

Proc. of the XXVII Intern. School on Physics of Semiconducting Compounds, Jaszowiec 1998

CONTRIBUTION OF Mn 3*d* ELECTRONS TO THE VALENCE BAND OF Sn_{0.9}Mn_{0.1}Te

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The synchrotron radiation in the energy range between 15 and 70 eV was used to investigate the electronic structure of the crystalline Sn_{0.9}Mn_{0.1}Te by means of the resonant photoemission spectroscopy. Fano-type resonance has been observed in the obtained constant initial energy curves with the resonant energy 50.6 eV and antiresonant energy 49.0 eV. The energy distribution curves taken at photon energies close to the Mn 3*p*–3*d* transitions allow us to conclude that Mn atoms contribute to the valence band mainly at energies of 4.0 eV and 7.8 eV below the valence band edge.

PACS numbers: 79.60.-i, 71.20.Nr

1. Introduction

Solid solutions of transition metal chalcogenides and semiconducting crystals are well known as semimagnetic (or diluted magnetic) semiconductors. A ternary compound Sn_{1-x}Mn_xTe, belonging to this group of materials, is a narrow gap semiconductor crystallising in the rock salt structure [1]. It differs markedly from the best known tetrahedrally bonded semimagnetic semiconductors based on II–VI compounds as Mn atoms substituting for cations are here surrounded by six anions forming a regular octahedron, contrary to the tetrahedral configuration in II–VI compounds. The symmetry of the surrounding of the Mn ion determines the crystal field splitting of its *d* shell and influences the interaction between this shell and the states originating from the anion orbitals. It should be pointed out that the exchange interaction of Mn 3*d* electrons leads to the anomalous magneto-transport and magneto-optical properties of semimagnetic semiconductors of the types II–VI and IV–V. The aim of the present paper was to investigate a contribution of Mn 3*d* electrons to the valence band of Sn_{0.9}Mn_{0.1}Te by means of photoelectron spectroscopy. This technique has been already used to identify the transition-metals-derived contribution to the band structure of many semimagnetic semiconductors [2–4].

2. Experimental conditions and results

The experiment was performed in HASYLAB at DESY, Hamburg, on the beamline FLIPPER II with synchrotron radiation of variable photon energy between 15 and 70 eV. The experimental set-up, consisting of interconnected UHV chambers, enabled *in situ* preparation and characterization of samples. At the beam-entrance side it was equipped with a plane grating monochromator operating over the photon-energy range of 15–200 eV. A cylindrical mirror electron energy analyser was used in the analysis chamber to measure photoelectron spectra. The total energy resolution achieved in photoemission experiments was about 0.2 eV. The material under investigation was crystalline $\text{Sn}_{0.9}\text{Mn}_{0.1}\text{Te}$ grown by the modified Bridgman method in the Institute of Physics, Polish Academy of Sciences. The clean surface of the sample was obtained prior to the photoemission experiment by filing *in situ* with a diamond file in UHV conditions ($p = 4 \times 10^{-8}$ Pa).

The Fano-like resonance was used to investigate the contribution of Mn 3d states to the valence band structure of $\text{Sn}_{0.9}\text{Mn}_{0.1}\text{Te}$. The resonance results from the interference between the direct photoemission processes of Mn 3d electrons and the discrete Mn 3p–3d transitions followed by the super-Coster–Kronig decay. Photon energy in the resonant photoemission experiment was tuned to the energy of optical absorption edge corresponding to the 3p–3d transitions in Mn^{2+} ions, around the energy of 50 eV. Photons with an energy value close to the resonance energy cause selective and local excitation of Mn ions. The relaxation of excited Mn ions leads to the additional emission of Mn 3d electrons. The contribution of resonant photoemission can be described by the Fano effect [5] and characterised by a Fano line shape. The resonance is observed in photon absorption and in photoemission spectra taken in constant-initial-state (CIS) or constant-final-state (CFS) modes. Constant-initial-state dependences have been measured for initial-states energies between 8.3 eV and 15 eV below the vacuum level using an exciting photon with energies 45–60 eV which are close to the energy corresponding to the 3p–3d transitions. The shape of the obtained experimental CIS curves, presented in Fig. 1, confirms the existence of a strong Fano-like resonance. The maximum of the resonance was found at a photon energy 50.6 eV, the minimum — at a photon energy 49 eV.

Energy distribution curves (EDS) taken at photon energies within the energy range of the resonance and antiresonance are presented in Fig. 2. The intensity of the signal was normalised according to the monochromator output and corrected for variations in photon flux. At lower exciting-photon energies, near to the antiresonance, photoelectron intensity plotted versus binding energy reveals two maxima. At exciting-photon energies approaching the resonance energy, the third maximum appears at the energy about 4 eV below the valence band edge. The photoemission connected with the internal 3p–3d transitions in Mn^{2+} ions is responsible for this phenomenon.

In order to distinguish the contribution of Mn 3d electrons to the valence band of $\text{Sn}_{0.9}\text{Mn}_{0.1}\text{Te}$ crystal, the spectrum recorded at antiresonance (for $h\nu = 49$ eV) has been subtracted from the spectrum taken at resonance (for $h\nu = 50.6$ eV), as shown in Fig. 3. The resulting differential spectrum reveals three

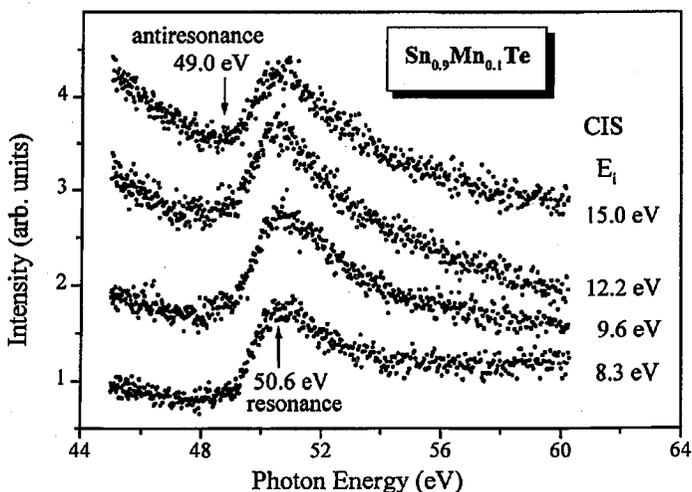


Fig. 1. Set of CIS spectra measured for photon energies near the Mn $3p-3d$ transition. Initial state energies E_i are determined with respect to the vacuum level. Individual spectra are shifted in vertical direction in order to improve the clarity of the figure. Resonant and antiresonant energies are indicated.

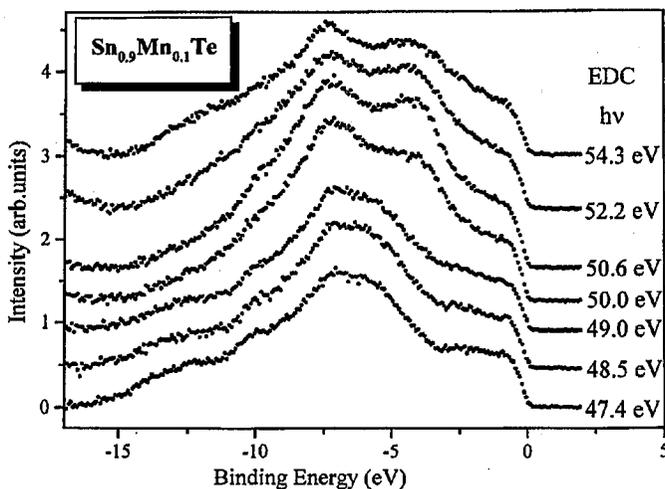


Fig. 2. Set of energy distribution curves (EDC) of the $\text{Sn}_{0.9}\text{Mn}_{0.1}\text{Te}$ valence band at various exciting photon energies $h\nu$ within the energy range 47.4–54.3 eV. Individual curves are shifted in vertical direction in order to improve the clarity of the figure. Energy scale is determined with respect to the valence band edge.

structures: one at the binding energy up to about 2.5 eV below the valence band edge, second one at 4.0 eV with the half-width 1.7 eV and third one at the binding energy 7.8 eV with a greater half-width.

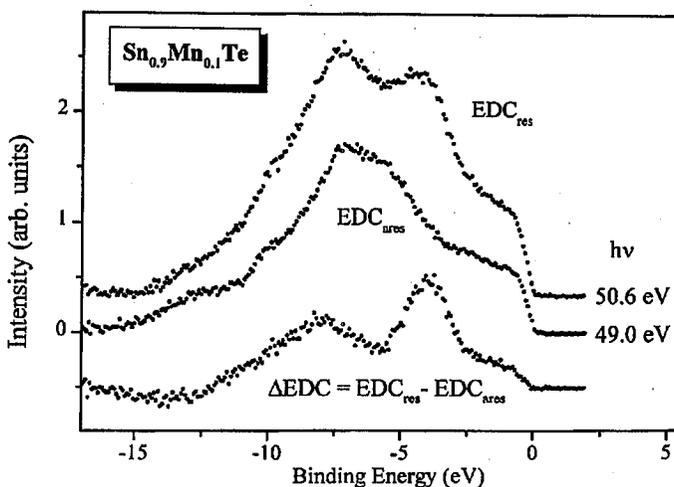


Fig. 3. Energy distribution curves (EDC) of the $\text{Sn}_{0.9}\text{Mn}_{0.1}\text{Te}$ valence band for resonant (EDC_{res}) and antiresonant (EDC_{ares}) photon energies and the difference between these two distribution curves (ΔEDC). Photon energies are respectively 50.6 eV (EDC_{res}) and 49.0 eV (EDC_{ares}). Remarks as in Fig. 2.

The shape of the differential spectrum is similar to that observed in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ [2] and in $\text{Zn}_{1-x}\text{Mn}_x\text{Y}$ as well as in MnY ($Y = \text{S, Se, Te}$) [6, 7]. Similarly to those papers we can assume that the most pronounced maximum at the energy 4.0 eV originates from Mn 3d electrons which do not hybridise with the valence band states. In the case of $\text{Sn}_{1-x}\text{Mn}_x\text{Te}$, because of octahedral symmetry, these are Mn 3d (t) states that have different symmetry than $s-p$ valence band states. The Mn 3d (e) electrons that have the same symmetry as the valence band states can hybridise with the valence band electrons. Therefore, their energy is changed by the hybridization, so the contribution of Mn 3d (e) electrons is responsible for the structure in the binding energy range up to 2.5 eV.

The deepest lying structure (7.8 eV below the valence band edge), similarly to another compounds, is not assigned to the Mn 3d density of states. This satellite structure results from transitions to the final state d^5 whereas the remaining structures of the valence band result from the transitions to the configuration $d^6\bar{L}$ (\bar{L} denotes a ligand hole).

Acknowledgment

The paper was partially supported by the Committee for Scientific Research (Poland) grant No. 2 P03B 089 10.

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