VALENCY OF Yb IN PbS AND PbTe DETERMINED BY XPS

Z. Gołacki

Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warsaw, Poland

AND M. Heinonen

Department of Applied Physics, University of Turku, ElectroCity
Tykistokatu 2D, 20520 Turku, Finland

X-ray photoelectron spectroscopy experiments on PbTe:Yb, PbS:Yb, PbTe, and PbS crystals have been performed using the monochromatized Al K_α radiation. The valence band spectrum of PbTe:Yb exhibits one set of peaks associated with divalent Yb initial states, but two sets associated with divalent and trivalent Yb are observed for PbS:Yb. The valency of Yb in PbTe:Yb is 2 (within an accuracy of the experiment) but in PbS:Yb the mixed valency of Yb is seen. These conclusions are confirmed by an analysis of Yb $4d$ spectra in PbTe:Yb and PbS:Yb crystals.

PACS numbers: 71.20.Nr, 79.60.–i

Ytterbium compounds show many interesting physical phenomena, e.g., Kondo effect, mixed valence, and existence of heavy fermions [1–3]. Yb monochalcogenides crystallize in the rock salt structure similarly as lead chalcogenides and form with them the mixed solid solutions. Depending on the host matrix the environment of Yb ions changes (S, Se or Te) and the lattice constant changes considerably. The lattice constant usually influences (chemical pressure) the valency of the ions with the tendency to induce a mixed valence (Ce, Sm, Eu, Tm and Yb). In the presented paper the effort was done to determine by X-ray photoelectron spectroscopy (XPS) the valency of Yb ions in PbTe and PbS, which is not obvious and need the experimental proof.

PbYbTe, PbYbS, PbTe, and PbS crystals were grown by the Bridgman method. Yb content was determined by the electron microprobe analysis to be equal 2 at.% for PbS:Yb and 3 at.% for PbTe:Yb. PbS:Yb samples were of n-type, PbTe:Yb samples were of p-type. No inclusions were found in the samples. The XPS spectra were recorded using a Perkin–Elmer small spot ESCA spectrometer equipped with an X-ray Al tube, a Rowland circle monochromator, and a hemispherical electron energy analyser. The spectral resolution was 0.7 eV. Samples were introduced into the preparation chamber with a vacuum better than

10^{-9} torr, cleaved, and then shifted to the measuring chamber with a vacuum better than 5×10^{-10} torr. Pb $4f$ and $5d$, Te $3d$ and $4d$, and S $2p$ spectra were measured for all the crystals (for the control of the experiment), but the attention was paid mainly to the valence band (VB) spectra and the $4d$ spectra of Yb ions. The experimental conditions — photon energy 1486.6 eV favour the bulk contribution of the photoelectron process.

The VB spectra of PbTe and PbS registered in this work are similar to those reported earlier in the literature [4]. The core levels spectra of Pb, Te, and S did not show any pronounced changes with doping by Yb.
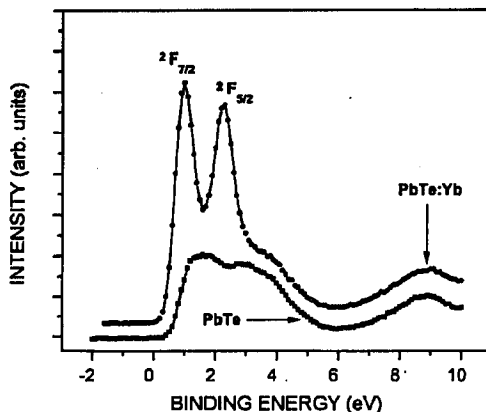

Fig. 1.   XPS valence band spectra for PbTe and PbTe:Yb.

Figure 1 shows the normalized VB photoemission spectra of PbTe:Yb, PbTe. The normalization takes into account the time acquisition and the photoemission intensity marked by intensity of the anion core lines. The difference between the PbTe and PbTe:Yb VB spectra is most pronounced near the Fermi level. The shape of the valence electrons energy distribution with two prominent peaks is characteristic for divalent Yb and corresponds to the $4f^{14} \rightarrow f^{13}$ photoionization process [5, 6]. These peaks can be assigned to the two states $^2F_{7/2}$ and $^2F_{5/2}$. The energy positions of maxima are 0.95 eV and 2.3 eV, respectively, the spin–orbit splitting of the $4f$ doublet is equal to 1.35 eV. This is typical value for the $4f$ electrons distribution in the divalent Yb [5, 6]. Due to a large photoionization cross section for the Yb $4f$ states, their influence on the valence band spectrum is distinctly seen, despite of the small Yb content.

Figure 2 presents the VB photoemission spectra of PbS:Yb, PbS and their difference. In comparison to PbTe:Yb the doublet characteristic for divalent Yb corresponding to $4f^{14}$ initial states is shifted towards the Fermi level and some additional structure appears at the energy 7–9 eV. This structure is caused by the existence of a trivalent Yb and corresponds to the $4f^{13}$ initial states.

Similar difference between PbS:Yb and PbTe:Yb, indicating a divalent character of Yb in PbTe and mixing valence in PbS is observed in Yb $4d$ spectra. Yb $4d$ spectrum of PbTe:Yb consists of 2 peaks with energies 181 and 191 eV
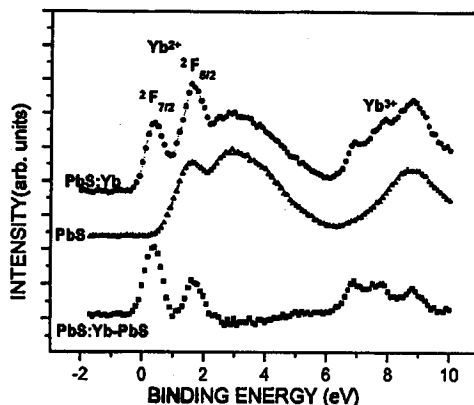
Fig. 2. XPS valence band spectra for PbS and PbS:Yb. The difference between the both spectra after normalization (PbS:Yb–PbS) is marked by the square points.
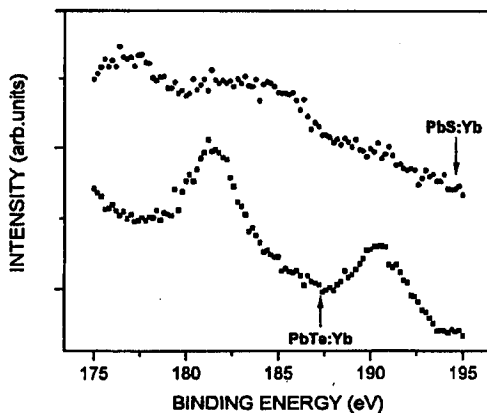

Fig. 3. Photoemission spectra of Yb $4d$ core level in PbTe:Yb and PbS:Yb.

corresponding to the $4d^{5/2}$ and $4d^{3/2}$ states, respectively (see Fig. 3). A similar position of the $4d$ maxima — 181.4 and 190.3 eV of divalent Yb was observed in Yb_4Bi_3 [7].

For PbS:Yb an additional broad structure appears with a binding energy of 180–187 eV. This spectrum is the superposition of two structures from divalent and trivalent Yb. These positions of $4d$ maxima of trivalent Yb observed in YbAs are approximately 183 eV and 197 eV [8].

In conclusion we found that the behaviour of Yb is different in PbTe and PbS. This conclusion is supported by the analysis of the transport properties of both crystals. PbTe:Yb is p-type semiconductor, while Yb doping causes n-type conductivity of PbS:Yb.

References

[1] N.B. Brandt, V.V. Moshchalkov, *Adv. Phys.* **33**, 374 (1984).

[2] C.M. Varma, *Rev. Mod. Phys.* **48**, 219 (1976).

[3] G.R. Stewart, *Rev. Mod. Phys.* **56**, 755 (1984).

[4] R.B. Shalvoy, G.B. Fisher, P.J. Stiles, *Phys. Rev. B* **15**, 2021 (1977).

[5] K.H.J. Buschow, M. Campagna, G.K. Wertheim, *Solid State Commun.* **24**, 253 (1977).

[6] R. Nyholm, Ib. Chorkendorf, J. Schmidt-May, *Surf. Sci.* **143**, 177 (1984).

[7] S. Suga, S. Ogawa, H. Namatame, M. Taniguchi, A. Kakizaki, T. Ishii, A. Fujimori, S.-J. Oh, H. Kato, T. Miyahara, A. Ochiai, T. Suzuki, T. Kasuya, *J. Phys. Soc. Jpn.* **58**, 4534 (1989).

[8] Jin-Seok Chung, En-Jin Cho, S.-J. Oh, *Phys. Rev B* **41**, 5524 (1990).