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Dense Kondo compound UCu_5Sn —electronic structure and x-ray photoemission

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Abstract

The electronic structure of the paramagnetic phase of the dense Kondo, moderate heavy-fermion compound UCu_5Sn was studied by x-ray photoemission and by calculations. The band structure was calculated using the tight-binding linear muffin-tin orbital method in the atomic sphere approximation. The calculated x-ray spectrum is in reasonable agreement with the experimental one. The electronic specific heat enhancement factor is $\gamma/\gamma_0 \approx 11$, pointing out the essential role played by the Kondo-type many-body interactions. A complex satellite structure of the core 4f spectrum from U is an indication of a possibly mixed valence state of uranium in UCu_5Sn .

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years a rapidly increasing interest has been attributed to the ternary uranium-based intermetallics, showing often strongly correlated electronic states (heavy quasiparticles) at low temperatures. Those ternaries which contain a transition metal in their compositions attract particular interest, for example URu_2Si_2 , UNi_2Al_3 , UPd_2Al_3 and $\text{U}_2\text{Pt}_2\text{In}$. They, except for the latter, are not only magnetically ordered heavy-fermion (HF) systems, but also display superconducting properties at low temperatures [1]. In turn the HF system $\text{U}_2\text{Pt}_2\text{In}$ does not magnetically order and is the first compound in the $\text{U}_2\text{T}_2\text{M}$ series exhibiting a so-called non-Fermi-liquid state [2]. As recently proposed [3, 4], the central point in the investigation of such compounds is the double role of the U f electrons, which on the one hand can be treated as well localized ones, and on the other hand at low temperatures usually behave as itinerant carriers with extremely large effective masses.

One of the remarkable characteristics, for example, of the UCu_5M ($\text{M} = \text{Al}, \text{In}, \text{Sn}$) family of compounds is the coexistence of magnetic order and Kondo lattice effects [5]. Usually Kondo lattices exhibit an antiferromagnetic ground state at low temperatures, which is true for UCu_5Al and UCu_5In [6], but not for UCu_5Sn [7]. This compound is a ferrimagnet [8, 9] and belongs to the family of moderate HF systems ($\gamma(0) = 330 \text{ mJ K}^{-2} \text{ mol}^{-1}$), in which the Kondo interactions ($T_K = 15 \text{ K}$) compete at low temperatures with the exchange interactions ($T_C = 54 \text{ K}$), in the simultaneous presence of the crystal field effect [8]. As proved in [9], the magnetic transition at T_C is due to the onset of the ferrimagnetic order in the unit cell of hexagonal CeNi_5Sn type having two different uranium atom sites, U[2(a)] and U[2(c)], where the value of magnetic moment for the U[2(a)] sublattice is about ten times larger than that in the U[2(c)] sublattice. Hence the antiferromagnetic coupling of these two sublattices of uranium atoms leads to the first example of a ferrimagnet among the HF systems known to date.

This large difference in the magnitudes of U[2(a)] and U[2(c)] moments, i.e. 2.2 and $0.2 \mu_B$, respectively, may arise from the different atomic distribution of surrounding ligands in their coordination polyhedra. Although the coordination numbers (CNs) are close to each other and amount to 18 for the 2(a) and 20 for the 2(c) sites, the atomic distribution is as follows: 12 Cu and six Sn in the case of U[2(a)] and 18 Cu and two Sn in the case of U[2(c)]. Besides other factors, only the fact of the larger number of d-metal atoms in the U[2(c)] polyhedron, having shorter $d_{\text{U-Cu}}$ and distinctly longer $d_{\text{U-Sn}}$ distances compared with those in the U[2(a)] polyhedron [9], can have an important meaning both in the 5f–6d hybridization and in the much stronger Kondo-like interaction just for the uranium atom at the 2(c) site.

In summary, all these facts presented above may suggest that there appears for the uranium atoms in the CeNi_5Sn -type unit cell some difference in their valence and local density of conduction electrons on the U[2(a)] and U[2(c)] atoms. Therefore, from the point of view of environment variation around the central uranium atom, and possible variable strengths of the 5f–ligand hybridization, we have recently started some systematic band structure studies of a few uranium ternary intermetallics.

Previously we have investigated the band structure and x-ray photoemission (XPS) of UCu_5Al [10], crystallizing in the tetragonal structure specific for this compound [6]. We have shown that there is a possibility that in this compound the initial 5f-electron configuration has rather a complex character in the vicinity of the Fermi energy, which in consequence leads to the occurrence in the 4f-electron core spectra of a very asymmetric main line and as many as two satellites. This is probably a result of the fact that the final electron configuration is $5f^n$, where $n = 2, 3$ and 4.

2. Experiment

The preparation of samples of UCu_5Sn used for XPS measurements was described in [9]. Briefly, the stoichiometric mixture of high-purity component elements (U 99.9%, Cu 99.99%, Sn 99.999%) was arc melted under a purified argon atmosphere. The obtained compound was then annealed for two weeks at 800°C in an evacuated sealed quartz ampoule. The EDAX analysis confirmed the stoichiometry of the compound. The XPS spectra were obtained with monochromatized Al $K\alpha$ radiation (1486.6 eV) at room temperature, using a PHI 5700/660 Physical Electronics spectrometer. The energy spectra of the electrons were analysed by a hemispherical mirror analyser with an energy resolution of about 0.3 eV. The Fermi level (E_F) was referred to the gold 4f-level binding energy (BE) at 84.0 eV. All spectra were measured immediately after breaking the sample in a vacuum of 5×10^{-10} Torr. This procedure was repeated several times, for each core-level and valence-band (VB) spectrum, until the O(1s)

Table 1. Structural parameters of UCu₅Sn at $T = 297$ K taken from [1] and Wigner–Seitz radii S_j (Å).

Atom (position)	x	y	z	S_j
U[2(a)]	0	0	0	2.082
U[2(c)]	1/3	2/3	1/4	1.890
Cu[12(k)]	0.8335	0.3329	0.1468	1.421
Cu[4(f)]	1/3	2/3	0.5433	1.355
Cu[2(d)]	1/3	2/3	3/4	1.397
Cu[2(b)]	0	0	1/4	1.397
Sn[4(f)]	1/3	2/3	0.0855	1.631

peak was negligibly small. (The details of the experimental procedure are as follows. The measurement chamber is connected with the sample preparation chamber, both in vacuum of 5×10^{-10} Torr. The sample is freshly broken and immediately introduced into the measurement chamber. The XPS spectrum is taken and if the oxygen O(1s) peak appears the procedure of breaking and measuring is repeated until the O(1s) peak is reduced to a minimum.) We did not observe an increase of the oxidation effect during the acquisition time.

3. Band structure calculation

The tight-binding linear muffin-tin orbital (TB-LMTO) in the atomic spheres approximation (ASA) [11, 12] was used to compute the electronic band structure of UCu₅Sn. The system is hexagonal (structure of CeNi₅Sn type with space group $P6_3/mmc$); its unit cell accommodates four formula units with $N = 28$ atoms [13]. In the ASA the unit cell is filled by the Wigner–Seitz atomic spheres characterized by the Wigner–Seitz radii S_j ($j = 1, \dots, N$). Their total volume is equal to the volume of the unit cell, $V = (4\pi/3) \sum_{j=1}^N S_j^3$. The input for the computations is the hexagonal unit cell as provided in [13] and the experimental values for the lattice constants at room temperature, $a = b = 4.9837$ Å, $c = 20.2944$ Å [13], were taken. There are two inequivalent positions of U and four of Cu in the unit cell. The compound UCu₅Sn is ferrimagnetic below $T_C = 54$ K [9], so it is in the paramagnetic state at room temperature, at which the XPS measurements were made. The calculations were performed for the paramagnetic phase. The unit cell containing 28 atoms was used with coordinates of atoms taken from [13] and quoted in table 1. The atomic configurations were assumed as core + $6p^65f^36d^17s^2$ for U, core + $3d^{10}4s^1$ for Cu and core + $4d^{10}5s^25p^2$ for Sn. In the ASA the overlap volume of the muffin-tin spheres chosen was 7.5%. The standard combined corrections for overlapping [11] were employed to compensate the ASA errors. The fully relativistic approach for the core electrons and the scalar relativistic approximation for the valence electrons were used. The Min–Jang [14] scheme for calculating the spin–orbit effects was employed. The exchange–correlation potential was chosen in the form proposed by Perdew *et al* [15] with nonlocal corrections. The self-consistent calculations were performed for 396 k -points in the irreducible wedge (1/24 BZ) of the Brillouin zone. The tetrahedron method [16–18] was used for integration in k -space. The iterations were repeated until accuracy of the energy eigenvalues within the error of 0.01 mRyd was achieved.

4. XPS spectra

The x-ray photoemission spectrum in a broad range of BE (0–1300 eV) is presented in figure 1. From this figure it is clear that there is only negligible contamination of the investigated sample by uranium oxides or carbides.

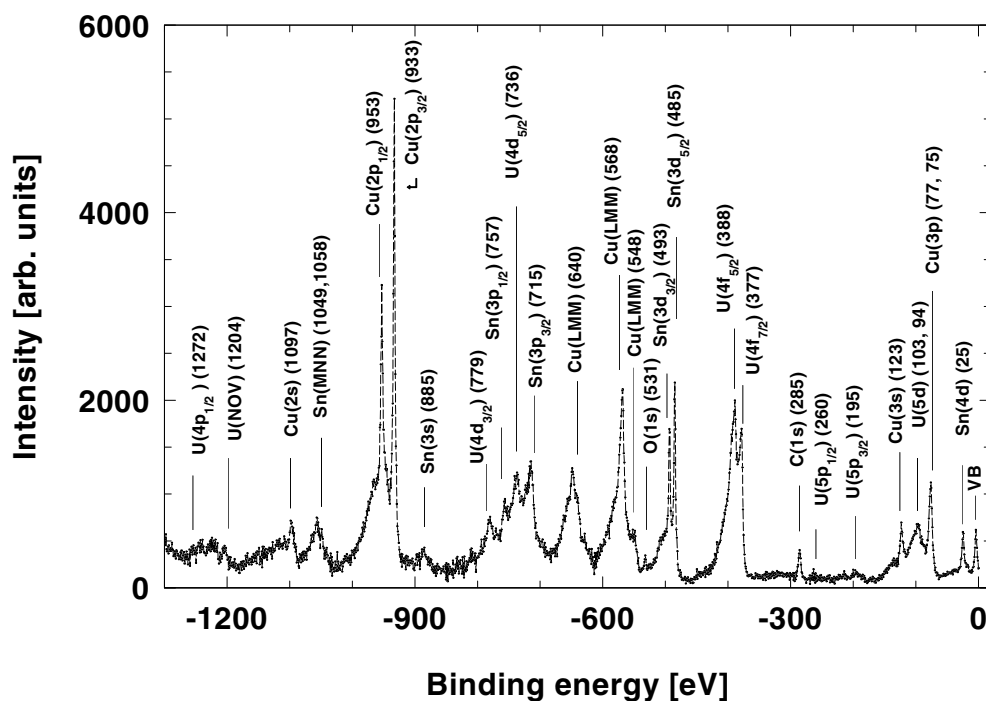


Figure 1. UCu_5Sn XPS spectrum in a broad energy range.

The XPS spectrum in the VB region for the UCu_5Sn compound is shown in figure 2. The shape of the spectrum between -6 and 0 eV is dominated by the Cu(3d) electrons and by hybridized U(5f) with spd valence electrons. The width of the band is about 6 eV.

The regions exhibiting the U(6p) (-18 eV) and Sn(4d) (-25 eV) peaks are also included. Comparing the XPS valence bands of Cu and U metals [10] with the VB of the UCu_5Sn compound, it turns out that the position of the maximum of the VB of UCu_5Sn centred at -4 eV is shifted by 0.7 eV in the BE as compared with the VB of pure Cu. The low-energy, about 1 eV wide, peak in the valence spectrum of UCu_5Sn is due to U(5f)-derived electrons. Its maximum is shifted toward the Fermi level by about 1 eV as compared with the corresponding peak for pure uranium metal.

The remaining s and p states have very low intensities and contribute over the entire VB, which matches well with the band structure calculation described below.

The U(4f) core-level spectrum of UCu_5Sn and its decomposition are shown in figure 3. The background is subtracted using the Tougaard method [19].

The spectrum shows a spin-orbit splitting corresponding to $4f_{7/2}$ and $4f_{5/2}$ components; each of them consists of a dominant asymmetric main line and two satellites at the higher-BE sides. The positions of the satellites are 2.5 and 7.3 eV higher in BE. The 2.5 eV satellite is also asymmetric and has a higher intensity than the 7.5 eV satellite, being more symmetric and with the lowest intensity. This kind of structure has also been observed in the core-level spectra of a few other uranium compounds, such as UM_2Al_2 ($M = \text{Ni}, \text{Pd}$) [20]. They were assigned as $5f^3$ and $5f^2$ final-state configurations, respectively, while the main line to the $5f^4$ one (see e.g. [20]). The line shape of core levels recorded by XPS is frequently referred to the many-body effect: the electron-hole interaction in the photoemission process [21, 22]. The simplest formulation of the theory is in terms of the analytical expression of Doniach and

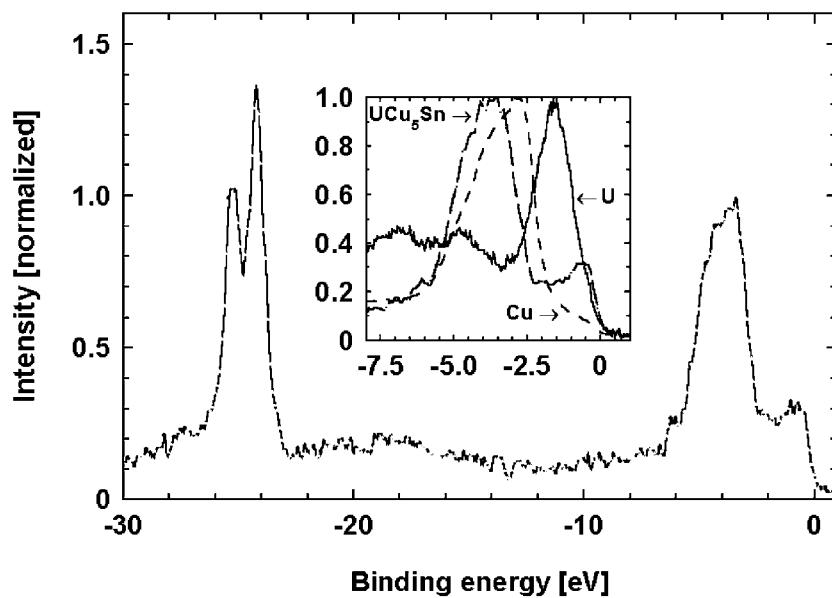


Figure 2. VB of the XPS. Inset: comparison of the VB spectrum of UCu_5Sn with those of pure U and Cu; all spectra are normalized to maximum intensity.

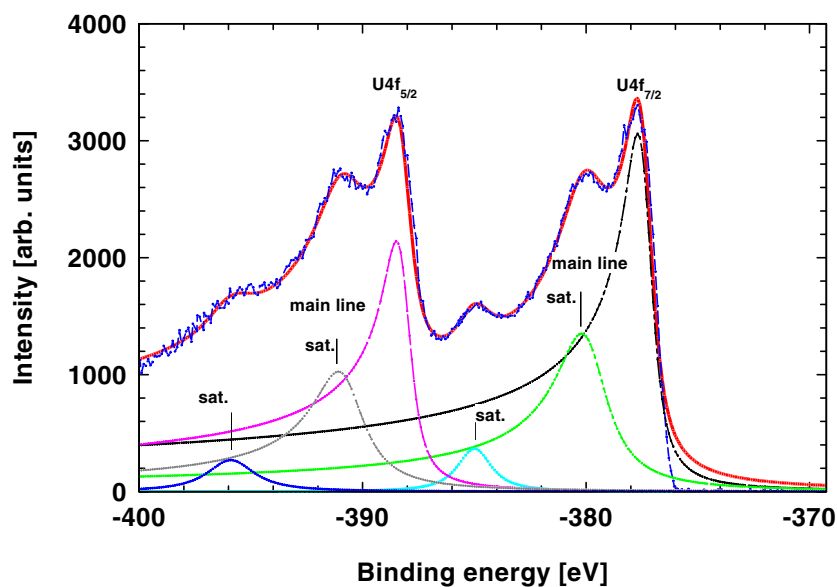


Figure 3. The measured XPS 4f core-level spectrum of UCu_5Sn (full curve) and its decomposition into main lines and satellites (broken curves).

Šunjić [23], where the asymmetry of the line is described by the singularity index α , which is a function of angular-dependent partial screening charges.

The origin of the satellites at about 2.5 eV higher BE is not clear. It seems that the occurrence of this satellite is characteristic for a few ternary compounds mentioned above

Table 2. DOS at the Fermi level (states/(eV unit cell)).

Atom (position)	Site-projected DOS	Type of DOS	Total and <i>l</i> -decomposed DOS
U[2(a)]	30.2680	Total	50.7107
U[2(c)]	13.7565	Total for s electrons	1.0101
Cu[12(k)]	3.0043	Total for p electrons	1.8885
Cu[4(f)]	1.8753	Total for d electrons	5.4531
Cu[2(d)]	0.2765	Total for f electrons	42.3590
Cu[2(b)]	0.5145		
Sn[4(f)]	1.0156		

containing apart from uranium also some transition metal, though such a structure has also been reported for the Pd-rich solid solutions U(Rh,Pd)₃ [21]. Similar satellites also appear in other studies [20, 21] and are interpreted as a result of the contribution of 5f², 5f³ and 5f⁴ states in the final state [20, 21]. However the contribution of the 5f³ satellite in the UCu₅Sn studied here is probably enhanced to some small degree by the existence of uranium oxides, which have their symmetric satellite at the same energy location.

According to Fujimori *et al* [20], the presence of the symmetric 7.3 eV peak (the 5f² final state) below the main line of UCu₅Sn gives evidence that the uranium atoms in this compound may be in the mixed valence state.

5. Calculated band structure and the XPS spectrum

The calculated band structure is presented in the form of the DOS plots in figures 4 and 5. The dominating features of the total DOS plots have their counterparts in the XPS spectrum. In figure 4 (top panel) the band of width about 0.5 eV near the Fermi energy, lying predominantly above E_F , is due to the f electrons from U atoms in the UCu₅Sn. The contributions from U atoms at the two inequivalent positions are significantly different as depicted in the insets in figure 5(a). One can see that the Fermi level is situated inside the U 5f band with a medium value of DOS. The broad band of width about 6 eV (figure 4) is dominated by contributions from 3d electrons from Cu with some admixture of U(6d) electrons. There appear some differences in the shapes of the Cu 3d bands from inequivalent positions of Cu (see figure 5). The heights of the peaks are roughly scaled by the numbers of atoms in the inequivalent positions of Cu in the unit cell: 12, 4, 2 and 2 for positions k, f, d and b, respectively. The narrow peak at the BE about 19.5 eV is determined by 6p electrons from U.

The strong narrow peak at BE of about 22.4 eV (figure 4), giving rise to a pronounced split feature of the XPS spectrum, is contributed by 4d electrons from Sn. The shape of this peak on an expanded energy scale is shown in figure 5(a) (bottom panel). The total and partial densities of states at the Fermi level are provided in table 2. The total DOS(E_F) is dominated by 5f electrons from U; of these contributions those from U[2(a)] are distinctly larger than those from U[2(c)]. The electronic specific heat coefficient calculated from DOS(E_F) is $\gamma_0 = 29.9 \text{ mJ K}^{-2} \text{ mol}^{-1}$. This value is much smaller than the experimental one, $\gamma = 330 \text{ mJ K}^{-2} \text{ mol}^{-1}$. The enhancement factor $\gamma/\gamma_0 \approx 11$ is slightly larger than that in UCu₅Al [10], the other member of this family of uranium compounds.

The calculated numbers of states are given in table 3; a remarkable feature is the charge transfer at U[2(a)], distinctly larger than that at U[2(c)], corroborating the different role played by U atoms in the two positions.

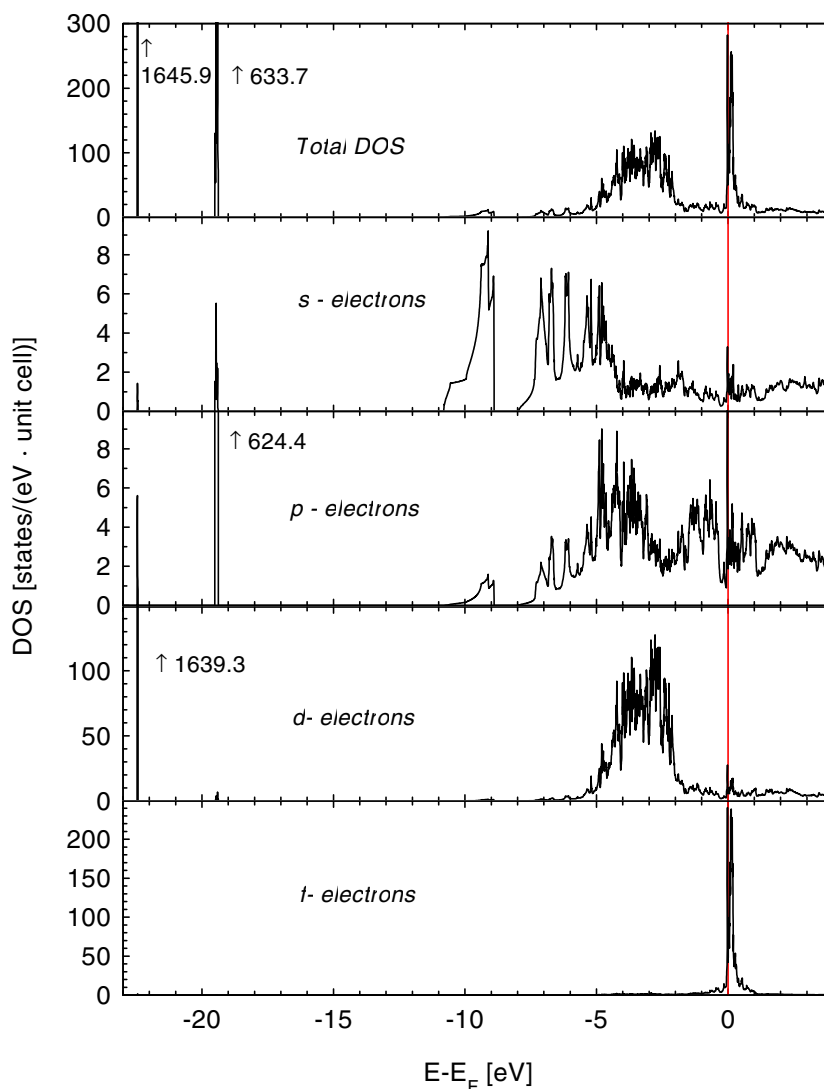


Figure 4. Calculated total and partial DOSs for UCu₅Sn.

A remarkable property of UCu₅Sn as found from neutron diffraction study [9] is the large difference between the ordered magnetic moments per U atom for the two inequivalent crystallographic positions, $m_{U[2(a)]} = 2.14 \mu_B$ and $m_{U[2(c)]} = 0.18 \mu_B$ [9]. Trying to understand this feature, calculations of the band structure with spin polarization were performed but gave no hint to understanding the large difference between values of local moments at the two inequivalent positions. The existence of the large magnetic moment on U[2(a)] is intuitively consistent with the existence of the sharp peak at the partial U[2(a)] DOS (cf figure 5(a)) and relatively low partial DOS for U[2(c)]. However, no quantitative theoretical estimate of $m_{U[2(a)]}/m_{U[2(c)]}$ can be given at the moment.

Perhaps the orbital contribution to the magnetic moments can be considered as the source of these differences in the moments, of course if they are not caused by many-body effects of a Kondo or other type.

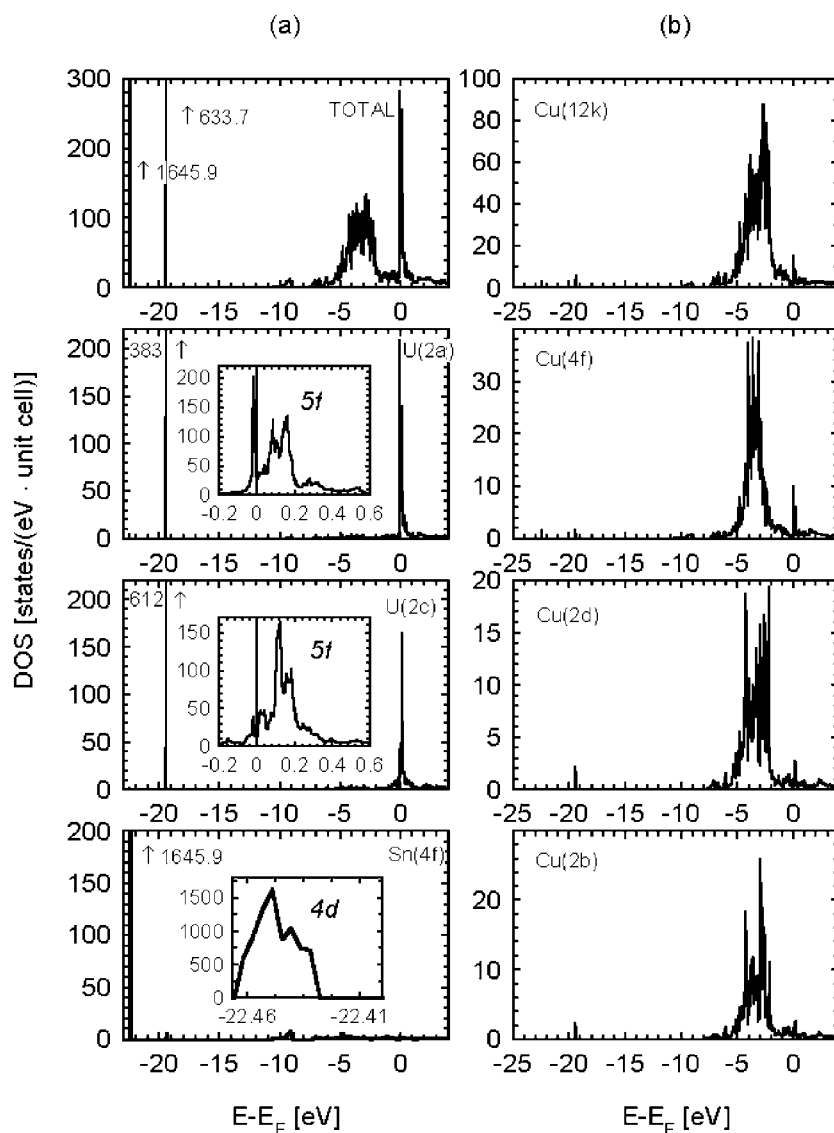


Figure 5. Atom-projected DOSs. Note the expanded scale in the insets.

The XPS spectrum was calculated in the standard way by weighting the partial densities of states for the constituent atoms of the compound with approximate atomic cross sections for photon scattering, provided in the tables [24], and convoluting them with a Gaussian function to account for the experimental resolution. The parameter for the Gaussian was taken as equal to the experimental resolution, $\delta = 0.3$ eV.

The calculated XPS spectrum is shown in figure 6. The part of the spectrum covering the range of the BE up to 6 eV contains contributions from Cu (mainly 3d states) and U (5f states). The contribution from Cu are dominant simply because there are more Cu atoms in the unit cell. In the inset in panel (b) of figure 6 contributions from the two U atoms in inequivalent positions are presented. Similarly, in panel (c) the line is split into parts from the four Cu

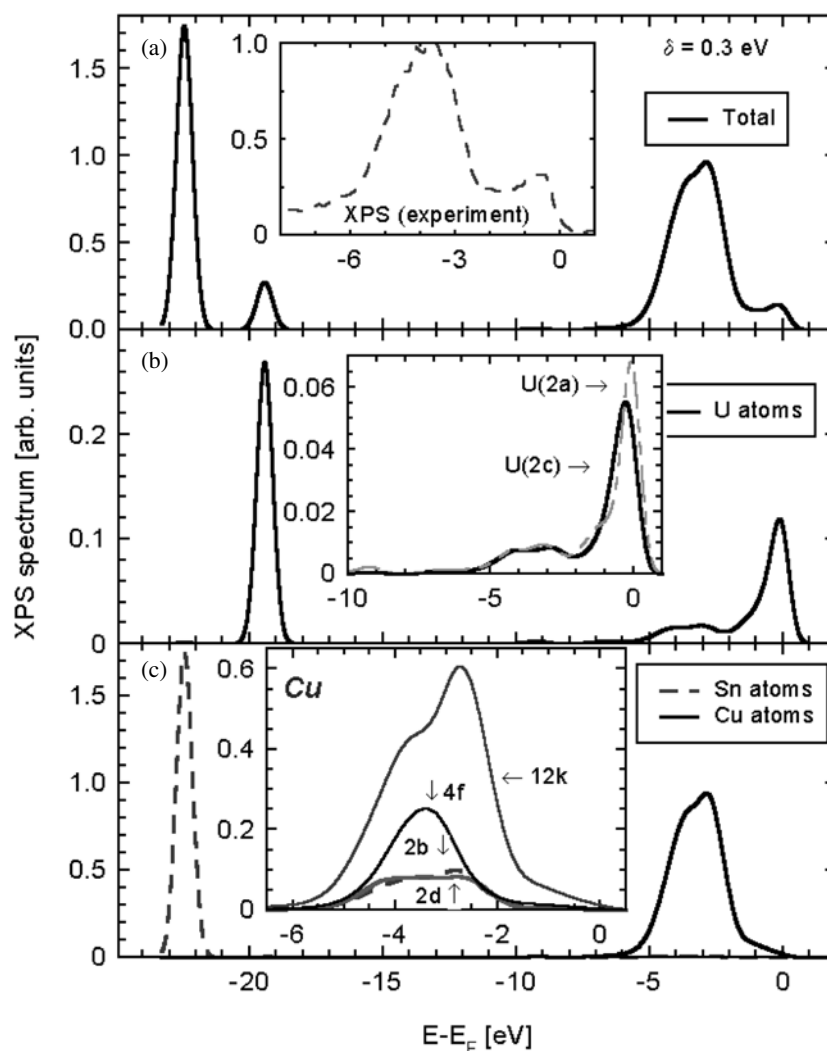


Figure 6. Calculated XPS spectra: (a) total (part of the experimental spectrum shown in the inset for comparison), (b), (c) contributions from U, Cu and Sn atoms. Insets in (b) and (c) exhibit the contribution from inequivalent crystallographic positions of respective atoms.

atoms in inequivalent positions. The calculated spectrum is in quite good agreement with the low-BE part of the measured XPS spectrum shown in figure 2.

The calculated modest peak at about 19.5 eV BE, resulting from U 6p electrons (figures 6(a), (b)), can be traced to a broad maximum in the experimental XPS curve in figure 2. The pronounced peak at about 22.5 eV BE in the calculated spectrum is determined by 4d electrons from Sn. Its position is lower by about 2.5 eV than the corresponding peak in the measured spectrum. Also the double-peak structure of the experimental line is not reproduced by calculations. Although there is slight evidence of such a structure in the DOS (see the inset in figure 5(a)), the details are then smeared out by the Gaussian factor with $\delta = 0.3$ eV in calculating the spectrum.

Table 3. Numbers of states (per atom).

Atom (position)	Electrons				Total
	s	p	d	f	(s + p + d + f)
U(2a)	0.6791	6.3288	2.4409	3.5141	12.9629
U(2c)	0.5462	6.1671	2.0839	3.1386	11.9358
Cu(12k)	0.7224	0.7820	9.5675	—	11.0719
Cu(4f)	0.6954	0.5412	9.4719	—	10.7085
Cu(2d)	0.7642	0.7696	9.4599	—	10.9937
Cu(2b)	0.7633	0.7383	9.4808	—	10.9824
Sn(4f)	1.4156	2.0887	10.0780	0.0561	13.6384
Total (per unit cell)	22.6184	47.9112	239.9406	13.5298	324.0000

6. Conclusions

The XPS study at room temperature combined with electronic band structure calculations for the paramagnetic phase of UCu_5Sn reveals characteristic similarities with properties of UCu_5Al [10], belonging to the same family of compounds. This is so even though its low-temperature properties are different: UCu_5Al is antiferromagnetic (below 18 K) whereas UCu_5Sn is ferrimagnetic ($T_C = 54$ K)—not a common property for HF systems.

The overall agreement of the measured XPS spectra with the calculated ones is reasonably good. A perfect agreement cannot be expected since the many-body effects in the dense Kondo system are not incorporated into the local density approximation underlying the LMTO calculations [11]. The ‘bare’ electronic specific heat coefficient calculated from the band structure is $\gamma_0 = 29.9 \text{ mJ K}^{-2} \text{ mol}^{-1}$. The experimental value is $\gamma = 330 \text{ mJ K}^{-2} \text{ mol}^{-1}$ [8,9], so the quite large enhancement factor $\gamma/\gamma_0 \approx 11$ is an indication of the importance of the many-body Kondo lattice effects. The band structure data suggest a higher degree of localization of 5f electrons on U in positions 2(a) than those in positions 2(c). The satellite structure of the core-level U(4f) spectra indicates that U atoms are perhaps in the mixed valence state as observed in other systems [20]. A quantitative explanation of the large difference in measured magnetic moments on U in the two inequivalent positions in the ferrimagnetic phase remains to be achieved.

Acknowledgments

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