Proceedings of the XX International School of Semiconducting Compounds, Jaszowiec 1991

REFLECTIVITY STUDY OF THE $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ CRYSTALS

B.J. KOWALSKI, Z. GOŁACKI AND B.A. ORŁOWSKI

Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warszawa, Poland

The room temperature reflectivity spectra of the $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ ($x = 0, 0.03, 0.05$) crystals have been measured in the visible and ultraviolet range from 1.7 to 12 eV. The structure of the spectra was interpreted in terms of the electronic band structure of the binary material (ZnSe). The experimental results were compared with the reflectivity spectra of the Fe-based semimagnetic semiconductors [1], and the interpretation was confronted with the conclusions derived from the photoemission experiments performed for $\text{Cd}_{1-x}\text{Co}_x\text{Se}$ [2] and the tight-binding CPA calculations of the band structure of $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ [3].

PACS numbers: 78.20.Ci

Investigation of a new class of Co-based semimagnetic semiconductors is a direct continuation of the earlier study of the Mn- and Fe-based materials. At present, the energy position of the d -states and their hybridization with the host orbitals can be studied in the system with seven d -electrons, too. Since these factors, together with the disorder occurring in the mixed crystal, influence strongly the band structure of the solid, the investigation of the interband optical transitions was chosen as an experimental method. In particular, the reflectivity spectroscopy in the wide energy range has proved to be a powerful tool for studies of the electronic structure of the semimagnetic semiconductors [1, 4]. The presence of the d -states of the transition metal ions manifests itself in the marked change of the strength and/or position of the maxima in the optical spectra. This is due to interaction of the transition metal orbitals with the initial and final states of the optical excitations observed in the binary crystal, and to the direct contribution of the d -states to the new optical transitions.

The $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ samples investigated in this work were polycrystalline, and their surfaces were mechanically polished and rinsed with alcohol. Two experimental set-ups were used during the measurements. The first one includes a high-pressure xenon lamp and a quartz prism monochromator. The spectra of the

reflectance coefficient for the energy range of $1.7 < h\nu < 4.5$ eV were taken with it. The measurements for the energy range of $4.0 < h\nu < 12$ eV were carried out with the second set-up based on the hydrogen lamp and the vacuum monochromator [5].

The reflectivity spectra obtained are shown in Fig. 1 together with the $\varepsilon_2(h\nu)$ curves obtained by means of a Kramers-Kronig analysis (Fig. 2). The reflectivity

Fig. 1. The reflectivity spectra of $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ at 300 K for three compositions.

maxima observed for the ZnSe sample correspond well to those previously reported [6]. According to this, they are interpreted as follows:

- the edge and the shoulder at 2.8 eV correspond to transitions at Γ ($\Gamma_8^v - \Gamma_6^c$, $\Gamma_7^v - \Gamma_6^c$);
- the maximum at 4.9 eV — transitions: $L_{4,5}^v - L_6^c$, $A_8^v - A_{10}^c$ (0.3, 0.3, 0.3), $L_6^v - L_6^c$, $A_6^v - A_{10}^c$ (0.3, 0.3, 0.3);
- the highest maximum at 6.9 eV with shoulders at 6.4, 7.6 and 8.3 eV — transitions: $X_7^v - X_6^c$, $\Delta_6^v - \Delta_{10}^c$ (0.6, 0, 0), $\Sigma_{7,8}^v - \Sigma_{9,10}^c$ (0.6, 0.6, 0), $\Delta_8^v - \Delta_{12}^c$ (0.6, 0, 0), $\Delta_6^v - \Delta_{12}^c$ (0.6, 0, 0).

The origin of the broad structure (with a maximum at 9.6 eV) is not determined finally yet.

The presence of the Co ions in the crystal leads to:

- the modification of the first edge and the shoulder at 2.8 eV,
- the decrease of the maximum at 4.9 eV (it becomes a shoulder for $\text{Zn}_{0.95}\text{Co}_{0.05}\text{Se}$),
- the strong decrease of the broad maximum at 9.6 eV,
- the marked broadening of the all features observed in the spectra.

According to the interpretation of the spectra of ZnSe, the modification of the structure at 2.8 eV is connected with the change of the energy gap width. This corresponds to the results of the photoemission experiments performed for

Fig. 2. The $\epsilon_2(h\nu)$ spectra obtained by means of a Kramers-Kronig analysis of the reflectivity spectra shown in Fig. 1.

$\text{Cd}_{1-x}\text{Co}_x\text{Se}$ [2]. The marked Co-derived contribution to the electronic density of states was revealed at the edge of the valence band. The decrease of the maximum at 5 eV can be connected with the strong modification of the energy bands at L by the Co-derived d -states. The same effect was observed for the Fe-based materials [1]. The broadening of the structure in the spectra is usually a sign of the disorder occurring in the mixed crystal. However, it must be noted that the relatively low content of Co (less than 5%) leads to the strong modification of the spectra. In particular, it is stronger than that observed for the Mn- and Fe-based semimagnetic semiconductors of the similar transition metal content. Perhaps, it is connected with the peculiarly strong exchange interaction reported by Mašek on the basis of the theoretical study of the Co-based materials [3].

References

- [1] B.J. Kowalski, A. Sarem, B.A. Orłowski, *Phys. Rev. B* **42**, 5159 (1990);
A. Sarem, B.J. Kowalski, B.A. Orłowski, *J. Phys. Condens. Matter* **2**, 8173 (1990).
- [2] V. Cháb, J. Mašek, B.A. Orłowski, B.J. Kowalski, *Acta Phys. Pol. A* **80**, 333 (1991);
B.A. Orłowski, B.J. Kowalski, V. Cháb, in *Proc. 9th Int. Conf. Vacuum Ultraviolet Radiation Physics, Honolulu 1989*, *Phys. Scr.* **41**, 984 (1990).
- [3] J. Mašek, *Acta Phys. Pol. A* **80**, 267 (1991).
- [4] A. Kisiel, M. Piacentini, F. Antonangeli, N. Zema, A. Mycielski, *Solid State Commun.* **70**, 693 (1987);

A. Kisiel, M. Piacentini, F. Antonangeli, J. Oleszkiewicz, A. Rodzik, N. Zema, A. Mycielski, *J. Phys. C* **20**, 5601 (1987).

[5] B.J. Kowalski, B.A. Orłowski, *Solid State Commun.* **76**, 1317 (1990).

[6] Experiment: J.F. Freeouf, *Phys. Rev.* **7**, 3810 (1973).

D. Theis, *Phys. Status Solidi B* **79**, 125 (1977);

theory: J.P. Walter, M.L. Cohen, Y. Petroff, M. Balkanski, *Phys. Rev. B* **1**, 2661 (1970);

J.R. Chelikowsky, M.L. Cohen, *Phys. Rev. B* **14**, 556 (1976).