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Electronic structures of RCuIn and R_2CuIn_3 (R = La, Ce, Pr)

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Electronic structures of ternary compounds RCuIn and R_2CuIn_3 (R = La, Ce, Pr) have been studied by the X-ray photoelectron spectroscopy. The valence bands and the XPS core levels were investigated. The two families of compounds crystallize in different hexagonal crystal structures: ZrNiAl-type for RCuIn and AlB_2-type for R_2CuIn_3. Analysis of the XPS valence bands indicates that they are mainly determined by the Cu 3d band. The analysis of the Ce 3d spectra based on the Gunnarsson-Schönhammer model gives the hybridization of the 4f electrons with the conduction band equal to 45 meV for CeCuIn and to 140 meV for Ce_2CuIn_3. The appearance of the $3d^94f^0$ component is a clear evidence of the intermediate valence behaviour for cerium. The 4f occupation number is 0.95 for CeCuIn and 0.92 for Ce_2CuIn_3. The analysis of the other core levels confirms a small influence of the atomic surrounding on the electronic structure.

Key words: *rare earth intermetallics; electronic properties; core level*

1. Introduction

RCuIn systems, where R is a rare earth element, have recently been extensively investigated. Isothermal sections of their phase diagrams and crystallographic data of the ternary compounds are collected in the review paper [1]. According to it, from 4 to 10 intermetallic compounds are formed in each system. Intermetallic phases containing 33 at. % of R, i.e. RCuIn and R_2CuIn_3 (R = La, Ce, Pr) are the subject of the present work.

RCuIn compounds crystallize in the hexagonal ZrNiAl structure type, where the R, Cu, In atoms occupy sites of Zr atoms – 3g, Ni atoms – 1b and 2c, and Al atoms – 3f [2]. The R_2CuIn_3 compounds crystallize in the AlB_2 structure type, where R atoms

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occupy sites of the Al atoms and atoms of the statistical mix ($Cu_{0.5}In_{1.5}$) occupy the sites of the B atoms [3]. In RCuIn compounds the rare earth atoms are located in pentagonal prisms with capped faces with the coordination number (*CN*) equal to 17. The coordination polyhedra (CP) for the Cu1 and Cu2 atoms are tricapped trigonal prisms (*CN* = 9) and the indium atoms have distorted tetrahexahedra (*CN* = 14). For R_2CuIn_3 compounds the CP of the rare earth atom is a hexagonal prism with capped bases (*CN* = 14), the (0.25 Cu + 0.75 In) atoms have tricapped trigonal prisms.

The differences in the crystal structures do not influence the magnetic properties. Magnetic data indicate that La compounds are Pauli paramagnets while those with Ce and Pr are Curie–Weiss paramagnets and down to 2 K do not order magnetically [4, 5].

The results of X-ray photoelectron spectroscopy (XPS) measurements for RCuIn and R_2CuIn_3 compounds (R = La, Ce, Pr) have been presented in this work.

2. Experimental details and results

Polycrystalline samples were fabricated by arc melting of high purity metals (rare earths with the purity not worse than 99.8 wt. % of the main component, electrolytic copper with the purity 99.92 wt. % Cu and indium with the purity 99.99 wt. % In) in titanium gettered argon atmosphere (*P* = 50 kPa). The chemical compositions of the alloys were checked for weight losses which did not exceed 1 wt. %. All the prepared ingots were then annealed at 870 K for 700 h in evacuated silica tubes and then quenched in water.

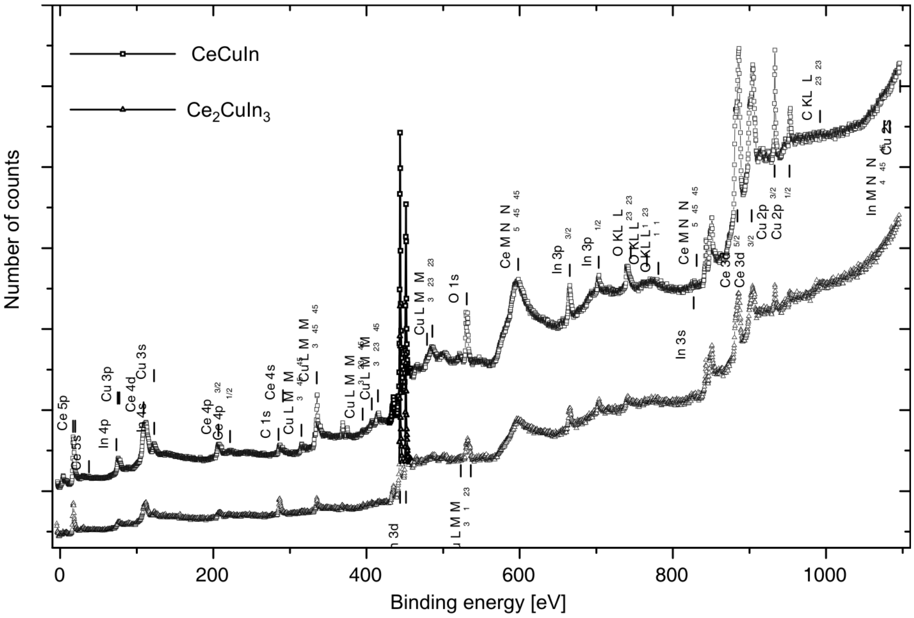

Fig. 1. XPS MgK_{α} spectra of CeCuIn and Ce_2CuIn_3

X-ray powder diffraction patterns were recorded at room temperature using CuK_α line with a Philips X'Pert type diffractometer. The XPS spectra were obtained at room temperature using the Leybold LHS10 and PHI 5700/600 Physical Electronic electron photoemission spectrometer with the AlK_α ($h\nu = 1486.6$ eV) and MgK_α ($h\nu = 1253.6$ eV) radiation in the vacuum of about 10^{-9} mbar. Details of the experiment have been described elsewhere [6].

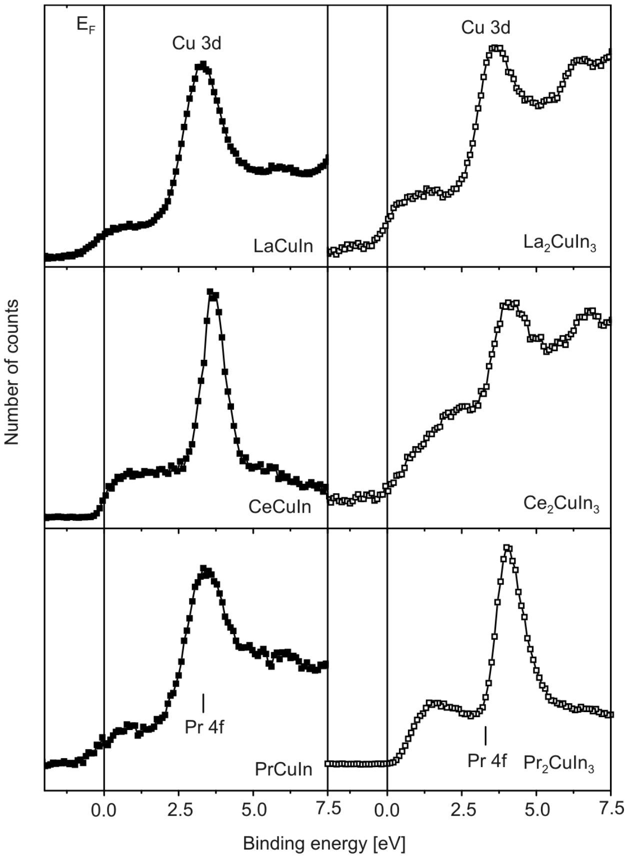

Fig. 2. XPS spectra of the valence bands in RCuIn and R_2CuIn_3. The bar gives the position of the Pr 4f peak in the metallic praseodymium. The Fermi level E_F, located at $E = 0$ eV, is marked by the vertical solid line

The X-ray analysis confirms that all the RCuIn (R = La, Pr) compounds are single phase with the ZrNiAl type structure, while the R_2CuIn_3 compounds have the hexagonal AlB_2-type structure. Analysis of these data indicates that the cell parameters are in good agreement with the published ones [2, 3]. Figure 1 shows the XPS spectra of CeCuIn and Ce_2CuIn_3 in a wide binding energy range of 0–1100 eV. The binding energies are related to the Fermi level ($E_F = 0$ eV). A small oxygen and carbon contamination is visible.

The XPS valence bands (VB) of all the investigated compounds are presented in Fig. 2. The band extends from the Fermi energy located at $E = 0$ eV to the binding energy of about 7.5 eV. The VB XPS spectra represent mainly the dominant contribution of the Cu 3d states. Below the Fermi level, a broad and weak peak corresponding to the R5d6s states is located. The peak corresponding to the Cu 3d states is at 3.2 eV for LaCuIn and at 4.1 eV for CeCuIn, Ce_2CuIn_3 and Pr_2CuIn_3. The peak corresponding to the Pr4f states observed for pure Pr metal at 3.5 eV [7] overlaps the peaks corresponding to the Cu 3d states.

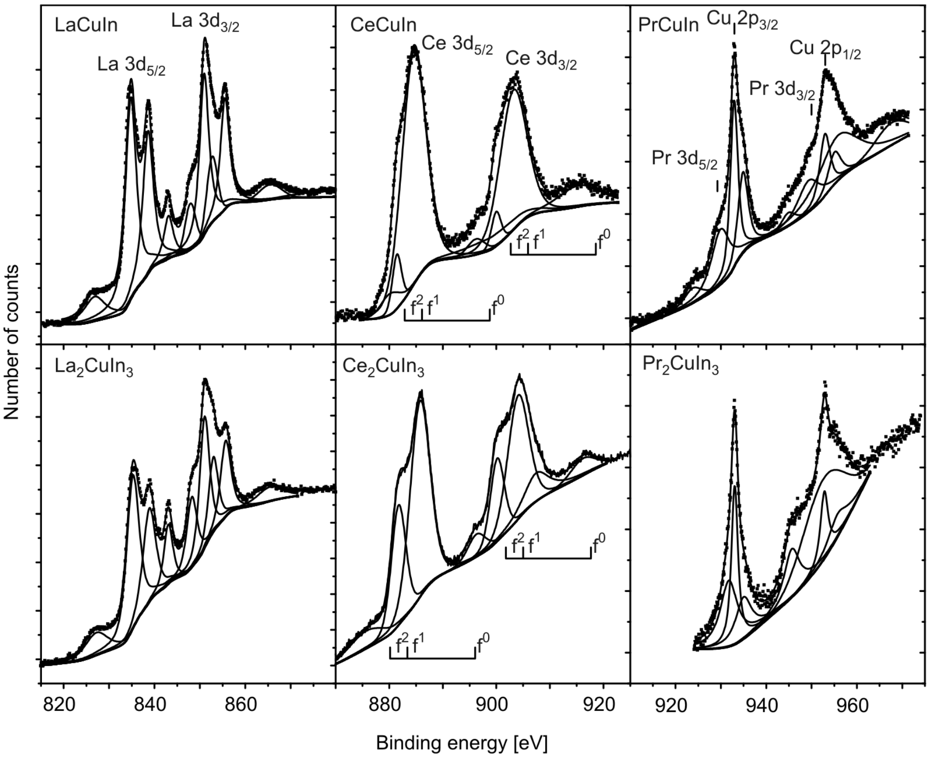

Fig. 3. Deconvoluted X-ray photoelectron spectra of the $R3d_{5/2}$ and $R3d_{3/2}$ electron states of La, Ce and Pr in RCuIn and R_2CuIn_3 (R = La, Ce, Pr)

Figure 3 illustrates the R3d XPS spectra of RCuIn and R_2CuIn_3 (R = La, Ce, Pr). For Pr compounds the observed peaks corresponding to the Pr $3d_{5/2}$ and Pr $3d_{3/2}$ overlap those of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ making the analysis impossible. The structure of the La and Ce compounds spectra has been interpreted in terms of the Gunnarsson –Schönhammer theory [8]. For all the investigated compounds the spin-orbit splitting dominates the spectral structure of R 3d XPS peaks and is equal 17.0 eV for La, 18.4 eV for Ce and 20.4 eV for Pr.

The individual peaks have a complex structure. At low binding energy side of the R $3d_{5/2}$ and R $3d_{3/2}$ the main lines of the shake down satellites are observed, which are known to account for the screened R 3d^{9}4f^{n+1} states. Based on the Doniach-Šunjić theory [9], the separation of these peaks gives the value of the intensity ratio $r_1 = I(\mathrm{f}^{n+1})/[I(\mathrm{f}^n)+I(\mathrm{f}^{n+1})]$. It was possible to determine the coupling parameter Δ using the measured intensities of the final R 3d^{9}4f^n and R3d^{9}4f^{n+1} states as well as calculation of the intensity ratio as a function of Δ previously published [10]. The coupling parameter Δ is defined as $\pi V^2\rho_{\max}$, where $\rho_{\max}$ is the maximum density of conduction states and V is the hybridization. The value of the intensity ratio r_1 equals 0.09 for CeCuIn and 0.29 for Ce$_2$CuIn$_3$,which corresponds to the Δ parameter 45 and 140 meV, respectively.

In the case of Ce compounds, the appearance of the f^0 contribution is a clear evidence of the mixed valence state. The intensity ratio $r_2 = I(\mathrm{f}^0)/[I(\mathrm{f}^0) + I(\mathrm{f}^1) + I(\mathrm{f}^2)]$ provides an estimate for the occupation of the final f states $n_{\mathrm{XPS}} = 1 - r_2$ being equal to 0.95 for CeCuIn and 0.92 for Ce$_2$CuIn$_3$.

In the next step, the positions of the core levels corresponding to the rare earth, copper and indium were analyzed. It was shown that the values of the level energies and values of the spin-orbit splitting are the same for RCuIn and R$_2$CuIn$_3$, both based on our experimental data as well as on the table values listed in Ref. [7] (see Table 1).

Table 1. Binding energies and respective values of the spin-orbit splitting energy ΔE [eV] for RCuIn and R$_2$CuIn$_3$ (R = La, Ce, Pr) and the data from Ref. [7]

Element	Parameter	LaCuIn	La$_2$CuIn$_3$	CeCuIn	Ce$_2$CuIn$_3$	PrCuIn	Pr$_2$CuIn$_3$	Table data
R	5d6s^2	0.7	0.9	2.0	1.95	0.7	1.3	
Cu	3d	3.2	3.6	4.0	4.0	3.3	4.0	
In	4d$_{5/2}$	16.0	16.3	16.9	16.8	16.2	17.1	16.6
	4d$_{3/2}$	16.8	17. 2	17.9	17.7	17.1	18.0	17.4
	ΔE	0.8	0.9	1.0	0.9	0.9	0.9	0.8
Cu	3p$_{5/2}$	75.1	75.5	75.6	76.2	75.1	75.8	75.2
	3p$_{3/2}$	77.6	78.1	78.3		77.4	78.4	77.2
	ΔE	2.5	2.6	2.7		2.3	2.6	2.0
R	4d$_{5/2}$	102.6	102.8	110.3	109.5	115.1	115.2	102.5 (La) 109.0 (Ce)115.1 (Pr)
	4d$_{3/2}$	105.2	105.6	112.1	112.5	120.0	117.7	105.3
	ΔE	2.6	2.8	1.9	3.0	3.9	2.5	2.8
Cu, In	3s, 4s	122.7	122.7	122.9	123.6	–	122.9	122.5 (Cu) 122.8 (In)
In	3d$_{5/2}$	443.7	443.6	443.8	443.8	443.3	443.9	443.9
	3d$_{3/2}$	451/0	451.1	451.3	451.3	450.9	451.5	451.4
	ΔE	7.6	7.5	7.5	7.5	7.6	7.6	7.5
R	3p$_{3/2}$	838.5	838.3	884.6	885.7	929.9	929.9	836.0 (La) 884.2 (Ce) 928.8 (Pr)
	3p$_{1/2}$	855.5	855.7	903.0	904.1	950.4	952.3	853.0 902.7 948.3
	ΔE	17.0	16.9	18.4	18.4	20.5	20.4	17.0 18.5 19.5
Cu	2p$_{3/2}$	932.9	933.0	933.1	933.2	933.9	934.0	932.5
	2p$_{1/2}$	952.7	953.0	952.9	953.1	954.4	954.4	952.5
	ΔE	19.8	20.0	19.8	19.9	20.5	20.4	20.0

3. Discussion and summary

The results of the XPS measurements indicate that in two series of the RCuIn and R_2CuIn_3 compounds the electronic structures are similar. This is in agreement with the magnetic data. In both systems, the magnetic moments of R^{3+} ions do not order down to 2 K for R = Ce and Pr or order antiferromagnetically for other rare earth elements. For all the compounds we have observed a narrowing of the Cu 3d peaks and their shift to higher binding energies (see Table 2).

Table 2. Values of the level energies and Γ_{FWHM} [eV] of Cu 3d peak in RCuIn and R_2CuIn_3 (R = La, Ce, Pr) and in pure Cu

Compound	E(Cu 3d)	Γ_{FWHM}
LaCuIn	4.2	1.0
La_2CuIn	3.6	1.6
CeCuIn	4.0	1.6
Ce_2CuIn_3	4.0	1.3
PrCuIn	3.4	1.6
Pr_2CuIn_3	4.0	1.1
Cu	3.0	2.4

These results indicate the more localized the 3d states. The analysis of the core levels for various elements gives information about the chemical shift which originates from the changes of the potential related to the formation of the compound. As a result, the binding energies of electronic levels are different in compounds and in pure elements.

Table 3. Binding energy shifts ΔE [eV] of core levels with respect to pure elements

Level	LaCuIn	La_2CuIn_3	CeCuIn	Ce_2CuIn_3	PrCuIn	Pr_2CuIn_3
Cu 3d	0.2	0.6	1.0	1.0	0.4	1.0
Cu $3p_{5/2}$	–0.1	0.3	0.4	1.0	–0.1	0.6
Cu $2p_{3/2}$	0.4	0.5	0.6	0.7	1.4	1.5
In $4d_{5/2}$	–0.6	–0.3	0.3	–0.2	–0.4	0.5
In $3d_{5/2}$	–0.2	–0.3	–0.1	–0.1	–0.6	0
R $4d_{5/2}$	0.1	0.3	1.3	0.5	0	0.1
R $3p_{3/2}$	2.5	2.8	0.4	1.5	1.1	1.1

Table 3 shows the chemical shifts of the most pronounced photoemission lines. In majority of the cases, the positive shift is observed for R = La, Ce, Pr and Cu and negative for indium. The negative shift on the In site may be related to some charge transfer towards these atoms.

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