Electronic structure and X-ray photoemission spectra of the half-Heusler compounds APtSn (A = Th, U or Ti, Zr, Hf)

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Introduction. The APtM group of equiatomic ternary alloys (A = Th, U or Ti, Zr, and Hf, while M=Sb or Sn) crystallize in the cubic MgAgAs-type structure (*F-43m* space group, 4 formula units in the unit cell). These compounds are so-called half-Heusler compounds, and present a rich variety of physical properties, especially semiconducting behaviour in their transport properties originating from the special symmetry of crystal structure [1, 2]. The overlap between the electronic orbitals of the A elements is much reduced due to the vacant A site, each second A site, in the complete Heusler type alloy: A_2PtM , is empty and hence the inversion symmetry in the crystal structure is lost. In the case of UPtSn, the large inter-uranium spacing of about 4.7 Å (below the Hill limit), leads to a large reduction in the U(5f)-T(4d)-M(s,p) hybridization causing a more localized kind of behaviour of the U(5f) electrons. In the paramagnetic state the magnetic properties are well described by the localized f-electron model, the temperature dependence of the magnetic susceptibility of UPtSn shows the Curie-Weiss behaviour towards high temperatures with an effective moment $\mu_{eff} = 3.45\mu_B$ and the paramagnetic Curie temperature θ_p, derived in a wide temperature range, is equal to -125 K [2]. The susceptibility of this compound, $\chi(T)$, exhibits quite anomalous behaviour at low temperatures. Below about 140 K first shows the tendency for leveling off and then at about 35 K, it increases rapidly to go through a small maximum at about 20 K, probably due to small ferromagnetic impurities. At the same time the heat capacity measurements show without ambiguity the transition probably into an antiferromagnetic order at the same temperature and yield the electronic specific heat coefficient to be about 10 mJ/K^2mol [1, 3].

As the measurements of electrical resistivity showed [1-3], the behaviour $\rho(T)$ is characteristic of semiconductors and its temperature dependence at higher temperatures may then be described by a gap function, $\rho(T) \approx \exp(\Delta/2k_BT)$, where Δ is 0.34 K [1]. At low temperatures $\rho(T)$ either decreases [1] or going through a maximum at different temperatures depending on a sample measured (60–140 K), then passes through a minimum at 9-16 K and dramatically increases towards lower temperatures. In order to describe the transport properties observed, previously a simple phenomenological model [2] has been proposed in which the band gap slowly diminishes and finally is closed at T = 0 K instead to collapse immediately at T_N, as is the case of UNiSn [4]. This suggests that the ordered state acts as an additional mechanism in a strong p-f mixing effect [5] towards closing the gap.

Previous synchrotron photoemission studies of valence band spectra [6] were measured in the photon energy range $h\nu$ = 22-130 eV. They showed the d-like density of states located well below the Fermi level, E_F, with the maximum being about 4.6 eV. The 5f states are close to the Fermi energy with a maximum at 0.75 eV and full width at half maximum of 1.6 eV. These results are consistent with a band gap in the paramagnetic state and a small γ value of 10 mJK^{-2} $mole^{-1}$.

Oppenner *et al.* [7] have adopted a model approach for a band-structure self-consistent description based on the local density approximation of density functional theory generalized with an on-site Coulomb correlation U (LDA + U) and shown that this model approach correctly describes a whole group of similar materials. For UPtSn they obtained an AF ground state which is semiconducting with a gap of 0.21 eV in the paramagnetic state. In this state the 5f density of states has a broad shape with its maximum at 0.85 eV, close to that found in the photoemission experiment [6].

ThPtSn is a suitable reference compound, because it has not occupied 5f electrons and remains paramagnetic semiconductor to the lowest temperatures [2]. In the case of ZrPtSn, the overall behaviour is qualitatively similar to that of found for UPtSn in that a local maximum is seen in $\rho(T)$ around 120K, a rather sharp minimum at 10K and finally, upon further cooling, $\rho(T)$ continues to rise sharply. We have also expanded our measurements and calculations on isostructural compounds TiPtSn and HfPtSn.

Computational and experimental details. The tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic sphere approximation (ASA) was used for band structure calculations [8, 9]. The exchange-correlation potential in the form proposed by von Barth and Hedin [10] was assumed for the calculations presented in Fig. 1(left panel).

Calculations were done for 3091 k-points in 1/24 segment of the Brillouin Zone. The initial atomic configuration of Pt was assumed as (Xe +$4f^{14}$) core +$5d^9 6s$; the configuration of Sn comprised (Kr) core +$4d^{10}5s^2 5p^2$. The remaining initial configurations were specified as follows: for Th: core +$6p^6 6d^2 7s^2$; and U: core +$6p^6 5f^3 6d7s^2$. As mentioned above, the resulting electronic band structure depends in some fine details upon the choice of the form of the exchange-correlation potential and the initial atomic configurations even if self-consistency is achieved within the assumed 0.01 mRy error in the energy eigenvalues, These differences are inherent in the TB-LMTO (ASA) approximations. The standard combined corrections [8] for overlapping muffin-tin spheres were applied. Fully relativistic treatment of the core electrons and the scalar relativistic approximation for the valence electrons was used [11]. Integrations in the k-space were done by the tetrahedron method [12-14]. The experimental values for the lattice constants: a = 6.736 Å for Th [3], and a= 6.6108 Å for U [3] were used in calculations.

The samples were prepared by arc melting appropriate amounts of constituent elements under argon gas. After melting the samples were wrapped in Ta foil and annealed in vacuum at 850 K for a week. The samples were identified by X-ray diffraction and determination of the lattice parameters. Only single phases were detected.

The X-ray photoemission spectra (XPS) were obtained with monochromatized Al K_α radiation (1486.6eV) at room temperature, using a PHI 5700/660 Physical Electronics Spectrometer. The emission spectra were analyzed by a hemispherical analyzer with energy resolution about 0.3eV. The samples were fractured mechanically in the preparation chamber under UHV conditions (5×10^{-10} Torr) and then moved into the main chamber. All spectra were recorded immediately after breaking in a vacuum about 5×10^{-10} Torr. The fractured samples contain a small amount of oxygen and carbon. The oxidation of all samples were checked several times during measurements by observing the O(1s) spectra. No effects of oxidation during the data acquisition time were observed.

Results. In Fig.1. (left panel), densities of states (DOS) calculated for APtSn compounds using von Barth-Hedin exchange-correlation potential [10] are summarized. A small energy gaps at top of the valence bands are the most important features of the electronic energy spectra of these compounds. The band structure calculations indicate on a complete filling of the valence for all of the APtSn compounds studied by us. Unfortunately, the actual values of the gaps between the occupied valence bands and the empty conduction bands have appeared to be sensitive to the assumptions made in implementing the local density functional theory.

Energy gaps calculated using the v. Barth-Hedin [10] or the Perdew et al. [15] exchange-correlation potentials are quite different (see Table below; all values expressed in meV).

compound → ↓ potential	ThPtSn	UPtSn	TiPtSn	ZrPtSn	HfPtSn
v. Barth-Hedin [10]	34	11	369	298	192
Perdew et al. [15]	< 6	10	254	150	25

The gap appears also to be sensitive to the choice of an initial atomic configuration of Sn atoms, *i.e.* they are different if all the ten 4d electrons of Sn are included either to "core" or to "valence band".

The sensitivity of the energy gap at the top of the valence band to the details of the TB-LMTO-ASA method chosen for the band structure calculation was the reason for undertaking computations by a different implementation of the general LDA treatment. To this end the full potential program LmtART 6.50 [16] has been used for recalculating the band structure of UPtSn. Unfortunately, no energy gap near the Fermi level was found, irrespective of using different forms of the exchange-correlation potential, taken from Refs.[10] or [15]. Instead, the total density of states at the Fermi level, DOS(E_F) = 3.758 states/(eV·formula unit) (for the exchange-correlation potential in the form of Ref. [10]) is pretty large. It gives, e.g., the theoretical estimate of the electronic specific heat coefficient γ_{th} = 8.85 mJ/K^2mol, as compared to the experimental value of 10 mJ/K^2mol. A very satisfying is the agreement between the calculated by the LmtART method splittings of the core and semicore levels with those formed from the measured XPS for UPtSn (see Fig. 6). The calculated splittings, compared with the measured ones (given in brackets) are as follows: U(4f): 11.02 eV (10.93 eV), Pt(4d): 16.83 eV (16.81 eV); Pt(4f): 3.56 eV (3.35 eV); Sn(3d): 8.7 eV (8.35 eV);

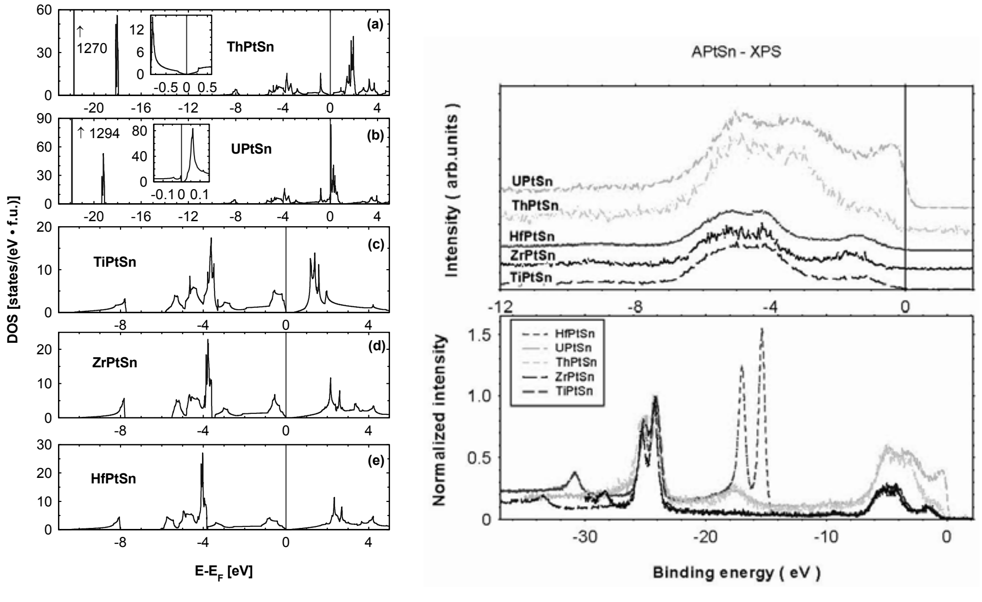

Fig.1. Left panel: the total DOS for (a) ThPtSn, (b) UPtSn, (c) TiPtSn, (d) ZrPtSn, and (e) HfPtSn; the insets in the (a) and (b) plots, in expanded scales, show the energy gap at the Fermi level. *Right panel*: the measured photoemission spectra.

Sn(4d):1.07 eV (0.94 eV). The total, local and partial densities of states calculated by the full potential LmtART method show shifts of the energy positions of some of the DOS(E) features presented in Fig. 1 (left panel).

Finally, calculations for UPtSn by the LmtART method [16] have revealed that the lowest total ground state energy has a magnetic state with the magnetic moments of 1.544 on U, -0.042 on Pt , and -0.020 on Sn (in μ_B). The orbital moments are -2.351, -0.014, and -0.003 for U, Pt and Sn, respectively. It also appeared from this calculation that the total energy of a non-magnetic state, with all the magnetic moments being suppressed, is higher by $\Delta E = 102$ meV per formula unit. The stable magnetic ground state is then an antiferromagnetic one but the exact type of the antiferromagnetic ordering has not been determined by our present calculations of the electronic structure. The stable antiferromagnetic ground state is also confirmed by TB-LMTO calculations. Since the experimental investigations [3] hint on a possibility of an antiferromagnetic ordering, any confirmation of such a ground state of UPtSn remains as an interesting challenge for a further investigation.

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