Electronic and volumetric effects in ternary compounds of ytterbium

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We present complete results of self-consistent electronic-structure calculations of Yb-based and Lu-based ternary intermetallic compounds, namely, $YbCu_4Ag$, $YbCu_4Au$, $YbCu_4Pd$, and $LuCu_4Ag$. All these materials show a characteristic peak in the optical conductivity at about 2–2.5 eV. From the analysis of the allowed interband transitions among the calculated bands at the Γ point, we explain the origin of this peak. $YbCu_4Ag$ is a Kondo system with a high Kondo temperature. $YbCu_4$-Au and -Pd order magnetically below 1 K. We give an interpretation of the origin of the different degree of f-d hybridization observed experimentally in these Yb-based compounds. [S0163-1829(96)01543-3]

I. INTRODUCTION

The cubic isostructural compounds $YbCu_4M$ (with M=Ag, Au, Pd) have been recently investigated via spectroscopic measurements,[1] because of their possible Kondo-lattice properties. Optical measurements[1] have revealed a heavy carrier plasma edge, related to the Kondo temperature, in $YbCu_4Ag$ but not in the other two compounds. Actually, $YbCu_4Ag$ is considered a heavy fermion system with a Kondo temperature estimated[2–4] between 60 and 100 K. It is paramagnetic down to the lowest temperatures whereas $YbCu_4Pd$, and $YbCu_4Au$ order antiferromagnetically below 1 K.[5]

The different ground states observed in these compounds result from the competition between three interactions: the crystal field interaction, the magnetic intersite Ruderman-Kittel-Kasuya-Yosida, interaction, and the intrasite Kondo effect. In systems where the $s-f$ Anderson hybridization is effective, the crossover between magnetic order and moment suppression depends, in different ways, on the hybridization parameter $\Delta(E_F)$ (Ref. 6) and the density of states at the Fermi level $\rho(E_F)$, through the moment coupling parameter J. Both $\Delta(E_F)$ and $\rho(E_F)$ are strongly dependent on the unit cell volume. It is therefore possible, in principle, to drive the system from one regime to another with experiments under pressure.

Bauer *et al.* have performed such experiments measuring transport properties in $YbCu_4Ag$,[7] transport and magnetic properties in $YbCu_4Au$.[8] They have found that the Kondo temperature T_K decreases with pressure whereas the magnetic temperature increases with pressure. They also infer that for enough high pressure a magnetic instability should occur also in $YbCu_4Ag$ as observed in $Yb_xCu_{1-x}Al$ (Ref. 9) at 100 kbar.

The importance of volume in the Kondo effect or, more generally, in the Anderson hybridization has been investigated extensively in Ce systems. In particular, in previous extended theoretical calculations[10] on, presumably moderate, heavy fermion systems like CeAg, CeCd, and CeZn, we pointed out the role of strictly electronic vs strictly volumic effects on the Anderson hybridization. In that case, the higher number of valence electrons in CeAg with respect to CeCd and CeZn had a much stronger influence on the mag-

nitude of the hybridization than volume. In any case, compression always led to an increase of hybridization.

The situation of the present compounds is analogous to that of the Ce intermetallics. In fact, they also are cubic compounds of transition metals with decreasing lattice constant, in the order $YbCu_4$-Ag, -Au, -Pd (like CeCd, CeAg, CeZn). Moreover the crystals with Ag and Au are isovalent, whereas $YbCu_4Pd$ has one valence electron less than the other compounds. They are therefore suitable to study the interplay of volumic vs electronic effects on their electronic properties.

However, there is an important difference between Ce and Yb. Yb is an anomalous rare earth element with a divalent configuration Yb^{2+}, i.e., a nonmagnetic ground state $^1S_0$, stable at low temperature. The volume of Yb in the divalent state is substantially larger[11] than the one in the trivalent magnetic configuration $^2F_{7/2}$. A tendency of Yb ions to valence transitions has been observed in several Yb compounds. In particular, experiments with applied magnetic fields have shown a negative volume magnetostriction at the onset of the trivalent magnetic state,[12] whence a tendency of Yb to magnetize under compression.

On the other hand Ce has, in normal conditions, a stable trivalent configuration with a magnetic ground state $^2F_{5/2}$. External pressure is known to depress magnetism in Ce compounds[13] increasing f delocalization and enhancing the f-band width.

The above discussion applies, anyway, more to band magnetism, e.g., Stoner criterium, than to more complicated situations where competing intrasite and intersite effects determine the ground states, like in the case of systems with localized moments.

The aim of the present paper is to carry out a theoretical investigation to study the interplay of volumic vs electronic effects on the ground state electronic structure of $YbCu_4Ag$, $YbCu_4Au$, $YbCu_4Pd$. In particular, we shall try to understand the relevance of the $f-d$ hybridization through the series both with respect to the unit cell volume and to the effective conduction band occupancy. To this aim it turns out to be useful to compare with the f-full analog $LuCu_4Ag$, for which we also perform calculations. As far as the hybridization is concerned, we are aware that our present discussion is qualitative. A quantitative estimate of the hy-
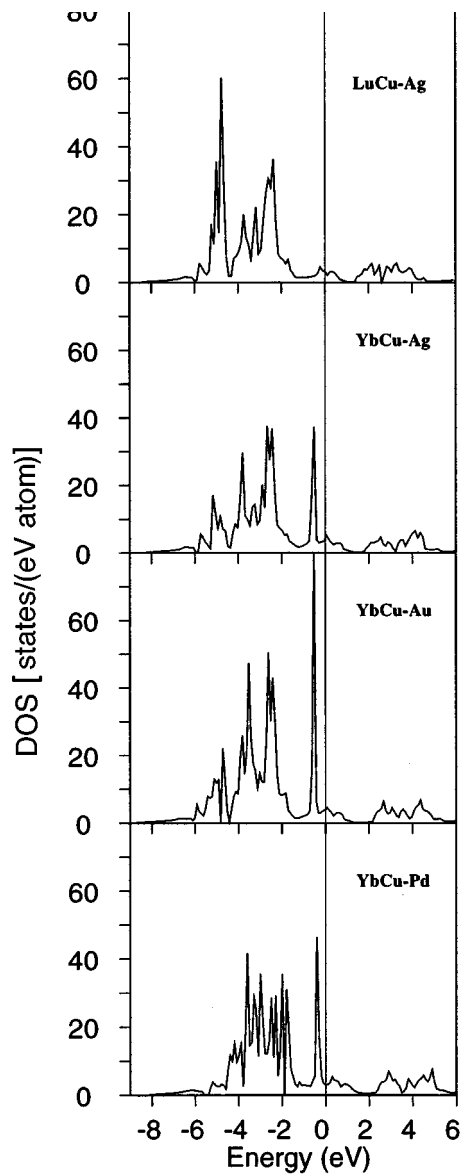
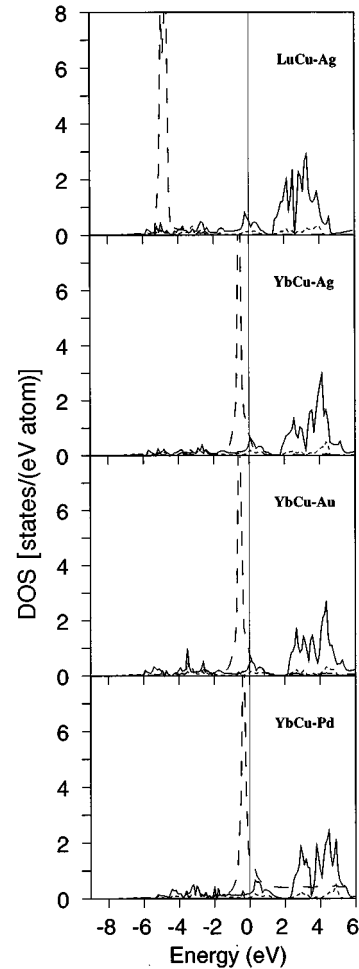FIG. 1. Total density of states for LuCu$_4$Ag (a), YbCu$_4$Ag (b), YbCu$_4$Au (c), and YbCu$_4$Pd (d).

FIG. 2. Partial density of states of f (long-dashed line), d (solid line), and p (dashed line) symmetry on the rare earth for LuCu$_4$Ag (a), YbCu$_4$Ag (b), YbCu$_4$Au (c), and YbCu$_4$Pd (d).

bridization in real materials is possible with techniques that overcome the intrinsic limitations of the local density approximation (LDA) (e.g., supercell calculations). However, we are interested in looking at the states involved in the hybridization and at its trend vs composition and volume: we therefore infer that the possible systematic error in the f-states position would not affect drastically our estimate. Moreover, it is known that in Ce and Yb compounds, as far as optical properties are concerned, possible renormalization effects on the hybridization matrix elements due to the correlation energy U are negligible[16,17] and of the order of unity.[18]

We presented very preliminary electronic-structure calculations of these compounds[14] and a short paper on the interpretation of the low temperature optical spectra of YbCu$_4$Ag and YbCu$_4$Au.[15] In the latter paper, we related many of the observed structures in the optical spectra to the allowed interband transitions deduced from band calculations. In particular, we assigned the characteristic optical structure at 2 and 2.4 eV in YbCu$_4$Ag and YbCu$_4$Au, respectively,[15] to a $\Gamma_4 \rightarrow \Gamma_3$ transition involving basically d states.

In the present work, we perform a symmetry analysis of the electronic states in order to find the allowed interband transitions for all the four compounds for further comparison with experiments. We restrict our analysis to interband transitions occurring at the point Γ in the energy range observed experimentally. Other points in the Brillouin zone may contribute to enhance the intensity of these transitions. The study of the paramagnetic phase in the analysis of the optical properties rather than the true magnetic ground state should not affect the results due to the very low ordering temperature and magnitude of the magnetic moments. Calculations have been performed at the experimental unit cell lattice constant for YbCu$_4$Ag, -Au, -Pd, and also at an expanded volume for YbCu$_4$Au, YbCu$_4$Pd, and LuCu$_4$Ag in order to check the volume-vs-electronic effect.

The paper is organized as follows: in the next section we present detailed results of the density of states (DOS's) of all compounds both at the experimental volume and at the YbCu$_4$Ag's volume, i.e., under expansion. In the third sec-
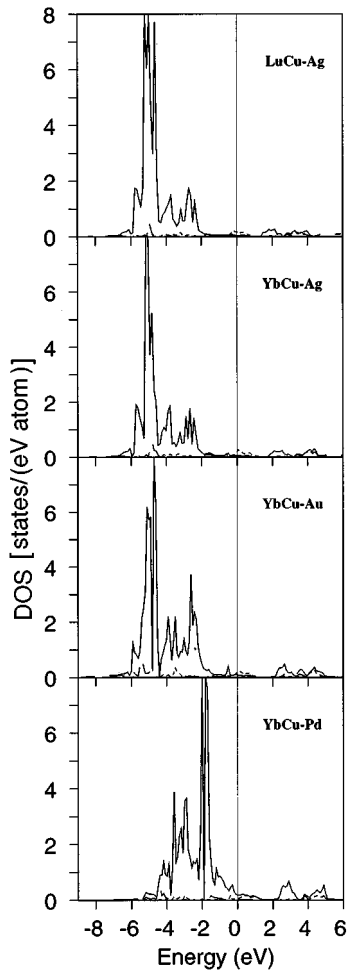
FIG. 3. Partial density of states of d (solid line) and p (dashed line) symmetry on Ag in LuCu$_4$Ag (a), Ag YbCu$_4$Ag (b), Au in YbCu$_4$Au (c), and Pd in YbCu$_4$Pd (d).

FIG. 4. Partial density of states of d (solid line) and p (dashed line) symmetry on Cu in LuCu$_4$Ag (a), YbCu$_4$Ag (b), YbCu$_4$Au (c), and YbCu$_4$Pd (d).

tion, we analyze the band structure giving details on the composition of the eigenvectors, according to the angular symmetry and atomic origin (charge character). On this basis we discuss the allowed optical transitions in the different compounds. Moreover, we discuss the reasons of the different strength of $f-d$ hybridization observed in these Yb-based compounds. In the final section, we discuss the results comparing with available experiments.

II. THE DENSITY OF STATES AND THE CHARGE DISTRIBUTION

The self-consistent calculations of the paramagnetic state for all the compounds have been performed using the *full-potential linearized augmented plane wave*[19] method within the (LDA) (Ref. 20) for exchange and correlation. The state density has been calculated using 60 and 80 special k points in the linear tetrahedron method.[21] All the compounds considered here are isostructural to MgSnCu$_4$, which has a fcc lattice with a basis of six atoms per unit cell. The experimental lattice costants are $a = 7.0814$, 7.0519, and 7.0396 Å for the systems with Ag, Au, and Pd, respectively.[22] Calculations at an expanded unit cell, equal to that of YbCu$_4$Ag,
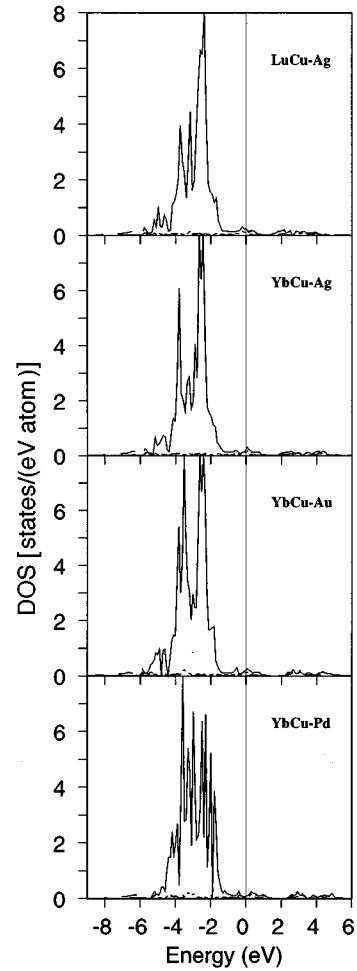
have also been done for Yb systems with Au and Pd and for LuCu$_4$Ag. The volume expansion corresponds to about 1% and 2% for YbCu$_4$Au and YbCu$_4$Pd, respectively.

We first focus on the spectral distribution of the electronic states. Figures 1–4 display plots of total and partial DOS's for the four compounds. A first glance to Fig. 1 indicates that the profile of the DOS's, in the energy range considered here, shows four main structures.

(A) At low energies there is a broad, quite intense structure extending from about -6 to -2 eV in all compounds. Inspection of the partial DOS's in Figs. 2–4 suggests that this structure can be attributed to essentially the sum of d states on Cu [Figs. 4(a)–(d)] and Ag, Au, Pd [Figs. 3(a)–(d)]. In LuCu$_4$Ag there is the additional superposition of the peak contributed by the full f shell of Lu [Fig. 2(a)].

(B) Approaching the Fermi energy, one finds the high narrow peak [Figs. 1(b)–(d)] due to the incomplete f states of Yb [Figs. 2(b)–(d)].

(C) The third important structure is the doubly peaked shoulder about 1.5 eV wide and roughly centered about E_F [Figs. 1(a),(b),(d)]. Notice that in YbCu$_4$Pd [Fig. 1(d)] this shoulder has shifted completely above E_F. This structure comes from d and p states mostly of Yb/Lu [Figs. 2(a)–(d)]

TABLE I. Angular momentum resolved integrated DOS per cell in the different muffin-tin spheres for the compounds considered.

Lu,Yb	s	p	d	f
LuCu$_4$Ag	0.53	0.53	1.26	14.08
YbCu$_4$Ag	0.46	0.46	0.90	13.79
YbCu$_4$Au	0.46	0.49	0.95	13.78
YbCu$_4$Pd	0.46	0.47	0.91	13.62
Ag, Au, Pd	s	p	d	f
LuCu$_4$Ag	0.43	0.32	9.0	0.01
YbCu$_4$Ag	0.45	0.28	9.01	0.01
YbCu$_4$Au	0.60	0.31	8.51	0.02
YbCu$_4$Pd	0.37	0.22	8.22	0.01
Cu	s	p	d	f
LuCu$_4$Ag	2.00	1.55	36.72	0.06
YbCu$_4$Ag	2.00	1.48	36.72	0.06
YbCu$_4$Au	1.98	1.51	36.79	0.06
YbCu$_4$Pd	1.98	1.47	36.78	0.06

and of the two metallic [Figs. 4(a)–(d)] atoms. The fact that this shoulder is present in Yb-based as well as Lu-based compounds indicates that it is quite independent of the hybridization of these states with f states at E_F. This is clearly confirmed by the plot of the partial DOS's on Lu [Fig. 2(a)], where no f states are present at E_F. The shift of the structure above E_F in YbCu$_4$Pd may be ascribable to the different number of non-f valence electrons with respect to the compounds with the noble metals. This emphasizes very well the importance of the nominal valence of the metallic components.

(D) The fourth structure in Fig. 1, roughly 3 eV wide and centered at about 3.5 eV is separated by a quasigap from the structure discussed in C. This structure is relevant to the optical spectra since it possibly represents the final states of dipole induced interband transitions.[15] In all compounds this structure shows a steep shoulder beginning at ≈ 2 eV: the distance between its lower edge and E_F is very close to the energy where the intense absorption peak is observed in the optical spectra of YbCu$_4$Ag,Au.[1,15] To assess the character of the states involved in this structure it is useful to look at the partial DOS's in Figs. 2–4: the major contribution is coming from d states on Yb [Figs. 2(b)–(c)] and Lu [Fig. 2(a)]. Experimental support to the DOS's described in points A, C, D comes from electron spectroscopy results by Kang *et al.*[27] discussed in the last section.

In what follows, we discuss the results obtained from the calculation of the partial DOS's per unit cell in the muffin-tin spheres at the Fermi level $\rho(E_F)$ and of the integrated charge $\int_{-\infty}^{E_F} \rho(E) dE$ for the different angular momenta ($l=s$, p, d, f) in the four compounds. In Table I we report data of the integrated density of states, within the muffin-tin spheres, for the different compounds and different l character.

The entries of Table I show negligible differences in the Yb-based compounds within the reasonable accuracy of the calculations. In particular, the number of occupied f states on Yb atom is practically the same (within $\simeq 1\%$), indicating

that the extra valence electron on Au and Ag with respect to Pd does not affect the total f occupancy significantly. In YbCu$_4$Pd, the lack of one s valence electron with respect to the other two compounds, affects the states on Pd a little. No appreciable differences occur on Yb or Cu. Finally, small differences essentially on Lu (within a few %) occur in LuCu$_4$Ag with respect to YbCu$_4$Ag. In particular, the total number of f electrons within the rare earth muffin-tin sphere increases by about 4% in the Lu system. This holds true even for the results obtained at the small expanded volume, reported above.

Concerning the DOS's at E_F as deducible from the plots in Figs. 1–4, we shall comment on the results with respect to two parameters, namely, the valence charge and the unit cell volume. In fact, important differences are found in the l-partial densities at the Fermi level.

(i) Let us first consider $\rho(E_F)$ on Yb atom. The f density depends inversely on the unit cell volume of the three compounds. It is found to be 72, 84 and 92 states/atom eV(10^{-2}) in YbCu$_4$Ag, Au, and Pd, respectively, but it grows considerably in YbCu$_4$Pd at the expanded volume, amounting to 136 states/atom eV(10^{-2}). The other l components are of comparable magnitude in the compounds with the noble metals, but change quite sensibly in YbCu$_4$Pd at both equilibrium and expanded volume. In particular, there is a depletion of s, p, and d states on Yb in the latter compound. Going over to $\rho(E_F)$ on Ag, Au, and Pd, we notice some differences for d states between Ag and Au and for p, d states between Ag/Au and Pd. Finally, comparing $\rho(E_F)$ on Cu we find a large decrease of all l components between the compounds with the noble metals and that with Pd. In fact, whereas in the systems YbCu$_4$Ag,Au the s, p, d, f density is of the order of 20, 55, 95, 0.9 states/atom eV(10^{-2}), in YbCu$_4$Pd there is a drop of 50–60 % of these values. On the other side the analogous quantities obtained at expanded volume show negligible differences.

(ii) It is very interesting now to focus on the results for the f-full system LuCu$_4$Ag. The electronic structure has been calculated at the same volume of the corresponding Yb-based system. Apart from the obvious drop of $\rho(E_F)(=2$ states/atom eV (10^{-2}) for f states on Lu with respect to Yb, there are relevant differences between the two systems in the s, p, and d DOS's on Yb and Lu atoms and in the s, p states on Ag and Cu. In particular, $\rho(E_F)$ of f and d states on Cu increases quite a lot in the Lu compound compared with the Yb one. In particular, the f density on Cu increases by 700% in the Lu-based compound. The latter datum, along with the decrease of $\rho(E_F)$ on Cu observed in YbCu$_4$Pd with respect to the two isovalent compounds, supports the idea that the states at E_F contributed by Cu are very sensitive to the number and symmetry of the external atomic configuration.

Altogether one can say that electronic effects (i.e., different number of valence electrons) affect largely the properties at the Fermi level, whereas volume (i.e., decreasing volume through the series, or expansion) affects only slightly the relative weight of the different l components in the charge distribution, with exception of $\rho(E_F)$ for f states on Yb.
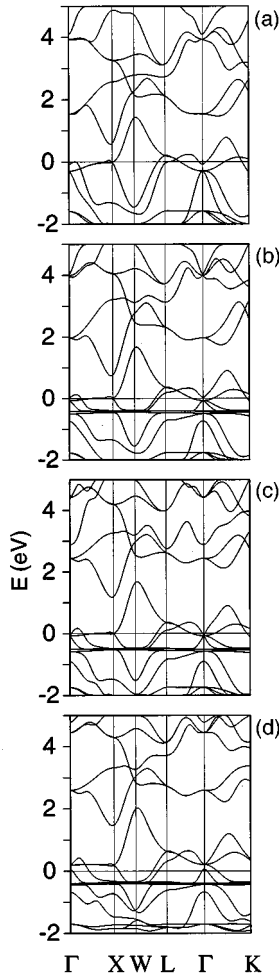
FIG. 5. Band structure of $LuCu_4Ag$ (a), $YbCu_4Ag$ (b), $YbCu_4Au$ (c), and $YbCu_4Pd$ (d).

III. BAND STRUCTURE, INTERBAND TRANSITIONS, AND HYBRIDIZATION

In this section, we present the band structure of the four compounds and a symmetry analysis of the electronic states. The goal is twofold.

First, we shall discuss the allowed electric dipole transitions for the interpretation of optical spectra. Second, we shall try to discuss at least qualitatively the degree of $f-d$ hybridization.

We have already reported the band structures of $YbCu_4Ag$ and $YbCu_4Au$ in a short paper.[15] The gross features of the two band structures are very similar to each other and to those of $YbCu_4Pd$. The states at lowest energy (from -8 to -6 eV) are characterized by a wide band with essentially s character of the three atoms. These are followed by the dense region of the d bands of Ag/Au/Pd and Cu between -5 and -2 eV, by the narrow f states of Yb near E_F (≈ -2 -1 eV), and by the region of the conduction states above it within $1-4$ eV.

The band structure of $LuCu_4Ag$ is characterized by the presence of the f states at low energy around -5 eV. These states are intermingled with d states of Ag and Cu. Finally, in both Yb- and Lu-based compounds, d states extend over a wide region above and below E_F hybridizing with antibonding s, p, and d states.

We shall focus on the region of energy ranging from -2 to 5 eV. The four panels in Fig. 5 display the energy bands for each compound calculated at the experimental lattice constant, except for $LuCu_4Ag$ obtained at $YbCu_4Ag$'s volume. The states included in this energy range are those more relevant to discuss the optical transitions and also the problem of the *hybridization*.

Since we need to know the symmetry and composition of the states with more detail, we have labeled the bands of Fig. 5 with the irreducible representation of the point group symmetry T_d at $k=0$. In the notation used,[23] the usual cubic harmonics, basis functions in the full cubic group O_h, have irreducible representations Γ_1, Γ_4 (threefold), and Γ_5 (threefold) for $l=3$, Γ_3 (twofold) and Γ_4 (threefold) for $l=2$, Γ_4 (threefold) for $l=1$, and Γ_1 for $l=0$. The basis functions of these five irreducible representations in T_d may have, however, different combinations of l,m components of spherical harmonics with respect to O_h.[23] Finally, we recall that the operator of the electric dipole has representation Γ_4.

The irreducible representation at Γ for the bands plotted in Fig. 5 are displayed in Table II along with the l character (%) of the eigenvectors. In the first column of each table we give progressive numbers to identify the different band manyfolds in order of decreasing energy. Comparing the band structure in Fig. 5 with the entries in Table II one can understand, at least at the Γ point, the origin of the differences among the compounds.

We first focus on the energy region $-0.5<E<4.5$ eV where interband transitions take place. This region is characterized in all compounds by the presence of empty states between 0 and 4.5 eV (see Fig. 5) belonging to the irreducible representations Γ_1, Γ_3, Γ_4 whose l character is given in Table II. The number of these bands varies, however, among the different compounds, as can be seen from the bold entries in Table II and in the plots of Fig. 5. In particular, we notice that $YbCu_4Pd$ has the highest number of empty states above E_F. The empty states common to the three Yb-based compounds by symmetry and composition are the Γ_4 triplet (2) in Ag and Pd systems, (1) in the Au system, and the Γ_3 doublet (3). The Γ_1 singlet (5) in $YbCu_4Pd$, (4) in $YbCu_4Ag$, Au is the first empty state for the Ag and Pd systems whereas it is occupied in the Au system.

Another interesting feature is the inversion of Γ_4 and Γ_1 highest states in $YbCu_4Au$ with respect to $YbCu_4Pd$ and $YbCu_4Ag$ where these bands are almost degenerate [see Fig. 5(b)]. In $YbCu_4Pd$ these states are well split apart, but the composition is quite different (see Table II). This inversion in $YbCu_4Au$ is joined by this analogous inversion between the second singlet and the triplet Γ_4 at the bands bottom (not reported). Both effects may be ascribed to the higher atomic weight of Au with respect to Ag or Pd which induces an inversion between bonding and antibonding states. The inversion at high energy affects the symmetry of interband transitions and has been observed in the optical spectra of $YbCu_4Au$.[15] In all Yb-based compounds the doublet Γ_3 is formed by more than 50% by d states of the Yb and of Ag/Au or Pd. Comparing $LuCu_4Ag$ with $YbCu_4Ag$ it is interesting to note that the states above E_F (see Table II) have a composition analogous to the corresponding states in $YbCu_4Ag$.

TABLE II. Irreducible representations at the Γ point for the energy bands reported in Fig. 5. Bold symbol denotes states above E_F. The l character of the major components in the eigenvectors is given at selected bands.

	YbCu$_4$Ag		YbCu$_4$Au	
1	Yb($s+f$ 9%)Ag(s 34%)Cu($s+d$ 9%)	Γ_1	Yb($p+d+f$ 12%)Au(d 10%)Cu($s+p+d$ 12%)	$\boldsymbol{\Gamma_4}$
2	Yb($p+d$ 14%)Ag(d 8%)Cu($s+p+d$ 13%)	Γ_4	Yb(f 5%)Au(s 36%) Cu($s+p+d$ 10%)	Γ_1
3	Yb(d 44%)Ag(d 11%) Cu(p 6 %)	$\boldsymbol{\Gamma_3}$	Yb(d 45%)Au(d 15%) Cu(p 5 %)	$\boldsymbol{\Gamma_3}$
4	Yb(f 39%)Cu(p 9%)	Γ_1	Yb(f 43%)Cu(p 8%)	Γ_1
5	Yb(d 21% f 17%)Ag,Cu($p+d$ 14%)	Γ_4	Yb(d 22% f 11%) Au,Cu($p+d$ 16%)	Γ_4
6	Yb(f 99%)	Γ_5	Yb(f 99%)	Γ_5
7	Yb(f 81%,d 5%)Ag,Cu(p 3%)	Γ_4	Yb(f 85% $p+d$ 4%)Ag,Cu(p 3%)	Γ_4
8	Yb(f 62%)	Γ_1	Yb(f 57%)	Γ_1
9	Cu(d 25%)	$\boldsymbol{\Gamma_5}$	Cu(d 25%)	$\boldsymbol{\Gamma_4}$
10	Cu(d 23%)	$\boldsymbol{\Gamma_4}$	Cu(d 23%)	$\boldsymbol{\Gamma_3}$
	LuCu$_4$Ag		YbCu$_4$Pd	
1	Lu($s+f$ 9%)Ag(s 32%)Cu($s+d$ 10%)	Γ_1	Pd(s 30%)Yb(1%),Cu(9%)	Γ_1
2	Lu($p+d+f$ 17%)Ag(d 8%)Cu($s+p+d$ 13%)	Γ_4	Yb(12%)Pd(12%)Cu(14%)	Γ_4
3	Lu(d 50%)Ag(d 12%)Cu(p 4%)	$\boldsymbol{\Gamma_3}$	Yb(d 43%)Pd(d 21%) Cu(p 4%)	$\boldsymbol{\Gamma_3}$
4	Lu($s+f$ 4%)Ag($s+f$ 2%)Cu($s+p+d$ 14%)	Γ_1	Yb($p+d+f$ 12%)Pd(d 12%)Cu($s+p+d$ 14%)	$\boldsymbol{\Gamma_4}$
5	Lu(d 29%)Ag($p+d$ 8%)Cu($p+d$ 8%)	Γ_4	Yb(f 35%)Cu(p 9%)	Γ_1
6	Cu(d 25%)	Γ_5	Yb(f 99%)	Γ_5
7	Cu(d 23%)	Γ_4	Yb(f 95%)	Γ_4
8	Cu(d 24%)	$\boldsymbol{\Gamma_3}$	Yb(f 66%)	Γ_1
9	Cu(d 24%)	$\boldsymbol{\Gamma_5}$	Cu(d 25%)	$\boldsymbol{\Gamma_5}$
10	Cu(d 23%)	$\boldsymbol{\Gamma_3}$	Pd(d 35%)Cu(d 13%)	$\boldsymbol{\Gamma_4}$

The results obtained so far may be used to predict at least some of the dipole allowed interband transitions in the four compounds. From a symmetry point of view, the allowed transitions are easily found from group theory. Tensorial multiplication among the representations of the initial states with the representation of the dipole operator gives the final states available to the transitions. Nothing may be said on the intensity of the transitions without explicit calculation of the matrix elements.

Since the typical medium-high energy conductivity spectrum of these compounds ranges from 1 to 6 eV,[1] it is reasonable to take as final states those indicated with bold characters in Table II, i.e., the bands plotted above E_F in Fig. 5. We take as initial states those included within one eV below E_F. Therefore we are led to consider possible transitions among initial states Γ_1, Γ_4, Γ_5 and final states Γ_1, Γ_3, and Γ_4. The following transitions are allowed: $\Gamma_1 \rightarrow \Gamma_4$; $\Gamma_4 \rightarrow \Gamma_1, \Gamma_4, \Gamma_3$; $\Gamma_5 \rightarrow \Gamma_3, \Gamma_4$.

A characteristic peak in the optical conductivity of the Yb-based compounds has been observed at about 2–2.5 eV.[1,15] Preliminary measurements[24] in LuCu$_4$Ag also indicate the presence of this characteristic peak. According to the present calculations we are led to ascribe the occurrence of this peak to interband transitions to the triplet Γ_3 above E_F from either occupied triplet Γ_4, Γ_5 closest to E_F. In particular, we think that the conductivity peak above is essentially due to the transition $\Gamma_4 \rightarrow \Gamma_3$ in YbCu$_4$Ag,Au and LuCu$_4$Ag, whereas in YbCu$_4$Pd it is presumably an indirect transition involving the same states but slightly aside the point Γ [see Fig. 5(d)]. As can be seen in Table II, the transition $\Gamma_4 \rightarrow \Gamma_3$ involves mainly initial states of hybridized f-d states of the rare earth with metallic states and final

states of mainly non-f origin. In LuCu$_4$Ag the f states in the initial Γ_4 triplet are replaced by Lu d states (see Table II). This interpretation is in agreement with the observation done in the preceding section when discussing the common structure of the DOS's in point D. As said at the beginning of the section, transitions at other symmetry points may also contribute to the intensity of the observed peaks as well as to other observed transitions. However, the band structure is such that not many contributions to the conductivity peaks in the energy range observed experimentally should have significant contributions from other lines than Δ and the surroundings of Γ along Λ and Σ. An analysis of the whole spectrum has been carried out for YbCu$_4$Ag and YbCu$_4$Au.[15] Thus, for example, it is easy to identify many other optical structure just by inspection of the band structures and Table I. There are six and four transitions to the empty states Γ_1, Γ_4, and Γ_3, from the states 5 to 8 in YbCu$_4$Ag. In YbCu$_4$Au there are five and four from the states labeled from 4 to 8.

We close the section with the discussion on the $f-d$ hybridization in the Yb-based compounds. As reported in the Introduction, a considerable Kondo temperature has been observed only in YbCu$_4$Ag. In the other two Yb compounds the ground state is magnetic, with a very low transition temperature. Pressure could possibly drive YbCu$_4$Au to a dense Kondo system, according to resistivity measurement.

The tendency of a system to have a large Anderson hybridization may be estimated from electronic calculations by considering the relative weight of f states in the density of states and in the eigenvectors near E_F. In fact, if we roughly assume that, for a fixed value of the total number of f electrons/Yb, the larger is $\rho_f(E_F)$ and the weaker is the hy-

bridization with other states, we may draw some qualitative conclusions on the three compounds. In the present case, since the number of f electrons/Yb is constant in the three compounds, the f-band hybridization is largest in YbCu$_4$Ag and decreases going to the compounds with a smaller volume. It decreases, however, also in the expanded Pd system. We may further support this criterion by the analysis of the eigenvectors of the bands involving Yb f states in Table II. Let us focus on the entries 4–7 of Table II, for the Yb-based systems.

In YbCu$_4$-Ag and -Au, the triplet Γ_4 (7) shows a strong mixing among d and f states of Yb and with other metallic states. This same triplet (7) is almost an unhybridized f state in YbCu$_4$Pd. The next triplet Γ_5 may be considered irrelevant to the hybridization in all compounds since it has 99% f character. It just contributes to increase the f DOS's at E_F. The next bands Γ_4 and Γ_1, entries 5, 4 in Table II, play a crucial role in determining the difference among the three Yb compounds. On one side the singlet Γ_1 has a similar composition in the three compounds with a strong presence of f states and appreciable presence of metallic states, stronger in the Ag and Au systems. On the other side, the Γ_4 triplet shows a large mixing of f states in the silver and golden systems with an intra-atomic hybridization among d and f states of Yb, much weaker in the Pd system. Moreover, inspection of the plots in Figs. 5(b)–(d), shows that this triplet Γ_4 is above the Fermi energy at $k=0$ in YbCu$_4$Pd and thus it does not contribute to $\Delta(E_F)$ and $\rho(E_F)$. It is close to E_F but separated from it by the singlet Γ_1 in YbCu$_4$Au, whereas it is the closest state to E_F in YbCu$_4$Ag. Therefore in YbCu$_4$Ag the Fermi surface crosses larger portions of the state Γ_4 where the hybridization is high. Thus, we conclude that the relative position of the triplet Γ_4 and singlet Γ_1 is a qualitative but strong indication of the origin of the different strength of the Anderson hybridization in these compounds.

It is interesting to see how the same states Γ_4 and Γ_1 are modified in LuCu$_4$Ag with respect to the Yb-based compound. This shows how the analysis of the eigenvectors is crucial to really understand the electronic structure of apparently similar band structures.

IV. CONCLUSIONS

In the present paper, we have determined the detailed electronic structure of YbCu$_4$Ag, Au, Pd, and LuCu$_4$Ag in order to highlight the interplay between electronic and volumic effect. We have also tried to estimate the different role of the Anderson hybridization in the three compounds as one of the causes of the high Kondo temperature observed only in YbCu$_4$Ag.

We conclude that the origin of the different ground states observed in these compounds is not due to the difference in volume. Electronic effects play by far a more important role. Regarding the hybridization, our calculations support that it is most effective in YbCu$_4$Ag, important in YbCu$_4$Au, and much weaker in the YbCu$_4$Pd, as also suggested by other authors.[7,8,5]

Many of the results obtained in the preceding sections

may be compared to existing experiments. In particular, we have interpreted a characteristic peak measured in the optical spectra[1] of YbCu$_4$Ag, Au, and Pd by an interband transition, direct or indirect, associated with initial states of mixed d and f character (Γ_4) and final states of essentially d character (Γ_3) (see Table II). An analogous conclusion may be drawn comparing the results of LuCu$_4$Ag with preliminary results of its conductivity spectrum.[24] In this case, the f states in the initial state Γ_4 are replaced by Lu d states (see Table II). Moreover, according to the results of band calculation[25] of isostructural YbCu$_4$In, the characteristic peak observed in the optical spectra by Marabelli and Bauer[26] at $\simeq 1.2$ eV, may also be interpreted as due to the same transitions as in the present compounds.

An interesting comparison may be done between the electronic structure obtained presently and the results of electron-spectroscopy by Kang et al.[27] In their paper, the authors aim to ascertain the presence of a Kondo resonance in the photoemission (XPS) and bremsstrahlung (BIS) spectra of the three Yb-based compounds, using the corresponding Lu-based compounds as a reference.

They conclude that the Yb ion is nearly trivalent in the three compounds, especially Pd, for which the Kondo resonance is practically absent in the BIS spectrum. For Au and Ag, the observed weak resonance may point to the existence of a Kondo energy scale characterized by T_K. In any case, T_K is largest in the Ag system and smallest in the Pd system. This conclusion agrees qualitatively with our findings of the preceding section and with recent results from resistivity experiments.[7,8] However, their suggestion of a very small T_K in YbCu$_4$Ag is in contrast with the findings of other authors.[1,4,7]

We find a good agreement between the calculated DOS's in Figs. 2–4 and the XPS spectra. Focusing on the occupied states, Kang et al.[27] assign Ag d states in LuCu$_4$Ag around -7 to -5 eV, which is comparable to our results in Fig. 4(a). For the three Yb-based compounds, the Cu $3d$ and Pd $4d$ states are located between -5 and -2 eV in the XPS spectra of YbCu$_4$Pd, whereas Ag $4d$ and Au $5d$ states are found between -7 to -5 eV. Comparing these results with the DOS's in Figs. 3(b)–(d), we see that indeed the Pd d states lie at higher energy with respect to the two partner compounds.

Turning to unoccupied states, Kang et al.[27] recognize the presence of Yb/Lu $5d$ states above E_F. They also underline that the Cu and Ag/Au/Pd d states do not play an important role at E_F whereas s, p states do. This agrees with the discussion in the preceding section.

One should not attempt to compare the f DOS's with the BIS spectra, since LDA electronic calculations are known to fail in giving the correct binding energy of the resonant f states at the correct energy with respect to E_F. However, in the case of Yb metal, photoemission measurements by Lang et al.[28] have shown that the energy corresponding to the XPS energy of the f state is -1.27 ± 0.1 eV with respect to E_F. This value, corresponding to the bare f states renormalized by the effect of the hybridization and correlation in the Anderson model, is not very different from what we find and falls in the energy range obtained in the photoemission data by Kang et al.[27]

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