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
(Received 22 July 1985)

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.

PACS numbers: 79.60.Cn, 71.70.Ms, 72.15.Qm, 76.30.Kg

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 results[4-9] 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 considerations[12] 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 Schönhammer[13] (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 commerical 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 electrons[23] 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 Ce[24] 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]

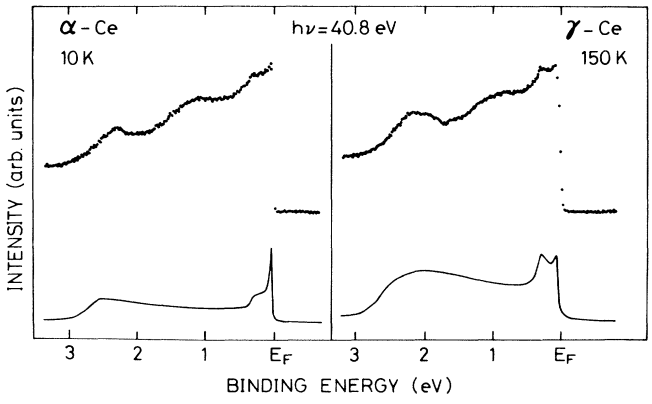

FIG. 1. Dots: outer-level photoelectron spectra of α- and γ-Ce. Full curves: result of a many-body calculation (including $4f$ spin-orbit interaction) for the f contribution to the photoemission spectra. The curves have been convoluted with Lorentzians of 20 and 60 meV FWHM for α- and γ-Ce, respectively, 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 $4f_{7/2}$

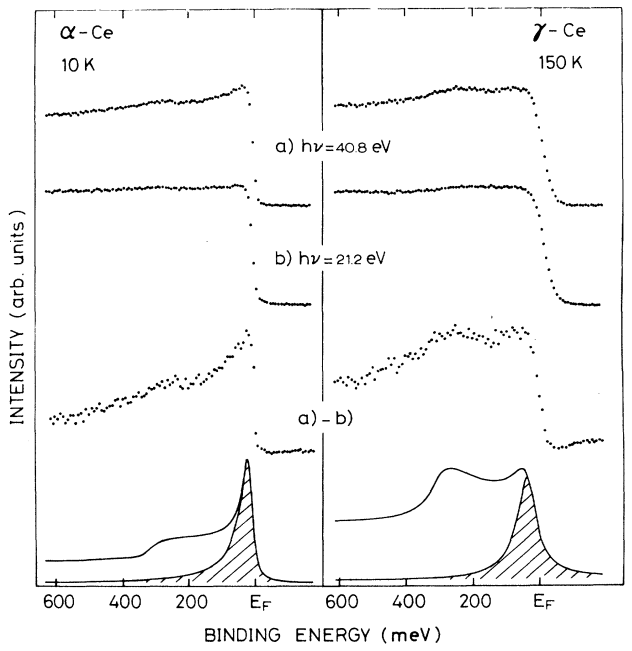

FIG. 2. Dots: outer-level photoelectron spectra of α- and γ-Ce within 500 meV below E_F. The curves labeled $a - b$ represent differences of weighted spectra a and b (see text). Full curves: model calculation (see caption of Fig. 1). The curves defining the hatched areas correspond to the particular 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 theory[25] and a Green's-function technique with decoupling procedure[26] 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 Yafet[27]) 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:

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

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 $a_0^{E,\epsilon}$ 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 variation[31] [$U(E_F)=0$]. 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]

The authors are indebted to H. Beck for his patient guidance through the many-body theory. This work has been supported by the Swiss National Science Foundation.

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