The resonant photoemission spectroscopy was applied to investigate the valence band electronic structure of semimagnetic semiconductor Pb$_{0.92}$Mn$_{0.08}$Se crystal and to determine the contribution of Mn 3d electrons to the valence band. The set of energy distribution curves and constant initial states spectra were taken for $h\nu$ energies in the region (40–60 eV) close to the Mn 3p–3d transition. The electrons Mn 3d hybridize and contribute to the valence band electrons of the crystal and main density of states contribution appears in the energy 3.5 ± 0.2 eV below the valence band edge.

PACS numbers: 71.20.Fi, 79.60.–i

1. Introduction

The crystal Pb$_{0.92}$Mn$_{0.08}$Se belongs to the family of semimagnetic semiconductors or diluted magnetic materials (DMM) based on IV–VI semiconductor compounds with Mn as a transition metal e.g. Pb$_{1-x}$Mn$_x$Te or Sn$_{1-x}$Mn$_x$Se [1–6]. These new materials are obtained by substitution of cation in IV–VI or II–VI compounds by transition metal cation like Mn, Fe and recently Co and Ni. The

---

*This work is supported partly by the Institute of Physics, Polish Academy of Sciences, and the State Committee for Scientific Research (Republic of Poland) (projects no. 20482 9101 and no. 20486 9101) and by BMFT under project 05 5GUABI.
substitution of the cation by transition metal leads to the appearance of the crystalline, chemical and magnetic disorder in the crystals. The electronic structure of these crystals is governed by three important factors: (i) hybridization of $s$–$p$ band electrons with $d$ electrons, (ii) 3$d$ electrons local correlation and (iii) local structure (structural, chemical and magnetic disorder). This creates an interesting problem for theoretical description of the electronic band structure of these crystals [7–9].

Recently a large effort has been devoted to understanding of the contribution of the electrons of transition metal ions to the valence band using the resonant photoemission experiment for Cd$_{1-x}$Mn$_x$Te [10], Fe$_x$O$_y$ [11] and Cd$_{1-x}$Fe$_x$Se [12, 13]. In the resonant photoemission experiment the photon energy is tuned relatively to the energy of optical absorption edge corresponding to the 3$p$–3$d$ transition. For the photon energy in the region of resonance energy the Mn ions are excited selectively and locally. The relaxation of excited Mn ions leads to the emission of the additional electrons according to the formula

$$3p^53d^5 + \hbar \nu = [3p^53d^5]^* = 3p^63d^4 + e^- \quad (*) \quad \text{— excited state}$$

and it enhances nonresonant photoemission expressed by the formula

$$3p^63d^5 + \hbar \nu = 3p^63d^4 + e^-.$$ 

Both of these effects are observed in the photoemission spectra in the region of resonant $\hbar \nu$ energy. The contribution of resonant photoemission can be described by the Fano effect [11] introduced for atomic systems and illustrated by a Fano line shape. For transition metal compounds the profiles of the line can be more complex.

2. Experimental conditions and results

The samples were grown by the modified Bridgman method in the Institute of Physics, Polish Academy of Sciences. The clean surface of the sample was obtained by argon ion bombardment and annealing in UHV conditions ($p = 3 \times 10^{-10}$ torr) and the spectra were taken in situ.

The resonant photoemission experiment was performed on the line FLIPPER II, with vacuum ultraviolet radiation of variable photon energy in the range between 10 and 130 eV obtained from synchrotron ring HASYLAB, Hamburg, Germany. The radiation impinges on the sample surface at an angle 45° with respect to the normal. The angle-integrated spectra were taken with an energy resolution 200 meV.

The set of the measured EDC’s is presented in Fig. 1. The two upper curves were measured for resonant and antiresonant radiation of $\hbar \nu$ energies, 50 eV and 48 eV relatively. The zero of energy scale corresponds to the vacuum level and it is located at a distance of 6 eV above the edge of the valence band (ionization energy). The valence band width is about 10 eV and the band is built of the following hybridized electrons: Pb 6$p$, Mn 4$s$, Mn 3$d$, Se 4$p$, Se 4$s$, and Pb 6$s$. The Pb 6$s$ electrons are located in the lower part of the valence band which possesses more-localized character than the upper part. The lower part of Fig. 1 presents the difference between EDC’s of resonant and antiresonant energies and is indicated as $\text{EDC(50)} – \text{EDC(48)}$. 
In Fig. 2 the constant initial states curves are presented. The measured position of the peak corresponds to the resonant energy for Mn 3p–3d transition.
in PbMnSe crystal. The precise position of the resonance was found as equal to $h\nu = 50.5$ eV. The antiresonant energy was found as a nearest minimum of the curves and its position was found as equal to 48.5 eV.

3. Results and discussion

The results present the contribution of the Mn 3d electrons to the valence band of the Pb$_{0.92}$Mn$_{0.08}$Se crystal (Fig. 1, lowest curve). The contribution consists of the strong peak with the maximum of energy equal to $9.5 \pm 0.2$ eV below the vacuum level or 3.5 eV below the valence band edge. A small contribution of the Mn 3d electrons can be mentioned above the peak, up to the valence band edge. In analogy to the contribution of Mn 3d electrons to the valence band of Cd$_{1-x}$Mn$_x$Te crystal, the contribution of Mn 3d measured for Pb$_{0.92}$Mn$_{0.08}$Te and Pb$_{0.2}$Sn$_{0.72}$Mn$_{0.08}$Te [6] corresponds to the localized electrons $d_e$ contribution while the $d_t$ electrons hybridize with other valence electrons. The relative height of the Mn 3d electrons contribution ($d_t/d_e$) is remarkably smaller for Pb$_{0.92}$Mn$_{0.08}$Se crystal than for Cd$_{1-x}$Mn$_x$Se [14] crystals. The exchange integrals of these two crystals have the similar relations.

The peak of the Fano type resonance presented in Fig. 2 is located at the 50.5 eV. It corresponds to the maximum of the Mn 3p–3d absorption equal to 50.0 eV [15].

References