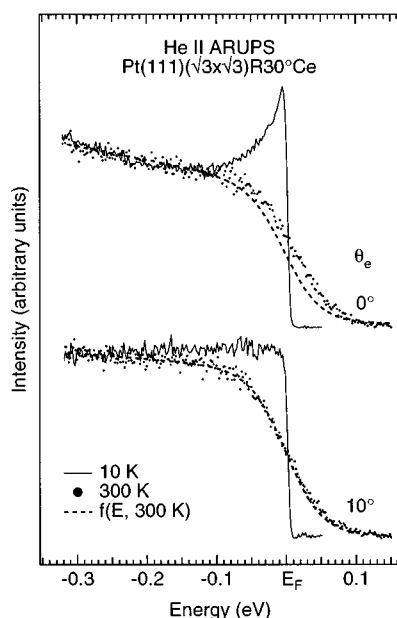
FIG. 3. Angle-resolved HeII UPS data at $\theta_e = 0°$ and 10° from nominal Pt(111)$(\sqrt{3} \times \sqrt{3})R30°$Ce at 10 and 300 K. The dashed line is the product of the Fermi function at 300 K and a linear fit to the 300 K data in the range $-0.3 \leq E \leq -0.15$ eV. The energy spacing between data points is 2 meV. $k_{\parallel}$ is along the $\bar{\Sigma}$ direction of Pt(111).

tenuation away from normal emission is observed for spectra measured with $k_{\parallel}$ along the $\bar{T}$ direction of Pt(111). In terms of $k_{\parallel}$, the Kondo peak is observed within the central 30% of the surface Brillouin zone in both directions measured.

A general feature observed in all HeII photoemission (and resonant photoemission) spectra from Ce-based materials is a peak at ~ 280 meV binding energy, understood to be a final-state feature of $j = \frac{7}{2}$ character.[4,19] This feature appears to be absent from the normal emission spectrum displayed in Fig. 2. There are suggestions that this peak is present at other emission angles, however. For example, in the $\theta_e = 4°$ spectrum shown in Fig. 2 a weak feature is seen, marked by an arrow, which could correspond to this spin-orbit final-state satellite. This interpretation is supported by the fact that there is no similar feature for the equivalent spectrum recorded from the La surface alloy.

Photoemission spectroscopy probes occupied electronic states. Due to the fact that thermal excitation markedly populates states to $\sim 2k_B T$ above E_F, as the temperature of a sample is raised a photoemission measurement increasingly examines the electronic structure above E_F. However, the temperature dependence of the spectral function of Kondo-based materials is particular. With increasing temperature the intensity of the Kondo peak, the tail of which is observed in photoemission from Ce-based materials, is reduced.[19] Figure 3 displays angle-resolved HeII photoemission spectra from Pt(111)$(\sqrt{3} \times \sqrt{3})R30°$Ce at two different temperatures, 10 and 300 K, for two angles of electron emission, $\theta_e = 0°$ and $\theta_e = 10°$. Also displayed for each angle is the Fermi function at 300 K (multiplied by a linear density of states obtained from fitting the 300 K spectrum in the range $-0.3 \leq E \leq -0.15$ eV). For the spectra recorded at $\theta_e = 10°$, where no

Kondo peak is seen at low temperature, nothing unusual is observed: the 300 K spectrum is broadened with respect to the 10 K spectrum, and its half-intensity point lies at E_F. The situation for the normal emission spectra is different. At 300 K, the intensity of the Kondo peak observed at low temperature has practically disappeared. However, the half intensity of the edge of the 300 K photoemission spectrum lies *not* at the Fermi level, but some 17 meV above it. This observation is strongly reminiscent of that made of the temperature dependence of photoemission spectra from polycrystalline CeSi$_2$,[5] a moderately heavy-fermion compound with a Kondo temperature generally accepted to be about 35 K. The interpretation of the polycrystalline data within the Kondo model scenario has been strongly backed up by a calculation performed within the noncrossing approximation (NCA).[5] The current observation is consistent with the presence of an anomalously large number of available excitations just above E_F for a restricted part only of reciprocal space. Furthermore, with the spectra intensity normalized as shown in Fig. 3, the normal emission spectrum recorded at 300 K has an integrated intensity from -200 to $+150$ meV which is 95% that of the 10 K spectrum. A loss of spectral weight in this energy region with increasing temperature is in line with the expectation based on the Kondo model, and to our knowledge, is a phenomenon which has no analogue in a normal metallic system.[19]

If the intensity variation of the peak is discarded, our spectra display the unconventional characteristics predicted by the single impurity model for a Kondo peak:[19,20] the proximity of the peak maximum to E_F determined by the resolution, the lack of observable dispersion, and the temperature evolution together ensure that this feature cannot account for a conventional dispersing band state. The fast angular dependence of the peak intensity is puzzling, however. By construction, any spectral function derived from the single impurity model contains no dependence on the photoelectron emission angle other than the anisotropy of the single electron f-matrix element. This cannot explain the observed effect, due to the geometry of our experiment (unpolarized light beam forming an angle of 45° with the electron emission direction). Diffraction of the photoelectrons as an explanation of the angular dependence cannot be definitively ruled out, although the observation that the peak is limited to an extremely narrow angle around normal emission does not favor this option.[21] Furthermore, similar effects have been observed at higher photoelectron energies, where the two spin-orbit split $4f$ components, which have practically the same energy, display different angular behaviors.[14]

For an ordered Ce-containing alloy, the single impurity model can only be considered as a first approximation towards a full description. Many properties of such heavy-fermion compounds unambiguously demonstrate coherence between the f states (Kondo lattice) at a sufficiently low temperature $(T \leq T^*)$.[22] Calculations based on a band formalism successfully explain certain low-temperature properties of heavy fermions, with the heavy effective masses being accounted for by renormalization. This procedure introduces an energy scale $k_B T^*$, within which the resulting quasiparticle bands around E_F exist.[23] Such a band-structure approach represents an attack on the heavy-fermion problem

from a direction different to that of the impurity model. However, this description of heavy fermions contains two essential features compatible with the peak revealed by our spectra: a confinement very close to E_F, and a dispersion too weak to be observable with our resolution. In the present state of development of theory and experiment, such an interpretation of our data can only be said to be speculative. The crystalline structure of our films is not precisely known, hindering the possibility of a realistic renormalized band calculation. Perhaps more fundamentally, what is missing in the band approach is the calculation of a spectral function. A link between the impurity and the renormalized band approaches to the heavy-fermion problem certainly exists, but it has never been explicitly worked out. In particular, the elaboration of the relation between T_K and T^* appears to be a very difficult task[24] which has not been treated rigorously to the best of our knowledge.

In the present study of an ordered alloy formed by deposition of Ce on Pt(111), the high-resolution photoemission spectra reveal a narrow peak whose aspects are in many ways compatible with previous heavy-fermion studies and spectral functions calculated within the single impurity model. The major exception to this is a very fast dependence of the intensity on the emission angle. It is anticipated that this observation is not in contradiction with a renormalized band approach, although the theoretical and experimental developments of this problem are not sufficiently advanced that a definitive statement can be made. We hope that our results will stimulate further progress.

[1] G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).

[2] N. Mårtensson, B. Reihl, and R. D. Parks, Solid State Commun. **41**, 573 (1982).

[3] F. Patthey, B. Delley, W.-D. Schneider, and Y. Baer, Phys. Rev. Lett. **55**, 1518 (1985).

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

[5] M. Garnier, K. Breuer, D. Purdie, M. Hengsberger, Y. Baer, and B. Delley, Phys. Rev. Lett. **78**, 4127 (1997).

[6] C. Gu, X. Wu, C. G. Olson, and D. W. Lynch, Phys. Rev. Lett. **67**, 1622 (1991).

[7] B. Kierren, T. Gourieux, F. Bertran, and G. Krill, Phys. Rev. B **49**, 1976 (1994).

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

[9] Y. Tanaka, M. Kamei, and Y. Gotoh, Surf. Sci. **360**, 74 (1996).

[10] T. Okane, M. Yamada, S. Suzuki, S. Sato, T. Kinoshita, A. Kakizaki, T. Ishii, T. Kobayashi, S. Shimoda, M. Iwaki, and M. Aono, J. Electron Spectrosc. Relat. Phenom. **80**, 241 (1996).

[11] B. Kierren, F. Bertran, T. Gourieux, N. Witkowski, D. Malterre, and G. Krill, Phys. Rev. B **53**, 5015 (1996).

[12] B. Kierren, F. Bertran, N. Witkowski, T. Gourieux, D. Malterre, M. Finazzi, K. Hricovini, and G. Krill, Surf. Sci. **352-354**, 817 (1996).

[13] W. Schneider, Th. Gantz, M. Richter, S. L. Molodtsov, J. Boysen, P. Engelmann, P. Segovia-Cabrero, and C. Laubschat, Surf. Sci. **377-379**, 275 (1997).

[14] A. B. Andrews, J. J. Joyce, A. J. Arko, J. D. Thompson, J. Tang, J. M. Lawrence, and J. C. Hemminger, Phys. Rev. B **51**, 3277 (1995).

[15] W. Di, K. E. Smith, and S. D. Kevan, Phys. Rev. B **45**, 3652 (1992).

[16] M. Garnier, D. Purdie, K. Breuer, M. Hengsberger, and Y. Baer (unpublished).

[17] A. B. Andrews, J. J. Joyce, A. J. Arko, Z. Fisk, and P. S. Riseborough, Phys. Rev. B **53**, 3317 (1996).

[18] H. Kumigashira, S.-H. Yang, T. Yokoya, A. Chainani, T. Takahashi, A. Uesawa, and T. Suzuki, Phys. Rev. B **55**, R3355 (1997).

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

[20] O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **50**, 604 (1983); Phys. Rev. B **28**, 4315 (1983).

[21] D. P. Woodruff and A. M. Bradshaw, Rep. Prog. Phys. **57**, 1029 (1994).

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

[23] G. Zwicknagl, Adv. Phys. **41**, 203 (1992).

[24] P. Fulde, J. Phys. F **18**, 601 (1988).