Photoemission study of the oxide-diluted magnetic semiconductor \( \text{Zn}_{1-x}\text{Mn}_x\text{O} \)

Master Thesis

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Chapter 1

Introduction

Diluted magnetic semiconductors (DMS) are semiconducting alloys whose lattices are made up in part of substitutional magnetic atoms, such as transition-metal and rare-earth metal ions [1]. From the view point of condensed matter physics, DMS are very attractive because they exist in the interdisciplinary region between semiconductor physics and magnetism, the two big fields of condensed-matter physics. From the view point of applications, DMS are interesting in that they combine semiconducting properties, such as optical and electrical controllability and magnetic properties. The most extensively studied and most thoroughly understood materials of this type are \( A_{1-x}^{II}M_{x}^{VI} \) alloys in which a fraction of the group II sublattice is replaced randomly by Mn, such as Cd\(_{1-x}\)Mn\(_{x}\)Te and Zn\(_{1-x}\)Mn\(_{x}\)Se. These II-VI DMS are of interest for several reasons. Their ternary nature enables us to tune the lattice constant and band parameters by varying the composition of the material. The random distribution of magnetic ions over the cation sublattice leads to important magnetic effects, e.g., the formation of a spin-glass-like phase at low temperatures. The substitutional Mn atoms in the \( A^{II}B^{VI} \) lattice are also characterized by highly efficient electroluminescence, which makes dilute \( A_{1-x}^{II}M_{x}^{VI} \) alloys important in the context of the optical flat panel display applications. Furthermore, the presence of localized magnetic ions in these semiconductor alloys leads to an exchange interaction between the sp band electrons and the d electrons associated with Mn\(^{2+}\), resulting in extremely large Zeeman splittings of electronic (band and impurity) levels. This spin-dependent properties leads to dramatic new effects, such as giant Faraday rotation, magnetic-field-induced metal-insulator transition, and the formation of bound magnetic polarons. In recent years, using semiconductor crystal growth and superstructure designing techniques, DMS quantum wells, super-
lattices, interfaces and quantum dot structures can be fabricated, and characteristic properties can be derived from quantum and electron correlation effects.

Recently DMS have attracted renewed interest. So far, magnetic interactions in DMS has been mainly non-ferromagnetic, namely, paramagnetic, antiferromagnetic, spin-glass-like etc. In recent years, In$_{1-x}$Mn$_x$As, Ga$_{1-x}$Mn$_x$As [2], Zn$_{1-x}$Mn$_x$Te [3] and modulation-doped quantum-well structure Cd$_{1-x}$Mn$_x$Te/Cd$_{1-y-z}$Mg$_y$Zn$_z$Te:N [4] showed carrier-induced ferromagnetism. This ferromagnetism is induced by holes doped into the semiconductor host together with the magnetic ions, and the induced Curie temperature seems to be related with the hole density. However, the origin of the carrier-induced ferromagnetism has been controversial yet.

So far, II-VI-based DMS where the anions are S, Se or Te chalcogen atoms have been extensively studied [1]. Zn$_{1-x}$Mn$_x$O is a new type of DMS in that its anion is oxygen. Effects of transition metal impurities in ZnO have been studied on the varistor characteristics [5] and optical properties [6]. The host semiconductor ZnO is a II-VI-group compound, and has recently attracted a great deal of attention because of intense commercial interest in short-wavelength semiconductor diode lasers like III-V wide-gap semiconductor GaN. Since ZnO is transparent for visible light if Zn$_{1-x}$Mn$_x$O exhibits ferromagnetism like III-V based DMS such as Ga$_{1-x}$Mn$_x$As and In$_{1-x}$Mn$_x$As [2], a new material, namely, a transparent magnet would be realized [7]. In Zn$_{1-x}$Mn$_x$O, the concentration of magnetic ions and that of carriers can be controlled independently by doping, e.g., Al, Ga or In donors unlike in the other DMS and that it may become a useful system for spin-controlled semiconductors engineering. In this work, we have studied the electronic structure of Zn$_{1-x}$Mn$_x$O by photoemission spectroscopy and subsequent configuration-interaction (CI) cluster-model analysis.

This thesis is organized as follows: First, we present the transition metal (TM) 2p core-level x-ray photoemission spectroscopy (XPS) of Zn$_{1-x}$TM$_x$O. Second, valence-band photoemission spectra of Zn$_{1-x}$Mn$_x$O are presented using resonant photoemission spectroscopy (RPES). Finally, I discuss the electronic structures of Zn$_{1-x}$TM$_x$O as well as the possibility of ferromagnetism in this system. The present work yields also useful information about the origin of the p-d exchange interaction in Zn$_{1-x}$TM$_x$O.
Chapter 2

Photoemission spectroscopy

2.1 Photoemission spectroscopy

Photoemission spectroscopy is a powerful technique to investigate the electronic structure in solids. In this section, I briefly present the principle of photoemission spectroscopy.

When the incident photon with the kinetic energy $h\nu$ hits on the sample, a photoelectron is emitted from the sample via the photoelectronic effect. The relationship between the kinetic energy of the photoelectron $E_{kin}^V$ relative to the vacuum level $E_{vac}$ and the binding energy $E_B$ relative to the Fermi level $E_F$ is given by the energy conservation as follows,

$$E_{kin}^V = h\nu - \phi - E_B$$

where $\phi$ is the work function of the sample. The schematic picture of this process is displayed in Fig.2.1. As the light source, the Mg K$\alpha$ (1253.6 eV)/Al K$\alpha$ (1486.6 eV) are often used for x-ray photoemission spectroscopy (XPS). For ultraviolet photoemission spectroscopy, the He I and II resonance lines or synchrotron radiation are often used. For such fixed incident photon energies, therefore, one can obtain photoemission spectra by counting the number of the photoelectrons as a function of kinetic energy $E_{kin}^V$. The binding energy is determined by the above the equation from the kinetic energy of the detected photoelectrons.

In the one electron picture, the obtained spectrum gives the density of states (DOS) of electrons $N(E)$ in the sample (Koopman’s theory) as shown in Fig.2.1 if one can regard both the photoemission cross section and the density of the unoccupied final states to be constant. However, in strongly correlated electron systems, one must
explicitly consider the energy difference between the $N$-electron and $(N-1)$-electron systems. Therefore the interpretation of the spectra become complicated, but one can obtain information about electron correlation effects by analyzing these spectra (see next section). It should be noted that photoemission measurement are sensitive to sample surface. Hence, I kept the surface clean throughout the measurements by Ar-sputtering under ultra-high vacuum conditions.

Figure 2.1: Schematic diagram of the photoemission process.
2.2 Resonant-photoemission spectroscopy

The resonant-photoemission spectroscopy (RPES) is the powerful technique to investigate subtle changes of impurity states in the host material [8]. Many these experiments were reported using synchrotron radiation which one can continuously vary photon energy.

Schematic diagram of RPES is shown in Fig.2.2. If the incident photon has an energy that is almost equal to the difference between a discrete $p$ core state and unoccupied $d$ state, besides the direct photoemisson process,

$$p^6d^N + h\nu \rightarrow p^6d^N + \epsilon_f,$$

the photoabsorption together with the super-Coster-Krönig transition,

$$p^6d^N + h\nu \rightarrow p^5d^{N+1} \rightarrow p^6d^{N-1} + \epsilon_f.$$

will occur. The energy levels in the final states created by these two processes have the same energy and the same electron configuration. Therefore, these two processes can interfere and the photoemisson intensity obeys so called Fano profile [9]. Since the interference enhancement occurs only for $d$ orbital, one can obtain the information for the $d$ partial DOS in the compounds.

2.3 Configuration-interaction cluster-model analysis

In order to obtain quantitative information from the photoemission spectra, I have made CI cluster-model analyses of the core-level and valence-band photoemission spectra. The CI cluster model has been a useful framework for understanding the electronic structure of DMS [10, 11]. For simplicity, I deal mainly with $\text{Zn}_{1-x}\text{Mn}_x\text{O}$, where the $\text{Mn}^{2+}$ ion has the $d^5$ configuration in the ground state. A more general formalism has already been given in Ref.[12]. In the CI picture, we consider a tetrahedrally coordinated ($\text{MnO}_4$)$^{6-}$ cluster by neglecting the weak trigonal distortion in the wurtzite crystal structure. The ground-state wave function $\psi_g$ and the final state wave functions of $\text{Mn} 2p$ core-level $\psi_c$ photoemission and the $\text{Mn} 3d$ valence-band $\psi_v$ photoemission are given by,
Figure 2.2: Schematic diagram of the resonant photoemission process.

\[
\psi_g = a_0|d^5\rangle + a_1|d^6 L\rangle + a_2|d^7 L^2\rangle + ..., \\
\psi_c = b_0|c d^5\rangle + b_1|c d^6 L\rangle + a_2|c d^7 L^2\rangle + ..., \\
\psi_v = c_0|d^4\rangle + c_1|d^5 L\rangle + c_2|d^6 L^2\rangle + ....
\]

where \(c\) and \(L\) denote a Mn 2p core hole and a O 2p hole, respectively. The cluster-model contains the following parameters: The ligand-to-3d charge-transfer energy is defined by \(\Delta \equiv E(d^6 L) - E(d^5)\) and the 3d-3d Coulomb interaction energy by \(U \equiv E(d^4) + E(d^6) - 2E(d^5)\), where \(E(d^n L^m)\) is the center of gravity of the \(d^n L^m\) multiplet. The multiplet splitting is expressed using Racah parameters \(B\) and \(C\), which are fixed at the values of the free Mn\(^{2+}\) ion \((B = 0.119 \text{ eV}, C = 0.412 \text{ eV})\) and are also expressed by Kanamori parameters \(u, u', j, j'\)[13] \((u' = u - 2j\) and \(j' = j\) in relation to \(u = A + 4B + 3C\),
\( u' = A - B + C, \ j = \frac{5}{2}B + C \). \( U \) is given by \( u - \frac{20}{9}j \). The charge-transfer and Coulomb interaction energies defined with respect to the lowest term of each multiplet are denoted by \( \Delta_{\text{eff}} = \Delta + \frac{70}{9}B + \frac{28}{9}C = \Delta + 2.2 \text{ eV} \) and \( U_{\text{eff}} = U + \frac{140}{9}B + \frac{56}{9}C = U + 4.4 \text{ eV} \), respectively. One-electron transfer integrals between Mn 3d and O 2p orbitals are expressed in terms of Slater-Koster parameters (\( p\sigma \)) and (\( pd\pi \)). We have fixed (\( p\sigma \)) = \( -2.16 \text{ (} p\pi \text{)} \) according to Harrison [15]. In Mn 2p core-level photoemission, we have introduced the Mn 3d-2p core-hole Coulomb attraction energy \( Q \) and assumed \( Q = 1.2U \). To reproduce the photoemission spectra, the line spectra calculated using the CI cluster model have been broadened by the Gaussian (representing the instrumental broadening and finite bandwidth effects) and Lorentzian (lifetime broadening which increases with binding energy) functions. Physically, larger \( \Delta, U \) and (\( p\sigma \)) values are expected due to the high electro negativity and the low electronic polarizability of the oxygen ions, and the short Mn-ligand bond length compared with these in the other II-VI DMS’s.

### 2.3.1 p-d exchange constant

Exchange interaction between the localized d electrons of magnetic impurities and the delocalized host sp electrons are characterized by the coupling constants \( N\alpha \) and \( N\beta \) [1]. \( N\alpha \) is the exchange interaction between the conduction band minimum (composed mainly of cation s orbitals) and transition-metal d electrons, namely, \( s-d \) exchange interaction. \( N\beta \) is the exchange interaction between the valence band maximum (VBM) (composed of mainly anion p orbitals) and transition-metal d electrons, namely, \( p-d \) exchange interaction. The exchange interaction is mainly derived from two parts: One is the potential exchange and the other is the kinetic exchange. At the \( \Gamma \) point, \( s-d \) hybridization is forbidden by symmetry, and therefore \( N\alpha \) is always positive, namely, the conduction electron spin tends to align parallel to the Mn\(^{2+}\) spin. On the other hand, the \( p-d \) exchange constant is mainly due to the kinetic exchange [14]. Using the three parameter values \( \Delta, U \) and (\( p\sigma \)), I have estimated the \( N\beta \) value[1, 10, 11, 14]. In the CI picture, the ground state is the lowest \( d^5L_0 \) configuration, where \( L_0 \) denotes a hole at the valence-band maximum (VBM), hybridized with the \( d^4 \) and \( d^6L_2^2 \) configurations. The energy difference between the lowest terms of the \( d^5L_0 \) and \( d^6L_2^2 \) configurations is given by \( \delta_{\text{eff}} = \Delta_{\text{eff}} - W_V/2 \). Here \( W_V \) is the width of the host valence band contributing to the hybridization term and is fixed at 2 eV. The lowest term
of $d^4$ is by $U_{\text{eff}} - \delta_{\text{eff}}$ higher than that of $d^5L_0$. For the Mn$^{2+}$ impurity, where the $t_2$ orbitals are half-filled, only those ligand holes whose spins are antiparallel to that of the Mn$^{2+}$ can be transferred into the unoccupied $t_2$ orbitals in the intermediate state and, consequently, the $p$-$d$ exchange becomes antiferromagnetic. The exchange constant $N\beta$ is then given by

$$N\beta = \frac{16}{S} \left( \frac{0.64}{u + 4j - \delta_{\text{eff}}} + \frac{1}{\delta_{\text{eff}}} \right) \left( \frac{1}{3}(pd\sigma) - \frac{2\sqrt{3}}{9}(pd\pi) \right)^2$$

For the Mn$^{2+}$ impurity, we have assumed that the total spin $S = \frac{5}{2}$ and the transfer integrals between $d^4$ and $d^5L$ are smaller by 20% than those between $d^6$ and $d^6L$ due to the contraction of the Mn 3d orbital with the ionization [16]. Expression for the other transition-metal $p$-$d$ exchange constants in terms of the electronic structure parameters are summarized in Appendix.
Chapter 3

Physical properties of Zn$_{1-x}$TM$_x$O

ZnO is easily doped with transition-metal ions at the cation site using non-equilibrium crystal growth technique [19]. So far, to the research on II-VI DMS using conventional solid-state reaction [1] has been restricted to the other calchogen based DMS, namely, S, Se and Te compounds because oxide materials were difficult to synthesize with high quality and their detailed growth mechanism were not known.

3.1 ZnO

ZnO is an intrinsic $n$-type semiconductor because interstitial-Zn and oxygen vacancies act as native donors. Its crystal structure is the wurtzite type with the lattice parameters $a=0.32$ and $c=0.52$ nm. Fundamental absorption edge occurs at 3.4 eV at room temperature. The conduction and valence band are mainly consist of Zn 4$s$ and O 2$p$ orbitals, respectively. Taking advantage of good optical transparency and high electric conductivity, transparent electrode materials for solar cells and flat-panel displays are being developed. Thin film ZnO with Al dopant is prepared by laser-MBE method or pulse-laser deposition (PLD) technique on sapphire(001) or better lattice-matched ScMgAlO$_4$(001) substrates. Lattice matching is usually need for the epitaxial growth, but ZnO/sapphire is not lattice-matched. ZnO growth mode is called higher-order epitaxy mode. ZnO on sapphire has large lattice mismatch, but this mode enable it to reduce lattice mismatch and produce ultrafine particle of diameters ranging 50-500 Å. This surface has a spiral structure and is thereby not atomically flat[17].
3.2 Zn$_{1-x}$TM$_x$O

ZnO is easily doped with transition-metal ions at the cation site using laser-MBE method or PLD technique [19]. The solubility limits of a series of transition metals in ZnO determined by x-ray diffraction are shown in Fig. 3.1. Mn$^{2+}$ and Co$^{2+}$ ions have high solubility because their ionic radii are the closest to that of Zn$^{2+}$ among all the TM ion dopants. Optical transitions derived from the transition metals have been observed (Fig.3.2) and complicated magneto-resistance effects have been studied (Fig.3.3), like the other II-VI chalcogen based DMS [1].

Figure 3.1: Solubility of transition metals in ZnO [20]

3.3 Zn$_{1-x}$Mn$_x$O

In the Zn$_{1-x}$TM$_x$O series, Zn$_{1-x}$Mn$_x$O has been most extensively investigated because the Mn$^{2+}$ ion has the highest solubility and Mn $d$ shell is half-filled simple electronic structure and has the total spin of $S=5/2$ because of Hund's coupling, like the other II-VI DMS A$^I_{1-x}$Mn$_x$B$^VI$. All A$^I$B$^VI$ compound with A$^I$= Zn, Cd or Hg and B$^VI$= S, Se or Te have a direct band gap at $k=0$ and their crystal structures are sustained zinc-blende or wurtzite-type with $x$ up to solubility limit. The lattice constants of A$^I_{1-x}$Mn$_x$B$^VI$ follow Vegard's law including Zn$_{1-x}$Mn$_x$O in Fig.3.4. Mn concentration dependence of absorption edge of Zn$_{1-x}$Mn$_x$O is also linear displayed in Fig.3.5 and expressed by $E_g = 3.273 + 1.32x$, expected from the other A$^I_{1-x}$Mn$_x$B$^VI$ DMS [1]. Low-temperature magneto-resistance of Zn$_{1-x}$Mn$_x$O (see, Fig.3.3) shows a similar behavior.
Figure 3.2: Optical absorption spectra of Zn$_{1-x}$TM$_x$O [20]

Figure 3.3: Magnetoresistance of Zn$_{1-x}$TM$_x$O (TM=Cr, Mn, Co and Ni) [20]

Figure 3.4: Mn content dependence of cell volume (top) and a- and c- axes lattice constants (bottom) for Zn$_{1-x}$Mn$_x$O films [18]
Figure 3.5: (a) Transmission spectra of Zn$_{1-x}$Mn$_x$O films measured at room temperature for various $x$ values. Numbers in the figure denote $x$. Inset: Photon energy dependence of $\alpha^2$ for deducing band gap ($E_g$) from the intersection of the dotted lines. (b) Variation of $E_g$ with Mn content. The solid line is fitted line expressed as $E_g = 3.273 + 1.32x$ (eV) [18].

to that of A$_{1-x}$Mn$_x$B$^{VI}$ and is understood as due to the spin splitting enhanced by the $s$-$d$ exchange interaction [36] and the rise of the Fermi level in the majority-spin subband due to the electron redistribution between the subbands [37]. The magnetic susceptibility of Zn$_{1-x}$Mn$_x$O showed a spin-glass behavior with the spin freezing temperature $T_F$ of about 13K in Fig.3.6. Magnetic-field dependence of the magnetization curve below $T_F$ is fitted to the modified Brillouin-function [1]. The exchange coupling constant between the nearest neighbors $J_1 = J_{d-d}$ has been obtained using a Curie-Weiss plot, and found to be the same order of magnitude as the other A$_{1-x}$Mn$_x$B$^{VI}$ DMS. Theoretically, strong antiferromagnetic interaction and the anion dependence of $J_1$ superexchange interaction is expected from fourth order perturbation calculation [14].

The above experiments show that Zn$_{1-x}$Mn$_x$O has similar physical properties to A$_{1-x}$Mn$_x$B$^{VI}$ DMS, and understood accordingly. However, two theoretical approaches have predicted that $p$-type Zn$_{1-x}$Mn$_x$O shows ferromagnetism with high Curie temperature [7, 32]. Synthesis and experiments on $p$-type material are strongly desired.
Figure 3.6: Magnetization normalized by that at 20 K for a Zn$_{0.64}$Mn$_{0.36}$O film measured during a zero-field-cooled (ZFC) and field-cooled (FC) runs in various magnetic fields. The curves are shifted vertically as represented by the dashed horizontal lines [23].

Figure 3.7: Curie-Weiss plot for a Zn$_{0.64}$Mn$_{0.36}$O film. The solid line represents a linear fit to the data for 120-300K with extrapolation to $T = 0$ K. Inset represents $-J_1/k_B$ derived from the fitting (circle) together with those for Zn$_{1-x}$Mn$_x$ Y ($Y=$O, S, Se and Te) (triangle). The error bars are determined from standard deviations of the fits for 80-300 K (bottom bar) and 200-300K (upper bar) [23]. The values of $-J_1/k_B$ for $Y=$S, Se and Te are derived from Ref.[1]
Chapter 4

Theories of carrier-induced ferromagnetism

Ferromagnetic III-V- and II-VI-based DMS and their quantum structures have been realized as in the preceding chapters. However, the origin of the carrier-induced ferromagnetism in DMS has been a controversial issue till now. To elucidate the mechanism of carrier induced ferromagnetism is desired since it will provide a useful guideline for material design of the DMS with the higher $T_c$. In this chapter, I summarize the three models for the origin of the carrier-induced ferromagnetism in DMS.

4.1 Introduction

Ferromagnetism in transition-metal compounds has been a long-standing issue in condensed-matter physics. Currently, colossal negative magnetoresistance in $R_{1-x}A_x\text{MnO}_3$ (R= rare-earth element, and A= divalent element) is upsurge of interest [44, 45]. Giant negative-magnetoresistance effect has also been observed in the III-V based DMS $Ga_{1-x}\text{Mn}_x\text{As}$ in the vicinity of a metal-insulator transition [21]. These common features may be a keypoint to understand the origin of the ferromagnetism in DMS. So far, several theories have been proposed and several problems remained unanswered:

1. Energy scale of $E_F$ and the $p$-$d$ exchange interaction.

2. Asymmetry of electron and hole doping.

3. Possibility of the ferromagnetism in the non-Mn transition-metal DMS.
There are three possible mechanisms to be considered here as the origin of the carrier-induced ferromagnetism. The first is the Ruderman-Kittel-Kasuya-Yosida (RKKY) model, the second is double-exchange (DE) model and the third is the $p-d$ exchange model.

4.1.1 RKKY model

One can consider the $s-d$ model (also called the Kondo-lattice model or Zener model),

$$H = -t \sum_{i,j,\sigma} (c_{i\sigma}^\dagger c_{j\sigma} + h.c.) + J_{pd} \sum_i \sigma_i \cdot S_i$$

where $J_{pd}$ represents the exchange interaction between spin of the carrier and spin of the TM. First, I consider the RKKY model. Ferromagnetism derived from RKKY interaction was first proposed for explaining ferromagnetic IV-VI semiconductors such as PbSnMnTe [46]. After, the carrier-induced ferromagnetism of III-V DMS Ga$_{1-x}$Mn$_x$As was discovered [2], the RKKY mechanism was applied to it. The RKKY exchange interaction between sites $i$ and $j$ is given by,

$$H = -J_{ij} S_i \cdot S_j, \quad \text{where } J_{ij} \text{ is given [47],}$$

$$J_{ij} = -\frac{2m_0 k_F^4}{\pi \hbar^2} J_{pd}^2 F(2k_F r_{ij}) \exp \left( -\frac{r_{ij}}{l} \right),$$

where $F(x) = -\frac{\cos x + \sin x}{x^2}$, $l$ is the mean free path of carriers and the exponential term $\exp(-\frac{r_{ij}}{l})$ represents the de-Gennes damping factor. (Here, I consider RKKY interaction in the three-dimensional for simplicity, RKKY model in other dimensions were already extensively discussed [32].) As DMS has much a smaller Fermi wavenumber compared to an ordinary metal, the ferromagnetic interaction become long-ranged and de Gennes factor suppresses the antiferromagnetic part. This simple expression for RKKY interaction furthermore shows that the Curie temperature is proportional to the carrier effective mass and the square of the $p-d$ exchange constant ($J_{pd} \propto N\beta$). Also, this theory predict that $p$-type materials are more advantageous for ferromagnetism because of the large effective mass and the stronger exchange interaction compared to $n$-type materials. Recently, Dietl et al [31] proposed a modified RKKY model (they called it as Zener model) which included spin-orbit interaction, too. In $p$-type materials, as the carrier concentration increases, the Fermi level approaches the $\Gamma_7$ spin-orbit split band and increases the DOS effective mass. As the DOS effective mass increases, the destructive effect of the spin-orbit interaction on the magnitude of the spin polarization become largely reduced. This explains why the Curie temperature of Ga$_{1-x}$Mn$_x$As is
higher than that of $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ if their hole concentration were the same order of magnitude. Also, as the anion element becomes lighter, $p$-$d$ hybridization become stronger. They predicted that semiconductors with lighter anion which are often wide-gap semiconductors may become ferromagnetic with a high Curie temperature shown in Fig. 4.1. However, the RKKY mechanism is based on perturbation theory and requires the condition that $E_F \gg |N\beta|$. This condition is not realistic, although RKKY mechanism explains many experimental results.

4.1.2 Double-exchange model

The DE model [50, 51], where the effective hopping for the Mn 3$d$ conduction electrons varies with the angle between the Mn 3$d$ spins due to strong Hund’s coupling ($J_{pd} < 0$ in the above $s$-$d$ model), has long been used to explain the coexistence of ferromagnetism and metallic conduction in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.2 < x < 0.4$).

Using the Korringa-Kohn-Rostoker (KKR) Green’s function method based on the local-density-approximation band structure calculation, Sato and Katayama-Yoshida show that doped holes in $\text{Zn}_{0.75}\text{Mn}_{25}\text{O}$ partially occupy Mn 3$d$ states and stabilize the ferromagnetic (FM) state against the anti-ferromagnetic (AFM) state which is stabilized in the electron-doped case, because the Mn 3$d$ band in the FM state is broader than that in the AFM state [7](Fig. 4.2). This mechanism that carrier induced-ferromagnetism in
Figure 4.2: Total DOS (solid line) and the local density of the Mn $d$ states (dotted line) in the hole-doped (Zn,Mn)O. N atoms replace the O atoms up to 25%. The DOS are shown for (a) the ferromagnetic states and (b) the anti-ferromagnetic states. In (b), the density of states per Mn atom is shown [7].
the III-V based DMS had been already pointed out by Akai [33]. When we compare hole-

and electron-doped cases, the electron-doped case does not show the ferromagnetism even for carrier concentration up to 80% shown in Fig.4.3. As far as the DE model is concerned, electron doping showed equivalent to hole doping from a view point of the stabilization of ferromagnetic states. They analyzed the KKR calculation and found that the doped electrons mainly occupied to the cation (Zn and Ga) 4s states and did not occupy Mn 3d states. As a result, an energy gain by the DE interaction was not expected. Moreover, the calculation showed that the magnetic ground states of the other 3d transition-metal ions (V, Cr, Fe, Co or Ni) doped into ZnO were ferromagnetic without any carrier doping (Fig. 4.4). This DE model is not restricted to $E_F \gg |N\beta|$ and does not relate the $T_c$ value and the $p-d$ exchange constant explicitly.

In the simple DE model, it is implicitly assumed that doped carriers are Mn d holes. However, in II-VI chalcogen-based-DMS and III-V based DMS, doped holes have mainly
Figure 4.4: Chemical trend of the magnetic states for 3d transition-metal atoms doped into ZnO. Results for 25% doping are shown. The total magnetic moment per transition-metal atom is also shown [7].

$p$-hole character. It is the shortcoming of the DE model.

### 4.1.3 $p$-$d$ exchange model

Recently, the $p$-$d$ exchange model [48, 49, 44] has been proposed to explain the colossal magnetoresistance in the thin films of Mn-perovskite compounds [45]. So far, the coexistence of ferromagnetism and metallic conduction has long been explained by the DE model. In the DE model, it is implicitly assumed that doped carriers are Mn $d$ holes or electrons. This assumption is not justified by both electron-energy-loss [54] and photoemission spectroscopies [55] in Mn-perovskite, which have shown that the ferromagnetic manganites ($x < 0.4$) are doped charge-transfer insulators with carriers mainly residing on the oxygen orbitals. This situation is similar to the ferromagnetism
in DMS because II-VI and III-V DMS are charge-transfer types, namely, they have a $\Delta < U$ type ground state.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.5}
\caption{(a): Energy diagram for a system with a charge-transfer type electronic structure. (b): Ferromagnetic ordering of the TM spins induced by the oxygen hole.}
\end{figure}

According to Khomskii and Sawatzky [44], I briefly discuss the $p$-$d$ exchange model. If we consider a charge-transfer type system with oxygen holes and treat these holes as localized, one should have the situation depicted in Fig.4.5 (a). I should mention that of course there is always hybridization between $d^nL$ and $d^{n-1}$ configurations in the
hole-doped ground state and they can be strongly mixed. In Fig.4.5 (b), the oxygen hole (spin $\frac{1}{2}$) sitting between the two TM ions would make their spins parallel [56]. Exchange interaction between the oxygen and the TM spins would be much stronger than that between TM ions themselves because $J_{TM-O}$ and $J_{TM-TM}$ are expressed by,

$$J_{TM-O} \sim \frac{t_{pd}^2}{|\Delta|} \quad \text{and} \quad J_{TM-TM} \sim \frac{t_{pd}^4}{|\Delta|^3},$$

where $t_{pd}$ is a hybridization matrix element between the TM $d$ and oxygen $p$ orbitals and $J_{TM-O}$ is expressed by the $p$-$d$ exchange constant $N\beta$ in DMS. If two TM-ions spin configuration is parallel, the energy gain is about two times larger than that of antiparallel configuration. Therefore, the $p$-$d$ exchange interaction causes two TM-ions spin ferromagnetic. On the other hand, in the ordinary DMS, antiferromagnetic superexchange interaction always exists and TM ions spin alignment is antiferromagnetic [14, 58]. This interaction always exists not only in $n$-type DMS but also in $p$-type DMS. However, antiferromagnetic superexchange interaction is derived from fourth-order perturbation and $p$-$d$ exchange constant is derived from second-order one and hence $p$-$d$ exchange contribution is larger than antiferromagnetic one. Therefore, ferromagnetism appear in $p$-type DMS. Similar model is often used for high-$T_c$ superconductor physics [57]. (This model is an effective Hamiltonian in the low energy region called $t$-$J$ model.)

Next, we consider the motion of oxygen holes. Of course the corresponding band would be a mixture of both oxygen $p$ and TM $d$ states, but in a zeroth-order approximation it can be understood as having predominantly $p$ character. Exchange interaction of the remaining TM spins ($d^n$ configuration) via this band may provide a mechanism for ferromagnetism, which in this case will exist together with the metallic conductivity. This picture would be identical to the already mentioned DE model. The $p$-$d$ exchange model is useful for explaining the ferromagnetism in DMS on the insulator side and the relationship between the ferromagnetism and the electronic structure of DMS. However, dilute and random substitutions of Mn ions in DMS makes the effective transfer integral $t_{pd}$ rather small. More elaborate $p$-$d$ exchange model is desired in considering ferromagnetism in DMS.

Recently, several new approaches for the origin of carrier-induced ferromagnetism in DMS were proposed [34, 35]. At this stage, however, the microscopic origin of the ferromagnetic mechanism in DMS remains to be clarified.
Chapter 5

X-ray photoelectron Spectroscopy of $\text{Zn}_{1-x} \text{TM}_x \text{O}$

Generally speaking, core-level photoemission spectra of transition-metal compounds show that the main peak and satellite structures. This indicates that the Coulomb correlation and hybridization effects are strong. Particularly, the $2p$ core-level spectra of transition-metal atoms are suitable for obtaining the electronic structure parameters because of the relatively high intensity and the simple structures compared to the other core levels. We have measured the transition-metal $2p$ core-level spectra of $\text{Zn}_{1-x} \text{TM}_x \text{O}$ ($\text{TM}=\text{Cr}, \text{Mn}, \text{Fe}$ and $\text{Ni}$).

5.1 Experiment

I have measured $\text{Zn}_{1-x} \text{TM}_x \text{O}$ with Al dopant, which were prepared by pulsed-laser deposition on sapphire (001) or ScAlMgO$_4$ (001) substrates (See, table 8.2).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$x$</th>
<th>substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Zn}_{1-x} \text{Mn}_x \text{O}$</td>
<td>0.13</td>
<td>sapphire</td>
</tr>
<tr>
<td>$\text{Zn}_{1-x} \text{Cr}_x \text{O}$</td>
<td>0.10</td>
<td>sapphire</td>
</tr>
<tr>
<td>$\text{Zn}_{1-x} \text{Fe}_x \text{O}$</td>
<td>0.10</td>
<td>sapphire</td>
</tr>
<tr>
<td>$\text{Zn}_{1-x} \text{Ni}_x \text{O}$</td>
<td>0.05</td>
<td>ScAlMgO$_4$</td>
</tr>
</tbody>
</table>

Table 5.1: Nominal concentration $x$ measured by EPMA and corrected by ICP
X-ray diffraction showed the wurtzite structure without impurity phase and electron probe microanalysis (EPMA) showed a homogeneous distribution of TM in the film. The content of the TM ions were determined by inductivity-coupled plasma (ICP) analysis. The carrier density of Zn$_{0.87}$Mn$_{0.13}$O was determined by Hall measurements to be 1.4x10$^{20}$ cm$^{-3}$. (The carrier density of the other sample are unknown.) The detailed sample preparation procedure and their optical and transport properties have been reported elsewhere [18]. X-ray photoemission (XPS) measurements were performed using the Mg $K\alpha$ ($h\nu = 1253.6$ eV) line and the Al $K\alpha$ ($h\nu = 1486.6$ eV) line. The energy resolution was about 1.0 eV in both lines from the Au $4f_{\frac{3}{2}}$ core-level spectrum. Photoelectrons were collected using a VSW hemispherical analyzer in the angle-integrated mode. All the measurements were performed in an ultra high vacuum below 2.0 x 10$^{-9}$ Torr at room temperature. To keep the sample surfaces clean, we repeated Ar-ion sputtering (1 kV). After sputtering, the TM content may change from the bulk value but the TM core-level XPS intensity agreed with the bulk values to within ±20%. In the core-level photoemission, the plasmon peak appears on the higher binding energy side of the main peak. The plasmon frequency $\omega_p$ is expressed by,

$$\omega_p = \sqrt{\frac{ne^2}{\epsilon_0 m}}$$

where n and m denote the density and the mass of electrons, respectively. The separation between the plasmon and the main peaks corresponds to the plasmon energy $\hbar\omega_p$. I have estimated the plasmon energies of Zn$_{1-x}$TM$_x$O and obtained $\hbar\omega_p \sim 20$eV.

5.2 Result

5.2.1 Zn$_{1-x}$Mn$_x$O

Mn-doped II-VI based DMS has been extensively studied. The valence state of the Mn ion was determined to be Mn$^{2+}$ from the total spin $S = \frac{5}{2}$ deduced from electron-spin resonance. The Mn content was determined by EPMA and corrected by ICP analysis. The carrier density was determined by Hall measurements to be 1.4x10$^{20}$ cm$^{-3}$ ($x = 0.13$). The experimental Mn 2p core-level spectrum for the $x = 0.13$ sample is shown in Fig. 5.1 (The result for $x = 0.07$ was almost identical to $x = 0.13$). The broad peak at 667 eV is Mn $L_{2,3}M_{2,3}M_{4,5}$ Auger emission. Each of the $j=3/2$ and $j=1/2$ spin-orbit components of the Mn 2p core level consists of the main peak and the satellite
Figure 5.1: Mn 2p core-level photoemission spectrum of Zn_{0.87}Mn_{0.13}O and its CI cluster-model analysis. The dashed curve represents the integral background. The bottom panel shows a decomposition of the spectrum into final-state configurations.

on the higher binding energy side of the main peak separated by $\sim 6$ eV. The presence of the satellite structure indicates that strong Coulomb interaction among the Mn 3d electrons and hybridization between the Mn 3d and ligand O 2p orbitals are important. The Mn 2p core-level spectrum has been fitted using CI analysis as shown in Fig. 5.1. By fitting the spectrum (Fig. 5.1), I have obtained $\Delta=7.0\pm 1.0$ eV, $U=5.0\pm 1.0$ eV and $(pd\sigma)=-1.4\pm 0.1$ eV, hence $\Delta_{\text{eff}} \approx 9$ eV and $U_{\text{eff}} \approx 9$ eV. The ground state contains 88% $d^5$, 11% $d^6L$ and 1% $d^7L^2$ configurations and the number of $d$ electrons is $n_d=5.1$. These parameters are similar to those for MnO, in which the Mn ion is octahedrally coordinated [30].
Figure 5.2: Cr 2p core-level photoemission spectrum of Zn$_{0.90}$Cr$_{0.10}$O and its CI cluster-model analysis. The dashed curve represents the integral background. The bottom panel shows a decomposition of the spectrum into final-state configurations.

5.2.2 Zn$_{1-x}$TM$_x$O ($TM=$Cr, Fe and Ni)

The solubility of Cr, Fe and Ni ions in II-VI compounds is much smaller than Mn-based DMS. Non-equilibrium crystal growth methods like molecular beam epitaxy has enabled us to introduce a large amount of these ions.

So far, Cr-doped DMS were very attractive material because its $p$-$d$ exchange interaction was ferromagnetic in the DMS [38], unlike the Mn-, Fe- and Co-doped DMS. Magnetic properties of Cr-doped DMS show characteristic features intermediated between the Mn- and Co-doped DMS and the Fe-based DMS because of a strong static Jahn-Teller distortion around the Cr ions [39]. In spite of Goodenough-Kanamori rules [41], that tetrahedral coordination always allows some AF superexchange channel for any $d$-orbital level occupancy, ferromagnetic superexchange interaction was proposed theoretically [40].
Figure 5.3: Fe 2p core-level photoemission spectrum of Zn$_{0.90}$Fe$_{0.10}$O and its CI cluster-model analysis. The dashed curve represents the integral background. The bottom panel shows a decomposition of the spectrum into final-state configurations.

Figure 5.2 shows the Cr 2p core-level spectrum of Zn$_{0.90}$Cr$_{0.10}$O and its CI cluster-model fit. Non-monotonic background including the structure around 598 eV is due to the energy loss (plasmon) satellite accompanying the Cr 2P$_{3/2}$ peaks. The plasmon energy obtained by the experimental spectrum (Fig.5.2) is about 20 eV and it is almost the same value as the calculated one. By fitting the spectrum using the CI cluster-model as shown in Fig. 5.2, I have obtained $\Delta=7.5\pm1.0$ eV, $U=4.5\pm1.0$ eV and $(pd\sigma)=-1.5\pm0.1$ eV, and hence $\Delta_{\text{eff}} \simeq 5.4$ eV and $U_{\text{eff}} \simeq 4.0$ eV. The ground state contains 81% $d^4$ and 18% $d^6L$ configuration and the number of $d$ electrons is $n_d=4.2$.

Fe-doped DMS shows Van-Vleck paramagnetism in the low temperature limit because the ground state has the $A_1$ symmetry due to the spin-orbit interaction which is non-degenerate [1] and it has a magnetic excited state $\sim 10$ cm$^{-1}$ above the ground state [1]. However, I assume the ground state of the Fe$^{2+}$ ion to be in the high-spin...
Figure 5.4: Ni 2p core-level photoemission spectrum of Zn$_{0.95}$Ni$_{0.05}$O and its CI cluster-model analysis. The dashed curve represents the integral background. The bottom panel shows a decomposition of the spectrum into final-state configurations.

configuration ($^5E$ symmetry with $S = 2$ ) in analyzing photoemission spectrum because the energy scale for photoemission spectrum is much larger than that of the spin-orbit interaction and I measured it at the room temperature. Figure 5.3 shows the Fe 2p core-level spectrum of Zn$_{0.90}$Fe$_{0.10}$O and its CI cluster-model fit. The Fe 2$p_{1/2}$ satellite is obscured by the overlapping due to O KLL Auger emission. By fitting the spectrum using the CI cluster-model analysis shown in Fig. 5.3, I have obtained $\Delta = 6.5 \pm 1.0$ eV, $U = 5.5 \pm 1.0$ eV and $(pd\sigma) = -1.3 \pm 0.1$ eV, hence $\Delta_{\text{eff}} \approx 8.4$ eV and $U_{\text{eff}} \approx 4.9$ eV. The ground state contains 89% $d^6$ and 11% $d^7 L$ configurations and the number of d electrons is $n_d = 6.1$.

There have been few experimental reports on DMS with Sc, Ti, V, Ni or Cu ions because of the low solubility of these ions in II-VI semiconductors. Magnetic circular dichroism experiment on Zn$_{1-x}$Ni$_x$Te [42] showed that Ni-doped DMS has AF $p-d$
exchange interaction, consistent with the recently cluster-model analysis [11]. Figure 5.4 shows the Ni 2p core-level spectrum of Zn_{0.9}Ni_{0.1}O and its CI cluster-model fit. This fit was made including full-multiplet structure. By fitting the spectrum as shown in Fig. 5.4, I have obtained $\Delta = 4.5 \pm 1.0$ eV, $U = 6.0 \pm 1.0$ eV and $(p\sigma) = -1.6 \pm 0.1$ eV, hence $\Delta_{\text{eff}} \simeq 5.9$ eV and $U_{\text{eff}} \simeq 5.9$ eV. The ground state contains 84% $d^7$ and 15% $d^7L$ and 1% $d^8L^2$ configurations and the number of $d$ electrons is $n_d = 8.2$.

From the above transition-metal 2p core-level spectra and cluster-model fitting were performed and summarized in Table 5.2. By the present analyses, I could understand the chemical trend in Zn_{1-x}TM_xO. As the atomic number of the TM ion increases (Cr $\rightarrow$ Mn $\rightarrow$ Fe $\rightarrow$ Ni), $\Delta$ becomes smaller and $U$ becomes larger. The electronic ground states of Zn_{1-x}TM_xO are more ionic characters compared to the other conventional DMS.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta(\Delta_{\text{eff}})$</th>
<th>$U(U_{\text{eff}})$</th>
<th>$(p\sigma)$</th>
<th>$n_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn_{1-x}Cr_xO</td>
<td>7.5 (5.4)</td>
<td>4.5 (4.0)</td>
<td>-1.5</td>
<td>4.2</td>
</tr>
<tr>
<td>Zn_{1-x}Mn_xO</td>
<td>7.0 (9.2)</td>
<td>5.0 (9.4)</td>
<td>-1.4</td>
<td>5.1</td>
</tr>
<tr>
<td>Zn_{1-x}Fe_xO</td>
<td>6.5 (8.4)</td>
<td>5.5 (4.9)</td>
<td>-1.3</td>
<td>6.1</td>
</tr>
<tr>
<td>Zn_{1-x}Ni_xO</td>
<td>4.5 (5.9)</td>
<td>6.0 (5.9)</td>
<td>-1.6</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Table 5.2: Electronic structure parameter sets and the ground state $d$ electron numbers of Zn_{1-x}TM_xO (TM=Cr, Mn, Fe and Ni)
Chapter 6

Resonant photoemission study of Zn$_{0.93}$Mn$_{0.07}$O

To obtain more detailed information about the electronic structure of Zn$_{1-x}$Mn$_x$O, we have measured valence-band photoemission spectra of Zn$_{1-x}$Mn$_x$O ($x = 0.07$) using resonant photoemission spectroscopy (RPES). I have obtained the Mn 3$d$ density of state (DOS), and electronic structure parameters $U$, $\Delta$ and $(pd\sigma)$ using CI cluster-model analysis.

6.1 Introduction

The valence-band structure is very important because physical properties of the material are largely determined to energy and momentum distribution of electron in it. In particular, Mn 3$d$ position in parent semiconductor DOS, which is very essential issue for its optical and electrical properties of Mn-based DMS, influences the $p$-$d$ exchange interaction and $d$-$d$ superexchange interaction. One-electron picture obtained from band structure calculation is very useful to understand the properties of the host semiconductor, but transition metal compounds band structure calculations are always insufficient for themselves because of the strong electron correlation effects and this is applied to DMS, too. RPES is a powerful technique to investigate subtle changes in the electronic structure induced by the impurity in the host material.
6.2 Experiment

Zn$_{1-x}$Mn$_x$O thin films ($x = 0.07$) with Al dopant were prepared by pulsed-laser deposition on ScAlMgO$_4$ (001) substrates. X-ray diffraction showed the wurtzite structure without impurity phase and electron probe microanalysis showed a homogeneous distribution of Mn in the film. The valence state of the Mn ion was determined to be Mn$^{2+}$ from the total spin $S = \frac{5}{2}$ deduced from an electron-spin resonance. The Mn content was determined by EPMA and corrected by ICP analysis. The carrier density was determined by Hall measurements to be $2.9 \times 10^{19}$ cm$^{-3}$ ($x = 0.07$). Detailed sample preparation procedure and their optical and transport properties have been reported elsewhere [18].

Photoemission experiment was performed at BL-18A of Photon Factory, High Energy Accelerator Research Organization. For valence-band measurements, synchrotron radiation in the energy range 20-80 eV was used. The resolution was estimated to be about 200 meV from the Fermi edge of Ta wire in contact with the samples. We chose the Zn 3d peak as a reference for the intensity normalization and the binding-energy calibration [The Zn 3d peak in ZnO is located at $E_B=8.81$ eV from valence band maximum (VBM) [24]] to correct for weak charging effect and possible band-bending effect. Photoelectrons were collected using a VG CLAM hemispherical analyzer in the angle-integrated mode. All the measurements were performed in an ultra high vacuum below $10^{-10}$ Torr at room temperature. To keep the sample surfaces clean, we repeated Ar-ion sputtering (1 kV) and annealing at 250°C. The low temperature annealing was done to prevent Al$_2$O$_3$ segregation. Because of the temperature constraint, low energy electron diffraction patterns of 1 x 1 were not clearly observed. After sputtering and annealing, the Mn content may change from the bulk value but the Mn core-level XPS intensity agreed with the bulk values to within ±20%.

6.3 Result

Figure 6.1 shows valence-band photoemission spectra of Zn$_{0.93}$Mn$_{0.07}$O were taken at various photon energies in the Mn 3p $\rightarrow$ 3d core excitation region, where resonant photoemission effect occurs. RPES can be used to extract the Mn 3d partial density of states (PDOS). Mn 3p $\rightarrow$ 3d core absorption occurs at photon energies above 50 eV as shown in the inset of Fig. 6.1. Interference between the normal photoemission and Mn
Figure 6.1: A series of Photoemission spectra of $\text{Zn}_{0.93}\text{Mn}_{0.07}\text{O}$ in the valence-band region. The inset shows the absorption spectra of $\text{Zn}_{0.93}\text{Mn}_{0.07}\text{O}$ recorded in the total electron yield mode.
3p-to-3d transition followed by a 3p-3d-3d Super-Koster-Krönig decay generates a Fano like intensity profile in the valence-band spectra and enhances the Mn 3d electron's emission. Binding energies are referenced to the VBM for the binary host ZnO. Similar experiments have been performed for other DMS such as Ga₁₋ₓMnxAs [25], Cd₁₋ₓMnxY [26, 27] and Zn₁₋ₓMnxY (Y=S, Se, Te) [28]. In Fig. 6.1, the peaks at 2.5 eV, 6 eV and 9 eV have mainly character of non-bonding O 2p, O 2p hybridization with Zn 4s and Zn 3d, respectively [29].

![Figure 6.2: Mn 3d PDOS of Zn₀.₉₃Mn₀.₀₇O and its CI cluster-model analysis. The inset shows comparison with the Mn 3d PDOS of Zn₀.₆₈Mn₀.₃₂Te, Zn₀.₈₁Mn₀.₁₉Se and Zn₀.₈₁Mn₀.₁₉S. Binding energies are referenced to the VBM of the host semiconductors. The bottom panel shows a decomposition of Mn 3d PDOS spectrum of the Zn₁₋ₓMnxO into final-state configurations.](image)

Figure 6.2 shows the Mn 3d PDOS of Zn₀.₉₃Mn₀.₀₇O, which has been obtained by subtracting the off-resonance spectrum ($h\nu = 49$ eV) from the on-resonance spectrum ($h\nu = 50.5$ eV) (see, Fig. 6.1). To remove oxygen 2p contribution as possible (in this
photon energy range, O 2p cross-section $\sigma_{O_{2p}}(h\nu)$ is about 10 times larger than the other chalcogen p states [53]), two spectra are normalized, first, Zn 3d area intensities and next, multiplied $\sigma_{Zn_{3d}}(h\nu)/\sigma_{O_{2p}}(h\nu)$. The inset shows the Mn 3d PDOS of the other II-VI chalcogenide-based DMS.[28] The spectral features of the II-VI-based II-VI DMS are similar to each other, showing three characteristic features: first shoulder (0-2 eV), main peak (3.5 eV), higher energy satellite structure (5-9 eV). Interpretation based on the one-electron energy level scheme is that the 3.5 eV peak is mainly the Mn 3d-e localized states and that the Mn 3d-$t_2$ states are more strongly hybridized with the anion p states and shows broad DOS (0-5 eV), but high energy satellite cannot be understood within the one-electron picture. On the other hand, CI cluster-model interpretation indicates that the shoulder and main peak are predominantly consist of $d^5L$ final states ($L$ denotes a O-2p hole) and the high energy satellite is derived from the unscreened $d^4$ atomic like final states and the charge-transfer final states. Note that the one-electron energy does not equal the value measured in photoemissson experiments ($d^5 \rightarrow d^4$) because of strong orbital relaxation and correlation effects. In either picture, the final states broad Mn 3d structure implies strong p-d hybridization. As shown in the inset of Fig. 6.2, Mn 3d PDOS spectrum for Zn$_{1-x}$Mn$_x$O is different from the other chalcogen-based DMS at a first glance, but one can see that the chemical trend is sustained in the whole series of materials. On going from Te to Se to S to O, the intensity of the first shoulder relative to the main peak becomes stronger, and the satellite structures weaker. These changes are rather abrupt between S and O due to the much higher electro negativity of oxygen than the other chalcogens.

To make more unambigious the conclusion on the electronic structure of Zn$_{1-x}$Mn$_x$O, more systematic studies of Zn$_{1-x}$Mn$_x$O samples ranging from $x = 0$ to the solubility limit ($x \approx 0.35$) with high electrical conductivity are necessary. Techniques to obtain atomically flat surfaces are also desired.
Chapter 7

Discussion

7.1 Chemical trend in II-VI diluted magnetic semiconductors

Now, I have obtained the electronic structure parameter sets for Zn_{1-x}MnxY (Y = O, S, Se and Te) and Zn_{1-x}TMxO (TM = Cr, Mn, Fe and Ni) by using CI cluster-model analysis. I summarize these parameters and discuss the possibility of ferromagnetism these compounds.

7.1.1 Anion dependence in Zn_{1-x}MnxY (Y = O, S, Se and Te)

The anion dependence of the electronic structure parameters of Zn_{1-x}MnxY (Y = O, S, Se and Te) are shown in Fig. 7.1. Chemical trend in these results is easily understood from the anion electronegativities like the trend in other transition-metal compounds [12].

7.1.2 Transition-metal-ion dependence in Zn_{1-x}TMxO (TM = Cr, Mn, Fe and Ni)

The transition-metal-ion dependence of the electronic structure parameters of Zn_{1-x}TMxO (TM = Cr, Mn, Fe and Ni) are shown in Fig. 7.2. Chemical trend in these results is easily understood. As the atomic number increases, the positive charge of the transition-metal ion increases, and then the d electron wavefunction shrinks. This explains why U increase with the atomic number. As for Δ, atomic number increases, the energy level
Figure 7.1: Anion dependence of the electronic structure parameters for \( \text{Zn}_{1-x}\text{Mn}_x\text{Y} \) 
\((Y = \text{O}, \text{S}, \text{Se} \text{ and Te})\)
Figure 7.2: Upper panel: Transition-metal ion dependence of electronic structure parameters of \( \text{Zn}_{1-x} \text{TM}_x \text{O} \) \( (\text{TM} = \text{Cr, Mn, Fe and Ni}) \). Lower panel: Transition-metal ion dependence of calculated the \( p-d \) exchange constants of \( \text{Zn}_{1-x} \text{TM}_x \text{O} \) \( (\text{TM} = \text{Cr, Mn, Fe and Ni}) \).
of the transition metal become deeper relative to the anion, making $\Delta$ smaller. Trend of the hybridization strengths ($pd\sigma$) is mainly governed by the interatomic distances between the transition metal ions and anions. As the interatomic distance decreases, the overlap of the 3$d$ orbitals with the anion $p$ orbitals increases the value of ($pd\sigma$). However, ($pd\sigma$) in Fig. 7.2 shows non-monotonic behavior. These uncertainties in the parameters were discussed in Ref [52] before. I think these parameters are effective ones and useful for understanding chemical trend of DMS.

7.1.3 $p$-$d$ exchange interaction in Zn$_{1-x}$TM$_x$Y

I have estimated the $N\beta$ values using the electronic structure parameters deduced from the CI cluster-model analysis (Lower panel in Figs. 7.1 and 7.2). Zn$_{1-x}$Mn$_x$O has a large $p$-$d$ exchange constant as those of the II-VI chalcogenide-based DMS and III-V-based DMS. While the $p$-$d$ hybridization strength in the ground state is much weaker in Zn$_{1-x}$Mn$_x$O than that in the other Mn-doped DMS. The origin of the large $N\beta$ value in Zn$_{1-x}$Mn$_x$O is the strong $p$-$d$ hybridization in the first ionization state because of the energy separation $U_{\text{eff}} - \delta_{\text{eff}}$ is small. In calculating $p$-$d$ exchange constant for Zn$_{1-x}$Cr$_x$O and Zn$_{1-x}$Ni$_x$O, I have considered Jahn-Teller distortion of them assuming that the population of the degenerate $t_2$ orbitals is equal [11]. In Zn$_{1-x}$Cr$_x$O and Zn$_{1-x}$Ni$_x$O, the positive $N\beta$ values are predicted. The energy denominator $-\delta_{\text{eff}} + u' - j$ (see Appendix) of the ferromagnetic contribution is small compared to antiferromagnetic parts in these compounds. In future, other experiments, for example, magneto-optical ones of Zn$_{1-x}$TM$_x$O are desired to compare the calculated and experiment $N\beta$ values.

7.2 Possibility of ferromagnetism in diluted magnetic semiconductors

First, I compare the $p$ and $n$-type Zn$_{1-x}$Mn$_x$O. The large $\Delta$ value deduced here indicates that in the ground state, the Mn impurity in Zn$_{1-x}$Mn$_x$O is in a relatively localized ionic state as in MnO [30]. This is very different from the other II-VI- and III-V-based DMS, which are characterized by small $\Delta$ (usually $\Delta < U$) and hence strong admixture of the Mn 3$d$ and the host valence band in the ground state.

In Zn$_{1-x}$Mn$_x$O, on the other hand, the valence holes will interact more strongly with the Mn 3$d$ electrons because the separation between the Mn 3$d$ occupied state
Figure 7.3: Schematic description of the electronic structure of $n$- and (hypothetical) $p$-type $\text{Zn}_{1-x}\text{Mn}_x\text{O}$. 
and the valence band $U_{\text{eff}} - \delta_{\text{eff}} \approx 1$ eV is rather small. A schematic description of the $n$- and $p$-type electronic structures of the Zn$_{1-x}$Mn$_x$O is shown in Fig. 7.3. In $n$-type Zn$_{1-x}$Mn$_x$O, electrons occupy mainly the Zn 4s and Mn 4s derived host-conduction band and the Mn 3d electron number change little. On the other hand, in the $p$-type Zn$_{1-x}$Mn$_x$O valence holes ($p$-holes) strongly hybridize with the Mn 3d states like the photo-produced hole in the photoemission final state dose. Moreover, the occupied Mn 3d electrons have a strong antiferromagnetic coupling with the valence holes (due to the large negative $N\beta$ value), and the Mn-Mn interaction becomes effectively ferromagnetic mediated by the polarization of the valence holes.

Next, I consider the other transition-metal-doped DMS. Dietl et al. derived the relationship between the $p$-$d$ exchange constant and Curie-temperature $T_c$ using $6\times6$ Kohn-Luttinger band-structure formalism,

$$T_c \propto x_{\text{eff}} (N\beta)^2$$

where $x_{\text{eff}}$ is the effective transition-metal concentration considered about the antiferromagnetic superexchange interaction [31]. If this theory can be applied, Zn$_{1-x}$Mn$_x$O is the best material in the Zn$_{1-x}$TM$_x$O series ($TM = \text{Cr, Mn, Fe and Ni}$) (I ignore the anti-ferromagnetic superexchange interaction contribution) for ferromagnetism.

As I considered about the DE model and $p$-$d$ exchange model, photoemission experiments of Zn$_{1-x}$Mn$_x$O and subsequent CI cluster-model analysis show that the ground state of $p$-type Zn$_{1-x}$Mn$_x$O has not only Mn 3d-hole character, but also considerable O 2p-hole character. This means that in the first approximation the $p$-$d$ exchange model is more appropriate model to describe the carrier-induced ferromagnetism in oxide-based DMS. In the $p$-$d$ exchange model, the ferromagnetic contribution $J_{TM-O}$ is proportional to $N\beta$ and this is the same as the model proposed by Dietl et al.. From the view point of the $p$-$d$ exchange model, Zn$_{1-x}$Mn$_x$O is favorable for ferromagnetism because of the large $|N\beta|$ value. However, smaller the $|U_{\text{eff}} - \delta_{\text{eff}}|$ is, the worse the perturbation approach becomes, and the electronic structure is no more simple charge-transfer type and a more elaborate approach become necessary.

In any case, once ferromagnetism appears, Zn$_{1-x}$Mn$_x$O will be a more controllable system than the other DMS in the sense that the carrier concentration and the Mn content can be varied independently in a wide range.
Chapter 8

Conclusion

In conclusion, I have measured the transition-metal 2p core-level photoemission spectra of $Zn_{1-x}TM_xO$ ($TM=Cr$, Mn, Fe and Ni) and valence-band photoemission spectra of $Zn_{0.93}Mn_{0.07}O$ and obtained the electronic structure parameters using CI cluster-model analysis. Using these parameters, we have estimated the $p$-$d$ exchange coupling constant $N\beta$. These values are summarized in Table 8.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta(\Delta_{\text{eff}})$</th>
<th>$U(U_{\text{eff}})$</th>
<th>$(pd\sigma)$</th>
<th>$n_d$</th>
<th>$N\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Zn_{1-x}Cr_xO$</td>
<td>7.5 (5.4)</td>
<td>4.5 (4.0)</td>
<td>-1.5</td>
<td>4.2</td>
<td>1.2</td>
</tr>
<tr>
<td>$Zn_{1-x}Mn_xO$</td>
<td>7.0 (9.2)</td>
<td>5.0 (9.4)</td>
<td>-1.4</td>
<td>5.1</td>
<td>-2.1</td>
</tr>
<tr>
<td>$Zn_{1-x}Fe_xO$</td>
<td>6.5 (8.4)</td>
<td>5.5 (4.9)</td>
<td>-1.3</td>
<td>6.1</td>
<td>-1.4</td>
</tr>
<tr>
<td>$Zn_{1-x}Ni_xO$</td>
<td>4.5 (5.9)</td>
<td>6.0 (5.9)</td>
<td>-1.6</td>
<td>8.2</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 8.1: Electronic structure parameter sets and $p$-$d$ exchange constants for $Zn_{1-x}TM_xO$ ($TM=Cr$, Mn, Fe and Ni)

In $Zn_{0.93}Mn_{0.07}O$, the Mn 3d PDOS is relatively high near the VBM. I predict that if one can dope the system with sufficient amount of holes, the holes will strongly hybridize with the Mn 3d state and will induce strong ferromagnetic coupling between the Mn 3d spins. In future, temperature-dependent photoemission studies of the other transition-metal based DMS and $p$ type-material will be very interesting to investigate the origin of ferromagnetism in DMS.
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Appendix

Atomic configurations and electronic structure parameters

Table 8.2: Ground state configuration, local moments and Racah parameters (in eV) $B$ and $C$, taken from [43], for $TM$ ions in $Zn_{1-x}TMxO$.

<table>
<thead>
<tr>
<th>TM ion (spin state)</th>
<th>Ground-state configuration</th>
<th>Local moment, $S$</th>
<th>Racah parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{2+}$ (HS)</td>
<td>$t_{2g}^4 e_{g}^2$</td>
<td>$\frac{5}{2}$</td>
<td>0.119, 0.412</td>
</tr>
<tr>
<td>Cr$^{2+}$ (HS)</td>
<td>$t_{2g}^2 e_{g}^2$</td>
<td>2</td>
<td>0.103, 0.425</td>
</tr>
<tr>
<td>Fe$^{2+}$ (HS)</td>
<td>$t_{3g}^3 e_{g}^2 e_{g}$</td>
<td>2</td>
<td>0.131, 0.484</td>
</tr>
<tr>
<td>Ni$^{2+}$ (HS)</td>
<td>$t_{2g}^1 t_{2g}^1 e_{g}^2$</td>
<td>1</td>
<td>0.135, 0.600</td>
</tr>
</tbody>
</table>

Table 8.3: Multiplet correction for $\Delta$ and $U$ of the TM ions.

<table>
<thead>
<tr>
<th>$d^n$</th>
<th>$\Delta_{\text{eff}}$</th>
<th>$U_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^4$</td>
<td>$\Delta - 4(-\frac{14}{9}B + \frac{7}{9}C) - 14B$</td>
<td>$A - \frac{7}{2}B$</td>
</tr>
<tr>
<td>$d^5$</td>
<td>$\Delta - 5(-\frac{14}{9}B + \frac{7}{9}C) + 7C$</td>
<td>$A + 14B + 7C$</td>
</tr>
<tr>
<td>$d^6$</td>
<td>$\Delta - 6(-\frac{14}{9}B + \frac{7}{9}C) - \frac{7}{2}B + 7C$</td>
<td>$A - \frac{7}{2}B$</td>
</tr>
<tr>
<td>$d^8$</td>
<td>$\Delta - 8(-\frac{14}{9}B + \frac{7}{9}C) - 6B + 7C$</td>
<td>$A + B$</td>
</tr>
</tbody>
</table>
$p$-$d$ exchange constant

\[ \text{Mn}^{2+} : N\beta = -\frac{16}{S} \left( \frac{0.64}{u + 4j - \delta_{\text{eff}}} + \frac{1}{\delta_{\text{eff}}} \right) \left( \frac{1}{3}(pd\sigma) - \frac{2\sqrt{3}}{9}(pd\pi) \right)^2 \]

\[ \text{Fe}^{2+} : N\beta = -\frac{16}{S} \left( \frac{0.64}{u + 3j - \delta_{\text{eff}}} + \frac{1}{\delta_{\text{eff}}} \right) \left( \frac{1}{3}(pd\sigma) - \frac{2\sqrt{3}}{9}(pd\pi) \right)^2 \]

\[ \text{Cr}^{2+} : N\beta = \frac{16}{S} \left( \frac{1}{\delta_{\text{eff}}} - \frac{1}{\delta_{\text{eff}} + 4j} \right) \left( \frac{1}{3}(pd\sigma) - \frac{2\sqrt{3}}{9}(pd\pi) \right)^2 \times \frac{1}{3} \]

\[ + \frac{16}{S} \left( \frac{1}{\delta_{\text{eff}} + 6j} + \frac{0.64}{-\delta_{\text{eff}} + u' - j} \right) \left( \frac{1}{3}(pd\sigma) - \frac{2\sqrt{3}}{9}(pd\pi) \right)^2 \times \frac{2}{3} \]

\[ \text{Ni}^{2+} : N\beta = \frac{16}{S} \left( \frac{0.64}{-\delta_{\text{eff}} + u' - j} - \frac{0.64}{-\delta_{\text{eff}} + u' + j} \right) \left( \frac{1}{3}(pd\sigma) - \frac{2\sqrt{3}}{9}(pd\pi) \right)^2 \times \frac{1}{3} \]

\[ + \frac{16}{S} \left( \frac{1}{\delta_{\text{eff}}} - \frac{0.64}{-\delta_{\text{eff}} + u' + 3j} \right) \left( \frac{1}{3}(pd\sigma) - \frac{2\sqrt{3}}{9}(pd\pi) \right)^2 \times \frac{2}{3} \]
References


[50] C. Zener, Phys. Rev. 82, 403 (1951)


