Fe 3d CONTRIBUTION TO THE VALENCE BAND OF CUBIC $Hg_{1-x}Fe_xS$ — RESONANT PHOTOEMISSION STUDY

B.J. Kowalski, B.A. Orlowski, W. Szuszkiewicz, B. Witkowska

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

AND R.L. Johnson

Universität Hamburg, II Institut für Experimentalphysik
Luruper Chaussee 149, 22761 Hamburg, Germany

Resonant photoemission spectra of cubic $Hg_{0.94}Fe_{0.06}S$ were measured for photon energies near to the energy of intra atomic Fe $3p^6 3d^6 \rightarrow 3p^5 3d^7$ transition. The difference between the spectra taken at resonance and antiresonance is presented as a measure of the energy distribution of Fe $3d$ derived states. The results obtained show that Fe $3d$ states contribute to the whole valence band with a distinct structure appearing at the band edge.

PACS numbers: 79.60.−i

Many of the diluted magnetic semiconductors (DMS) based on II–VI compounds have been extensively investigated since the 70s. Their electric, magnetic and optical properties were determined and band structures described [1–5]. However, this is still not the case for those solid solutions which would contain mercury sulphide as a non magnetic component. This compound is an exception among the other, tetrahedrally bonded, members of the II–VI family. Its natural form (α-HgS) is a wide gap semiconductor of a cinnabar crystal lattice. The cubic modification of mercury sulphide, β-HgS, is stable at above 550 K but it transforms upon cooling into α-HgS [6]. Thus, big size, bulk monocrystals of cubic HgS have not been available to experimentators until quite recently. Some information about crystal structure and electronic properties was obtained from experiments performed for a powder produced by chemical precipitation [7], a natural polycrystalline material highly doped with Fe (metacinnabar) [8], or vacuum-evaporated thin films [7].

However, a technique of stabilization of the cubic lattice in big monocrystals of HgS grown by means of an equilibrium method has been recently proposed [9]. It is based on doping the crystals with a transition metal (e.g. Fe, Co) or selenium. That achievement made it possible to investigate further properties of β-HgS with prospects to compare the results with those known for HgTe and HgSe as well as for the cinnabar form of HgS. Moreover, a new group of solid solutions (DMS, among others) has been obtained. The opportunity arose to fill the gap in the set of data concerning properties of II–VI based diluted magnetic semiconductors.

In this paper we report the results of the valence band density of states distribution study performed for cubic $Hg_{0.94}Fe_{0.06}S$ by means of photoemission. In order to reveal the Fe $3d$ derived contribution built into the valence band we applied resonant photoemission spectroscopy. Energy distribution curves (EDC) were measured for the photon energy range covering the Fe $3p$–$3d$ absorption edge (50–57.5 eV). The comparison of the spectra taken at resonance and at antiresonance energies enabled us to visualise emission from Mn $3d$ derived states. The complementary data were also obtained by a constant initial state (CIS) technique.

The photoemission experiments were performed in the FLIPPER II system built in HASYLAB at DESY (Hamburg, Germany). The set-up consists of interconnected UHV chambers designed for the sample preparation and extended characterization of solids. The analysis chamber is equipped with a cylindrical mirror electron energy analyser and a low-energy electron diffraction (LEED) facility. The system is attached to a beamline of the storage ring DORIS II via a plane grating monochromator designed to operate over the photon energy range of 15–200 eV. The total energy resolution achieved in photoemission experiments was 100 meV. The FLIPPER II system has been described in detail in Ref. [10].

The samples investigated were prepared by a modified Bridgman method in the Institute of Physics, Polish Academy of Sciences in Warsaw. It was checked by X-ray diffraction that $Hg_{0.94}Fe_{0.06}S$ forms the uniform solid solution with a zinc-blende crystal structure. The chemical composition was determined by the SEM microprobe and EDXRF (energy-dispersive X-ray fluorescence) analysis. Clean surfaces were prepared by cleavage *in situ* under UHV conditions.

As it was shown by means of many experiments and calculations [1–5] the unusual properties of DMS are defined by the interaction of the open shell transition metal (TM) ions with host semiconductor environment. In particular, exchange interaction between localised TM $3d$ spins and the band electrons as well as the sp–d hybridization had to be taken into account if any proper description of electronic band structure of DMS was to be constructed [1–5].

On the other hand, many experiments were done to verify the theoretical predictions of the strength of the hybridization and distribution of transition metal $3d$ derived states in the valence bands of many different DMS. Photoemission and optical spectroscopies was found to be the most useful tools for those investigations. The band mapping photoemission techniques gave the detailed information used to draw the $E(k)$ diagrams of the band structures in the entire Brillouin zone [11]. However, TM derived contributions to the valence bands did not manifest themselves clearly in those results. The resonant photoemission techniques filled that gap. These methods proved to be useful for investigation of transition metal compounds [12–14], and were also applied to reveal and identify the TM derived contribution to the band structure of many DMS [15–17].

The resonant enhancement of photoemission intensity from open shell systems is well known as being the result of a quantum mechanical interference between two processes leading to the same final state [18]. For Fe containing compounds we observe Fe $3p^6 3d^6 + h\nu \rightarrow 3p^6 3d^5 + e^-$ and Fe $3p^6 3d^6 + h\nu \rightarrow 3p^5 3d^7 \rightarrow 3p^6 3d^5 + e^-$ [19].

The interference results in the strong modulation of the photoemission cross

section around the photon energy of about 56 eV. It manifests itself as a Fano-like resonance occurring in X-ray absorption and photoemission spectra taken in constant-initial-state (CIS) or constant-final-state (CFS) modes. Consequently, Fe 3d derived contribution to the photoelectron energy distribution curve (EDC) can be clearly revealed by comparison of the spectra taken at the resonance and antiresonance photon energies.
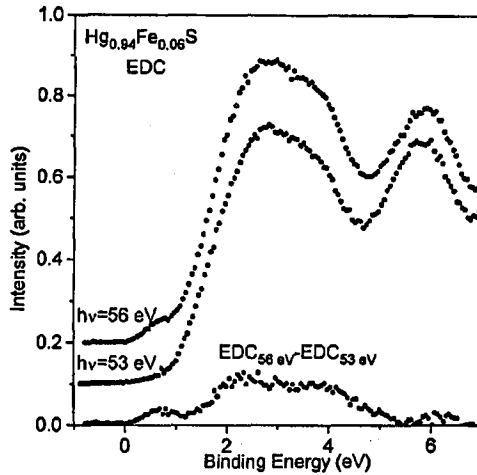

Fig. 1. The EDCs (i.e., number of emitted electrons plotted as a function of their energy) taken at the resonance (56 eV) and antiresonance energies (53 eV) and normalised to match the intensity at the high energy tail of the spectra. The difference spectrum is a measure of the Fe 3d derived density of states distribution. The origin of the energy scale was set at the Fermi level position measured on a reference metallic sample. The binding energy region shown in the figure corresponds to the position of the valence band in II–VI compounds.

The results of the resonant photoemission experiment performed for $Hg_{0.94}Fe_{0.06}S$ are shown in Fig. 1. The overall shapes of the spectra correspond well to those observed for other II–VIs. The first maximum at 2.8 eV occurs due to the emission from the upper part of the valence band while the second one (at 5.8 eV) is connected with transitions from the high density of states region at the bottom of the band at the X point of the Brillouin zone (dominated by the contribution of cation s states [4]).

The shape of the Fe 3d derived density of states distribution is visualised by subtracting the spectrum taken at antiresonance from that recorded at resonance (Fig. 1). In the difference spectrum we revealed structures at 0.7, 2.3, and 3.9 eV. These energies correspond well to those found for structures characteristic of the Fe 3d partial density of states in $Cd_{0.89}Fe_{0.11}Se$ (0.5, 2.3, 3.7 eV, respectively) [20]. However, the relative intensities of the features at 2.3 and 3.9 eV are markedly different for these two compounds. As it was shown by means of a

configuration-interaction (CI) calculation [20], these structures correspond mainly to transitions to the charge transfer configuration of $d^6\underline{L}$, where $\underline{L}$ denotes a ligand hole. Thus, we can expect that the changes in their intensities result from a modification of $p\text{-}d$ hybridization strength.

Development of β-HgS crystal growth technology enabled us so far to study the samples of the composition up to $x = 0.06$. The full interpretation of the structures observed still needs more experimental results, particularly for higher values of x. It is believed that the Fe solubility limit in HgS has not been achieved yet and we hope that some new crystals rich in Fe ions will be soon grown and investigated.

Acknowledgments

References

[1] *Semiconductors and Semimetals*, Eds. R.K. Willardson, A.C. Beer, J.K. Furdyna, J. Kossut, Vol. 25, Academic Press, Boston (MA) 1988.

[2] J.K. Furdyna, *J. Appl. Phys.* **64**, R29 (1988).

[3] J. Kossut, W. Dobrowolski, in: *Handbook of Magnetic Materials*, Ed. K.H.J. Buschow, Vol. 7, North-Holland, Amsterdam 1993, p. 231.

[4] S.H. Wei, A. Zunger, *Phys. Rev. B* **35**, 2340 (1987).

[5] B.E. Larson, K.C. Hass, H. Ehrenreich, A.E. Carlsson, *Phys. Rev. B* **37**, 4137 (1988).

[6] G.G. Roberts, E.L. Lind, E.A. Davis, *J. Phys. Chem. Solids* **30**, 833 (1969).

[7] K.J. Siemsen, H.D. Riccius, *Phys. Status Solidi B* **37**, 445 (1970).

[8] R. Zallen, M. Slade, *Solid State Commun.* **8**, 1291 (1970).

[9] W. Szuszkiewicz, B. Witkowska, E. Dynowska, J. Górecka, to be published.

[10] R.L. Johnson, J. Reinchardt, *Nucl. Instrum. Methoths Phys. Res.* **208**, 791 (1983).

[11] B. Velický, J. Mašek, G. Paolucci, V. Cháb, M. Surman, K.C. Prince, *Festkörperprobleme* **XXV**, 247 (1985).

[12] A. Kakizaki, K. Sugano, T. Ishii, H. Sugawara, S. Shin, *Phys. Rev. B* **28**, 1026 (1983).

[13] R.J. Lad, V.E. Henrich, *Phys. Rev. B* **39**, 13478 (1989).

[14] L.C. Davis, *Phys. Rev. B* **25**, 2912 (1982).

[15] L. Lay, M. Taniguchi, J. Ghijsen, R.L. Johnson, *Phys. Rev. B* **35**, 2839 (1987).

[16] M. Taniguchi, M. Fujimori, M. Fujisawa, T. Mori, J. Souma, Y. Oka, *Solid State Commun.* **62**, 431 (1987).

[17] M. Taniguchi, Y. Ueda, I. Morisada, Y. Murashita, T. Ohta, I. Souma, Y. Oka, *Phys. Rev. B* **41**, 3069 (1990).

[18] L.C. Davis, L.A. Feldkamp, *Phys. Rev. B* **23**, 6239 (1981).

[19] B. Sonntag, P. Zimmermann, *Rep. Prog. Phys.* **55**, 911 (1992).

[20] Y. Ueda, M. Taniguchi, T. Mizokawa, A. Fujimori, I. Souma, Y. Oka, *Phys. Rev. B* **49**, 2167 (1994).