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RESONANT PHOTOEMISSION SPECTRA OF $Zn_{1-x}Co_xS$ VALENCE BAND

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We report the results of a resonant photoemission study of $Zn_{1-x}Co_xS$. A Co $3d$ derived contribution to the valence band spectra was revealed as a 5 eV wide structure with two maxima: at the edge of the valence band and about 4 eV below the edge. The results were compared with the total DOS distribution resulting from tight binding–coherent potential approximation calculations.

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1. Introduction

Semiconducting mixed crystals containing transition metal (TM) ions built into the cation sublattice are usually referred to as semimagnetic or dilute magnetic semiconductors (SMSC or DMS). These terms emphasize the most important characteristics of the compounds: interconnection of their magnetic and semiconducting properties. This experimentally observed phenomenon is a direct manifestation of strong interaction between TM magnetic ions and delocalized valence band electrons. Basic properties of TM ions are determined by the number of electrons occupying the $3d$ shell. On the other hand, the basic features of the band structure are determined by selection of the host semiconductor, usually a II–VI

compound. Different combinations of these two components give us various materials: from zero gap semimetals to wide gap semiconductors, with subsystem of magnetic ions consisting of Mn, Fe, Co or Ni.

The wide-gap Zn-based members of the family appeared as routinely grown crystals rather lately if compared with Hg- and Cd-based prototypes of SMSCs. Nowadays, however, they attract growing attention [1]. They offer us possibility to study nature and strength of interaction between magnetic ions and semiconducting system with a relatively wide gap. From the point of view of possible applications they could be used as a suitable material for light emitters in the high energy part of the visible spectrum.

As it was mentioned above, the most important point giving the insight into properties of semimagnetic semiconductors is a character of interaction between electrons localized in TM d shells and those occupying valence band. Of course, it strongly depends on the relative energy position of TM d levels and bands of the host semiconductor. On the other hand, mutual interaction modifies both the TM d shell and the valence band structure leading to formation of the new, unified electronic structure of the semimagnetic semiconductor. Since photoemission spectroscopy was well known as a useful tool for band structure investigations it was quite early applied for revealing TM $3d$ contribution to the valence band of SMSC [2]. The band mapping techniques show clearly some band structure modifications induced by presence of TM $3d$ states, but for relatively low photon energies usually used in these methods (20–40 eV) additional density of $3d$ states manifests itself relatively weakly [3]. Fortunately, some complementary data can be acquired by means of resonant photoemission technique, successfully applied in studies of electronic structure of open-shell metal compounds [4]. In spite of its angle integrated character this method gives very sensitive tool to determine contribution of TM $3d$ electrons to the valence band. Comparing the spectra taken at resonance and at off-resonance photon energies we can reveal and identify the contribution connected with TM d shell. We can determine its shape and energy position with respect to the bands of the crystal.

In the paper we present the results of the resonant photoemission study of $Zn_{1-x}Co_xS$ crystal. The revealed Co $3d$ related contribution to the valence band density of states distribution corresponds well to those observed for other SMSC. The qualitative accordance with the results of tight binding–coherent potential approximation (TB-CPA) calculations was also proved.

2. Experimental conditions

The reported resonant photoemission experiments were performed in a photoemission spectrometer attached to the FLIPPER II beamline in Hasylab at DESY (Hamburg, Germany). The system was equipped with an analysing and a preparation chambers. The FLIPPER II monochromator allowed us to use synchrotron radiation of the photon energy in the range from 20 to 200 eV [5]. Photoelectron energy was measured with a cylindrical mirror analyser (CMA). The energy resolution was kept at 0.2 eV.

The sample was cut off from the bulk $Zn_{0.9}Co_{0.1}S$ crystal grown by chemical transport method using iodine as the transporting agent. Synthetized and then

powdered CoS was used as a starting material with powdered ZnS. The crystal growth process was performed in silica tube (diameter 20 mm, length 100 mm) with a conical tip. The horizontal furnace with the temperature conditions was taken like for growth of ZnS crystal. The sharp zone was maintained at 920°C. The transport process was performed for two weeks and typical crystals of size $8 \times 8 \times 5$ mm^3 were grown. The growth process was performed in the Institute of Physics, Polish Academy of Sciences, Warsaw, Poland.

The sample, a plain parallel plate of the dimensions of about $5 \times 5 \times 1$ mm^3, was cut off from the bulk $Zn_{0.9}Co_{0.1}S$ crystal. Its surface was mechanically and chemically polished, then cleaned in a preparation chamber by Ar^+ ion bombardment and annealing in UHV. Since the preparation chamber was directly connected with the analysing one, the prepared sample was kept under UHV conditions until the measurements were completed.

Since $Zn_{1-x}Co_xS$ is a wide gap material of low conductance, an electron flood gun was used to compensate charging effects occurring during measurements.

3. Experimental results and discussion

The energy range of synchrotron radiation available in the FLIPPER II system fully enabled us to measure photoemission spectra for $Zn_{1-x}Co_xS$ under resonance as well as off-resonance conditions with respect to the intra-atomic Co $3p$–$3d$ transition (61 eV) [6]. This helped us to distinguish emission from Co $3d$ states from that outcoming from the valence band.

Figure 1 shows the set of energy distribution curves (EDCs) taken for the photon energies $h\nu$ from 56 to 65 eV. Since some charging effects and thus shifts of the spectra along the energy scale could not be excluded, the spectra were aligned to keep the energy position of Zn $3d$ peak constant. They were also normalized in accordance with the height of that maximum. One can easily follow the increase in emission in the valence band region when the photon energy is tuned to the Co $3p$–$3d$ resonance energy. However, even though the resonant increase in the emission is not uniform in the electron binding energy range investigated, one cannot clearly reveal any details of the Co $3d$ states distribution in the valence band region in the original EDCs. Thus, in order to visualize the shape of the Co $3d$ contribution, we subtracted the spectrum taken at $h\nu = 59$ eV (anti-resonance) from that obtained for the resonance energy (61 eV). The procedure resulted in the curve shown in Fig. 2.

In order to confirm the result of the subtraction procedure, constant initial states (CIS) curves have been drawn for the initial state energies scanning the electron binding energy region of the revealed photon energy dependent contribution (Fig. 3). All the CIS spectra have the shape characteristic of the Fano resonance curve [7]. The resonance energy obtained from the spectra corresponds well to the energy of Co $3p$–$3d$ transition. Dominant resonance or anti-resonance character of the curve illustrates the strength of hybridization coupling the initial state with the band continuum [8].

The shape of the curve of Fig. 2 suggests that the density of Co $3d$ states is spread in energy over the whole valence band region. The only two particularities which can be revealed are: a clearly resolved maximum at the edge of the valence

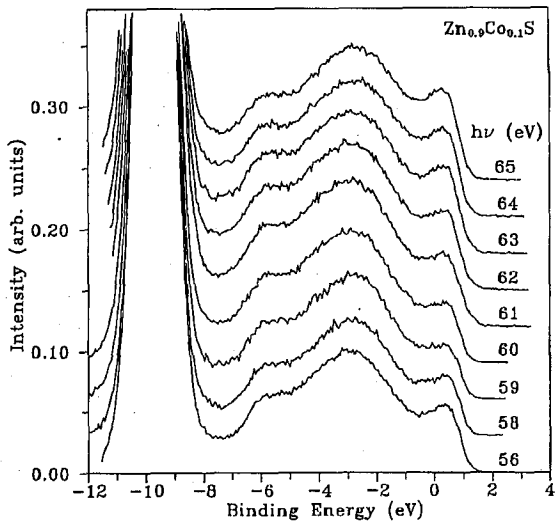

Fig. 1. The set of the energy distribution curves (EDCs) of the valence band of ZnCoS crystal taken for the photon energies $h\nu$ region from 56 to 65 eV including the resonant energy 61 eV.

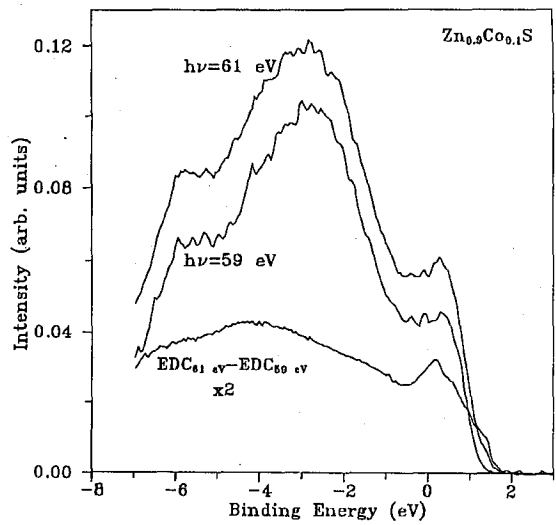

Fig. 2. The EDCs measured for $h\nu = 61$ and 59 eV. The lowest curve presents the results of subtraction of anti-resonant curve $h\nu = 59$ eV from resonant curve $h\nu = 61$ eV.

band and a flat maximum at about 4 eV below the edge. While the first closely reminds the maxima observed at the edges of the valence bands for other Fe- and Co-containing SMSCs [3], the latter is in contrast with the pronounced maxima derived from TM $3d$ states usually revealed in the middle of the valence band for Hg- and Cd-based SMSCs [3, 9]. The feature observed at the edge of the

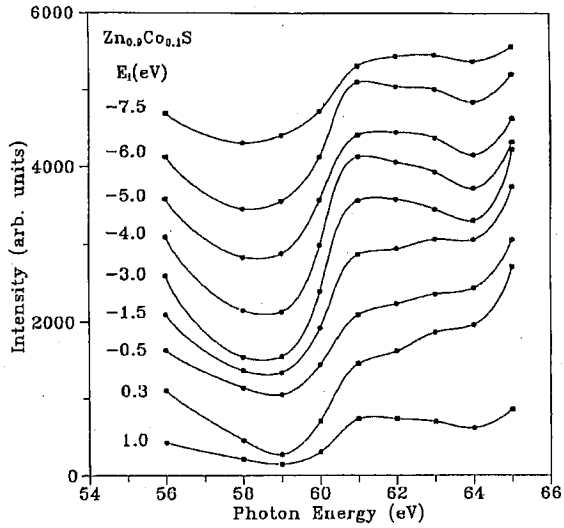

Fig. 3. The set of constant initial states (CIS) curves drawn for the initial state energies E_i (eV) measured relatively to the valence band edge.

valence band is connected with presence of the sixth (in Fe) or sixth and seventh (in Co) electrons in TM 3*d* shell. It does not occur for Mn-containing materials. This maximum manifests itself as emission from occupied *d* orbitals of *e*-type symmetry (in the tetrahedral crystal field) and of minority spin state [10]. The other pronounced maximum usually observed in resonant photoemission spectra of SMSCs was ascribed to the emission from the *e*-symmetry *d* orbitals of the opposite spin which are occupied when five electrons occur in the shell. Since *d* orbitals of *e*-symmetry do not hybridize with host crystal valence band, the electrons emitted from them occur in relatively narrow peaks in the spectra. On the contrary, the *t*-type orbitals which hybridize with *p*-states of anions are responsible for the broad band of TM 3*d* derived states detected in the resonant photoemission experiment in the whole valence band energy region [9, 10].

Similar arguments can be used to explain qualitatively the shape of the Co 3*d* related contribution revealed for $Zn_{1-x}Co_xS$. The distinct maximum at the edge of the valence band clearly confirms presence of additional electronic states, localized in energy and weakly interacting with orbitals of the host crystal constituents. By analogy, they can be ascribed to *e*-symmetry Co 3*d* states. The other part of the curve of Fig. 2 should correspond to the widely spread (due to hybridization) contribution of *t*-symmetry states as well as non-hybridizing *e*-symmetry states concentrated at the energy of about 4 eV below the valence band maximum.

A more detailed interpretation needs comparison with results of $Zn_{1-x}Co_xS$ band structure calculations. The valence band density of states distribution was calculated by means of tight binding–coherent potential approximation approach [11, 12] in order to interpret the measured XPS–EDCs [13]. Since neither final states effects nor energy dependence of the matrix elements were taken into ac-

count, we can use them only for a qualitative comparison with our results. However, the sharp maximum at the edge of the valence band and some broad Co $3d$ derived contribution to the valence band density of states are well reproduced by the theory. In comparison to the Mn based SMSC where d_e and d_t electrons of Mn have the same spin, in the case of Co the d_e electrons can have both polarizations — spin up or spin down. The exchange splitting of d_e electrons leads to the appearance of the electrons above the top of the ZnS valence band.

4. Summary

The resonant photoemission experiments were performed for $Zn_{1-x}Co_xSe$ in the photon energy range adjusted to Co $3p$–$3d$ transition. The distinct maximum at the edge of the valence band as well as the broad structure spread over the whole valence band were revealed as Co $3d$ derived contribution to the density of states distribution. The first was ascribed to e-symmetry Co $3d$ states of minority spin direction and the latter to t-symmetry states hybridizing with orbitals of the host crystal constituents and non-hybridizing e-symmetry states of majority spin direction, concentrated at energy of about 4 eV below the valence band maximum.

The obtained results are consistent with experimental data acquired for other SMSC as well as with available results of TB–CPA calculation results.

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