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Effects of Ce-Lu substitution on the *d* valence states of Laves phases

L. Duò, P. Vavassori, and L. Braicovich
Dipartimento di Fisica, Politecnico di Milano, piazza Leonardo da Vinci 32, 20133 Milano, Italy

G. L. Olcese
Istituto di Chimica Fisica, Università di Genova, Corso Europa 26, 16132 Genova, Italy

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The legitimacy of the extraction procedure of the 4*f* spectral function for Ce intermetallic compounds by modeling the non-*f* states in terms of isostructural substitutions of the rare-earth species is analyzed by combined ultraviolet direct and inverse photoemission spectroscopy on $CeCo_2$, $LuCo_2$, $CeRh_2$, and $LuRh_2$. We find that the occupied states show a strong sensitivity to the *R* substitution when the *R* atoms interact strongly with the metal as in the extended 4*d* *M* wave functions (Rh) while the variations are negligible in the case of 3*d* *M* partner (Co). The more delocalized empty states are sensitive to the Ce-Lu substitution both in RCo_2 and RRh_2 systems. The results are discussed in terms of the different spatial extent of Ce and Lu 5*d* wave functions and of the degree of intermixing with the *M* partner *d* valence states.

I. INTRODUCTION

In recent years the spectroscopic study of Ce and Ce-transition metal (*M*) compounds has attracted considerable attention, with particular emphasis on their electronic and magnetic properties.[1] In these compounds the energy overlap between the *f* states and the more delocalized *d* states, which are very important in the Ce-*M* chemical bond, makes it difficult to disentangle the two contributions both in photoemission spectroscopy (PES) and inverse photoemission (IPES). In many cases[2] by implicitly assuming that the rare-earth (*R*) substitution does not alter the *d*-partial density of states (*d*-PDOS), the Ce *f*-related spectral functions have been obtained by difference spectra with similar compounds containing a completely empty (e.g., Y and La) or completely filled (e.g., Lu) *f* shell.

The aim of this work is to assess the limits of applicability of this approach through a quantitative analysis of the substitution effects in *R* compounds. This is achieved by a systematic study of PES and IPES (in the ultraviolet) on the Ce-Lu substitution in a number of Laves phase intermetallic compounds[3] with the same crystal structure and similar lattice parameters (upon *R* substitution), namely, $CeCo_2$, $LuCo_2$, $CeRh_2$, and $LuRh_2$. These cubic Laves phases are interesting because, besides allowing isostructural *R* substitutions, they are characterized by a large *R*-*M* coordination number and represent, therefore, a good test to evaluate the sensitivity of the electron states to the variation of *R* partner. The reason of the choice of Lu as a substituting element of Ce is twofold: on one hand, in order to be able to study the whole *d* PDOS, it is important to avoid the presence of the *f* states in a wide energy range spanning both filled and empty states; this rules out the possibility of using La,[4] which has a strong 4*f* emission in the region between ~4 and ~7 eV above E_F;[5,6] on the other and, the differences in the shape of the *d* wave functions should be minimized, in order to avoid a severe distortion of the charge distribution around the *R* sites; from this point of view Lu appears more appropriate than Y.[7]

We find that in the occupied states of $CeCo_2$, the Ce-Lu substitution has a negligible effect, while a sizable modification is present in empty states; on the other hand, $CeRh_2$ is more sensitive to substitution, both in occupied and in empty states, i.e., the substitution effects are larger in the compounds having the greater *R*-*M* hybridization. The experimental trends are rationalized in terms of the interplay between (i) the different spatial extent of Ce vs Lu 5*d* wave functions, (ii) the different spatial extent of Co 3*d* vs Rh 4*d*, and (iii) the lattice parameters variation upon substitution. This explains also the greater sensitivity of empty states to substitution due to the greater wave functions extent.

II. EXPERIMENT

The IPES spectrograph[8] is based on an ultraviolet grating dispersing photons on a flat field. Spectra are collected by scanning the electron energy (isochromat mode); at various photon energies $h\nu$, the spectra are acquired simultaneously so that they are strictly comparable. The full width at half maximum (FWHM) is ~0.4 eV for $h\nu=12$ eV (Ref. 8). Pt spectra have been taken for the energy calibration[9] during the same experiment. The spectra are normalized on line, to the current impinging onto the sample.

Photoemission spectroscopy data has been measured with a 150-mm hemispherical analyzer using He I radiation ($h\nu=21.2$ eV) with FWHM=0.15 eV. The rather broad angular definitions both in IPES and in PES, to-

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gether with the polycrystalline nature of the samples, ensure that all measurements are **k** integrated.

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. All crystals are cubic Laves phases with the $MgCu_2$ structure type (Ref. 4). The number of nearest neighbors is, for the R (M) site, 12 (6) M atoms and 4 (6) R atoms. In Table I the atomic distances, $d[R\text{-}R]$, $d[R\text{-}M]$, and $d[M\text{-}M]$, are given.

All the samples have been mechanically scraped *in situ* with 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. 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 keeping the samples at ~ 100 K during the scraping and the measurements, without any temperature increase. Sample cleanliness and surface stoichiometry[10] have been accurately checked by x-ray core-level spectroscopy.

III. RESULTS

Figure 1 presents the PES results on $CeCo_2$ (dots) and $LuCo_2$ (line) [Fig. 1(a)] and on $CeRh_2$ (dots) and $LuRh_2$ (line) [Fig. 1(b)] at $h\nu=21.2$ eV, normalized to their maximum intensity. While there are strong similarities between the $CeCo_2$ and $LuCo_2$ profiles with the maximum intensity (A) reached at 0.35 eV below E_F, substantial line-shape variations upon R substitution are present in RRh_2: the dominant peak (B), at ~ 1.15 eV below E_F in $LuRh_2$, moves to a larger binding energy (BE ~ 1.65 eV), resulting in a centroid shift for $CeRh_2$; furthermore, the weight of the shoulder A close to E_F becomes lower compared to the maximum intensity.

Figure 2 gives the IPES results at $h\nu=10.4$ and 13.4 eV for $CeCo_2$ (dots) compared with the spectrum of $LuCo_2$ (line, $h\nu=13.4$ eV). In the spectra four features can be identified in $CeCo_2$ ($LuCo_2$) at about 0.8 eV (0.8 eV, A), 2.2 eV (1.8 eV, B), 3.8 eV (3.2 eV, C), and 5.4 eV (4.6 eV, D) eV above E_F. Finally, Fig. 3 displays IPES results at $h\nu=11.7$ and 13.4 eV in $CeRh_2$ and $LuRh_2$ (line, $h\nu=13.4$ eV). Two structures are visible in the spectra located in $CeRh_2$ ($LuRh_2$) at ~ 0.8 eV (0.8 eV, A) and 4.8 eV (3.2 eV, B) eV above E_F. Despite some intensity variations, the energy, of the IPES features shown in Figs. 2 and 3, is constant within a large $h\nu$ range (Refs. 3 and 11).

TABLE I. Summary of the R-R, R-M, and M-M nearest-neighbors distances d of $CeCo_2$, $LuCo_2$, $CeRh_2$, and $LuRh_2$, respectively. All the compounds have the $MgCu_2$ cubic Laves phases structure type.

Compound	$d[R\text{-}R]$ (Å)	$d[R\text{-}M]$ (Å)	$d[M\text{-}M]$ (Å)
$CeCo_2$	3.10	2.97	2.53
$LuCo_2$	3.08	2.95	2.51
$CeRh_2$	3.27	3.13	2.67
$LuRh_2$	3.21	3.08	2.62

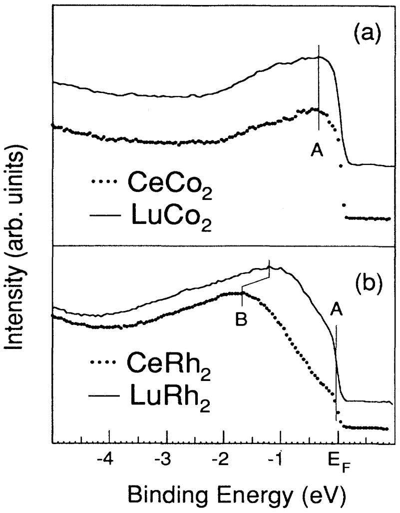

FIG. 1. (a) Intensity normalized PES results for $CeCo_2$ (dots) and $LuCo_2$ (line), with $h\nu=21.2$ eV. The maximum intensity A lies at 0.35 eV below E_F. (b) Same as (a) but for $CeRh_2$ (dots) and $LuRh_2$ (line). The peak intensity B lies at 1.15 (1.65) eV for $LuRh_2$ ($CeRh_2$).

IV. DISCUSSION

The chemical bonds in the compounds under study involve a low d occupancy atom (R) and a much higher d occupancy atom as Co and Rh. On the basis of the present knowledge on the electron states of these compounds (Refs. 3, 11, and 12), we can qualitatively state that the occupied d DOS's have a dominant Co (Rh) character with a redistribution of the small Ce (or Lu) d contribution to higher BE's than in pure R. On the other hand, the empty states region well above E_F is dominated by the R d-derived states and in the intermediate region,

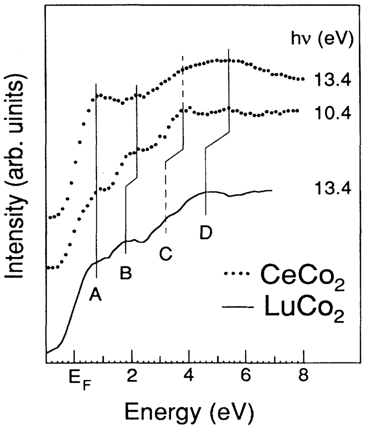

FIG. 2. Intensity normalized IPES results for $CeCo_2$ (dots) and $LuCo_2$ (line), measured in the isochromat mode at $h\nu=10.4$ and 13.4 eV. Features A, B, C, and D on $CeCo_2$ ($LuCo_2$) lie at 0.8 (0.8), 2.2 (1.8), 3.8 (3.2), and 5.4 (4.6) eV above E_F, respectively. The weaker features are represented as dashed lines.

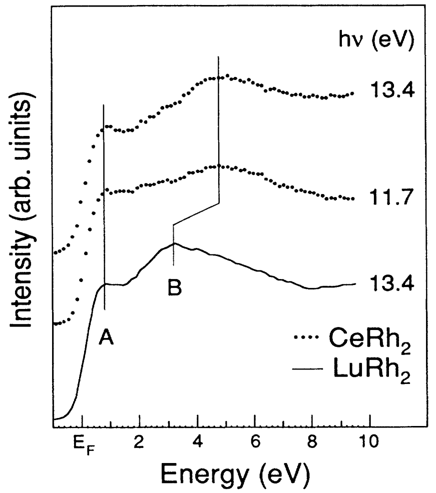

FIG. 3. Same as Fig. 2 but for $CeRh_2$ (dots) and $LuRh_2$ (line) at $h\nu = 11.7$ and 13.4 eV. Features *A* and *B* on $CeRh_2$ ($LuRh_2$) lie at 0.8 (0.8) and 4.8 (3.2) eV above E_F, respectively.

i.e., just above E_F, a contribution from empty Co (Rh) *d* states is still present.[11]

As far as the relative sensitivity of the measurements to *d* vs. *f* states is concerned, we have shown in a previous work[5] that in the $h\nu = 10-30$ eV range, IPES changes from a mostly *d* to a *f* sensitive regime due to the $h\nu$ dependence of cross sections. This happens also in *R*-*M* compounds.[11] Thus, at low $h\nu$ ($< \sim 15$ eV), a direct comparison between *d*-like states in Ce- and Lu-based compounds can be performed. In direct photoemission, due to the low *f* occupation the He I spectrum is *d* sensitive. Within this framework, one can, therefore, address the sensitivity of the *d* PDOS with respect to the variation of *R* partner in different chemical environments.

A. Occupied *d* states

Since the PES profiles are mainly related to the *M d* PDOS, their possible variations, upon Ce-Lu substitution, must be understood in terms of *M*-*M* and *M*-*R* chemical interaction. The former depends only on the *M*-*M* nearest-neighbors distance, which decreases by only 0.02 (0.05) Å for *M*=Co (Rh) upon Ce-Lu substitution, because of the smaller Lu atomic size. The *R*-*M* overlap is influenced by the different Ce vs Lu 5*d* wave-function width as well: actually, this effect is definitely larger than the tiny lattice contraction and results in a lower Lu 5*d*-*M d* than Ce 5*d*-*M d* hybridization. Therefore, in the case of Ce*M* a shift to larger BE may occur, due to the stronger *R*-*M* hybridization, as compared to Lu*M*. Indeed this happens in *R*-Rh_2 and not in RCo_2.

The marked similarity between the PES results of $CeCo_2$ and $LuCo_2$ [Fig. 1(a)] can be understood in terms of the pronounced localization of the Co 3*d* wave function on the atomic site, so that both Co 3*d*-Co 3*d* and *R* 5*d*-Co 3*d* overlap integrals do not undergo remarkable variations upon substitution. This is further supported by a recent work[13] on YCo_2 and a number of RCo_2 compounds (*R* =Ce, Pr, Nd, and Sm) showing a strong overall line-shape similarity among the *d*-sensitive PES results despite different combinations of wave-function widths and lattice parameters.

The strong difference between the PES results of $CeRh_2$ and $LuRh_2$ [Fig. 1(b)] has, thus, to be attributed to the much wider radial distribution of the Rh 4*d* orbitals, generating a stronger sensitivity to the Ce-Lu substitution. The shift of the valence-band peak [feature *B* in Fig. 1(b)] to higher BE and the consequent reduction of the DOS close to E_F (feature *A*) as compared to $LuRh_2$, thus, represent the experimental evidence that the increased *R*-Rh hybridization pulls down the bonding states depleting the region close to E_F.

We add that strong modifications of the *d*-sensitive UV PES profiles has been previously observed[14] in a compound similar to $CeRh_2$, namely, $CeRu_2$, upon substitution of Ce with La. All these findings seem to suggest that, at variance with the case of 3*d M*'s, when dealing with extended *d* valence states like those of 4*d M*'s (and *a fortiori 5d M's*) *R substitutions do perturb the non-f valence states* below E_F, unless a proper matching between the effects of the lattice and the wave-function variation takes place as in the case of Ce_7Rh_3 vs Lu_7Rh_3.[15]

B. Unoccupied *d* states

Figure 2 shows some differences between the *d*-sensitive IPES spectra for $CeCo_2$ and $LuCo_2$ at variance with the PES results. In both compounds there are four structures (*A*–*D*), in agreement with theoretical site-selective PDOS calculations (Refs. 3, 11). Apart from *A*, the other features are systematically found at larger energies in $CeCo_2$ with shifts of about 0.4 eV (*B*), 0.6 eV (*C*) and 0.8 eV (*D*). While feature *A* still contains a sizable contribution of Co 3*d* holes, and, similarly, to the occupied electronic states is unchanged upon *R* substitution, the structures *B* to *D* are mainly due to *R* 5*d*-like holes.[11] This region of the spectrum is, therefore, driven by the *R*-*R* 5*d* interaction, which is larger in the case of $CeCo_2$. The effect is a shift of the Ce 5*d* antibonding states, far from E_F in $CeCo_2$ compared to $LuCo_2$. It is worth noting that this shift seems to increase on going from *B* to *D*, i.e., increasing the antibonding character of the involved states.

A similar situation occurs in the low $h\nu$ IPES comparison between $CeRh_2$ and $LuRh_2$. In fact, the results of Fig. 3 clearly show doubly peaked line shapes for both compounds with feature *A* (Rh-derived) at a fixed position and the broad structure *B* (*R*-derived) shifted to a higher energy in $CeRh_2$. Again, we interpret this experimental evidence as the effect of a stronger *R*-*R* 5*d* interaction in the case of $CeRh_2$. Furthermore, the intensity ratio between the features *A* and *B* of Fig. 3 is lower for $CeRh_2$ than $LuRh_2$. This is the empty states counterpart on $CeRh_2$ of the "hybridization gap"[16] effect across E_F, shown by feature *A* in Fig. 1(b).

In the RCo_2 case, the more pronounced sensitivity of the empty *d* electron states to the Ce-Lu substitution, as compared to the occupied *d* states, should be attributed to the larger spatial extent of the *R* 5*d* wave functions with respect to the Co 3*d*, consistently with the PES results on $R\mathrm{Co}_2$ vs $R\mathrm{Rh}_2$. This seems to indicate that even in cases like $R\mathrm{Co}_2$, where R substitution effects are negligible in the occupied valence states, the states lying above E_F show a strong sensitivity to small variations of the radial functions.

V. CONCLUSIONS

We have presented a combined UV PES and IPES investigation in the *d* sensitive regime on CeCo_2, CeRh_2 and on the isostructural Lu substituted compounds (LuCo_2 and LuRh_2) in order to discuss the sensitivity of the partial *d*-DOS to the substitution effects. In the occupied electron states, where the M *d*-derived signal is predominant, the substitution effects are significant when the hybridization between the R and the M orbitals is large ($M=\mathrm{Rh}$), and becomes negligible in the case of the more contracted Co 3*d* shell, whereas for the empty states, whose spatial extent is larger, the effect is clearly present even in $R\mathrm{Co}_2$, although less pronounced than in $R\mathrm{Rh}_2$. Moreover, we have presented a rationale on this effect based on the spatial extent of the involved wave functions.

These results may, therefore, represent a useful guideline to indicate in which cases a quantitative evaluation of the *d* PDOS in CeM compounds can be accurately performed, in terms of the *d* PDOS of an isostructural compound with a substituting R element, and in which cases, instead, these kinds of comparisons are not fully legitimate.

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