

Université de Neuchâtel

Faculté des Sciences

**Etude par spectroscopie d'électrons à haute
résolution des excitations de faible énergie dans
les systèmes hybridés**

Thèse
sous forme réduite
avec un résumé

Travail effectué dans le groupe du professeur Yves Baer et présenté
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François Patthey

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Etude par spectroscopie d'électrons à haute
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dans les systèmes hybridés

de Monsieur François Patthey

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FACULTÉ DES SCIENCES

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

Messieurs Y. Baer, H. Beck, G. Krill (Nancy)
et J. Flouquet (Grenoble)

autorise l'impression de la présente thèse.

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Le doyen:



F. Persoz

Résumé

Introduction

La spectroscopie d'électrons est une technique permettant d'obtenir des renseignements sur la structure électronique d'un solide, d'un liquide ou d'un gaz. Nous avons effectué des mesures en photoémission ultraviolette à haute résolution sur des composés du cérium et de l'ytterbium que l'on nomme systèmes à valence intermédiaire.

Systèmes à valence intermédiaire

Lorsque, dans un solide, une couche électronique à grand nombre quantique orbital est partiellement occupée comme la couche $4f$ dans les lanthanides, les électrons de cette couche, quoique ayant une faible énergie de liaison, restent quasi-localisés sur leur site. Toutefois, ils peuvent par hybridation avec la bande de conduction participer à la liaison. Il en résulte un nombre non-entier d'électrons de valence ce qui justifie le nom de systèmes à valence intermédiaire.

Les systèmes à valence intermédiaire montrent des comportements très particuliers en raison du caractère à la fois localisé et itinérant des électrons $4f$. Par exemple:

- instabilité structurelle
- chaleur spécifique électronique très élevée à basse température (fermions lourds)
- susceptibilité magnétique qui passe d'un comportement type Curie-Weiss à haute température (moments magnétiques locaux) à un comportement type Pauli à basse température (magnétisme des électrons itinérants)
- effet Kondo dû à la diffusion des électrons de conduction sur les moments magnétiques localisés.

D'une manière générale on peut dire que l'état de valence intermédiaire qui se manifeste dans un grand nombre de propriétés des solides est un effet à N corps si bien que les spectres de photoémission présentent des structures qu'il est impossible d'interpréter de manière intuitive.

Théorie

Dans les lanthanides, l'extension spatiale des orbitales $4f$ étant petite par rapport au rayon atomique, il est possible, en première approximation, d'utiliser le modèle à une impureté de Anderson. On a donc un niveau $4f$ localisé et une bande de conduction couplés par un terme d'hybridation. Nous calculons l'état fondamental et les spectres de photoémission en faisant les deux approximations suivantes qui sont particulièrement adaptées au cas du cérium et de ses composés:

- la répulsion coulombienne entre deux électrons dans le niveau $4f$ est considérée

comme étant infinie. On interdit donc la double occupation du niveau $4f$.

- on passe à la limite où la dégénérescence du niveau $4f$ est infinie ce qui simplifie grandement les calculs.

Le calcul montre que l'hybridation donne lieu à une accumulation d'excitations de faible énergie qui apparaissent dans le spectre de photoémission comme un pic au niveau de Fermi. On nomme habituellement ce pic le pic de Kondo.

Partie expérimentale

Les mesures ont été effectuées sur un appareil XPS standard équipé d'un analyseur d'électrons électrostatique. Les photons ultraviolets (environ 20 et 40 eV) sont produits dans une décharge d'hélium. L'accent a été mis sur la haute résolution instrumentale qui est essentiellement déterminée par l'analyseur d'électrons. Afin de s'approcher de la limite théorique nous avons d'une part stabilisé toutes les tensions et d'autre part écranté soigneusement le champ magnétique qui est la cause principale de perturbations. Nous avons ainsi gagné un facteur 5 dans la résolution instrumentale par rapport aux mesures existantes.

Résultats et discussion

Les mesures présentées dans ce travail ayant fait l'objet de publications nous nous contentons ici de les énumérer, la liste des publications correspondantes figurant en dernière page.

Le cérium métal: $\alpha - Ce$ et $\gamma - Ce$

Système fortement hybridé: le CeN

Systèmes à fermions lourds: $CeCu_6$ et $CeAl_2$

Effet de la température: le $CeSi_2$

Un cas parmi les composés de l'ytterbium: $YbAl_3$

Conclusions

De ce travail nous pouvons tirer deux enseignements: le premier concerne l'utilisation de la photoémission à haute résolution en général et le second son utilisation pour l'étude des systèmes à valence intermédiaire.

Tout d'abord on peut raisonnablement prétendre que la spectroscopie d'électrons est une technique assez sensible pour étudier les excitations de faible énergie dans les solides. Ainsi, en poussant encore la résolution instrumentale, on doit être capable de disséquer les premiers meV à partir du niveau de Fermi qui sont intimement reliés aux propriétés du système proche de l'état fondamental et ainsi de mettre en évidence des phénomènes tels que:

- haute densité d'excitations dans les systèmes à fermions lourds
- effets du champ cristallin
- gap dans les supraconducteurs
- pertes d'énergies dans les solides
- toutes autres excitations de faible énergie telle que phonons, excitations magnétiques, etc.

En ce qui concerne les systèmes à valence intermédiaire, nous avons pu nous convaincre de la validité du modèle à une impureté pour les décrire. En particulier, l'observation des deux composantes spin-orbite du niveau f^1 dans le cérium (encore jamais clairement distinguées) et l'estimation de leurs intensités relatives nous a permis, en accord avec les résultats des autres spectroscopies (XPS, EELS et BIS), de caractériser les composés du cérium que nous avons étudiés. Nous avons ainsi pu conclure que tous ces composés métalliques du cérium que nous avons étudiés, des plus hybridés ($\alpha - Ce$ et CeN) aux moins hybridés (fermions lourds) appartiennent au même régime: le régime de Kondo.

Il n'en va pas de même du seul composé de l'ytterbium que nous avons étudié et qui appartient au régime de valence mixte caractérisé par un nombre d'occupation du niveau f proche d'un demi-entier. Au vu de mesures antérieures, il semble que cela soit également le cas pour d'autres composés de l'ytterbium ($YbAu$, $YbCu$, $YbAl_2$, etc.). Une importante conséquence de cette observation est que, en dépit de la contraction des lanthanides, l'hybridation dans les lanthanides lourds n'est pas forcément plus faible que dans les lanthanides légers. Il est d'autre part possible que certains composés d'ytterbium comme le $YbCu_2Si_2$ appartiennent au régime de Kondo mais cela reste à démontrer comme rest à démontrer que l'hybridation est un mécanisme essentiel dans toute la série des lanthanides avec peut être certaines singularités comme dans les composés d'euporium qui montre une dépendance

en température du nombre d'occupation du niveau $4f$ tendant à impliquer qu'il existe un régime (que l'on pourrait appeler régime des fluctuations de valence) dans lequel la température a autant d'effet que l'hybridation sur le mélange de configurations. Il ne fait aucun doute que ces questions seront résolues plus ou moins complètement dans un proche avenir avec l'aide de toutes les techniques expérimentales parmi lesquelles la spectroscopie d'électrons joue certainement un rôle important.

Liste de publications

Le cérium métal: $\alpha - Ce$ et $\gamma - Ce$

Low-Energy Excitations in $\alpha - Ce$ and $\gamma - Ce$ Observed by Photoemission
F.Patthey, B.Delley, W.D.Schneider and Y.Baer
Phys.Rev.Lett. 55, 1518 (1985)

Système fortement hybridé: le CeN

High-Resolution Photoemission Study of CeN : a Narrow-Band Material.
F.Patthey, S.Cattarinussi, W.D.Schneider, Y.Baer and B.Delley
Europhys.Lett. 2, 883 (1986)

Systèmes à fermions lourds: $CeCu_6$ et $CeAl_2$

Characterization of the heavy-fermion system $CeCu_6$ by high-energy
electron spectroscopies
F.Patthey, B.Delley, W.D.Schneider and Y.Baer
Phys.Rev. B 34, 2967 (1986)

Spectroscopic evidence for an unrealized heavy-electron state in $CeAl_2$
F.Patthey, B.Delley, W.D.Schneider and Y.Baer
Phys.Rev. B 35, 5963 (1987)

Effet de la température: le $CeSi_2$

High-Temperature Collapse of the Kondo Resonance in $CeSi_2$ Observed
by Photoemission
F.Patthey, B.Delley, W.D.Schneider and Y.Baer
Phys.Rev.Lett. 58, 2810 (1987)

Un cas parmi les composés de l'ytterbium: $YbAl_3$

Characterization of the hybridized $4f$ states in $YbAl_3$ by high-energy
spectroscopies
F.Patthey, J.M.Imer, B.Delley, F.Hulliger, W.D.Schneider and Y.Baer
Phys.Rev. B 36, 7697 (1987)

Un exemplaire complet de ce travail de thèse est déposé à la bibliothèque de
l'université de Neuchâtel, 26 avenue du 1^{er} Mars 2000 Neuchâtel

Low-Energy Excitations in α - and γ -Ce Observed by Photoemission

F. Patthey, B. Delley, W.-D. Schneider, and Y. Baer
Institut de Physique, Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland
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uv-photoemission spectra of the α and γ phases of Ce have been measured with an unprecedented resolution (20 meV). A detailed many-body calculation based on the Anderson impurity model and including the $4f^1$ spin-orbit splitting has been performed. It accounts perfectly for the fine structures observed in the spectra. Within the energy range corresponding to the ground-state lowering by the f - d hybridization, the f contribution to the spectra reveals the density of low-energy excitations culminating at E_F .

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The unusual character of the isostructural $\gamma \rightarrow \alpha$ phase transition in Ce metal has always been attributed to some drastic modification of the electronic structure. Many different models based on more or less intuitive ideas have been proposed to explain the exceptional manifestations of this transition.¹⁻³ The accumulation of many different experimental results⁴⁻⁹ has gradually confirmed the assumption that the $4f$ -occupation number n_f undergoes only a minor reduction of about 10% upon the phase transition, in agreement with a very early prediction based exclusively on thermochemical data.¹⁰ It became then more and more evident that the fundamental mechanism driving this transition is a change of the mixing between the extended conduction-band states and the atomiclike $4f$ states.^{9,11} The various formalisms developed for the calculation of the electronic states in periodic solids are not adapted to take into account the coupling between these two kinds of states which have completely different single-particle Coulomb correlation energies. They yield Bloch eigenstates which can hardly account for the local character remaining in the mixed states. Nevertheless, sophisticated considerations¹² appear to bring out many-body aspects of the excitations in such systems.

The Anderson impurity model offers the simplest framework where local and extended states can be treated on an equal footing. Gunnarsson and Schönhammer¹³ (GS) have used it to calculate the f contribution to the excitation spectra of Ce and of its compounds. At the present time, this model has shown great success since it simulates correctly the very different types of excitation spectra observed in these solids which need only to be characterized by a limited number of simple parameters.¹⁴⁻¹⁶ Up to now the validity of the GS model could only be tested within the current resolution (100-500 meV) achieved in electron spectroscopies.¹⁷ From the best-resolved (100 MeV) photoemission study of α - and γ -Ce published recently,¹⁸ it has been inferred that models pinning one f feature to the Fermi level in both phases of Ce are inappropriate. This conclusion is unreliable since the resolution was not sufficient to observe the

fine structures near E_F predicted by the GS model.

The aim of this study is to show that with an improved instrumental resolution and at low temperature these low-lying excitations can be clearly observed in photoemission spectra. This is a fundamental challenge since these excitations correspond to the relevant energy scale of the quasi-ground-state measurements (transport properties, specific heat, etc.). In addition, the consequences of the spin-orbit interaction in photoemission spectra can be easily studied and are found to be correctly accounted for by the GS model.

The samples of metallic Ce were obtained *in situ* by repeated evaporation onto a sapphire plate at room temperature for γ -Ce (with use of a closed-cycle He refrigerator). The pressure did not rise above 1×10^{-10} Torr during the evaporation. The measurements were performed with our combined XPS-BIS-EELS apparatus^{19,20} which has been equipped with a commercial rare-gas discharge lamp used to produce the He-resonance lines He I (21.2 eV) and He II (40.8 eV). We have developed an additional pumping stage for this lamp so that a total pressure of 3×10^{-10} Torr could be maintained in the spectrometer during the measurements. The spectra of α -Ce were recorded at 10 K and those of γ -Ce at 150 K, in order to reduce the thermal broadening at the Fermi level. All of the instrumental parameters influencing the resolution (geometry, magnetic fields, voltages) were tuned so that a total instrumental linewidth of 20 meV, including the contribution of the light source, could be obtained. This resolution was determined from the Fermi edge width of Ag measured at 10 K.

Figure 1 shows the outer-level spectra of α - and γ -Ce excited with He II radiation. The overall features of these spectra are in agreement with the well-known f -excitation distribution with two maxima, one just at E_F , and the other one at around 2 eV.^{11,18,21} This f contribution is superimposed on the contribution from other symmetries. At the bottom of Fig. 1 is also displayed the result of the GS-model calculation (see later) for the f -excitation spectrum. In order to extract the f contribution from the experimental spectra,

one can take advantage of the very rapid photon energy dependence of the cross section between f and other symmetries.²² As shown in Fig. 2, the two spectra taken at 40.8 and 21.2 eV have been weighted and subtracted from each other, in order to reproduce as well as possible the computed f spectra in the 500-meV range below the Fermi energy. The new striking feature observed at high resolution is the presence of two peaks, one at E_F , and the other one at 280 meV. Their intensity ratios are very different in the two phases. The possibility of a surface shift can immediately be ruled out, since a surface sensitivity enhancement by variation of the escape angle of the emitted electrons²³ did not modify these spectra. The two structures which have precisely the energy separation of the $4f_{7/2}$ and $4f_{5/2}$ levels in atomic Ce²⁴ must reflect the spin-orbit splitting. However, they do not simply account for final-state multiplets as in the case of heavy rare-earth materials, but, as a consequence of the hybridization between f and band states, they correspond to a rather complicated many-body response of the system to the creation of a hole by photoionization.

In order to interpret these experimental spectra and to obtain the relevant parameters characterizing the α and γ phases of Ce within the Anderson impurity model, we have performed a first-order calculation with the GS model, where the spin-orbit interaction is included.¹³ The hybridization parameter Δ was adjusted to obtain the f -occupation numbers n_f (0.98 in γ -Ce and 0.88 in α -Ce) resulting from a second-order calculation of lower resolution but fitted to many different spectroscopic results (XPS, BIS, and EELS).¹⁷

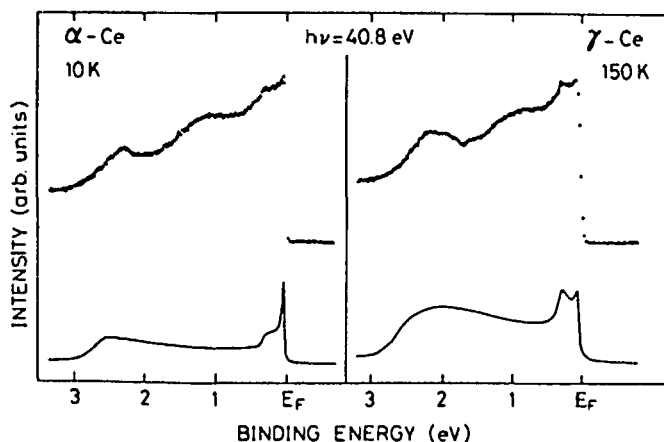


FIG. 1. Dots: outer-level photoelectron spectra of α - and γ -Ce. Full curves: result of a many-body calculation (including $4f$ spin-orbit interaction) for the f contribution to the photoemission spectra. The curves have been convoluted with Lorentzians of 20 and 60 meV FWHM for α - and γ -Ce, respectively, in order to simulate the influence of finite resolution and temperature.

The band was assumed to have a semielliptical shape, a total width of 8 eV, and an occupied width of 2.5 eV. With the uncoupled $4f_{5/2}$ level 1.2 eV below the Fermi energy and a spin-orbit splitting of 280 meV, the best agreement between theory and experiment is found for $\Delta = 82$ meV in γ -Ce and $\Delta = 105$ meV in α -Ce. In Fig. 1 the comparison over the whole bandwidth of the total measured spectrum (He II) accounting for all contributions with the model calculation for the f contribution can only be qualitative but appears to be quite satisfactory; the agreement becomes excellent over the 500-meV range below E_F displayed in Fig. 2, where the experimental $4f$ contribution has been approximately extracted (spectrum $a - b$). The essential information obtained in this analysis is that a modest 30% increase of the hybridization parameter Δ already accounts correctly for the important changes observed in the photoemission spectra upon the γ - α transition. In γ -Ce the structure at 280 meV originates predominantly from the excitation of the $4f_{7/2}$ level. When Δ increase in α -Ce, more $4f_{7/2}$ character is admixed to the initial state, leading to a loss of atomic character which spreads and washes out the intensity of the $4f_{7/2}$

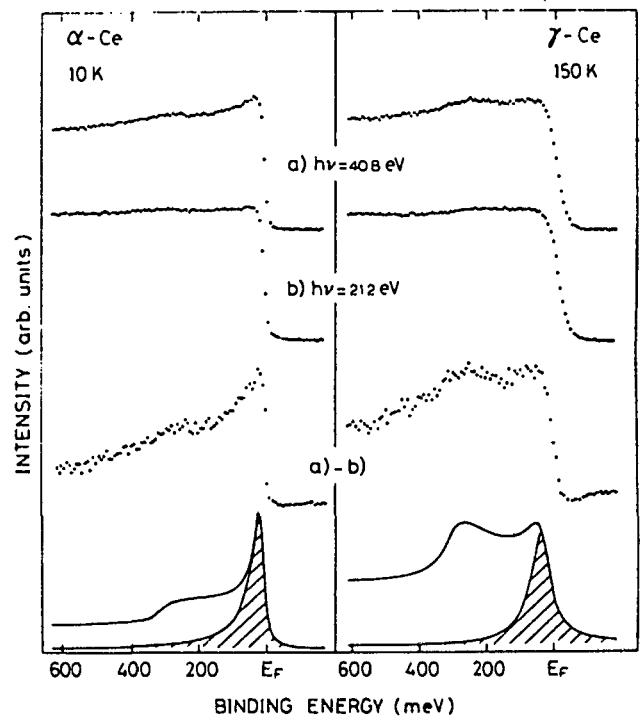


FIG. 2. Dots: outer-level photoelectron spectra of α - and γ -Ce within 500 meV below E_F . The curves labeled $a - b$ represent differences of weighted spectra a and b (see text). Full curves: model calculation (see caption of Fig. 1). The curves defining the hatched areas correspond to the particular transitions occurring within the energy range δ (see text). The relative intensities of the α - and γ -Ce spectra have not been normalized.

structure. We note that recently a self-consistent perturbation theory²⁵ and a Green's-function technique with decoupling procedure²⁶ have predicted qualitatively the excitation spectra that we have measured in the two phases of Ce.

One of the fundamental motivations for the performance of spectroscopic studies is to deduce ground-state properties of electronic systems from their excitation spectra. This task is to some extent accomplished when the parameters defined in the Anderson impurity model are determined. One can attempt to go beyond these numbers by a formal analysis of the structure of the N -electron ground state and of the $(N-1)$ -electron final states involved in the considered photoemission process. The singlet ground state (given by Varma and Yafet²⁷) has to lowest order the form

$$|\phi_0\rangle = a_0|0\rangle + \int d\epsilon a_\epsilon|\epsilon\rangle.$$

It is expanded in the basis functions $|0\rangle$ formed only of band states filled up to the Fermi energy and in the functions $|\epsilon\rangle$ formed of a band with a hole at the energy ϵ and of one f electron. For a nonvanishing hybridization parameter Δ , the ground state is separated by an energy gap δ from the excited N -electron state continuum of the same symmetry. δ is the energy lowering of the ground state resulting from the f - d hybridization (Ref. 13, Appendix C). The final states with energy E can be written in a similar way:

$$|\phi_E^\mu\rangle = a_0^{E,\mu}|\epsilon\mu\rangle + \int d\epsilon' a_{\epsilon'}^{E,\mu}|\epsilon\epsilon'\mu\rangle.$$

Again there are two types of basis functions: (i) The function $|\epsilon\mu\rangle$, characterized by the quantum number μ , represents a band with one hole at ϵ and no f electron; (ii) the functions $|\epsilon\epsilon'\mu\rangle$ represent a band with two holes at ϵ and ϵ' , and one f electron. It is important to notice that for any fixed choice of ϵ and μ , the lowest final state (split-off final state) is also separated from the continuum of final states by an energy gap δ . Therefore, the transitions of lowest energy lead to the split-off final states which correspond to the pole of the f Green's function. The f -dipole matrix element between these initial and final states couples only $|\epsilon\rangle$ and $|\epsilon\mu\rangle$. Since the coefficient $a_0^{E,\mu}$ has the same value in each split-off state, the spectral density $\rho(E)$ is simply proportional to a_ϵ^2 . If the lowest final-state energy is taken as the origin of the total energy scale, then $E = \epsilon$ for the considered split-off states. In the low-energy range $0 \leq \epsilon \leq \delta$, transitions of another type cannot occur, and one finds the relation $\rho(\epsilon) = (1 - n_f)a_\epsilon^2$. The spectral density in this narrow region of the spectrum reflects directly the weight of the basis state $|\epsilon\rangle$ in the ground state. It forms a tail falling off rapidly from its maximum value at E_F ($\epsilon = 0$):

$\rho(E_F) = n_f^2\pi/N_f\Delta$.¹³ If the complete spectral density is normalized to n_f , the weight of these particular transitions is $n_f(1 - n_f)$. This contribution has been extracted from our calculation and has been convoluted with a Lorentzian in order to simulate the instrumental resolution and the thermal broadening (see caption of Fig. 2). The result is displayed by the curves defining the hatched areas in Fig. 2. The parameters resulting from the best fit of the theory to the experimental spectra yield the values $\delta = 5$ meV for γ -Ce and $\delta = 26$ meV for α -Ce. The finite resolution reduces the peak heights (particularly for γ -Ce), but it preserves their relative areas which are 2% and 12% of the total integrated intensity (n_f) in γ - and α -Ce, respectively. The experimental spectra reveal clearly the existence of these particular excitations within δ and provide the first evidence that high-energy spectroscopy is adapted to probe this crucial low-energy range, closely related to the ground state.

In the spin-fluctuation limit, where the f population is very close to 1, δ/k_B is called the Kondo temperature and $\rho(\epsilon)$ within δ the Kondo peak.¹³ In the light of the present investigation, the early attempts^{28,29} to identify as a Kondo peak the 2-eV maximum in photoemission spectra of γ -Ce and Ce compounds was a misinterpretation. The increase of δ upon the γ - α transitions of Ce deduced from the present study is in qualitative agreement with thermodynamical descriptions of this transition proposed within related formalisms.^{2,3}

The concept of single-particle eigenvalues is not apparent in the GS model, but it is interesting to notice that it provides a picture of the f -excitation spectra, showing some striking similarities with the spectra of correlated band states,³⁰ despite the rather different nature of these two systems. The f -excitation spectra within δ have a metallic character in the sense that, as in a single-particle approach to a metallic band, a population variation is possible at E_F for an infinitesimal total energy variation³¹ [$U(E_F) = 0$]. All of these final states contain the same f population as the initial state and can be compared to the adiabatic single-particle part of a photoionization band spectrum. The other types of final states reflect the correlation: They are at least separated from E_F by δ , and for increasing energy they contain a lower f population, i.e., a more pronounced f -hole character.³²

On the other hand, when remaining within the Anderson impurity model, the low-energy region of the spectra, formed of the split-off final states, can certainly be interpreted in terms of a localized Fermi liquid.^{27,33,34}

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High-Resolution Photoemission Study of CeN: a Narrow-Band Material.

F. PATTHEY, S. CATTARINUSSI, W.-D. SCHNEIDER and Y. BAER

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

B. DELLEY

Laboratories RCA ltd - CH-8048 Zürich, Switzerland

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Abstract. – The outer level electronic structure of polycrystalline CeN films is studied at low-temperature by photoemission using HeI and HeII excitation sources. The *f*-emission spectra are analysed successfully within the Anderson single-impurity model yielding a narrow band of low-energy excitations within $\delta = 15$ meV above E_F . Towards higher energies the spectra reveal an excitation due to the spin-orbit interaction of the ground state *f*-population. In substoichiometric CeN the hybridization between *f*- and band states is weakened leading to a more atomiclike *f*-ionization peak around $\epsilon_f = -1.2$ eV.

The unconventional physical and chemical properties of many rare-earth materials are originating from the interaction of the incomplete 4*f*-shell with the band states of the solid. The nonnegligible wave function overlap of the predominantly atomiclike 4*f*-states with the extended states [1] and the small 4*f*-ionization energies of the order of the bandwidth give rise to a weak hybridization between these two kinds of states of completely different character. This hybridization is responsible for the participation of the *f*-states in the chemical bond [2] and it is expected to play the key role in the heavy-electron behaviour discovered recently [3].

The compound CeN, crystallizing in the NaCl structure, shows rather unusual properties among the other rare-earth nitrides. Its room-temperature lattice constant of 5.019 Å [4] is anomalously small so that the Ce-Ce distance of 3.55 Å lies just between those of γ -Ce (3.65 Å) and α -Ce (3.43 Å). Each Ce-atom is surrounded by 6N neighbours at a distance of 2.51 Å giving rise to an appreciable Ce4*f*-N2*p* wave function overlap. The low-temperature magnetic susceptibility of CeN is very low, displaying a remarkable similarity with the one of LaN. Above 1000 K a moment approaching the Ce³⁺ free-ion value [5] is obtained. On the other hand, the linear coefficient of specific heat γ is vanishingly small in LaN [6] and it is ~ 8.3 mJ mol⁻¹ K⁻² in CeN [5] indicating the contribution of the *f*-states to the specific heat.

In an early attempt to clarify the electronic structure of CeN an X-ray photoemission study (XPS) of a single crystal sample was performed [7]. The unusual sharp peak observed at E_F with a full width at half maximum (FWHM) corresponding to the experimental resolution of ~ 0.3 eV was interpreted as emission peak from a localized $4f^1$ state being degenerate with the f^0 configuration. The peculiar $3d$ - and $4d$ -core spectra were thought to reflect the presence of two degenerate $4f$ populations in the initial state as predicted by the configuration fluctuation model [8]. A subsequent resonant photoemission study of the outer levels around the Ce $4d$ threshold revealed a further structure of f -character at ~ 1.2 eV below E_F . Since this structure is not discernible in the XPS spectra, which have much less surface sensitivity than the UPS spectra, it was attributed to the excitation of the $4f$ states assumed to have a larger binding energy at the surface [9, 10].

These experimental observations stimulated different band theory calculations of the electronic structure of CeN. Qualitative agreement with the XPS spectra is obtained when substantial (N $2p$) – (Ce $4f$) hybridization is included in the computation [11, 12]. This approach gains credibility by the fact that calculations for the reference compound LaN yield only a very low density of state at E_F [13, 14] in agreement with the very small experimental γ -value. Recently, the surface electronic structure of CeN was calculated in a layer-by-layer decomposition of slab bandstructure results [15]. This study, though yielding reasonable agreement with the XPS-spectra, does not support the picture of surface shifted $4f$ states [9, 10]. Instead, surface vacancies of N [16] or complicated final-state effects are suggested to be at the origin of the 1.2 eV peak in the UPS spectra.

Band theories of correlated electronic systems using a mean-field approach are rather successful in determining ground-state properties like lattice constants or the f -occupation n_f , but the calculated eigenvalue distribution can never be directly compared to excitation spectra [2]. An attempt to simulate the photoemission final state in the Ce-pnictides by a supercell calculation [17, 18] was rather successful but offered no explanation for the 1.2 eV peak in CeN.

A totally different approach to the f -state in solids has been chosen by GUNNARSON and SCHÖNHAMMER [2]. Based on the Anderson single-impurity model which includes the mixing between localized and extended states, they computed within the sudden approximation the ground and excited states relevant for the electron-spectroscopies. This scheme for the calculation of high-energy f -spectra of light rare-earth materials appears to be very successful [19]. In CeN this approach yields a surprisingly good simulation not only of the core spectra, but also of the outer level XPS and BIS excitations [20]. The parameters obtained from this study still seemed to be compatible with the existence of a configuration fluctuation mechanism in CeN.

This situation motivated us to study with high-resolution at low-photon energies the outer level excitations of CeN where the emphasis is on the following questions. i) Does the sharp peak observed with XPS at E_F correspond to emission from localized f states? ii) Can the single-impurity model still account for a situation which seems to be quite satisfactorily modelled by the band theory approach? iii) What is the origin of the 1.2 eV peak observed in surface-sensitive photoemission?

The photoemission measurements were performed in a spectrometer equipped with a commercial gas discharge lamp producing photons of 21.2 eV (HeI) and 40.8 eV (HeII) [21]. The CeN sample was prepared by gas reaction *in situ*. During evaporation and deposition of Ce on a heated (~ 800 K) tungsten foil mounted on the cryo-tip of a closed-cycle He-refrigerator, a partial pressure of 10^{-6} Torr N was maintained. Subsequent flash-annealing cycles with temperatures up to ~ 2000 K yielded CeN samples of high quality as determined by the excellent agreement of their room-temperature UPS spectra with XPS spectra obtained from CeN single crystals [7]. The photoexcitation spectra presented in this study

(except fig. 1a)) were recorded at a sample temperature of ~ 30 K with a resolution of 50 meV as measured at the Fermi edge of CeN. Spectra taken at higher resolution (28 meV) showed no more fine structure so that advantage could be taken of a higher counting rate at lower resolution. The difference between $h\nu$ (HeI) and the total width of the spectrum has been evaluated to determine a work-function of $\phi = (2.72 \pm 0.1)$ eV for a well-annealed polycrystalline CeN film.

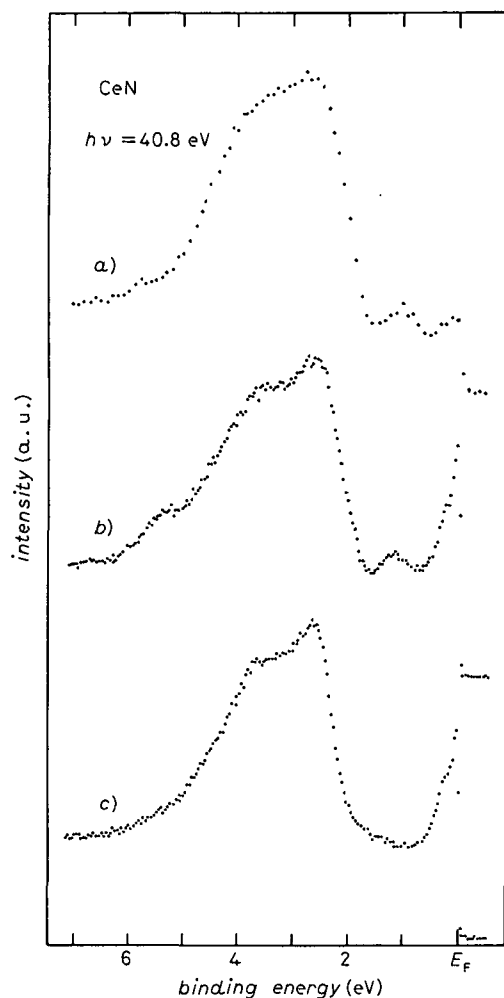


Fig. 1. - Photoemission spectra of the outer states of CeN obtained with HeII radiation. *a*) Unannealed film measured at room temperature. *b*), *c*) Films measured at ~ 30 K after subsequent annealing steps (see text).

Figures 1*a*)-*c*) display the outer level spectra of CeN obtained with HeII radiation at various stages of sample preparation. The spectrum of fig. 1*a*), taken at room-temperature from an unannealed film, shows a remarkable similarity with previous spectra obtained from a CeN single crystal at comparable photon energies [9,10]. The dominating emission structure centred around 5 eV originates essentially from N $2p$ derived states and the peak at E_F is due to f -emission. In particular the 1.2 eV peak is clearly visible. Spectra recorded after subsequent sample annealing show a continuous intensity reduction of this peak (fig. 1*b*)) until finally it becomes practically undiscernible in fig. 1*c*). At this stage the spectra

resemble closely the XPS spectra of a CeN single-crystal [7], indicating that a carefully prepared surface of a CeN film yields a spectrum free from this extra structure. The origin of the 1.2 eV peak will be discussed later.

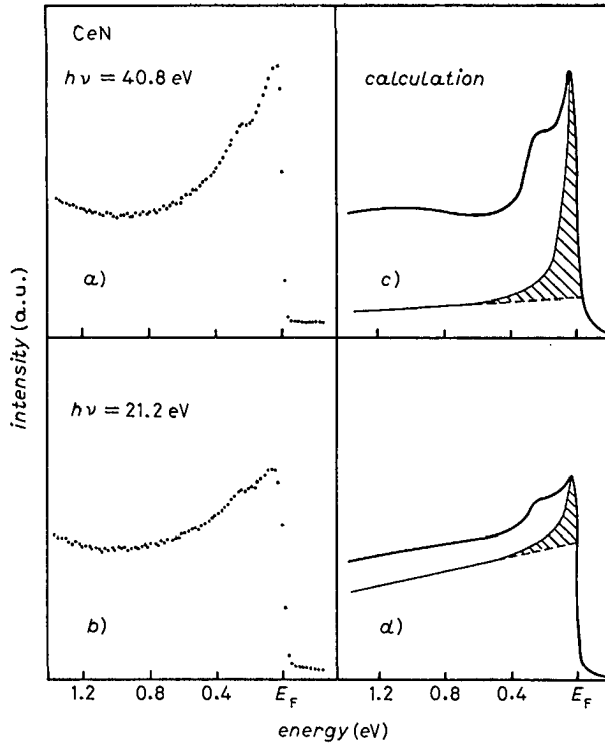


Fig. 2. - *a*), *b*) UPS spectra of CeN within 1.3 eV below E_F . *c*), *d*) Result of a many-body calculation (including the $4f$ -spin-orbit interaction) for the f - and p -contributions to the photoemission spectra. Upper curves: Sum of p -contributions (dashed curves) and f -contributions weighted by their cross-section ratios. The curves defining the hatched areas correspond to the split-off final states (see text).

Figures 2*a*) and *b*) display the spectra obtained from a well-annealed CeN sample in the energy range up to 1.3 eV above E_F using HeII and HeI radiation, respectively. It appears that the peak at E_F , assumed to be sharp in XPS spectra, has in fact a FWHM of about 300 meV, a factor of 10 larger than the resolution of the UPS measurement. This observation already casts doubts on the earlier interpretation of this peak in terms of a long-lived f^0 -final state assumed to be degenerate with the f^1 initial state. On the other hand, this peak is followed by a shoulder at about 280 meV corresponding to the energy of the atomic $4f_{5/2}$ - $4f_{7/2}$ spin-orbit splitting as already observed in Ce-metal [21]. These two features demonstrate that a pure atomlike description of the spectra is not suitable.

The Anderson single-impurity model has provided a clue for an understanding of such excitations in Ce-systems. For this reason a first-order many-body calculation including the spin-orbit interaction in the impurity scheme [2] has been performed. It has been constrained to yield the value of the ground-state f -occupation n_f , obtained in an earlier study of CeN from a fit to many different excitations (XPS and BIS outer levels, XPS and EELS $3d$ core levels) [19]. The valence and conduction bands of semi-elliptical shape used earlier have been replaced by one band of Lorentzian shape (FWHM = 6 eV, maximum 3 eV

above E_F), whereas the valence band derived mainly from N $2p$ states (see fig. 1) is ignored. This choice of the band shape near E_F for the model calculation can be justified by its similarity to the density of states of the isostructural compound LaN having practically no occupied f -states [13] and to the photoemission spectrum of CeN in the $4d$ - $4f$ antiresonance, where the f -emission is practically suppressed [9, 10]. From these works we have estimated that the range from E_F to 1 eV used for the adjustment of the spectral weight contains about $0.2p$ electrons. In the same energy range the many-body calculation yields 0.3 f electrons.

Figures 2c) and d) display the calculated spectra for both HeII and HeI excitations. Since the experimental spectra contain contributions from the band (dashed curve) and the f -states a weighted superposition of these two contributions has been calculated (upper full curve) and compared with the data. Best agreement is obtained for weighting coefficients corresponding roughly to photoexcitation cross-section ratios $\sigma(0.3f)/\sigma(0.2p) \approx 1/3$ and $\approx 3/1$ for HeI and HeII, respectively [22]. A Lorentzian broadening of FWHM = 60 meV has been included to account for the instrumental resolution, the lifetime broadening and the temperature. The data are best fitted with the values $\Delta = 150$ meV for the hybridization parameter and $\epsilon_f = -1.0$ eV for the difference in total energy between f^1 and f^0 configuration without hybridization. The striking agreement between the calculated and the experimental spectra gives confidence in this type of analysis. In the ground state the computation yields a partial f -occupation of 0.86 for $j = 5/2$ and 0.04 for $j = 7/2$. The energy lowering of the ground state due to the hybridization is found to be $\delta = 15$ meV, a value between those of γ -Ce (6 meV) and α -Ce (26 meV). The energy region of the split-off states [2], where the f -occupation in the final state is the same as in the initial state, is indicated in fig. 2c) and d) by the curves defining the hatched areas. Towards higher energies the excitations acquire more and more f -hole character and account for final states having no close relationship to the ground state. For this reason, the excitation spectra of such systems cannot be simply derived from ground-state band calculations and only in the energy region confined within δ a comparison between the impurity approach and the band approach can be attempted. Within δ , one can anticipate that the excited final state can be related to the adiabatic single-particle part of a photoionization band spectrum [21]. If δ is taken as a measure of the adiabatic spectrum width, it is at least one order of magnitude smaller than the calculated f -bandwidth [11, 12, 15]. On the other hand, coherence effects which are present in a lattice lead to corrections to the impurity result. These effects, however, are smaller by a factor $1/n_f$ ($N_f = 6$, in the present case) than on-site effects [23]. Therefore, to leading order in $1/N_f$, it is consistent to analyse the data for the lattice within the single-impurity model.

A special attention will be devoted to the shoulder at 280 meV above E_F (ground state), an energy corresponding to the atomic value of the $4f_{5/2}$ - $4f_{7/2}$ spin-orbit splitting. In CeN the impurity calculation of the hybridized ground state yields fractional j -populations of 95% and 5% for $j = 5/2$ and $j = 7/2$, respectively, consequently the excited states, located about 280 meV above the ground state, have approximately 95% $4f_{7/2}$ character and 5% $4f_{5/2}$ character. A fractional j -population of this excited state becomes possible by the hybridization-mediated screening of a hole with $j = 5/2$. In contrast to the singularity at E_F , this structure has a smooth energy distribution, since it is embedded in the continuum of the band states with which it hybridizes. We want to point out that this type of excitation evidently probes the multiplet structure of the $4f$ ground state population of Ce. In the rare-earth elements following Ce these multiplets are numerous and spread in a larger energy range. For a nonvanishing hybridization, they can be excited in photoemission spectra so that the interpretation of previous resonant photoemission experiments on light rare-earth compounds [24-26] has to be reconsidered critically.

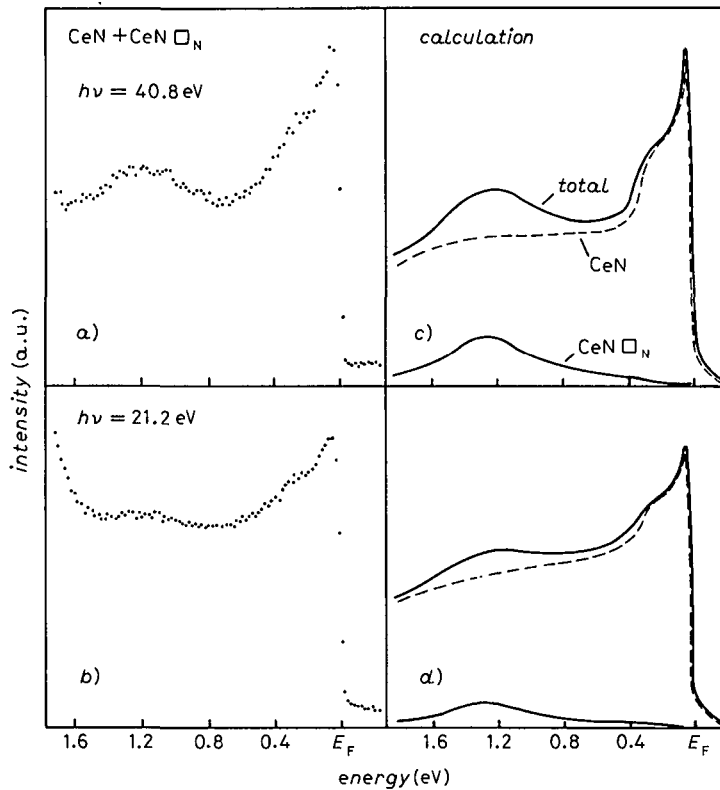


Fig. 3. - *a*), *b*) UPS spectra of substoichiometric CeN within 1.6 eV below E_F . *c*), *d*) Result of the many-body calculation. Bottom curves: f -contribution from vacancy-surrounded Ce-atoms. Dashed curves: many-body calculation for CeN as in fig. 2. Upper curves: sum of the contributions from stoichiometric and substoichiometric CeN.

Finally, we address the question of the origin of the 1.2 eV structure observed in fig. 1*a*) and *b*). First of all, the f -character of this structure is demonstrated by its resonant behaviour at the $4d$ - $4f$ excitation threshold [9, 10]. Secondly, it is known that the nitrides can accommodate up to 40% N-vacancies, while the metal atoms rest approximately at their lattices sites [27, 28]. For surface layers the N-deficiency might be even higher. The single-impurity model appears to be well adapted to simulate the resulting weakening of the f - p hybridization by modifying the parameters Δ and ϵ_f . Since our aim is to show only qualitatively the consequences of substoichiometry on excitation spectra, we have performed a calculation neglecting the statistical distribution of N-vacancies around each Ce-atom and ignoring the concomitant changes in the conduction bands. Figures 3*c*), *d*) display the result of the many-body calculation for the two excitation spectra with appropriate weighting factors as in fig. 2. The contribution to the spectrum of a surface film with N-deficiency (denoted $\text{CeN}\square_N$) is simulated with $\Delta = 50$ meV and $\epsilon_f = -1.2$ eV (full curves in the bottom), whereas the bulk contribution of stoichiometric CeN is calculated as previously with $\Delta = 150$ meV and $\epsilon_f = -1.0$ eV (dashed curves). Both changes of the parameters account for the hybridization weakening and f -localization increase ($n_f \approx 1$) near vacancy sites and lead to a dramatic intensity reduction of the excitations near E_F . For this reason, practically only the f^0 -ionization peak around ϵ_f broadened by $N_f \Delta$ [2] survives in the spectra of $\text{CeN}\square_N$. The sum of the two contributions is represented in fig. 3 by the

upper full curves. The agreement with the experimental spectra is encouraging and underlines the internal consistency of the spectra analysis within the single impurity model. The appearance of similar structure in photoemission spectra of substoichiometric early transition metal nitrides [28] and carbides [29] suggests the existence of a similar hybridization weakening involving the *d*-states.

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Characterization of the heavy-fermion system CeCu₆ by high-energy electron spectroscopies

F. Patthey, W.-D. Schneider, and Y. Baer

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

B. Delley

Laboratories RCA Ltd., CH-8048 Zürich, Switzerland

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The heavy-fermion system CeCu₆ has been studied by photoemission and inverse photoemission spectroscopies. The spectra are analyzed within the Anderson single-impurity model and the relevant parameters deduced from the comparison between theory and experiment. This oversimplified formalism explains why, even with our markedly improved experimental conditions, the manifestations of heavy electrons around the Fermi level still cannot be discerned in the spectra.

The hybridization of the f states with the band states in rare-earth-metal and actinide compounds appears to be one of the most important mechanisms which can modify the behavior of these states in solids. The situation is particularly interesting in the intermediate regime where either localized¹ or itinerant manifestations of the f states can be observed, depending upon the probe which is used and the temperature of the sample. This is one feature of the heavy-fermion systems in which the f states appear to have a rather normal localized behavior at high temperature, whereas their low-temperature properties can be analyzed as if they were originating from a dramatically narrow band corresponding to a mass renormalized by a factor which can exceed 100.²

Attempts to reveal by electron spectroscopies the aspects of the electronic structure responsible for these exotic properties have already been made,³⁻⁶ and they have shown the difficulty of this task. The aim of the present study is to investigate one extreme case at low temperature with the best possible resolution and to analyze the results within the Anderson single-impurity model. Among the heavy-fermion systems, the Ce compounds are more favorable than the U compounds for this type of study since a Ce atom can bind at most only one f electron. We have chosen to investigate CeCu₆ which crystallizes in a stable phase and shows quite unconventional properties,⁷⁻¹⁰ in particular, one of the largest low-temperature linear coefficients of specific heat ($\gamma \approx 1600$ mJ/molK²). The behavior of the f electrons can already be anticipated from the orthorhombic structure of this compound.¹¹ Each Ce atom is surrounded at an average distance of 3.146 Å by 19 Cu atoms forming a cage. The neighbor Ce atoms are separated by 4.83 Å (a spacing $\sim 32\%$ larger than in γ -Ce) and have no direct contact. The f states can be visualized as embedded in a Fermi sea with their wave-function tails overlapping only weakly with the diffuse sp -band states of Cu. In first approximation, the single impurity model appears to be well adapted to account for this situation so that we shall use the Gunnarsson-Schönhammer (GS) model¹² based on it to analyze the different spectra.

The polycrystalline CeCu₆ sample used in this study was prepared by melting the stoichiometric amounts of the constituents in a levitation furnace. The x-ray analysis

showed that within the detection limit the sample was formed of a single phase. The x-ray photoemission (XPS), UV photoemission (UPS), and bremsstrahlung isochromat (BIS) measurements were performed in the same instrument where the sample was cooled at about 15 K with a closed-cycle He refrigerator and its surface cleaned regularly by scraping *in situ* with an Al₂O₃ file.

In the analysis of our electron spectroscopy data of CeCu₆, it is the best agreement of the GS calculation with all types of spectra (XPS, UPS, BIS) which has dictated the choice of the following parameters entering the single-impurity Hamiltonian:^{12,13} $\epsilon_f = -1.2$ eV, $U_{ff} = 7$ eV, and $U_{fc} = 11.5$ eV. A second-order calculation has been performed for the core-level spectra, whereas for the high-resolution photoemission spectrum the calculation had to be limited to the first order. The consistency of these two calculations is obtained by requiring that they yield the same value of the initial f population n_f . Figure 1 shows the computed and measured XPS spectra of the $3d$ shell. The diagram at the bottom of the figure displays for the two spin-orbit-split components the energies of the relevant basis states in the presence of the core hole. In this representation the hybridization between f and band states is ignored ($\Delta \equiv 0$) so that no configuration mixing can take place.¹³ The full curve is the $3d$ spectral function predicted by the GS calculation and broadened by convolution with a Lorentzian of full width at half maximum (FWHM) ≈ 3 eV. When compared with the experimental spectrum (dots), it appears immediately that the spectral weight is essentially concentrated on the position of the uncoupled f^1 states. This is a consequence of the small value of the hybridization parameter Δ which produces between the rather close f^1 and f^2 configurations only a very weak mixing, barely discernible in the calculated curve. Invoking the sudden approximation, this observation provides a first qualitative indication of a nearly pure f^1 initial state. A closer inspection of the experimental peaks shows that their shapes are not Lorentzian and that they contain weak structures. In a recent study of the $3d$ core levels of different heavy-fermion systems including CeCu₆ (Ref. 6), this feature can also be observed, and it is even more pronounced in CeCu₂Si₂ and CeAl₃. These structures are most likely to be attributed to the excitation of

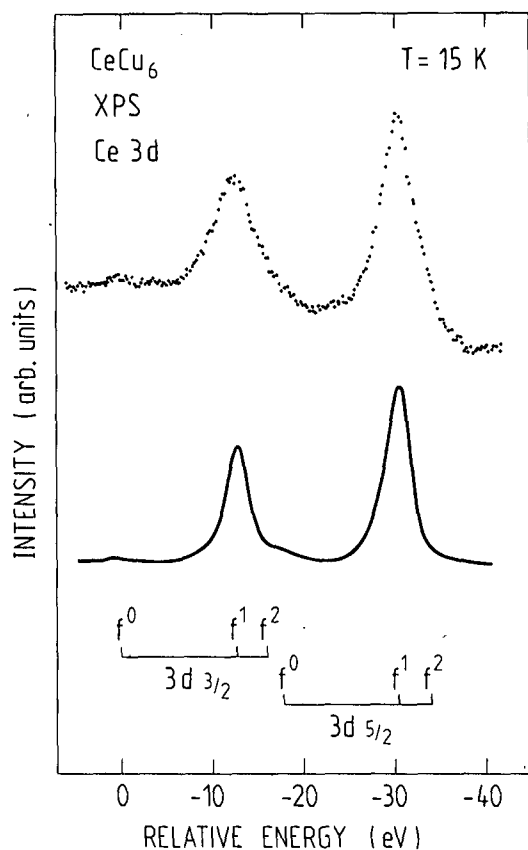


FIG. 1. Photoemission spectrum of the Ce 3d level in CeCu₆. Bar diagram: positions assumed for the uncoupled ($\Delta=0$) final states. Solid curves: spectral function calculated with the GS model. Dotted curves: XPS spectrum.

the $3d^9 4f^1$ multiplets which are known.^{14,15} The strength of these structures varies strongly in the different compounds and one has to be aware that in such cases the shoulder on the low-energy side of each line cannot be assigned to a f^1 - f^2 mixed state. This would require such unrealistically large values of Δ that the model could not simulate correctly the other structures observed in the different types of spectra. The energy separation of the f^0 and the f^1 uncoupled states is sufficiently large to prevent the f^0 final state from any sizable mixing. For this reason its intensity accounts directly for the weight $1 - n_f$ of this configuration in the ground state. In contrast to the 3d spectrum of CeCu₆ published previously,⁶ the presence of this final state is unambiguously observed in our spectrum and it could be simulated by the model calculation which yields $(1 - n_f) \approx 0.005$ according to the values of the parameters given previously.

Figure 2 shows the XPS and BIS spectra of the outer levels of CeCu₆. A close similarity between the photoemission spectra of CeCu₆ and Cu metal¹⁶ is observed. This is in fact not surprising since the Cu neighbors have approximately the same separation as in pure Cu metal. The Cu 3d band is only shifted by a few tenths of an eV toward higher energies in CeCu₆, and between E_F and 2 eV the valence-band intensity is enhanced by the presence of the Ce states. As explained below, the 4f peak expected at E_F is too weak to be observed with the resolution of 0.3 eV

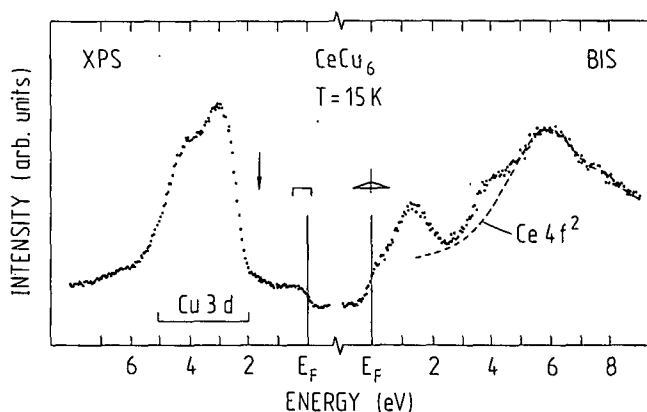


FIG. 2. XPS and BIS spectra of the outer states of CeCu₆ (see text).

achieved in XPS. The calculated position of the low-energy maximum in the 4f excitation spectrum¹² is indicated by an arrow. It is only revealed in the experimental spectrum by a weak hump, as a consequence of the high dilution of the Ce atoms in this compound.

In the BIS spectrum, the presence of the f shell is clearly observed as a leading peak centered at 6 eV and showing the typical feature resulting from the f^2 -multiplet intensities predicted by the fractional parentage coefficients and broadened by short lifetimes (dashed line).¹⁷ When compared to Ce metal, these multiplets are shifted 2 eV away from E_F . This increase of the final-state energy reflects the fact that the valence electrons at E_F originate mainly from Cu atoms so that they are not very efficient in the screening of the additional localized charge on an isolated Ce atom. This trend can be observed when the concentration of La and Ce atoms is decreased in alloys of these elements with transition metals.¹⁸ The strong peak with a maximum at 1.3 eV above E_F is likely to be mainly ascribed to the empty 5d states of Ce (Ref. 19). Furthermore, in this energy range, the BIS spectrum of pure Cu (Ref. 20) shows pronounced oscillations which certainly contribute to the first peak and to the shoulder in the flank of the f^2 intensity. The GS model predicts in BIS a f^1 -to- f^2 intensity ratio of about $(1 - n_f)$, so that from a rough estimate of the f^2 signal, the expected f^1 signal has been sketched as a Lorentzian at E_F above the spectrum. With the BIS instrumental resolution of ~ 0.6 eV it is evident that this $4f^1$ intensity cannot be discerned in the experimental spectrum.

The small energy range above E_F indicated in Fig. 2 has been investigated at high resolution (20 meV) with UPS. The experimental spectrum shown in Fig. 3(a) does not reveal any intensity enhancement in the 100-meV range above E_F . Even when it is recorded with an extreme resolution of 12 meV, the Fermi edge displayed in the inset of Fig. 3 appears to have a quite conventional shape. At first sight this observation is very surprising since the unconventional properties of CeCu₆ at low temperature are attributed to a very high density of low-energy quasiparticle excitations. The fact that these excitations are not apparent in photoemission spectra measured at finite resolution and temperature can be simply explained in terms of

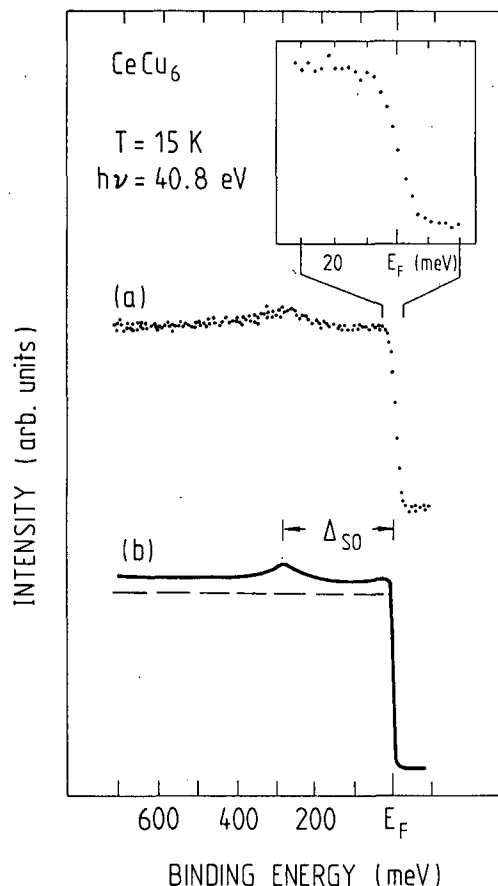


FIG. 3. UPS spectrum of CeCu_6 in the small energy range above E_F indicated in Fig. 2. (a) Experimental spectrum measured with a resolution of 20 meV. (b) Simulation of the spectrum by the GS calculation (see text). Inset: Fermi edge measured with a resolution of 12 meV.

the many-body states used to describe the ground and excited eigenstates derived from the single-impurity Hamiltonian. The photoemission spectral function for the f symmetry calculated within the sudden approximation accounts for two distinct types of many-body final states. The first type (split-off states) corresponds to the minimum total energy with one hole at the energy ϵ , and it forms a narrow distribution $\rho_f^s(\epsilon)$, which is maximum at E_F and falls abruptly within an energy range δ defining the relevant energy scale for the metalliclike f excitations of the system. The final states of the other type are distributed at energies larger than δ so that they do not overlap with $\rho_f^s(\epsilon)$ within the narrow range δ above E_F . In the limit $\epsilon_f \gg \Delta$, the f -level occupation is very close to 1, $T_K = \delta/k_B$ is the Kondo temperature and $\rho_f^s(\epsilon)$ the Kondo peak.¹² One can show that $\rho_f^s(\epsilon)$ reflects exactly the weight distribution of the f character which is mixed to the band states in the singlet initial ground state. This type of excitation has been recently observed and analyzed in γ - and α -Ce (Ref. 21). In photoemission, the maximum of the Kondo peak at E_F is proportional to $1/\Delta$ so that it diverges when $\Delta \rightarrow 0$ ($\delta \rightarrow 0$) but its integrated weight $n_f(1 - n_f)$ vanishes. For heavy-fermion systems the single impurity model yields a first approach to the very high

density of low-energy many-body excitations, it shows how these are related to the structure of the many-body ground state, and it predicts their intensity in high-energy spectra. These facts cannot be simply translated into the single-particle language, but one can intuitively identify $\rho_f^s(\epsilon)$ with the adiabatic bandlike part of a f -emission spectrum²¹ or, more abstractly, it can be considered as a Fermi-liquid manifestation.²²

The values of the parameters given previously and resulting from the best simulation of the spectra of CeCu_6 yield the limits $n_f(1 - n_f) \lesssim 0.005$ and $\delta \lesssim 1$ meV. This is very close to the complete $4f^1$ localization limit and the dramatically weak weight $n_f(1 - n_f)$ of the Kondo signal is not surprising since for $\Delta = 0$ ($n_f = 1$) it vanishes and the whole spectral weight is concentrated on a $4f^0$ final state located at ϵ_f above E_F . For a finite Δ , this $4f^0$ peak is replaced by a continuum starting from the energy δ above E_F and showing a maximum at an energy moving from ϵ_f toward higher energies when Δ increases. In contrast to the Kondo peak, these states account for a more atomiclike response of the system to a sudden electron emission and they do not reflect a pre-existing structure of the many-body ground state.¹²

In the GS simulation of the experimental spectrum shown in Fig. 3(b), the f contribution has been superposed on a constant intensity (dashed line) assumed to originate from the band states. Within the first 100 meV above E_F , the calculation confirms that the Kondo peak is too weak to be observed under the present experimental conditions. The structure predicted and observed at the spin-orbit splitting energy ($\Delta_{SO} = 280$ meV) above E_F is also due to the f screening mechanism responsible for the Kondo peak. The only difference in this case is that it is not the $\frac{5}{2}$ but the $\frac{7}{2}$ j component which is involved. For this reason it does not reflect an aspect of the initial state which has a nearly pure $j = \frac{5}{2}$ character since $k_B T$ and δ are much smaller than Δ_{SO} . For a weak hybridization, the fact that this type of final state has more intensity than the Kondo peak might be simply due to its position closer to the center of gravity ($\sim \epsilon_f$) of the total f -excitation spectrum.

The present approach to this problem within the GS model has two drawbacks. The first one is that it cannot account in a lattice for the coherence effects which induce a splitting of the Kondo peak. This point will become important for photoemission only if a resolution better than δ can be achieved. More serious is the fact that the present GS calculation implies $T = 0$ and remains approximately valid only for $T \lesssim T_K$. This condition appears to be not quite satisfied in our measurement. When T becomes larger than T_K , one can anticipate that the hybridization mechanism, which at $T = 0$ gives rise to the energy lowering δ of the singlet ground state, will be modified at $T > 0$ by thermal mixing with nonsinglet states. The predicted consequences are a broadening²³ and/or a weakening²⁴ of the Kondo peak in photoemission spectra. One cannot exclude that in our CeCu_6 spectrum measured at 15 K with a resolution of 12 meV (inset, Fig. 3) the Kondo peak is already washed out.

This study shows that within the oversimplified framework of the single impurity model, the manifestations of the very heavy electrons in photoemission are correctly

predicted. In the extreme situation encountered in CeCu_6 , the weight of the Kondo peak is too weak to be directly detected with the resolution and the low temperature which could be reached until now, but there are no fundamental obstacles to the improvement of these conditions. In the light of the conclusion of the present work, the re-

cent spectroscopic studies devoted to the heavy-fermion problem^{3-5,25} have to be reconsidered critically.

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Spectroscopic evidence for an unrealized heavy-electron state in CeAl_2

F. Patthey, W.-D. Schneider, and Y. Baer

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

B. Delley

Laboratories RCA Limited, CH-8048 Zürich, Switzerland

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The compound CeAl_2 has been studied at low temperature (15 K) by high-resolution (< 20 meV) photoemission using He I and He II excitation sources. The spectra analysis within the Anderson single-impurity model for $T=0$ reveals that the extrapolated low-energy parameter $\delta=0.2$ meV is consistent with the analysis of the specific heat performed within the same formalism. The extreme narrowness of the density of low-lying excitations predicted for $T=0$ indicates that CeAl_2 would be a heavy-electron metal if the magnetic ordering below 4 K did not prevent the formation of a coherent Kondo lattice.

The great popularity of photoemission must be attributed to the fact that it is commonly considered one of the most direct methods to probe the density of the electronic states (DOS) in solids. However, when the correlation of the outer states becomes so pronounced that manifestations of their atomic character are observed, the relationship between measured spectra and DOS is no longer straightforward.¹ In the extreme case of $4f$ states, the simple single-particle picture becomes almost meaningless and fails to account for many properties involving their excitations. In particular, at low temperatures the quasi-equilibrium methods (specific heat, susceptibility, transport properties) applied to the study of systems containing Ce reveal very unusual manifestations. Clearly this situation results from a very high density of many-body excitations just above the ground state, which behave in many respects like heavy electrons.

The single-impurity model has proved to yield a first approach to important aspects of this problem.² It has been used to calculate the spectral functions of high-energy spectroscopies and the comparison with experiments has demonstrated that it contains the essential mechanisms allowing one to account for the observed final-state excitations. However, the experimental resolution commonly achieved is about two orders of magnitude larger than the low-energy excitations responsible for the unusual properties of heavy-fermion systems. We have shown³⁻⁵ that already with a resolution improvement of a factor 10, the information extracted from photoemission spectra can be linked to results obtained by low-energy methods. The aim of this Rapid Communication is to demonstrate that this approach reveals original aspects of the more complicated situation encountered in CeAl_2 . When the temperature is decreased in this system, the lowest total energy corresponds to a magnetically ordered state^{6,7} which prevents the completion of spin compensation.

The polycrystalline CeAl_2 sample was prepared by melting stoichiometric amounts of the constituents in a levitation furnace. An x-ray diffraction analysis confirmed the MgCu_2 crystal structure of the sample. The photoemission measurements were performed in a spectrometer

equipped with a commercial gas-discharge lamp producing very narrow photon lines of 21.2 eV (He I) and 40.8 eV (He II).³ The sample was cooled at about 15 K with a closed-cycle He refrigerator. Clean surfaces were obtained by frequently scraping *in situ* with an Al_2O_3 file and spectra were taken with a total resolution of 18 meV.

Figures 1(a) and 1(b) show, between 4 eV and $E_F=0$

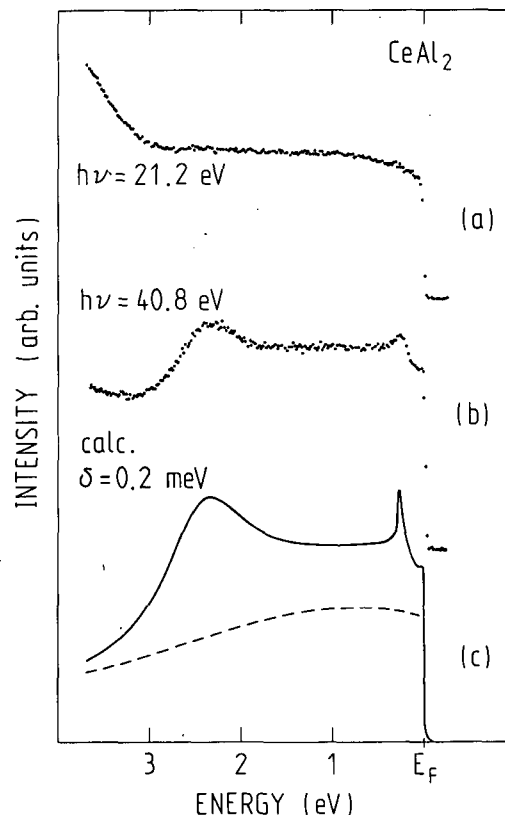


FIG. 1. (a) and (b) Photoemission spectra of CeAl_2 measured with a resolution of 25 meV. (c) Simulation of the spectrum (b) by a many-body calculation including spin-orbit and crystal-field splitting (see text).

eV, the photoemission spectra of CeAl_2 excited with the two photon energies. When the photon energy is raised from 21.2 to 40.8 eV, the $4f$ to spd cross-section ratio increases by a factor of the order of 10 and two structures around 2.5 and 0.3 eV emerge from the rather featureless conduction band obtained at $h\nu=21.2$ eV. The intensity increase above 3 eV must be attributed to the accumulation of secondary electrons. By comparison with the spectra of α - and γ -Ce (Ref. 3) these two structures are readily identified with final states of predominantly $4f^0$ and $4f^1_{7/2}$ character, respectively. The present spectra are consistent with previous photoemission results^{8,9} taken with a resolution which is roughly a factor of 10 poorer. Figures 2(a) and 2(b) display an enlarged view of the excitations extending from E_F to 0.6 eV. The 40.8-eV spectrum reveals clearly around 0.3 eV the emission accounting for the $4f_{7/2}$ final-state screening and, when compared to Fig. 2(a), it shows also a weak enhancement of the intensity near the Fermi energy. A more detailed interpretation of these spectra, however, is only possible on the basis of a model calculation.

Down to temperatures of about 10 K, resistivity data¹⁰ and specific-heat results¹¹ of CeAl_2 are well accounted for by a single-impurity model including the crystalline-field splitting of the $4f$ states.¹² At 4 K a transition occurs to an antiferromagnetically ordered state^{6,7} with a magnetic

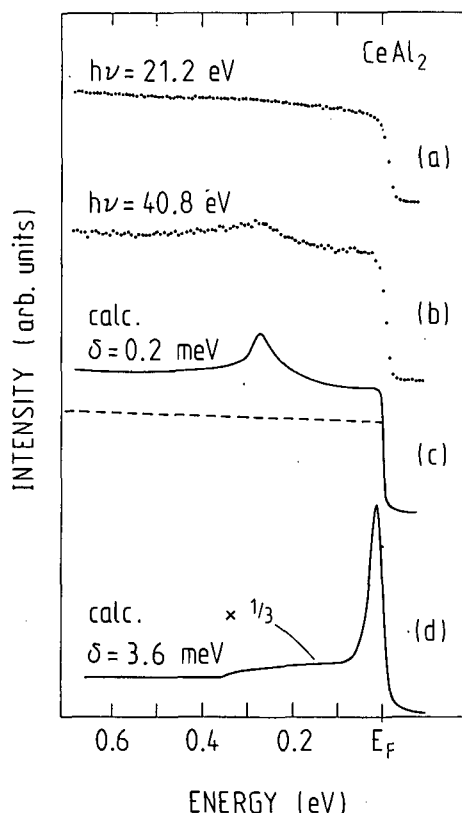


FIG. 2. (a) and (b) Photoemission spectra of CeAl_2 in a restricted energy range above E_F , measured with a resolution of 18 meV. (c) Simulation of the spectrum (b) by a many-body calculation. (d) Many-body calculation corresponding to the measured γ value interpreted with the single-impurity model.

moment per site reduced by about 10% when compared to the value expected for the Γ_7 doublet.¹¹ This observation demonstrates that at this temperature the spin compensation due to the Kondo effect ($T_K \approx 5$ K) has just started. In the magnetic phase a further spin compensation is assumed to be quenched by the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. Our photoemission measurements have been performed at 15 K so that only the lowest Γ_7 crystal-field level is populated [$E(\Gamma_8) - E(\Gamma_7) \approx 10$ meV (Ref. 6)] and the magnetic interaction is not yet acting. In order to remain within the framework of the previous studies devoted to CeAl_2 and also because it is the only one which is tractable at the present time, in a first step we shall simply use the single-impurity model at $T=0$ to analyze our photoemission data. The validity and limitations of this approach will be discussed at the end of the paper. Early attempts^{8,9} have already been made to interpret the high-energy (≈ 2 eV) $4f$ peak observed in CeAl_2 in terms of hybridization strength Δ , and to compute the Kondo temperature from the parameters obtained in photoemission. At this time the difficulty was that no formulation of the photoemission spectral function was available within the single-impurity model.

The present calculation, performed within the Gunnarsson-Schönhammer (GS) formalism,² takes into account a crystal-field splitting of 10 meV between the quartet Γ_8 and the doublet Γ_7 of the $j = \frac{5}{2}$ component but ignores the splitting of the $j = \frac{7}{2}$ component 280 meV above the Γ_7 level. The conduction band is assumed to be of Lorentzian shape with 3-eV full width at half maximum (FWHM) and centered at 0.8 eV below E_F . This simple band mimics very roughly the calculated DOS of LaAl_2 (Ref. 13) and is consistent with the shape of the HeI spectrum near E_F . The spectra shown in Figs. 1(c) and 2(c) are calculated with the parameters $\epsilon_f = -1.8$ eV, $\Delta = 80$ meV, $\Delta_{s.o.} = 280$ meV, $E(\Gamma_8) - E(\Gamma_7) = 10$ meV, and a Lorentzian broadening of 20 meV, accounting for the instrumental resolution. Best agreement with experiment is obtained with a cross-section-weighted sum of the conduction band (dashed curve) and of the f contribution (solid curve). Apart from the shape of the $4f_{7/2}$ structure, which may be affected by lifetime broadening not included in the calculation, the agreement between the model and the experiment is quite convincing. With the single-impurity parameters deduced from this comparison, we obtain $n_f = 0.999$ for the f occupation in the ground state and $\delta = 0.2$ meV for the energy lowering resulting from the hybridization. Furthermore, the calculation confirms that most of the f character in the ground state derives from the Γ_7 doublet (0.998), whereas in the excitation spectra the intensities originating from Γ_8 and Γ_7 are of the same order of magnitude, but so far have not been resolved experimentally. From this type of analysis one can conclude that Ce in CeAl_2 would form a Kondo lattice ($|\epsilon_f| \gg \Delta$, $\delta \ll \Delta$) at $T < T_K$ if no magnetic transition would take place. It is a simple matter to estimate what would be the linear coefficient of the specific heat $\gamma(T \rightarrow 0)$ from our determination of $T_K = \delta/k_B \approx 2.3$ K. For the degeneracy $N_f = 2$ of the Γ_7 ground state, the exact scaling relation between the strong-coupling scale T_0 and the Kondo scale T_K is given by $T_0 = T_K/1.29$.¹⁴ One can then express

$C(T \rightarrow 0)/T$ as¹⁵

$$\gamma(T \rightarrow 0) = N_A \pi k_B^2 / 4.65 \delta \quad (1)$$

(N_A is Avogadro's constant), which yields, for our value of δ , $\gamma(T \rightarrow 0) \approx 2400$ mJ/K²mol. It is interesting to notice that this result is in fair agreement with the analysis of the specific heat above the magnetic transition¹¹ based on a very simple Kondo model.¹⁶ This enormous extrapolated value of $\gamma(T \rightarrow 0)$ indicates that CeAl₂ would become at low temperature an extreme heavy-fermion metal, like CeAl₃ (Ref. 17) and CeCu₆ (Refs. 18 and 19), if the magnetic order did not interrupt the formation of a coherent Kondo lattice. As a matter of fact, the outer-level excitations observed in CeCu₆ (Ref. 4) are nearly identical to those in CeAl₂. Unfortunately, in the latter case a broad plasmon hinders the detection of the extremely weak f^0 component of the $3d$ core-level spectra which provides an independent determination of δ in CeCu₆. In the magnetic phase below 4 K the measured γ value of CeAl₂ is 135 mJ/K²mol,¹¹ roughly a factor of 20 smaller than the value obtained from Eq. (1) with the single-impurity parameters extracted from our spectroscopic data at 15 K. If the observed γ is tentatively interpreted as resulting from a pure Kondo screening acting incoherently on each Ce site, a Kondo temperature $T_K = 42$ K ($\delta = 3.6$ meV) is obtained [Eq. (1)]. In order to demonstrate that this assumption is not compatible with our high-resolution photoemission spectra, we have calculated a spectral function with Δ increased by roughly a factor of 2 to obtain $\delta = 3.6$ meV, while the other parameters have not been modified. The resulting spectrum shown in Fig. 2(d) is reminiscent of CeN (Ref. 5) but is in total disagreement with the present experiment. This situation is consistent with the observation¹¹ that the average moment in the Γ_7 state has a 10% reduction in the magnetic phase which can be expected to prevent the development of a more complete spin compensation when $T \rightarrow 0$. A simple model based on the persistence of the Kondo effect in the magnetic phase has been proposed to explain the specific heat at low temperature.¹¹ An alternative explanation has also been given recently in terms of magnetic excitations.²⁰ This low-temperature range will be soon accessible to photoemission experiments which might bring a valuable contribution to the elucidation of this problem.

This analysis of the low-lying excitations observed with photoemission in CeAl₂ and other Ce systems³⁻⁵ yields an indisputable demonstration that the single-impurity model at $T = 0$ K contains the relevant mechanism allowing us to simulate in detail the spectra. Furthermore, the low-energy parameter δ extracted from the fits is consistent with the analysis of the specific heat performed within the same formalism. The success of this model is gratifying,

but the foundation of this agreement is not rigorously established and raises many interesting questions which will be briefly discussed.

(i) The single-impurity model ignores the coherence effects expected to induce a gap near E_F .²¹ If the hybridization energy of each f site with the band is much larger than the energy lowering resulting from the coherence, one can assume that the value n_f derived from the single-impurity model predicts correctly the weight of the $4f$ states hybridized to the band states at E_F . This condition should be sufficient to ensure that the spectral functions account correctly for spectra measured with a resolution larger than the gap width.

(ii) Spectra measured at $T > T_K$ are analyzed with the single-impurity model at $T = 0$. The validity of this approximation is confirmed by a calculation based on the single-impurity model at finite temperature.²² It shows that up to temperatures not too far above T_K the weight of the $4f$ signal pinned at E_F remains approximately constant. The same conclusion can be drawn from a calculation of $n_f(T)$ with the Bethe ansatz,²³ indicating that for $T < \Delta/k_B$ (≈ 800 K for CeAl₂) and $N_f = 2$, the f population remains rather temperature independent in the Kondo limit.

(iii) Our model calculation is performed to the lowest order in $1/N_f$, despite the fact that the degeneracy of the Γ_7 ground state is only $N_f = 2$. This approximation certainly does not yield a well-converged ground state; however, one can invoke again the exact calculation with the Bethe ansatz²³ which yields for $S = \frac{1}{2}$ a singlet in agreement with the present approach. A very good fit to the data of the model calculation is also obtained for $N_f = 6$ when crystal-field splitting is not taken into account. It increases the value of δ only by a factor of 3 so that this difficulty affects merely the accuracy of the parameters deduced from this analysis.

(iv) Our local model requires the formation of a singlet ground state on each Ce site so that within an energy range of the order of δ extending from E_F , one band electron per Ce ion must be available for the spin compensation. This is obviously impossible in a lattice and the Kondo effect remains incomplete.²⁴ Other approaches may not be confronted with this difficulty,²⁵ but it remains that the density of the band states near E_F is a key parameter for the ground state reached when $T \rightarrow 0$. For example, it is most likely that the increase of this density is responsible for the transformation of the magnetic ground state in CeAl₂ into a Kondo-like ground state in CeAl₃.

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High-Temperature Collapse of the Kondo Resonance in CeSi₂ Observed by Photoemission

F. Patthey, W.-D. Schneider, and Y. Baer

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

and

B. Delley

RCA Laboratories, Ltd., CH-8048 Zürich, Switzerland

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uv-photoemission spectra of CeSi₂ have been measured with a resolution of 18 meV in the temperature range $15 \text{ K} < T \leq 300 \text{ K}$. The spectral analysis has been performed within the Anderson single-impurity model using the noncrossing approximation and including $4f$ -spin-orbit and crystal-field splittings. It accounts perfectly for the observed flattening of the fine structures in the spectra when the temperature increases. This study confirms indisputably the many-body nature of the low-lying excitations around E_F observed with photoemission.

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The low-energy electronic excitations within $k_B T$ play an essential role in the transport properties, the magnetic susceptibility, and the electronic specific heat of condensed matter. For normal metals the correlation between the conduction electrons does not lead to dramatic deviations from the nearly free-electron model down to the lowest temperatures. In highly correlated electronic systems, however, an important enhancement of the low-temperature specific heat is observed which can be formally accounted for by renormalizing the electron mass in the free-electron-model formulas. Recently, a new class of metals containing elements at the beginning of the $4f$ and $5f$ series has been discovered which exhibit a variety of extremely anomalous low-temperature properties.¹ For example, the linear coefficient of the specific heat γ ($T \rightarrow 0$) reaches magnitudes of the order of 1 J/mole K^2 , which would correspond to an effective electron-mass enhancement of a factor of 1000 in the free-electron model. Hence, the term heavy-electron metal^{2,3} has been coined to characterize these systems. A possibility to visualize an extremely high specific heat in a single-particle approach is to consider that it can be attributed to the fraction of the thermally excited electrons in a band of width $k_B T_0$, $C(T) \sim nk_B(T/T_0)$.⁴ In heavy-electron systems this approach yields bandwidths of the order of 1 meV, which is typically 10^{-3} of the Fermi energy in usual metals. A simple single-particle origin of such a high and narrow density of low-energy excitations appears, however, not to be tenable. The essential arguments against this description are (i) that the ground state would clearly favor ferromagnetism and (ii) that the number of electrons forming such peaks is not sufficient to account for the large entropy observed at $T > T_0$.⁴

It is now generally accepted that the weak hybridization between the extended electron states and the highly correlated f -electron states is the key mechanism that

gives rise to the many-body nature of the heavy-electron manifestations.⁵ For dilute Ce systems, the Anderson single-impurity model, containing this hybridization as an essential ingredient, predicts^{6,7} that with decreasing temperature a resonant structure ("Kondo resonance") develops within an energy $k_B T_0 = \delta$ above E_F , which sets a new energy scale to all low-temperature properties. The impurity model is obviously not adapted to account for any coherence effect between the different f sites in a lattice.⁴ However, it has appeared to be very successful in the interpretation of high-energy spectroscopic data,⁵ and recently, the low-lying excitations within δ have been directly observed with high-resolution (20 meV) photoemission in Ce metal⁸ and CeN.⁹ The aim of the present Letter is to investigate the temperature-dependent development of the Kondo resonance in order to obtain a conclusive test of the many-body concepts invoked to explain the unconventional temperature dependence of the properties of heavy-electron systems.

As a suitable candidate for this investigation, the compound CeSi₂ was chosen. It crystallizes in the tetragonal α -ThSi₂ structure, where each Ce atom is bonded to twelve silicon atoms at an interatomic distance of 3.13 Å.¹⁰ The magnetic susceptibility shows a breakdown of the Curie-Weiss law at low temperatures without any indication of ordering.^{11,12} Heat-capacity measurements exclude magnetic ordering or crystal-field transitions below 70 K down to 0.1 K and yield a linear coefficient of the specific heat $\gamma(T \rightarrow 0) \approx 100 \text{ mJ/K}^2 \text{ mole}$.^{11,12} These facts point to $4f$ -spin compensation by the conduction electrons at low temperature and consequently CeSi₂ has been considered as a dense Kondo system.¹³ $\gamma(T \rightarrow 0)$ is already strongly enhanced when compared to normal metals, but is still 1 order of magnitude smaller than in extreme heavy-electron compounds^{14,15} such as CeCu₆ in which the photoemission Kondo peak of weight $n_f(1 - n_f)$ (n_f is the f population per Cu atom)

and width δ is too weak to be detected with the best resolution achieved presently.¹⁶ From the relationship¹⁷ $\gamma \sim 1/\delta$ it appears immediately that CeSi₂ can be expected to offer a favorable situation for studying the behavior of the Kondo peak.

The polycrystalline sample of CeSi₂ was prepared by melting stoichiometric amounts of Ce and Si in a levitation furnace. Homogenization was achieved by repeated melting and subsequent tempering at 1100 K for 2 days. Analysis of the Debye-Scherrer patterns showed that only a single phase with the α -ThSi₂ structure was present.¹⁸ The photoemission measurements were performed in a spectrometer equipped with a commercial gas-discharge lamp producing the very narrow photon lines of 21.2 eV (HeI) and 40.8 eV (HeII).⁸ The sample was cooled at about 15 K with a closed-cycle He refrigerator. Elevated temperatures up to 300 K were obtained by the heating of the cold finger during refrigeration. During the measurements the vacuum was 3×10^{-10} Torr and the oxygen and carbon contamination of the surface was maintained below the detection limit by frequently scraping *in situ* with an Al₂O₃ file. The spectra were taken with a total resolution of 40 meV [Fig. 1(a)] and 18 meV [Figs. 1(c)–1(f)].

Figure 1(a) shows, between 4 eV and $E_F = 0$ eV, the

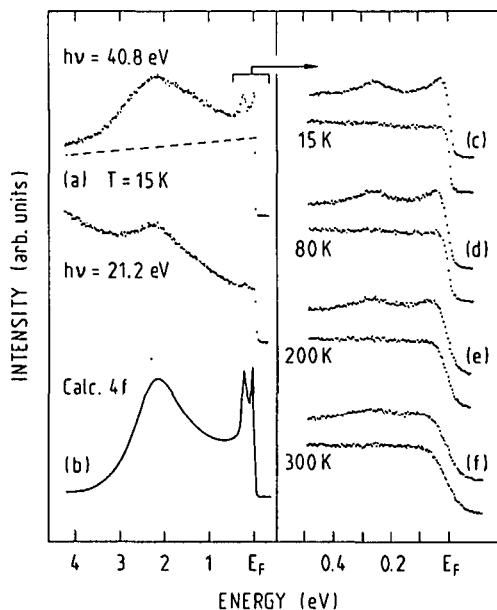


FIG. 1. (a) Photoemission spectra of CeSi₂ measured at $T = 15$ K with a resolution of 40 meV. The dashed line indicates the emission intensity from non- f -symmetry states. (b) Simulation of the f contribution by a many-body calculation for finite temperature including $4f$ spin-orbit and crystal-field splittings. The curve has been convoluted with a Gaussian of 40 meV FWHM in order to account for the instrumental resolution. (c)–(f) Photoemission spectra of CeSi₂ (upper curves, HeII excitation; lower curves, HeI excitation) in a narrow energy range above E_F measured with a resolution of 18 meV at the indicated sample temperatures.

photoemission spectra of CeSi₂ excited with the two photon energies at the lowest sample temperature (15 K) which could be obtained. For $h\nu = 21.2$ eV the spectrum contains essentially a broad structure around 2 eV which, by comparison with x-ray photoemission spectra,¹⁹ must be partly attributed to emission from Si states of $3p$ character. When the photon energy is raised to 40.8 eV, the $4f/3p$ cross section increases by a factor²⁰ of 6 and, in addition to the strengthening of the broad 2-eV peak, two sharp structures emerge near the Fermi energy, which can only be barely discerned at 21.2 eV. This cross-section dependence clearly reveals the f character of the three emission features. The emission intensity from states of other symmetries is estimated to be roughly given by the dashed line in Fig. 1(a). Our spectra are consistent with previous resonant photoemission data²¹ which were recorded at room temperature with a resolution roughly a factor of 10 poorer and consequently could not resolve the interesting peaks close to E_F . By comparison of the present results with those of Ce metal,⁸ the structures around 2 and 0.3 eV are identified with final states of mainly $4f^0$ and $4f^{1/2}$ character, respectively. The peak at E_F originates from the low-lying excitations closely related to the ground state.

Many properties of heavy-electron systems show two quite distinct regimes at temperatures far above and below T_0 . This may be the most characteristic symptom pointing to the many-body nature of the anomalous low-temperature properties of this class of solids. It is a fundamental experimental challenge to investigate the evolution of the low-energy excitations concomitant to the transition between these two regimes. For increasing sample temperatures, Figs. 1(c)–1(f) display, in an enlarged view of the region extending from E_F to 400 meV, the $4f^1$ spin-orbit-split final states excited with HeII (upper curves) and HeI (lower curves) radiation. The step between the data points is 5 meV and all spectra have been accumulated (3 h for HeI excitation and 30 h for HeII excitation) until 6×10^3 counts are obtained at 400 meV. At 15 K it is the instrumental resolution which sets the limit of the peak height at E_F . The break in the slope of the Fermi edge near the top of the peak [Fig. 1(c)] which appears to be shifted by about 35 meV towards higher energies is most likely caused by crystal-field splitting (see below). Unfortunately, the amplitude of this splitting in CeSi₂ has never been determined to the best of our knowledge. As the temperature increases, this first peak above E_F is progressively washed out and has completely disappeared at 300 K where the thermal broadening of the Fermi edge is about 100 meV ($\sim 4k_B T$). The $4f^{1/2}$ final states around 280 meV form a rather symmetric peak at 15 K, which is also attenuated with increasing temperature but remains clearly visible.

In order to obtain a quantitative description of the temperature dependence of the excitation spectra, we have calculated the spectral functions for the Ander-

son Hamiltonian using the "slave boson" approach in the noncrossing approximation.^{6,22} To reduce numerical problems in the low-temperature regime, the Boltzmann-weighted spectral functions were computed self-consistently according to Müller-Hartmann.²³ Since these functions have no simple analytic continuation, we do the self-consistent calculations on the real axis with an energy resolution of 1×10^{-4} eV which is just sufficient at the lowest temperatures considered here. It should be noticed that the crystal-field (CF) splitting of the $j = \frac{5}{2}$ state has important consequences as already discussed for CeAl₂.²⁴ In the present case, for a tetragonal symmetry three doublets²⁵ are formed, thereby the ground-state degeneracy N_f is lowered from 6 to 2. Since the existence of a CF splitting of $\Delta_{CF} = 35$ meV between the ground state and the first excited doublet is compatible with the present data we have included such a CF splitting in our spectra calculation. For the interpretation of the present data it is sufficient to assume simply the degeneracy of the two excited $4f_{5/2}^1$ CF levels at 35 meV and of all $4f_{7/2}^1$ CF levels at $\Delta_{s.o.} = 280$ meV so that the degeneracies of the ground state and the excited states are $N_f = 2, 4,$ and $8,$ respectively. The band is assumed to be centered at 0.5 eV above E_F and to have a Gaussian shape of FWHM = 3 eV. The spectrum shown in Fig. 1(b) represents the f contribution to the excitation spectrum calculated with the parameters $T = 15$ K, $\epsilon_f = -1.6$ eV, $\Delta = 95$ meV, $\Delta_{s.o.} = 280$ meV, $\Delta_{CF} = 35$ meV, and a Gaussian broadening of 40 meV accounting for the instrumental resolution. With the single-impurity parameters deduced from this comparison we obtain $n_f = 0.97$ for the f occupation in the ground state and $\delta = 3$ meV for the energy lowering resulting from a single-site hybridization, so that the corresponding Kondo temperature is $\delta/k_B = 35$ K.

Figures 2(a)–2(d) show the f contribution to the experimental spectra, obtained from the difference of the HeII and HeI excitation spectra [Figs. 1(c)–1(f)] weighted by the same cross-section ratio for all temperatures. These experimentally derived f spectra are compared in Fig. 2 with the computed f -spectral functions [Figs. 2(e)–2(h)] for the corresponding sample temperatures with use of the same single-impurity parameters as above. The curves have been convoluted with Gaussians of 18 meV accounting for the instrumental resolution. Since the peak around 2 eV [Figs. 1(a) and 1(b)] shows practically no temperature dependence, only the spectral region of the $4f$ spin-orbit-split final states above E_F is shown. Apart from the width of the experimental structures which is partly determined by lifetime broadening not included in the calculation, the agreement between experiment and model for the whole spectral range and for all temperatures is striking. It proves that this many-body calculation yields a correct description of the temperature dependence of our experimental spectra. The formation of the singlet ground state giving rise to

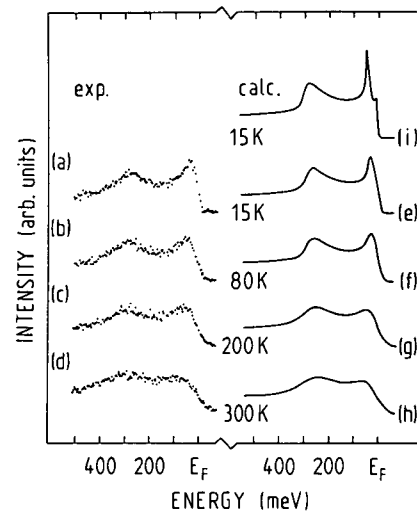


FIG. 2. Comparison between experimentally derived and computed f spectra of CeSi₂. The curves (a)–(d) represent differences of the weighted spectra shown in Figs. 1(c)–1(f). The curves (e)–(h) are the result of a many-body calculation for the corresponding temperatures including $4f^1$ spin-orbit and $4f_{5/2}^1$ crystal-field splittings. A convolution with Gaussians of 18 meV FWHM has been performed in order to account for the finite instrumental resolution. The uppermost curve (i) represents the calculated f spectrum for $T = 15$ K without instrumental broadening.

the Kondo resonance close to E_F requires a sharp cutoff in the occupation of the extended states and therefore can only develop at sufficiently low temperatures ($T \lesssim T_0$). When $k_B T$ increases and exceeds $k_B T_0$, non-singlet states of higher energy become more and more populated so that the Fermi-liquid behavior transforms gradually into an atomiclike behavior. The spectra of Figs. 2(a)–2(d) yield the first unmistakable observation with photoemission of this progressive transition appearing as a collapse of the extremely narrow and intense distribution of the low-energy many-body excitations when the temperature is raised above T_0 .

In general, for relatively small crystal fields such that the energy separation Δ_{CF} between ground state and the first excited doublet is of the order δ (CF = 0) (obtained without CF), the Kondo peak remains the prominent feature of the photoemission spectrum near E_F .²⁴ For $\Delta_{CF} > \delta$ (CF \neq 0), however, the Kondo temperature is reduced²⁶ and by a weight transfer from the Kondo peak the CF levels would become apparent in sufficiently well-resolved spectra. The present data of CeSi₂, recorded with a resolution of 18 meV, seem to be not too far from this situation, as indicated by the uppermost curve (i) in Fig. 2 representing the calculated spectrum for $T = 15$ K without instrumental broadening. It remains that an important fraction of the intensity observed in the peak pinned at E_F must be attributed to the many-body resonance formed of split-off states.²⁴ Their distribution reflects the weight of the f character in the hy-

bridized basis states used in the simplest formulation of the singlet ground state at $T=0$ K.²⁷ In fact the many-body character of the peak at E_F is also clearly demonstrated by its spectral weight at low temperature. If it would correspond to the excitation of single-particle states for which the Koopmans' approximation is valid, the integrated intensity of this peak alone should account for $n_f \approx 1$ instead of $n_f(1-n_f) = 0.03$,²⁸ i.e., a factor of 30 larger than observed experimentally.

The flattening of the $f_{5/2}$ and $f_{7/2}$ structures when the temperature increases may seem to be in contradiction with the observation of a rather important peak located within 1 eV above E_F in the x-ray photoemission spectrum of a CeSi₂ sample at 300 K.¹⁹ The explanation of this situation must be looked for in the facts that the relative f cross section increases substantially from 40-eV to 1500-eV photon energy and that at high temperature the $f_{5/2}$ and $f_{7/2}$ intensities are only spread in this energy range but have not vanished. When measured with the x-ray-photoemission-spectroscopy resolution of 300 meV it is then obvious that the corresponding intensity distribution has the appearance of a single peak located at E_F . This feature should not be confused with the Kondo peak which can only be observed at low temperature and with a sufficiently high resolution.

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Characterization of the hybridized $4f$ states in YbAl_3 by high-energy spectroscopies

F. Patthey, J.-M. Imer, W.-D. Schneider, and Y. Baer

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

B. Delley

Schweizerisches Institut für Nuklearforschung, Badenerstrasse 569, CH-8048 Zürich, Switzerland

F. Hulliger

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich, CH-8093 Zürich, Switzerland

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The intermetallic compound YbAl_3 has been studied by bremsstrahlung isochromat spectroscopy, x-ray photoemission, and high-resolution (< 20 meV) uv photoemission using HeI and HeII lines. The spectra analysis with the Anderson single-impurity model for $T=0$ reveals a ground state with an important hybridization of f states with band states, corresponding to an f population $n_f=13.5$. In contrast to all investigated metallic Ce systems which are in the Kondo regime, YbAl_3 is found to be in the mixed-valence regime. A rough calculation provides an explanation for the comparable hybridization strengths observed in Ce and Yb systems.

During the last decade special attention has been devoted to the lanthanide systems showing manifestations of the Kondo effect, of heavy fermions and of mixed valence.¹⁻³ It is now generally accepted that the origin of these unconventional properties must be looked for in the weak coupling between the atomiclike $4f$ states and the band states of the solid. The particular mechanism responsible for the ground-state stability of these systems is rather directly reflected by their excitation spectra within the low-energy range defined by the total energy lowering δ which results from the hybridization.⁴ For Ce systems only, photoemission spectra have been recorded with a sufficiently high resolution to give access to these low-lying excitations.⁵⁻⁷ Their analysis within the single-impurity model appeared to be compatible with the low-temperature specific heat.

Heavy lanthanides also show unusual properties originating most likely from the same hybridization mechanism. Yb compounds offer a situation perfectly analogous to the one met in Ce or La, if the role of occupied and empty $4f$ states is interchanged and the energy scale inverted.⁸ This mirror property of Ce and Yb systems allows us to use exactly the same single-impurity model in both cases. However, for Yb the values of the parameters defined in this model may be different from those characterizing the Kondo limit found for Ce, so that one can hope to verify experimentally the existence of one of the other regimes predicted by this theory.⁹⁻¹¹

The intermetallic compound YbAl_3 , displaying puzzling properties, was chosen for this investigation. From the lattice constant which fits fairly well in the systematics of the trivalent heavy rare-earth aluminides,¹² one could conclude that the Yb ions are very close to the magnetic trivalent configuration. However, at low temperatures the magnetic susceptibility does not follow the Curie law expected for this configuration.¹² An anomalously large coefficient of the specific heat has been reported,¹² suggesting an f -symmetry admixture to the Fermi surface.

Mössbauer isomer shift measurements showed that the valence of Yb in YbAl_3 has no temperature dependence and a fractional value of 2.7 was obtained from the data analysis.¹³ X-ray photoemission spectroscopy (XPS) has revealed two sets of final-state f multiplets which were interpreted as originating from a ground state consisting of the two nearly degenerate $4f^{13}$ and $4f^{14}$ ionic configurations¹⁴ fluctuating in time.¹⁵ Within this intuitive model of valence fluctuations, one of the characteristic symptoms revealing this situation in f photoemission spectra is the pinning at E_F of the lowest component of the $4f^{13}$ multiplets.¹⁶ With the resolution currently achieved in XPS, the validity of this criterion seemed to be verified many times. However, photoemission spectra of YbAl_2 , taken at $h\nu=70$ eV with a resolution of 170 meV, showed that the first f component is not located at E_F but 240 meV above it.¹⁷ This unexpected observation has been tentatively attributed to some incomplete relaxation of this photoemission final state.¹⁷ The different results obtained for Yb systems can be hardly reconciled with conventional arguments and there is an urgent need for a unified description of their properties. The aim of the present Communication is to show that the observation of the low-energy excitations with high-resolution photoemission yields a decisive contribution to this problem.

The polycrystalline YbAl_3 sample was grown from Al flux in an evacuated Al_2O_3 tube. An x-ray analysis confirmed the single-phase cubic Cu_3Au -type structure of the sample.¹² The electron spectroscopic measurements were performed in an apparatus combining x-ray photoemission spectroscopy (XPS), bremsstrahlung isochromat spectroscopy (BIS), and uv photoemission spectroscopy (UPS) excited with the two narrow HeI and HeII resonance lines at 21.2 and 40.8 eV.⁵ The total instrumental resolution of these techniques was 0.3, 0.4, and < 20 meV, respectively. The sample was cooled to about 25 K using a closed-cycle He refrigerator in order to sharpen the Fermi edge and to prevent oxygen diffusion from the

bulk to the surface. The contamination could be maintained below the limit of detection by frequently scraping the sample with an Al_2O_3 file.

The analysis of the spectra has been performed within the single-impurity model. Advantage was taken of the mirror property of Ce and Yb systems previously mentioned to carry out a Gunnarsson-Schönhammer (GS)-type calculation⁴ of the spectral function at $T=0$. It included the $4f^{14}$ configuration and the $4f_{7/3}^{13}$ and $4f_{5/3}^{13}$ states separated by 1.26 eV (Ref. 18) but could not take into account the $4f^{12}$ configuration, which is about 8 eV above the ground state. In the hole language, it is convenient to define ϵ_f as the total energy difference between the two lowest unhybridized $f_{7/2}^{13}$ and f^{14} configurations and this parameter has a negative value since without hybridization $f_{7/2}^{13}$ would be the ground state of YbAl_3 . The coupling strength between f and band states is taken into account by the parameter Δ .⁴ The band is simulated by a Lorentzian of 6 eV full width at half maximum (FWHM) and centered 2 eV above the Fermi level. In order to still obtain an estimate of the $4f^{12}$ contribution (without multiplet splitting) to the final states, a much simpler calculation in the zero-bandwidth limit¹⁹ has also been performed.

Figure 1 displays the XPS (a) and BIS (b) spectra recorded at 25 K and the corresponding single-impurity calculations for $T=0$ (c), (d). In the XPS spectrum the $4f^{12}$ final-state multiplets are clearly recognized between 5 and 11 eV below the Fermi energy. Near E_F two narrow peaks are observed with an energy splitting of 1.2 eV and an intensity ratio of about 8:6. These observations allow us to identify them with $4f_{7/2,5/2}^{13}$ final states as encountered in Yb-metal²⁰ but shifted by ≈ 1 eV towards E_F . Spectra taken at room temperature (not shown here) display an enhanced $4f^{12}$ multiplet intensity already ob-

served in XPS spectra of YbAl_3 (Ref. 14) and YbAl_2 .²¹ For YbAl_3 this excess of intensity could be widely reduced by cleaning the sample surface so that we attribute it to the occurrence of the $4f^{12}$ multiplets of Yb oxide formed by oxygen diffusion from the bulk to the surface region of the sample. The measurement of the BIS spectrum shown in Fig. 1(b) required a particular care since even at low temperature the electron beam induced a fast formation of Yb oxide immediately detected as a $4f^{14}$ final state about 1.5 eV above E_F . The first peak at E_F is less pronounced than in the BIS spectrum of YbAl_2 ;²¹ therefore, in accordance with the stoichiometry difference, we identify it with f emission while the broad maximum extending towards higher energies is attributed to the emission from band states.

Figure 1(c) displays the zero-bandwidth model calculation for XPS where the $4f^{12}$ spectral weight is concentrated in a 2 eV FWHM Lorentzian since multiplet splitting has been discarded. All other structures are broadened by Lorentzians of 0.3 eV FWHM to account for the instrumental resolution. The values of the different parameters has been chosen in such a way that the calculation reproduces the $I(4f^{13})/I(4f^{12})$ intensity ratio. The ground-state f occupation n_f is found to be 13.4. For U_{ff} , the value of 7 eV corresponding to the center of gravity of the $4f^{12}$ multiplet is roughly the same as found in most Ce systems.²² The calculation for the BIS spectrum, also shown in Fig. 1(d) will be discussed below.

In order to obtain detailed information concerning the low-energy excitations, high-resolution uv spectra were recorded [Figs. 2(a)–2(d)]. At these low photon energies, however, photoemission becomes extremely surface sensitive, as demonstrated by spectra (a) and (c). By comparison with the spectra of Yb metal^{23,24} and YbAl_2 (Ref. 17) the structures at 1.2 and 2.4 eV are identified as origi-

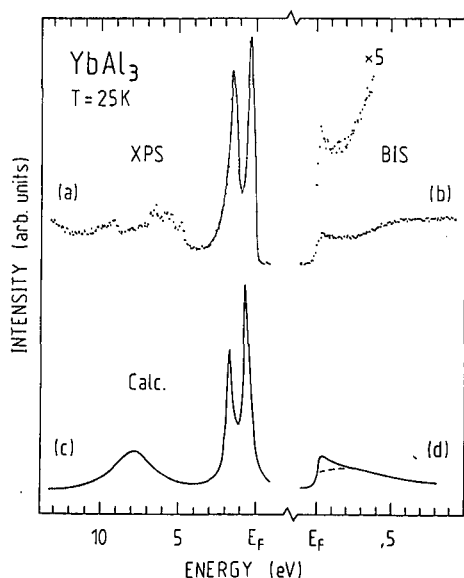


FIG. 1. (a) XPS and (b) BIS spectra of YbAl_3 . (c) Simulation of the f -photoemission spectrum within the zero bandwidth approximation. (d) Simulation of the BIS spectrum by a GS calculation of the f excitations superimposed on a Lorentzian band (dashed line).

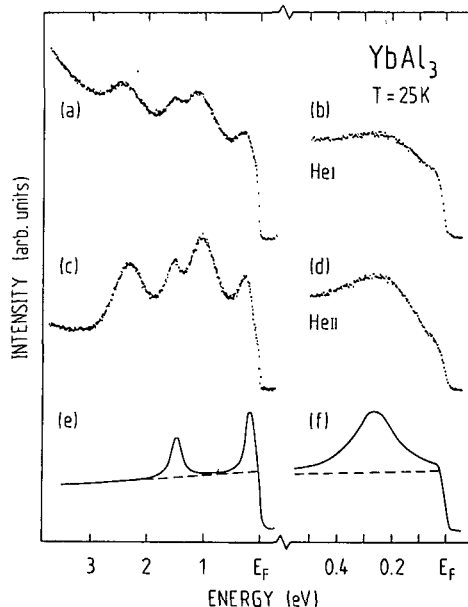


FIG. 2. (a)–(d) uv-photoemission spectra of YbAl_3 ; (a), (c) in the full range of surface and bulk $4f$ excitations; (b), (d) in a narrow energy range above E_F . (e), (f) Calculation simulating the bulk contribution to the spectra (c) and (b) (see text).

nating from divalent Yb ions ($4f^{14}$ configuration) present at the surface where the coordination is different.²⁵ The bulk 4f emission is recognized near E_F and at 1.5 eV, in agreement with the peak positions observed in the much less surface sensitive XPS spectrum [Fig. 1(a)]. In the low-energy flank of the first peak near E_F a weak shoulder reveals the Fermi edge; therefore, the energy region of this peak has been measured in detail. The resulting spectra displayed in Figs. 2(b) and 2(d) illustrate the enhancement of the cross-section ratio between 4f and band states when the photon energy increases and demonstrate unambiguously that the top of the f emission peak is located at 240 meV and not at E_F .

Figures 2(e) and 2(f) display the calculated f-photoemission spectra of the bulk (solid curve above the dashed line) computed within the GS model. The contribution from the band states (dashed line) is adjusted to give the best agreement with HeII experiment. In this model calculation the experimental position of the first peak is obtained for the parameters $\Delta=80$ meV and $\epsilon_f = -0.2$ eV yielding a ground state which contains an f population $n_f=13.6$ and is lowered by $\delta=240$ meV with respect to the uncoupled $4f_{7/2}^{13}$ state. Since for a zero bandwidth the simple model underestimates n_f and by omission of the $4f^{12}$ configuration the GS model overestimates n_f , a value of 13.5 seems reasonable for YbAl₃. The agreement between measured and calculated spectra is gratifying but not quite perfect. The fact that the experimental spectrum is broader than the simulated one is not surprising since lifetime broadening and electron-hole pair excitations are not included in the model. With the same parameters we have calculated the f spectral function for BIS. The result shown in Fig. 1(d) includes the contribution of the band estimated from XPS and is broadened by the experimental resolution of 0.4 eV. The total f contribution, normalized with respect to XPS by the factor $(N_f - n_f)/n_f = 1/27$, is essentially the continuation of the tail of the 4f photoemission peak. The comparison with experiment shows that this f signal superimposed to the emission from band states can only be discerned near E_F .

It is now instructive to contrast this spectra analysis of YbAl₃ with those performed previously for different metallic Ce systems.^{5-7,26,27} In these latter it has always been found $-\epsilon_f \gg \Delta$, with ϵ_f between -1 and -2 eV and Δ of the order of 50 to 150 meV. These conditions are typical for the Kondo regime in which the f population n_f is very close to the integral value 1 and the energy lowering δ ranges from < 1 meV in heavy-electron systems like CeCu₆ (Ref. 26) to 25 meV in α Ce.⁵ In YbAl₃ the value $-\epsilon_f=200$ meV is substantially smaller than for Ce systems while the hybridization strength Δ is of the order of $-\epsilon_f$. It results a fractional hole number $n_f^h \approx 0.5$ far from integral values and an important energy lowering $\delta=240$ meV. This energy gain of the ground state is very large compared to kT for $T < 300$ K so that no variation of n_f is expected in this temperature range. Within the single-impurity model the condition $-\epsilon_f \approx \Delta$ character-

izes the mixed valent regime^{9-11,28} which appears to be rather different from the oversimplified concept of configuration fluctuation proposed earlier to explain photoemission spectra showing distinct features of two 4f populations. In fact, the photoexcitation induces transitions to a low-energy continuum of final states starting at the Fermi energy identified with the ground state with $n_f=13.5$. Towards higher energies this continuum transforms gradually into a practically pure $4f_{7/2}^{13}$ state at the first peak maximum. At 1.5 eV appear the final states attributable to the $4f_{5/2}^{13}$ component and between 5 and 11 eV to the $4f^{12}$ multiplets. This interpretation of the photoemission spectrum shows that the total energy lowering resulting from the hybridization is directly given by the energy position of the $4f_{7/2}^{13}$ peak referenced to the Fermi energy.

The present interpretation of the electronic structure of YbAl₃ rests exclusively on the analysis of the outer level spectra. The reason for this is twofold: (i) the 3d levels usually considered are not accessible with the Al K α line in Yb and (ii) the spectra of the less bound 4p and 5p levels²⁹ display a very rich multiplet structure (not shown here). The interpretation of such spectra would require a GS calculation including as basis states all possible atomic multiplets. This is a difficult task that we have not attempted since it would add to our otherwise complete spectra analysis only the determination of the Coulomb energy U_{fc} between a core hole and an f electron.

The formal analysis of the excitation spectra of YbAl₃ within the single impurity model appears to be very successful. However, the comparable magnitude of the coupling strengths Δ in Ce and Yb systems is totally unexpected if only the 4f wave-function contraction across the lanthanides is considered. In simple molecular orbital theories the coupling strengths are often taken to be proportional to the corresponding overlap matrix elements. We have estimated the overlap matrix elements S between an f orbital and plane waves at the Fermi energy of a jellium corresponding to the electron density of aluminum. In this approximation we used the $kr \rightarrow 0$ asymptotic form of $j_3(kr)$, representing the f-partial wave in the plane-wave expansion around the Yb nucleus. We find $S(\text{Yb}, n_f=13)=5.4$, $S(\text{Yb}, n_f=14)=44$, $S(\text{Ce}, n_f=0)=6.7$, $S(\text{Ce}, n_f=1)=24$. This behavior of the overlap integrals originates from the tails of the 4f wave functions, which in both cases become more intense when the potential is weakened by an f-count increase. Starting from trivalent configurations where the tail is weaker for f^{13} than for f^1 , the hybridization induces a positive variation of n_f in Yb and a negative one in Ce. If this relative population change is large enough (as in YbAl₃) it can cancel the intensity difference of the tails obtained in the pure trivalent configurations. This mechanism is likely to explain the occurrence of similar hybridization strengths in Ce and Yb systems.

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