

Electronic Structure of TmPdIn

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Electronic structure of a ternary TmPdIn compound, which crystallizes in the hexagonal ZrNiAl-type structure, was studied by X-ray photoemission spectroscopy and ultraviolet photoemission spectroscopy. Density of states in the valence band was calculated by means of the augmented plane wave/local orbital method based on density functional theory. The results showed that the valence band is formed mainly of Tm 4*f* and Pd 4*d* states. In the ultraviolet photoemission spectra one can distinguish Pd 4*d* maximum and Tm 4*f* multiplet peaks, which are displaced with respect to those of pure Tm.

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1. Introduction

Rare earth based intermetallics of RTX stoichiometry (R — rare earth, T — *d*-electron element, X — *p*-electron element) exhibit a great variety of intriguing physical properties. The structural and magnetic data, for such systems, are summarized in reviews [1, 2]. Our investigations are concentrated on the compounds with R = Tm and the hexagonal ZrNiAl-type crystal structure which have the complex magnetic properties at low temperatures [3–5].

TmPdIn, which is investigated in this work, crystallizes in the hexagonal ZrNiAl-type structure. The magnetic and specific heat data indicate that below $T_N = 2.65$ K it is an antiferromagnet [6].

In this work the results of X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) for TmPdIn are presented and compared to density functional theory (DFT) calculations.

2. Experimental details

A polycrystalline sample of TmPdIn was synthesized by arc melting the stoichiometric amounts of the constituent elements of high purity (3N for Tm and 4N for Pd and In) in titanium-gettered argon atmosphere. Subsequently, the buttons were annealed in an evacuated quartz tube at 873 K for one week. A quality of the product was checked by powder X-ray diffraction (XRD) performed at room temperature using XPERT-PRO PAN-alytical powder diffractometer with Cu K_α radiation. The XRD data were analyzed using the Rietveld type refinement program, FullProf [7].

The X-ray photoemission spectra were obtained at room temperature using VG Scienta R4000 photoelectron analyzer with a monochromatized radiation of Mg K_α ($h\nu = 1253.6$ eV) and the overall resolution of 1.0 eV. Binding energies refer to the Fermi level ($E_F = 0$). The valence band was also investigated by means of UPS at 14 K with energy of 21.2 eV (He(I)) and 40.8 eV (He(II)). The corresponding energy resolution

was 25 meV. Sample surface was prepared by scratching with a diamond file in ultrahigh vacuum of 5×10^{-10} mbar. Energy calibration was based on the measurements of Au 4*f* states of pure gold and Fermi edge on Cu polycrystal for XPS and UPS, respectively.

Band structure calculations were performed in full-relativistic mode using Elk FP-LAPW/APW+lo code [8] with local spin-density approximation (LSDA) and the Perdew-Wang exchange-correlation potential [9, 10].

3. Results

The obtained XRD pattern (Fig. 1) corresponds well to the hexagonal crystal structure of the ZrNiAl-type. In the crystallographic unit cell, atoms are located at the following unique sites: Tm in 3g: $x_R, 0, \frac{1}{2}$, In in 3f: $x_{In}, 0, 0$ and Pd in 2b: $0, 0, \frac{1}{2}$ and 2c: $\frac{1}{3}, \frac{2}{3}, 0$. The Rietveld analysis yields the refined structure parameters which are shown in Table I.

TABLE I

Crystal structure parameters of TmPdIn.

Parameter	Value
a	7.631(4) Å
c	3.731(3) Å
V	188.1(2) Å ³
x_R	0.2607(4)
x_{In}	0.5916(4)
R_{Bragg}	6.90
R_{prof}	8.09

The calculated total density of states for TmPdIn and the contributions from Tm, Pd, and In are shown in Fig. 2. The Tm 4*f* states are split by spin-orbit interaction, as well as Coulomb on-site repulsion and form a series of peaks between -3.6 and -7.2 eV. The calculated density of Pd 4*d* states reaches the maximum at -3.2 eV. The In 5*p* states are located in the region from -2 to 5 eV while In 5*s* are between 5.5 and 9 eV with the low intensity.

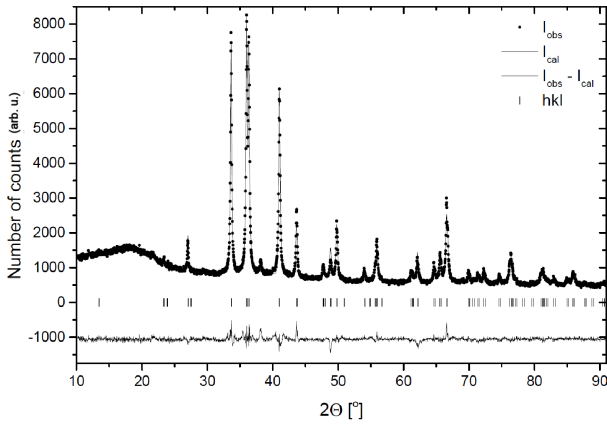


Fig. 1. X-ray diffraction pattern obtained for TmPdIn with Cu K_{α} radiation at room temperature. Experimental data are marked with black points, solid line denotes a result of Rietveld analysis.

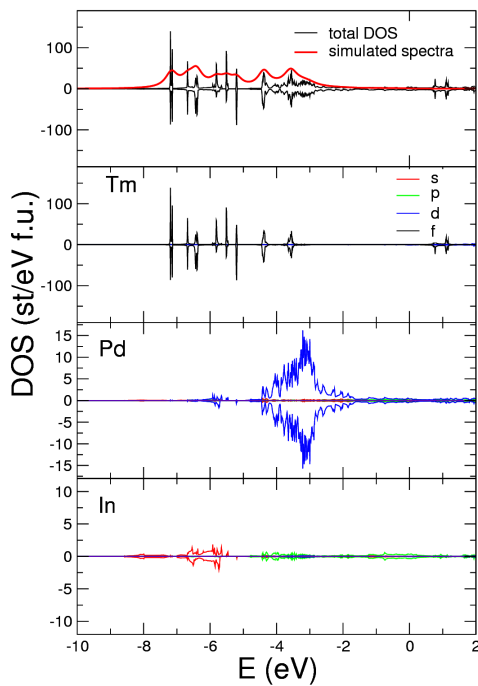


Fig. 2. Total and partial (corresponding to particular orbitals) densities of states (DOS) calculated by means of APW+lo method for the valence band of TmPdIn. Positive and negative DOS values are shown for opposite spin directions. The red line superimposed on the total DOS is a simulated XPS spectrum obtained from the contributions of partial DOS-es with proper photoionization cross-sections and experimental broadening.

The valence band spectra obtained by XPS and UPS with He(I) and He(II) are shown in Fig. 3. The XPS spectrum of the valence band is dominated by a multiplet structure originating from Tm $4f$ electrons. However, the positions of the multiplet peaks are displaced with respect to those observed in metallic thulium [11]. Additional peak with strong intensity observed at ≈ 3.8 eV in the spectra of He(I) and He(II) is related to Pd $4d$

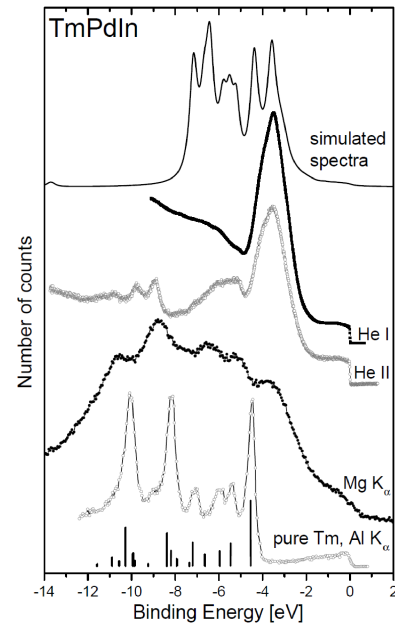


Fig. 3. Valence band of TmPdIn measured with He(I), He(II) (UPS) and Mg K_{α} (XPS) radiation at $T = 14$ K. The spectrum for pure Tm obtained with Al K_{α} radiation from [11] is shown for comparison. Bars denote positions and intensities of the calculated peaks [11]. The uppermost curve is the XPS spectrum simulation from Fig. 2.

states. The multiplet structure is not well seen in the He(I) spectra.

The experimental results are compared to the simulation of XPS spectra obtained from theoretical calculations presented in Fig. 2. The theoretical density of states (DOS) curves were convolved with Gaussian function in order to correct for experimental broadening and the resulting simulated spectra are shown in both Fig. 2 and Fig. 3. Their shape reflects the results of the experiment in particular for XPS. The theoretical results showed multiplet splitting with the maxima at the energies of -7.2 , -6.6 , -6.38 , -5.8 , -5.47 , -5.15 , -4.37 , and -3.6 eV. This simulated multiplet has a similar shape to that observed experimentally but the energies are rescaled. The large and broad peak related to Pd $4d$ states found around -3.2 eV in the calculations is well seen in He(I), He(II) and XPS spectra. Indium $5p$ and $5s$ states have low DOS in the calculations and they are rather unnoticeable in the experiment. Tm $5d$ and $6s$ states should also contribute near the Fermi energy forming a broad plateau but they have low values of calculated DOS and probably low spectral intensity.

It may be concluded that XPS spectra are well reproduced by the calculations. They consist mostly of Tm $4f$ multiplet and Pd $4d$ contributions. He(II) spectrum exhibits one additional peak at 9.5 to 10 eV, which is found neither in XPS spectrum nor in the calculations. Its origin is not known but as He(II) measurements are characterized with higher surface sensitivity it may be related to surface states.

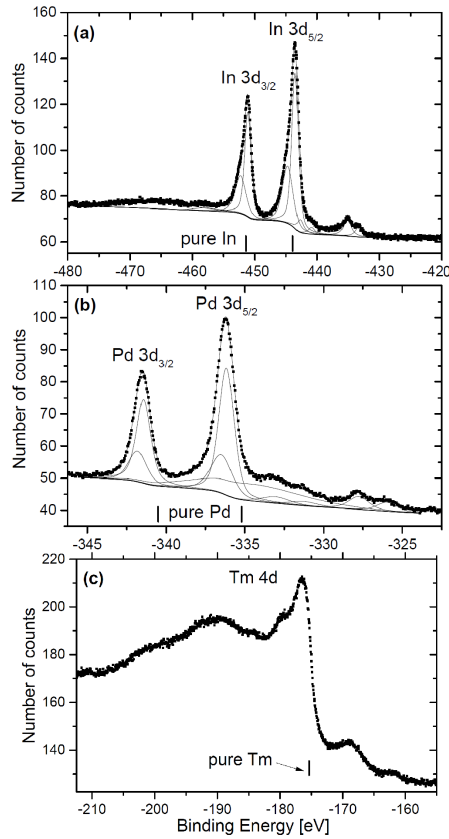


Fig. 4. XPS spectra for TmPdIn obtained with Mg K_{α} radiation. Spectra for In 3d (a), Pd 3d (b) and Tm 4d (c) are shown. Binding energies for pure In, Pd and Tm are shown.

TABLE II

Binding energies for In 4d, In 3d, Tm 4f and Pd 3d core levels obtained from XPS performed with Mg K_{α} . Determined spin orbit splitting values Δ are also given. The data for pure elements are taken from [12].

State	TmPdIn [eV]	Pure element [eV]
In 4d _{5/2}	16.45	16.6
In 4d _{3/2}	17.2	17.4
Δ	0.75	0.8
Tm 5p _{3/2}	25.5	25.0
Tm 5p _{1/2}	32.4	31.8
Δ	6.9	6.8
Pd 3d _{5/2}	336.2	335.2
Pd 3d _{3/2}	341.4	340.5
Δ	15.2	15.3
In 3d _{5/2}	443.5	443.9
In 3d _{3/2}	451.1	451.4
Δ	7.6	7.5

The XPS spectra for selected core levels are shown in Fig. 4. At 176.5 eV the maximum corresponding to the Tm 4d state is detected. This value is between those for pure metallic Tm (175.5 eV) and Tm in oxides (177.4 eV) [12]. This confirms that the bonding in TmPdIn has a small deviation from the bonding in pure

metal, which is characteristic of intermetallics. The energy values of core levels in TmPdIn are listed in Table II. The obtained values are close to the binding energies for pure elements [13].

4. Summary

In this work we investigated the electronic structure of TmPdIn. The obtained spectra indicate that the Pd 4d states are located below Fermi level (≈ 3.5 eV) and overlap with the Tm 4f state ($^4I_{15/2}$). This suggests the considerable hybridization of 4f and 3d electrons which should influence the magnetic properties of this compound. The energies of Tm 4f and Tm 4d states are close to metallic Tm. However, clear shifts in the Tm 4f multiplet peaks are observed with respect to pure Tm.

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