

# Electronic structure and photoemission studies on Kondo semimetal $U_2Ru_2Sn$

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**Abstract.** Electronic structure is studied of the compound  $U_2Ru_2Sn$  showing Kondo type anomalies. The X-ray photoemission spectrum (XPS) on a single crystal was measured and the crystal structure refinement was done. The electronic band structure was calculated by the tight-binding linear muffin-tin orbital method in the atomic sphere approximation, with non-local corrections to the exchange-correlation potential and spin-orbit effects included. The XPS valence band is well reproduced by the calculated one. Calculations suggest metallic character of  $U_2Ru_2Sn$  and give the electronic specific heat coefficient by a factor 1.4 larger than the experimental value reported in literature.

**PACS.** 71.20.-b Electron density of states and band structure of crystalline solids – 82.80.Pv Electron spectroscopy (X-ray photoelectron (XPS), Auger electron spectroscopy (AES), etc.)

## 1 Introduction

In recent years there have been rising interests in so-called Kondo semiconductors. To this class of materials belong several cubic systems, like e.g.  $Ce_3Pt_3Bi_4$ , or the orthorhombic cerium ternaries  $CeTM$  ( $T = Ni, Rh; M = As, Sb, Sn$ ) [1,2]. The most important compounds in this series  $CeNiSn$ ,  $CeRhAs$ , and  $CeRhSb$  crystallize in the  $\varepsilon$ - $TiNiSi$ -type structure, while the metallic  $CeRhP$  compound adopts the tetragonal  $LaPtSi$ -type structure [3,4]. Although  $CeRhBi$  has the orthorhombic structure as its arsenide and antimonide counterparts, it is a Fermi liquid heavy fermion system [5]. The name of this class of compounds comes from the observation that their transport properties show a Kondo or an intermediate valence behaviour at higher temperatures and a gap opening at the Fermi level at low temperatures. All these compounds are non-magnetic to the lowest temperatures. The development of an energy gap  $\Delta/k_B$  of a few Kelvin especially in the latter non-cubic systems, called by Kasuya [6] *exotic Kondo insulators* (metals), is considered to be associated with the hybridization of the  $f$  states with conduction band electrons which makes them a “spin gap”. If a clear V-shaped gap formation for  $CeTM$  ternaries is manifested by NMR [7] and tunnelling-spectra (e.g. [8]) measurements, simultaneously a large residual coefficient of electronic heat capacity at  $T$  approaching 0 K is observed (see for

example [9]). Hence, the observed a V-shape pseudo-gap located at the Fermi level classifies these systems rather as semimetals than semiconductors. Moreover, the recent Shubnikov–de Haas (SdH) oscillations, observed for a high quality  $CeNiSn$  single crystal [10], provide clear evidence about metallic character of this prototype Kondo semiconductor. In turn, high-resolution photoemission spectroscopy experiments made for  $CeRhAs$  and  $CeRhSb$  [11] at low temperatures are interpreted in terms of a pseudogap formation in their densities of states (DOS). Also the investigated electronic structure of pure and alloyed  $CeNiSn$  [12,13] and  $CeRhSb$  [14] by self-consistent spin-polarized linear muffin-tin orbital (LMTO) calculations clearly indicated the presence of indirect gap, however being much sensitive on alloying. Nevertheless, the LMTO calculations gave a small value of the DOS at  $E_F$ , confirming a pseudogap formation. The valence band XPS spectra were also compared with calculations of the electronic structure [13,14]. Furthermore, the  $3d$  and  $4d$  core-level of Ce XPS spectra have been studied [14], which clearly indicated the intermediate valence of Ce in  $CeRhSb$  in agreement with the susceptibility results (i.e. an observation of broad high temperature maximum in  $\chi(T)$ .)

In this work we turn our attention to the semimetallic uranium ternary compound  $U_2Ru_2Sn$ , which belongs to a series of ternaries  $U_2T_2Sn$ , where  $T$  is a transition metal. All these ternaries crystallize in an ordered version of the tetragonal  $U_3Si_2$ -type structure (P4/mbm) [15]. In

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**Table 1.** Crystal data and structure refinement for  $U_2Ru_2Sn$ .

Wavelength	0.71073 Å
Crystal system, space group	tetragonal, P4/mbm
Unit cell dimensions	$a = 7.497(1)$ Å $c = 3.563(1)$ Å
Volume	$200.26(7)$ Å <sup>3</sup>
Z, Calculated density	2, 13.216 Mg/m <sup>3</sup>
Absorption coefficient	$93.869$ mm <sup>-1</sup>
F(000)	644
Theta range for data collection	5.44 to 34.31 deg.
Reflections collected / unique	2530 / 252 [ $R(int) = 0.0973$ ]
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	252 / 0 / 12
Goodness-of-fit on F <sup>2</sup>	1.280
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0358$ , $wR2 = 0.1134$
R indices (all data)	$R1 = 0.0406$ , $wR2 = 0.1206$
Extinction coefficient	0.041(4)

this paper we give for the first time the crystal structure refinement of this compound.

The Kondo semimetal assignment to this compound, being the first one among actinide compounds, was based on the observation of the resistivity rise upon cooling below 30 K [16] and intermediate-valence behaviour of the susceptibility [17]. Then, the Hall effect, <sup>119</sup>Sn NMR, thermopower, heat capacity and thermal conductivity measurements performed on the polycrystalline samples of  $U_2Ru_2Sn$  [18,19] have been reported. Indeed, all these measurements, performed down to lower temperatures, suggest the existence in the DOS of this compound a narrow energy gap of about 75 K. Thus, the energy gap of this compound is about one order of magnitude larger than that for the CeTM-type compounds. Nevertheless, a carefully reasoned comparison with the archetypal Kondo semimetal CeNiSn brings several striking resemblances (see Ref. [18]). Very recent magnetoresistivity (MR) and magnetic susceptibility measurements made on a  $U_2Ru_2Sn$  single-crystal of this non-magnetically ordered Kondo semimetal [20] indicate its highly anisotropic properties. For example the resistivities yield band-gap values, which differ by two orders of magnitude depending on the direction of the current. Also the magnetoresistivity and magnetic susceptibility are highly anisotropic. The transverse MR is always positive and varies quadratically with an applied magnetic field  $B$ . A puzzling maximum and a sign change which both occur around  $T = 25$  K are observed in the temperature dependences of transverse and longitudinal MR, respectively. Thus, this temperature corresponds to the temperature of the inflection point  $T_{inf}$  in the  $\rho(T, j||a)$  dependence and may signalize some reconstruction in the electronic structure taking place at low temperatures.

In this paper we present results of refinements of the crystallographic data and measurements of the XPS spectra together with computation of the electronic band

structure and the XPS spectrum for the compound  $U_2Ru_2Sn$ .

## 2 Experimental

The polycrystalline sample was prepared by melting constituents in an arc furnace under titanium gettered atmosphere of ultrahigh-purity. The purity of elements was: U (99.98%), Ru (99.99%) and Sn (99.999%). The X-ray pattern showed no evidence for the existence of any parasitic phases.  $U_2Ru_2Sn$  in the form of single-crystalline sample was obtained by Czochralski method. Microprobe examination, made with a Philips SEM515 scanning electron microscope and EDAX PV9800, have shown a good homogeneity and composition close to the nominal one of the sample. No impurity elements were detected.

For the X-ray refinement of the structure a very small single crystal was isolated from the crushed sample and examined by means of a KUMA DIFFRACTION KM-4 four circle automatic diffractometer equipped with a CCD camera, using graphite monochromatized Mo  $K_\alpha$  radiation. An analytical absorption correction has been applied. The compound is tetragonal, of  $U_2Si_3$ -type with space group P4/mbm [15]. A careful analysis of the data has revealed the occupancy factor for each atom to be of 1.00(1). It has further shown that the structure is completely ordered. Details are summarized in Tables 1 and 2. The measured lattice parameters (at wavelength 0.79073 Å, temperature 293(2) K) are  $a = 7.4970(10)$  Å,  $c = 3.5630(10)$  Å, in a fair agreement with recently published data [15,17]. Atomic coordinates and both isotropic and anisotropic displacement parameters are listed in Table 2. Clearly,  $U_2Ru_2Sn$  is isostructural to many other uranium 2 :2: 1 stannides [15].

The XPS spectra were collected with monochromatized Al  $K_\alpha$ , 1486.6 eV, radiation at room temperature. The energy spectra of emitted electrons were analysed by

**Table 2.** Structural parameters of  $U_2Ru_2Sn$  (tetragonal, P4/mbm).

Atom	$X$	$y$	$z$	$U_{(eq)}$	$U_{11}$	$U_{33}$	$U_{12}$
U	0.1686(1)	0.6686(1)	0.5	0.009(1)	0.010(1)	0.007(1)	0.001(1)
Sn	0.0	0.0	0.0	0.009(1)	0.007(1)	0.012(1)	0
Ru	0.1356(2)	0.3644(2)	0.0	0.013(1)	0.011(1)	0.016(1)	-0.002(1)

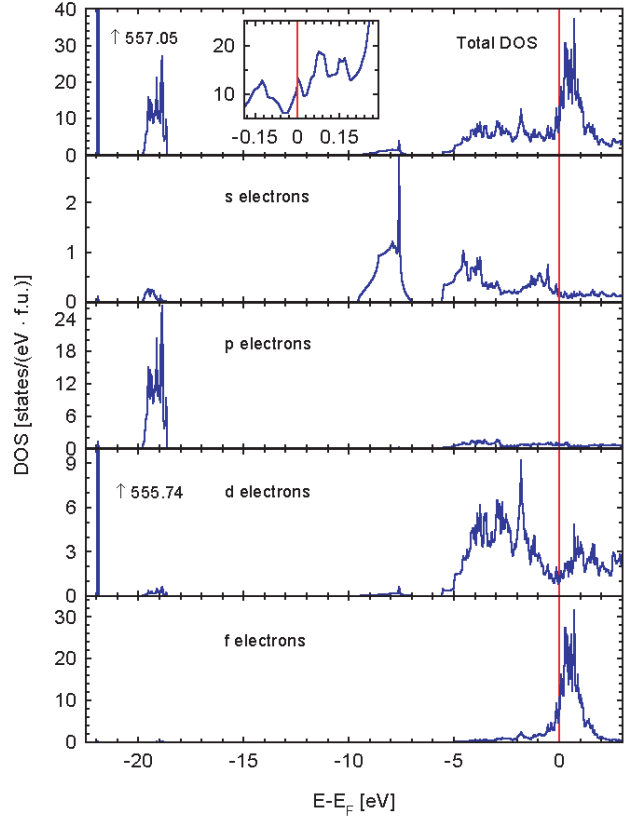
$U_{11} = U_{22}, U_{23} = U_{13} = 0$

a hemispherical mirror analyser with an energy resolution of about 0.3 eV. The Fermi level was referred to gold, to the  $4f$ -level of binding energy 84.0 eV. The spectra were measured in vacuum of  $5 \times 10^{-10}$  Torr, immediately after cleaving the sample in situ. We repeatedly cleaved the sample in situ about every 10 min in order to check if we had for each time the same spectrum. This gave us a proof that we dealt with a high quality (001) cleaved plane for each breaking, being pure and having flat surfaces. These planes were obtained from single-crystalline bars cut along the [001] axis and also used in transport measurements [20]. No effects of oxidation during the data acquisition time were observed. In addition we have confirmed by XPS analysis that the surface stoichiometry composition of the sample was only different from the ideal 2: 2: 1 within 2% for each element in the sample.

### 3 Electronic structure

The electronic band structure was calculated by the tight-binding linear muffin-tin orbital method (TB-LMTO) in the atomic sphere approximation (ASA) [21, 22]. The room temperature experimental values of the lattice parameters (Tab. 1) were assumed for computations. In the crystal structure of  $U_2Ru_2Sn$  each type of atoms occupy equivalent positions in the unit cell. The unit cell accommodates two formula units, the positions of atoms are given in Table 2. In the ASA the volume of the unit cell is divided into the Wigner-Seitz (W-S) atomic spheres of the radii 1.7242 Å, 1.4751 Å and 1.9340 Å for U, Ru and Sn atoms, respectively. The average Wigner-Seitz radius is 1.6846 Å. No magnetic ordering was discovered for  $U_2Ru_2Sn$ , therefore only the results of computations without spin polarization will be presented below. (The spin-polarized calculations were also done but they lead to a strongly unstable ferromagnetic state with the magnetic moment of  $2.8 \mu_B$  per formula unit.)

The starting atomic configurations were assumed as core  $+6p^65f^36d^17s^2$  for U, core  $+4d^75s^1$  for Ru and core  $+4d^{10}5s^25p^2$  for Sn. The overlap volume of muffin-tin spheres for the chosen W-S radii  $S_j$  was 9.15%. The standard combined corrections for overlapping W-S spheres [21] were applied to compensate the ASA errors. The fully relativistic treatment was used for the core electrons and the scalar relativistic approximation was adopted for the valence electrons. The spin-orbit effects were taken into account within the Min-Jang scheme [23]. The Perdew et al. [24] exchange-correlation potential with non-local corrections were used. The self-consistent calculations were performed for 495  $k$ -points in the irreducible wedge (1/16) of the Brillouin zone. The iteration proce-



**Fig. 1.** Total density of states (DOS) for  $U_2Ru_2Sn$  and its contributions from  $s, p, d$  and  $f$  electrons. In the inset in the upper panel the total DOS around the Fermi energy is shown in an expanded energy scale.

dure was ended when the self-consistency within 0.01 mRy error was achieved. For the integration in the  $k$ -space the standard tetrahedron method was used [25–27].

The computed partial densities of states (DOS) for the constituent atoms in the compound multiplied by the respective weight factors proportional to the atomic cross-sections for photon scattering (provided in Ref. [28]) and convoluted with the Gaussian function gave the calculated X-ray photoemission spectra. The parameter for the Gaussian distribution was taken equal to the experimental resolution  $\delta = 0.3$  eV.

### 4 Results and discussion

The calculated electronic structure of  $U_2Ru_2Sn$  gave density of states (DOS) plots presented in Figures 1–2. The total DOS in the uppermost panel of Figure 1 is decomposed into contributions from  $s, p, d$  and  $f$  electrons in

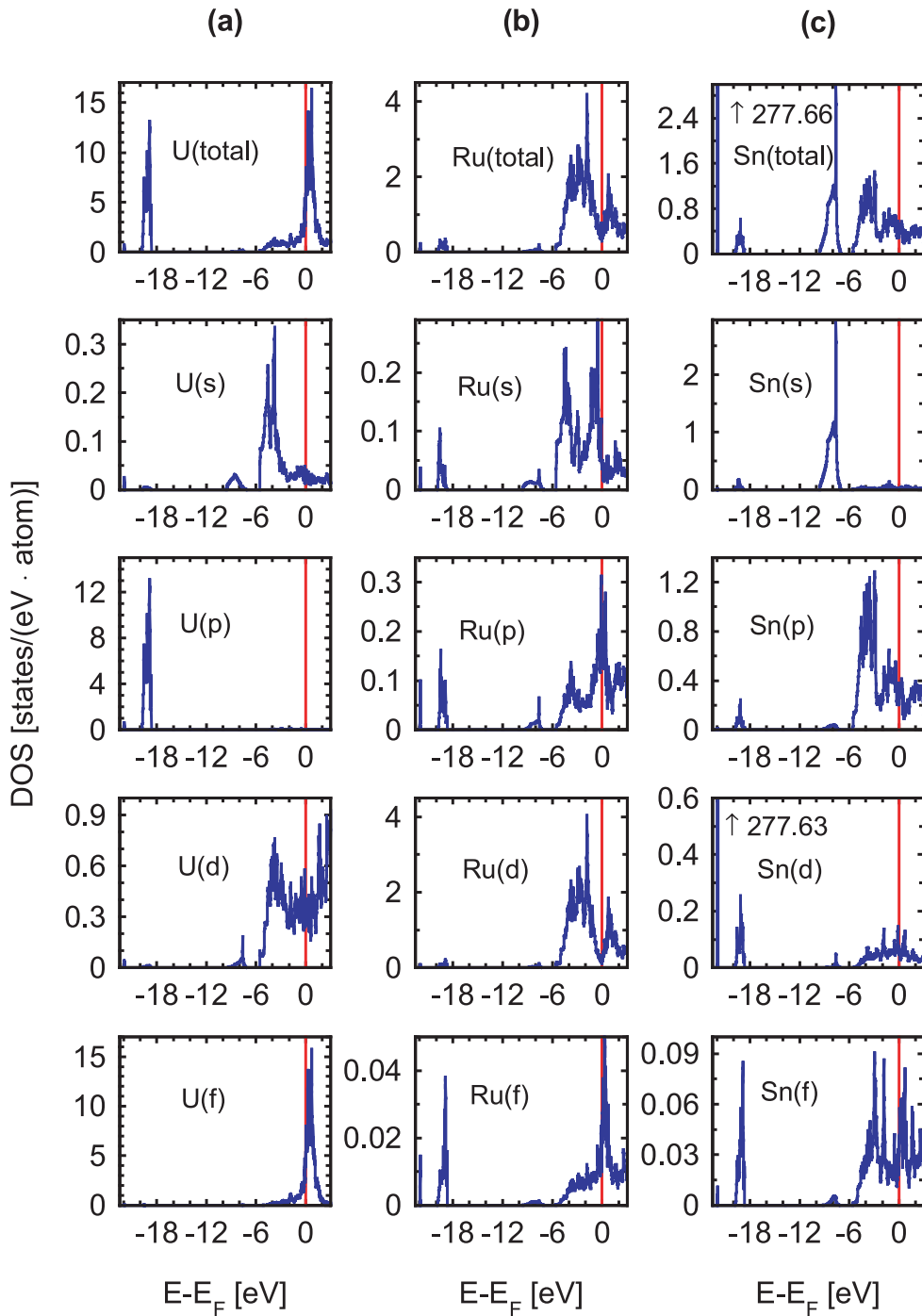


Fig. 2. Site projected and partial contributions to DOS.

respective panels (note the different vertical scales). The inset in the uppermost panel of Figure 1 displays on an expanded energy scale the important region near the Fermi energy ( $E_F$ ). Site-projected DOS are presented in Figure 2 (a, b and c) for the U, Ru and Sn atoms, respectively.

In the total DOS a few characteristic features can be observed. The valence band from about  $-5$  eV to the Fermi level (taken as  $E_F = 0$ ) is dominated by contributions from the  $d$ -electrons, mainly from Ru. Also appreciable contributions to this region of the valence band come from the Sn  $p$ -electrons, U  $d$ - and  $s$ -electrons. The

unoccupied part of DOS above  $E_F$  consists of a rather wide ( $\sim 2$  eV) band due to the  $5f$  electrons from U with a signature of spin-orbit splitting and a quite substantial contribution from the Ru  $d$ -electrons. A gap of the order 2 eV separates the main valence band from not very pronounced contributions coming essentially from the Sn  $s$ -electrons. The band of width  $\sim 1$  eV centred at about  $-19$  eV and showing some structure is due to the U  $p$ -electrons (94.9%) with small contributions from the Ru (0.9%) and Sn (0.6%)  $p$ -electrons. The very narrow strong peak at  $\sim -22$  eV results from the Sn  $d$ -electrons which

**Table 3.** DOS at the Fermi level for  $U_2Ru_2Sn$  compound (states/(eV (atom or f.u.))).

Atom	Electrons				Total ( $s + p + d + f$ )
	$s$	$p$	$d$	$f$	
U	0.032	0.049	0.370	4.778	5.229
Ru	0.048	0.203	0.226	0.022	0.499
Sn	0.019	0.311	0.071	0.036	0.437
Total (per f.u.)	0.179	0.815	1.263	9.636	11.893

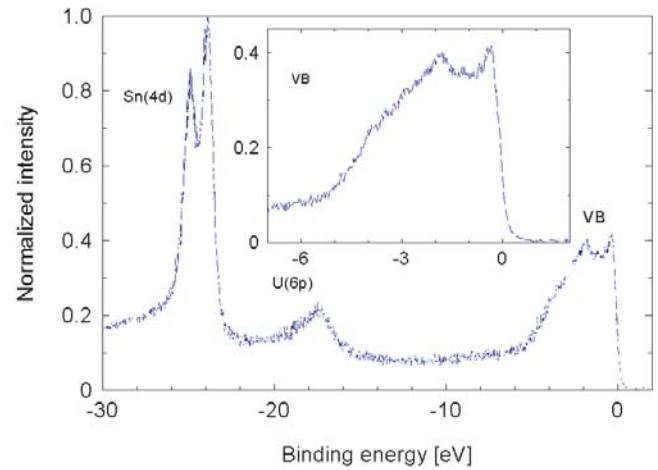
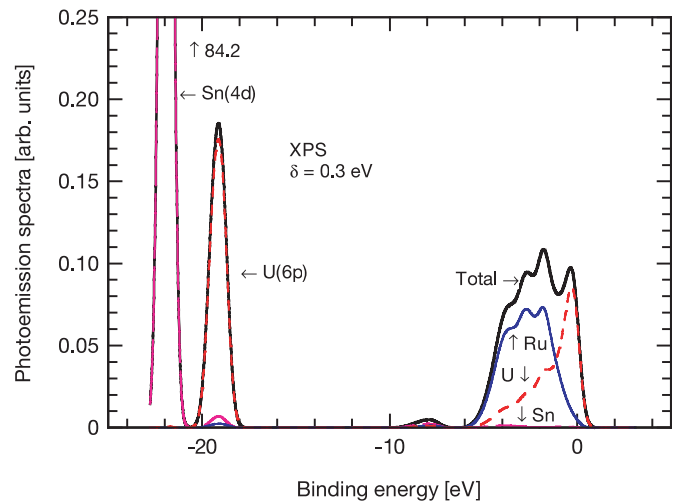
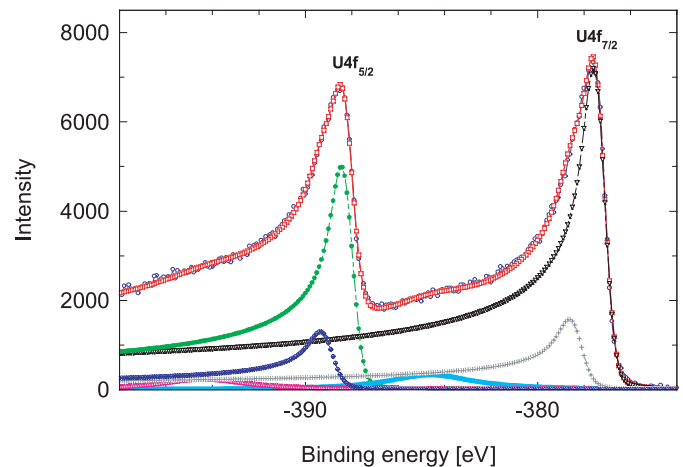
**Table 4.** Numbers of states for  $U_2Ru_2Sn$  compound (per atom or f.u.).

Atom	Electrons				Total ( $s + p + d + f$ )
	$s$	$p$	$d$	$f$	
U	0.4734	5.9519	2.0430	3.0255	11.4938
Ru	0.6368	0.4942	6.7975	0.0479	7.9764
Sn	1.7085	2.8969	10.2794	0.1748	15.0596
Total (per f.u.)	3.9289	15.7891	27.9604	6.3216	54.0000

appear to be to a much extent localised. The general features of the electronic band structure of  $U_2Ru_2Sn$  calculated here are quite similar to the ones obtained for other members of the family of  $U_2T_2M$  isostructural compounds [29,30].

The low binding energy part of the measured XPS spectrum is shown in Figure 3. The inset presents the valence band in an expanded energy scale. The theoretical spectrum is given in Figure 4. The valence band is rather well reproduced by calculations. The lowest-energy narrow peak results from the U  $5f$  electrons. At higher binding energies (B.E.) the contributions from the Ru  $4d$  electrons dominate. The second maximum observed at a B.E. . . of  $-2$  eV nearly coincides with the corresponding peak in the theoretical curve. The positions and shapes of the features at higher (absolute) values of B.E. are not reproduced so well by calculations. The calculated position of the peak from the U  $6p$ -electrons is at a B.E. of about  $-19$  eV in contrast to the experimental peak at about  $-17.5$  eV. Also the calculated peak from the Sn  $4d$ -electrons is shifted in B.E. by about 2 eV with respect to the centre of the spectral weight associated with the experimental Sn  $4d$  line (Fig. 3). The calculated Sn  $4d$  line does not show the splitting seen in the experiment.

The spectrum due to the U  $4f$ -core electrons is given in Figure 5. The  $4f$  spectrum shows two asymmetric lines resulting from  $4f_{7/2}$  and  $4f_{5/2}$  levels, split by the spin-orbit interaction. The two-line structure with a separation of about 11 eV is typically observed in a number of uranium compounds. A trace of weak satellites can be seen from the

**Fig. 3.** Measured XPS spectrum of  $U_2Ru_2Sn$ . The valence band in an expanded energy scale is presented in the inset.**Fig. 4.** Calculated XPS spectrum. The contributions to the valence band from U (broken line), Ru (light line) and Sn (long-dash) are shown. The line at the binding energy  $-19$  eV is decomposed into the dominant contribution from U  $6p$  electrons, small one from Ru and even smaller from Sn.**Fig. 5.** Measured XPS spectrum from U  $4f$ -core electrons. The two spin-orbit split lines  $4f_{5/2}$  and  $4f_{7/2}$  are decomposed into the asymmetric main lines and satellites.

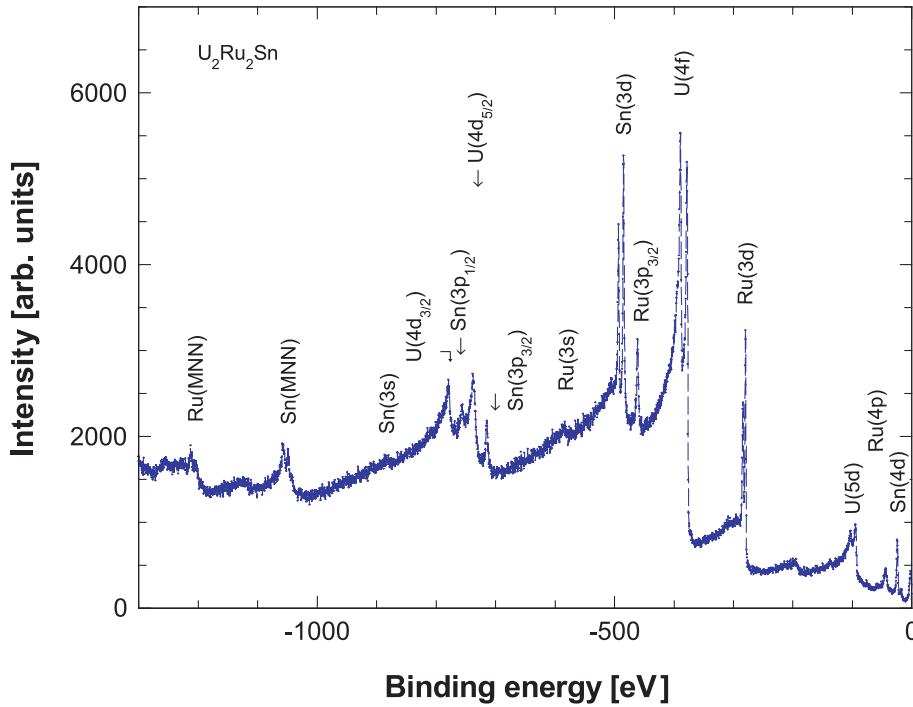


Fig. 6. XPS of  $U_2Ru_2Sn$  in a broad binding energy range.

raw experimental data. The standard procedure of subtracting the background [31] was applied and the deconvolution of the total core level curve had been made. The asymmetric lines were fitted to the line shapes proposed by the Doniach-Šunjić theory [32]. The value 0.46 was taken for the singularity index  $\alpha$ . As a result one gets a decomposition into an asymmetric main line accompanied by two asymmetric satellites: one at about 1 eV higher binding energy and a weak and broad satellite at about 7 eV higher binding energy with respect to the main line (see Fig. 5). The physical origin of the asymmetry of the main lines is the screening of the ( $4f$ ) core-hole potential by the  $5f$  electrons on neighbouring U atoms [33,34]. The 7 eV-satellite is often found in uranium compounds however in the present case it unexpectedly appears to be quite small and broad. Their intensity is related to the degree of the  $5f$  electron localization [35]. The low intensity of these 7 eV-satellites in the present case would indicate a rather itinerant character of  $5f$  electrons. The asymmetric satellites at 1 eV B.E. with respect to the main lines are reminiscent of similar satellites, but at about 3 eV B.E., which have been found in previous studies on several ternary uranium compounds (see for example Ref. [37] and discussion therein). The structure of the  $4f$  lines, consisting of the main line and two satellites, is interpreted as resulting from contributions of  $5f^2$ ,  $5f^3$  and  $5f^4$  final states in the photoemission processes. This interpretation is compatible with the so-called dualism of the  $5f$  electrons behaviour encountered in intermetallic uranium compounds [38]. It was reported in literature that uranium oxides gave a symmetric peak at about 3 eV higher B.E. with respect to the main line [36]. The uranium oxides peak was a reason of concern in the previous studies of uranium compounds having the

7 eV, 3 eV satellite structures of the  $4f$  lines (e.g. [37]). However for  $U_2Ru_2Sn$  the satellite structure is different with 1 eV satellites instead of 3 eV ones. Therefore this provides a proof that uranium oxides do not contribute to the  $4f$ -spectrum of  $U_2Ru_2Sn$ . Moreover, the high quality of the crystal used in the present investigations together with experimental precautions suggests that oxides contributions in Figure 5 are unlikely. This conclusion also arises from the analysis of the XPS spectrum made in a broad energy range which is displayed in Figure 6.

## 5 Conclusions

$U_2Ru_2Sn$  has very peculiar properties. Its transport properties indicate on a Kondo-semiconducting [17] or semimetallic [19] behaviour according to various sources. On the other hand, the quite large value of  $\gamma(0) \cong 20$  mJ/(K<sup>2</sup> mol) of the electronic contribution to the specific heat was reported [39], which had recently been confirmed by low-temperature heat capacity measurements of Tran et al. [18] ( $18 \pm 1$  mJ/(K<sup>2</sup> mol), clearly indicating on a metallic character of this compound. The band structure calculations give a finite DOS at the Fermi level thus supporting the idea of a metallic state. Calculated from DOS( $E_F$ ) value of the Sommerfeld coefficient is  $\gamma_{th} \approx 28$  mJ/(K<sup>2</sup> mol). The measured value of  $\gamma(0)$  is significantly smaller than for  $U_2T_2Sn$  ternaries [39]. It is strange however that the calculated value  $\gamma_{th}$  exceeds the measured  $\gamma(0)$ . A likely explanation may be the inaccuracy of the TB-LMTO-ASA method in treating the highly correlated  $5f$  electrons on U. A small shift of the steep shoulder of the U  $5f$  contribution to the density of

states near  $E_F$  could have a dramatic effect on  $DOS(E_F)$  and hence on  $\gamma_{th}$ .

In conclusion one can observe that the calculated valence band XPS spectrum is in a rather good agreement with the experimental one providing some confidence in the validity of the band structure calculations based upon the density functional theory to systems with  $5f$  electrons. The DOS in the vicinity of the Fermi energy shows a V-shaped pseudo-gap at about 0.04 eV below the Fermi level. It is not clear if this feature is related to the Kondo pseudo-gap which is invoked to explain the transport properties and is anticipated from many body effects. The satellite structure of the  $4f$  line, discussed in details above, supports the view of the dual nature of  $5f$  electrons, partly localized and partly itinerant.

Further theoretical and experimental works are needed to explain the very interesting properties of  $U_2Ru_2Sn$ , which behaves completely different than the other members of the  $U_2T_2M$  family.

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