

Co 3d-level position in ZnS:Co semiconductors

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Experimental studies of x-ray photoelectron and Co $L\alpha$ x-ray emission spectra of the ZnS:Co semiconductor were carried out. It was established that Co ions are present in isovalent Co^{2+} configuration and that the Co 3d impurity states are localized above the top of the valence band by 1.0 ± 0.2 eV.

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I. INTRODUCTION

Interest in the study of the electronic structure of wide-gap II–VI semimagnetic semiconductors (ZnS, ZnSe, CdTe, etc.) increased substantially in recent years, motivated both by the construction of ZnSe-based semiconductor lasers operating in the blue-green region of the spectrum and due to ferromagnetism with high Curie temperature. Doping with 3d elements changes the optical properties of these compounds and gives rise to magnetic effects depending on the energetic position of the 3d ion states and their interaction with the host bands (see, for example, Ref. 1). Therefore, it is very important to know the positions of the 3d impurity levels.

The positions of the 3d impurity levels relative to the valence band or the conduction band in the II–VI semiconductors have been established by optical absorption measurements.² For Mn-doped II–VI semiconductors (ZnS:Mn, ZnSe:Mn, CdTe:Mn), the energy positions of Mn 3d impurity states have been deduced both by means of photoelectron spectroscopy^{3–5} and using a combination of x-ray emission Mn $L\alpha$ spectra and the Mn 2p binding energies determined from x-ray photoelectron spectroscopy experiments.^{6–8} It was found that Mn 3d impurity states are localized at 2–3 eV under the valence-band edge.^{4,5,8} According to optical data, Co 3d impurity levels should be localized in the forbidden band.²

In this work we have carried out a direct observation of the Co 3d impurity levels in ZnS:Co using x-ray emission and x-ray photoelectron spectroscopies. The combination of these two methods allowed us to determine the position of the Co 3d states relative to the valence-band edges.

II. EXPERIMENT

Single-crystal samples of ZnS and $\text{Zn}_{1-x}\text{Co}_x\text{S}$ ($x \approx 0.05$) were grown by a chemical transport method. The x-ray pho-

toelectron spectra were measured on a PHI 5600 ci Multi-technique System x-ray photoelectron spectrometer using monochromatic Al $K\alpha$ radiation. The samples were cleaved in vacuum before the measurements to expose a clean surface for investigations. An x-ray emission experiment was performed at the bulk branch line of beamline I511 at MAX II (MAX-lab National Laboratory, Sweden). The Co $L\alpha$ x-ray emission spectrum was obtained using a high-resolution Rowland-mount grazing-incidence grating spectrometer with a two-dimensional detector⁹ at an exciting photon energy of 815 eV. The measurements were done at room temperature.

III. RESULTS AND DISCUSSION

The x-ray photoelectron Co 2p spectrum of the doped semiconductors ZnS:Co is shown in Fig. 1. For comparison, the Co 2p spectra of the oxides CoO and LiCoO_2 and the Co 2p spectrum of the monosulfide CoS, reproduced from the paper of Riesterer *et al.*¹⁰ are shown. The background formed by secondary electrons has been subtracted from the spectra.

The Co 2p x-ray photoelectron spectra show satellites labeled as *B* and *D*. The complex structure of the Co 2p spectrum is mainly attributed to the charge-transfer processes. The well-screened $2p^5 3d^{n+1}L$ states correspond to main maxima (*A* and *C*), and the poorly screened $2p^5 3d^n$ states correspond to the satellites (*B* and *D*). Here *L* denotes a hole on a ligand and *n* is equal to 7 for divalent cobalt ions (CoO and CoS) and to 6 for Co^{3+} ions (LiCoO_2). One can see that the energy distances between the satellites and the main lines in the Co 2p spectra of CoO, CoS, and ZnS:Co are approximately equal, whereas in LiCoO_2 (where the ground-state configuration is $3d^6$) these distances are much larger. Thus, one can conclude that the cobalt ions in ZnS:Co have the ground-state configuration $3d^7$. It correlates with

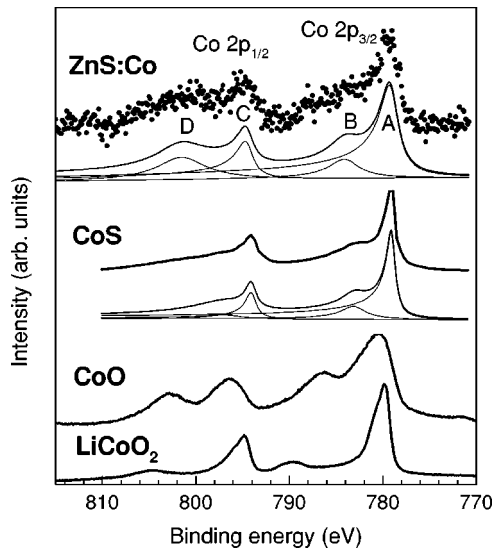


FIG. 1. X-ray photoelectron Co $2p$ spectra of the compounds of ZnS:Co, CoS, CoO, and LiCoO₂. The spectrum of cobalt monosulfide is taken from the paper of Riesterer *et al.* (Ref. 10). The spectra are corrected for the background created by secondary electrons. The spectra for ZnS:Co and CoS are separated into components.

the optical and EPR data which have been done previously on these samples.¹¹ According to a qualitative analysis of the Co $2p$ spectra, the cobalt-sulfur bond in ZnS:Co is more covalent than in CoS.¹²

To determinate the energy positions of the Co $3d$ impurity states of ZnS:Co relative to the valence-band edge, we have used a combination of Co $L\alpha$ x-ray emission and Co $2p$ x-ray photoelectron spectra. The Co $L\alpha$ spectra arise due to the electronic transition $3d4s \rightarrow 2p_{3/2}$, so they reveal $3d$ partial states in the valence band. The Co $2p_{3/2}$ binding energy (peak A in Fig. 1) is equal to 778.90 ± 0.05 eV. With this result we can convert the Co $L\alpha$ spectrum of ZnS:Co into the binding-energy scale, as illustrated in Fig. 2.

The Co $L\alpha$ spectrum of the ZnS:Co semiconductor is compared with the x-ray photoelectron valence-band spectrum of ZnS. Doping with Co atoms leads to some broadening of the core-level lines as well as of the valence-band spectrum. That occurs due to a distortion of the crystal lattice of the doped crystals and different charge effects for the surface and the volume of the crystals.¹¹ This effect makes it difficult to determine an exact position of the energy top of the valence band. That is why we have chosen for comparison the spectrum of the nondoped crystal. It is necessary to point out that the positions of the x-ray photoelectron peaks do not depend on the Co-impurity concentration.¹²

The energy top of the valence band (in the binding-energy scale) is determined by linear extrapolation of the steep edges of the valence-band spectrum to the base line. The top of the valence band, determined that way, has a binding energy of 2.00 ± 0.05 eV. By using these data we found that the Co $3d$ impurity states are localized above the top of the valence band by 1.0 ± 0.2 eV.

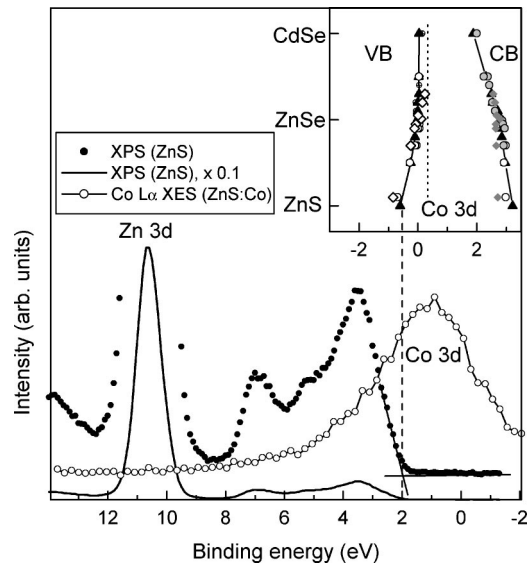


FIG. 2. X-ray photoelectron spectrum of the valence band of ZnS and Co $L\alpha$ x-ray emission spectrum of ZnS:Co. The inset presents the position of the Co $3d$ (optical transition $d^7 \rightarrow d^6$) energy level in respect of the valence-band and conduction-band edges through the whole composition range of the CdSe–ZnSe–ZnS solid solutions obtained using the internal reference rule (Ref. 13). The data are taken from the papers of Surkova *et al.* (Refs. 14 and 15) for $T = 300$ K.

This result correlates well with one obtained from optical measurements^{14,15} (see also inset in Fig. 2) where the Co $3d$ impurity level in ZnS:Co is found to be localized at 0.93 eV above the valence-band edge.

IV. CONCLUSION

In conclusion, we have determined the position of Co $3d$ states with respect to the valence-band edges by combination of x-ray emission and x-ray photoelectron spectroscopies and found good agreement with the relevant optical data obtained using the conception of the internal reference rule.¹³ Such good coincidence shows that in the case of ZnS:Co the interaction between the $3d$ impurity and host valence-band states is negligible and that the Co ions are present in isovalent Co²⁺ configuration.

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