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SYNCHROTRON RADIATION PHOTOEMISSION STUDIES OF Fe 3*d* STATES IN $Cd_{1-x}Fe_xSe$

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The angle integrated resonant photoemission measurements of $Cd_{1-x}Fe_xSe$ were performed for different Fe concentrations ($x = 0.00$, 0.07, 0.14) 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 CdSe results, two additional structures, whose intensity depends on Fe content, which were assigned to Fe 3*d* states of *e* symmetry with spin up and down, respectively. The hybridization of the t_2 component of the 3*d* electrons of Fe in the valence band is discussed.

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1. Introduction

In recent years the class of diluted magnetic semiconductors (DMS), in which the group II element is randomly replaced with Fe^{2+} ion, has become of great interest because of the significantly different magneto-optical properties observed in comparison with those of Mn-substituted II–VI compounds. Unlike the well-known Mn-based DMS [1], the Fe-based II–VI compounds show a very low solubility of Fe, creating some difficulties in obtaining single phase samples for studying the electronic properties.

In $Cd_{1-x}Fe_xSe$ the transition metal Fe^{2+} ions replace randomly the Cd cations in the wurtzite structure of the host CdSe crystal [2].

It is believed that, similarly to the Mn-based DMS's [3–5], there is a large exchange interaction between the Fe $3d$ electrons, which leads to the spin splitting of the Fe $3d$ states into two groups of sublevels (spin-up and spin-down). Within the tetrahedral crystal field each of these states is further split into a doublet e at low energy and a triplet t_2 at high energy. The six $3d$ electrons of the Fe^{2+} ion fill the five e and t_2 spin-up states and one of the e spin-down states. The e states remain localized both in the valence band (VB) and in the energy gap while the t_2 states are supposed to hybridize with the anion (Se) and cation (Cd) p- and s-like states, causing further distortion of the electronic band structure and modification of the density of states. Very few experimental data are available for the $Cd_{1-x}Fe_xSe$ compounds [6–11] and the attempt of describing the Fe $3d$ states behavior while interacting with the CdSe electronic structure results rather incomplete. At first Kisiel et al. [8] suggested a model, based on reflectivity measurements, in which the $3d^1 e\downarrow$ state is located at about 0.6 eV above the top of the VB [6, 7] while the t_2 level hybridizes with the upper part of the VB, mostly originating from the Se $5p$ atomic states. The filled $e\uparrow$ states lie below them as a localized state. Taniguchi et al. [9] using their photoemission results suggested that the filled t_2 states are spread over the entire VB due to hybridization. More recently Sarem et al. [10] suggested, according to a model working for wide-gap DMS's, a new scheme for the Fe $3d$ states in CdSe. In this paper we report the results of resonant photoemission measurements on $Cd_{1-x}Fe_xSe$ showing the contribution of the $3d$ states of Fe^{2+} to the valence band in the ternary compound.

2. Experiment

The photoemission measurements on $Cd_{1-x}Fe_xSe$ ($x = 0.0, 0.07, 0.14$) were performed using the conventional ultra-high vacuum equipment for photoelectron spectroscopy available at the Iowa-Montana soft X-ray beamline at the University of Wisconsin Synchrotron Radiation Center* in the photon energy range between 30 eV and 70 eV with an average photon-energy resolution of 0.1 eV [12]. Angle-integrated energy distribution curves (EDC) were measured with a commercial double-stage cylindrical mirror analyser operating at 10 eV pass energy. The kinetic energy of the emitted electrons was detected with an average overall resolution of 0.2 eV.

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The samples were grown through a modified Bridgman method and their nominal Fe content was checked by using the linear dependencies of the lattice parameters $a(x)$ and $c(x)$, measured by means of X-ray diffraction techniques, on the Fe concentration x [13]. The X-ray test showed a single phase wurtzite structure for the samples used in our measurements.

Measurements were performed at room temperature on samples scraped *in situ* under ultra-high vacuum conditions.

3. Results and discussion

EDC's for $Cd_{0.86}Fe_{0.14}Se$ were measured at several photon energies between 30 eV and 70 eV and some selected examples obtained at photon energies close to the Fe $3p$–$3d$ threshold are reported in Fig. 1. The spectra of the ternary compound are compared with those obtained for pure CdSe samples at the same photon energies. All the spectra were normalized to the integrated Cd $4d$ intensity scaled by the Cd concentration $(1 - x)$ and aligned to the Cd $4d$ peak energy position which is not expected to shift with composition [14]. The zero of the binding energy scale was set at the top of the CdSe valence band whose value was determined by

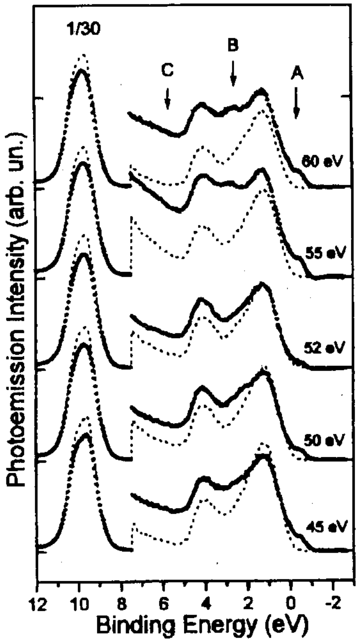

Fig. 1. Selected photoelectron energy distribution curves for the valence band and Cd $4d$ core emission from $Cd_{0.86}Fe_{0.14}Se$ (full dots) and CdSe (dashed line) at several photon energies. The spectra are aligned to the Cd $4d$ core level position and the zero of the energy is at the top of the valence band for pure CdSe.

linear extrapolation of the leading edge of the VB photoelectron feature. The valence-band spectrum of pure CdSe has been discussed in detail elsewhere [15]. The two prominent structures were assigned to the Se $4p$ states with an increasing contribution of the Cd $5s$ state moving towards deeper binding energy. From Fig. 1 it is evident that new features appear in the valence band region due to the presence of Fe. At photon energies below the Fe $3p$–$3d$ threshold near 52 eV two new structures are observed: the one at 0.5 eV over the top of the CdSe valence band is always evident, while the second one, whose energy position is about 3.0 eV below the top of CdSe valence band, becomes more pronounced as the photon energy increases. The latter structure becomes much more prominent passing through the Fe $3p$–$3d$ absorption edge, where a resonant behavior is expected for the Fe $3d$ photoelectrons. The photoelectron resonance takes place in this region as a result of the interference between the direct excitation process of the Fe $3d$ electrons ($3p^6 3d^6 \rightarrow 3p^6 3d^5 + \varepsilon l$) and the discrete Fe $3p \rightarrow 3d$ excitation process followed by a super Coster–Kronig decay ($3p^6 3d^6 \rightarrow 3p^5 3d^7$, $3p^5 3d^7 \rightarrow 3p^6 3d^5 + \varepsilon l$). Evidence of the resonant behavior of the new structure is given by measuring the constant initial state (CIS) spectra in the photon energy region between 45 eV and 65 eV. The CIS spectra, normalized to the photon flux, obtained for the binding energies indicated by the arrows in Fig. 1, are reported in Fig. 2. The general behaviors of

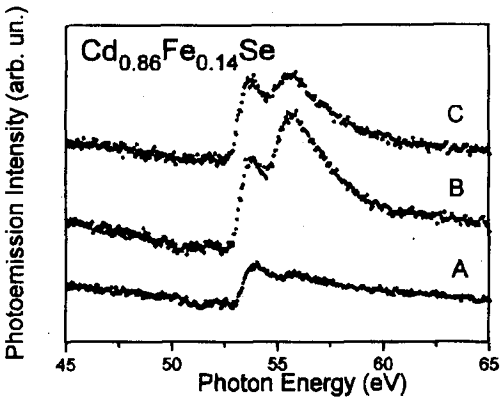

Fig. 2. CIS spectra obtained for initial energies marked as A, B and C in Fig. 1 in $Cd_{0.86}Fe_{0.14}Se$. The spectra are normalized to the photon flux and the background contribution from pure CdSe is subtracted.

the three curves are quite similar to each other and closely resemble the atomic Fe $3p \rightarrow 3d$ absorption spectrum [16] apart from the intensity ratio between the two peaks. The B feature in the EDC's has a very strong resonant effect, expecially in the 55–57 eV absorption region, while the A feature shows a resonance effect that is half of the intensity of the B feature in the 52–55 eV region. The C curve, which is taken at an energy strongly influenced by inelastically produced secondary electrons, shows two peaks of equivalent intensity. The origin of the B and A features in the VB photoelectron spectra is assigned to the filled e spin-up states and the partially filled *e* spin-down state, respectively, whose energy positions with respect to the top of the CdSe valence band are in good agreement with those reported by previous authors [6, 8, 9, 11]. In this scheme it is evident that the *e* spin-up and *e* spin-down states show the same coupling with the Fe $3p^6 3d^6 \rightarrow 3p^5 3d^7(^4P)$ transition [16], giving the resonant structure in the 52–55 eV photon energy range, because the intensities of the two jumps scale proportionally with the number of electrons present in the spin-up and spin-down states (2:1). In the 55–57 eV the *B* feature shows a very strong resonance in correspondence with the Fe $3d^7(^4F)$ final state [16], whereas structure *A* shows a weak behavior supporting a strong difference in the interaction of the states involved in the resonance.

In order to identify the contribution of the filled t_2 spin-up states to the ternary compound valence band, we computed the VB photoelectron intensity difference spectra at some selected photon energies in the resonance region. The difference spectra were performed in two ways: the first method consisted in subtracting the EDC VB spectrum of $\mathrm{Cd_{0.86}Fe_{0.14}Se}$ measured out of resonance (50 eV, 52 eV photon energies) to the spectrum measured above resonance at 55 eV photon energy; each spectrum was normalized to the Cd 4*d* area. The second method is based on the direct difference between the EDC VB spectra of the $\mathrm{Cd_{0.86}Fe_{0.14}Se}$ and of the pure CdSe taken at the same photon energy and normalized to Cd 4*d* area scaled by the $(1-x)$ concentration factor. A set of photoelectron difference spectra is shown in Fig. 3. The first method can be applied only for few photon energies around the resonance threshold, while the second method gives results at all photon energies allowing to follow the change of the spectral features. Looking

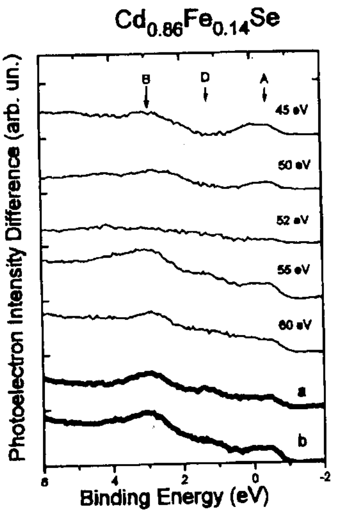

Fig. 3. Photoelectron difference curves obtained from EDC's $\mathrm{Cd_{0.86}Fe_{0.14}Se}$–CdSe subtraction (solid line) at several photon energies and resonance–antiresonance difference curves (thick line) obtained for $\mathrm{Cd_{0.86}Fe_{0.14}Se}$ at 55–52 eV (a) and 55–50 eV (b) photon energies.

at the evolution of the difference spectra ($Cd_{0.86}Fe_{0.14}Se$–CdSe) while changing the photon energy across the resonance, there clearly appears a new band in addition to the A and B features. This new band (D) is positioned at about 1 eV below the top of the CdSe VB and fills the minimum present in the 45 eV and 50 eV curves. The same band appears also in the resonance–antiresonance difference curves (a and b in Fig. 3). In the 55–60 eV photon energy interval, an intensity increase in the high energy part of the difference curves is observed. This can be due to the strong influence of additional secondary electrons generated in the resonant process. The energy position of the D feature is in correspondence to the maximum of the predominant Se $4p$ peak in the valence band EDC of pure CdSe. This allows us to assign the D feature to the t_2 states hybridized with the Se p-like states. Our assignment is supported by a band structure calculation performed on $Zn_{0.5}Fe_{0.5}Se$ showing a strong contribution of d-character density of states of Fe to the total density of states in this energy region [17]. The t_2 photoelectron emission results to be weaker than the e emission probably due to a strong hybridization with the valence states. We cannot exclude a small contribution of the t_2 emission from the higher energy part of the valence bands, where the intensity gain due to the secondary electrons may hide their effect [9].

In conclusion, from resonant EDC spectra measured around the Fe $3p$–$3d$ absorption threshold in $Cd_{0.86}Fe_{0.14}Se$, we could identify the Fe $3d$ e spin-down state at 0.5 eV above the top of the CdSe VB, the e spin-up state at about 3.0 eV below the top of the VB. We found also evidence of Fe $3d$ states spread in the region of the Se $4p$ VB maximum, which we assigned to the hybridized t_2 spin-up state.

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