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High resolution photoemission study of well-ordered cerium surface compounds

Travail de thèse effectué dans le groupe du professeur Yves Baer et présenté à l'institut de physique de l'Université de Neuchâtel pour l'obtention du titre de docteur ès sciences.

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Michael Garnier

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IMPRIMATUR POUR LA THÈSE

Etude par photoémission à haute résolution de composés de surface ordonnés à base de cérium

de M. Michael Garnier

UNIVERSITÉ DE NEUCHÂTEL

FACULTÉ DES SCIENCES

La Faculté des sciences de l'Université de Neuchâtel sur le rapport des membres du jury,

MM. Y. Baer (directeur de thèse), H. Beck,
et W.-D. Schneider (Uni. Lausanne)

autorise l'impression de la présente thèse.

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Liste des publications

(1)
M. Garnier, K. Breuer, D. Purdie, M. Hengsberger, Y. Baer and B. Delley, Phys. Rev. Lett. **78** (1997), 4127
Applicability of the single impurity model to photoemission spectroscopy of heavy fermion Ce compounds

(2)
M. Garnier, D. Purdie, K. Breuer, M. Hengsberger, Y. Baer and B. Delley, Phys. Rev. Lett. **81** (1998), 1349
Reply to "$CeSi_2$ Photoemission Spectra at 5 meV Resolution" by A.J. Arko and J.J. Joyce, preceding page

(3)
M. Garnier, D. Purdie, K. Breuer, M. Hengsberger and Y. Baer, Phys. Rev. B **56** (1997), 11399
Momentum-resolved photoemission of the Kondo peak in an ordered Ce-containing alloy

(4)
M. Garnier, D. Purdie, K. Breuer, M. Hengsberger and Y. Baer, Phys. Rev. B **58** (1998), 9697
Comparative photoemission study of Pt(111)($\sqrt{3}$x$\sqrt{3}$)R30°Ce and Pt(111)(2x2)La

(5)
M. Garnier, D. Purdie, K. Breuer, M. Hengsberger and Y. Baer, Phys. Rev. B **58** (1998), 3515
High resolution photoemission from an ordered Ce/Be alloy

(6)
K. Breuer, S. Messerli, D. Purdie, M. Garnier, M. Hengsberger, G. Panaccione, Y. Baer, T. Takahashi, S. Yoshii, M. Kasaya, K. Katoh and T. Takabatake, Europhys. Lett. **41** (1998), 565
Photoemission study of the Kondo insulator Ce3Bi4Pt3

Le texte complet de cette thèse est déposé à la Bibliothèque de l'Institut de Physique de l'Université de Neuchâtel.

Résumé

Les composés à base de cérium font partie de la catégorie des composés dite "fermions lourds" en raison de leurs propriétés physiques. Ces propriétés découlent principalement du comportement inhabituel des électrons 4f du cérium, qui hésitent entre un comportement localisé et un comportement de bandes. L'étude par photoémission de ces composés peut donc permettre d'éclaircir l'influence de ces électrons, et de déterminer si le modèle couramment utilisé pour décrire les spectres de photoémission (modèle SIM, dit "modèle à une impureté") est réellement applicable.

Jusqu'à maintenant l'étude par photoémission de ces composés s'est principalement focalisée sur des composés polycristallins (pour des raisons de facilité de préparation). Le but de cette étude est d'étendre une telle étude à des composés cristallins préparés *in situ*. Notre nouvel équipement pour la photoémission à haute résolution (jusqu'à 5 meV de résolution en énergie) est directement relié à une chambre permettant de préparer et de caractériser de tels échantillons.

Le premier but de cette thèse aura néanmoins été une étude de composés polycristallins afin de tenter de mettre fin à une longue polémique dont l'objet est l'applicabilité du SIM (voir publications **(1)** et **(2)**). Nos mesures sont en très bonne adéquation avec les prédiction du SIM. L'étape suivante a été la préparation de composés de surface cristallins. Le SIM, par construction, ne prédit pas de dépendance angulaire des spectres de photoémission (pas de corrélations entre les électrons 4f), et la mesure de tels composés en dépendance angulaire permet de tester les limites du SIM. Deux échantillons ont été préparés: cérium sur Pt(111) et cérium sur Be(0001). Après déposition du cérium et recuit, on a obtenu deux surfaces cristallines. Le Ce/Pt(111) est décrit dans **(3)** et **(4)** tandis que le Ce/Be(0001) est décrit dans **(5)**. Pour résumer, le premier a montré une forte dépendance angulaire des spectres de photoémission, et le deuxième n'a montré aucune dépendance angulaire.
Un dernier échantillon a été mesuré: il s'agit de l'isolant de Kondo $Ce_3Bi_4Pt_3$ **(6)**, dont l'état fondamental isolant est supposé être fortement dépendant de la qualité cristalline de l'échantillon.

En conclusion, cette étude a permis de mettre en lumière l'importance des effets angulaires dans les composés à base de cérium. Les composés polycristallins peuvent bien être décrits par le SIM, mais les composés cristallins nécesitent un modèle tenant compte de la corrélation entre les électrons 4f.

Publication n° 1

Applicability of the Single Impurity Model to Photoemission Spectroscopy of Heavy Fermion Ce Compounds

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Photoemission spectra measured with an energy resolution of 5 meV from Ce-based heavy fermion materials are presented. The spectra add strong support to the interpretation of the peak at the Fermi level in terms of the spectral function calculated within the single impurity model. This work clearly demonstrates that if reliable information on heavy fermion compounds is to be obtained using photoemission spectroscopy, it is necessary to work with an instrumental resolution approaching kT_K, where T_K is the Kondo temperature. [S0031-9007(97)03272-9]

PACS numbers: 79.60.Bm, 71.27.+a

Heavy fermions probably constitute the most widely studied class of highly correlated electron systems. When a rare earth is involved, the $4f$ states are weakly hybridized with the band states and at low temperature behave as an exceptionally narrow metallic band dominated by a very high correlation. In the Kondo description, the $4f$ local moment is gradually screened and a many-body singlet ground state is formed at $T = 0$ K. With increasing temperature, magnetic states become excited and the $4f$ states gradually recover their atomic character. The characteristic temperature separating these two regimes is the Kondo temperature, T_K, and $\delta = kT_K$, expressing the energy gain of the system per rare earth atom coming from the formation of the singlet state. The resulting unconventional properties (transport, magnetism, specific heat) are successfully predicted within the single impurity model (SIM), which is considered to contain the essential ingredients for describing the situation [1]. It has been particularly appealing to observe the states responsible for these manifestations in systems considered to be homogeneous dense Kondo compounds directly using electron spectroscopies. Calculations of spectral functions of these correlated systems based on the SIM [Gunnarsson-Schönhammer (GS) model [2], noncrossing approximation (NCA) [3]] differ markedly from the quasiparticle density of states, and they display signatures of the ambivalent nature of this many-body state; the high energy excitations account for its atomic character (bare energy of the $4f$ electrons and their intra-atomic Coulomb correlation energy), whereas the low-energy excitations display its exceptional metallic character generated by an extremely narrow renormalized band (Kondo peak) centered, for Ce compounds, above the Fermi level, E_F. In this model, δ completely characterizes the Kondo peak. Both the position of the peak and the weight of its occupied part are given by δ. The peak intensity at E_F scales with $1/\delta$.

In Ce-based heavy fermion systems, the Kondo energy scale, δ, typically ranges between 0.1 and 50 meV. This parameter thus sets extremely severe resolution conditions in photoemission studies. The most powerful technique for the disentanglement of the $4f$ states from the band states consists of the exploitation of synchrotron radiation to take advantage of the huge $4f$ cross section resonance at the Ce $4d$ threshold (120 eV). However, resolution limits in this energy range are currently of the order of 40 meV, and energy calibration with monochromatized radiation is not trivial. The other possibility commonly used to extract the $4f$ signal from photoemission spectra is offered by the conventional increase of the $4f$ cross section between the photon energies 21.2 eV (He I) and 40.8 eV (He II) delivered by He discharge lamps. These two intense lines have a very narrow natural width (≤ 2 meV), so that the resolution is essentially determined by the quality of the electron energy analysis. A few years ago, direct and inverse photoemission studies of Ce compounds produced spectra which seemed to demonstrate the essential characteristics of the spectral function based on the SIM [4,5]: the scaling of the Kondo peak intensity with T_K, and its nonconventional temperature dependence. This interpretation of the photoemission spectra has been disputed, however, with the claim that a conventional model provides a sufficient explanation for all photoemission observations [6–9]. This claim raises a very fundamental question which urgently needs to be cleared up [10,11], so that confidence in the capacity of photoemission to reveal many-body effects in correlated electron systems may be restored.

Recent technical improvements in the available electron spectrometers allow us now to achieve a total energy resolution of ~5 meV, a new condition which allows the relevant energy range δ containing the characteristic many-body excitations of moderately heavy fermions to be studied with more confidence. Our samples, prepared

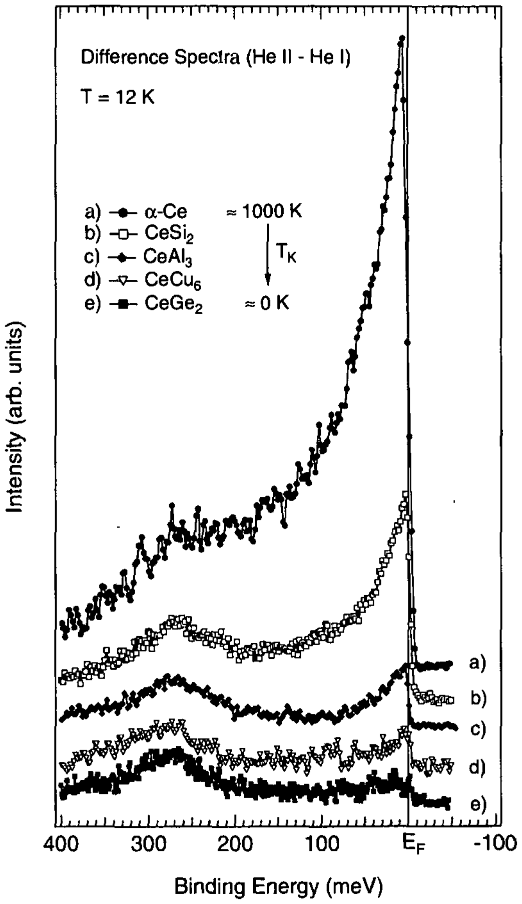

FIG. 3. Difference spectra (He II − He I) for a series of heavy fermion Ce compounds which span a wide range of T_K. The original spectra were recorded with high energy resolution ($\Delta = 5$ meV) and at 12 K.

is probably an artefact showing the limit of our subtraction technique for very weak $4f$ signals. We note that the FWHM of the peak decreases only by a factor of approximately 2 from α-Ce to CeCu$_6$ and does not reflect directly δ. We deliberately refrain from a quantitative analysis of the line shapes and intensities of the peaks since, quite apart from the difficulties involved in determining an absolute value for T_K, the spectra are measured from surfaces, at different values of T/T_K, and they certainly contain excitations of crystal field split levels and probably of phonons and electron-hole pairs.

In conclusion, this study presents photoemission data of some simple Ce-based Kondo compounds, demonstrating the necessity of an extremely high energy resolution. These new spectra are fully consistent with the SIM and cannot be analyzed with a conventional model. In the particular case of CeSi$_2$: (a) the peak at E_F cannot be accounted for by a DOS simulated by a Lorentzian line located 20 meV below E_F; (b) the linewidth and shape of the Kondo peak is consistent with a SIM calculation; and (c) the temperature dependence of this peak reflects the thermal population of the empty part of the Kondo resonance, in agreement with NCA calculations. In a series of simple heavy fermion compounds, it is seen that the Kondo temperature is a key parameter determining the weight of the Kondo peak and that an instrumental resolution approaching kT_K is essential if reliable information on heavy fermions is to be obtained. These conclusions are limited to the compounds measured in this study, but they do invite that the other data, used to suggest an approach different from SIM [9], be confirmed with better resolution.

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Publication n° 2

Garnier *et al.* Reply: Arko and Joyce [1] make two claims regarding our $CeSi_2$ data and the associated analysis [2]: an unphysical background subtraction, and a mundane temperature dependence of the spectra. The relative normalization of the He I and He II spectra as carried out in our paper [2] was somewhat arbitrary. Arko and Joyce propose an upper limit for the intensity of non-f states in the He II spectrum. However, for this they have a complicated procedure involving many steps [3], each one with severe uncertainties, and one must anticipate a large error radius for the final calibration. In order to clear this situation we have performed a relative intensity calibration of $CeSi_2$ and $LaSi_2$ spectra. For each compound, He I and He II spectra have been measured without modifying any other experimental condition. The relative intensities of the He II spectra of the two compounds have then been obtained by normalizing their He I spectra to the same intensity between -1 eV and E_F (inset in Fig. 1). This procedure is simple and robust. Figure 1 shows the raw spectra of $CeSi_2$ and $LaSi_2$, the resulting difference spectra, and our previous noncrossing approximation (NCA) calculation [2], obtained with the same code used in Ref. [4]. As anticipated, this improved procedure simply adds a nearly constant $4f$ contribution, and the characteristic near-E_F two-peak structure is not challenged. Even if the agreement between the theoretical prediction obtained for the parameters imposed by the properties of $CeSi_2$ and the experiment is not quite perfect, our opinion is that this comparison demonstrates that the single impurity model contains the essential physical concepts determining the spectral function. Similarly, our observation of the characteristic peak ratio evolution as a function of kT_K [2] cannot credibly be disputed on the basis of such background arguments.

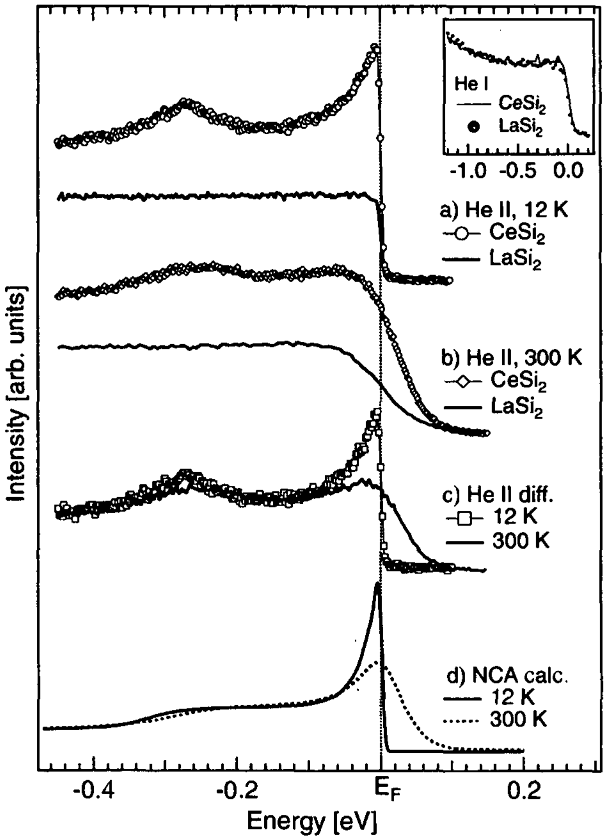

FIG. 1. He II ultraviolet photoemission spectroscopy data from $CeSi_2$ and $LaSi_2$ at (a) 12 K and (b) 300 K. The $LaSi_2$ spectra represent the non-$4f$ spectral contribution, relative normalization based on the He I spectra (inset) where any $4f$ contribution is negligible. (c) Difference spectra representing the Ce $4f$-spectral funciton for $CeSi_2$ at 12 and 300 K. (d) NCA calculations of the Ce $4f$ spectral function using the parameters for $CeSi_2$ [2].

Arko and Joyce simulate our data using a simple mathematical model that is without any physical basis. It involves at least five fitting parameters which have been modified [1,5] following the resolution improvement of our data [2]. For example the $4f_{5/2}$ peak has been moved from below to above E_F, in agreement with the Kondo peak position. It is hardly surprising that they always manage to obtain a better fit to spectra than the NCA simulation with imposed parameters.

Arko and Joyce claim that there is clearly no buildup of extra intensity above E_F at 300 K. We completely disagree with this statement and invite the reader to form his own opinion through an inspection of the data in Fig. 1. This anomalous intensity is also seen in their model since the peak multiplied by a Fermi function is now located above E_F.

The view advocated in the previous Comment is in stark opposition to that expressed in a recent report on photoemission [6].

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$CeSi_2$ Photoemission Spectra at 5 meV Resolution

New PES (photoemission spectra) data for $CeSi_2$ at 5 meV resolution are presented in [1]. The authors once again claim agreement with NCA (noncrossing approximation), using an apparent new code (now similar to ours) and new parameters. Though we disagree with many statements in [1], we focus on (a) the unphysical nature of their non-f background subtraction and (b) our ability to explain their temperature dependence by mundane, conventional effects. The important new information from the 5 meV resolution of [1] is that the angle-integrated occupied $4f_{5/2}$ density of states (DOS) is peaked at E_F rather than at -20 meV as previously reported [2].

The faulty background subtraction of [1] is immediately obvious in Fig. 1(a) where we present near-E_F data from [1] but now extended to -4.0 eV with data from [3]. Similarly from [3] we show the $LaSi_2$ PES to simulate the non-f background, but now modified with $CeSi_2$ data (the $LaSi_2$ and $CeSi_2$ line shapes at 12 K and 21.2 eV are nearly identical) above -0.4 eV for 5 meV resolution. With non-f background normalization exactly as in [1], a zero, or even negative $4f$ intensity is obtained throughout the subtracted spectrum, except above -0.4 eV,. which was all that was presented in [1]. This translates into an unphysical vanishing or even negative f^0 peak which, from resonant photoemission, is known to be as intense as the $4f_{5/2}$, and which is central to NCA. Thus immediately there is absolutely no agreement with NCA nor with published data. The discrepancy with NCA worsens with a more correct non-f normalization [upper limit shown in Fig. 1(a)]. This is obtained by comparing the $CeSi_2$ and $LaSi_2$ PES intensities at 21 and 40.8 eV with O-$2p$ intensities from a submonolayer of oxygen on the surface, and additionally by comparing the $4f$ spectrum, after background subtraction, to resonant PES which measures primarily $4f$ photocurrent. With this non-f subtraction the $4f_{7/2}$ at 300 K is peaked at ≈ -50 meV rather than at E_F where both Ref. [1] and NCA would have it. Also, the occupied width of the $4f_{5/2}$ at 12 K is at least 3 times the NCA predictions. The apparent "good fit" above -0.4 eV to NCA in [1] (and even this is poor when data are overlayed) is purely an artifact of the arbitrary, nonphysical data reduction.

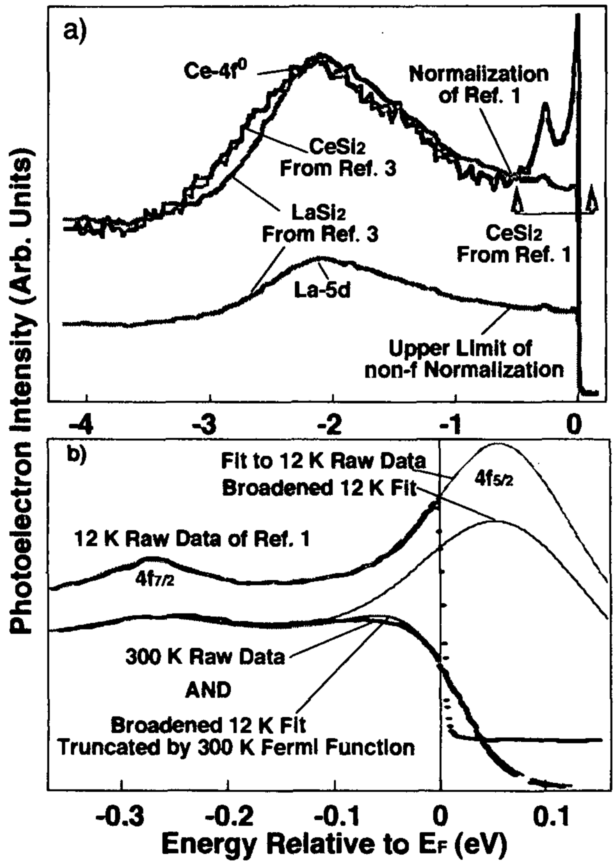

FIG. 1. (a) Composite scans with new and old data along with correct normalization (see text). (b) Raw data of [1] along with fits.

Temperature dependence is explained without resort to any model. The raw 12 K spectrum of [1] in Fig. 1(b) can be represented in analytic form by two Lorentzians (at -0.272 and $+0.06$ eV, FWHM $=$ 0.204 and 0.210 meV) plus a background. Although the fitted $4f_{5/2}$ peak at 0.06 eV suggests the centroid of the DOS occurring above E_F only the first 50 meV or so are sampled at 300 K, so that the line shape above 50 meV is irrelevant. The raw 300 K spectrum is almost exactly reproduced from the fitted 12 K analytic form simply by broadening the 12 K fit with a 120 meV Gaussian to equal the broadening clearly visible in the $4f_{7/2}$ data peak (most likely due to phonons since NCA does not broaden the $4f_{7/2}$), and truncating with a 300 K Fermi function. There is clearly no need for a 3 meV wide feature at 3 meV above E_F to yield the 300 K spectrum. Further, the shift in the $4f_{5/2}$ peak position with T is opposite of NCA predictions. There is clearly no buildup of extra intensity above E_F at 300 K. Thus in view of the shift and exact fit at 300 K, a conventional approach adequately describes the temperature dependence.

Similar subtractions were employed for the remaining spectra shown in Fig. 3 of Ref. [1]. Conclusions drawn thereof need reevaluation.

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[2] F. Patthey *et al.*, Phys. Rev. Lett. **58**, 2810 (1987).
[3] D. Malterre *et al.*, Adv. Phys. **45**, 299 (1996).

Publication n° 3

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

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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)(2×2)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)

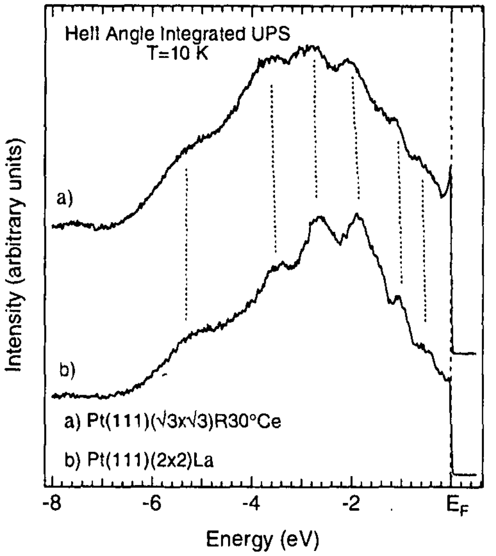

FIG. 1. Angle integrated HeII UPS data from Pt(111) $(\sqrt{3}\times\sqrt{3})R30^\circ$Ce and Pt(111)(2×2)La (nominal designations, see text). The feature appearing at E_F in the Ce/Pt(111) alloy spectrum is associated with the presence of $4f$ electrons. The spectra were recorded with an instrumental resolution of 5 meV.

$(\sqrt{3}\times\sqrt{3})R30^\circ$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) $(\sqrt{3}\times\sqrt{3})R30^\circ$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) $(\sqrt{3}\times\sqrt{3})R30^\circ$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 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]

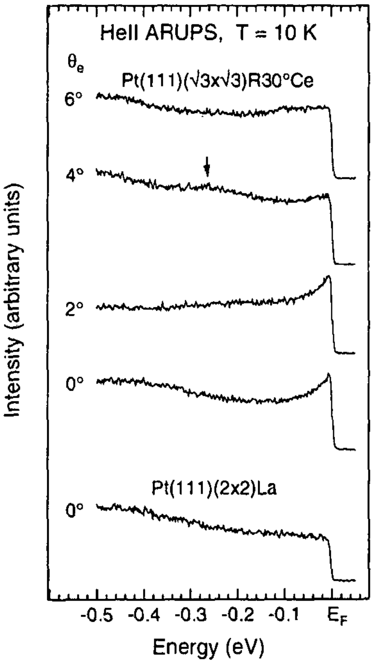

FIG. 2. A selection of angle-resolved HeII UPS data from Pt(111)$(\sqrt{3}\times\sqrt{3})R30^\circ$Ce, and the normal-emission angle-resolved HeII spectrum of Pt(111)(2×2)La. The arrow indicates a possible signature for the spin-orbit peak (see text). $k_\parallel$ is along the $\bar{\Sigma}$ direction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

Figure 2 shows a selection of HeII angle-resolved photoemission spectra in the near E_F region from Pt(111) $(\sqrt{3}\times\sqrt{3})R30^\circ$Ce, together with the normal emission ($\theta_e = 0^\circ$) HeII spectrum from Pt(111)(2×2)La. All off-normal angle-resolved data shown were recorded with $k_\parallel$ along the $\bar{\Sigma}$ 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 $\theta_e = 30^\circ$ in the direction shown, an angle putting $k_\parallel$ past the second $\bar{\Gamma}$ 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) $(2\times2)R30^\circ$Ce,[14] our measurements indicate the reappearance of the Kondo peak at the second $\bar{\Gamma}$ point, suggesting the presence of surface umklapp scattering. The same peak at-

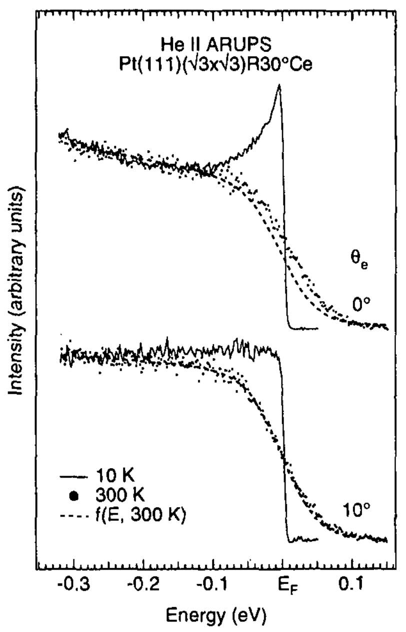

FIG. 3. Angle-resolved HeII UPS data at $\theta_e=0°$ and 10° from nominal Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce at 10 and 300 K. The dashed line is the product of the Fermi function at 300 K and a linear fit to the 300 K data in the range $-0.3\leq E\leq -0.15$ eV. The energy spacing between data 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 $\sim 2k_BT$ 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 phenomenom 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_BT^*, 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.

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Publication n° 4

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Comparative photoemission study of Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce and Pt(111)(2×2)La

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Careful examination of the low-energy electron diffraction image from Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce shows the designation to be only approximate and suggests a close structural similarity to Pt(111)(2×2)La. This is backed up by angle-resolved photoemission spectroscopy, which reveals the valence-band structure of the two alloys to be remarkably similar. The use of the La alloy to identify the non-f features in the photoemission spectra of Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce is thus put on a firm footing. The Kondo peak in He II angle-resolved ultraviolet photoemission spectroscopy data of Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce is observed at the first and second $\bar{\Gamma}$ points, suggesting the presence of surface umklapp scattering. [S0163-1829(98)10039-5]

I. INTRODUCTION

Despite the advances made in the field of heavy fermion materials through the application of photoemission,[1,2] the surface sensitivity of this technique can be seen as a shortcoming when measuring scraped polycrystalline compounds.[3] By using well-ordered single-crystal samples one can hope to further understanding of these heavy fermion systems past the single impurity model (SIM), based on the Anderson Hamiltonian. This model, although successful, can only be viewed as a first approximation to a full description of the problem. Recent progress in the preparation of Ce-containing samples which display long-range surface order has been made through evaporation of Ce onto single-crystal substrates.[4–18] In our laboratory, we have applied high-resolution ultraviolet photoemission spectroscopy (UPS) to examine the low-energy excitations in a well-ordered thin-film Ce-containing alloy: Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce.[19] In an attempt to identify the $4f$ contribution to the spectra, a second alloy was prepared in which the Ce was replaced by La.[19] Despite the different low-energy electron diffraction (LEED) pattern displayed by the La-containing alloy, Pt(111)(2×2)La, a detailed comparison between the two systems holds. This will be demonstrated in the current paper. We present a close examination of the LEED images from the two systems and a comparison of the d-band valence-band structure as revealed by He I angle-resolved UPS.

II. SURFACE PREPARATION AND DIFFRACTION RESULTS

The Pt(111) substrate was cleaned by standard sputtering-annealing cycles (Ar$^+$ 1 kV, 800 °C), to give a chemically clean and well-ordered surface, as indicated by Auger electron spectroscopy and LEED measurements, respectively. Evaporation of Ce was carried out in a pressure better than 2×10^{-10} Torr, using a quartz microbalance to ensure a rate of typically 1 Å/min. We have mainly studied samples prepared by depositing 4 ML of Ce on the clean substrate, as this use of a relatively thick Ce coverage prevents problems of mixed phases observed at lower Ce concentrations.[4,5] After evaporation of Ce the sample was annealed at 600 °C for 10 min. Such a treatment produces the LEED pattern shown in Fig. 1(a). By comparing this LEED pattern to that of the clean substrate, shown superimposed in the figure, a quasi-($\sqrt{3}\times\sqrt{3}$)$R30°$ symmetry is identified. The contraction of the LEED pattern observed for the surface alloy over that of the clean substrate [Fig. 1(a)] means that a more precise identification for the surface is ($1.1\sqrt{3}\times1.1\sqrt{3}$)$R30°$, one which does not appear in the phase diagram for the Ce/Pt(111) system proposed by Tang *et al.*[4] Such a LEED pattern was observed by Tang *et al.*[4] and Baddeley *et al.*,[5] but only ever in conjunction with a quasi-(2×2) image. We observed this mixed pattern after evaporation of a lesser quantity of Ce (~2 ML).

The same procedure was followed for preparation of the La/Pt(111) sample (annealing at 700 °C), resulting in a (2

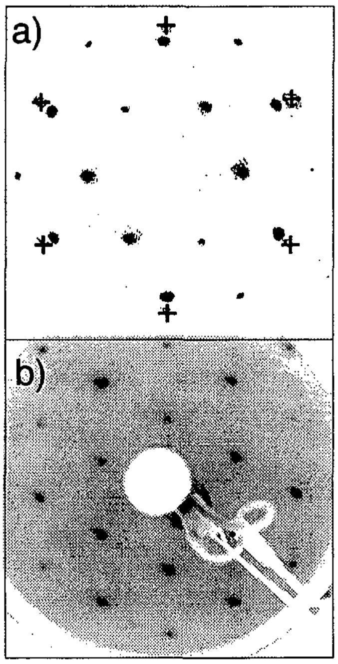

FIG. 1. (a) LEED pattern of Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce at $E_p=104$ eV. Superimposed is the equivalent LEED pattern for Pt(111) (crosses). (b) LEED pattern of Pt(111)(2×2)La at $E_p=104$ eV. The azimuthal orientation of the underlying substrate in both images is the same.

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$\times 2)$ LEED pattern for ~4 ML coverage, Fig. 1(b). This seems to be a precise designation. During initial evaporations of La, a superimposed $(2\times 2)R30°$ LEED pattern was also observed. This symmetry was not seen after the first few treatments. Such surface alloy systems have a complicated evolution[5] and it is possible that residual quantities of the evaporant produce a seed favoring formation of the nonrotated (2×2) phase.

The $(1.1\sqrt{3}\times 1.1\sqrt{3})R30°$ designation for the Ce/Pt alloy gives a surface lattice vector of $1.9a$, where a is the substrate lattice vector. This is 5% less than the surface lattice vector for Pt(111)(2×2)La. Without the dilation observed for Ce/Pt, the mismatch between the two systems would be nearer 15%. This provides a first indication that despite the difference in the LEED patterns of our two samples, the two thin-film alloy crystal structures are very similar. This speculation is supported by the observation that the lattice constants of CePt_n and LaPt_n, $n=2$, 3, and 5 are identical to within 0.5% for corresponding n.[20,21] The valence-band photoemission spectra presented below show indeed that the electronic structures of these two surfaces are closely related.

The Ce/Pt(111) system was found to be very stable. Although the intensity of the $4f$ structure seen in photoemission spectra (see next section) vanishes after 10–20 min of exposure to the UV radiation of our He lamp, a simple annealing of the sample at 600 °C for 10 min was found to rejuvenate the surface. The insensitivity of the surface to any residual contamination, despite the known high reactivity of cerium, is probably due to the alloy's structure. The passive nature of this sample is in line with other studies of Ce/Pt alloy formation on Pt(111) (Refs. 4 and 5) and suggests the presence of a pure Pt layer at the surface. Although there is a disagreement in these previous studies concerning the stoichiometry of the thin-film alloy, both structural models proposed, CePt_{2+x} (Ref. 4) and CePt_5,[5] allow the presence of a surface terminated uniquely by Pt. The model based on CePt_5 is one that covers five different surface structures observed.[5] Whatever the true microscopic details might be, it seems likely that the underlying structure of our surface bears close resemblance to those of the earlier studies.

III. PHOTOEMISSION RESULTS

Photoemission measurements were performed using a hemispherical electron analyzer and a high intensity 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. All spectra reported here were recorded at 10 K. The off-normal angle-resolved spectra for $\mathrm{Pt}(111)(\sqrt{3}\times\sqrt{3})R30°\mathrm{Ce}$ presented have all been measured along the $\overline{\Gamma K}$ direction of Pt(111). As discussed in the previous section, the LEED data suggest that the structures of the two alloys studied are very similar, the main difference being a rotation of 30° when compared with the underlying substrate. Photoemission data from Pt(111)(2×2)La were thus recorded with the Pt sample rotated azimuthally by 30°.

Angle-resolved He I (21.2 eV) photoemission spectra from the two surfaces under consideration are displayed in Fig. 2. The two data sets correspond to equivalent symmetry directions and show transitions between bands, those of the initial state being formed by hybridization of the Pt $5d$ electrons with the Ce valence electrons ($5d$, $6s$ levels). Although a detailed interpretation of the angle-resolved spectra would require more information than the surface symmetry available to us, it is seen that each major structure observed in a He I angle-resolved ultraviolet photoemission spectrum of Pt(111)(2×2)La is reproduced in the equivalent $\mathrm{Pt}(111)(\sqrt{3}\times\sqrt{3})R30°\mathrm{Ce}$ spectrum. However, away from normal emission there is a shift of the spectral features towards the Fermi level for the Ce-containing alloy. This is unambiguously seen for those features lying between −1.5 eV and E_F, and is particularly evident in the spectra recorded at $\theta=9°$ and 12° (Fig. 2). The origin of this difference lies in the Ce $4f$ occupation. This orbital provides inefficient screening, and so, in the atomic situation, the occupied Ce $5d$ levels are expected to lie deeper in energy than those of La. In the solid state the situation is more complicated and the energies of the transitions observed with angle- resolved photoemission are modified. A more quantitative discussion of the spectra of Fig. 2 would require calculation and precise knowledge about the structural details of the two alloys, but the important feature is the remarkable similarity of the two data sets, showing that the band structures of these two surfaces are extremely close to one another. This supports the conjecture made on the basis of the LEED data that the two surface alloys are closely related, and adds strength to the use of such a comparison as a method to determine which features in the spectra derive from the $4f$ electrons.[19]

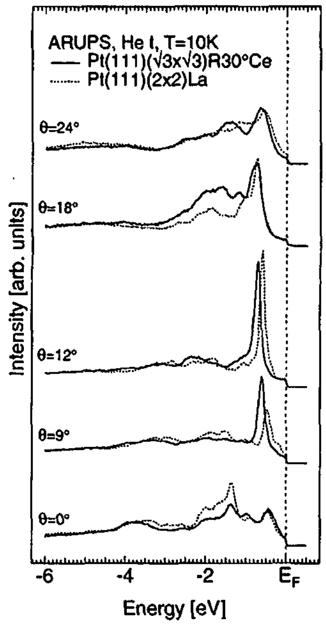

FIG. 2. Angle-resolved He I photoemission spectra of $\mathrm{Pt}(111)(\sqrt{3}\times\sqrt{3})R30°\mathrm{Ce}$ and Pt(111)(2×2)La. For details regarding the directions of measurement, see text.

The Ce $4f$-photoionization cross section for He I photons is negligibly small and so to obtain the contribution of the $4f$ electrons we have to consider spectra measured with He II radiation. Under these conditions, angle-integrated photoemission reveals the presence of a sharp peak cut at the Fermi level uniquely in the Ce-containing alloy.[19] This peak is due to the Ce $4f$ electrons and is identified with the tail of the Kondo resonance, which is usually seen in photoemission spectra from polycrystalline Ce compounds.[1]

The SIM, which is usually used to describe the photoemission spectra of Ce compounds,[2] treats the Ce atoms as isolated impurities. Possible interaction, direct or indirect, between Ce atoms is thus ignored. With the intention of looking for possible momentum dependence in the Kondo peak, we have performed He II angle-resolved UPS of the Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce surface alloy in the near-E_F region. The details of these measurements, the angular and temperature dependencies of the Kondo peak are discussed in more detail elsewhere.[19] In brief summary, we have not been able to measure any dispersion of the peak maximum. The peak is situated 4 meV below E_F and we believe its position to be determined purely by our instrumental resolution (5 meV). Away from normal emission its intensity rapidly decreases.[19] At $\theta = 26°$, however, there is an indication of the reappearance of the Kondo peak (Fig. 3). This angle lies close to the second $\bar{\Gamma}$ point of the surface Brillouin zone. This observation is similar to an independent one made on a single crystalline Ce/Pt system at higher photon energy (120 eV),[6] suggesting that an effect of surface umklapp scattering is being observed.

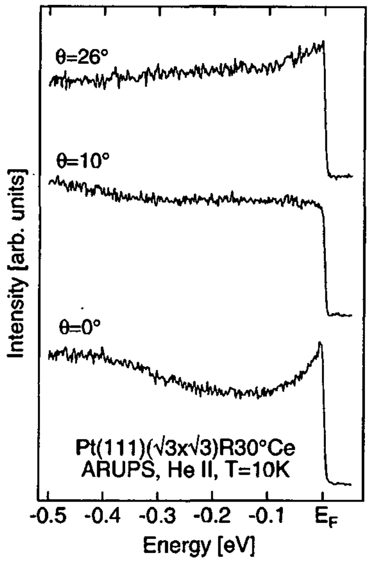

FIG. 3. Angle-resolved He II photoemission spectra of Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce in the near E_F. The azimuthal orientation is as in Fig. 2.

IV. SUMMARY

The two surface alloys Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce and Pt(111)(2×2)La have been examined using LEED and photoemission. The LEED data suggest that the two systems are closely related structurally. This is supported by angle-resolved photoemission data that demonstrate remarkable similarity in the electronic structure of the two surfaces. The Ce $4f$ contribution to the photoemission spectra is thus easily isolated by comparing He II data from the two systems.

ACKNOWLEDGMENT

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Publication n° 5

PHYSICAL REVIEW B VOLUME 58, NUMBER 7 15 AUGUST 1998-I

High-resolution photoemission from an ordered Ce/Be alloy

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Photoelectron spectroscopy at high-energy resolution (5 meV) has been performed on a crystalline Ce/Be alloy film, prepared by *in situ* evaporation of Ce onto Be(0001). At 12 K, the f spectral function displays a narrow peak at E_F, corresponding to the occupied tail of the Kondo resonance. The Kondo resonance retains significant intensity at 300 K, as revealed by temperature-dependent data. Angle-resolved spectra show no k dependence. [S0163-1829(98)05028-0]

It is commonly believed that the single impurity model (SIM) contains the essential concepts for understanding the unconventional properties of heavy electron compounds. From this basis and with model densities of states, the spectral functions for the usual electron spectroscopies (XPS, UPS, BIS, XAS, and EELS) have been calculated.[1] These spectral functions contain all structures observed, including those not explained by any other conventional model, and many photoemission studies have been compared to such model spectra with a view to demonstrating the validity of the SIM.[2] Although the conceptual limitations of the SIM have never been hidden,[3] the claim has been made that as an approach to explaining the spectroscopy the SIM is false, and that a conventional density of states is sufficient.[4] The principal objections concern the peaks close to the Fermi energy (E_F), which are considered to have an intensity, width, and temperature dependence not related to the Kondo temperature (T_K). That the electrons in heavy fermion materials can exist in a coherent state at very low temperature has been demonstrated by the observation of de Haas–van Alphen oscillations.[5] This is a situation that is outside the capabilities of the SIM, but which has been successfully described within a renormalized band approach.[6] Evidence of coherence has also emerged from photoemission measurements on crystalline surfaces, which have shown a momentum dependence of the $4f$ intensity and a dispersion of the $4f$ peaks. Although it is commonly quoted that coherence takes place at temperatures far below T_K, an explicit theoretical basis for this statement does not seem to exist.[7]

The simplest and best documented type of heavy fermion material treated within the SIM is cerium and its compounds, and the considerations developed in the current paper will be limited to this case. Evidence of angular dependence in $4f$ photoemission spectra was first obtained on crystalline Ce/Pt films.[8] Photoemission at very high resolution was subsequently used to study the same system, and the pronounced k dependence of the Kondo peak intensity was confirmed.[9] However, no definitive evidence of a sizable dispersion was revealed in these later measurements. Furthermore the temperature dependence of the Kondo peak in this system displays a behavior consistent with that predicted by NCA calculations. Momentum dependence of the photoemission spectra of $CeSb_2$ has been reported,[10] but the lack of published properties of this compound makes its heavy fermion character uncertain. Single crystalline $CeBe_{13}$ has also been investigated with angle resolved photoemission both at the $4d$ resonance[11] and at low photon energy ($h\nu=40$ eV).[10] Surfaces cleaved in different orientations yield extremely different $4f$ spectra so that their relevant Kondo temperatures cannot be specified. From the data analysis an important momentum dependence of the intensity and a dispersion of the $4f$ structures is deduced and a conventional interpretation of their temperature dependence is proposed.

The strong hybridization of the $4f$ states of Ce atoms embedded in the rather free-electron-like sp band of Be offers a favorable situation for studying the $4f$ photoemission signal of a crystalline heavy fermion compound. In the present study, we have produced a single-crystalline Ce/Be thin film by surface reaction. Be(0001) was mechanically polished prior to insertion into our vacuum system where it was cleaned by conventional sputtering and annealing cycles (Ar^+ 2.5 keV, 1000 K). The surface thus produced exhibits a good sixfold symmetry low-energy electron diffraction (LEED) pattern and a clean Auger spectrum. Evaporation of ~ 18 ML Ce onto the clean substrate was performed in the low 10^{-10} mbar range at a rate of typically 1 Å min^{-1}. This leads to a complete extinction of the LEED spots. The reaction and recrystallization of the surface film was carried out by annealing progressively up to 925 K over a period of about 40 h. This results in a sharp 1×1 LEED pattern observed at room temperature. The Auger spectrum indicates a Ce concentration lower than in $CeBe_{13}$, although the unknown concentration of Ce as a function of depth makes it difficult to precise stoichiometry. The important aspect for this study is that our sample be monocrystalline. This is confirmed by the LEED data. The very low reactivity of this surface demonstrates that the outermost layer consists exclusively of Be atoms.

Photoemission spectra were recorded with a total energy resolution of 5 meV using a high-intensity He uv lamp and a hemispherical electron analyzer. The base pressure of the instrument was in the low 10^{-11} mbar range. As previously observed with Ce/Pt single-crystalline films, uv irradiation of the cold sample (12 K) creates surface damage, which results in a weakening of the $4f$ signal. This effect restricted continuous measurement of the Ce/Be films to periods of ~ 40 min, after which the sample was annealed for 30 min at 925 K to restore the surface quality.

Figure 1 presents the angle integrated He II ($h\nu=40.8$ eV) photoemission spectrum of the valence band measured

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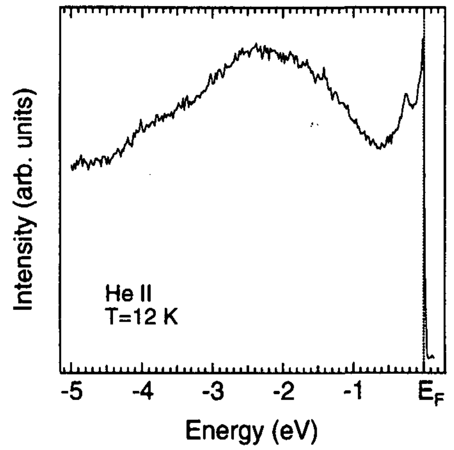

FIG. 1. Angle integrated He II valence band of Ce/Be recorded at $T = 12$ K.

at 12 K. The photoemission cross section for the Be valence band electrons at this photon energy is low and their contribution to the spectrum is a featureless background. The large peak between -4.5 and -0.7 eV reflects the Ce $5d$ band states and $4f^0$ final states which overlap in energy. This structure will not be discussed further, as we focus our attention on the two narrow peaks at low binding energy. These are systematically observed in heavy-fermion compounds.[2] The peak pinned at E_F is commonly interpreted as reflecting the quasiparticles formed by hybridization of the $4f$ states with the band states (i.e., all non-f states in the vicinity of E_F). It is this feature that is responsible for the heavy-fermion properties at low temperature and that, within the SIM, is identified with the occupied tail of the Kondo resonance. The second peak accounts for excited final states originating from the spin-orbit split $4f_{7/2}$ component.

He I and He II angle-integrated spectra recorded at different temperatures in a narrow energy range extending from -0.5 to $+0.2$ eV are shown in Fig. 2. For He I excitation ($h\nu = 21.2$ eV), the relative cross section of the $4f$ states is very low and the corresponding spectra account almost exclusively for the extended band states. As expected for a density of states that contains no rapid variation close to E_F, the temperature evolution of the spectra simply reflects the thermal broadening of the Fermi function and the Fermi level is located at half-intensity of the edge. However, a completely different situation is encountered in the He II spectra. Now the $4f$ cross section is significant. For increasing temperatures, the two $4f$ peaks are gradually suppressed, leaving at 300 K a broad structure and a half-intensity of the spectral cutoff located some 40 meV above E_F. The magnitude of this edge shift is much larger than previously observed in the single-crystalline Ce/Pt thin film alloy,[9] but comparable to that seen with polycrystalline CeSi$_2$.[12] This observation is assumed to reflect the thermal excitation of an extremely high density of states lying just above E_F, a situation compatible with the Kondo resonance as predicted by NCA calculations of the spectral function within the SIM.[13]

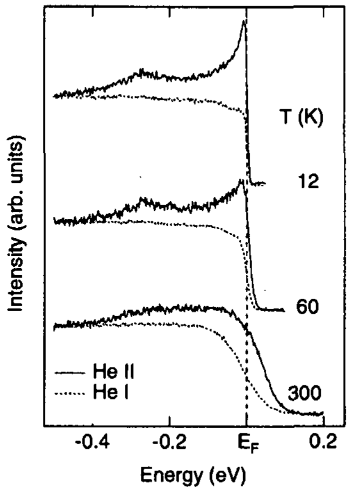

FIG. 2. He I and He II angle-integrated photoemission spectra of Ce/Be recorded at 12, 60, and 300 K. The normalization between He I and He II spectra is arbitrary.

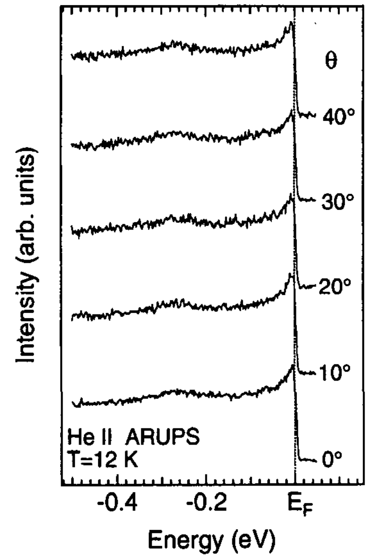

FIG. 3. Angle-resolved He II photoemission spectra of Ce/Be at $T = 12$ K. Spectra are recorded in the $\overline{\Gamma M}$ direction with an angular resolution of ± 1°. The first surface Brillouin zone boundary ($\bar{M}$) is crossed at $\theta = 31°$ for emission at the Fermi level.

Figure 3 shows He II angle-resolved photoemission spectra in the near-E_F region of this single-crystalline Ce/Be alloy film. In the measurements presented here the momentum vector parallel to the surface, $\mathbf{k}_{\parallel}$, varies along the $\overline{\Gamma M}$ direction. The general shape of these low-temperature angle-resolved spectra is the same as that of the angle-integrated spectrum. Indeed, within the accuracy and statistics of this measurement, no variation of the shape and intensity of the low-energy $4f$ signal can be observed as a function of angle. The position of the peak close to E_F is determined by the sample temperature and our instrumental resolution. The peak position is fully compatible with its origin being the cutoff tail of a feature centered above the Fermi level, leaving no margin for assuming a meaningful dispersion. This observation strengthens an interpretation of this peak in terms of the occupied tail of the Kondo resonance.

This photoemission study is only the second carried out with such a high-energy resolution on an ordered surface of a cerium-based Kondo system. In both this case and the earlier one of Ce/Pt (Ref. 9) the characteristic spectral shape predicted by the SIM is qualitatively observed and, within our experimental constraints, no dispersion of the peak maximum at E_F is seen. Furthermore the temperature dependence reveals the existence of a high density of states above E_F, compatible with the Kondo resonance. The difference in the spectral characteristics of these two samples is in the momentum dependence of the Kondo peak. For Ce/Pt a strong k dependence is observed,[9] whereas in the current case of Ce/Be no such dependence is seen. By construction coherence effects are not contained in the SIM and in order to explain effects due to the lattice one has to look for models that explicitly include its existence. Local density approximation (LDA) band calculations with an f band phenomenologically renormalized to reproduce the very high effective masses of heavy-fermions systems, yield a successful interpretation of de Haas–van Alphen data obtained in such compounds.[6] A preliminary model calculation within this approach for angle-resolved photoemission of γ-Ce shows that the f intensity disperses above E_F within a small energy range of the order of the characteristic temperature.[14] A pronounced momentum-dependent intensity is also shown. The occupied part of this computed DOS culminating at the Fermi level, is qualitatively compatible with the k dependence observed in photoemission data of Ce/Pt films.[9] The absence of dispersion in the Ce/Be alloy film might be attributed to the more isotropic nature of the free-electron-like Be valence band electrons hybridizing with the $4f$ state. More calculations and experiments will be necessary to corroborate this hypothesis. Another theoretical approach to the problem starts from the periodic Anderson model (PAM), within which different calculations have recently been performed. In the symmetric case,[15,16] coherence gives rise to the opening of a low-temperature gap at E_F. This is commonly assumed to explain the peculiar properties of the Kondo insulators, a view backed up by the observation of a pseudogap in the high-resolution photoemission spectra of $Ce_3Bi_4Pt_3$.[17] It is also interesting to notice that the correlation strength among the conduction electrons has a strong influence on their spectral shape.[16] A more complex situation is predicted by model calculations in the asymmetric PAM.[18] Various magnetic phases are stabilized in different concentration ranges of the conduction electrons, and for a low concentration the Kondo scale is significantly reduced compared to the SIM value. The amplitude of this reduction shows a very strong dependence upon the choice of the f Coulomb correlation and the hybridization strength. The inclusion of the $4f$ degeneracy always present in Ce compounds is anticipated to reduce the difference between the periodic and the single impurity models. At the present stage of development of such calculations it not straightforward to relate with confidence the results presented to the real conditions realized in the measured samples. Furthermore, no predictions exist concerning momentum effects in the $4f$ spectral functions.

The recent photoemission studies of monocrystalline Kondo systems demonstrate the importance of lattice effects that cannot be described within the SIM. In neither of the Ce-based monocrystalline films studied at very high resolution up to the present has any indication been found requiring a fundamental revision of the qualitative interpretation of the peak observed at E_F in terms of occupied tail of the Kondo resonance. The new and puzzling aspect is that the angular dependence of its intensity observed in Ce/Pt films is completely absent from the Ce/Be films spectra. More measurements of very different single-crystalline surfaces will be required to confirm such contrasted behaviors. This type of observation contains valuable information, which can be expected to stimulate the calculation of new spectral functions and to guide the choice of the relevant parameters determining the strength of momentum dependent effects in a Kondo lattice.

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Publication n° 6

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Photoemission study of the Kondo insulator $Ce_3Bi_4Pt_3$

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PACS. 71.28+d – Narrow-band systems; intermediate-valence solids.

Abstract. – The electronic structure of the Kondo insulator $Ce_3Bi_4Pt_3$ has been studied by high-resolution photoelectron spectroscopy. Indications of the unusual electronic structure are observed: the $4f$ derived peak near the Fermi level is located at a binding energy of 20 meV and is not cut-off by the Fermi edge as in conventional Kondo systems; for low photon energies, where the $4f$ contribution is negligible and the conduction band states are probed, a loss of spectral intensity in the same energy range is observed. These observations are related to the opening of a gap at low temperature, confirming the picture that hybridisation between a localised $4f$ state and the conduction band is responsible for the insulating character of this material.

Kondo insulators have recently emerged as a new class of material, characterised by a novel ground state containing a small energy gap [1]-[3]. Compounds within this class contain a partially filled f (or possibly d) shell. They are non-magnetic and insulating at low temperature and exhibit local moments at elevated temperature, where they cannot be distinguished from conventional Kondo systems. A prototypical Kondo insulator is $Ce_3Bi_4Pt_3$. Various measurements of this material have shown evidence for the presence of a gap: transport measurements reveal a temperature dependence compatible with an activation energy of 3 meV [4]; optical reflectivity shows a depletion of spectral weight below 100 K beginning at 35 meV [5]; and inelastic neutron scattering measurements demonstrate the presence of a 12 meV gap in the magnetic excitation spectrum [6]. Moderate substitution of Ce by La destroys the insulating character and leads to a conventional (moderately) heavy-fermion state, as evidenced by the decreasing resistivity and the increase in the value of the specific heat [4], [7].

The origin of the insulating ground state is believed to originate from the hybridisation of a localised f-state with one half-filled conduction band, the small value of the gap being related to strong electronic correlations. It is currently unclear whether a local model, based

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on the Kondo formalism, or a band model, properly renormalised to take correlations into account, provides the better starting point for describing the electronic structure. Calculations performed within the Anderson lattice model and those for a two-band model both predict a 4*f* density of states (DOS) dominated by two sharp peaks which straddle a gap [8], [9]. Direct evidence for the gap-forming mechanism by electron spectroscopy has not be given to date. The application of photoemission as a probe of Kondo insulators is a formidable challenge, as the size of the gap imposes stringent limits on the energy resolution necessary, and photoemission studies have therefore been scarce. Susaki *et al.* reported measurements on polycrystalline YbB_{12} [10], a Kondo insulator characterised by an activation energy of 5 meV [11]. In this work, agreement of the spectra with the single impurity model was claimed, as a "Kondo peak" was observed at a position compatible with the thermodynamic data. In addition, a loss of spectral weight in the vicinity of the Fermi level (E_F) indicative of the opening of an energy gap was reported. These results have been contested [12], but a recent photoemission study on the effects of Lu-substitution in YbB_{12} confirms the existence of a partially developed gap (pseudogap), which closes with increasing Lu content [13]. In the current paper we report high-resolution photoemission measurements on $Ce_3Bi_4Pt_3$. Contrary to Yb-containing compounds, the maximum of the conventional Kondo resonance in Ce-based systems is located above E_F. Our measurements on single-crystalline samples reveal unusual spectral features that can be related to the depletion of states at E_F characteristic of the opening of an energy gap.

High-resolution photoemission experiments were performed in Neuchâtel using a spectrometer equipped with a 200 mm hemispherical electron analyser and a high-intensity He discharge lamp. The spectra presented here were taken with an energy resolution of $\sim$ 6 meV, as determined by the width of a Ag Fermi edge. All measurements were undertaken in a quasi–angle-integrated mode to facilitate comparison with the momentum-integrated spectral function and to obtain reasonable statistics before sample deterioration sets in. The base pressure in the measurement chamber was in the low 10^{-11} Torr range, rising to 1×10^{-10} Torr during operation of the lamp. Complementary resonant photoemission measurements were undertaken at the Swiss-French beamline SU3 of the Super-Aco storage ring in Orsay, France. It has to be noted that a precise energy calibration of our resonant photoemission data is not possible due to the occurrence of energy shifts of the order of 10-20 meV in the monochromatised photon beam during the course of the measurements. The position of E_F in these spectra has therefore somewhat arbitrarily been chosen to coincide with the midpoint of the Fermi cut-off. Single crystals of $Ce_3Bi_4Pt_3$ were grown by the Bridgman method [14] and characterised by powder X-ray diffraction. The activation energy as determined from transport measurements was in good agreement with the value previously reported [4]. Preparation of clean surfaces was accomplished by *in situ* cleavage. For comparison, additional measurements were undertaken on scraped surfaces of polycrystalline samples. These were prepared by alloying Pt_3Bi_4 and Ce metal in an argon atmosphere using a tri-arc furnace, and subsequent annealing at 1020 K for a week.

For an understanding of the electronic structure of Kondo insulators, detailed knowledge of the *f*-states is of primary interest. Two approaches are possible for the extraction of the Ce 4*f*-states: resonant photoemission at the Ce $4d \to 4f$ threshold (122 eV); and the use of cross-section effects, taking difference spectra of measurements recorded at two photon energies with markedly different 4*f* cross-sections. For the latter method the two most intense lines from a He discharge lamp, He I (21.8 eV) and He II (40.8 eV), are widely employed. In this study both means to disentangle the 4*f*-DOS are employed.

Figure 1 (a) shows a valence band photoemission spectrum of $Ce_3Bi_4Pt_3$ taken at the Ce 4*f*-resonance, with an energy resolution of 50 meV. At this photon energy the Ce 4*f*-states

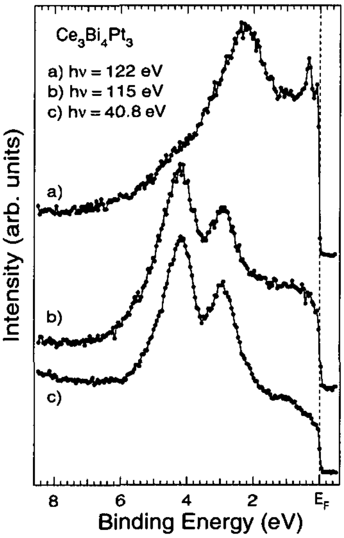

Fig. 1. – Valence band photoemission spectra of cleaved $Ce_3Bi_4Pt_3$ taken with different photon energies: (a) on resonance ($h\nu = 122$ eV); (b) off-resonance ($h\nu = 115$ eV); (c) He II ($h\nu = 40.8$ eV).

can be expected to dominate. The strongest spectral feature is a peak at 2.4 eV binding energy, which is readily ascribed to emission from $4f^0$ final states. A peak at around 300 meV binding energy and one just below E_F are due to transitions to states with $4f^1$ final-state character. These structures will be discussed in detail later. The spectrum taken at the Ce $4f$-antiresonance (115 eV) and that taken with He II photons, figs. 1 (b) and (c), have a remarkably similar structure. They both exhibit a double peak structure with maxima at binding energies of 2.8 and 4.0 eV. These peaks are related to states of predominantly Pt $5d$ character [15]. The extraction of the f-states from photoemission spectra taken with these photon energies is therefore seen to be delicate, although, as shown below, not impossible. Measurements performed at resonance certainly provide the best means of isolating the Ce $4f$-states, but the energy resolution obtainable with He discharge lamps is currently one order of magnitude better than that currently achievable at 120 eV.

Low-temperature spectra in the region close to E_F are shown in fig. 2. The spectrum from cleaved $Ce_3Bi_4Pt_3$ taken at the Ce $4f$-resonance with an energy resolution of 50 meV (fig. 2 (a)) reveals two peaks not unlike those commonly observed in Ce-based heavy-fermion systems. One is located at around 300 meV binding energy, and is ascribed to a final-state excitation of $j = \frac{7}{2}$ character, while the other, located close to E_F, is in conventional Kondo systems interpreted as the Kondo peak, the occupied tail of the Kondo resonance, broadened by crystal-field split sidebands. At the resolution achieved for this measurement, it is impossible to distinguish the spectrum of fig. 2 (a) from that of a conventional Kondo system with low or intermediate hybridisation between the conduction band and $4f$-electrons. Despite the difficulty in extracting the $4f$-spectral function (see fig. 1), measurements with our laboratory source can reveal differences in the electronic structure between $Ce_3Bi_4Pt_3$ and a metallic Kondo system. High-resolution spectra from cleaved $Ce_3Bi_4Pt_3$ at 10 K taken with He II and He I radiation are displayed in fig. 2 (b) and (c), respectively. In the former, structure due to Ce $4f$-states is observed as a shoulder at the position of the spin-orbit final-state excitation and as a feature with a maximum at a binding energy of 20 meV. No such structure is seen

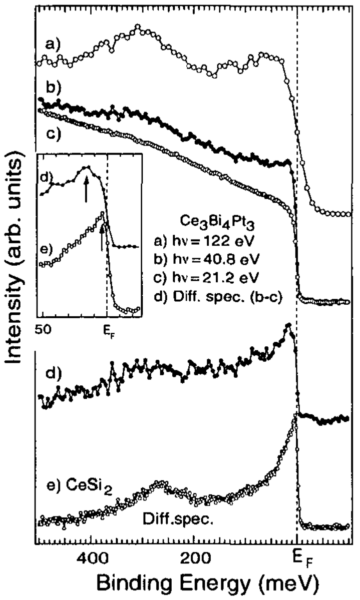

Fig. 2

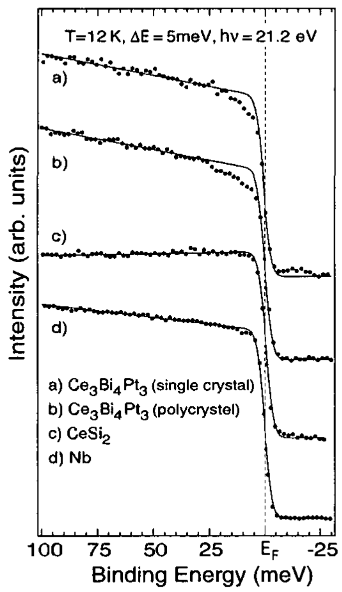

Fig. 3

Fig. 2. – High-resolution photoemission spectra from single-crystal $Ce_3Bi_4Pt_3$ taken with photon energies of: (a) 122 eV (ΔE = 50 meV, T = 30 K); (b) 40.8 eV ($\Delta E \sim$ 6 meV, T = 12 K); and (c) 21.2 eV ($\Delta E \sim$ 6 meV, T = 12 K). (d) Difference spectrum He II – He 1 (b – c) representing the $4f$ contribution. (e) The difference spectrum for the conventional Kondo system $CeSi_2$. The inset shows the spectra (d) and (e) in the immediate vicinity of E_F.

Fig. 3. – Photoemission spectra from the near E_F region taken at 12 K and with an excitation energy of 21.2 eV (He I). (a) Single-crystalline $Ce_3Bi_4Pt_3$; (b) polycrystalline $Ce_3Bi_4Pt_3$; (c) polycrystalline $CeSi_2$; and (d) polycrystalline Nb.

in the He I spectrum on the other hand. The difference between the He II and the He I excited spectrum can be used to isolate these Ce f-states. The difference spectrum, shown in fig. 2 (d), exhibits the same general features as the on-resonance spectrum. The most notable characteristic of this spectrum is the location of the maximum 20 meV below E_F. To illustrate the significance of this observation, the corresponding difference spectrum for $CeSi_2$, a typical moderately heavy-fermion system whose measured $4f$-spectral function is successfully calculated within the single-impurity model [16], is shown in fig. 2(e). Here the Kondo peak has a maximum at 4 meV, a value determined by the instrumental resolution and the thermal broadening at the Fermi level. The inset of fig. 2 shows the region in the close vicinity of E_F for spectra (d) and (e), with arrows indicating the positions of the maxima of the two $4f$-spectral features. It is tempting to relate the depletion of $Ce_3Bi_4Pt_3$ spectral weight below a binding energy of 20 meV to the insulating character of this compound, especially as optical experiments reveal a loss of spectral weight in the same energy range at low temperature [5]. Moreover, the measurement agrees qualitatively with the calculated DOS [8], [9]. We note, however, that finite intensity at E_F is present in spectrum (d), implying an incomplete opening of a gap in the $4f$-density of states. This point is discussed in more detail below.

Figure 3 shows He I photoemission spectra from $Ce_3Bi_4Pt_3$ in the near-Fermi level region. The sample temperature was 12 K, and the best experimental conditions available to us were used. At this excitation energy the contribution from Ce $4f$-states is negligible and the mainly Pt-derived conduction band states are probed. In addition to the experimental spectra, fits based on a linear extrapolation of the density of states between 100 and 30 meV binding energy are depicted. These fits take into account the Fermi function at 12 K and the experimental resolution. The spectra from single- and polycrystalline $Ce_3Bi_4Pt_3$ (fig. 3(a) and (b)) show very similar behaviour. They are linear between 100 and ~ 20 meV binding energy and, when compared to the linear extrapolation, lack spectral intensity in the region between 20 meV and the Fermi level. Nevertheless, the spectra show a well-pronounced Fermi edge, and a full gap of the size of the transport gap is not observed. Spectra taken under the same conditions from polycrystalline samples of the moderately heavy-fermion system $CeSi_2$ (fig. 3(c)) and from metallic Nb (fig. 3(d)) coincide almost exactly with the linear fit, confirming the depletion of spectral weight near E_F in $Ce_3Bi_4Pt_3$ as a subtle but real effect. The depletion of spectral weight is thus an intrinsic property of $Ce_3Bi_4Pt_3$ and reflects the incomplete opening of a gap for the non $4f$-states. The fact that very similar behaviour is encountered for ordered single-crystalline surfaces and for scraped surfaces from polycrystalline samples with no comparable long-range order may suggest that the mechanism responsible for the gap opening is of rather local character.

The observation common to figs. 2 and 3 is a depletion of spectral weight in the vicinity of E_F starting at 20-25 meV. This is observed for both the localised $4f$-electrons and for the conduction band states, indicating that the hybridised nature of the electronic states at E_F is responsible for the gap formation. In no case, however, has a full gap been observed. This scenario is strongly reminiscent of the behaviour observed in photoemission studies of other strongly correlated insulators. For example, the gap opening observed in YbB_{12} is also incomplete [10], [13]. FeSi, a narrow-gap semiconductor exhibiting properties quite similar to those of Kondo insulators, has also been studied by high-resolution photoemission [17], [18]. Here a partial gap opening is observed, and it has been speculated that disorder and the perturbation induced by the surface prevent observation of the opening of a full gap by photoemission [18]. A similar situation can be envisioned for $Ce_3Bi_4Pt_3$, although the small difference between the poly- and monocrystalline spectra seems to imply that long-range order does not play the same role as in FeSi. This might indicate that different mechanisms are responsible for the insulating ground state in these two materials. In a similar context, it has to be noted that even bulk-sensitive measurements on Kondo insulators are strongly affected or even dominated by extrinsic effects at low temperature, and that a truly insulating ground state has yet to be observed for any Kondo insulator [2], [5]. The additional perturbation caused by the surface is likely to magnify these effects for a surface-sensitive technique such as photoelectron spectroscopy. The subtle nature of the effect observed here indicating the gap opening is therefore not seen to be surprising.

In summary, we have studied the Kondo insulator $Ce_3Bi_4Pt_3$ by means of photoelectron spectroscopy, using the best resolution currently available. Spectra taken at the Ce $4f$-resonance condition are best suited to reveal the Ce $4f$-states, but the resolution attainable at a photon energy of 122 eV is not sufficient to allow the spectra to be distinguished from those of conventional metallic Kondo systems. Measurements of spectra at He discharge energies suffer from the domination of states other than Ce $4f$, but can be undertaken with a significantly superior energy resolution. A careful analysis of the spectra reveals that the Kondo peak is located at a binding energy of 20 meV, and not at E_F as in conventional metallic Kondo systems. A depletion of spectral weight between the energy of this peak's maximum and E_F is observed for both the f-states and the conduction band states, and is related to the opening of an energy gap at low temperature. The similar behaviour observed for both the conduction band states and the localised $4f$-electrons is a clear indication that the states at E_F, which are responsible for the unusual electronic structure, are formed by hybridisation.

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