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## X-RAY PHOTOELECTRON SPECTROSCOPY AND X-RAY DIFFRACTION STUDIES OF $Zn_{1-x}Co_xS$ DILUTED MAGNETIC SEMICONDUCTOR CRYSTALS\*

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X-ray photoelectron spectroscopy and powder X-ray diffraction studies of diluted magnetic semiconducting alloys  $Zn_{1-x}Co_xS$ , in the composition range  $0 \leq x \leq 0.18$ , were performed. The analysis of XPS spectra has shown that admixture of Co into ZnS lattice does not affect the shape and position of Zn 2*p* core level, whereas certain modification of the S 2*p* peak shape was observed. The detected binding energy of Co indicated similarity between Co-S and Co-O bond structure. Significant contributions of Co 3*d*<sup>7</sup> electrons to the valence band density of states were revealed.

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For more than two decades numerous research projects have been concentrated on the II-VI diluted magnetic semiconductors (DMS) based on the transition metal (TM) ions, mainly Mn and Fe (see [1, 2]). During last years a widespread scientific interest of this topic has also included the II-VI DMS with Co [3]. Substitution of cation by magnetic ion, which occurs in a DMS, results in hybridization of the 3*d* states of TM with the *sp* band states of a host semiconductor. This inevitably leads to modification of the crystal band structure and of its valence band density of states (DOS) distribution, which can be effectively investigated by means of ultraviolet photoemission spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). The latter method seems sometimes more advantageous since, besides the valence band, it also enables us to observe the atomic core levels thus providing additional information concerning the nature of chemical bonds. Up to now, photoelectron spectroscopy has been rarely applied for investigating the electronic properties of the Co-based II-VI DMS [4].

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The goal of our paper was to perform systematic XPS studies, supported by X-ray diffraction (XRD) measurements, of the DMS alloys  $\text{Zn}_{1-x}\text{Co}_x\text{S}$  in the composition range  $0 \leq x \leq 0.18$ .

The  $\text{Zn}_{1-x}\text{Co}_x\text{S}$  samples were grown at the Institute of Physics, Polish Academy of Sciences, by chemical vapor transport using iodine as a transport agent. X-ray microprobe analysis enabled us to determine precisely a composition of the crystals. This was followed by the XRD studies performed by a conventional X-ray powder diffractometer. They confirmed that all the samples had zinc blende structure. The diffractograms showed no traces of other phase and/or the Co precipitations. For selected crystals the lattice constant was determined by the Bond method using the high resolution single crystal diffractometer equipped with four-crystal monochromator [5]. We found that the lattice constant of our crystals shows linear  $x$  dependence, known from the literature.

The XPS measurements were performed in a Perkin-Elmer 5000 ESCA spectrometer equipped with a hemispherical analyzer. The spectra were collected within two different excitation modes, namely by using a standard Mg  $K_\alpha$  (1253.6 eV) X-ray source (mode 1) or an Al  $K_\alpha$  (1486.6 eV) X-ray source with a Rowland circle geometry monochromator (mode 2). The crystals were cleaved under UHV.

Mg  $K_\alpha$  excitation provided high accuracy of determining the binding energies for particular core levels. Within this mode no surface charging effects were observed — accidental appearance of charging resulted in a systematic shift (by additive constant) of the whole energy scale, which was corrected by reference to the adventitious carbon line [6]. On the other hand, the use of the second mode, due to its higher energy resolution (0.5 eV) and better peak-to-background ratio, enabled us to perform more detailed analysis of a shape of the core lines of constituent atoms, as well as of the valence band. Within this mode, slight non-linear surface charging, due to complex discharging processes [7] was usually observed. Therefore, low energy electron bombardment of the crystal surface provided by flood gun (neutralizer) was performed during the measurement to reduce this effect.

XPS measurements have shown that the introduction of Co to a ZnS lattice, in the composition range  $x \leq 0.18$ , does not affect the binding energy and the shape of Zn  $2p$  core level, within experimental accuracy. This suggests that the Zn-S bond length in the crystals studied remains unchanged, similarly as e.g. in the case of Cd-Te bond in the  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  alloys [8]. The above result seems rather obvious since in our compounds every Zn atom is surrounded by S atoms as the nearest neighbours.

On the other hand, certain changes of the S  $2p$  anion line shape due to an admixture of Co-S bonds have been observed, as shown in Fig. 1 by the representative set of the S  $2p$ -core level XPS spectra recorded for ZnS,  $x = 0.05$  and  $x = 0.18$ . This refers specially to the crystal with the highest Co content (here,  $x = 0.18$ ) whereas for lower composition ( $x \leq 0.05$ ) a binding energy and a shape of the S  $2p$  peaks seem almost unchanged. Under assumption of a random substitution of Zn by Co atoms in a cation sublattice this effect can be ascribed to the difference of binding energies of the S  $2p$  electrons bounded to Co and Zn. Since

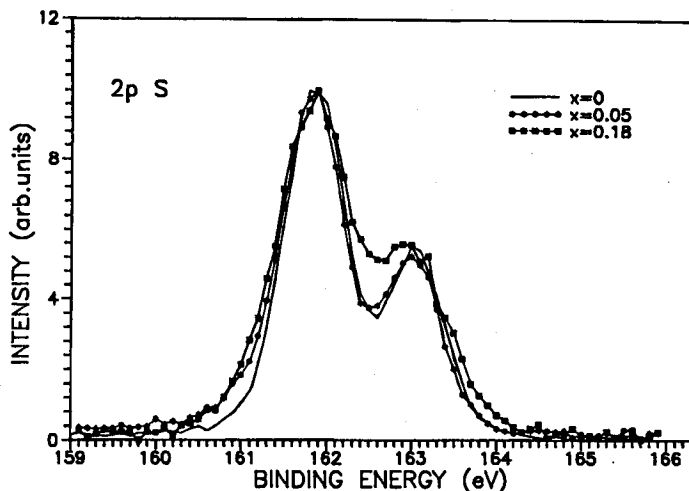


Fig. 1. XPS 2p doublet of sulphur in ZnS and  $\text{Zn}_{1-x}\text{Co}_x\text{S}$  with  $x = 0.05$  and  $x = 0.18$  as a function of photoelectron binding energy.

both Co and Zn atoms are divalent and differ only by the structure of the 3d shell, one could not expect significant differences between these binding energies, even for a Co content comparable to that of constituent components. A more detailed analysis of the S 2p spectra in these crystals, intentionally performed to estimate a contribution of Co-S bond, will be included in the next paper [9]. The preliminary estimate indicates that the above binding energy difference does not exceed 0.8 eV.

The Co 2p line was detected in the XPS spectrum for all the samples studied, including the lowest Co content,  $x = 0.01$ . The binding energies of Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub> core levels were found constant within the composition range ( $x \leq 0.18$ ) and equaled 780 eV and 794 eV, respectively. This suggests a similarity between Co-S and Co-O bonds [10]. A systematic increase of background intensity in the vicinity of Co 2p<sub>1/2</sub> peak with Co content was also observed.

Figure 2 gives the XPS spectra of valence band (VB) recorded for  $\text{Zn}_{1-x}\text{Co}_x\text{S}$  DMS alloys with a composition ranging from pure ZnS up to  $x = 0.18$ . For better comparison, the spectra were normalized to the first maximum height. They were found to depend significantly on  $x$  and gave evidence of a contribution of Co 3d electrons to the VB DOS of ZnS.

It can be seen that the increase of Co content induced certain spectral features in a vicinity of the top of VB. These led to broadening of the valence band by almost 1 eV and to appearance of the additional structure (DOS) in the energy gap (see  $x = 0.18$  — Fig. 2). It is worth to emphasize that this is the first experimental evidence of the Co-related DOS found in the energy gap of ZnS due to formation of pseudobinary DMS compound, whereas the impurity-limited case of ZnS:Co is widely known in the literature (e.g. [11]).

Also a pronounced modification of the VB spectrum, induced by Co admix-

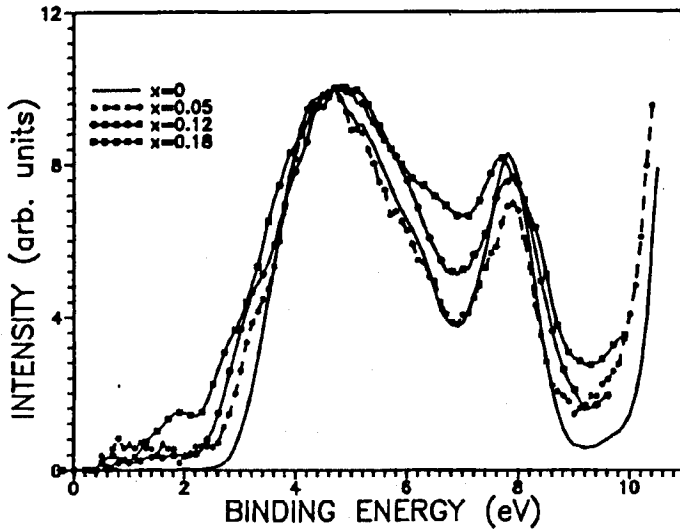


Fig. 2. XPS valence band spectra of ZnS and  $Zn_{1-x}Co_xS$  with  $x = 0.05$ ,  $x = 0.12$ , and  $x = 0.18$ .

ture, in the energy range from 5.5 eV to 7.5 eV (Fig. 2), in the minimum of the VB DOS characteristic of II-VI compounds, was observed. This strictly coincides with the earlier UPS results for  $Cd_{1-x}Co_xSe$  [4]. Similar effect has been reported for different II-VI compounds alloyed with Mn or Fe (e.g. [4, 12, 13]) thus indicating a more general tendency.

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