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Electronic structure of $CeRhIn_5$ and $CeIrIn_5$

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We have performed the full potential linearized augmented plane-wave (FP-LAPW) calculations of the layered cerium compounds $CeRhIn_5$ and $CeIrIn_5$, which belong to a novel, intensively investigated family of heavy fermion (HF) materials. The ground states of this compounds can be tuned between antiferromagnetism (AFM) and superconductivity (SC) by external pressure or doping. We have carried out X-ray photoelectron spectroscopy (XPS) experiments to compare recorded valence band spectra with theoretical calculations. We have also analysed the XPS 3d Ce spectra, to estimate the occupation of the Ce 4f shell and the hybridisation between 4f and conduction electrons. We have found and discussed the influence of the lattice parameter a and the df interatomic hybridization effect on the properties of ground state in the series of $CeMIn_5$ compounds.

Key words: *heavy fermions; electronic structure; XPS; superconductivity*

1. Introduction

Recently, much attention have attracted studies of the relationship between magnetism and superconductivity in HF compounds. In these materials, evolution of ground states as a function of pressure or chemical environment frequently is discussed in terms of Doniach's model [1, 2]. This model considers a subtle competition between the local on-site exchange interaction (Kondo effect) compensating the local magnetic moment, and the long-range magnetic interaction, which can lead to magnetic order through the Ruderman–Kittel–Kasuya–Yoshida (RKKY) mechanism. In few classes of HF compounds, the SC near the boundary between the magnetic and nonmagnetic region can be extorted either by pressure or doping in order to suppress the magnetic order.

$CeMIn_5$ (M = Co, Rh or Ir) are good examples of such materials. $CeCoIn_5$ and $CeIrIn_5$ are HF superconductors at ambient pressure with T_C = 2.3 K and 0.4 K, respectively [3, 4], while $CeRhIn_5$ ordered antiferromagnetically below T_N = 3.8 K ex-

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hibits a transition to the superconducting state with $T_C \approx 2.2$ K at the pressure 2.5 kbar [5, 6]. All of those compounds are found to be located near the quantum critical point (QCP) in the Doniach phase diagram and are very intensively investigated. However, their unconventional ground states are still somewhat controversial. To understand the ground state properties, we calculated electronic structure of $CeRhIn_5$ and $CeIrIn_5$ by the FP-LAPW method. The results of the band structure calculations are compared with the XPS valence band spectra. We also investigated the Ce 3d XPS spectra, from which the occupation number of the Ce 4f shell and the hybridization energy between 4f shell and conducting band were determined. We present the results of GGA + U calculations for different correlation energies U and analyse the f–f correlation effects.

2. Experimental details

Polycrystalline samples of $CeRhIn_5$ and $CeIrIn_5$ were prepared by arc melting stoichiometric amounts of the elemental metals (Ce 99.99%, Rh 99,9%, Ir 99,99%, In 99,995% in purity) on a water cooled cooper hearth in an ultra-high purity Ar atmosphere with an Al getter. Each sample was remelted several times to promote homogeneity, and then annealed at 800 °C for 7 days. The samples were examined by X-ray powder diffraction analysis (XRD) and found to consist of a single phase. The lattice parameters (listed in Table 1) were obtained from the XRD patterns analysis using the POWDER-CELL program, and are in good agreement with those previously reported [7–10]. The XPS spectra were obtained with monochromatized Al K_α radiation at room temperature using a PHI 5700 ESCA spectrometer.

Table 1. Lattice parameters for $CeCoIn_5$, $CeRhIn_5$ and $CeIrIn_5$ (space group $P4/mmm$)

Lattice parameter	Compound		
	$CeCoIn_5$ [21]	$CeRhIn_5$	$CeIrIn_5$
a [Å]	4.601	4.652	4.668
c [Å]	7.54	7.542	7.515

The electronic structure was studied by the full potential linearized augmented plane-wave (FP-LAPW) method [11] using the experimental lattice parameters. The gradient corrected local spin density exchange (LSD XC) potential in the form proposed by Perdew, Burke and Ernzerhof [12] was included. In the calculations, the core levels were treated completely relativistically, while for valence states relativistic effects were included either in a scalar relativistic treatment [13] or with the second variational method using the scalar-relativistic eigenfunctions as basis, including spin-orbit coupling [14]. $CeMIn_5$ compounds are strongly correlated systems, we therefore go beyond the standard generalized gradient approximation (GGA) and include orbital dependent potentials in methods GGA + U, introduced by Anisimov et al. [15], with an approximate correction for the self-interaction correction.

3. Results and discussion

Figure 1 shows the results of numerical calculations of the total electronic density of states (DOS) for paramagnetic $CeRhIn_5$ and $CeIrIn_5$. The DOSs were convoluted by Lorentzians with a half-width of 0.35 eV to account for the instrumental resolution. The partial DOSs were multiplied by the corresponding cross sections [16]. A background, calculated by means of the Tougaard alghoritm [17], was subtracted from the

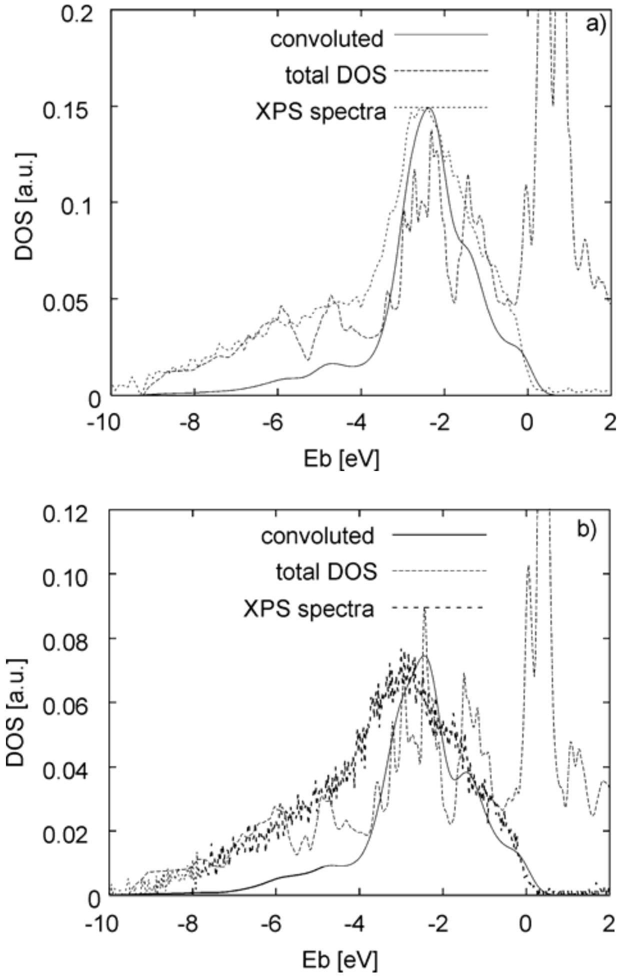

Fig. 1. XPS valence band spectra for paramagnetic $CeRhIn_5$ (a) and $CeIrIn_5$ (b)

XPS data. The agreement between the calculated and measured XPS valence band spectra is good. The spectra reveal that the valence bands of $CeRhIn_5$ and $CeIrIn_5$ have a major peak mainly due to the d states of Rh or Ir located near the Fermi level. The second peak centred at about 5 eV is mainly due to the In states. The Ce 4f states give only negligible contribution to the total XPS spectra of $CeRhIn_5$ and $CeIrIn_5$.

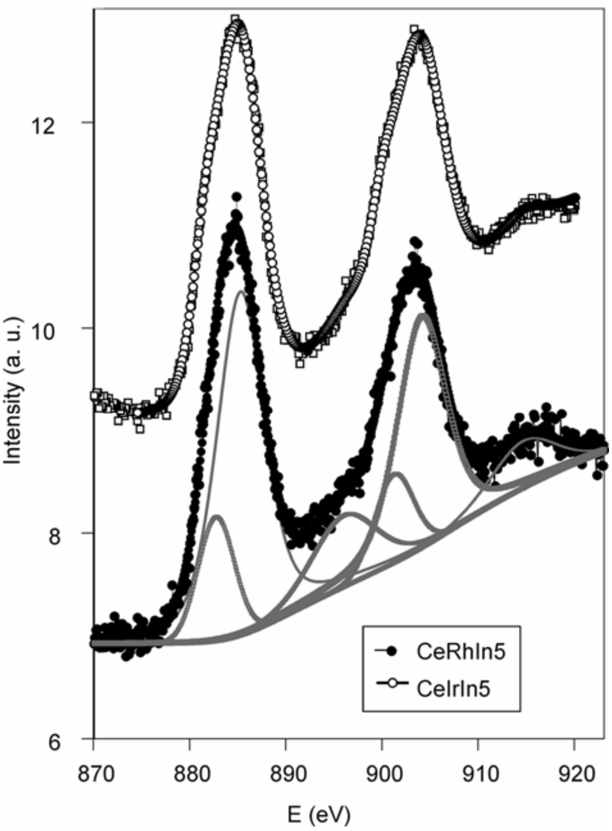

Fig. 2. Ce 3d XPS spectra for $CeRhIn_5$ and $CeIrIn_5$. For $CeRhIn_5$, separated and overlapping peaks attributed to the $4d^9f^2$, $4d^9f^1$ and $4d^9f^0$ final states are also shown

Figure 2 shows the Ce 3d XPS spectra for $CeRhIn_5$ and $CeIrIn_5$. Three final-state contributions f^0, f^1 and f^2 exhibit a spin-orbit splitting Δ_{SO} = 18.6 eV. The separation of the overlapping peaks in the Ce 3d XPS spectra was made on the basis of the Doniach–Šunjić theory [18]. The appearance of the f^0 components suggest the mixed valence behavior of Ce, while the f^2 peaks located at the low-binding energy side of the f^1 components are attributed to the hybridization between the f states and the conduction band. Based on the Gunnarson–Schönhammer (GS) theoretical model [19, 20], we have estimated the f-occupation number n_f and the hybridization energy Δ for the both compounds. The n_f value is 0.89 for $CeRhIn_5$ and 0.95 for $CeIrIn_5$. Our

FP-LAPW calculations as well as the FP-LMTO [21] indicate that Ce is nearly trivalent in CeRhIn$_5$ and in CeIrIn$_5$, which is in contradiction to the results obtained from the Ce 3d XPS spectra. The hybridization energy Δ is ca. 89 meV for CeRhIn$_5$, while for CeIrIn$_5$ Δ is slightly higher (92 meV) which could be explained by the following: the SC ground state of CeIrIn$_5$ is equivalent to that of CeRhIn$_5$ under external pressure, which usually increases hybridization effect (see also discussion of the resonant df XPS spectra in Ref. [22]).

The spin-polarized calculations make preference for the magnetic ground state in both compounds and the magnetic moment is calculated only for Ce (considering for simplicity the ferromagnetic order and magnetic moments along the c axis). The electronic structures of CeRhIn$_5$ and CeIrIn$_5$ are similar (compare Figs. 3 and 4). For CeRhIn$_5$ we have also performed antiferromagnetic (AF) calculations, an AF order, however, has a very small effect on the magnitude of magnetic moments and the shape of DOSs.

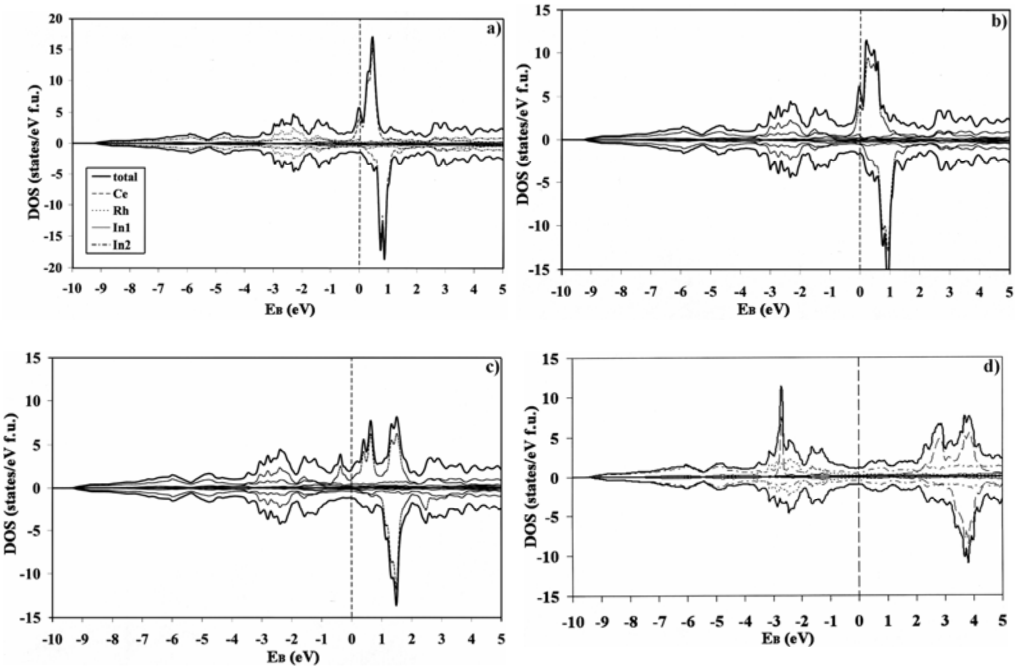

Fig. 3. Total and partial spin up and spin down DOSs for CeRhIn$_5$ calculated by the following methods: GGA (a), GGA + SO (b), GGA + SO + U (1.65 eV) (c) and GGA + SO + U (6.8 eV) (d)

The FP-LAPW calculations beyond the GGA allowed us to investigate the strength of the correlation effects of the Ce 4f electrons in CeRhIn$_5$. The GGA + U calculations give the best agreement of the calculated magnetic moment to the experimental value of ca. 0.37μ_B [23] for the correlation energy $U = 1.65$ eV. This U-value is slightly larger than that of ca. 1.5 eV, acquired from FP-LMTO [21].

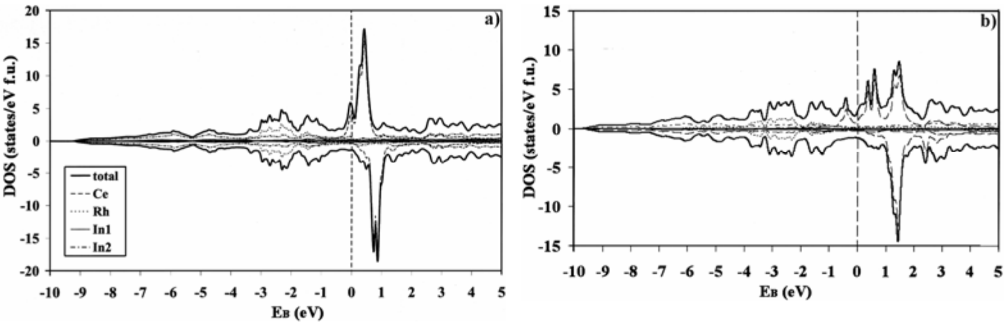

Fig. 4. Total and partial spin up and spin down DOSs for CeIrIn$_5$ calculated by: GGA (a) and by GGA + SO + U (1.75 eV) (b)

In Figure 3, we have shown for comparison the total and partial DOSs for CeRhIn$_5$ calculated by GGA, GGA + SO and GGA + SO + U method with $U = 1.65$ eV and $U = 6.8$ eV, respectively (typical value of Ce compounds). The correlation energy in the GGA + U calculations causes progressive localization of the 4f states and leads to a change of the ground state from itinerant to localized, while the GGA calculations suggest the itinerant magnetism. In our opinion the Ce 4f states are on the border between localization and itinerancy.

Table 2. Density of states at the Fermi level DOS (E_F), calculated (M_c) and experimental (M_{exp}) values of the total magnetic moment on Ce atom in CeRhIn$_5$ and in CeIrIn$_5$

Parameter	CeRhIn$_5$				CeIrIn$_5$			
	GGA	GGA + SO	GGA + SO + U (1.65 eV)	GGA + SO + U (6.8 eV)	GGA	GGA + SO	GGA + SO + U (1.65 eV)	GGA + SO + U (6.8 eV)
M_c [μB]	–	0.201	0.37	0.444	–	0.195	0.364	0.435
M_{exp} [μB]	0.37 [23]				–			
DOS [E_F]	6.79	7.19	3.33	2.1	6.56	7.26	3.3	2.03

The nature of the ground state of CeMT$_5$, discussed here on the basis of the Doniach model [1, 2], depends both on the exchange J(f–s) coupling and the DOS (E_F). However, the DOS (E_F) of the CeMIn$_5$ series are almost the same (Table 2), therefore in framework of this model, the magnetic or nonmagnetic behaviour results from the strength of $J \sim 1/V$, where V is a unit cell volume. Increasing the pressure or chemical substitution, which both lead to decreasing of the lattice parameters a, could provoke the magnetic–nonmagnetic phase transition due to the change of J coupling. Another reason of the magnetic/nonmagnetic ground state is a hybridization between Ce 4f and M 3d states along c axis, which could delocalize the f states and in consequence form the nonmagnetic ground state, too.

Table 3. The pf and df hybridization parameter for Ce–In1 (0.5, 0.5, 0), Ce–In2 (0, 0.5, 0.3103(6)) and Ce–M interactions, calculated by FP-LMTO method and the total fp (V_{pf}) and fd (V_{df}) hybridization energies estimated by Kumar et al. [24] using parameters from the tight binding approximation of Harrison, summing the values over all nearest neighbours

Compound	pf and df hybridization parameter×10^3 [eV^2]			Hybridization energy [eV]	
	Ce–In1	Ce–In2	Ce–M	V_{df}	V_{pf}
$CeCoIn_5$	6.08	14.36	0.19	0.307	2.066
$CeRhIn_5$	5.88	15.27	0.58	0.572	2.03
$CeIrIn_5$	6.16	17.04	0.77	0.627	2.031

Nonmagnetic $CeCoIn_5$ and AF $CeRhIn_5$ are good examples of the situation (i), their lattice parameters *a* are distinctly different (Table 1), whereas the fd hybridization strengths are very similar (see Table 3). Moreover, a transition to the SC state observed under a pressure of ~1.6 kbar in the magnetic $CeRhIn_5$ [5, 6] could be attributed to strong lattice contraction (i.e., increasing of *J*), experimentally observed [24].

The second reason (*ii*) is clearly documented when one compares the properties of $CeRhIn_5$ and $CeIrIn_5$; their unit cell volumes are very similar (Table 1), while the fd hybridization energies are different. On the base of (ii), we can understand the magnetic or nonmagnetic properties of the respective compounds at $T = 0$.

Note, that the interatomic hybridization between Ce 4f and In 5p states is dominant in the $CeMIn_5$ series (Table 3), however, this energy is the same in $CeRhIn_5$ and in $CeIrIn_5$, therefore it cannot decide about the ground state behaviour. The most important effect, we believe, is attributed to the fd hybridization strength, nevertheless, this energy is about one order in magnitude weaker than the fp interaction.

4. Conclusions

The magnetic/nonmagnetic character of the ground state of the $CeMIn_5$ is the result of the competition between effect of pressure exerted in the direction parallel to the basal plane of the unit cell and the hybridization between Ce 4f and the transition metal d-states. Both, strong fd hybridization and contraction of the lattice parameter *a* cause delocalization of the 4f states and, in consequence, lead to demagnetization and probably to a superconducting ground state.

We have found, that Ce in $CeRhIn_5$ and $CeIrIn_5$ are nearly trivalent, and the hybridization between the f states and the conduction electrons is stronger in $CeIrIn_5$. This suggests that f electrons in the superconducting $CeIrIn_5$ are more delocalized than those in AF $CeRhIn_5$, but generally the electronic structure of the both compounds is very similar. When strong correlation effects between the f electrons were taken into account by the GGA + U approach ($U \approx 1.65$ eV), the calculated total magnetic moment on the cerium atom in $CeRhIn_5$ is well compared to that obtained from neutron diffraction. The GGA + U calculations show that the 4f electrons both in

$CeRhIn_5$ and $CeIrIn_5$ are closed to the border which separates the localized and delocalized (itinerant) states.

Acknowledgements

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