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Towards a Self-Consistent Determination of the Mixing Parameters in the Anderson Model: An Application to the 4*f*-Excitation Spectra of YbP

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A method is presented for computing the mixing parameters in the Anderson model for heavy-rare-earth compounds, based on a linear combination of atomic orbitals fit to a self-consistent band-structure calculation. An appropriate average of these parameters is used in a many-body calculation of the valence-band x-ray-photoemission and inverse-photoemission spectra of YbP, with the Coulomb integral U as the only adjustable quantity. The calculated inverse-photoemission spectrum agrees qualitatively with room-temperature low-resolution data by Baer *et al.*

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The orbitally degenerate Anderson impurity model[1] has become an important tool for the analysis of high-energy spectra of light-rare-earth materials.[2-4] Thanks to its comprehensive treatment and extension by Gunnarsson and Schönhammer[2] (GS), all the features observed in x-ray photoemission (XPS), x-ray absorption, electron-energy-loss spectroscopy, and bremsstrahlung isochromat (BIS) spectroscopy can be satisfactorily accounted for with only six parameters (the degeneracy N_f and position ϵ_f of the f level, its coupling Δ to extended states of bandwidth $2B$, the Coulomb interaction U between the f electrons, and the interaction U_{fc} between a core hole and the f electrons).

GS start from a variational calculation of the ground state,[5] which in its simplest form is written

$$|\phi_0^{(1)}\rangle = A\left[1+\sum_{\mathbf{k},n,m,\sigma} a_{\mathbf{k}n}^{m} f_{m\sigma}^{\dagger} c_{n\mathbf{k}\sigma}\right]|0\rangle, \qquad (1)$$

where $|0\rangle$ represents the unperturbed Fermi sea of valence and conduction electrons, and the second term in the parentheses generates all possible states obtainable by the transfer of a Bloch electron, labeled by the band index n and wave vector $\mathbf{k}$, into a localized level with the crystal-field label $m=\{\Gamma_{,j}\}$. The transfer is controlled by the mixing parameters $V_{\mathbf{k}m}^{n}$, which also determine the coefficients $a_{\mathbf{k}n}^{m}$. The simplicity of the GS theory rests on the observation that these matrix elements satisfy

$$\sum_{\mathbf{k},n} V_{\mathbf{k}m}^{n} V_{\mathbf{k}m'}^{n*}\delta(\epsilon-\epsilon_{\mathbf{k}}^{n}) \equiv |V_\Gamma(\epsilon)|^2\delta_{mm'}. \qquad (2)$$

$|V_\Gamma(\epsilon)|^2$ is then replaced by a Γ-independent average, modeled by a semielliptical or constant function of energy or by an experimental valence photoemission spectrum. With this *Ansatz*, the values found for Δ $\{\equiv\pi\max[|V(\epsilon)|^2]\}$ in the various applications[2-4] typically vary between a few hundreths and a few tenths of an electronvolt, that is, in a range accessible to high-accuracy *ab initio* calculations.

Here, we apply the GS formalism to a system with one f hole, specifically to the calculation of the valence XPS and BIS spectra of YbP, a compound in which the Yb ion has a stable (with respect to a full shell) $4f^{13}$ configuration. That this problem can be mapped onto the one originally formulated for the $4f^1$ configuration of Ce has been pointed out before.[4,6] What is new in our treatment is that we explicitly calculate mixing parameters $V_{\mathbf{k}m}^{n}$ for a realistic band structure[7] and from them construct the function $|V(\epsilon)|^2$. Furthermore, we determine the position of the f level by imposing charge neutrality, accounting for the fact that we deal with a concentrated system.

The ground level for the $4f^{13}$ configuration of Yb is a $J=\frac{7}{2}$ multiplet, separated from the excited ($J=\frac{5}{2}$) level by a spin-orbit splitting of $\simeq 1.2$ eV, i.e., much larger than ϵ_f, which we find to be less than 0.2 eV away from the Fermi energy. This implies that $N_f=8$ and that the excited multiplet can be neglected in the self-consistency procedure, in contrast to the situation in the light rare earths, where it strongly affects the ground-state energy and $4f$ occupancy n_f.[2] Four of the five parameters necessary to interpret valence spectra are therefore known *a priori.*

Our procedure for constructing $|V(\epsilon)|^2$ consists of five steps: (i) a determination of the band structure of the compound under consideration; (ii) a Slater-Koster (SK) linear combination of atomic orbitals (LCAO) parametrization[8,9] of the bands; (iii) a recalculation of the disperison of the extended states with those SK parameters which do not involve the $4f$ orbitals; (iv) an evaluation of the mixing matrix elements between these LCAO bands and the $4f$-crystal-field orbitals, again by use of the optimized parameters obtained from the SK fit; (v) the construction of the 7×7 matrix equivalent of the GS $|V(\epsilon)|^2$ function, describing the coupling between all possible pairs of $4f$

orbitals via the extended states, and, finally, the definition of a mean coupling per orbital as the average of the eigenvalues of this matrix.

(i) We start from a self-consistent, semirelativistic, "warped muffin-tin" linearized augmented plane-wave calculation for YbP, with the local-density approximation (LDA) for exchange and correlation. From it, we expect to obtain an accurate description of the extended states as well as a close estimate of the total $4f$ *charge* on each Yb ion, even though the LDA is known to misrepresent the details of the *density* for localized orbitals.[10] The latter expectation is based on the observation that, because of the lanthanide contraction, all of the $4f$ charge is contained in the metal-centered muffin-tin sphere, with a vanishingly small density at the sphere radius, $r_{\mathrm{MT}}=2.647$ a.u. The f-hole occupancy we obtain is $n_f=0.89$ "per impurity."

(ii) In our LCAO parametrization of the band structure, we consider the rare-earth $4f$, $5d$, and $6s$ and the phosphorous $3s$ and $3p$ orbitals, with first- and second-neighbor metal-ligand, ligand-ligand, and metal-metal interactions, except for the direct f-f and the f-ligand coupling, where we take into account only nearest neighbors. We further make the two-center approximation for all transfer integrals involving f orbitals. This leads to 57 independent parameters, with which we fit a total of 342 eigenvalues at 21 independent points of the irreducible Brillouin zone, with a rms deviation of 8.5 mRy. (For comparison, Dorrer, Eibler, and Neckel[11] obtained a rms deviation of 9.4 mRy in a 45-parameter fit to the band structure of ScP at 29 independent points of the irreducible Brillouin zone.) The assumption here is that corrections to the LDA $4f$ wave function in the outer region of the muffin-tin sphere are small.

(iii) The advantage of the LCAO parametrization is that it allows a separation "by hand" between bandlike and localized ($4f$) states, while at the same time providing values for the mixing-matrix elements between the two. The relevant bands for our problem are those derived from the Yb d and P p orbitals, and we have diagonalized the 8×8 matrix representing the p-d complex, using the parameters obtained from our fit. The corresponding partial densities of states are shown in Fig. 1. *They contain all the effects due to the presence of the* $4f$ *electrons, except the hybridization.* The latter, we find, is dominated by nearest-neighbor ligand-metal ($pf\sigma$) interactions (0.197 ± 0.0027 eV) followed by ($pf\pi$) interactions (-0.181 ± 0.0027 eV) and *second*-neighbor metal-metal ($df\sigma$) coupling (-0.159 ± 0.0095 eV),[12] all other integrals being at least a factor of 2 smaller than ($df\sigma$).

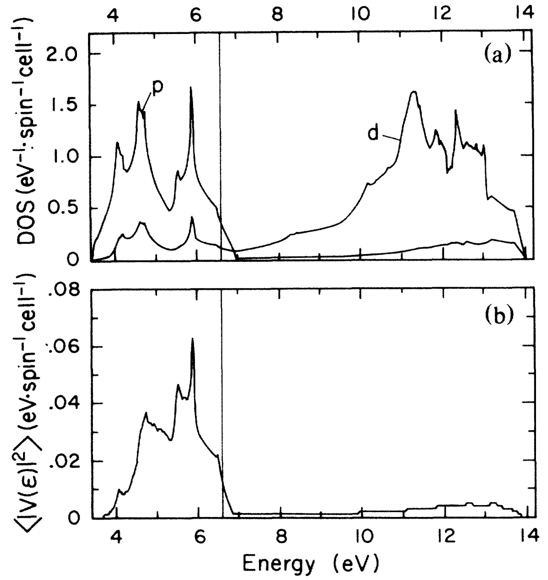

FIG. 1. (a) LCAO phosphorous-$3p$ and ytterbium-$5d$ partial densities of states in YbP. (b) Average coupling of the many-body $4f$ level of Yb to the phosphorus-$3p$-derived valence band in YbP.

(iv) The coupling of the (many-body) f level to the extended states involves single-particle matrix elements between Bloch and $4f$-hole orbitals, and can be reduced to linear combinations of the above two-center integrals. By expressing the Bloch waves in orthogonal LCAO and the f orbitals in cubic harmonics corresponding to the three irreducible representations $a_{2\mathrm{u}}$ (basis: xyz), $t_{1\mathrm{u}}$ [basis: $x_1=x(5x^2-3r^2)$, y_1,z_1], and $t_{2\mathrm{u}}$ [basis: $x_2=x(y^2-z^2),y_2,z_2$], we obtain (a is the lattice constant)

$$V^{p_x}_{\mathbf{k}x_1}=N^{-1/2}\{2(pf\sigma)\cos(k_xa/2)-(\tfrac{3}{2})^{1/2}(pf\pi)[\cos(k_ya/2)+\cos(k_za/2)]\} \tag{3a}$$

and

$$V^{p_x}_{\mathbf{k}x_2}=N^{-1/2}(\tfrac{5}{2})^{1/2}(pf\pi)[\cos(k_ya/2)-\cos(k_za/2)] \tag{3b}$$

for the coupling of the p_x component of each band at $\mathbf{k}$ with the x_1 and x_2 crystal-field oribtals, respectively. Similarly, the p_y (p_z) component couples only to y_1 and y_2 (z_1 and z_2).

The d-f interaction takes place between the e_g-like components of the band and the $t_{1\mathrm{u}}$ crystal-field orbitals; we shall ignore it, even though ($df\sigma$) is not smaller than ($pf\pi$). Our justification for this is twofold: First, the e_g-like spectral density in the energy range relevant for the GS calculation, i.e., close to the Fermi level, is 4 to 5 times smaller than its p-like counterpart; second, only three of the seven crystal-field orbitals interact with these bands, which reduces the average coupling per orbital accordingly. Finally, the $a_{2\mathrm{u}}$ orbital does not couple to the bands at all.

(v) We can now consider processes in which an electron jumps from a given crystal-field orbital α_i into the band and back to an orbital β_j, by evaluating the following sums with the tetrahedron integration method[13]:

$$F_{\alpha_i\beta_j}(\epsilon) = \sum_{\mathbf{k},\nu} c^{\nu *}_{p_\alpha}(\mathbf{k})\, c^{\nu}_{p_\beta}(\mathbf{k})\, V^{p_\alpha^*}_{\mathbf{k}\alpha_i} V^{p_\beta}_{\mathbf{k}\beta_j}\, \delta(\epsilon-\epsilon^{\nu}_{\mathbf{k}}), \tag{4}$$

where α,β label the components x, y, or z, and i and j take either the value 1 (for t_{1u}) or 2 (for t_{2u}). ν is a band index, which goes from 1 to 8, and $c^{\nu}_{p\beta}(\mathbf{k})$ is the p_β component of the normalized eigenvector for band number ν at the point $\mathbf{k}$. While at a given $\mathbf{k}$ point transitions between different crystal-field orbitals are possible, the sum over $\mathbf{k}$ introduces full cubic symmetry in the intermediate-states coupling, making $\mathbf{F}$ diagonal.

The strong on-site Coulomb interaction makes the occupation of each orbital by the hole equally probable, so that one only needs the average:

$$\langle |V(\epsilon)|^2\rangle \equiv \tfrac{1}{7}\,\mathrm{Tr}\mathbf{F}(\epsilon). \tag{5}$$

As seen in Fig. 1, the shape of this function is similar but not identical to that of the p-projected density of states. As a final step, we cut off the high-energy tail of $\langle |V(\epsilon)|^2\rangle$ and invert the energy scale, thereby going over to hole description.

What follows is a straightforward application of the GS theory to first order in $1/N_f$. The constraint $n_f=0.89$ leads to a value $\epsilon_f=-0.18$ eV for the position of the (hole) f level, i.e., the many-body $4f^{13}$ $(^2F_{7/2})$ state of the isolated impurity lies 0.18 eV *above* E_F. Including the interaction with the bands lowers the ground-state energy of the hole by 12 meV. For the record, the single-particle $4f$-crystal-field energies obtained from the SK fit to the band structure lie around 1.25 eV *below* E_F, with a total splitting of 20 meV.

In Fig. 2, we show the $4f$-BIS spectrum for two different situations: (a) with a Lorentzian broadening of 20 meV which, in terms of the thermal smearing of the Fermi edge, $\Gamma=4kT$, corresponds to a temperature of $\simeq 60$ K; (b) the same at room temperature, with and without a Gaussian of width 0.5 eV (FWHM) to account for the finite instrumental resolution.[13] The low-temperature spectrum is dominated by the $4f^{14}$ peak at 0.27 eV, corresponding to the filling of the $4f$ shell by the incoming electron. The next important structure is a Kondo resonance at less than 5 meV above E_F. We attribute the remaining features to band-structure effects. At room temperature, the Kondo resonance has been completely absorbed by what was just a small spike beside it, and the result is a shoulder on the low-energy side of now one single peak. This spectral density can be directly compared to the one computed by Bickers, Cox, and Wilkins,[4] in which the Kondo resonance is still much higher than the f^{14} peak and below the Fermi level. Finally, the spectrum with instrumental broadening included has only a bump centered at $\simeq 0.22$ eV, with a total width of 0.70 eV. Preliminary measurements by Baer *et al.*[14] show a similar feature centered at $\simeq 0.65$ eV and of width $\simeq 1$ eV. That the observed width is larger than the computed one is consistent with the fact that we have not considered radiative or Auger decays of the final $4f^{14}$ state into band states in our calculation. One possible reason for the difference in peak positions is that the $l=3$ component of the density in the Yb-centered muffin-tin sphere not only accounts for the true $4f$ charge of the rare-earth ion but also for possible f-like contributions in this sphere from overlapping charge densities from neighboring ions. Our procedure therefore only yields a *lower bound* for n_f.

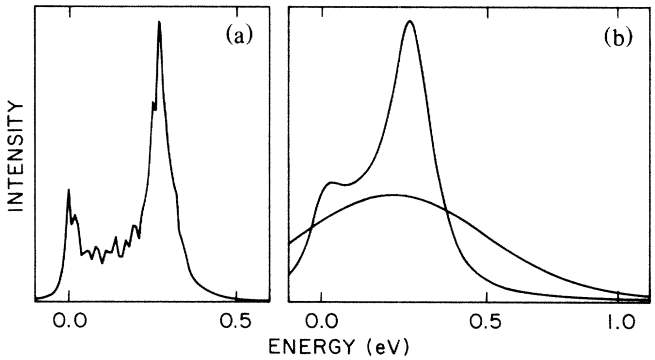

FIG. 2. Calculated $4f$-BIS spectra of YbP with (a) a thermal broadening $\Gamma=4kT$ of 20 meV corresponding to $T=60$ K, and (b) the same at room temperature, with and without the convolution with a Gaussian (FWHM $=0.5$ eV) to account for the instrumental resolution.

The photoemission data[14] show a multiplet structure corresponding to a $4f^{12}$ final state, starting with $^3H_6$ at $\simeq 6.2$ eV below E_F, and a negligible intensity at the Fermi level, pointing to a full phosphorus p band. Our computed XPS spectra are shown in Fig. 3. They consist of a large peak at the position of the first multiplet, obtained with $U=6.4$, and a smaller Kondo resonance above E_F. Since our variational calculation for the ground state ignores the excited $F_{5/2}$ level of the isolated impurity, we do not reproduce the spin-orbit sideband of the Kondo resonance computed by Bickers, Cox, and Wilkins.

In summary, we have presented a systematic method for determining the mixing parameters in the Anderson model for heavy-rare-earth materials. These results can be used in a GS calculation to produce valence XPS and BIS spectra given the one remaining undetermined parameter (U) which currently must be taken as adjustable. The approach accounts to a large extent for the concentrated nature

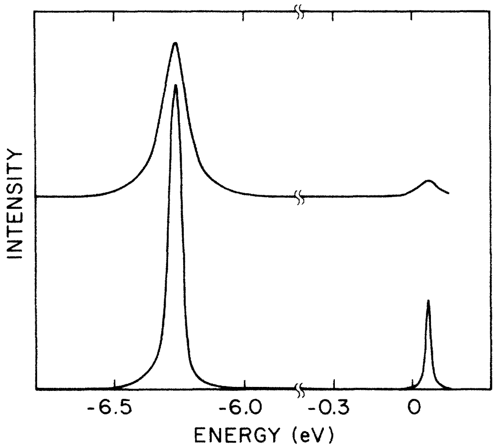

FIG. 3. Calculated $4f$-XPS spectra of YbP. Bottom curve: with a thermal broadening $\Gamma = 4kT$ of 20 meV, corresponding to $T \simeq 60$ K. Top curve: same at room temperature.

of the system, but ignores coherence effects, which is amply justified by the low ordering temperature (0.41 K) for this compound.[15] Through the use of a more realistic structure for the hybridization of the f level with the bands based on an *ab initio* calculations,[16] the GS parametrized model has been brought one step closer to a first-principles theory of high-energy spectroscopies.

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