4f Photoemission from Rare-Earth Systems

M. D. Nunez-Regueiro[a] and M. Avignon
Laboratoire d'Etudes des Propriétés Electroniques des Solides, Centre National de la Recherche Scientifique, 38042 Grenoble Cedex, France
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The $4f$ spectral density of the Falicov-Kimball model is calculated within the "resonance broadening" approximation. This allows a qualitative interpretation of the double-peak structure observed in $4f$-derived photoemission for the light–rare-earth systems: A partial delocalization of the f electrons into the d band is deduced in the γ-α transition for Ce; the two peaks move away from the Fermi energy with the f level as one goes from Ce to Pr to Nd. The only feature obtained in Sm-based systems can be understood within the same picture.

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The finding of similar bimodal structures in the $4f$-derived photoemission spectra for the two phases γ and α of Ce[1] and its compounds[2] has reactivated the discussion about the elusive nature of these systems. Recent results by Parks *et al.*[3] for neighboring compounds seem to show that the two-peak structure is not unique to Ce-based systems, but a common property of the light rare earths. Furthermore, the energy separation between the two features remains constant, but they move together as one goes from Ce to Pr to Nd. Wieliczka, Olson, and Lynch[4] confirm the double structure for Pr, shifted to higher binding energies compared to Ce. Also, high-resolution photoemission for metallic Ce shows[5] a slight but significant shift for the feature at the Fermi level in α-Ce as one goes to the γ phase. Although the higher-binding-energy peak is always related to the position of the $4f$ level, E_0, different interpretations are given for the low-binding-energy peak.

Günnarsson and Schönhammer[6] proposed a model in which screening effects are neglected and the double structure is attributed to correlations in the ground state. They calculated the $4f$ spectral density for the Anderson impurity in the limit of large f degeneracy and interpreted the feature close to the Fermi level as a Kondo-type (or Abrikosov-Suhl) resonance. The $4f$ spectra for Ce compounds can be qualitatively reproduced with the assumption of a very large f-d hybridization ($V \sim 0.1$ eV) and an important f occupation ($\langle n^f \rangle > 0.7$). As other spectroscopies can be interpreted with the same parameter values, the model is appealing. There are, however, some puzzling points: The bimodal structure is observed at room temperature for noncollapsed Kondo systems also; and the hybridizaton, although one order of magnitude larger than expected, and scaled now by the degeneracy, is not enough to reproduce the experimental widths. Moreover, the Abrikosov-Suhl resonance is expected to decrease in intensity but not to move as the f level E_0 becomes deeper, at variance with experimental results for Pr and Nd compounds. In this calculation the f-d Coulomb interaction, which is an important parameter for these systems,[7] is not taken into account as it is claimed that it can implicitly be included in the model as a renormalization of the f-level position E_0 and f-f Coulomb repulsion U.[6]

In constrast, Liu and Ho[8] attributed the double structure to the screening potential created by the photoemission process: A shakedown satellite appears due to the f-d correlation. In their subsequent related papers[9] they build up a mixed-valent state by promoting f electrons into the conduction band. But they calculated the spectra using the exact result obtained when only one hole is created in an f^1 system, which does not correspond to a real mixed-valent situation. Also, Riseborough[10] has recently discussed the importance of the f-d interaction but, again, only in this low density of conduction electrons limit.

In fact, if such screening effects are so important in photoemission they must be relevant to the ground state. In this paper, we show that the $4f$ spectral density is strongly modified when the f-d Coulomb interaction G is considered and the effect of the itinerancy of the d electrons on the localized ones taken into account. As the f electrons have much longer lifetime than the d ones, they can "see" their motion: They are being resonant between two energies E_0 and $E_0 + G$. This is just Hubbard's "resonance broadening" correction,[11] which yields one or two peaks depending on the G value compared to the d bandwidth $2W$, and it is this effect which becomes principally responsible for their width, and not the hybridization. This Green's-function decoupling procedure evaluates the eventually mixed-valent state self-consistently (as has been done by Oh and Doniach[12] for the core spectrum): This puts in evidence the importance of the band filling. The relative weight of the peaks becomes a function of the number of conduction electrons. In contrast with previous models, the low–binding-energy feature is not pinned at the Fermi level ϵ_F, but both features move down with the bare f level E_0. Depending on the occupation of both types of states, one or both features are below ϵ_F. This allows, for the first time, an explanation of the valence spectra of both light and heavy rare earths within the same picture.

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We consider the periodic Falicov-Kimball[13] Hamiltonian

$$H=\sum_{i,j}t_{ij}d_i^{\dagger}d_j+E_0\sum_i f_i^{\dagger}f_i+G\sum_i n_i^f n_i^d, \tag{1}$$

where the first term describes the conduction states, the second the localized f levels, and the last one the local Coulomb repulsion between them. The f Green's functions are

$$(\omega-E_0)\langle\langle f_i,f_i^{\dagger}\rangle\rangle=1+G\langle\langle n_i^d f_i,f_i^{\dagger}\rangle\rangle, \tag{2}$$

$$(\omega-E_0-G)\langle\langle n_i^d f_i,f_i^{\dagger}\rangle\rangle=\langle n_i^d\rangle+\sum_j t_{ij}\langle\langle(d_i^{\dagger}d_j-d_j^{\dagger}d_i)f_i,f_i^{\dagger}\rangle\rangle. \tag{3}$$

The usually invoked Hartree-Fock result corresponds to an approximation of Eq. (2). The only effect of the G term in that case is to shift the unique peak, without width in energy when $V=0$. The Hubbard I decoupling[11] always yields (i.e., for all G/W ratios) two peaks at E_0 and E_0+G, with relative weights depending on the d occupation but also without width in energy. In this aproximation the last terms in Eq. (3), which describe the effect of the motion of the d electrons on the f_i site considered, are neglected. We claim that including these terms is crucial when describing the f states. In fact, the f electrons are in resonance between these two energies, depending on whether there is a conduction electron or not on the same lattice site; the rate of this switching is given by the d itineracy. If we approximate the equations of motion for these terms as in Ref. 11,

$$\begin{aligned}F_1(\omega)\langle\langle d_i^{\dagger}d_jf_i,f_i^{\dagger}\rangle\rangle&\approx t_{ij}\langle\langle(n_i^d-\langle n^d\rangle)f_i,f_i^{\dagger}\rangle\rangle+\sum_{l\neq i}t_{jl}\langle\langle d_i^{\dagger}d_lf_i,f_i^{\dagger}\rangle\rangle,\\ F_2(\omega)\langle\langle d_j^{\dagger}d_if_i,f_i^{\dagger}\rangle\rangle&\approx t_{ij}\langle\langle(n_i^d-\langle n^d\rangle)f_i,f_i^{\dagger}\rangle\rangle+\sum_{l\neq i}t_{jl}\langle\langle d_l^{\dagger}d_if_i,f_i^{\dagger}\rangle\rangle,\end{aligned} \tag{4}$$

where

$$F_i(\omega)=\frac{(\omega-E_0)(\omega-E_0-G)}{\omega-E_0-G(1-\langle n^f\rangle)},\quad F_2(\omega)=F_1(-\omega+2E_0+G). \tag{5}$$

Their sum can be evaluated as follows:

$$\sum_j t_{ij}\langle\langle(d_i^{\dagger}d_j-d_j^{\dagger}d_i)f_i,f_i^{\dagger}\rangle\rangle\simeq[\lambda_1(\omega)-\lambda_2(\omega)]\langle\langle(n_i^d-\langle n^d\rangle)f_i,f_i^{\dagger}\rangle\rangle, \tag{6}$$

with

$$\lambda_i(\omega)=F_i(\omega)-\{\tilde{F}[F_i(\omega)]\}^{-1}, \tag{7}$$

where $\tilde{F}(\omega)$ yields the d density of states, and we have considered a semielliptical band. When we include these terms, the f Green's function reads

$$\langle\langle f_i,f_i^{\dagger}\rangle\rangle\frac{\omega-E_0-G(1-\langle n_i^d\rangle)-[\lambda_1(\omega)-\lambda_2(\omega)]}{(\omega-E_0)(\omega-E_0-G)-[\lambda_1(\omega)-\lambda_2(\omega)](\omega-E_0-G\langle n^d\rangle)}, \tag{8}$$

and accounts for the effects we have discussed. Although the index i in Eq. (8) distinguishes partial d occupation on the f_i site considered, we have used average $\langle n^d\rangle$ occupation for all lattice sites. This must not qualitatively change the results.

For small ratio G/W, the weighted mean of the two resonances is found at $\tilde{E}_0\approx\langle n^d\rangle(E_0+G)+(1-\langle n^d\rangle)E_0$ [Fig. 1(a)]. For large G/W there are two features [Fig. 1(b); secondary peaks are not significant, as they are an artifact of the band-edge singularities]. As the integrated area of the higher-binding-energy peak is $1-\langle n^d\rangle$, more than one electron per site is necessary to have the lower-binding-energy peak at or below ϵ_F. Weight from the former feature is transferred to the latter one with increasing $\langle n^d\rangle$. Both peaks move down from ϵ_F with the f level E_0 (Fig. 2).

As a result of the G interaction, the f level is broadened in energy, and the peaks have an important width. It is not hybridization, but an effect due to the inhomogeneity of the system. It is not a lattice effect; the same behavior is found for the impurity. In a forthcoming publication we show that the hybridization, although necessary to have a fluctuating valent state, does not introduce significant changes when treated in a mean-field approximation.

Then, for large enough ratio G/W the system must be metallic and have an important f occupation to present a bimodal $4f$ spectra: This is the case of Ce. The intensity transfer between the peaks in the γ-α transition[1,4] is consistent with a partial promotion of the f electrons into the band (see Fig. 2) although smaller than previously thought (only 0.2 or 0.3).

It seems that the same physics is involved in the neighboring systems.[3] Hamiltonian (1) is relevant to integral valence as well as mixed valence. If one assumes that our calculation describes the f^n shell, there

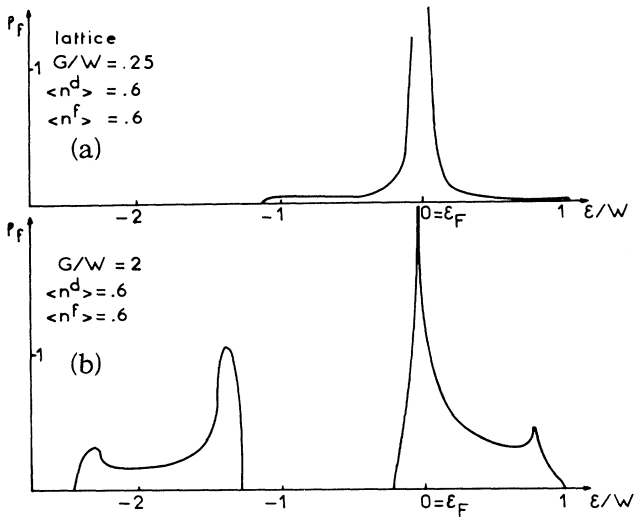

FIG. 1. f-spectral density within the "resonance broadening" approximation. (a) Small ratio G/W; there is only one peak, at ϵ_F in the intermediate valence case. (b) Large ratio G/W; there are two features. For $\langle n^f\rangle + \langle n^d\rangle > 1$ both peaks can be below $\epsilon_F(\epsilon = 0)$.

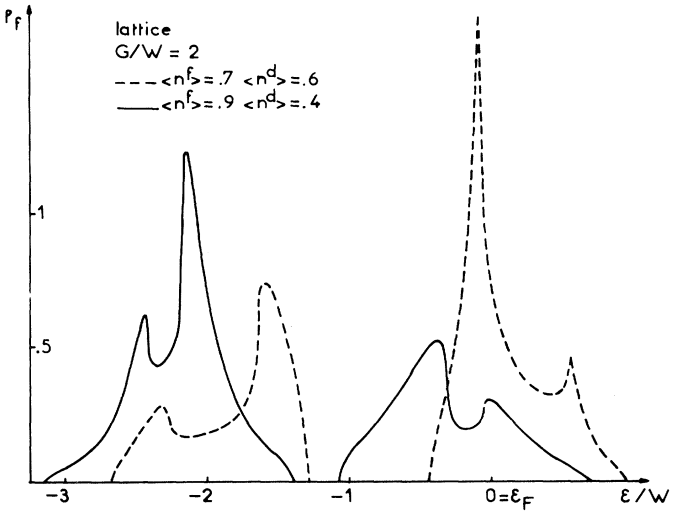

FIG. 2. Effect of delocalizing 0.2 f electron into the d band. The low-binding-energy peak increases weight and shifts to ϵ_F.

is agreement with the fact that both features go down from ϵ_F with E_0 as one goes from Ce to Pr to Nd compounds. E_0 has to be considered as a quasiparticle energy and represents the energy required to excite an f electron from the f^n shell into the conduction band.[14] For different alloys it is difficult to compare $\langle n^d\rangle$. However, from this simplified model (all degeneracies have been neglected) one can speculate that the effective number of itinerant electrons acting on the Ce ions is more important in $CePd_3$ than in $CeRu_2$.[3]

For Sm-based systems, the situation for the f unstable electron is different. Although the G/W value is important, the 2^+ valent state is semiconducting (there is no "resonance broadening" effect) and in the mixed-valent phase as $\langle n^d\rangle = 1 - \langle n^f\rangle$ only part of one peak is seen by direct photoemission; the other one is above ϵ_F.

We conclude that results for the Anderson model cannot be trivially extended to include the f-d Coulomb interaction G. It has been shown that the "resonance broadening" effect allows an interpretation of the $4f$ spectra of both light and heavy rare earths, with the same Hamiltonian largely used to describe common macroscopic properties. More effect is necessary to include correctly both the G term and the hybridization before ruling out this or Günnarsson and Schönhammer's interpretation. Even within a Kondo collapse picture, the f-d interaction can be at the origin of the $4f$ double structure observed by photoemission in Ce compounds.

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[a]Present address: Centro Atomico Bariloche, Instituto Balseiro, 8400 Bariloche, Argentina.

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