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Effect of spin-orbit coupling on the electronic structure of bismuthide YbAuBi

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The electronic structures of ternary ytterbium YbAuBi and YbAuSn compounds were studied by X-ray photoemission spectroscopy (XPS) and *ab initio* methods (LMTO-ASA, FP LMTO, FPLO). The results showed that the valence bands in these compounds are formed by the 4f orbitals of ytterbium and 5d orbitals of transition metals. Full relativistic band calculations (FP LMTO and FPLO) with spin-orbit coupling have shown that the 4f peak consists of two peaks that correspond to the Yb $4f_{7/2}$ and $4f_{5/2}$ doublet.

Key words: *rare earth compounds; electronic structure; photoelectron spectroscopy; ab initio methods; FPLO; FP LMTO*

1. Introduction

Ternary YbTM (T – transition metal, M – Sn, Bi) compounds crystallise into different crystallographic structures (MgAgAs, LiGaGe, Fe_2P, CaLiSn, TiNiSn). The magnetic, thermodynamic, and transport properties of this series of ytterbium compounds were studied by Kaczorowski et al. [1]. They found that the compounds YbTBi, with T = Cu, Ag, and Au, and YbTSn, with T = Ag, Au, and Zn, are nonmagnetic with divalent ytterbium ions [1]. In YbPdBi, YbRhSn, and YbPtSn, however, they observed localised magnetism with trivalent Yb ions.

Recently, Szytula et al. [2] studied their electronic structure by X-ray photoemission spectroscopy. The XPS measurements indicated that YbAuSn and YbAuBi are divalent, while YbRhSn and YbPtSn are trivalent. The band structure of Yb compounds was calculated in the past by various *ab initio* methods [4–10], within the

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local spin density (LSD) approximation using various contributions to the exchange potentials [4–9]. The divalent, trivalent, or intermediate valence of Yb depends on the type of elements in the ytterbium compounds.

2. Experimental and theoretical methods

The electronic structures of YbTX compounds were obtained by X-ray photoemission spectroscopy (XPS) and by *ab initio* calculations. Measurements were carried out on polycrystalline samples [1]. The XPS spectra were measured at room temperature using a Multipurpose Electron Spectrometer PHI5700/600 with AlK_α monochromatised radiation ($h\nu = 1486.6$ eV) and a Leybold LHS10 Electron Photoemission Spectrometer with MgK_α radiation ($h\nu = 1253.6$ eV) [2]. The experimental procedure is described in Ref. [2].

The electronic densities of states (DOS) of YbTM have been calculated by the spin-polarised self-consistent tight binding linear muffin tin orbital (TB LMTO) method in the atomic sphere approximation (ASA) [11, 12] for experimental lattice parameters [1]. The scalar-relativistic approximation for band electrons and the full relativistic treatment of frozen core electrons were applied. The exchange correlation potential was assumed in the form of von Barth and Hedin [13], and gradient corrections were also included [14]. The results of calculations are presented in [2] and [3]. Scalar-relativistic (without spin orbit coupling) LMTO-ASA calculations gave a single, large peak due to the 4f electrons of Yb near the Fermi level. The position of Au was close to that observed in XPS spectra [2].

In this paper, we present the electronic structure of YbAuBi calculated by the FP LMTO (LmtArt) [15, 16] and FPLO [17] methods. The band structure was calculated for the experimental lattice parameter (structure type MgAgAs, $a = 0.6848$ nm). In both methods, we applied spin-orbit coupling. In the FPLO scheme, the calculations were performed using the full relativistic version of the full potential local orbital minimum basis. For the site–centre potentials and densities, expansions into spherical harmonics were used up to $l_{max} = 12$. The number of k points in the irreducible part of the Brillouin zone was 484. The parameterisation of the exchange-correlation potential in the framework of the local spin density approximation was used in the form proposed by Perdew–Wang [18].

3. Results

The electronic structure was measured for YbAuBi and YbAuSn, and we calculated the band structure for YbAuBi including the spin-orbit coupling. In Figure 1, we present the XPS spectra of the valence bands of YbAuSn, YbAuBi, and of metallic Yb. We observed two peaks below the Fermi level, corresponding to the Yb $4f_{7/2}$ and $4f_{5/2}$ doublet, similar to that in metallic Yb. In the region of higher binding energies, 5

$< E <$ 10 eV, the peaks correspond to the 5d states of Au and p-electron states of Sn and Bi.

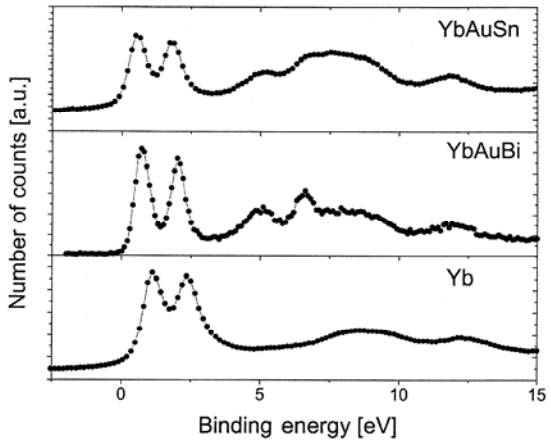

Fig. 1. XPS spectra of the valence bands of YbAuBi, YbAuSn, and metallic Yb

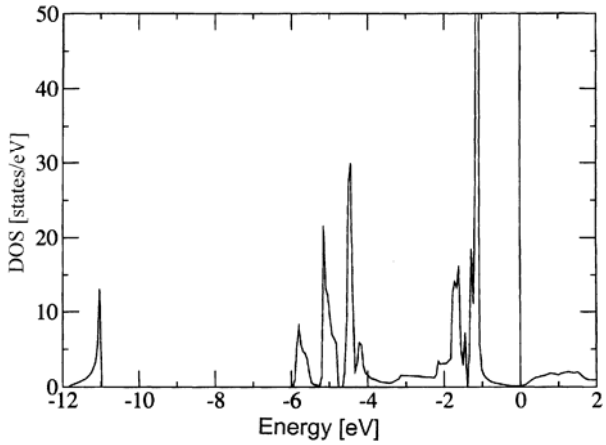

Fig. 2. The total density of states of YbAuBi (scalar-relativistic FPLO)

Recently, we presented the electronic structures of YbAuSn and YbAuBi [2] calculated by the TB LMTO–ASA method [11, 12]. We observed one main peak below the Fermi level as well as contributions from the 5d electron states of Au and p-electron states of Sn and Bi for higher binding energies. In this work, we present fully relativistic full potential band calculations including spin-orbit coupling. Scalar relativistic full potential calculations (FPLO and FP LMTO) give similar shapes of the densities of states (only one main peak below the Fermi level, see Fig. 2.) to those seen in TB LMTO-ASA results [2]. The number of 4f electrons obtained from scalar relativistic FPLO and LMTO-ASA methods are 13.94 and 13.91, respectively.

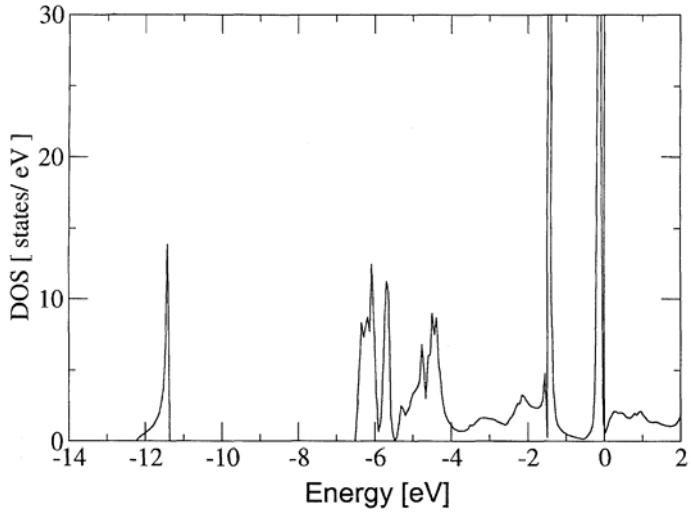

Fig. 3. The total density of states of YbAuBi (full relativistic FPLO)

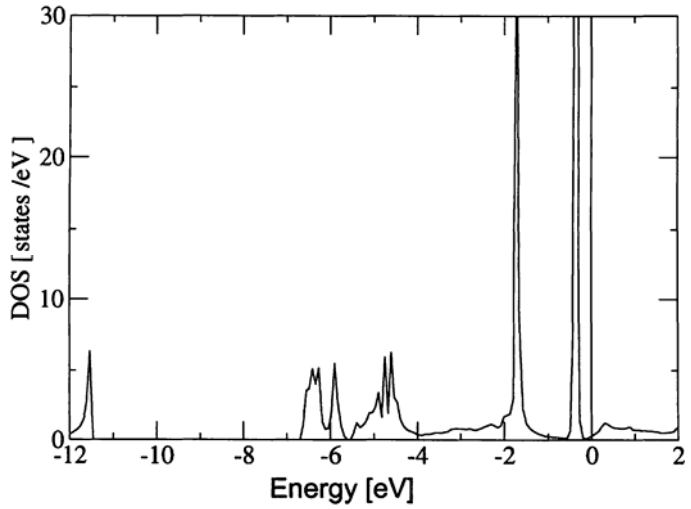

Fig. 4. The total density of states of YbAuBi (FP LMTO)

In Figures 3 and 4, we present the total density of states (DOS) for YbAuBi, obtained by the FPLO [17] and FP LMTO [15,16] methods. The total DOS in Fig. 3 is plotted for two spin directions, however the DOS obtained from the FP LMTO method is for only one spin direction. We observe a 4f feature below the Fermi level, consisting of two peaks, one corresponding to Yb $4f_{7/2}$ and the other to the $4f_{5/2}$ doublet. The splitting of the peaks is about 1.5 eV, close to that of the XPS spectra [2]. The number of 4f electrons of Yb obtained from the FPLO and FP LMTO methods are 13.61 and 13.76, respectively.

4. Conclusions

We present the XPS spectra of YbAuSn and YbAuBi compounds and *ab intio* fully relativistic full potential (FPLO and FP LMTO) calculations of the electronic structure of YbAuBi. FP LMTO and FPLO calculations (including S-O) give a splitting of the 4f states of Yb similar to that from photoemission measurements. Both methods give very similar results. The scalar relativistic (TB LMTO and FPLO) methods also give similar shapes of the densities of states – one main 4f peak below the Fermi energy. Our *ab initio* calculations confirmed that the ytterbium ion is divalent in YbAuBi as well as YbAuSn (not discussed here).

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