

Electronic structure of CeRh₂Sn₄

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We performed a study of the compound CeRh₂Sn₄, not investigated so far. Our samples were carefully characterized by X-ray powder diffraction analysis and by locally resolved, energy dispersive X-ray spectroscopy (EDXS). We present a combined experimental and theoretical study based on X-ray photoelectron spectroscopy (XPS) data together with *ab initio* band structure calculations. The Ce 3d XPS spectrum indicates a small mixed valence of Ce. Analysis of the 3d⁹4f² weight using the Gunnarsson–Schönhammer theory suggests a hybridization between Ce 4f states and the conduction band of about 85 meV. The valence band spectrum, dominated by Rh 4d states, is in a very good agreement with the calculated one.

Key words: *electronic structure; XPS; FPLO*

1. Introduction

Many cerium based ternary compounds of Ce-T-X-type, where T is a transition metal and X is a p-element, exhibit unusual physical phenomena such as heavy-Fermi (HF) liquid or non-Fermi-liquid types of behaviour in a metallic state or a Kondo-lattice/valence-fluctuation type of state. The stability of paramagnetic or magnetically ordered ground state in such compounds strongly depends on the on-site hybridization energy among conduction and f electrons, the bare f-level position in the conduction band, the magnitude of intrasite Coulomb interaction and the number of electrons occupying the f-shell.

CeRhSn has attracted great interest during the last years due to its non-Fermi liquid character of low-temperature physical properties [1–6], having been explained in terms of the Griffiths phase. Moreover, in this system, Ce is in a mixed valence state and the Ce 4f states strongly hybridize with the conduction band. It is interesting to examine in detail the effect of stoichiometry and crystal structure on the formation of different ground states of the compound in the system Ce–Rh–Sn. Here, we present a study of a new compound CeRh₂Sn₄ which has not been investigated so far.

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2. Experimental

A polycrystalline sample of CeRh_2Sn_4 was prepared by arc melting of the elemental metals (Ce 99.99%, Rh 99.95% and Sn 99.99% in purity) in stoichiometric amounts on a water cooled hearth in an ultra-high purity Ar atmosphere with an Al getter. Our sample was remelted several times to promote homogeneity and annealed at 800 °C for 7 days. The sample was characterized by X-ray powder diffraction (XRD) analysis performed on a Siemens D-5000 diffractometer using CuK_α radiation. The lattice parameters obtained from the XRD patterns analysis using the POWDER-CELL program are in agreement with those previously reported [7]. The composition of the sample was examined by energy dispersive X-ray spectroscopy (EDXS) microanalysis. The quantitative measurements were performed at many points on the polished surface.

The electronic structure was studied by the Full Potential Local Orbital (FPLO) Minimum Basis method [8] within the local density approximation (LDA) using the experimental lattice parameters. In the scalar-relativistic calculations, the exchange and correlation potential of Perdew and Wang [9] was used. As the basis set, Ce (4f, 5s, 5p, 5d, 6s, 6p), Rh (4s, 4p, 4d, 5s, 5p) and Sn (4s, 4p, 4d, 5s, 5p, 5d) states were employed. The lower-lying states were treated fully relativistically as core states. The Sn 5d states were taken into account as polarization states to increase the completeness of the basis set. The treatment of the Ce (4f, 5s, 5p), Rh (4s, 4p) and Sn (4s, 4p, 4d) semicorelike states as valence states was necessary to account for non-negligible core–core overlaps. The spatial extension of the basis orbitals, controlled by a confining potential $(r/r_0)^4$, was optimized to minimize the total energy. A k -mesh of 90 points in the irreducible part of the Brillouin zone (400 in the full zone) was used.

The X-ray photoelectron spectroscopy (XPS) data were obtained with monochromatized AlK_α radiation at room temperature using a PHI 5700 ESCA spectrometer. The spectra were recorded immediately after breaking the sample in a ultra-high vacuum of 10^{-10} Torr. Calibration of the spectra was performed according to [10]. Binding energies were referenced to the Fermi level ($\varepsilon_{\text{F}} = 0$).

3. Results and discussion

Figure 1 shows a part of a polished surface of the sample. The composition of the main phase (phase 1) was examined at a few points and was found not to be in agreement with stoichiometric CeRh_2Sn_4 . Rather, under the used conditions, the phase $\text{Ce}_{1.2}\text{Rh}_2\text{Sn}_{3.8}$ (see Table 1) forms with the content of ~85 %. There are pieces of an additional phase, marked as phase 2, between the larger grains of the main phase. We found also few grains of a third phase. Based on the combined EDXS and XRD analysis we obtained a fraction of ~9% of RhSn_2 (phase 3) and ~6% of $\text{Ce}_3\text{Rh}_4\text{Sn}_{13}$ (phase 2) in the bulk CeRh_2Sn_4 sample.

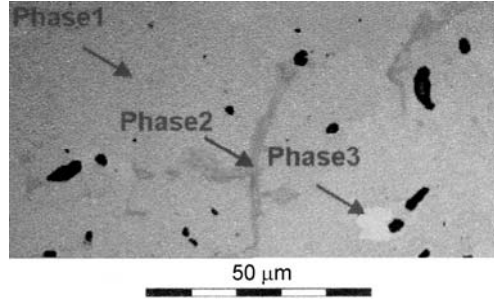


Fig. 1. A part of the polished surface of the sample

Table 1. Average atomic concentrations of Ce, Rh and Sn in phases detected in the sample, estimated on the basis of the EDX patterns analysis

Phase	Ce	Rh	Sn
	at. %		
1	17.34	28.61	54.06
2	16.84	20.14	63.02
3	1.96	32.82	65.21

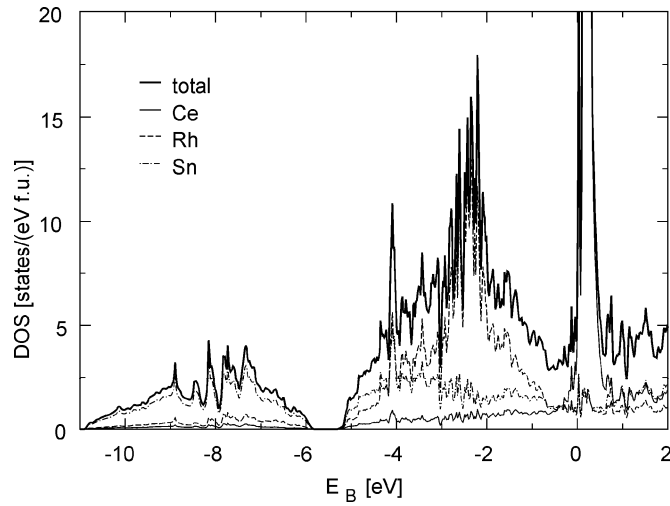
Fig. 2. The total and partial DOS on Ce, Rh and Sn for CeRh_2Sn_4

Figure 2 shows the results of the numerical calculations of the total and partial densities of states (DOS) for paramagnetic CeRh_2Sn_4 within LDA. The partial l-resolved DOSs were multiplied by the corresponding cross sections [10]. The results were convoluted by a Fermi function for 300 K and by pseudoVoigt function with a full-width-half-maximum (FWHM) of 0.4 eV and 0.4 eV for Lorentzian and Gaussian, respectively, to take into account the live-time broadening of the hole states, the

instrumental resolution and phonon broadening. A background, calculated by means of the Tougaard algorithm [12], was subtracted from the XPS data.

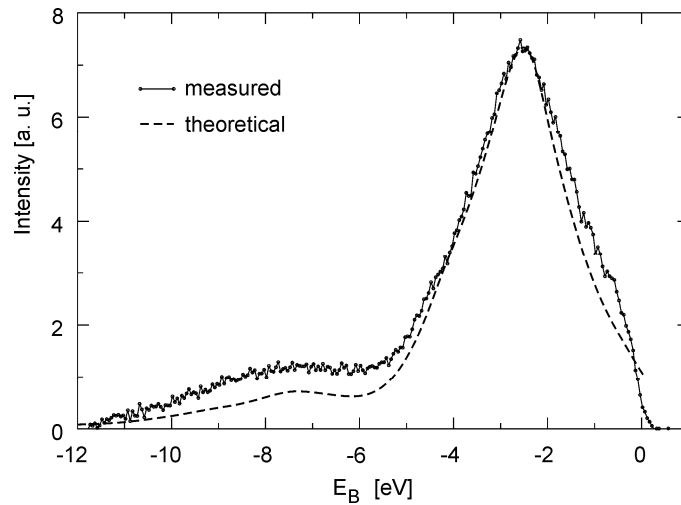


Fig. 3. Measured XPS valence band spectrum and the spectrum calculated by the FPLO method within LDA approximation for paramagnetic CeRh_2Sn_4

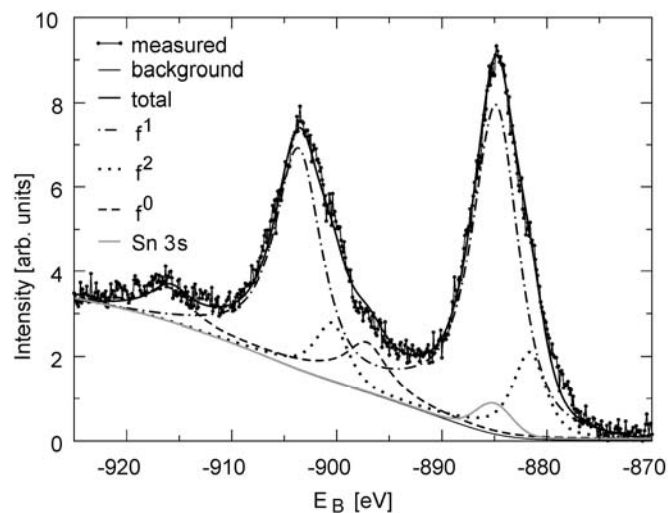


Fig. 4. The Ce 3d XPS spectrum deconvoluted based on the Gunnarsson-Schönhammer theory [15, 16]

The agreement between the calculated and measured XPS valence band spectra is good (Fig. 3). The spectrum reveals that the valence band of CeRh_2Sn_4 has a major peak mainly due to the d states of Rh located at about 2.5 eV and Sn 5p states. The second peak centered at about 8 eV is mainly due to the Sn 5s states. The Ce 4f states

give only a negligible contribution to the total XPS spectra of CeRh_2Sn_4 . The Ce 3d core-level XPS spectrum for CeRh_2Sn_4 is presented in Fig. 4.

Three final-state contributions f^0 , f^1 and f^2 are clearly observed, which exhibit a spin-orbit splitting $\Delta_{\text{SO}} \approx 18.8$ eV. This value is in agreement with the one calculated by the FPLO method (18.83 eV). There is also an overlap of the Ce 3d photoemission lines with the Sn 3s peak at the binding energy of 885 eV. The separation of the overlapping peaks in the Ce 3d XPS spectrum was done on the basis of the Doniach-Šunjić theory [13]. The appearance of the f^0 components suggests a mixed valence behaviour of Ce, while the f^2 peaks located at the low-binding energy side of the f^1 components appear when the core hole becomes screened by an extra 4f electron. Such a situation may occur due to a hybridization of the 4f shell with the conduction band. Consequently, the intensity of the f^2 peak with respect to the sum of the intensities of the f^1 and f^2 peaks could reflect the degree of the hybridization. The hybridization energy Δ , which describes the hybridization part of the Anderson impurity Hamiltonian [14], is defined as

$$\Delta = \pi V_{fs}^2 N(E)_{\text{max}}$$

where V is the hybridization matrix element and $N(E)_{\text{max}}$ is the maximum value of DOS. We estimated Δ from the ratio $r = I(f^2)/[I(f^1) + I(f^2)]$, in accordance with the procedure given by Gunnarsson and Schönhammer [15, 16]. For CeRh_2Sn_4 , we obtained $\Delta \approx 85$ meV, which is significantly smaller than that for CeRhSn (~ 120 meV) suggesting that the Ce 4f states of CeRh_2Sn_4 are more localized than those of CeRhSn .

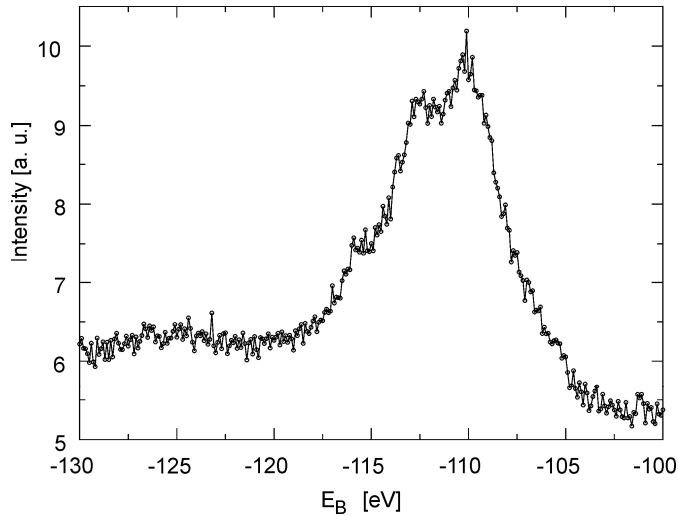


Fig. 5. The Ce 4d XPS spectrum for CeRh_2Sn_4

Based on the Gunnarsson-Schönhammer theory we also estimated the Ce 4f occupation number n_f from the intensity ratio: $I(f^0)/[I(f^0) + I(f^1) + I(f^2)]$. We obtained $n_f \approx 0.92$ which

suggests that the valence of Ce in CeRh_2Sn_4 is close to $3+$. This is consistent with the Ce 4d XPS spectrum (Fig. 5) where one can observe a multiplet structure between the binding energies 104 eV and 119 eV. These lines have been assigned to the $3d^9f^1$ final state. There is no evidence for additional peaks which could be attributed to the Ce $3d^9f^0$ states.

4. Conclusion

A sample of nominal composition CeRh_2Sn_4 was characterized by the XRD analysis and by EDXS. It was found that the main phase corresponds to the composition $\text{Ce}_{1.2}\text{RhSn}_{3.8}$. The core-level XPS spectra exhibited that Ce in $\text{Ce}_{1.2}\text{Rh}_2\text{Sn}_{3.8}$ is nearly trivalent and the hybridization between Ce 4f states and conduction band is of about 85 meV which suggests that in $\text{Ce}_{1.2}\text{Rh}_2\text{Sn}_{3.8}$ Ce 4f states are rather well localized. The valence band spectrum calculated on the basis of FPLO results within the LDA is dominated by Rh 4d states and is in a very good agreement with the measured one. Specific heat, magnetic susceptibility and resistivity measurements are in progress.

Acknowledgements

The authors thank for financial support from the Project No. 1 PO3B 052 28, for the Grant No. N202 010 32/0487 of Ministry of Education and Science and for the DFG, Emmy Noether program.

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Received 7 May 2006
Revised 1 September 2006