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# VALENCE BAND ELECTRONIC STRUCTURE OF HgMSe (M = Mn, Fe, Co)

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The synchrotron radiation in the energy range between 40 and 80 eV was applied to investigate the electronic structure of $Hg_{0.7}Mn_{0.3}Se$, $Hg_{0.88}Fe_{0.12}Se$ and $Hg_{0.93}Co_{0.07}Se$ crystals by means of the resonant photoemission spectroscopy. The set of energy distribution curves was measured in the region near the M (M = Mn $3d^5$, Fe $3d^6$, Co $3d^7$) $3p$–$3d$ transitions. In order to determine thoroughly the Fano type resonance energy the constant initial states curves were measured.

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## 1. Introduction

HgSe crystallizes in the zinc blende structure and belongs to the inverted band structure semiconductors with a negative band gap. The conduction band minimum of HgSe has $\Gamma_8$ symmetry and it is located above the maximum of the valence band $\Gamma_6$ [1, 2]. For low concentration of transition metal (M $3d$) atoms, the band $\Gamma_6$ is lying below $\Gamma_8$ and the band gap is negative like in the HgSe crystal. With an increase in the number of M $3d$ atoms the $\Gamma_6$ band moves up approaching $\Gamma_8$ band and then overlapping the M $3d$ states.

The $Hg_{1-x}M_xSe$ $(0 < x < 1)$ compounds belong to the group of semimagnetic semiconductors (SMSC) or diluted magnetic materials (DMM) [3, 4]. The electronic structure of these ternary alloys is strongly influenced by [5]:

- crystalline, chemical and structural (local structure) disorder,

- local correlation of $3d$ electrons,
- hybridization of $s$–$p$ valence band electrons with M $3d$ electron states.

The interaction of M $3d$ electrons with the valence band electronic structure leads to the anomalous magneto-transport and magneto-optical properties. The investigations of these properties are stimulated by an interest in the origin of these properties and possible applications of these semimagnetic semiconductors to infrared detectors and other magneto-transport and magneto-optical devices [6].

The resonant photoemission spectroscopy was recently used to study the contribution of the transition metal ions $3d$ electrons to the valence band of transition metal compounds like e.g. $\mathrm{Fe}_x\mathrm{O}_y$ [7], $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ [8] and $\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{S}$ [9]. In the resonant photoemission experiment the photon energy $h\nu$ is tuned to the energy in the region of the M $3p$–$3d$ transition core resonances. For these photon energies the M ions are excited selectively and locally. The relaxation of the core excited M ions leads to the emission of outer $3d$ electrons.

The enhancement of the M $3d$ electron emission is caused by the coupling of the discrete excitation

$$3p^6 3d^n + h\nu = [3p^5 3d^{n+1}]^* \qquad (^* \text{ – excited state})$$

with

$$3p^6 3d^n + h\nu = 3p^6 3d^{n-1} + \mathrm{e}^-$$

continuum channel via the autoionization of the $[3p^5 3d^{n+1}]^*$ excited states.

For an isolated resonance interacting with several continua the cross-section is given by a Fano type profile

$$\sigma = \sigma_a + \sigma_b (q + \varepsilon)^2/(1 + \varepsilon^2) \ldots, \tag{1}$$

where $\varepsilon = (h\nu - E_\mathrm{r})/\Gamma$ ($E_\mathrm{r}$ — resonance energy, $\Gamma$ — FWHM). The shape of the resonance is determined by the asymmetry parameter $q$ which is positive for the M $3p$–$3d$ resonances causing the cross-section to go through a minimum below the resonance maximum. $\sigma_a$ represents the noninteracting and $\sigma_b$ — the interacting part of the continuum excitation.

In the $h\nu$ energy region close to the resonant energy both interacting and noninteracting ionizations contribute to the photoemitted electron current. For transition metal compounds the profiles of the line can be more complex. The transition metal ions are selectively excited according to following one of the formulae:

$$\mathrm{Mn}\ 3p^6 3d^5 + h\nu = [\mathrm{Mn}\ 3p^5 3d^6]^* = \mathrm{Mn}\ 3p^6 3d^4 + \mathrm{e}^-,$$

$$\mathrm{Fe}\ 3p^6 3d^6 + h\nu = [\mathrm{Fe}\ 3p^5 3d^7]^* = \mathrm{Fe}\ 3p^6 3d^5 + \mathrm{e}^-,$$

$$\mathrm{Co}\ 3p^6 3d^7 + h\nu = [\mathrm{Co}\ 3p^5 3d^8]^* = \mathrm{Co}\ 3p^6 3d^6 + \mathrm{e}^-.$$

The processes discussed above result in an enhancement of the photoemission only for photon energies close to the M $3p$–$3d$ resonances [10–12].

## 2. Experimental conditions

The crystals used in this study were grown by a modified Bridgman method at the Institute of Physics, Polish Academy of Sciences. The crystals obtained were uniform in composition and the X-ray diffraction measurements of the samples did not show any segregation of the additional transition metal ions. The surface of the crystals was cleaned by the argon ion bombardment (600 eV) and annealing (150°C) in the preparation chamber. The spectra were taken in the analyzing chamber in ultra high vacuum conditions ($p = 10^{-10}$ Tr).

The resonant photoemission experiment was performed in the energy range between 40 eV and 80 eV at the beam line Flipper II [13] with application of the synchrotron radiation obtained from the storage ring DORIS in HASYLAB (Hamburg, Germany). The Flipper II line monochromator was found to be a very good system to avoid second order peaks of the diffraction grating. The energy resolution ranged from 150 meV to 250 meV. The angle of light incidence was 45° measured with respect to the surface normal.

## 3. Results and discussion

Figures 1a, b and c present the set of the energy distribution curves (EDCs) of the $Hg_{0.7}Mn_{0.3}Se$, $Hg_{0.88}Fe_{0.12}Se$ and $Hg_{0.93}Co_{0.07}Se$, respectively. The zero of the energy scale corresponds to the edge of the valence band and is located about 5.5 eV below the vacuum level.

In $Hg_{0.88}Fe_{0.12}Se$ and $Hg_{0.93}Co_{0.07}Se$ crystals (Fig. 1b and c) the valence band remains like the HgSe crystal valence band. It is 6 eV wide and consists of two distinct peaks. In ternary crystals the valence band is built of the following electron states: Hg $6s^2$, M $3d^n4s^2$, and Se $4p^4$. The top part of the valence band is mainly built by hybridized Se $4p$ and Fe $3d$ wave functions. In the lower part of the valence band the main contribution comes from Hg $6s$ and M $4s$ electrons. The lower part of the valence band photoemission spectrum is about 2.2 eV wide and possesses the maximum at 5 eV below the valence band edge.

The valence band of the $Hg_{0.7}Mn_{0.3}Se$ crystal (Fig. 1a) reveals somewhat different structure. Because of remarkably high concentration of Mn ($x = 0.3$) the contribution of the Mn $3d$ states leads to the appearance of the well visible peak of the valence band corresponding to the Mn $3d^5$ electrons contribution. For the $h\nu$ energies close to the $3p$–$3d$ resonance the valence band EDC displays a strong peak 6 eV wide and two not very distinct shoulders.

Another kind of the photoemission experiment [14] is the measurement of the constant initial states (CIS) curves, where the electrons detected are emitted from the same initial states. The CIS curves are taken by scanning simultaneously the photon energy and the energy of the analyzed electrons. In that way the emission current from the same electronic states with binding energy $E_i$ (referred to the vacuum level) can be observed for different $h\nu$ energies. When the $h\nu$ energy approaches the resonant energy of the particular ion (M $3p$–$3d$) the photoemission current is expected to increase.

In Figs. 2a, b and c the sets of constant initial states spectra for $Hg_{0.7}Mn_{0.3}Se$, $Hg_{0.88}Fe_{0.12}Se$ and $Hg_{0.93}Co_{0.07}Se$ are presented. The position of the maximum of

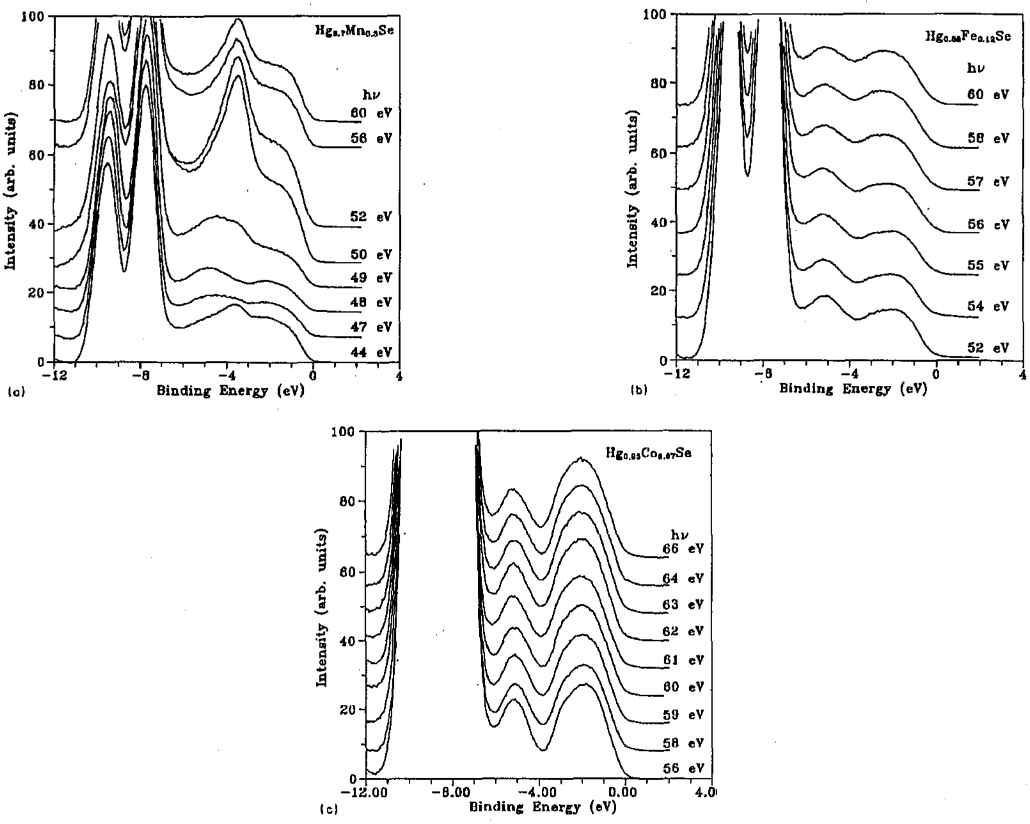

Fig. 1. The set of energy distribution curves obtained for: (a) the $Hg_{0.7}Mn_{0.3}Se$ crystal in the energy range 44–60 eV, close to the resonance energy for Mn (50 eV); (b) the $Hg_{0.88}Fe_{0.12}Se$ crystal in the energy range 52–60 eV, close to the resonance energy for Fe (56 eV); (c) the $Hg_{0.93}Co_{0.07}Se$ crystal in the energy range 56–66 eV, close to the resonance energy for Co (62 eV).

the curves corresponds to the energy of the Fano resonance. The value of the Fano resonance energy was found at 50 eV for Mn (Fig. 2a), at 56 eV for Fe (Fig. 2b) and at 61 eV for Co (Fig. 2c). The minima located below the Fano-type resonance peaks occur at the places corresponding to the antiresonance energies, that means energies in which the nonresonant part of the cross-section ($\sigma_a$, see formula (1)) remains and the contribution of M 3*d* states to the valence band should have a minimum. The absorption spectra corresponding to the M 3*p*–3*d* transitions have a sharp maximum for Mn 3*p*–3*d* transitions [10, 11] while for Fe and Co the absorption curves possess splitted peaks.

In order to determine where the contribution of the 3*d* transition metal ions states to the valence band density of states (DOS) reaches the highest value, the curves corresponding to the antiresonance energies were subtracted from each of

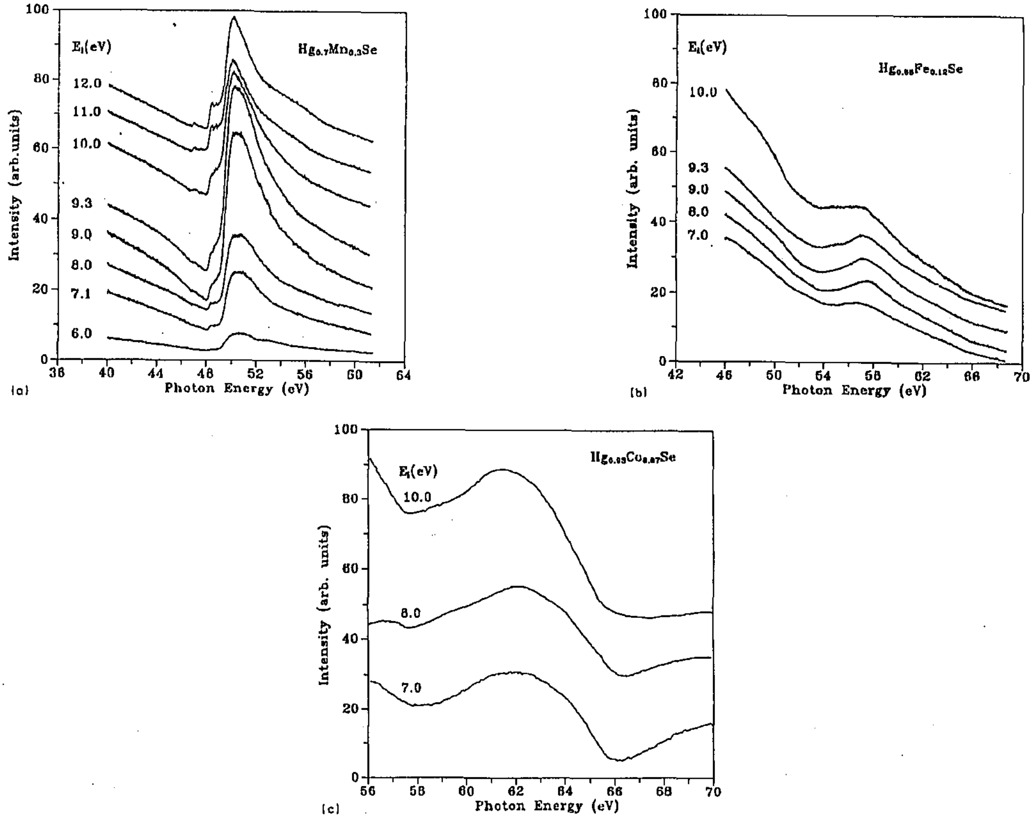

Fig. 2. The set of constant initial states curves measured for crystals $Hg_{0.7}Mn_{0.3}Se$ (a), $Hg_{0.88}Fe_{0.12}Se$ (b), $Hg_{0.93}Co_{0.07}Se$ (c) in the resonant energy region for different initial $E_i$ states.

the other curves, e.g. a curve corresponding to 48 eV from Fig. 1a was subtracted from the curve corresponding to: 60 eV, 56 eV, 52 eV, 49 eV, 47 eV and 44 eV from the same Fig. 1a. In Fig. 1b a curve corresponding to 54 eV was subtracted from the curves obtained for 60 eV, 58 eV, 57 eV etc. The results of these subtractions are presented in Figs. 3a, b and c. Figure 3a shows the set of curves which have a maximum at $-3.5$ eV $\pm 0.2$ eV below the valence band edge or 9 eV $\pm 0.2$ eV below the vacuum level (first ionization potential of HgSe equals 5.5 eV). The position of the maximum corresponds to the main contribution of Mn $3d^5$ states to the valence band DOS of the $Hg_{0.7}Mn_{0.3}Se$ crystal.

The curves from Fig. 3b and c do not possess as sharp maxima as it was obtained for a ternary crystal with Mn. The Fe $3d$ and Co $3d$ electrons contribution seems to be more spread over the whole valence band than it is for Mn $3d$ electrons.

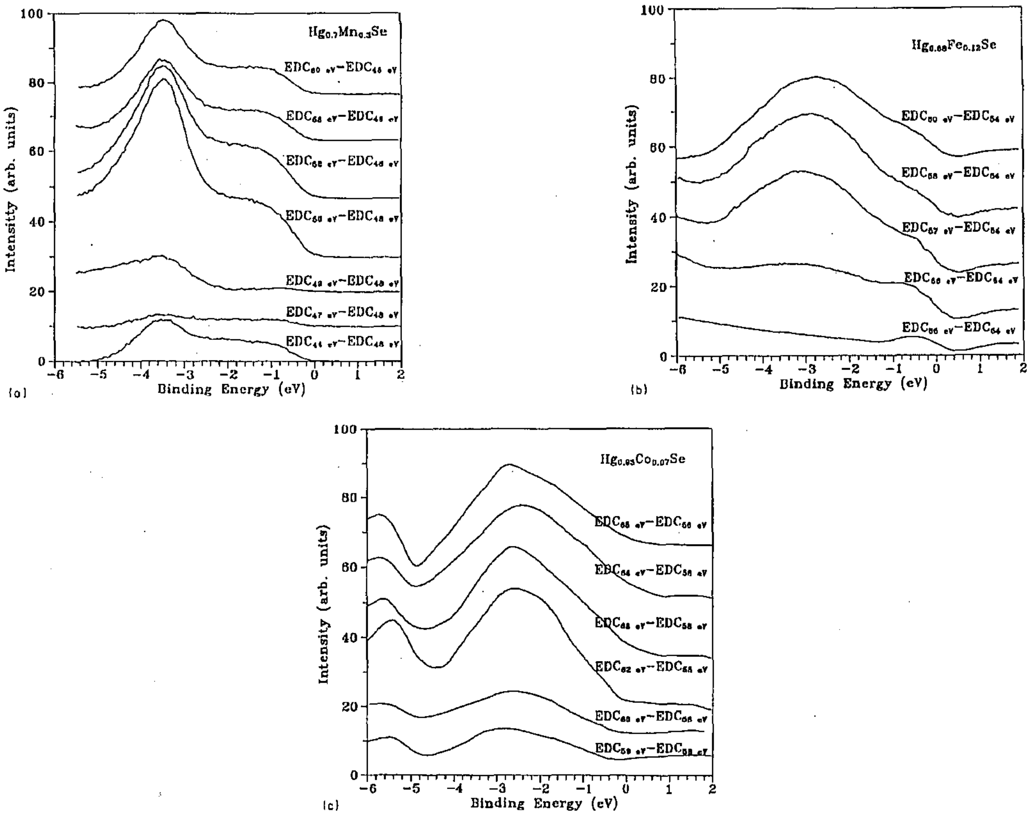

Fig. 3. The set of the difference of the EDCs of the $Hg_{0.7}Mn_{0.3}Se$ (a), $Hg_{0.88}Fe_{0.12}Se$ (b), $Hg_{0.93}Co_{0.07}Se$ (c) crystals and EDC of the antiresonance curve (obtained for $h\nu =$ 48, 54, 58 eV, respectively).

## 4. Summary

The valence band electronic structure of $Hg_{0.7}Mn_{0.3}Se$, $Hg_{0.88}Fe_{0.12}Se$ and $Hg_{0.93}Co_{0.07}Se$ crystals was investigated by means of the resonant photoemission spectroscopy. The set of energy distribution curves (EDCs) was measured in the region near the M (M = Mn, Fe, Co) $3p$–$3d$ resonant transitions. The valence band was found to be built of Hg $6s^2$, M $3d^n4s^2$ and Se $4p^4$ electrons. The differences among the EDC curves (resonant or others minus antiresonant) present the contribution of M $3d$ states to the valence band and indicate their hybridization with the other Hg and Se states. The EDCs well correlate to the DOS distribution in the valence band of $Cd_{1-x}M_xSe$ (M = Mn, Fe and Co) calculated by Masek [15]. From the constant initial state curves the Fano type resonant energies were determined as follows: for Mn = 50 eV, for Fe = 56 eV and for Co = 61 eV. The shape of the CIS spectra of M $3d$ atoms was found to be very similar to the absorption spectra of M $3d$–$3p$ transitions [10, 11].

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