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XAFS Studies of Diluted Magnetic Semiconductors $\text{Zn}_{1-x}\text{M}_x\text{S}$ (M = Mn, Co)

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Abstract. X-ray absorption near edges structure (XANES) spectra of the Diluted Magnetic Semiconductors (DMS) system $\text{Zn}_{1-x}\text{M}_x\text{S}$ (M=Mn, Co) have been measured at the Mn and Co $L_{3,2}$ -edge using sample current mode. Analysis of the M $L_{3,2}$ -edge XANES spectra for $\text{Zn}_{1-x}\text{M}_x\text{S}$ revealed the presence of a white line feature in each series, whose intensity increased linearly with concentration x . The white line feature is assigned to M $2p_{3/2}$ and $2p_{1/2}$ photoelectron excitations to nonbonding $3d(e)$ states and to the relatively broadened band of M $3d(t_2)$ - S $3p$ hybridized antibonding states. The rate of increase of $L_{3,2}$ white line intensity with x is associated with the difference in the degree of p - d hybridization of states between M $3d$ and S $3p$.

1. INTRODUCTION

The most widely studied II-VI-based Diluted Magnetic Semiconductors (DMS) have been those containing Mn^{2+} as the substitutional magnetic cation [1]. In recent years, Fe- and Co-based DMS have also been successfully grown and investigated [2]. In an earlier extended x-ray absorption fine structure (EXAFS) study [3, 4], we found evidence for tetrahedral bond weakening in these and other Mn-based DMS alloys, which can be attributed to Mn $3d$ - and anion valence p -orbital hybridization resulting in decreased amount of charge available for the making of sp^3 bonds. More recently, analysis of the S K -edge x-ray absorption near edge structure (XANES) spectra for $\text{Zn}_{1-x}\text{M}_x\text{S}$ [5], has revealed a concentration- and transition-metal-type-dependent pre-edge resonance peak which was attributed to S $1s$ photoelectron excitation to the unoccupied S $3p$ - M $3d(t_2)$ hybridized antibonding states. The main density of M $3d$ - S $3p$ hybridized states' features is expected to be observed for excitations involving final S p states or final M^{2+} $3d$ states in $\text{Zn}_{1-x}\text{M}_x\text{S}$. In order to deduce information on the electronic structure based on photoelectron excitations occurring on the magnetic ions, we have undertaken a study presented here of Mn and Co $L_{3,2}$ -edge XANES of $\text{Zn}_{1-x}\text{M}_x\text{S}$.

2. EXPERIMENTAL

The samples used in these studies have been reported previously [5]. The samples were ground and sieved to a fine powder (particle size < 400 mesh) and rubbed onto an adhesive indium tape for room-temperature sample current measurements in high vacuum (5×10^{-9} torr). X-ray absorption spectra of $\text{Zn}_{1-x}\text{M}_x\text{S}$ (M=Mn, Co) have been measured at the Mn and Co $L_{3,2}$ -edge at the Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan, using high-energy spherical grating monochromator (HSGM) beamline with an electron beam energy of 1.3 GeV and a maximum stored current of 200 mA.

3. RESULTS AND DISCUSSIONS

Figs. 1 and 2 show the M $L_{3,2}$ -edge XANES spectra of $\text{Zn}_{1-x}\text{M}_x\text{S}$ (M = Mn, Co). All of the spectra shown have been normalized by the incident intensity I_0 and, after subtraction of pre-edge background at L_3 -edge, scaled to the maximum of the peak heights (labeled A). Using the dipole-selection transition rule, we attribute the white line features at the Mn (Co) $L_{3,2}$ -edge (labeled L_3 and L_2) XANES to photoelectron transitions from the $\text{Mn}^{2+}(\text{Co}^{2+})$ $2p_{3/2}$ and $2p_{1/2}$ ground states to the final unoccupied $\text{Mn}^{2+}(\text{Co}^{2+})$ $3d$ electron states. The shape of the $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ ($\text{Zn}_{1-x}\text{Co}_x\text{S}$) alloys' spectra were found to be nearly identical at Mn (Co) $L_{3,2}$ -edge throughout the range of x values in each series. In contrast to the generally single-peaked feature observed at the Co $L_{3,2}$ -edge XANES spectra of $\text{Zn}_{1-x}\text{Co}_x\text{S}$, a rather complicated Mn $L_{3,2}$ -edge XANES spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ was observed, exhibiting strong multiplet and crystal effects [6,7]. As seen in Figs. 1 and 2, peak A is accompanied by a lower-intensity peak (labeled B) located just above the Mn L_3 -edge, while the L_2 -edge white line feature exhibits a peak doublet in the spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{S}$. Conversely, the Co $L_{3,2}$ -edge white line features of $\text{Zn}_{1-x}\text{Co}_x\text{S}$ are exhibited as relatively broad, individual peaks, respectively. The full width at half maximum (FWHM) of peak A was found to be ~ 1.1 eV for $\text{Zn}_{1-x}\text{Mn}_x\text{S}$, irrespective of x , while for peak B it was found to increase from ~ 0.36 eV at $x = 0.06$ to ~ 0.50 eV at $x = 0.40$. The FWHM of peak A increased uniformly from 2.0 eV at $x = 0.06$ to 2.3 eV at $x = 0.30$ for $\text{Zn}_{1-x}\text{Co}_x\text{S}$. The

relatively broader FWHM of peak A for $\text{Zn}_{1-x}\text{Co}_x\text{S}$ can be attributed to peaks A and B, in the case of Mn $L_{3,2}$ -edge XANES spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{S}$, being unresolved at the Co L_3 -edge (see inset of Figs. 1 and 2). Careful analysis shows a progressive increase of the combined integrated intensity of features A and B with increasing Mn concentration in $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ alloys. Similarly, there is a monotonic increase in the integrated intensity of feature A with Co content in the $\text{Zn}_{1-x}\text{Co}_x\text{S}$ alloys. In addition, the high energy satellite structure (labeled C), occurring ~ 3 eV above the Mn and Co L_3 -edge main feature in the XANES spectra, has been observed as occurring more pronouncedly for $\text{Zn}_{1-x}\text{Mn}_x\text{S}$, and less pronouncedly for $\text{Zn}_{1-x}\text{Co}_x\text{S}$. The intensity of this satellite structure was found to increase with x and is presumably caused by the excitation of Mn(Co) $2p_{3/2}$ photoelectrons to $4s$ states in the conduction band [8].

Figure 1: Normalized Mn $L_{3,2}$ -edge absorption spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{S}$. The white line region of Mn L_3 -edge is inset on a magnified scale.

Figure 2: Normalized Co $L_{3,2}$ -edge absorption spectra of $\text{Zn}_{1-x}\text{Co}_x\text{S}$. The white line region of Co L_3 -edge is inset on a magnified scale.

Our results can be explained on the basis of an electronic structure model in which the Mn $3d$ and S $3p$ bands of $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ alloys are derived from their respective atomic levels (please see Fig. 6 of Ref. 5 for a schematic representation). Because the structure surrounding Mn^{2+} (Co^{2+}) ions in $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ ($\text{Zn}_{1-x}\text{Co}_x\text{S}$) exhibits T_d group symmetry, the magnetic-transition-metal $3d$ states are split into e doublets (having lower energy than the undistorted $3d$ orbitals) and t_2 triplets (having higher energy than the undistorted $3d$ orbitals) by the crystal field. Due to $3p$ electrons on neighboring S atoms having t_2 symmetry, there is no p - d hybridization for the Mn(Co) $3d(e)$ states on symmetry grounds. Therefore, the $3d(e)$ levels remain local, as is evidenced by the fact that the peak in the XANES spectra associated with photoexcitations of $2p$ electrons to these final states remains dispersionless with x . In contrast, the $3d(t_2)$ are strongly hybridized with the S $3p$ states of the same symmetry, and contribute to the broadening of bands derived from these states in the density-of-states of $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ alloys. We attribute the white line feature of Mn(Co) $L_{3,2}$ -edge to dipole allowed transitions of photoelectrons from Mn^{2+} (Co^{2+}) $2p_{3/2}$ and $2p_{1/2}$ states to the unoccupied $3d$ states above the Fermi level. More specifically, a reasonable conclusion is that the white line feature of $L_{3,2}$ -edge corresponds predominantly to Mn(Co) $2p_{3/2}$ and $2p_{1/2}$ electrons making transitions to a relatively narrow band of Mn(Co) $3d(e)$ and to a broadened band of Mn(Co) $3d(t_2)$ - S $3p$ hybridized antibonding states.

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