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Electronic properties of $ThCu_5Sn$ and $ThCu_5In$ compounds*

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$ThCu_5In$ and $ThCu_5Sn$ alloys crystallize in an orthorhombic $CeCu_5Au$-type structure with the *Pnma* space group. *Ab-initio* band structure calculations have been performed based on the full-potential local-orbital (FPLO) method. The calculated densities of electronic states are used to obtain photoemission spectra. The spectra of valence bands are predominated by 3d electrons located on Cu atoms.

Key words: *actinide compounds; electronic structure; photoemission spectra*

1. Introduction

Uranium compounds have recently attracted attention because of many interesting properties such as the Pauli paramagnetism, spin fluctuations, heavy fermions, magnetic ordering, or superconductivity. Many of these properties are related to the uranium 5f electrons which show an intermediate character between the localized 4f electron system and itinerant character of 3d electrons. The role of 5f electrons is important in actinides and the question is if they are localized or itinerant or perhaps the two configurations coexist giving rise to a new character of the electronic structure, referred to as the duality of the behaviour of 5f electrons. It is very useful to compare properties of isostructural systems with and without 5f electrons treating the systems with thorium as reference ones. Results of investigations of the electronic structure of UCu_5M (M = In, Sn) have recently been published [1, 2]. X-ray phase analyses of annealed and as-cast $ThCu_5In$ and $ThCu_5Sn$ alloys indicated that they are isostructural and that their structure is similar to that of UCu_5In(Sn) ($CeCu_5Au$ type structure being an ordered variant of the $CeCu_6$ type, space group *Pnma*) [3, 4]. The aim of this paper is to calculate the band structure of $ThCu_5In$(Sn) employing the *ab-initio* method.

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2. Method of calculations and results

In order to study electronic structure of the $ThCu_5M$ compounds (M = In, Sn), we used the full-potential local-orbital (FPLO) method [5] based on the local spin density approximation (LSDA) [6]. The fully-relativistic mode was used in the calculations. The calculations were carried out for the orthorhombic structure with 28 atoms per unit cell (four formula units, see Fig. 1 and Table 1) and experimental values of the lattice constants [3]: a = 8.305 Å, b = 5.068 Å, c = 10.600 Å, for $ThCu_5In$, and a = 8.286 Å, b = 5.080 Å, c = 10.554 Å for $ThCu_5Sn$.

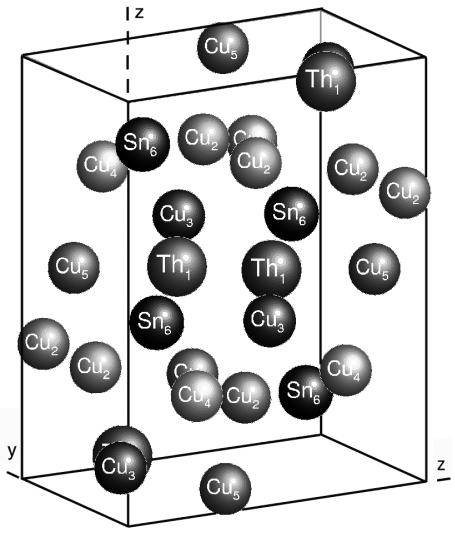

Fig. 1. Crystallographic structure of the $ThCu_5M$ (M = In, Sn) compounds

Table 1. Atomic positions [3] and the site projected densities of electronic states (DOS) at the Fermi level[a]

Atom	Position	DOS [states/(eV atom)]
Th(4c)	0.2538, 0.2500, 0.5600 0.2530, 0.2500, 0.5579	0.834 0.877
Cu1(8d)	0.0683, 0.5011, 0.3115 0.0699, 0.5020, 0.3116	0.309 0.306
Cu2(4c)	0.0583, 0.2500, 0.1037 0.0638, 0.2500, 0.1029	0.322 0.292
Cu3(4c)	0.3186, 0.2500, 0.2454 0.3195, 0.2500, 0.2460	0.305 0.263
Cu4(4c)	0.4144, 0.2500, 0.0162 0.4159, 0.2500, 0.0174	0.331 0.341
In(4c)	0.1397, 0.2500, 0.8604	0.324
Sn(4c)	0.1381, 0.2500, 0.8582	0.200

[a]The upper coordinates for Th and Cu atoms describe positions for $ThCu_5In$ cell and the lower for $ThCu_5Sn$ one.

For the calculations we assumed the following configurations of atoms: core (1s ... 5p electrons) + semi core (5d6s) + valence electrons (6p7s7p6d5f) for Th atoms, core (1s ... 2p electrons) + semi core (3s3p) + valence electrons (4s4p3d) for Cu atoms, and core (1s ... 3p electrons) + semi core (3d4s) + valence electrons (4p5s5p4d) for In and Sn atoms. The calculations were performed for the reciprocal space mesh containing 343 points within the irreducible wedge of the Brillouin zone using the tetrahedron method [7] for integrations. The LSDA exchange-correlation potential was assumed in the form proposed by Perdew and Wang [8]. The self consistent criterion was equal to 10^{-8} Ry for the total energy.

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 [9].

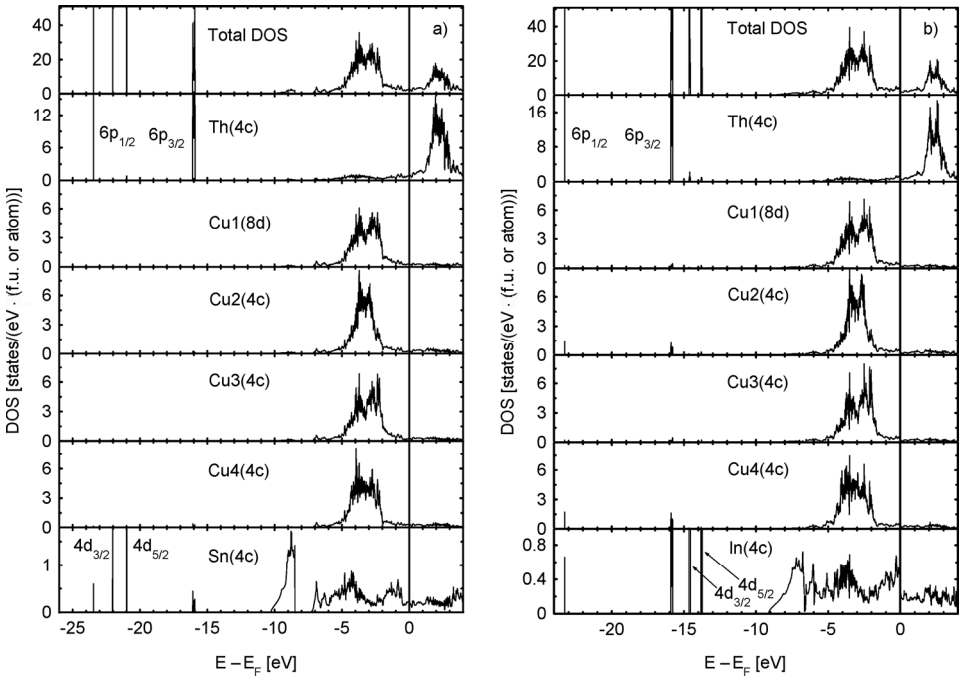

Fig. 2. Total and local DOS plots for the a) $ThCu_5Sn$, b) $ThCu_5In$ compounds

The DOS plots are presented in Fig. 2. Most of bands which form the valence bands for $ThCu_5M$ systems are located between about –10 eV and the Fermi level. The valence bands are formed mainly by Cu(3d) electrons located between –5 and –1 eV. The bottoms of valence bands are formed by Sn(4s) and In(4s) electrons. In the case of $ThCu_5Sn$, Sn(4s) electrons and the main part of valence band are separated by the gap of about 1.2 eV wide. Below the valence bands, we observe very narrow and tall peaks formed by flat bands occupied by the Th(6p), In(4d) and Sn(4d) electrons. The total

DOS at the Fermi level is equal to 2.73 and 2.59 states/(eV·f.u.) for $ThCu_5In$ and $ThCu_5Sn$, respectively. This means that the Sommerfeld coefficients in the linear term of the specific heat are equal to 6.43 and 6.10 mJ/(mol·K^2). These values are close to that obtained for $ThIn_3$, 5.28 mJ/(mol·K^2) [10]. The contributions provided by particular atoms are collected in Table 1. The Cu atoms provide about 40% and single thorium atom about 30% contribution to the total DOS at the Fermi level. The Th(6p) electrons for $ThCu_5In$ are slightly moved toward binding energies higher than in the case of $ThCu_5Sn$ one, conserving similar spin-orbit splitting (see Figs. 2 and 3).

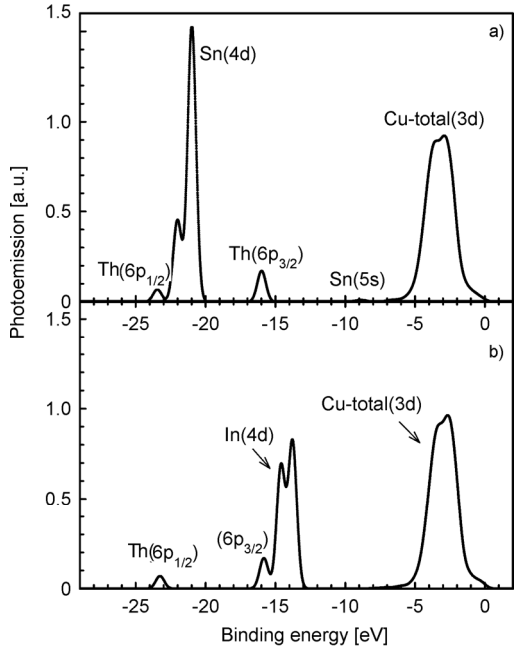

Fig. 3. X-ray photoemission spectra calculated for: a) $ThCu_5Sn$, b) $ThCu_5In$; $\delta = 0.3$ eV

A larger difference exists for 4d electrons on Sn and In atoms. The positions of the peaks are quite different, and smaller spin-orbit splitting gives single two-peak bands in the photoemission spectra. In both cases the calculated spin-orbit splitting is similar to the experimental one.

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