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## RESONANT PHOTOEMISSION STUDY OF $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ VALENCE BAND\*

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The phenomenon of Fano type resonant photoemission was used to distinguish the Fe electrons derived partial contribution to the valence band of a semimagnetic semiconductor  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ . The states appearing at the middle of the valence band correspond to the Fe 3d electrons while the step of the density of states obtained at the valence band edge region corresponds to the hybridized *s-p-d* electrons.

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The  $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$  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 the ternary crystal electronic structure of the valence band is affected by the 3d electrons correlations (Anderson Hamiltonian) and their hybridization in *s-p-d* build valence band [2, 3].

Recently a large amount of effort has been devoted towards understanding of the valence band structure of materials with the transition metal ions component, using the resonant photoemission experiment [4-7]. The photon energy is tuned to the cation  $3p-3d$  optical absorption edge. The state excited in the transition  $3p^6 3d^n - 3p^5 3d^{n+1}$  couples with the photoionization continuum  $3p^6 3d^{n-1} + e^-$

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(see Fig. 1 where both of the transitions corresponding to the resonance photon energy are presented; right hand side describes the ionization of one  $d$ -electron to the free-electron states, like in a nonresonance photoemission process, while the left hand side corresponds to the excitation to the discrete state of the ion). This coupling of the states leads to the enhancement of the Fe-derived contribution to the photoemission spectra, according to the Fano effect. In a case of atomic system, the excitation spectra are described by a Fano line shape [8, 9], but in transition metal compounds, the profiles can be more complex.

By taking the difference between valence band spectra measured from transition metal compounds at photon energies just in  $3p - 3d$  resonance and out of the resonance, the contribution from the nonresonating valence states should be subtracted and the resulting difference spectrum yields a measure of the transition metal derived contribution into the valence states. This states may either be purely transition metal  $3d$  states or  $3d$  derived states that are formed due to hybridization with neighboring ligand electrons.

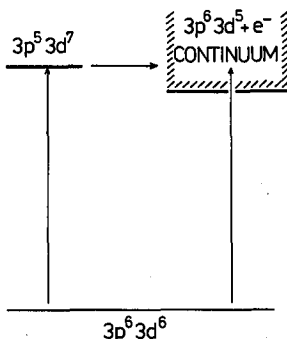


Fig. 1. The diagram of the transition energies to illustrate the resonant photoemission. In the right hand side of the figure the ionization of one  $d$ -electron to the free-electron states (like in a nonresonance photoemission process) is presented and in the left hand side of the figure the excitation to the discrete state of the ion is described. The state excited in the  $3p^6 3d^n - 3p^5 3d^{n+1}$  transition couples with the photoionization continuum  $3p^6 3d^{n-1} + e^-$ . This leads to the Fano effect, which manifests itself in a resonant photoemission experiment.

The photoemission experiments were performed on TGM-4 beamline at the storage ring BESSY in Berlin. The vacuum chamber was equipped with toroidal analyzer [10, 11] and preparation chamber. The set of Energy Distribution Curves (EDC) was measured in the  $h\nu$  energy range between 30 and 100 eV with a special attention taken to the resonant energy region for  $h\nu$  energy in the region between 50 and 60 eV. The crystals of  $Cd_{1-x}Fe_xSe$  were grown by modified Bridgman method in the Institute of Physics, Polish Academy of Sciences. The samples of dimension  $3 \times 3 \times 8 \text{ mm}^3$  were cutted with plane  $3 \times 3 \text{ mm}^2$  parallel to the surface (1010). The sample was mounted on sample holder and cleaved in situ in the

preparation chamber at a pressure of  $5 \times 10^{-10}$  Torr. The samples with composition  $x = 0$  and  $x = 0.1$  were investigated for comparison.

In Fig. 2 the measured EDC's for  $Cd_{1-x}Fe_xSe$  crystals obtained in the reso-

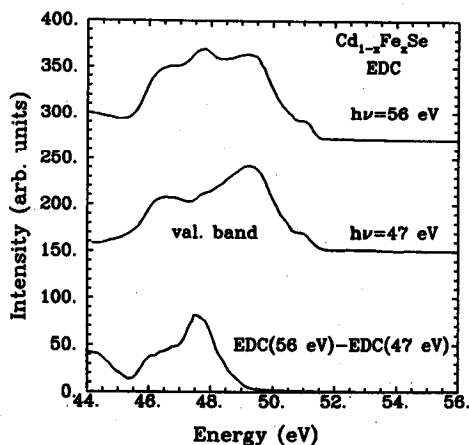


Fig. 2. The Energy Distribution Curve's (two upper curves of the figure) obtained for  $Cd_{0.9}Fe_{0.1}Se$  crystals using the different  $h\nu$  energies — resonant  $h\nu = 56$  eV and not resonant  $h\nu = 47$  eV; the lowest curve of the figure presents the difference between resonant and not resonant curves.

nant energy ( $h\nu = 56$  eV) and out of the resonance ( $h\nu = 47$  eV) are compared. The difference of the resonant curve and the curve taken out of the resonance is presented as the lowest curve in Fig. 2. The contribution of the Fe 3d electrons to the valence band appears as the remarkably high peak in energy 3.7 eV below the valence band edge of ternary crystal.

The height of the peak increases remarkably due to resonance effect in  $h\nu = 56$  eV. The small contribution of Fe 3d electrons appearing at the upper part of the valence band above the main contribution peak and even above the valence band edge of CdSe crystal, can be treated as corresponding to the contribution of the hybridized  $s - p - d$  valence band electrons. On the basis of the one-electron band picture [7, 12] the main peak (3.7 eV) possesses the origin of  $e_g$  electrons which do not hybridize with the Se 4p electrons and being localized electrons highly contribute to the measured density of states in the valence band region. The contribution of Fe 3d states in the whole valence band region is obtained due to  $t_{2g}$  electrons which hybridize with Se 4p electrons and spread their contribution over the whole valence band. At the upper part of the valence band of  $Cd_{1-x}Fe_xSe$  the appearance of the  $e_g$  electron is expected with the spin opposite to spin of the rest of the Fe d electrons. In the presented results the contribution of Fe 3d electrons in the upper part of the valence band of  $Cd_{1-x}Fe_xSe$  appears almost as well out of the resonance as in the resonance. This is rather not expected for a case of Fe 3d  $e_g$  electrons contribution in this region but indicates rather the  $t_{2g}$  character

of electrons.

We conclude, that the contribution of Fe  $3d^6$  electrons in the region above the valence band edge of CdSe was not found as the expected big contribution from  $d e_g$  electrons but it was found as resulting from  $s - p - d$  hybridization. This whole Fe  $3d^6$  contribution is similar to the contribution of Mn  $3d^5$  electrons to the valence band of  $Cd_{1-x}Mn_xTe$  (calculated by Masek and Velicky [3]).

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