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Photoemission spectra of some uranium compounds

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Electronic structures of some ternary uranium compounds (U_2Ru_2Sn and UCu_5M, M = Al, In, Sn) have been studied by theoretical (*ab-initio* calculations) and experimental (X-ray photoemission) methods. The band structure calculations have been performed based on the full potential local orbital method. The calculated densities of electronic states have been used to obtain photoemission spectra, then compared with experimental ones. A satisfactory agreement between the measured spectrum and that obtained from the calculated electronic structure has been achieved.

Key words: actinide compounds; electronic structure; photoemission spectra

1. Introduction

Uranium intermetallic compounds, especially those containing a transition metal T and a p-metal M, constitute an interesting class of materials. In recent two decades, they have attracted particular interest because of their frequent anomalous behaviour at low temperatures, mainly caused by a simultaneous occurrence of the magnetically ordered state together with heavy fermion and sometimes even with superconducting states.

The family of compounds UCu_5M (M = Al, In or Sn) is characterized by the coexistence of magnetic order (antiferromagnetic for M = Al and In; ferrimagnetic for M = Sn) and Kondo lattice effects, by moderate electronic specific heat enhancement

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($\gamma/\gamma_0 \approx 8$ for Al; $\gamma/\gamma_0 \approx 11$ for both In and Sn) and possibly a mixed-valence ground state [1–3]. U_2Ru_2Sn is a non-magnetically ordered Kondo semimetal [4, 5] exhibiting highly anisotropic properties. The aim of the present work is to extend our knowledge on the electronic structure of these compounds by fully relativistic *ab-initio* calculations and to compare the results with results of experimental photoemission investigations.

2. Computational details

The electronic structure of the UCu_5M (M = Al, In, Sn) and U_2Ru_2Sn compounds was studied by the full potential local orbital (FPLO) method [6] based on the local spin density approximation (LSDA) [7]. The fully relativistic mode was used in the calculations. The calculations were carried out for experimental values of the lattice constants [1–4]. We assumed the following configurations of atoms: core + semi core electrons (5d6s) + valence electrons (6p7s7p6d5f) for U atoms, core + semi core electrons (3s3p) + valence electrons (4s4p3d) for Cu atoms, core + semi core electrons (4s4p) + valence electrons (5s5p4d) for In, Sn and Ru atoms, and finally core + semi core electrons (2s2p) + valence electrons (3s3p3d) for Al atoms. The calculations were performed for the reciprocal space mesh containing at least 133 points within the irreducible wedge of the Brillouin zone, using the tetrahedron method [8] for integrations. The LSDA exchange correlation potential was assumed in the form proposed by Perdew and Wang [9]. The self consistency criterion was equal to 10^{-8} Ry for the total energy. The calculations were performed without spin polarization even in the case of UCu_5M (M = Al, Sn, In) because their temperatures of magnetic ordering are well below the room temperature at which the XPS measurements were made.

The theoretical X-ray photoemission spectra (XPS) were obtained from the calculated densities of electronic states (DOS) convoluted by Gaussian with a half-width equal to 0.3 eV and scaled using the proper photoelectronic cross sections for partial states [10].

3. Results and discussion

The results of *ab-initio* calculations based on the FPLO method are presented in Fig. 1 (left panel) together with our earlier results (right panel). General shapes of the valence bands are similar and we refer reader to our earlier papers [1–4], where a detailed discussion is presented. In this short paper we focus our attention on differences introduced by the fully relativistic FPLO method. In all cases, the valence bands close to the Fermi level are dominated by U(5f) electrons, for slightly higher binding energies the main contributions are provided by Cu(3d) electrons and Ru(4d) ones.

The fundamental differences between the present results and the earlier ones are related to the spin-orbit splitting which can be observed in FPLO results in DOS plots (Fig. 1) and photoemission spectra (Fig. 2). A small splitting between 4d subbands ($Sn(4d^{3/2})$ and $Sn(4d^{5/2})$, $In(4d^{3/2})$ and $In(4d^{5/2})$) results in characteristic double-peak structures in photoemission spectra. Much larger splitting is observed between $U(6p^{1/2})$ and $U(6p^{3/2})$ electrons. In both cases, the calculated spin-orbit splitting is similar to the experimental one. The splitting between $U(5f^{5/2})$ and $U(5f^{7/2})$ is observed only in DOS plots, the most of 5f states are located above the Fermi level and these states are not detected by XPS.

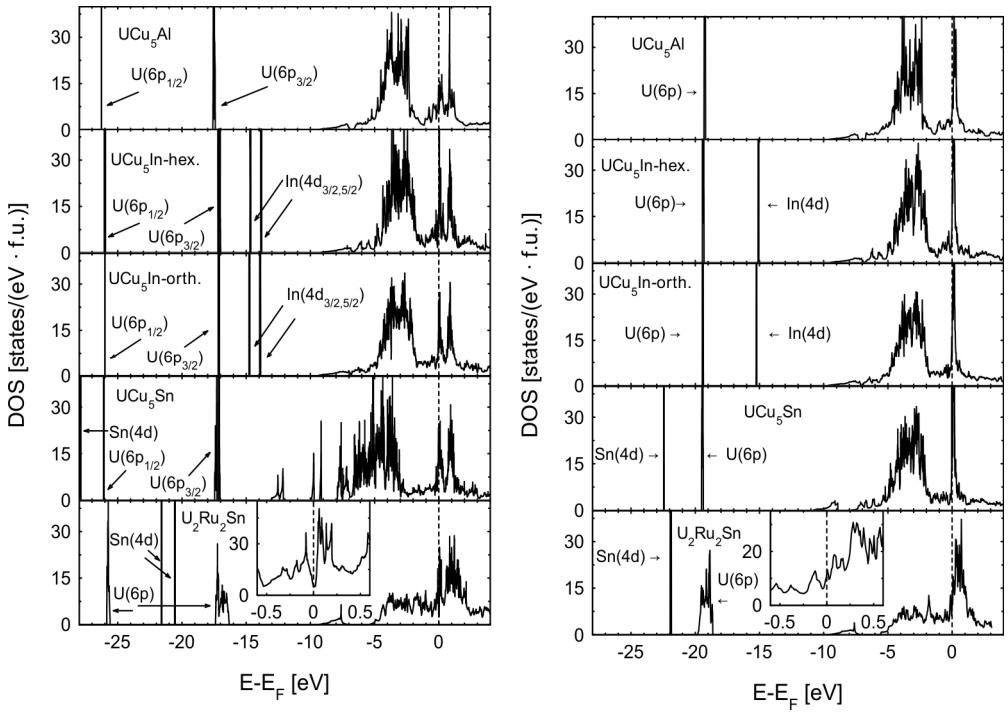

Fig. 1. The total DOS plots for the UCu_5M (M=Al, Sn, In) and U_2Ru_2Sn compounds. For UCu_5In, two cases are considered: hexagonal and orthorhombic unit cells. The left panel presents results obtained by the FPLO method and the right panel those obtained by the TB LMTO ASA method

The change of computational method leads to reconstruction of DOS plots and their values at the Fermi level. These values are collected in Table 1. Especially interesting is the case of U_2Ru_2Sn, experimentally found to be a Kondo semiconductor [12] or semimetal [13]. Earlier calculations [4] gave the Sommerfeld coefficient larger than the experimental one, what was attributed to the inaccuracy of the TB-LMTO-ASA method in treating the highly correlated 5*f* electrons on U. In the present results the Fermi level is located in a V-shaped pseudo-gap, what classifies the system as semimetal. The ratio γ/γ_0 has a correct value higher than 1.

Table 1. Densities of electronic states at the Fermi level (DOS ($E = E_F$) [states/(eV·formula unit)] calculated by the FPLO and TB LMTO [1–4] methods; the calculated (γ_0) and experimental (γ) values of the Sommerfeld coefficient in the linear term of the specific heat [mJ/(K^2·mol)]

Method	Parameter	Compound				
		UCu_5Al	UCu_5Sn	UCu_5In hex.	UCu_5In orth.	U_2Ru_2Sn
	γ	170 [14]	330 [15, 16]	Unknown	240 [17]	18 [18]
TB LMTO	DOS ($E = E_F$)	9.14	12.68	18.87	9.24	11.89
	γ_0	21.5	29.9	44.4	21.7	28.0
	γ/γ_0	7.91	11.04	–	11.06	0.64
FPLO	DOS ($E = E_F$)	11.49	13.62	13.55	16.77	5.07
	γ_0	27.02	32.12	32.26	39.40	11.94
	γ/γ_0	6.29	10.28	–	6.09	1.51

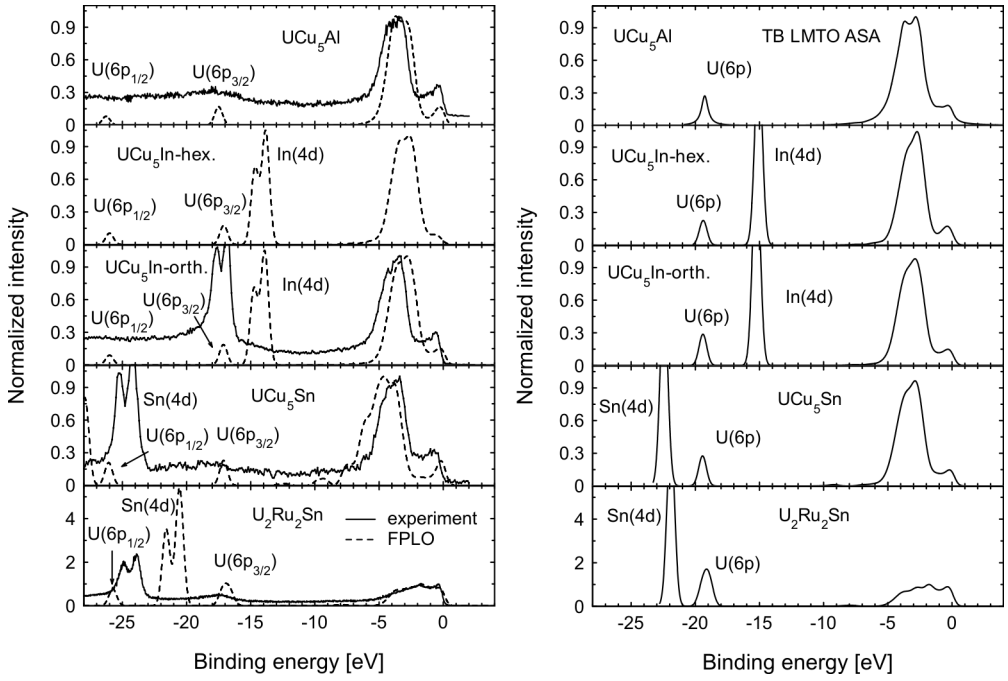

Fig. 2. Photoemission spectra of UCu_5M (M = Al, Sn, In) and U_2Ru_2Sn; For UCu_5In hexagonal and orthorhombic unit cells are considered; the left panel presents experimental results (solid line; not measured for hexagonal UCu_5In) and obtained by FPLO (dashed line) method; the right panel shows results obtained by the TB LMTO ASA method

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