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## SYNCHROTRON RADIATION PHOTOEMISSION STUDIES OF Mn 3d STATES IN $Zn_{1-x}Mn_xSe^*$

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The angle integrated resonant photoemission measurements of  $Zn_{0.9}Mn_{0.1}Se$  have been performed in the photon energy range between 30 eV and 70 eV using synchrotron radiation. The ternary compound valence band photoemission spectra show, in comparison to the ZnSe results, additional structures, whose intensity depends on Mn content. These new features have been assigned to transitions from the Mn 3d states of  $e$  symmetry with spin up. The hybridization of the  $t_2$  component of the 3d electrons of Mn in the valence band is discussed.

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For several years the Mn-doped II-VI semimagnetic semiconductors compounds, well-known also as diluted magnetic semiconductors (DMSs), have attracted considerable attention due to their interesting magnetic and semiconducting behaviour such as extremely large Faraday rotation, giant magneto-resistance and large values of the  $g$ -factor [1-4].

In  $Zn_{1-x}Mn_xSe$  [5], up to  $x < 0.33$ , the transition metal  $Mn^{2+}$  ions replace randomly the Zn cations in the zinc-blende structure of the host ZnSe crystal. The

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large exchange interaction produces the spin splitting of the  $3d$  Mn states into two groups of sublevels (spin-up and spin-down), where the spin-up set is completely filled. Within the tetrahedral crystal field of ZnSe each of these split into a doublet  $e$  at low energy and a triplet  $t_2$  at high energy. The five  $3d$  electrons of the  $\text{Mn}^{2+}$  ion fill the five  $e$  and  $t_2$  spin-up states [4]. The  $e$  states remain localized in the valence band (VB) while the  $t_2$  states hybridize with the anion (Se) and cation (Zn)  $p$ - and  $s$ -like states, causing further distortion of the electronic band structure and modification of the density of states [3]. The large amount of data available on many Mn-based DMSs, especially Cd-compounds, have allowed to solve some controversies on the identification of Mn  $3d$  features in the valence band density of states of ternary compound. Three features have been identified as connected with the presence of Mn: a major structure at 3.3–3.8 eV below the top of the valence band, a weak structure in the 0–2 eV range and a broad structure in the 6–9 eV range. Although the experimental framework is well stated the theoretical interpretation of these structures and the expected degree of hybridization with the Se  $p$ -derived valence band is still controversial. In order to contribute to clarify the mechanisms of  $p$ - $d$  hybridization in the DMS compounds is interesting to test the models developed for  $\text{Cd}_{1-x}\text{Mn}_x\text{Y}$  ( $\text{Y}=\text{Se}, \text{Te}, \text{S}$ ) in the case of other DMS compounds. Very few data are available for the  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  samples [6–9]. In this paper we report the results of resonant photoemission measurements performed on  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{Se}$ .

The photoemission measurements were carried out at the Grasshopper Mark V soft X-ray beamline of the University of Wisconsin Synchrotron Radiation Center [10] using a conventional ultra-high vacuum experimental set-up for photoelectron spectroscopy equipped with a commercial double-stage Cylindrical Mirror Analyser operating at 15 eV pass energy. Measurements have been performed at room temperature on samples scraped *in situ* under ultra-high vacuum conditions.

The energy distribution curves (EDC) spectra were measured at several photon energies between 30 eV and 70 eV and some selected examples obtained for photon energies close to the Mn  $3p$ - $3d$  threshold are reported in Fig. 1 for  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{Se}$  compared with those obtained for pure ZnSe at the same photon energies. All the spectra were normalized to the integrated Zn  $3d$  intensity scaled by the Zn concentration ( $1 - x$ ) and aligned to the Zn  $3d$  peak energy position which is not expected to shift with composition [11]. The zero of the binding energy scale has been set at the top of the ZnSe valence band whose value was determined by linear extrapolation of the leading edge of the VB photoelectron feature. The valence band spectrum of pure ZnSe has been discussed in detail elsewhere [10]. The two prominent structures were assigned to the Se  $4p$  states with an increasing contribution of the Zn  $4s$  state moving towards deeper binding energy. Our data on ZnSe show, in comparison with the recent results from Ref. [7], better definition of the VB EDC spectra. This result could be attributed to the different treatment of the sample surfaces. In fact, our samples were scraped preserving the crystalline structure of the sample surfaces whereas in Ref. [7] the surface was treated by subsequent processes of Ar sputtering and annealing. The latter treatment does not guarantee for the surface crystalline structure even if Auger spectroscopy shows clean and stoichiometric surfaces. From Fig. 1 it is evident

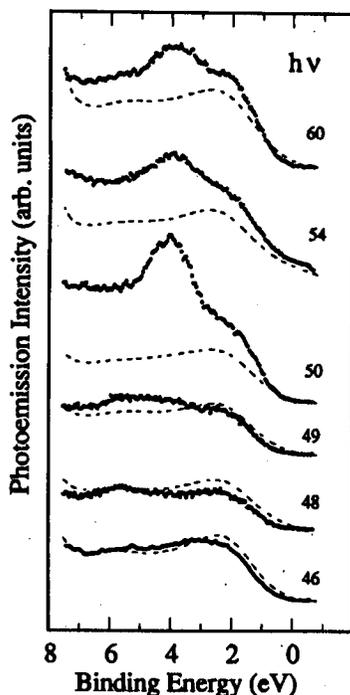


Fig. 1. Selected photoelectron energy distribution curves for the valence bands from  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{Se}$  (full dots) and  $\text{ZnSe}$  (dashed line) at several photon energies. The spectra are aligned to the  $\text{Zn } 3d$  core level position and the zero of the energy is taken at the top of the valence band of pure  $\text{ZnSe}$ .

that new features appear in the valence band region due to the presence of Mn. At photon energies below the Mn  $3p$ - $3d$  threshold near 46–48 eV the two EDCs are very similar, even if probably there exists a broadening of  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{Se}$  VB EDC due to bulk intrinsic disorder of the crystal or to the re-distribution of the electronic states due to the interaction of  $t_2$  spin-up states with the Se  $4p$  states in the upper part of the valence band. Passing through the Mn  $3p$ - $3d$  absorption edge (49–50 eV), where a resonant behaviour is expected for the Mn  $3d$  photoelectrons, a strong peak appears at about 4.0 eV below the top of the  $\text{ZnSe}$  valence band together with an enhancement of the photoelectron emission all over the valence band. The photoelectron resonance takes place in this region as a result of the interference between the direct excitation process of the Mn  $3d$  electrons ( $3p^6 3d^5 \rightarrow 3p^6 3d^4 + \epsilon l$ ) and the discrete Mn  $3p \rightarrow 3d$  excitation process followed by a Super Coster-Kronig decay ( $3p^6 3d^5 \rightarrow 3p^5 3d^6$ ,  $3p^5 3d^6 \rightarrow 3p^6 3d^4 + \epsilon l$ ). The peak at 4.0 eV is generally attributed to the localized  $e$  spin-up states. In order to identify the contribution of the filled  $t_2$  spin-up states to the valence band of the ternary compound, we computed the VB photoelectron intensity difference spectra subtracting the VB EDC spectrum of  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{Se}$  measured out of resonance (48 eV photon energy) from the spectrum measured above resonance at 50 eV

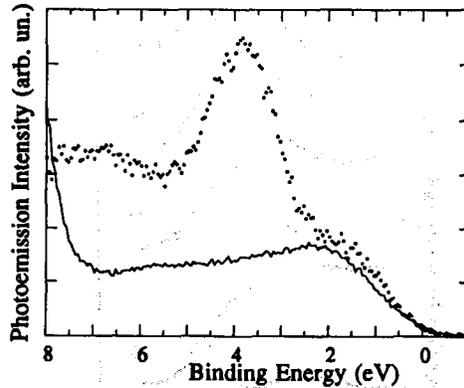


Fig. 2. Photoelectron difference curves obtained from resonance (50 eV)-antiresonance (48 eV) EDCs curves (full dots) obtained for  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{Se}$  compared with the pure ZnSe valence band EDC (solid line) taken at 50 eV.

photon energy; each spectrum was normalized to the Zn 3d area. In Fig. 2 there is reported the result of the resonance-antiresonance difference spectrum performed on  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{Se}$  together with the VB of ZnSe. The difference spectrum clearly shows the contribution of Mn states to the VB of the ternary compound. Beside the previously discussed peak at about 4.0 eV the difference spectrum shows two new features. The first one, at about 2.0 eV, is a broad band located in correspondence to the first peak of the valence band EDC of ZnSe. The second structure is present at higher binding energies between 6 eV and 8 eV showing up as an almost constant increase in the photoemission signal. We assign this features to the  $t_2$  states that hybridize with Se 4p states. This hybridization seems to be spread all over the valence band. Recent band structure calculations performed on  $\text{Zn}_{0.5}\text{Mn}_{0.5}\text{Se}$  [9, 12] support our assignment, showing a strong contribution of  $d$ -character spin-up density of states of Mn to the total density of states in the topmost part of the valence band, and with a less extent towards higher binding energies. Alternatively configuration interaction calculations predict a satellite structure in connection with transitions starting from the  $e$  states in the 6–9 eV binding energy region [3].

In conclusion, from resonant EDC spectra measured around the Mn  $3p$ - $3d$  absorption threshold in  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{Se}$ , we derived a partial density of Mn  $3d$  states which is consistent with the results available for  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  [2, 3, 13] and  $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$  [14]. We found evidence of localized Mn  $e$  states at 4.0 eV below the top of ZnSe valence band and we identify the hybridization of the  $t_2$  spin-up states as spread all over the valence band.

## References

- [1] W.M. Becker, *Semicond. Semimet.* **25**, 35 (1988).
- [2] A. Franciosi, S. Chang, R. Reifenberger, U. Dębska, R. Reidel, *Phys. Rev. B* **32**, 6682 (1985).

- [3] L. Ley, M. Taniguchi, J. Ghijsen, R.L. Johnson, A. Fujimori, *Phys. Rev. B* **35**, 2839 (1987).
- [4] Su-Huai Wei, A. Zunger, *Phys. Rev. B* **35**, 2340 (1987).
- [5] K. Smith, J. Masela, R. Kershaw, K. Dwight, A. Wood, *Mater. Res. Bull.* **23**, 1423 (1988).
- [6] A. Franciosi, S. Chang, C. Caprile, R. Reifenberger, U. Dębska, *J. Vac. Sci. Technol. A* **3**, 926 (1985).
- [7] R. Weidemann, H.E. Gumlich, M. Kupsch, H.U. Middelmann, *Phys. Rev. B* **45**, 1172 (1992).
- [8] L.P. Fu, W.Y. Yu, A. Petrou, J. Warnock, B.T. Jonker, *Phys. Rev. B* **48**, 18272 (1993).
- [9] H. Xiaoguang, H. Meichun, *J. Phys., Condens. Matter* **1**, 5371 (1989).
- [10] L. Ley, R.A. Pollak, F.R. McFreely, S.P. Kowalczyk, D.A. Shirley, *Phys. Rev. B* **9**, 600 (1974).
- [11] A. Wall, A. Franciosi, D.W. Niles, R. Reifenberger, C. Quaresima, M. Capozzi, P. Perfetti, *Phys. Rev. B* **41**, 5969 (1990).
- [12] R. Markowski, private communication.
- [13] B.A. Orlowski, K. Kopalko, W. Chab, *Solid State Commun.* **50**, 749 (1984).
- [14] A. Franciosi, C. Caprile, R. Reifenberger, *Phys. Rev. B* **31**, 8061 (1985).