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Empty and filled valence-electron states of Lu–transition-metal compounds: An uv spectroscopy study

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A joint uv-photoemission ($h\nu=21.2$ and 40.8 eV) and inverse-photoemission ($h\nu=11-17$ eV) spectroscopy investigation is reported on Lu and some Lu–transition-metal (M) compounds, namely $LuCo_2$, $LuRh_2$, and Lu_7Rh_3 focused on the Lu and the M d-derived filled and empty electron states. The analysis is performed by considering the substitution effects of a $3d$ with a $4d$ M partner ($LuCo_2$ vs $LuRh_2$) and by changing the stoichiometry and structure within the Lu-Rh phase diagram ($LuRh_2$ vs Lu_7Rh_3 vs pure Lu). In $LuRh_2$ the electron states, both below and above the Fermi level (E_F), appear at lower energy (i.e., more bounded) as compared to $LuCo_2$. Lu_7Rh_3 shows a strong narrowing of the Rh d band below E_F, due to a strongly decreased Rh-Rh interaction whereas above E_F a similarity with pure Lu at high-electron energies and a significant redistribution of the Rh $4d$ states are observed. A critical discussion of the results considering (i) the crystal structures and the atomic coordinations, and (ii) thermochemical estimations is performed. A comparison of the $LuCo_2$ data with published theoretical results indicates that the d-derived empty electron states are appropriately described within a single-particle picture at variance with the d occupied states for which remarkable discrepancies between theory and experiment are found probably due to the larger radial extent and more pronounced delocalization of the antibonding empty states with respect to the filled states. Some general consequences of these effects will be discussed.

I. INTRODUCTION

The spectroscopic study of rare-earth (R) metals and their compounds has attracted a great deal of interest in the past years, and a lot of information has been obtained by means of different spectroscopies.[1] The case of R-transition-metal (M) compounds has been thoroughly investigated both experimentally[2] and theoretically[3] (particularly for Ce compounds because of the greater hybridization of Ce $4f$ states with the valence states, compared to the other R's), and interesting phenomena connected to the interaction of the $4f$ electrons and the environment have been put into evidence (e.g., valence fluctuations in a variety of compounds). The study of these important problems took advantage of the generally strong $4f$ signal intensities present in both photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES). On the other hand, this makes access to the d-derived electron states more difficult, so that far fewer works have been dedicated to the more delocalized d states which are responsible for most of the chemical interaction in these compounds. Among them an important case is represented by RPd_3 compounds,[4–6] where split-off narrow d states have been detected above the Fermi level (E_F). Furthermore in a recent work[7] on d-sensitive photoemission from a variety of RCo_2 Laves phases (R=Y, Ce, Pr, Nd, and Sm) the full legitimacy of a bandlike description for the occupied d states has been questioned.

It is thus timely to investigate further the d states in R-M compounds by exploiting both occupied and empty states spectroscopy in the d-sensitive regime through ultraviolet PES and IPES at different photon energies. Here we approach this problem by studying Lu compounds: the Lu $4f$ shell is completely filled with a binding energy (BE) of the $4f$ core level of about 10 eV,[8] therefore eliminating any ambiguity in disentangling the f- and the d-like contributions to the spectra at variance with the case of other R's. In this field we have selected two topics.

(i) The substitution of a $3d$ with a $4d$ M partner belonging to the same column of the Periodic Table in the very important case of cubic Laves phases; thus we have chosen $LuCo_2$ and $LuRh_2$. Note that these compounds are also important for their magnetic properties.[9]

(ii) The change of stoichiometry and structure among systems belonging to the same phase diagram; thus we have compared $LuRh_2$ with Lu_7Rh_3, taking advantage of the strong excitation cross section for the Rh $4d$-derived states, and of the great effects expected in the occupied d region which is much wider than in $LuCo_2$. To this end we have added measurements for elemental Lu as well.

We rationalize the experimental trends in terms of the hybridization variations among the states of nearby atoms; in particular we show and explain the strong shift of the d-derived features toward lower kinetic energies (KE's), for both occupied and empty states, upon substitution of the $3d$ with the $4d$ M partner in an isostructural situation ($LuCo_2$ vs $LuRh_2$), and the marked narrowing of the occupied d density of states (DOS) together with

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the presence of a Rh d-like signal at energy as high as ~ 3 eV above E_F upon Lu enrichment (Lu_7Rh_3 vs $LuRh_2$).

Moreover we compare the experimental results for $LuCo_2$ with partial-density-of-states (PDOS) calculations[10] for an isostructural model system such as YCo_2, finding good agreement in the energy region above E_F, and some remarkable discrepancies below E_F, thus arguing that, for these compounds, a single-particle picture of the electron states is more appropriate for describing the empty states which have a larger spatial extension compared to the occupied states.

II. EXPERIMENT

A. The apparatus

The experimental apparatus consists of three chambers for the sample preparation and the IPES and PES measurements.

The IPES spectrograph[11] is based on an ultraviolet grating, dispersing photons with $h\nu$ in the 10–25-eV range on a flat field. Spectra are collected by scanning the electron energy (isochromat mode); for a given sample the spectra at various photon energies are acquired simultaneously so that they are strictly comparable. The full width at half maximum (FWHM) is between ~ 0.4 and ~ 0.9 eV in the $h\nu$ range 12–25 eV (Ref. 11). Pt spectra have been taken for the energy calibration[12] during the same experiment. The spectra are normalized on line to the current impinging onto the sample.

Photoelectron spectra have been measured with a 150-mm hemispherical analyzer using He I and He II radiation ($h\nu = 21.2$ and 40.8 eV, respectively) with FWHM=0.25 eV. The He II satellites have very little influence on the measurements, and their contribution has been removed from the spectra. Also an x-ray source (with Mg $K\alpha$ and Al $K\alpha$ lines) was available.

The rather broad angular definitions both in IPES and PES together with the polycrystalline nature of the samples ensure that all the measurements are **k** integrated.

B. The samples

Polycrystalline samples have been prepared by induction melting from stoichiometric amounts of the components in Ta crucibles after Ar purging. They were annealed at 800–900 °C for several days to obtain homogeneous polycrystals; the quality has been checked by x-ray diffraction and microprobe analysis. In Table I the crystal structures, the number (n) and distance (d) to the nearest-neighbor atoms (for the Lu and M sites) are given for the various compounds investigated, together with the heat of formation (ΔH) estimated according to the Miedema scheme.[13] The two Laves phases ($LuCo_2$ and $LuRh_2$) have the same crystal structure with very similar lattice parameters. In Lu_7Rh_3 the average[14] Lu-Lu coordination is very similar to that of pure Lu; moreover a small Lu-Rh bond length is present, while the Rh atoms are far from each other.

C. surface preparation and analysis

All the samples have been mechanically scraped *in situ* by means of a diamond file at a pressure lower than 5×10^{-10} mbar. The base pressure during the data collection was lower than 2×10^{-10} mbar. With a current density of $\sim 50\ \mu A/cm^2$ for the IPES measurements, we did not notice any extra contamination connected with electron bombardment. The main contribution to surface contamination at room temperature comes from surface segregation of impurities from the interior of the sample; this has been avoided by scraping and keeping the samples at ~ 100 K during the measurements without any temperature increase. Sample cleanliness has been checked via the O 1s and C 1s signals (by x rays), and the O 2p signal at about 6 eV below E_F (by uv radiation). No signal was detectable from the O 1s and C 1s core levels. From the O 2p signal an amount of contaminant lower than 0.05 layer has been estimated after $\sim$1-h acquisition. For safety the acquisition time on each clean surface has been limited to ~ 30 min. The sum of these acquisitions on each sample is presented in the IPES data given below.

A very important point is that the surfaces of the samples under study have shown the same stoichiometry of the bulk within an experimental accuracy of a few percent; this has been accurately checked by use of core-level peak intensities of x-ray PES.[15]

III. EXPERIMENTAL RESULTS

An overview of all PES results is given in Fig. 1, summarizing the spectra measured at two different photon energies, i.e., 40.8 (lower panel) and 21.2 eV (upper

TABLE I. Summary of the structural types and crystal parameters of Lu, $LuRh_2$, $LuCo_2$,and Lu_7Rh_3. The number n of nearest-neighbor atoms and the relative distances d are given for both Lu and the transition-metal (M) sites. Due to the presence of three slightly different inequivalent Lu sites, the corresponding numbers for Lu_7Rh_3 are given as mean values. In the last column is also listed the heat of formation (ΔH) estimated for each compound according to the Miedema scheme (Ref. 13).

		Lu				M				
	Structure	Lu-Lu		Lu-M		M-M		M-Lu		$-\Delta H$
Compound	type	n	d (Å)	n	d (Å)	n	d (Å)	n	d (Å)	(Kj/mol)
Lu	hcp	12	3.51							
$LuCo_2$	$MgCu_2$	4	3.08	12	2.95	6	2.51	6	2.95	38
$LuRh_2$	$MgCu_2$	4	3.21	12	3.08	6	2.62	6	3.08	79
Lu_7Rh_3	Th_7Fe_3	11.3	3.6	2.6	2.8	6	4.3	6	2.8	59

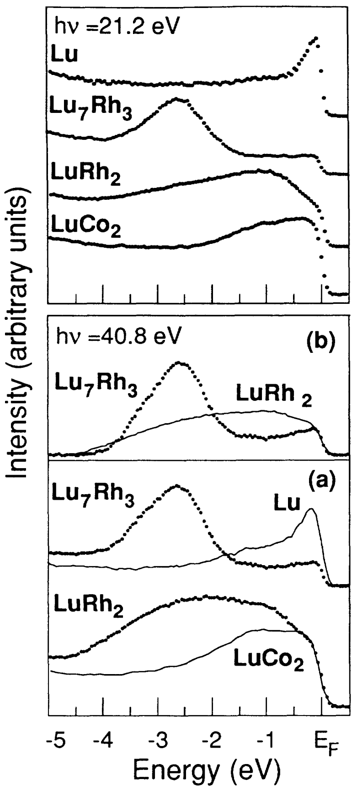

FIG. 1. Summary of PES results for LuCo$_2$, LuRh$_2$, Lu$_7$Rh$_3$, and pure Lu excited with He II ($h\nu$=40.8 eV—lower panel), and with He I ($h\nu$=21.2 eV—upper panel). For the intensity normalization of the spectra, see the text.

panel). A close similarity between the two sets of spectra is apparent. The normalization of the spectra at $h\nu$=40.8 eV proceeds as follows.

(i) In Fig. 1(a) two pairs of spectra are compared (LuCo$_2$ vs LuRh$_2$ and Lu$_7$Rh$_3$ vs Lu); within each pair the spectra are normalized to the same area of the Lu $4f$ level (not shown), i.e., basically to the same Lu concentration;

(ii) In Fig. 1(b) the spectra of LuRh$_2$ and Lu$_7$Rh$_3$ are compared after normalization to the same Rh atomic concentration; this has been achieved from the spectra normalized to the same Lu $4f$ area by multiplying the Lu$_7$Rh$_3$ spectrum by the stoichiometry factor $(\frac{7}{3})\times 2=4.7$; in this case the spectra are shown after subtraction of an integral background.

For $h\nu$=21.2 eV the $4f$ signal is very small and superimposed to the secondary electron signal, so that the above normalization is not possible and the spectra are arbitrarily normalized to the same height.

Some facts are immediately evident from the results of Fig. 1: the valence-band (VB) signal is broader in LuRh$_2$ than in LuCo$_2$, resulting in a higher BE position for the VB centroid (-1 eV for LuCo$_2$ and -1.8 eV for LuRh$_2$); moreover the VB emission is much stronger in LuRh$_2$ than in LuCo$_2$ relative to the same Lu concentration. In Lu$_7$Rh$_3$ a pronounced narrowing of the VB is seen with the peak position located at ~2.5 eV below E_F, i.e., much deeper in energy than the main peak of elemental Lu.

The counterpart of the previous results in terms of empty state spectroscopy is summarized in Fig. 2, where the three panels refer to LuCo$_2$, LuRh$_2$, and Lu$_7$Rh$_3$ compared with pure Lu. The IPES results are shown at three different $h\nu$'s: 11.7, 13.4, and 17.1 eV. For $h\nu$'s higher than ~17 eV the spectral shapes do not undergo remarkable modifications and therefore are not presented here. LuRh$_2$ shows, at all $h\nu$'s, a well-defined structure close to E_F (with an increasing intensity at higher $h\nu$'s) followed by a broad structure having a maximum at ~3.3 eV above E_F. In LuCo$_2$ at $h\nu$=11.7 and 13.4 eV, two structures are seen close to E_F together with a broad feature similar to that displayed by LuRh$_2$ but clearly peaked at higher energy (~4.6 eV above E_F), whereas the spectrum at $h\nu$=17.1 eV appears quite featureless. The IPES spectra of Lu$_7$Rh$_3$ show a broad structure clearly visible in all spectra, including pure Lu, with a maximum at ~5.7 eV, i.e., a much higher energy than in LuRh$_2$. Moreover in Lu$_7$Rh$_3$ an extra feature appears at about 3 eV showing a strong $h\nu$ dependence.

In the inset of Fig. 2 we show a typical IPES Pt spectrum ($h\nu$=21 eV) measured in the same run; the narrow d-holes Pt peak (FWHM=0.7 eV) shows that the spectral

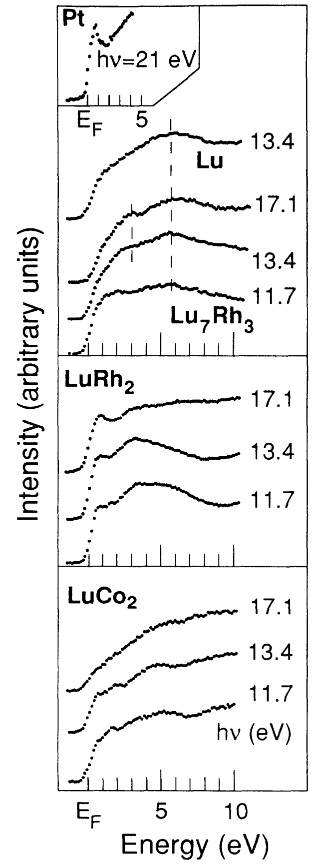

FIG. 2. Summary of IPES results from LuCo$_2$, LuRh$_2$, Lu$_7$Rh$_3$, and pure Lu measured in the isochromat mode at three photon energies (11.7, 13.4, and 17.1 eV). The inset gives the IPES spectrum for pure Pt at $h\nu$=21 eV.

features width detected at high $h\nu$'s in the Lu-based compounds is not due to instrumental limitations.

IV. DISCUSSION

The chemical bonds in the present compounds involve a low *d* occupancy atom (Lu) and a much higher *d*-occupancy atom such as Co and Rh. Thus we expect some analogy to the intermetallics of near-noble metals (Ni and Pd) and low-occupancy *d* atoms studied extensively by Fuggle *et al.*;[16] as a guideline we will extend this scheme to the present case. When Pd (or Ni) is diluted in early *d* hosts (including *R*'s) its *d* states are strongly hybridized with the *d* state's partner element, while retaining some unoccupied states. This results in a decreased width of occupied *d* bands with respect to elemental Pd (Ni), with a centroid shift to larger BE's. In the present case the *d* occupancy is lower than in Ni and Pd, and this should result in a larger fraction of *M d*-derived empty states. Therefore we can qualitatively expect that the occupied *d* DOS's have a dominant Co (Rh) character with a redistribution of the small Lu *d* contribution to higher BE's than in Lu metal. On the other hand, we expect that the empty region well above E_F is dominated by Lu *d*-derived states, and that in the intermediate region, i.e., just above E_F, a contribution from empty Co (Rh) *d* states is present.

Within this framework one can therefore address the nature of the *d* states, including arguments about the excitation cross sections, and the legitimacy of a bandlike description for these states.

A. Orbital assignments and excitation cross sections

(i) Both experimental solid-state cross sections of *d*- vs *sp*-derived states[17] and qualitative considerations of the calculated atomic dipole cross sections[18] show that our spectra are basically sensitive to states originated by *d* orbitals; thus they will be interpreted in terms of *d*-state excitations.

(ii) In all the compounds investigated here the main spectral features both in PES and IPES are seen in a rather broad $h\nu$ range, and appear basically at a constant energy referred to as E_F. It is therefore reasonable to neglect joint-density-of-states effects on the position of the features.

(iii) The stronger emission of $LuRh_2$ compared to $LuCo_2$, at the same Lu concentration, shown in Fig. 1(a) is consistent with a dominant *M d* contribution to the VB region, as anticipated above, and with a larger Rh 4*d* than Co 3*d* cross section (Ref. 18). Moreover in the $LuRh_2$ vs Lu_7Rh_3 comparison of Fig. 1(b), normalized to the same Rh concentration, the areas below the two VB spectra have about the same value, suggesting that the Rh 4*d* cross section is not significantly influenced by solid-state effects, at variance with other compounds.[19] Thus the atomic cross sections can be used for an estimation of the Lu 5*d* vs Rh 4*d* PES sensitivity, which should increase on going from $h\nu=40.8$ to 21.2 eV by factors of ~5 (with Co) and ~8 (with Rh). This rules out the presence of a relevant Lu 5*d* PES signal, which would therefore result in a severe modification of the VB line shape, between the He I and He II spectra.

(iv) In IPES results for $LuRh_2$ (Fig. 2) the increasing intensity vs $h\nu$ shown by the feature close to E_F, and the opposite trend found for the broad structure well above E_F, are consistent with the previously mentioned general scheme, i.e., with a sizable Rh 4*d* contribution near E_F and a dominant Lu 5*d* contribution at higher KE; in fact the calculation atomic Rh 4*d* cross sections increase with $h\nu$ while the Lu 5*d* cross sections decrease in this $h\nu$ range (Ref. 18). Considering this cross-sections behavior vs $h\nu$, the Lu_7Rh_3 IPES feature at ~3 eV above E_F (Fig. 2) can be interpreted as a mostly Rh-like signal. This large extension of the Rh *d* states above E_F compared to pure Rh is consistent with the significant redistribution of the empty Rh *d* states due to the strong Rh-Lu interaction (see Table I). A similar feature is not detected in diluted *R*-Pd (and *R*-Ni) compounds[20] due to the greater *d* occupation of Ni and Pd.

(v) In $LuCo_2$ IPES we see clear features at low $h\nu$'s while the spectrum at 17.1 eV is featureless; this cannot be due to experimental resolution, as already discussed (see inset of Fig. 2), and could be connected to similar effects reported in uv IPES from some low-*d*-occupancy *M*'s.[21]

(vi) The IPES measurements on pure Lu, displayed in Fig. 2 for $h\nu=13.4$ eV, show some discrepancies with previous x-ray bremsstrahlung isochromat spectroscopy (BIS) results;[2] these differences cannot be attributed to the increased *f* sensitivity of the x-ray spectroscopy compared to the uv measurements reported herein because, due to the f^{14} configuration of Lu, in both cases the spectra are mainly sensitive to the *d*-derived states. A closer comparison indicates that in both spectra the most intense peak is clearly visible at ~6 eV above E_F, while the structure located at ~2 eV in BIS is seen only as a slope change in IPES, and the minimum at ~4 eV disappears in the uv spectrum. A similar effect on going from uv to x-ray IPES has been previously reported for a number of *M*'s (Refs. 21 and 23) including the case of early 5*d M*'s (e.g., Hf, Ta, and W). These works have interpreted the aforementioned differences mainly in terms of a more efficient electron-hole pair production in the uv IPES which results in a more intense background, and have shown that adding a proper background to the theoretical DOS calculations almost completely fills the minimum in the DOS placed around 3–4 eV above E_F, in agreement with the experimental results. The case of Lu can be placed in the same framework, and gives further experimental support to these systematic IPES vs BIS line-shape variations.

B. General properties of the *d* DOS

Having assigned the dominant contributions to the measured spectral features, one can now discuss the main differences between the compounds herein investigated according to the two topics mentioned in Sec. I.

(i) In the $LuCo_2$ vs $LuRh_2$ comparison one finds a marked shift of the occupied valence *d* states to a higher BE in $LuRh_2$, together with a corresponding shift (about 1.3 eV) to a lower energy of the main structure in empty states. We interpret the BE gain of the $LuRh_2$ states below E_F in terms of the larger spatial extension of the Rh 4*d* wave function compared to the more contracted Co 3*d* wave function; on the basis of the Herman and Skillman[24] atomic wave functions it is easily seen that the increase in spatial extension is definitely larger than the increase in the interatomic distance, so that the average hybridization is stronger in $LuRh_2$ than $LuCo_2$. It is noteworthy that this trend is in qualitative agreement with the estimations for ΔH (Table I), giving double the value for $LuRh_2$ (-79 Kj/mol) as for $LuCo_2$ (-38 Kj/mol). Note that the broadening and the average shift of the occupied *d* states in $LuRh_2$ cannot simply be attributed to the small increase of the spin-orbit splitting ($\Delta E_{\mathrm{s.o.}}$) in the atomic base ($\Delta E_{\mathrm{s.o.}}[\mathrm{Co}]=0.23$ eV and $\Delta E_{\mathrm{s.o.}}[\mathrm{Rh}]=0.44$ eV). We point out that a trivial interpretation of this energy shift in terms of a larger Rh *d* occupation compared to Co, reminiscent of the different configurations in isolated atoms (d^8 in Rh and d^7 in Co) has to be ruled out; in fact many theoretical studies of R-M_2 Laves phases have shown that the energy position of the DOS features is largely dependent on the crystal structures, which in this case are strictly equivalent, and it si quite insensitive to the *d* occupation of the *M* partner.[25] Furthermore it is worth noting that in pure metals Co and Rh have calculated *d* occupations of 7.87 and 7.99, respectively,[26] i.e, very similar values.

The shift of the main empty peak in $LuRh_2$ with respect to $LuCo_2$ is consistent with the above argument; in fact this structure is mainly due to Lu 5*d* states, and in $LuRh_2$ the Lu-Lu nearest-neighbor distance increases with respect to $LuCo_2$, suggesting a trend toward lower energies because of the smaller hybridization, in analogy with theoretical results for $CeRu_2$, where the *d* DOS extracted from a published calculation[27] shows a feature at ~ 3 eV above E_F,[28] i.e., to significantly lower energy than for *R* compounds with 3*d* *M* partners (Ref. 10).

(ii) In the Lu_7Rh_3 vs $LuRh_2$ comparison the dominant Rh 4*d* contribution to the occupied states is dramatically narrowed upon increasing Rh dilution. We explain this fact, which shows some analogies to the case of dilute Ni and Pd *R* compounds (Ref. 16), as the consequence of the strong reduction of the Rh-Rh 4*d* wave-function overlap compared to $LuRh_2$. On the other hand, it should be noted that PES results for Lu_7Rh_3 show a small DOS close to E_F without any clear peak similar to the narrow structure of elemental Lu; this is consistent with the small Rh-Lu nearest-neighbor distance in Lu_7Rh_3 which is responsible for a considerable redistribution of the Lu 5*d* occupied states in the VB. The narrowing of occupied states in Lu_7Rh_3 has no counterpart in the empty states; in fact the main IPES feature of Lu_7Rh_3 is similar to that of Lu metal, showing a rather broad feature centered at about 5.7 eV above E_F. This analogy can be understood in terms of the similarity of the Lu-Lu coordination between the two cases (Table I). Furthermore in Lu_7Rh_3 IPES the structure close to E_F, mainly related to the Rh *d* states, is less pronounced than in $LuRh_2$ due both to the smaller Rh concentration and to the broader distribution of the Rh 4*d* empty states as mentioned above. These observations indicate that, for crystallographic reasons, the upper part of the Lu empty *d* states is much less sensitive to the presence of Lu-Rh bonds than the lower (occupied) *d* states.

C. Comparisons with YCo_2

Y-M_2 Laves phases are expected to be excellent models for Lu-M_2 Laves phases since the Y 4*d* and Lu 5*d* atomic wave functions have very similar radial widths; this similarity is even stronger than for any other lanthanide 5*d* wave functions. Moreover YCo_2 and $LuCo_2$ have the same crystal structure and very similar lattice parameters ($a=7.1$ Å in $LuCo_2$, and $a=7.2$ Å in YCo_2). Note also that the similarity between PDOS's of YCo_2 and $LuCo_2$ has been documented theoretically (Ref. 25). For these reasons we will use published theoretical results for YCo_2 (Ref. 10), performed in a tight-binding *d*-band model, to compare with our experimental results for $LuCo_2$. More recently better theoretical results have become available, in a narrower energy range, such as linear muffin-tin orbital atomic sphere approximation (LMTO-ASA) calculations in the local-spin-density (LSD) approximation of Ref. 7, which, in the case of YCo_2, give perfectly consistent results with those of Ref. 10 used here, thereby supporting the present choice. To the authors' knowledge, calculations for $LuRh_2$ and YRh_2 are not available, and calculations for $LuCo_2$ have not been published in the wide energy range needed to discuss our data. Thus the above discussion of the differences between $LuCo_2$ and $LuRh_2$ cannot be improved on a theoretical basis at present.

Figure 3 shows a comparison of the $LuCo_2$ PES ($h\nu=40.8$ eV) and IPES ($h\nu=13.4$ eV) experimental results (dotted) with the calculations of Ref. 10 (thin lines),

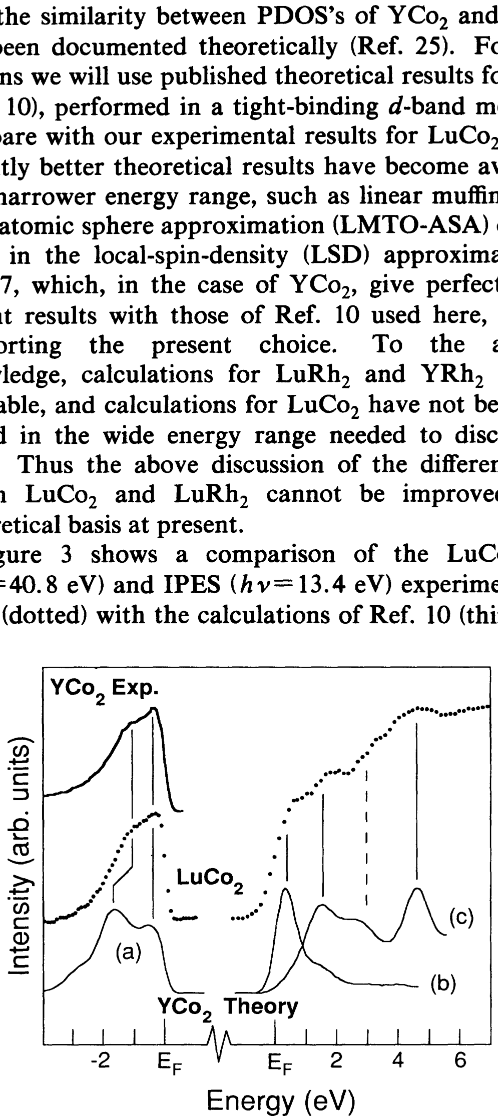

FIG. 3. Comparison between $LuCo_2$ measured spectra (dotted), theoretical *d* DOS of YCo_2 (thin line) taken from Ref. 10, and PES results (at $h\nu=112$ eV) for YCo_2 (thick line) taken from Ref. 7. The $LuCo_2$ PES spectrum is excited with $h\nu=40.8$ eV, and the IPES spectrum is the isochromat at $h\nu=13.4$ eV. The theoretical curve *a* is the occupied *d* PDOS of Co, while lines *b* and *c* are the empty *d* PDOS of Co and Y, respectively. All the theoretical curve have been broadened to account for the experimental resolution. For further details, see the text.

and with PES results at $h\nu = 112$ eV (solid line) reported in Ref. 7 for YCo_2; since the reported PES spectra are mainly sensitive to the Co *d*-derived states,[29] for the theoretical counterpart below E_F we use the Co PDOS (line *a*), while we present both Co and Y PDOS's (lines *b* and *c*, respectively) in the empty-state region. The theoretical DOS's have been broadened with an appropriate Gaussian function to account for the experimental resolution. Due to the uncertainties in evaluating the IPES background and the relative weights of the Co 3*d* and Y 4*d* PDOS's, no attempt has been made to fit the experimental IPES spectrum, thus limiting the comparison to the number and position of the spectral features. The theoretical curves are ground-state calculations, so that the comparison given in Fig. 3 neglects final excited-state effects.

The strong similarity between $LuCo_2$ and YCo_2 PES line shapes gives strong experimental support to the legitimacy of the comparison between $LuCo_2$ and YCo_2 as far as the *d* states are concerned.

It is immediately apparent that the comparison between theory and experiment is much more satisfactory for empty states than for occupied states.

In the region above E_F the experimental and theoretical curves show three clear features that are in excellent correspondence, as indicated by the vertical lines at about 0.35, 1.5, and 4.6 eV; moreover the theoretical shoulder at 2.9 eV above E_F perhaps has a counterpart in the measurements (vertical dashed line). Consistent with the general scheme given above and with the PDOS line shapes, one can thus state that the first feature at 0.35 eV is derived mostly from Co, while the second feature at 1.5 eV is basically derived from the low-*d*-occupancy element, although there is a considerable overlap between the two contributions in this energy region; the third feature at 4.6 eV is instead almost entirely due to the Lu 5*d* empty states.

The comparison between theory and experiment in the occupied-state region proceeds in the same manner as for other RCo$_2$ systems containing light *R*'s (Y, Ce, Pr, Nd, and Sm) studied below E_F in Ref. 7: the experimental structure at ~0.35 eV below E_F is well described by the theory, whereas the same kind of discrepancy regarding the position of the deeper feature (at a BE of ~1.1 eV in the experiment, and ~1.7 eV in the theory) has been put into evidence (see Fig. 3). This has been related to the presence of non-negligible correlation effects therefore questioning the full legitimacy of a band model description. Our data suggest that the situation is the same in a typical heavy-*R* system such as $LuCo_2$.

However, the present work adds further relevant information to this crucial topic. The above-mentioned agreement with a single-particle ground-state calculation of the empty states implies that final-state (electron addition) effects are strongly reduced. The lowering of the correlation energy can be interpreted in terms of the larger spatial width for the empty *d* states, compared to the filled *d* states, resulting in a decreased on-site Coulomb interaction. This can be interpreted qualitatively in terms of the larger radial extent for the atomic Lu 5*d* wave function with respect to the Co 3*d* wave function. Moreover the usually more pronounced delocalization among nearby atoms, typical of the antibonding empty states, can make a further contribution to this effect. According to this interpretation it can be noted that Lu has the most contracted *d* shell among the *R* species, so that in all the other RCo$_2$ Laves phases the situation could be even more favorable as far as the bandlike scheme for empty *d*-state spectroscopy is concerned. On the other hand, in these systems the interaction with the 4*f* charge is in general more pronounced than in $LuCo_2$, which has closed contracted *f* shell; this could present further difficulties for a ground-state description of the unoccupied states. This problem deserves further investigation with particular emphasis on light-*R* intermetallics with 3*dM*'s.

V. CONCLUSIONS

We have presented a combined uv PES and IPES investigation of some Lu-*M* compounds ($LuCo_2$, $LuRh_2$, and Lu_7Rh_3); this allowed extensive spectroscopic investigations of the *d* states responsible for the chemical bond in *R*-*M* intermetallics, since Lu has a closed 4*f* shell thus avoiding any IPES 4*f* signal, and giving a rather wide energy window without 4*f* signal as far as PES is concerned.

We have interpreted the results in terms of various degrees of hybridization in the chemical bond connected with the different extension of the atomic basis functions, and with crystallographic data. This has been achieved in two ways.

(i) By substituting a 3*d* with a correspondent 4*d* transition element in the cubic Laves phases ($LuCo_2$ vs $LuRh_2$), i.e, within the same structure, we have found a shift of both occupied and unoccupied states to lower energy, in qualitative agreement with the greater spatial extension of the Rh 4*d* wave functions and with thermochemical estimations.

(ii) By changing stoichiometry and structure in the Lu-Rh system ($LuRh_2$, Lu_7Rh_3, and pure Lu); here the narrowing of the occupied valence states and the persistence in Lu_7Rh_3 of a broad empty-state feature are understood in terms of the modification of the local coordination. This originates a significant redistribution of the Lu and Rh *d* states, and shows a similarity of Lu_7Rh_3 and pure Lu at energies higher than ~4 eV above E_F.

We also compared our $LuCo_2$ measurements with YCo_2 DOS calculations (Ref. 10). We found good agreement between IPES results and empty ground-state *d* DOS, though this comparison is not as good when dealing with occupied electron states. Thus the present data suggest that in $LuCo_2$ a bandlike description is more appropriate for the empty states due to their greater radial width, which reduces the electron addition effects in IPES. Some general consequences of this argument also have been discussed.

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