

BAND STRUCTURE OF TERNARY YbTM (T = TRANSITION METAL, M = Sn, Bi) COMPOUNDS

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Abstract Electronic structure of ternary ytterbium YbTBi (T = Au, Ag, Cu, Pd) and YbTSn (T = Ag, Au, Pt, Rh) compounds has been calculated by *ab-initio* spin-polarised Tight Binding LMTO method. *Ab-initio* band calculations indicate that YbTSn and YbTBi (T = Ag, Au, Cu) compounds are non-magnetic with the divalent ytterbium ions. In YbPdBi the small magnetic moment $m = 0.25 \mu_B$ is observed.

1. INTRODUCTION

The ternary YbTM compounds crystallise into different crystallographic structures (MgAgAs, LiGaGe, Fe₂P, CaLiSn, TiNiSn). The magnetic, thermodynamic and transport properties of the series of ytterbium compounds were measured by Kaczorowski *et al.* [1]. They found that the compounds YbTBi with T = Cu, Ag, Au and YbTSn with T = Ag, Au and Zn were nonmagnetic with the divalent ytterbium ions [1], however in YbPdBi, YbRhSn and YbPtSn they observed localised magnetism with trivalent Yb ions. The low-temperature specific heat measurements indicated a large value of the specific heat γ coefficient ($\gamma = 300\text{-}500 \text{ mJ/K}^2 \text{ mole}$). Recently, Szytuła *et al.* [2] studied the electronic structure by X-ray photoemission spectroscopy. The XPS measurements had shown that YbAuSn and YbAuBi compounds were divalent, while the YbRhSn and YbPtSn were trivalent. The band structure of Yb compounds was calculated in the past by the different *ab-initio* methods [3-10] within the local spin density (LSD) approximation using the various contributions to the exchange potentials [3-6]. Temmerman *et al.* [5] studied the total energy differences between divalent and trivalent configurations of Yb ions in series of ytterbium compounds. They found the relation between valence and localisation energy of *f* electrons [5]. In Yb compounds there are possible two electronic configurations: $4f^{13} (spd)^3$ (trivalent Yb³⁺) and: $4f^{14} (spd)^2$ (divalent- Yb²⁺). The divalent, trivalent or intermediate valence of Yb depends on the type of elements in the ytterbium compounds.

In this paper we present the electronic structure of YbTBi and YbYSn compounds which crystallise in the different type of crystallographic structures (MgAgSn, LiGaGe, Fe₂P, CaLiSn, TiNiSn). In Section 2 we give outline of the method and the results are presented in Section 3.

2. METHOD OF CALCULATIONS

The electronic density of states (DOS) of YbTM (T = transition metal, M = Sn, Bi) have been calculated by the spin-polarised self-consistent tight binding linear muffin tin orbital (TB LMTO) method in the atomic sphere approximation (ASA) [12-13] for the experimental lattice parameters. The scalar-relativistic approximation for band electrons and the fully relativistic treatment of the frozen core electrons were applied. The values of the atomic sphere radii were taken in such a way that the sum of all atomic sphere volumes was equal to the volume of the unit cell. The exchange correlation potential was assumed in form of von Barth and Hedin [14] and the gradient corrections were also included [15]. The self-consistent spin-polarised band calculations were performed for 216-270- k points in the irreducible wedge of the Brillouin zone, depending on the type of structure. The band calculations were performed for the full hybridisation between s , p , d and f electrons of ytterbium, transition metal and Sn or Bi. We have also applied the scheme proposed by Brooks *et al.* [16] in which the $4f$ states of Yb were treated as open core states. In such a model the number of $4f$ electron of Yb was fixed to 14.

3. RESULTS

The band structure and magnetic properties were calculated for two series of compounds: YbTBi (T = Cu ($3d^{10} 4s^1$), Pd ($4d^{10}$), Ag ($5s^1 4d^{10}$), Au ($6s^1 5d^{10}$)) and YbTSn (T = Rh ($5s^1 4d^8$), Pt ($6s^1 5d^9$), Ag ($5s^1 4d^{10}$), Au ($6s^1 5d^{10}$)). The T elements (excluding Pt and Rh) have the d shell completely occupied by 10 electrons. The atomic volume of the unit cell changes from $V = 0.3212$ (nm³) for YbAuBi [1] to $V = 0.1428$ (nm³) for YbCuBi [1]. The total densities of states (DOS) for paramagnetic YbTBi (T = Ag, Au, Pd, Cu) and YbTSn (T = Au, Ag, Rh, Pt) are presented in Figs. 1 and 2, respectively. For all ytterbium compounds the high peak from $4f$ states of Yb is located below the Fermi energy. The contribution to the density of states at the Fermi level $N(E_F)$ from $4f$ states is the greatest for the cubic YbPdBi ($N(E_F) = 4.6$ (states/(eV f.u.))). Two systems (YbRhSn and YbPtSn) with the hexagonal type structure (Fe₂P) have $N(E_F) = 3.33$ and 3.06 (states/(eV f.u.)), respectively. In those compounds the number of $4f$ electron of Yb is smaller than 14 ($13.77 < n_{Yb} < 13.82$) (Table 1) and this result indicates that ytterbium is trivalent in those compounds. In YbTBi (T = Au, Ag, Cu) the Fermi level is located in the valley on the right side of the $4f$ peak. The density of states $N(E_F)$ is small ($0.61 < N(E_F) < 0.91$ (states/(eV f.u.))) and the compounds are paramagnetic. In YbTBi compounds the peak in the DOS from $6p$ states of Bi are located between (12 eV < E < 11 eV). The main contribution to the photoemission spectra comes from $3d$ states of the transition T elements. For T = Au and Ag the main peak is located between 6.5 eV < E < 4 eV, however for T = Cu and Pd the peak of d states is moves towards the Fermi level and it is located between (5.6 eV < E < 1 eV). In the $4f$ peak in the paramagnetic YbPdBi we observe one high peak and the second smaller near 0.5 eV. Between the peaks is a valley. The spin polarised LMTO calculation has show a small magnetic moments on ytterbium $m_{Yb} = 0.23\mu_B$, palladium $m_{Pd} = 0.01\mu_B$ and bismuth $m_{Bi} = 0.01\mu_B$). The DOS for the ferromagnetic YbPdBi is presented in Fig. 3. We observe a small displacement of the $4f$ peak from majority and minority spin band of Yb. The contribution to

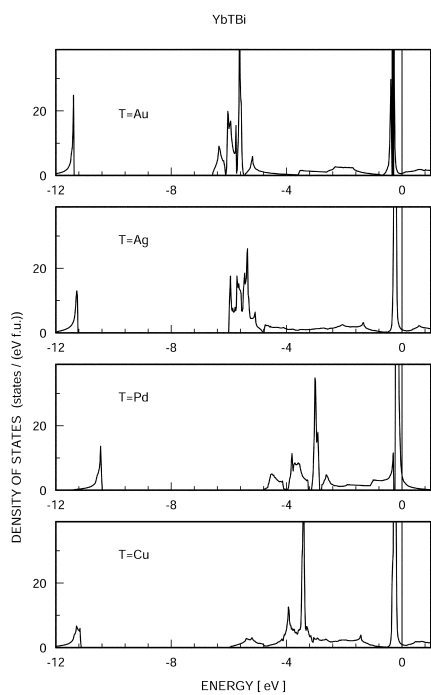


Fig. 1. The total density of states for the paramagnetic YbTBi (T = Au, Ag, Pd, Cu). The vertical line denotes the Fermi level

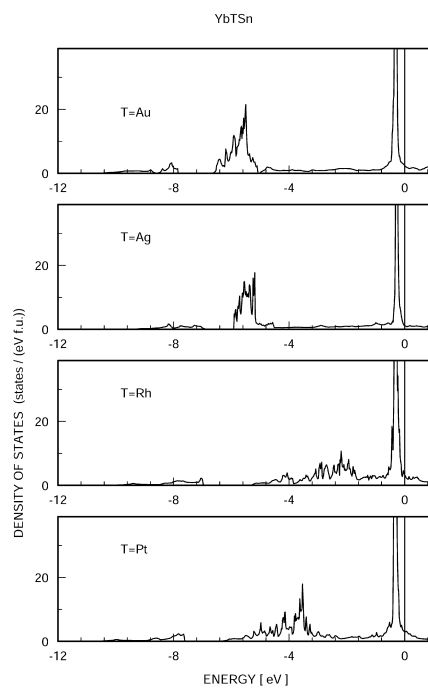


Fig. 2. The total density of states for the paramagnetic YbTSn (T = Au, Ag, Rh, Pt). The vertical line denotes the Fermi level

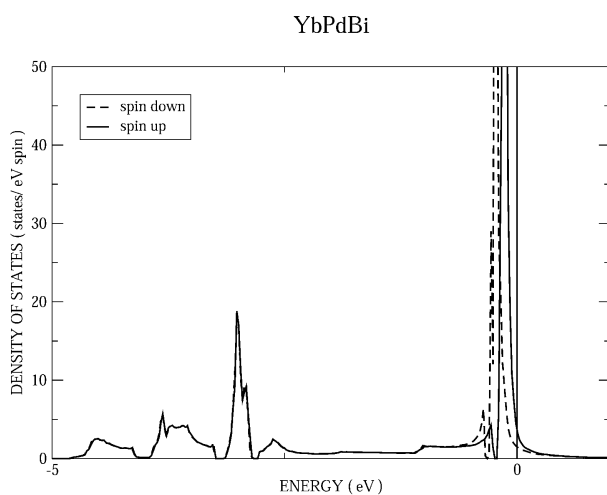


Fig. 3. The density of states for the ferromagnetic YbPdBi. The dash and solid lines denote the DOS for minority and majority spin band. The Fermi level is denoted by vertical line

the density of states at the Fermi level is mainly from the majority $4f$ electron states. The general shape of the total density of states for YbAuSn and YbAgSn is similar to YbAuBi and YbAgBi, respectively. The peak due to $3p$ electrons of Sn is located near $E = 8$ eV. The number of $4f$ electrons in those compounds is close to 14 what suggests that ytterbium is divalent in these systems. The value of $N(E_F)$ is greater for YbTSn ($T = \text{Ag, Au}$) than for YbTBi ($T = \text{Ag, Au}$) (Table 1). In the case of YbRhSn and YbPtSn the peaks from $4d$ and $5d$ electrons are broad and are located between $5.5 \text{ eV} < E < 1 \text{ eV}$. The density of the Fermi level is about 3 (states/eV f.u.) (Table 1). The *ab-initio* calculations indicate that electronic configuration in Yb is close to trivalent.

Table 1. Electronic density of states at the Fermi level $N(E_F)$ for two models: full hybridisation (*spdf*) and *f* electrons into core (*spd*)

Compound (structure)	$N(E_F)$ [states/(eV f.u.)]		Number of $4f$ electron $n_{\text{Yb}}(4f)$
	(<i>spdf</i>)	(<i>spd</i>)	
YbCuBi (LiGaGe)	0.91	0.39	14.00
YbPdBi (MgAgAs)	4.60	2.36	13.80
YbAgBi (LiGaGe)	0.89	0.42	14.00
YbAuBi (MgAgAs)	0.61	0.30	13.91
YbRhSn (Fe2P)	3.55	1.82	13.77
YbPtSn (Fe2P)	3.06	1.07	13.82
YbAgSn (CaLiSn)	1.55	0.67	13.98
YbAuSn (TiNiSn)	2.41	1.36	13.98

We have also performed the band calculations for the Brooks *at al.* [16] model in which the f electrons were included into the core, and we consider hybridisation only between *spd* electrons. In Table 1 we listed the values of the density of states at the Fermi level for the model with full hybridisation and for the case when the $4f$ electrons were included into core. The values of $N(E_F)$ listed in Table 1 indicate that the contribution from $4f$ electrons to the density of states at the Fermi level is more than 50% of the total value.

4. CONCLUSIONS

In this paper we presented the band structure of YbTBi and YbTSn compounds, which crystallised into different crystallographic structures. Our *ab-initio* self-consistent LMTO calculations indicate that the electronic configuration of ytterbium depends on the type of T element. For $T = \text{Ag, Au}$ and Cu the number of $4f$ electrons of Yb is close to 14 (divalent configuration). In YbPdBi, YbRhSn and YbPtSn the number of $4f$ electrons is less than 14 ($13.77 < n_f < 13.82$) what suggest that the electronic configuration of Yb is close to trivalent.

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