

Photoemission study of $\text{CeRh}_{1-x}\text{Pd}_x\text{Al}$. The effect of Pd doping on electronic structure

W. GŁOGOWSKI, A. ŚLEBARSKI*

Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland

In view of a contrasting behaviour of Pd-containing and Rh-containing systems, we investigate solid solutions $\text{CeRh}_{1-x}\text{Pd}_x\text{Al}$ in order to determine the dependence of their electronic properties on the number of the conduction electrons. We present structural and X-ray photoemission spectroscopy (XPS) data for $\text{CeRh}_{1-x}\text{Pd}_x\text{Al}$. We also discuss the influence of the number of free electrons in the conduction band on the stability of the crystallographic structure and the occupation number of the f-shell.

Key words: *strongly correlated electron system; electronic structure*

1. Introduction

Ce-based Kondo-lattice systems exhibit unusual physical, behaviour such as of the heavy-Fermi (HF) liquid (e.g., CeRhSb , CeNiSn for $T > \sim 10$ K, $\text{Ce}(\text{Ni,Pt})\text{Sn}$ [1]) and non-Fermi liquid (NFL) types, in the metallic state (e.g., CeRhSn [2]) or Kondo-lattice insulating type state (CeRhSb [3] and CeNiSn [4]). Recently, we suggested that the NFL behaviour in CeRhSn may be due to the existence of Griffiths phases in the vicinity of the quantum critical point [2], whereas in CeRhAl [5] the disorder leads to an unconventional metallic state, which does not fit within the framework of FL theory [5].

The stability of paramagnetic as a magnetic ground state in the Kondo-lattice limit [6] is strongly dependent on the number of electrons per atom. In the series of compounds, CeRhSb , CeRhSn , and CeRhAl , the number of valence electrons per formula unit is 18, 17, and 16, respectively. In the case of momentum-dependent hybridisation, the gap formed at $T \rightarrow 0$ for CeRhSb may vanish, e.g. in CeRhSn . CeRhAl is expected to be an insulator, this, however, is not the case [7]. For CeRhAl , we have recently observed [5] a coexistence of antiferromagnetic ordering ($T_N = 3.8$ K) and the NFL-like behaviour.

In view of the diverse behaviour of CePdAl with respect to CeRhAl , it is of interest to examine the solid solution $\text{CeRh}_{1-x}\text{Pd}_x\text{Al}$, to see the effect of decreasing the

*Corresponding author, e-mail: slebar@us.edu.pl

number of s -states (conduction states, if one treats d -electrons as almost localized) on the properties ground state. The aim of this work is to investigate the crystallographic and electronic structure of this series of compounds.

2. Experimental details and discussion

The samples of $\text{CeRh}_{1-x}\text{Pd}_x\text{Al}$ were prepared by arc melting, and were then annealed at 800 °C for 3 weeks. The lattice parameters were acquired from diffraction patterns using the Powder-Cell program. X-ray photoelectron spectroscopy spectra (XPS) were obtained with monochromatised Al K_α radiation using a PHI 5700 ESCA spectrometer. The samples were found to be orthorhombic ($e\text{-TiNiSi}$ structure, space group $Pnma$) for $0 \leq x \leq 0.8$, whereas CePdAl crystallizes in a hexagonal structure (ZrNiAl -type, space group $P6_2m$). In Figure 1, we compare the X-ray diffraction (XRD) spectra measured and calculated for the orthorhombic samples CeRhAl , $\text{CeRh}_{0.4}\text{Pd}_{0.6}\text{Al}$, and hexagonal CePdAl .

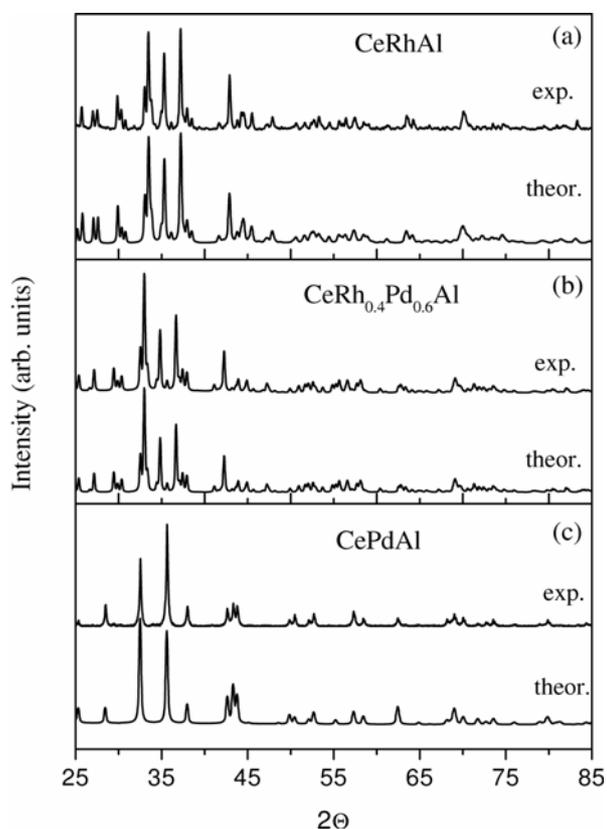


Fig. 1. XRD spectra and their calculated counterparts for CeRhAl , $\text{CeRh}_{0.4}\text{Pd}_{0.6}\text{Al}$, and CePdAl

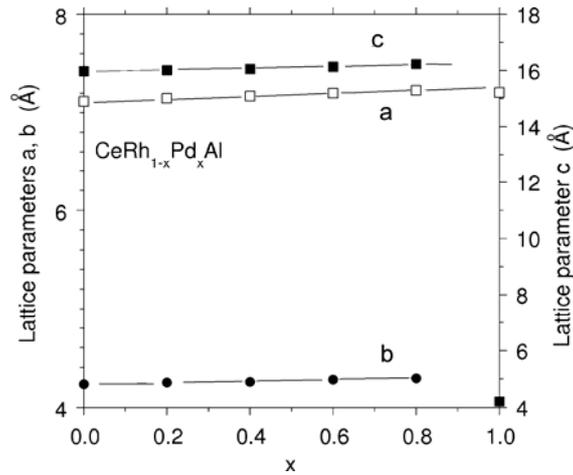
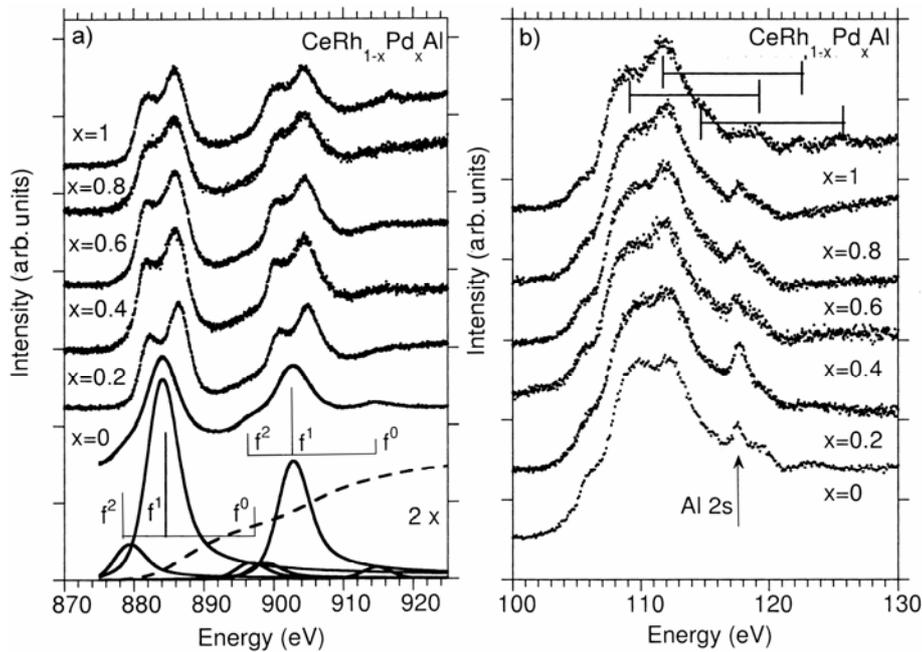
Fig. 2. Lattice parameters of $\text{CeRh}_{1-x}\text{Pd}_x\text{Al}$ 

Fig. 3. Ce 3d XPS (a) and Ce 4d XPS (b) spectra obtained for $\text{CeRh}_{1-x}\text{Pd}_x\text{Al}$. The f^0 , f^1 , and f^2 components in (a) are separated on the basis of Doniach–Šunjić theory. The satellite lines observed in the 3d XPS spectra of CePdAl are interpreted as plasmon losses with an energy of $\hbar\omega_p \approx 11$ eV

Figure 2 shows the lattice parameters for the $\text{CeRh}_{1-x}\text{Pd}_x\text{Al}$ series, determined from the best fit to the XRD spectra obtained experimentally. The volume of the unit cell systematically increases with x , whereas for CePdAl it rapidly decreases. $\text{CeRh}_{1-x}\text{Pd}_x\text{Al}$ samples with $x \leq 0.8$ have an orthorhombic $\text{Pd}_2(\text{Mn},\text{Pd})\text{Ge}_2$ -type structure,

which is a kind of a mixture of the orthorhombic CeRhSb and hexagonal CeRhSn-type structures [8], whereas the structure of CePdAl is hexagonal of the ZrNiAl-type [9].

Figure 3a shows the Ce 3d XPS spectra obtained for the series of compounds CeRh_{1-x}Pd_xAl. The contributions of the final states f^1 and f^2 are clearly observed, which exhibit a spin-orbit splitting of 18.6 eV. The presence of the f^0 component clearly marks the intermediate valence character of Ce atoms only for CeRhAl. Gunnarsson and Schönhammer (GS) have explained how to determine the properties of the initial f-state from Ce 3d XPS spectra [10] which are related to the final f-states. It is possible to estimate the hybridisation energy Δ from the ratio $r = I(f^2)/[I(f^1)+I(f^2)]$ (for details, see Ref. [10]), when the peaks of the 3d XPS spectra that overlap in Figs. 3 and 4 are separated (the method is described in Refs. [11–13]). The value of Δ is ~ 200 meV for CePdAl, ~ 190 meV for CeRh_{1-x}Pd_xAl samples with $x \leq 0.8$, and for CeRhAl it drastically decreases to ~ 70 meV.

The occupation number n_f of CeRh_{1-x}Pd_xAl is 0.9, whereas for the remaining CeRh_{1-x}Pd_xAl compounds $n_f \rightarrow 1$. We attribute the peak located at ~ 917 eV at the high-energy side of the f^1 component (see Fig. 4) in the 3d XPS spectra of CePdAl to plasmon losses with an energy of $\hbar\omega_p \approx 11$ eV. The same energy plasmons are visible in the Ce 4d XPS spectrum of CePdAl (see Fig. 3b).

There is a further evidence for the fluctuating valence of Ce in CeRhAl, as shown in Fig. 3b. The Ce 4d XPS spectra of CeRhAl exhibit two peaks, at ~ 119 and 123 eV, which can be assigned to the f^0 final state [10]. The indicated splitting of 3.1 eV has almost the same value as the spin-orbit splitting of the La 4d states.

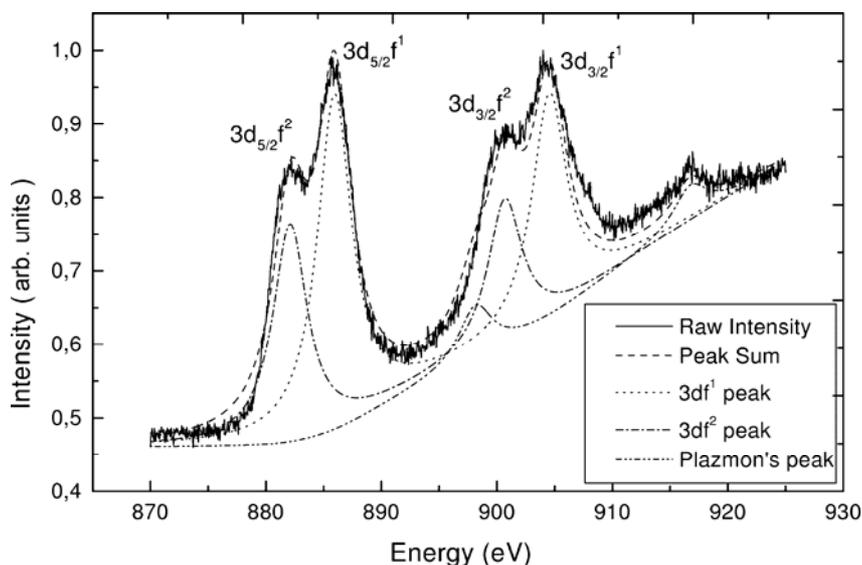


Fig. 4. Deconvolution of 3d Ce XPS spectra for CePdAl. The high-energy peaks located at 898 and 916.5 eV are of plasmon origin

We conclude that the Ce atoms of the components of the series $CeRh_{1-x}Pd_xAl$ containing Pd have stable f-shell configurations ($n_f = 1$), whereas $CeRhAl$ is an MV system. An increasing number of valence electrons (i.e. increasing x value) stabilize the occupation of the f shell ($n_f \rightarrow 0$). It is possible that both the stable configuration of Ce and the increasing number of conduction electrons give rise to the hexagonal structure of $CePdAl$ in the $CeRh_{1-x}Pd_xAl$ series of alloys.

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