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## 4f CONTRIBUTION TO VALENCE BAND OF $Pb_{1-x}RE_xS$ (RE = Eu, Gd) STUDIED BY RESONANT PHOTOEMISSION

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Resonant photoemission experiments were carried out in order to reveal the contributions of partly filled Eu 4f<sup>7</sup> and Gd 4f<sup>7</sup> shells to the valence bands of  $Pb_{0.95}Eu_{0.05}S$  and  $Pb_{0.95}Gd_{0.05}S$  crystals. The coupling between these orbitals and the host electronic states is discussed.

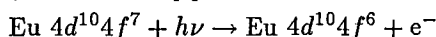
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Lead chalcogenides, narrow-gap semiconductors of IV-VI group, attract persistent, strong interest because of their optical and electric properties as well as of possibility to form many solid solutions with parameters suitable for many applications. They can be alloyed with tin chalcogenides in order to adjust the band gap of the mixed crystal to the chosen photon energy if an infrared detector is to be constructed [1]. Solid solutions of IV-VI compounds with rare earth (RE) chalcogenides became promising materials for infrared diodes and lasers, especially since non-equilibrium epitaxial methods (like molecular-beam epitaxy (MBE)) were applied to grow quantum-well systems [2, 3]. Apart from the possible applications, the efforts to prepare and investigate the rare earth containing, IV-VI based ternary crystals are stimulated by many interesting physical phenomena which can be studied in these materials. One of them is the rapid increase in the energy gap with the composition ratio of the crystal observed for  $Pb_{1-x}Eu_xSe$  [3] or  $Pb_{1-x}Eu_xTe$  [4, 5]. Investigations of luminescence should also be mentioned as an example, since they give important information about intra-ion transitions

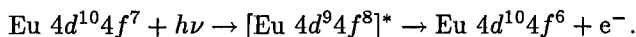
in the RE  $f$  shell and, simultaneously, about processes of efficient energy transfer to the luminescence centres.

Solid solutions of rare earth and lead chalcogenides belong to the family of diluted magnetic semiconductors (DMS) (semimagnetic semiconductors). It is well known that their basic properties are determined by interaction between magnetic ions system and band electrons of the host crystal. In particular, information about energy distribution of  $d$  (for transition metals) or  $f$  (for rare earth elements) states is crucial for the analysis of strength of the above-mentioned interaction.

Resonant photoemission technique turned out to be a very useful tool for research of transition metal or rare earth elements contributions to the electronic band structure of solids [6–8]. The resonant enhancement of photoemission intensity observed for systems containing open-shell atoms is a result of the coupling between two processes leading to the same final states. For crystals containing Eu atoms, we consider [9]:



and



This quantum interference selectively stimulates emission from the rare earth  $4f$  states for the photon energy tuned to the energy of intra-ion  $4d-4f$  transition. The direct manifestation of the resonance can be observed in photoemission spectra taken in constant-initial-state (CIS) or constant-final-state (CFS) regimes. Due to its Fano-type shape [10] (a maximum at energy near to the resonance following a minimum at the antiresonance energy) we can determine the photon energies at which the emission from the RE  $f$  derived states is enhanced or attenuated. The strong resonant enhancement of some features observed in the photoelectron energy distribution curves (EDC) enables us to reveal the partial contribution of the  $f$  states to the emission from the valence band. Subtracting the spectrum obtained at antiresonance photon energy from that recorded at resonance we obtain the difference curve which is a measure of  $4f$  states derived contribution to the valence band.

The samples were grown by the Bridgman method in the Institute of Physics, Polish Academy of Sciences. The crystal composition was determined by the electron microprobe measurements. The crystal structure and homogeneity of the samples were tested by X-ray diffraction experiments. The clean surfaces for photoemission measurements were prepared *in situ* by scraping the samples with a diamond file.

The resonance photoemission experiments were performed at the FLIPPER II beam line [11] in the HASYLAB synchrotron radiation laboratory in Hamburg, Germany. Photoelectron energy distribution curves as well as CIS spectra were measured for the photon energy ranges of 130–150 eV and 140–160 eV for  $\text{Pb}_{0.95}\text{Eu}_{0.05}\text{S}$  and  $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$ , respectively. The intensity of the spectra was normalised to the monochromator output and corrected for variations in photon flux.

Figure 1 shows the photoemission spectra taken for  $\text{Pb}_{0.95}\text{Eu}_{0.05}\text{S}$  and  $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$ . The curves were taken for the photon energies near to the

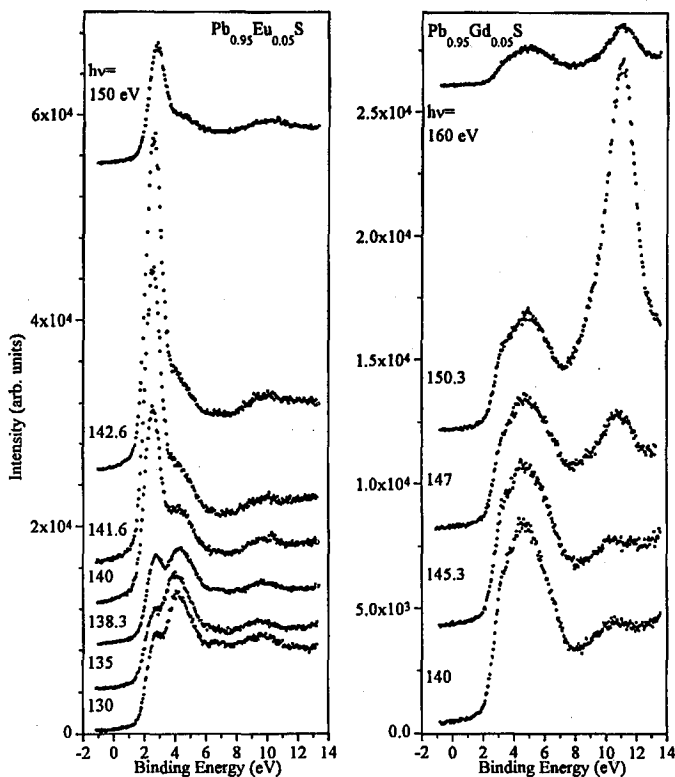


Fig. 1. The sets of energy distribution curves (EDC's) of  $Pb_{0.95}Eu_{0.05}S$  and  $Pb_{0.95}Gd_{0.05}S$ . The binding energy zero is set at the Fermi level.

energies of Eu 4d-4f and Gd 4d-4f transitions. It was determined by comparison of these EDC's and analysis of the CIS curves that the energies of 135, 142.6 eV for  $Pb_{0.95}Eu_{0.05}S$  and 145.3, 150.3 eV for  $Pb_{0.95}Gd_{0.05}S$  correspond to the antiresonance and resonance, respectively.

Figure 2 shows the difference spectra obtained from the EDC's recorded on and off resonance. For both materials the 4f derived contributions are well localised in energy but their positions with respect to the valence band are markedly different. In  $Pb_{0.95}Eu_{0.05}S$  it was revealed at the edge of the valence band. In  $Pb_{0.95}Gd_{0.05}S$  the corresponding maximum occurred deeply in the valence band, at the binding energy bigger by 8.5 eV. The strength of the resonant enhancement of the emission is similar in both materials.

Since rare earth atoms can occur in chemical compounds in many different charge states, mixed valency is the rule rather than the exception for these elements introduced as dopants into the solids. By comparison with the results reported for other Eu-containing crystals [12] we found that europium ions occur in  $Pb_{0.95}Eu_{0.05}S$  in the  $Eu^{2+}$  state. A weak structure observed in the difference spectrum (Fig. 2) at 10 eV can be ascribed to  $Eu^{3+}$  state. It was shown for MBE

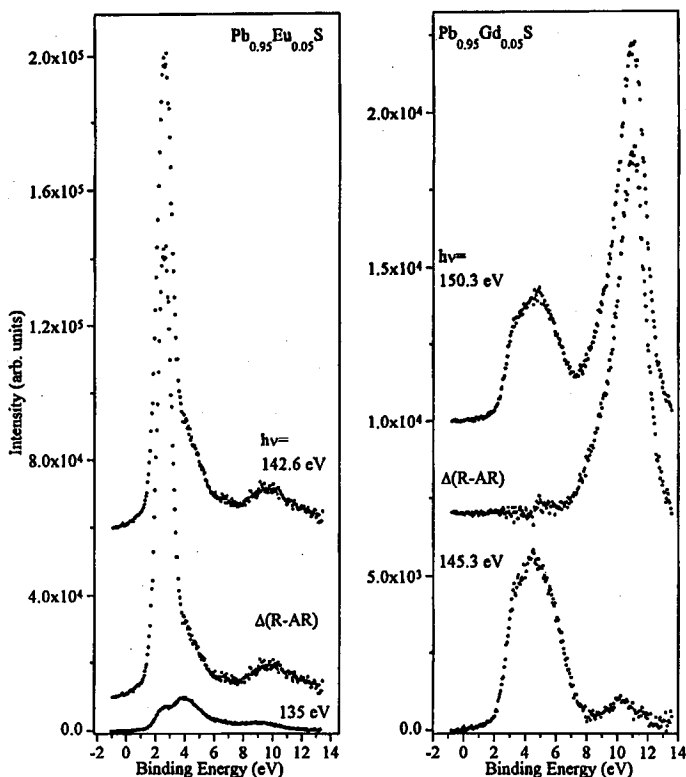


Fig. 2. The difference curves ( $\Delta(R - AR)$ ) obtained from the spectra taken on and off resonance for  $\text{Pb}_{0.95}\text{Eu}_{0.05}\text{S}$  and  $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$ . For  $\text{Pb}_{0.95}\text{Gd}_{0.05}\text{S}$ , the EDC's were additionally normalised to match the heights of the maxima corresponding to the valence band. In this way we corrected the difference spectrum for the photon energy dependence of the valence band photoemission cross-section.

grown  $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$  layers [12] that  $\text{Eu}^{3+}$  ions could occur at surface of the sample due to the cleaning procedure ( $\text{Ar}^+$  bombardment and annealing). Thus, the weakness of the structure observed at 10 eV proves that scraping the sample can be safely applied in order to prepare the surface for angle-integrated photoemission measurements of RE containing IV-VI crystals.

The width of the RE derived maxima in difference spectra is strongly dependent on the  $4f^{n-1}$  final-state multiplet splitting as well as on possible  $4f$ -ligand hybridization. It is difficult to distinguish these influences on the shape of the spectra presented, before any results of suitable theoretical calculations (e.g. in the configuration-interaction scheme) are available. However, we can compare the maxima in the difference spectra with the shapes of calculated photoemission spectra of the  $4f$  states in the rare-earth metals [13]. For Eu as well as for Gd, the calculated spectrum consists of many components (due to final-state multiplet splitting) merging into one maximum because of broadening. The slope of the

maximum is less steep on the lower binding energy side due to decreasing intensity of the components. The maximum obtained for  $Pb_{0.95}Gd_{0.05}S$  (Fig. 2) corresponds well to the theoretical prediction. On the contrary, for  $Pb_{0.95}Eu_{0.05}S$  one can discern some additional contribution to the main maximum, deeper in energy than the main peak. If we assume that this additional contribution is a satellite caused by 4f-ligand hybridization (as it was reported for RE halides [14]), then we can expect that the hybridization in  $Pb_{1-x}Eu_xS$  is stronger than in  $Pb_{1-x}Eu_xTe$ . For the telluride no satellite was found near the  $Eu^{2+}$  peak [12]. Such a trend would be consistent with the conclusions derived from the results of resonant photoemission experiments performed for transition-metal based diluted magnetic semiconductors [15].

Even if the detailed analysis of the results is still in progress they give the independent information about the energy positions of Eu 4f and Gd 4f states with respect to the valence band. Thus, they can be confronted with the experimental data concerning other properties of  $Pb_{0.95}Eu_{0.05}S$  and  $Pb_{0.95}Gd_{0.05}S$ . In particular, the strong Eu 4f derived contribution occurring at the edge of the valence band should manifest itself clearly in magneto-transport and magneto-optical phenomena.

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