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Electronic band structure and X-ray photoemission studies of ternaries APdGe (A = Th,U) in the paramagnetic state

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Among uranium transition metal germanides, UPdGe reveals fascinating magnetic and electrical properties. We have recently performed electronic band-structure calculations of this compound and its non-5f electron counterpart ThPdGe in the paramagnetic state. The obtained theoretical electron densities of states (DOS) were compared with newly measured X-ray photoemission spectra (XPS). For UPdGe some disagreement was observed probably due to the predominant localized character of 5f electron states observed in the XPS spectra.

Key words: *electronic structure; photoemission; intermetallic compounds*

1. Introduction

It has been known for some time that UPdGe, crystallizing in the orthorhombic TiNiSi-type crystal structure (*Pnma*), exhibits an interesting complex magnetic behavior and very specific electrical properties [1]. This system undergoes two magnetic transitions at 28 and 50 K, into ferro- and antiferromagnetic state, respectively. At the lowest temperatures, a simple canted ferromagnetic arrangement of the moments within the orthorhombic *ac* plane was first proposed [2] but based on magnetic space group analysis and neutron diffraction studies [1, 3] it has been recently suggested to form a collinear ordering of uranium moments along the orthorhombic *b* axis. It is worth underlining that the collinear ferromagnetic state exists rather at temperatures 20–30 K but below 20 K a conical structure with the net magnetic moment along the *c* axis was reported [4]. This finding agrees well with the recent study of thermopower

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and magnetoresistivity. In the temperature range from 28 to 50 K, a sinusoidally modulated antiferromagnetic structure was proposed [2]. As concerns electrical properties of UPdGe, the most interesting fact is that it reveals a giant value (73%) of magnetoresistivity at the transition temperature from ferro- to antiferromagnetic state [1].

This paper is considered to be the first step in understanding the magnetic and electrical properties based on the electronic structure studies of UPdGe and its non-5f electron counterpart ThPdGe in the paramagnetic state. With this aim fully relativistic (4-component) band-structure calculations were performed, using the full-potential local-orbital (FPLO) minimum-basis code [5] with the local density approximation (LDA) of the exchange-correlation potential. The 5f electrons were assumed to be itinerant. We used experimental lattice parameters $a = 7.054$ Å, $b = 4.357$ Å, $c = 7.617$ Å for UPdGe [6] and $a = 7.7006$ Å, $b = 4.3753$, $c = 7.5994$ Å just found for ThPdGe. For both compounds the atom positions were taken as those published in Ref. [3] for UPdGe. We obtained theoretical band energies $\mathrm{E_n}(\mathbf{k})$ and total DOS as well as for particular atomic sites and for all the atoms in the unit cell separately. To verify these computations, the partial DOSs for the constituent atoms in each system were multiplied by the respective weight factors proportional to atomic cross-sections on photon scattering [7]. The results were summed and convoluted with a Gaussian to simulate the energy resolution δ of the analyser used in the XPS experiment.

Theoretical XPS obtained in this way were compared with the experimental ones, collected with monochromatised AlK_α (1486.6 eV) radiation on the polycrystalline samples of UPdGe and ThPdGe at room temperature. The energy spectra of emitted electrons with an energy resolution of ~ 0.3 eV were analysed theoretically assuming $\delta = 0.3$ eV. The XPS spectra in a broad range of binding energies (0–1300 eV) were recorded under ultrahigh vacuum of 10^{-10} Torr at room temperature using a PHI 5700/660 Physical Electronics photoelectron spectrometer. Each spectrum was recorded immediately after braking the sample in vacuum. The oxidation of the samples was checked by inspecting the O 1s spectra before and after each measurement. Except for a small contribution of uranium dioxide, in the measured samples also some contamination from carbon was found.

2. Results and discussion

The behaviour of calculated band energies $E_n(\mathbf{k})$ in UPdGe is strongly anisotropic. Narrow band gaps open along a number of main symmetry directions $\mathbf{k}$. For other $\mathbf{k}$ mostly semimetallic character of bands is predicted by the theory. The spin-orbit coupling of U 5f states is of the order of 1 eV. Although the Fermi level E_F cuts the U $5f_{5/2}$ peak yielding a relatively high value of DOS at E_F, a pseudogap opens in the vicinity of E_F. In the region of valence band the contributions from Pd and Ge to the total DOS are very similar to each other for UPdGe and ThPdGe. As we expected, the non-occupied Th 5f states in ThPdGe are shifted far above E_F. Nevertheless, a very small part of these electronic states may exist also at E_F. For UPdGe, a distinct hybridisation of the U 5f states with the U 6d and Pd 4d as well as Ge 4sp states around E_F is apparent. Analogously, a hybridisation between the Th 5f with Th 6d and Pd 4d and Ge 4sp states is highly probable.

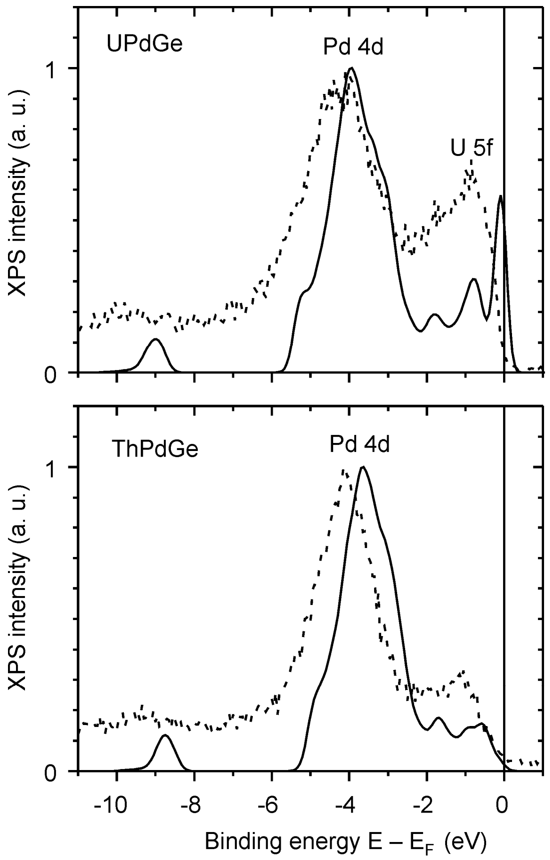

Fig. 1. The theoretical (solid line) and experimental (dashed line) XPS intensity determined for UPdGe and ThPdGe

In this paper, we limit our presentation to comparison of the theoretical and experimental XPS data for UPdGe and ThPdGe in the binding energy region of valence electrons. The obtained results are shown in Fig. 1. The analysis of the calculated XPSs for both compounds reveals that in this range of energy (for AlK_α radiation) we can observe mainly large and very similar contributions originating from the Pd 4d states having a wide peak centred at about 4 eV. This feature is well reproduced by the experimental XPS. Additionally, for UPdGe there is a pronounced contribution of the U $5f_{5/2}$ states located just below E_F. However, in our experiment the maximum of this contribution is shifted from E_F by about 1 eV towards lower energies. This distinct discrepancy is probably connected with a more localised character of U 5f states in UPdGe, which is well visible in the experimental XPS. Moreover, this contribution is spread in the energy region more than 3 eV, which supports the idea of distinct localisation of 5f electrons in UPdGe due to the formation of the final multiplet. This aspect will require more detailed studies with the UPS technique.

3. Conclusions

To understand the magnetic and electrical properties of UPdGe we studied its electronic structure as well as the structure of its non-magnetic counterpart ThPdGe in the paramagnetic state. We performed fully relativistic and full-potential band-structure calculations using modern FPLO code. The obtained theoretical band energies and electron DOSs were compared with the experimental XPS data. We believe that we achieved a satisfying agreement between the theoretical and experimental data as to the conduction bands, but an apparent disagreement was observed for the U 5f band in UPdGe probably due to its more localised character in this compound being well marked in the experimental XPS spectra.

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