

Electronic structure of selected ternary samarium compounds

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Introduction

The ternary RPdSn or RPdIn compounds have been intensively investigated in the past with respect to their crystal structure, magnetic and transport properties [1-5]. Most of them are ruled by f-d interactions. However, in compounds with hexagonal type of crystal structure some properties are connected with the frustration in R sublattice. Such interesting mechanism leads to the possible existence of the mixed valence, heavy fermion or Kondo effect.

The first group of compounds RPdSn where R=Ce-Dy crystallize in the orthorhombic TiNiSi type of crystal structure (*Pnma* space group) whereas with R=Er-Sc crystallize in the hexagonal Fe₂P structure (*P-62m* space group). The compound HoPdSn can exist in both structures and it depends on heat treatment of the sample [1,3]. The second group of compounds RPdIn (R=La-Sm,Y, Gd-Lu) with 4d elements crystallize in the ZrNiAl - type hexagonal structure (*P-62m* space group) [2,4,5].

The susceptibility of the polycrystalline SmPdSn compound deviates from Curie - Weiss behavior. As it was previously reported this compound exhibits antiferromagnetic ordering with T_N about 12K. However, in low temperature range there was noticed one more peak which is probably connected with complex magnetic structure [1,3,6].

The GdPdIn compound exhibits ferromagnetic phase transition at $T_C=102K$ and Curie - Weiss behaviour with the paramagnetic Curie temperature $\theta_p=96.5K$ [2] whereas the SmPdIn single crystal is a ferromagnet below 54K and $0.21\mu_B/Sm$ along the easy magnetization *a* - axis [4]. In mixed compounds SmPdSn_{1-x}In_x and Gd_xSm_{1-x}PdIn the ordering temperatures are lower than 80K [6]. Additionally, the *M(H)* magnetization curves for SmPdSn and SmPdSn_{0.5}In_{0.5} are not saturated [6]. It may be connected with the complex magnetic structure. For Gd_xSm_{1-x}PdIn studied compounds *M(H)* is almost saturated at 7T. The value of M_s equals $0.21\mu_B/f.u.$, $3.36\mu_B/f.u.$ and $7.52\mu_B/f.u.$ for $x=0.0$, $x=0.5$ and $x=1.0$, respectively. The estimated value of magnetocaloric effect (MCE) is rather low and only for compounds which contain Gd is close to 1 [J/kgK] at the applied magnetic field of 1T [6].

The compounds with samarium seem to be interesting due to possible existence of mixed valence state of samarium ions. As it was previously reported the free Sm atom is divalent $(4f^6)(sd)^2$ while the trivalent $(4f^5)(sd)^3$ state is explained as the transfer of one 4f electrons to the conduction band. The divalent state is stabilized at the surface and the trivalent is essentially visible in bulk samarium [7-10]. Some samarium compounds exhibit the intermediate valence state and even similar like the pure samarium the valence transition at the surface. The core level splitting between Sm³⁺ and Sm²⁺ states is about 7.6eV. The separation of the final 4f multiplet structure $4f^5$ and $4f^4$ allow to distinct the two possible configurations. In spite of using photoemission methods sometimes it is difficult to point out whether Sm spectra are a bulk or surface phenomena. However, one of the best method which can be used to distinguish between emission from the bulk or the surface samarium atoms is the tilting samples from the normal direction. Sometimes there is observed an increase of the intensity of Sm³⁺(3d_{5/2}) photoemission line with the decrease of the takeoff angle [7].

Here we are focused on the influence of indium and gadolinium substitution on the electronic structure of the SmPdSn_{1-x}In_x ($x=0.0, 0.5, 1.0$) and Gd_xSm_{1-x}PdIn ($x=0.0, 0.5, 1.0$) compounds. To the best of our knowledge the electronic structure of studied compounds is reported here for the first time. According to this investigation we were able to deduce the valence state of samarium ions in both systems.

Experimental details

The polycrystalline samples SmPdSn_{1-x}In_x ($x=0.0, 0.5, 1.0$) and Gd_xSm_{1-x}PdIn ($x=0.0, 0.5, 1.0$) were prepared by arc-melting from high purity elements under argon atmosphere. The melted samples were then wrapped in tantalum foil, placed in quartz tubes and annealed at 850°C for one week. After annealing all studied samples were single phase and their crystal structure was checked by means of X-ray diffraction (XRD) using Siemens D5000 diffractometer. The XPS measurements were performed with the use of PHI 5700/660 Physical Electronics spectrometer. The spectra were analyzed at room temperature using monochromatized Al K α radiation (1486.6eV). The surfaces of the samples were mechanically cleaned by scrapping with a diamond file or cleaving in the preparation chamber under high vacuum of 10^{-10} Torr. After cleaning the samples were immediately moved into the main chamber. This procedure was repeated until the intensity of C1s and O1s photoemission lines was to neglect or do not change in further cleaning of the surfaces of the samples. All XPS measurements were performed in vacuum of 10^{-10} Torr.

Results and discussion

Fig.1a displays the valence band (VB) spectra in the broad energy range with core levels In4d and Sn4d. Each VB spectrum was normalized with respect to the Pd4d. The spin - orbit (L-S) splitting between 4d_{5/2} and 4d_{3/2} indium states is about 0.85eV and between tin states

about 0.9eV. This band does not change an energy shift and forms maximum located at about 3.8eV below the Fermi level (E_F). The Gd4f level for compounds containing gadolinium is shifted in comparison to pure Gd (8eV). For GdPdIn this level is located at about 8.7eV and for Gd_{0.5}Sm_{0.5}PdIn at about 8.9eV below E_F . This energy shift can be connected with the change of surroundings of Gd atoms. The cusp visible in VB at about 5.7eV is typical for trivalent Sm³⁺(4f) states which give the contribution to VB below 5eV. The divalent Sm states should be visible above 5eV. The intensity of states at the Fermi level $N(E_F)$ is the highest for SmPdSn and the lowest for GdPdIn (Fig.1b). It could be connected with the contribution of Sn5p and Sm²⁺(4f) which are located below 5eV. One can notice that $N(E_F)$ is the highest for the compound which exhibits the lowest magnetization.

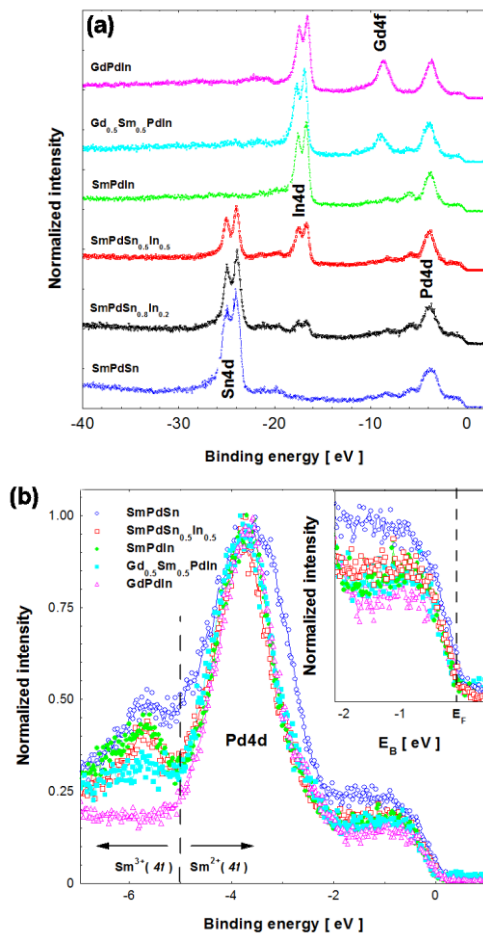


Figure 1. (a) The VB spectra in broad energy range for all studied compounds; (b) The VB near by the Fermi level (E_F) normalized to Pd4d states. Inset represents the intensity of states just below E_F .

Fig.2a represents Sm 3d spectra taken at 45° takeoff angle and normalized to the maximum. There are visible several core level lines. The highest intensity of states is observed for Sm³⁺ lines which are located at about 1081.8eV ($3d_{5/2}$) and 1073.3eV ($3d_{3/2}$) energy range. Each line of Sm³⁺ is composed of several peaks according to multiplets produced by ionization of samarium trivalent state. However for In-rich

compounds one of these peaks at about 1084eV is enhanced by In M₅N₄S₄ Auger line. Similar behaviour is observed for divalent samarium line Sm²⁺($3d_{5/2}$) located at about 1073.3eV. One of its components is enhanced by In M₄N₄S₄ Auger line (1076 eV). Therefore is difficult to estimate the 3+/2+ intensity ratio r , the coupling parameter Δ and the occupation number of f shell n_f by fitting 3d spectra using Gunnarson–Schönhammer model [12]. The separation between divalent and trivalent samarium peaks equals about 8.5eV.

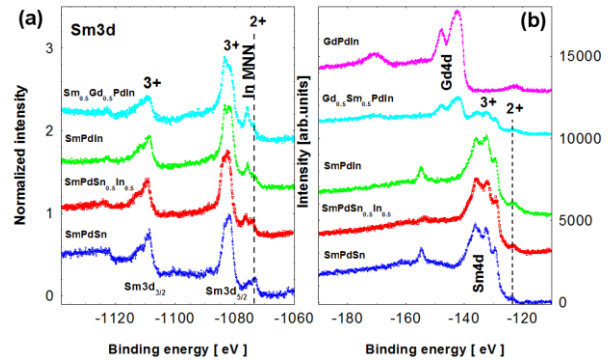


Figure 2. XPS photoemission core level spectra of the (a) Sm3d region; (b) Sm and Gd 4d region.

The 4d spectra are presented in Fig.2b. The overlap between divalent and trivalent samarium states and much more complicated multiplet structure of Sm4d than Sm3d states make the first spectra less attractive for detailed analysis. The observed Sm4d multiplet structure is typical for Sm³⁺ states. However at about 123eV is visible sharp peak which is typical for Sm²⁺ states. Some part of divalent spectrum is hidden under the stronger trivalent component.

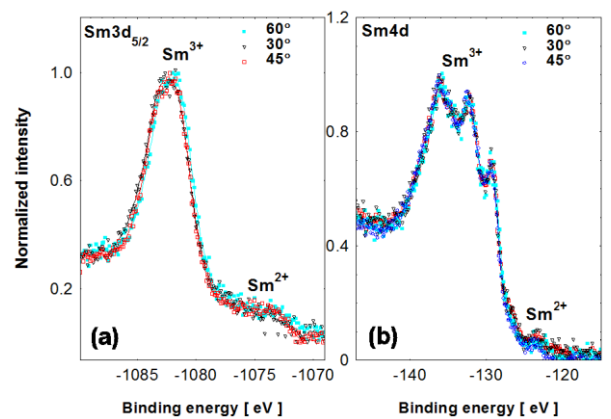


Figure 3. XPS photoemission spectra of the samarium core level (a) 3d; (b) measured by tilting the SmPdSn sample in three chosen takeoff angles.

We have also performed measurements by tilting the samples from the normal emission direction (45°) in order to enhance emission from the bulk (30°) and surface (60°) states. We have not observed significant change of the (3+)/(2+) intensity ratio with the change of takeoff angle. Fig.3. represents an example of this kind

of performed measurements for the SmPdSn compound. This behaviour can be related to the roughness of the surface. Therefore we have performed all investigation on the cleaved samples and scrapped by a diamond file. The results in both cases were nearly similar. Therefore we can conclude that the mixed valence state of samarium ions observed in studied compounds is not connected with the valence transition at the surface but rather with comes from bulk states.

Concluding remarks

From all measurements performed for the SmPdSn_{1-x}In_x ($x=0.0, 0.5, 1.0$) and Gd_xSm_{1-x}PdIn ($x=0.0, 0.5, 1.0$) compounds the following conclusions can be drawn:

- The change of the valence band spectra near by the Fermi level (E_F) is visible. The intensity of states at the Fermi level is the highest for the SmPdSn and the lowest for GdPdIn compounds. It is connected with the contribution of each elements to the valence band, some hybridization effects and f-d interactions.
- The samarium core level spectra exhibit the contribution of Sm³⁺ as well as Sm²⁺ states. The separation between divalent and trivalent Sm3d parts equals about 8.5eV. These two kind of peaks do not change with the tilting the samples during measurements. Therefore we claim that the mixed valence state of samarium ions in studied compounds comes from bulk states and not from the valence transition at the surface.

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