Fe 3d CONTRIBUTION TO $Hg_{1-x}Fe_xSe$ VALENCE BAND BY MEANS OF ANGLE-RESOLVED PHOTOEMISSION

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The Angle-Resolved Photoemission Electron Spectroscopy (AR PES) was applied to investigate the electronic structure of HgSe and $Hg_{1-x}Fe_xSe$ crystals for (110) surface. The measured set of Angle-Resolved Energy Distribution Curves (AR EDCs) permits to determine some of the elements of the electronic band structure $E(k)$ (energy-momentum dependence for ΓKX and ΓX directions in the Brillouin zone) for measured crystals. The Fe 3d contribution gives the states laying over the edge of the valence band of HgSe crystal (0.25 eV), and into the valence band.

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The $Hg_{1-x}Fe_xSe$ ternary crystal belongs to the family of Semimagnetic Semiconductors (SMSC) or Diluted Magnetic Materials (DMM) [1, 2]. These materials are obtained by substitution of cation in II–VI compounds by transition metal cation like Mn, Fe and recently Co. This substitution of the cation leads to the appearance of the crystalline, chemical and magnetic disorder, and it is causing that the electronic structure of the valence band is governed by the hybridization of s-p-d electrons in the valence band [2, 3]. In comparison to the substitutional Mn^{2+} which possesses only spin momenta ($S = 2.5$ and $L = 0$) the Fe^{2+} is a more general case, since it possesses both spin and orbital momenta ($S = 2$ and $L = 2$). The simple quantitative results of calculation of energy levels of Fe^{2+} ion in hexagonal environment was recently presented by Twardowski [4]. The Mn 3d electrons contribute to the valence band but they are not giving any contribution over the valence band edge of II–VI compounds [5, 6] while Fe 3d electrons contribute as well in the valence band as over the edge of II–VI compounds valence band [7–11].

The Angle-Resolved Photoemission Electron Spectroscopy (AR PES) was applied to investigate the electronic structure of HgSe and $Hg_{1-x}Fe_xSe$ crystals for (110) surface. The experiment was performed with vacuum ultraviolet radiation of variable photon energy in the range between 15 and 110 eV obtained from synchrotron ring SUPER-ACO in LURE, Orsay, France.

The clean surface of the crystals (zinc-blende structure) was obtained by the cleavage in UHV conditions ($p = 3 \times 10^{-10}$ Torr) along the cleavage plane (110) and the AR PES spectra were taken *in situ*.

The comparison of the Angle-Resolved Energy Distribution curves corresponding to the valence band of HgSe and $Hg_{1-x}Fe_xSe$ crystals are presented in Fig. 1. It shows that the valence band edge of $Hg_{1-x}Fe_xSe$ crystal is located in the
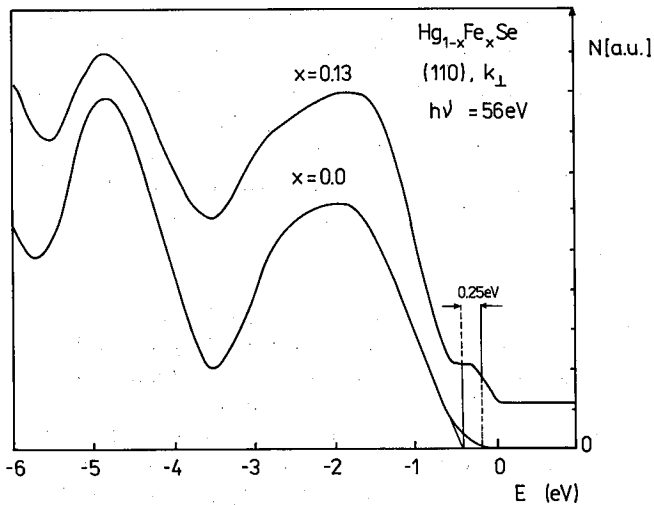

Fig. 1. The comparison of the edges of the valence bands of the HgSe and $Hg_{1-x}Fe_xSe$ crystals.

distance of 0.25 eV over the edge of HgSe crystal. The whole valence band width of $Hg_{1-x}Fe_xSe$ is bigger on 0.25 eV than the valence band width of HgSe crystal. Taking the analogy to the results obtained for $Cd_{1-x}Pb_xF_2$ ternary crystal valence band change with the composition x [12] one can treat the $Hg_{1-x}Fe_xSe$ valence band density of states distribution as a sum of the density of states of the valence bands of FeSe and CdSe crystals taken with the same crystalline structure.

For curve corresponding to the $Hg_{1-x}Fe_xSe$ valence band presented in Fig. 1 it is well visible additional density of states appearing in the binding energy 3.0 eV and in the region over this energy up to the valence band. This additional density of states corresponds to the contribution of the Fe $3d$ electrons. This kind of contribution appears as well in near the same region of the valence band of $Cd_{1-x}Fe_xSe$ [7–11].

The contributions of the Fe $3d$ states to the valence band in the edge region of $Hg_{1-x}Fe_xSe$ (edge of HgSe valence band is shifted on about 0.25 eV due to Fe

contribution, Fig. 1) and of $Cd_{1-x}Fe_xSe$ (edge of CdSe valence band is shifted on about 0.6 eV due to Fe contribution [7–11]) well corresponds to the position of the contribution of the Fe impurity in HgSe (0.23 eV over the valence band edge [10]) and in CdSe (0.64 eV over the valence band edge [13]).
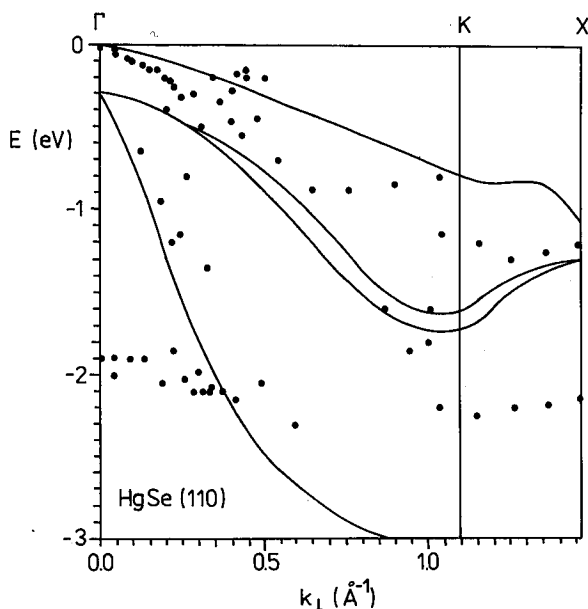

Fig. 2. The top part of the valence band structure of HgSe crystal as determined in presented work (points) in comparison to the calculated band structure by Bloom and Bergstresser [14].

In Fig. 2 the top part of the valence band structure of HgSe crystal is presented as it was determined from angle-resolved photoemission experiment (points in Fig. 2). The continuoues lines correspond to the top part of the valence band structure obtained from calculation by Bloom and Bergstresser [14].

The contribution of the Fe $3d^6$ electrons to the region over the top of the valence band of HgSe was found in distance 0.25 ± 0.05 eV and it well corresponds to the position of Fe impurity level in 0.23 eV over the valence band edge.

Good agreement of the measured and calculated band structure of the valence band was found along ΓK direction. Remarkable discrepancy between measured and calculated [14, 15] band structure was observed on the KX direction.

Acknowledgement

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