

X-ray absorption spectroscopy study of diluted magnetic semiconductors: $Zn_{1-x}M_xSe$ ($M=Mn, Fe, Co$) and $Zn_{1-x}Mn_xY$ ($Y=Se, Te$)

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(Received 18 September 2000; published 29 March 2001)

We have investigated $3d$ electronic states of doped transition metals in II-VI diluted magnetic semiconductors $Zn_{1-x}M_xSe$ ($M=Mn, Fe, Co$) and $Zn_{1-x}Mn_xY$ ($Y=Se, Te$), using the transition-metal $L_{2,3}$ -edge x-ray absorption spectroscopy (XAS) measurements. In order to explain the XAS spectra, we employed a tetragonal cluster model calculation, which includes not only the full ionic multiplet structure but also configuration interaction (CI). The results show that CI is essential to describe the experimental spectra adequately, indicating the strong hybridization between the transition metal $3d$ and the ligand p orbitals. In the study of $Zn_{1-x}Mn_xY$ ($Y=Se, Te$), we also found considerable spectral change in the Mn $L_{2,3}$ -edge XAS spectra for different ligands, confirming the importance of the hybridization effects in these materials.

DOI: 10.1103/PhysRevB.63.155203

PACS number(s): 71.23.An, 75.50.Pp, 78.70.Dm

I. INTRODUCTION

There has been active studies on diluted magnetic semiconductors (DMS's) for the last two decades because of their unique magneto-optical and magnetotransport properties such as giant negative magnetoresistance, extremely large electronic g factor, large Faraday rotation, etc.^{1,2} Recently the interest has surged again because of their possible applications to "spintronics" based on the semiconductor technology.³ DMS's, which are made by substitution of small amount of late $3d$ magnetic transition-metal (TM) atoms such as Mn, Fe, and Co ions into cation sites in the II-VI or III-V compound semiconductors, involve both semiconductor physics and magnetism. The band gap energy turns out to change with the doping concentration.⁷ Moreover, in some DMS's, the variation of the doping concentration was found to induce magnetic phase transitions, such as paramagnetic to spin glass phase and spin glass to antiferromagnetic phase,¹ and even ferromagnetism can also be induced by injecting carriers or photon irradiation.⁸

Here our studies are mainly focused on the electronic structure of II-VI based DMS's. The II-VI compounds such as ZnSe and ZnTe have a zinc blende crystal structure, in

which the cation Zn^{2+} ions are under the tetrahedral T_d site symmetry. The TM doping induces merely small changes of the lattice constants within the crystal structure. The $(4sp)^2$ electrons of the TM atoms, which act similar to the Zn $(4sp)^2$ electrons, participate in the ligand p -Zn $4sp$ bonding-antibonding states. These states, which correspond to the respective valence band and conduction band of the host semiconductor, are hardly affected by the doping.^{1,4} Meanwhile, the TM $3d$ electrons provide rather localized additional band states, which is expected to be located energetically in the wide band gap of the bonding-antibonding states. Optical absorption studies of DMS's showed the intra-atomic d - d transitions which can be understood by the $3d$ Coulomb multiplets excited from the corresponding ionic high-spin ground state.^{5,6} In spite of the ionic characteristics, the TM $3d$ electrons are known to make strong covalent bonding with ligand p electrons. Furthermore, this covalent bonding, which is often represented by " p - d " hybridization, is expected to play an important role in the interesting magnetotransport and magneto-optical properties such as giant Faraday rotation and Zeeman splitting.¹

In order to understand the electronic structure of these DMS's, several photoemission spectroscopy measurements

have been performed, mostly utilizing $3p \rightarrow 3d$ resonance phenomena near the TM $3p$ absorption edge.^{9,10} This technique enables us to separate out the TM $3d$ contribution to the electronic structure, and one can extract a sort of the $3d$ partial spectral weight. The resulting $3d$ spectral weight was found to be distributed in a very wide range of the valence band, no matter what the doping concentration is, indicating the strong p - d hybridization of ligand p band and the TM $3d$ orbitals. Meanwhile, the $3d$ spectral line shape does not agree with the band structure calculations.^{11,12} For such reasons, the TM $3d$ partial spectral weights have been tried to be interpreted in terms of a many-body approach such as a cluster model calculation with configuration interaction^{5,10} (CI) or an Anderson impurity model calculation.¹³ These model calculations, which are characterized by phenomenological physical quantities such as TM $3d$ on-site Coulomb energy, p - d hybridization, and the ligand p to TM $3d$ charge transfer energy, have been very successful in describing the electronic structure of TM compounds.¹⁴

Soft x-ray absorption spectroscopy (XAS) is another powerful high-energy probe to investigate the electronic structure of transition metal compounds.¹⁵ Especially in diluted systems, XAS has big advantages over the photoemission measurements. Figure 1 shows XAS spectra at TM $L_{2,3}$ -edges of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ ($x=0.059$), $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ ($x=0.049$), and $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ ($x=0.050$), which result from TM $2p \rightarrow 3d$ dipole transitions. The spectra are dominated by the large $2p$ core hole spin-orbit coupling energy, which divides them into roughly the L_3 and L_2 regions at low and high photon energy, respectively. The absorption process is a local process and its energy is determined by the characteristic core-hole energy. Despite the fact that the systems contain relatively small concentration of TM atoms, all the spectra nicely reveal the complex spectral structure, which originates from the $2p$ core-hole- $3d$ Coulomb multiplets, and one can determine important physical quantities to understand the electronic structure by analyzing them.

The photoemission spectroscopy is known to directly probe the electronic structure and the TM $3p$ -edge resonant photoemission spectroscopy enables us to extract the TM $3d$ partial spectrum. However, the extracted spectrum somehow differs from the true TM $3d$ electronic structure because of the different transition matrix elements in the resonant process from those in the direct photoemission process. Hence it is worthwhile to verify the physical quantities determined from the TM $3p$ -edge resonant photoemission studies by analyzing the XAS results. Furthermore, in a view of the experimental technique, the XAS is rather bulk sensitive, different from the resonant photoemission spectroscopy, and the results are much less sensitive to the surface condition of samples. Only a few XAS studies, however, have been performed for DMS's so far.¹⁶⁻¹⁹ Further, the reported studies were mostly focused on XAS spectra of the ligand atoms such as S K edge¹⁷ and Te L_1 edge and L_3 edge.¹⁸ The studies concluded qualitatively that the p - d hybridization is strong and the p - d hybridization strength depends on the ligand ions.¹⁹ However, quantitative analysis for the electronic structure has not been carried out.

In this paper, we report high-resolution XAS studies to

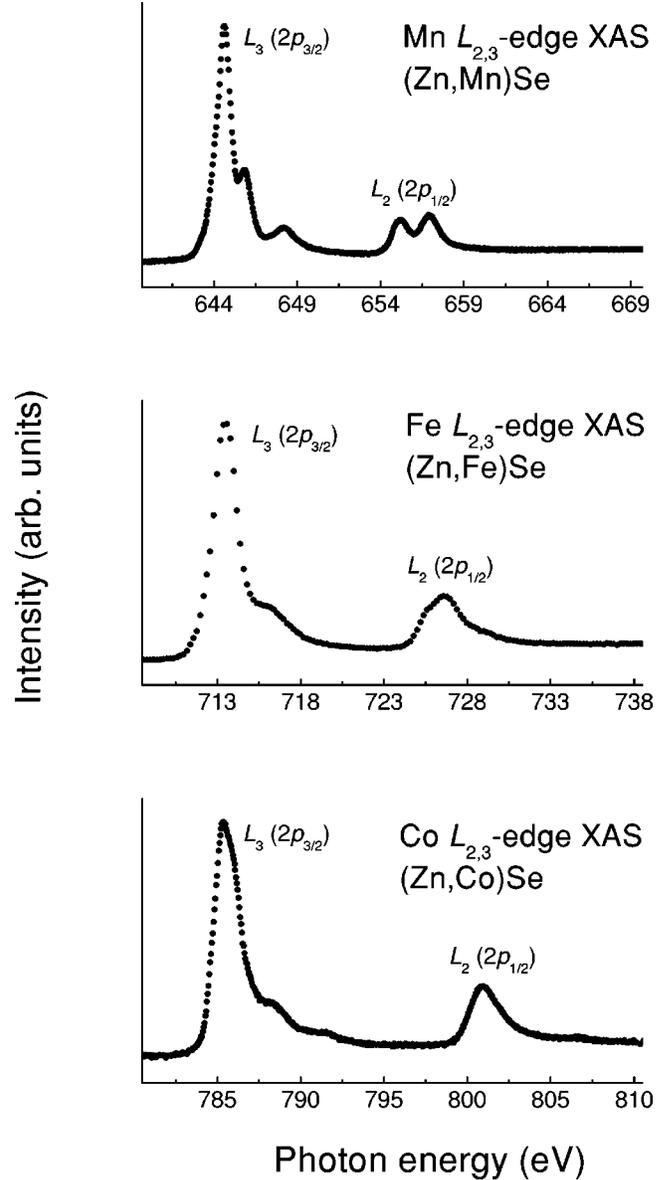


FIG. 1. Experimental XAS spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ ($x=0.059$), $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ ($x=0.049$), and $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ ($x=0.050$) at the TM $L_{2,3}$ edges.

investigate the electronic structure of various II-VI DMS's. The XAS spectra at the TM $L_{2,3}$ edges are analyzed by using a tetrahedral cluster model calculation including CI as well as the full ionic multiplets. Previously, the model calculations for TM $L_{2,3}$ -edge XAS spectra were performed only for condensed systems such as divalent Ni compounds²⁰ Ti_2O_3 ,²¹ CoO ,²² and LiVO_2 (Ref. 23) and showed that the CI considerably affects the XAS spectrum. Thus it is also important to elucidate how the effects of CI appear in the XAS spectra of diluted systems such as DMS's.

II. EXPERIMENT

The samples used in this study were $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ ($x=0.059$), $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ ($x=0.049$), and $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ ($x=0.050$) thin films grown by molecular beam epitaxy on the

TABLE I. Parameters used to calculate TM $L_{2,3}$ XAS spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ ($x=0.059$), $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ ($x=0.049$), and $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ ($x=0.050$). See text for detailed explanations. All the values are given in eV.

	Δ	$V_{pd\sigma}$	U	Q	B	C	F_{pd}^2	G_{pd}^1	G_{pd}^3	ζ_{2p}	κ	Γ_2	Γ_3
Mn^{2+}	5.0	1.0	8.0	10.0	0.119	0.412	6.321	4.606	2.618	6.846	0.8	0.45	0.35
Fe^{2+}	3.0	0.9	3.6	4.5	0.131	0.484	6.793	5.004	2.844	8.200	0.8	0.70	0.45
Co^{2+}	2.5	0.8	4.8	6.0	0.138	0.541	7.259	5.397	3.069	9.748	0.7	1.00	0.50

GaAs (001) substrate and a $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ ($x=0.60$) single crystal with (110) surface. The details of the sample growth and characterization were reported elsewhere.⁴ All the samples preserve the zinc blende crystal structure. The XAS measurements were carried out at the Dragon high-resolution soft-x-ray beam line²⁴ at the National Synchrotron Light Source, Brookhaven National Laboratory. The energy resolution of incoming photon was set to be about 0.5 eV in the full width at half maximum (FWHM). The spectra were collected with a total electron yield channeltron. The photon incident angle was set to be 60° with respect to the surface normal for convenience. The variation of the spectrum with the incident angle turns out to be negligible even for the $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ ($x=0.60$) sample. Before the measurements, the single-crystalline sample was cleaved *in situ* and the thin-film samples, which had been pre-etched using 1:3 mixture of NH_4OH (29%):methanol,²⁵ were annealed *in situ* at 300°C by radiation heating for about 3 h.²⁶ The measurements were performed at room temperature and the base pressure was maintained below 2×10^{-10} Torr.

III. CALCULATIONAL METHOD

We have employed a tetrahedral cluster model calculation to analyze the XAS spectra. The cluster consists of a central TM atom and its four nearest neighbor ligand atoms, and the model calculation includes not only the full multiplets of TM $3d$ electrons but also configuration interaction. The model is characterized by the on-site $3d$ Coulomb energy $U \equiv E(d^{n+1}) + E(d^{n-1}) - 2E(d^n)$, the ligand-to- $3d$ charge-transfer energy $\Delta \equiv E(d^{n+1}\underline{L}) - E(d^n)$, and the cation- d -ligand- p hybridization strength V . The initial configuration states are spanned over the ionic ground state $3d^n$ and the charge-transferred states $3d^{n+1}\underline{L}, \dots, 3d^{10}\underline{L}^{10-n}$, where \underline{L} denotes a ligand- p hole. The multiplets of the $3d$ electron configurations in the charge transferred states are taken into account explicitly while the total symmetry is preserved to be the same as the ionic ground state symmetry. The $3d$ Coulomb exchange interactions are represented by Racah parameters B and C . Although the Racah parameters can vary slightly in different configurations, we import the values from Ref. 5 and fix them in all configurations for the sake of simplicity. The on-site Coulomb U and the charge transfer energy Δ are treated as control parameters in the calculation and defined with respect to the lowest-energy $3d$ multiplet state of the corresponding configurations.

Similarly, the final states are also spanned over $2p3d^{n+1}, 2p3d^{n+2}\underline{L}, \dots, 2p3d^{10}\underline{L}^{9-n}$ configuration states. The Coulomb energies between the $2p$ core-hole and a $3d$ electron

are represented by the $2p$ - $3d$ Slater integrals F_{pd}^2 , G_{pd}^1 , and G_{pd}^3 , and the spin-orbit coupling of the $2p$ core-hole is taken into account with ζ_{2p} . The involved parameter values are borrowed from Ref. 27 and fixed for all configurations. The Slater integrals are scaled down by a reduction factor κ in order to account for the solid state screenings.²⁸ The average Coulomb interaction Q between a TM $2p$ hole and a $3d$ electron is set to be an empirical value of $1.25U$ as widely adopted in the core-level spectroscopy studies.

The hybridization interactions are expressed in terms of the Slater-Koster parameters $V_{pd\sigma}$ and $V_{pd\pi}$: $V_t \equiv \langle t|H|L_t \rangle = \sqrt{\frac{4}{3}}V_{pd\sigma}^2 + \frac{8}{9}V_{pd\pi}^2$ and $V_e \equiv \langle e|H|L_e \rangle = (2\sqrt{6}/3)V_{pd\pi}$, where $t(e)$ and $L_t(L_e)$ are TM- $3d$ and ligand- p orbitals with $t_{2g}(e_g)$ symmetry orbitals under T_d tetrahedral point group symmetry, respectively. For simplicity, we apply the empirical relation $V_{pd\sigma} = -2V_{pd\pi}$.²⁹ The crystal-field interaction $10Dq$ is fixed to be 0.25 eV in all the calculations, and the reason will be explained later. Here TM $3d$ spin-orbit coupling is neglected. It is known that the $3d$ spin-orbit coupling can be quenched when the ground-state orbital symmetry is either A or E ,²⁷ and indeed, the ground state symmetries of Mn^{2+} , Fe^{2+} , and Co^{2+} ions are 6A_1 , 5E , and 4A_2 under the T_d symmetry, respectively.

The initial ground state is obtained in the modified Lanczos method. Then the XAS spectra are calculated by the continued fraction expansion.³⁰ The calculated spectrum is broadened with a Lorentzian function, which accounts for the core-hole lifetime, and finally with a Gaussian function for the experimental resolution (0.5 eV). The Lorentzian broadenings Γ_2 for L_2 -edge and Γ_3 for L_3 -edge spectra are presented in Table I.

IV. RESULTS AND DISCUSSION

A. CI effects on the cluster model calculation

The calculated TM $L_{2,3}$ -edge XAS spectra for Mn^{2+} , Fe^{2+} , and Co^{2+} ions, which are in a tetrahedral cluster, are presented in Fig. 2 in comparison with the corresponding experimental XAS spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ ($x=0.059$), $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ ($x=0.049$), and $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ ($x=0.050$), respectively. Now the photon energy is presented relative to that of the corresponding main L_3 multiplet peak with the highest intensity. In order to investigate the role of configuration interaction, the calculation has been performed for the orders of the charge transferred states.

In the zeroth order calculations, which are denoted by \underline{L}^0 , the charge transferred states are neglected, i.e., the ionic calculations. Meanwhile in the m th order calculations, denoted

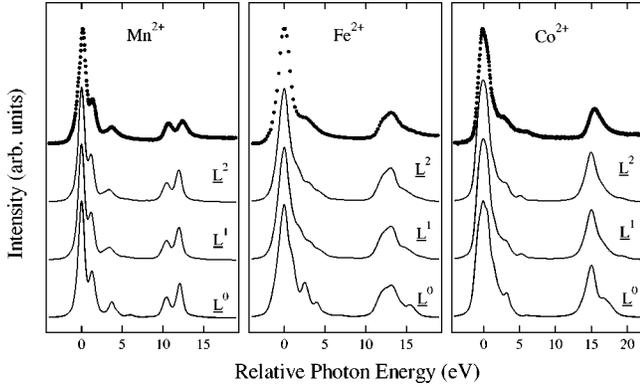


FIG. 2. Experimental (dots) and Calculated (lines) $L_{2,3}$ XAS spectra of Mn^{2+} , Fe^{2+} , and Co^{2+} ions in a tetrahedral cluster depending on the number of configurations employed. \underline{L}^n denotes a configuration, which contains a \underline{L}^n term in the initial and final states, up to which was included in the calculations. See text for detailed information on employed parameter values.

by \underline{L}^m , the charge transferred states are included up to the configuration states with m ligand holes, i.e., the calculations with the configuration states of $3d^n$, $3d^{n+1}\underline{L}^1$, \dots , $3d^{n+m}\underline{L}^m$ for the initial states and the configuration states of $2p3d^{n+1}$, $2p3d^{n+2}\underline{L}^1$, \dots , $2p3d^{n+m+1}\underline{L}^m$ for the final states. The spectra are normalized by the intensity of the L_3 main peak. For a given TM ion, the same parameter set is employed for the \underline{L}^0 , \dots , the \underline{L}^m calculations.

When we take into account only the \underline{L}^1 charge transferred states, we find that the calculated spectrum changes considerably from the \underline{L}^0 spectra, especially in the cases of Fe^{2+} and Co^{2+} ions.³¹ But the \underline{L}^2 spectra are nearly the same as the \underline{L}^1 spectra, indicating that the CI effects on the spectrum converge very rapidly. It is because the energies of the $3d^{n+2}\underline{L}^2$ and $2p3d^{n+3}\underline{L}^2$ configuration states already become much higher than those of $3d^{n+1}\underline{L}^1$ and the $2p3d^{n+2}\underline{L}^1$ states, due to the strong on-site Coulomb interaction. Thus we will consider, from now on, only the result of calculations which include configurations up to $d^{n+2}\underline{L}^2$ and $2pd^{n+3}\underline{L}^2$. Here the parameter values are chosen to give the \underline{L}^2 spectra, which agree well with the corresponding experimental ones.

As can be seen in Fig. 2, the spectrum is strongly disturbed by CI, especially in the high-energy region of the main L_3 multiplet peak. The peak separation becomes reduced and the sharp peak structure is smeared out with CI. Although similar trend might be reproduced just by increasing the crystal field splitting $10Dq$ value without including CI,²⁷ we believe CI is essential for proper interpretation of the XAS spectra for the following reason. When we increase the value of $10Dq$ without including CI, the pre-edge structure is well separated from the main peak and grows rapidly. At the same time the L_2 -edge spectrum becomes very complicated except for a Co^{2+} ion,³² neither of which is observed in the experimental spectra. Hence, $10Dq$ value should be small for Mn^{2+} and Fe^{2+} ions but large for a Co^{2+} ion if one fits the experimental spectra without CI. It

is, however, hard to believe that the $10Dq$ value, which reflects the hybridization strength in the calculation, changes abruptly along this series.³³

In the comparison of the calculated spectra with the experimental ones, the agreement is rather good in overall. But one can still recognize some minor disagreement, which is expected to arise from the uncertainties in Slater integrals and spin-orbit coupling parameters and the solid state effects which have been left out in the cluster model. Each final state multiplet may have different lifetime, and thus for the better fit, one should apply an appropriate core-hole-lifetime broadening for each multiplet state. The solid state effects seem to be rather severe in the spectrum of a Co^{2+} ion, and thus we employed the reduction factor κ smaller than other TM ions.

The parameter values for the best fit are tabulated in Table I. The ligand-to- $3d$ charge transfer energy Δ of Mn, Fe, and Co DMS's are 5.0, 3.0, and 2.5 eV, respectively. Here Δ is defined with respect to the lowest TM $3d$ multiplet energy. The decreasing behavior of Δ value along the series agrees with the decrease of the difference in the electronegativity between TM and ligand atoms. These values are similar to them obtained from the $d-d$ optical-absorption study.⁵ The hybridization parameter $V_{pd\sigma}$ are determined to be 1.0, 0.9, and 0.8 eV for Mn, Fe, and Co DMS's, respectively. The small decrease of $V_{pd\sigma}$ with the increasing atomic number is also consistent with the expected contraction of the $3d$ electron wave function, but these values are somewhat smaller than those obtained from the analysis of photoemission spectra.^{5,10} This is probably due to the small reduction of the effective hybridization strength in the XAS final states induced by the strong Coulomb potential by the localized core orbitals as pointed by Gunnarsson and Jepsen.³⁴ A similar behavior is also observed in the analysis of the Ni compounds using the Anderson impurity model.²⁰

B. Hybridization effect

In order to study the details of the hybridization effect, we compared the XAS spectra of $Zn_{1-x}Mn_xSe$ and $Zn_{1-x}Mn_xTe$ where different ligands will give variations in the charge-transfer energy Δ and the hybridization interaction $V_{pd\sigma}$. As can be seen in Fig. 1, the Mn L_3 -edge XAS spectrum shows a simple and distinguishable multiplet structure, and thus is very appropriate to study the variation of the hybridization effect. Figure 3 shows the experimental XAS spectra of $Zn_{0.941}Mn_{0.059}Se$ and $Zn_{0.4}Mn_{0.6}Te$ at the Mn L_3 edge together with the corresponding calculated ones. The XAS spectrum of $Zn_{1-x}Mn_xSe$ was examined for different Mn concentration (x value), and it was found that the variation of the spectral line shape was negligible. This indicates that the x-ray absorption is rather local process. The experimental spectra show four peak structure, a highest intensity peak (denoted by A), two high-energy peaks at about 1 eV (denoted by B) and 3.5 eV (denoted by C) above, and a small pre-edge structure (denoted by D), for both compounds. This structure is mainly originated from the Mn $2p^53d^6$ XAS final state multiplets of the Mn^{2+} ion.

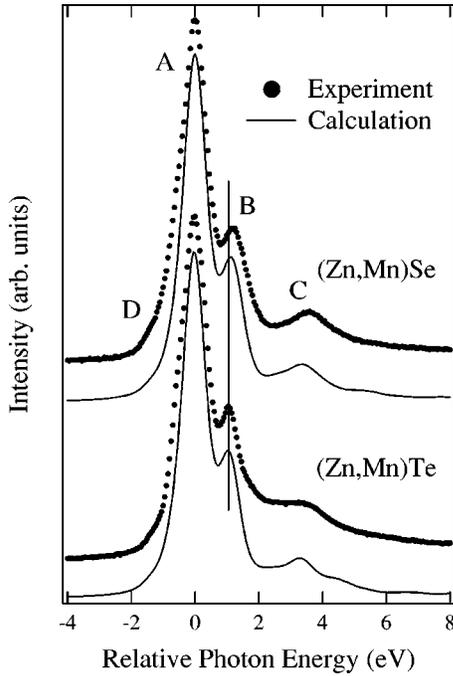


FIG. 3. Experimental (dots) and calculated (lines) XAS spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ ($x=0.059$) and $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ ($x=0.60$) at the Mn L_3 edge. The vertical line is a guide for the peak position. For parameter values of the calculations, refer to text.

The spectra display the common multiplet structure, but one can still recognize considerable difference in the relative peak energies and intensities for different ligand ions. For examples, the relative energy of the peak *B* is lower for Te-ligand ions, while the width of the peak *C* is narrower for the Se-ligand ions. The best fits for the multiplet of these two compounds were obtained with the parameter values of $\Delta = 5.0$ eV and $V_{pd\sigma} = 1.00$ eV for $\text{Zn}_{0.941}\text{Mn}_{0.059}\text{Se}$ and $\Delta = 3.8$ eV and $V_{pd\sigma} = 0.90$ eV for $\text{Zn}_{0.4}\text{Mn}_{0.6}\text{Te}$. Other parameters such as the on-site Coulomb interaction U and the crystal-field interaction $10Dq$ are fixed to be 8.0 and 0.25 eV, respectively, since they are expected to be hardly affected by the variation of the ligand ions. In the picture, Δ and $V_{pd\sigma}$ mainly determine the hybridization strength between TM- d and ligand- p orbitals.

As can be seen in the figure, the calculated spectra show good overall agreement with the experimental ones. Chemical trends of the parameter values are consistent with the electronegativity of ligand ions and also with the nearest neighbor distances between Mn and ligand ions. According to the Harrison's scheme,²⁹ the bond-length (d) dependence of $V_{pd\sigma}$ is $d^{-3.5}$, but the obtained values yield $d^{-1.4}$ dependence using a simple central-force model³⁵ for the Mn-anion bond length. Such a disagreement, which was also observed by Larson *et al.*, may be attributed to the chemical difference between Te and Se ions.¹² The agreement in the region of the second satellite is not as good as the first satellite, especially in $\text{Zn}_{0.4}\text{Mn}_{0.6}\text{Te}$. We suspect that this is probably due to the magnetic interaction between Mn^{2+} ions in this Mn-rich compound, which can affect the spectral shape considerably.³⁶

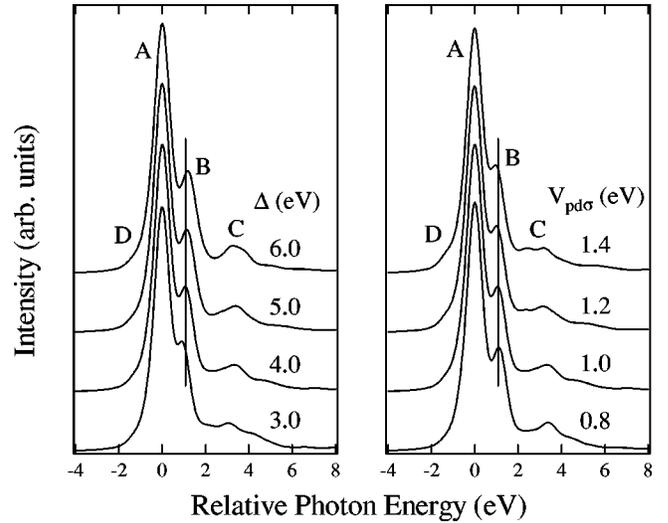


FIG. 4. Calculated L_3 XAS spectra of a Mn^{2+} ion in a tetrahedral cluster. Left panel: As a function of Δ . $V_{pd\sigma}$ is fixed to 1.0 eV. Right panel: As a function of $V_{pd\sigma}$. Δ is fixed to 4.0 eV. The vertical line is a guide for the peak position.

It is worthwhile to understand how the XAS spectrum is affected by the parameters Δ and $V_{pd\sigma}$. Figure 4 shows the XAS spectra as a function of Δ for a fixed $V_{pd\sigma} = 1.0$ eV in the left panel and the spectra as a function of $V_{pd\sigma}$ for a fixed $\Delta = 4.0$ eV in the right panel. First, the calculation results show that the position of the peak *B* is closer to the peak *A* and its intensity becomes smaller when the hybridization effect increases by decrease of Δ or increase of $V_{pd\sigma}$. Second, the structure *C* in the experimental spectrum seems to be a single peak structure. However, it turns out to consist of several multiplet states. Third, the pre-edge structure *D* is mainly induced by the crystal-field splitting $10Dq$. This structure is absent at $10Dq = 0$ but becomes distinguishable for large $10Dq$ value.²⁷ In our parameter set with small $10Dq$, the structure *D* is barely recognized as in the experimental results. In practice, it is difficult to determine the exact value of $10Dq$ from the fitting of XAS spectra, and we simply fixed $10Dq = 0.25$ eV just enough to show the structure *D*.

V. CONCLUSION

Electronic states of doped $3d$ transition metal ions in II-VI diluted magnetic semiconductors (DMS's) have been studied by the TM $L_{2,3}$ -edge XAS spectrum. The spectra of various DMS's are presented and interpreted in terms of a tetrahedral cluster model calculation including both a full multiplet structure and configuration interactions. The calculation results show that the inclusion of CI is essential to describe the XAS spectra of the doped TM ions with reasonable physical parameter values. This means that the hybridization between the TM- $3d$ and ligand- p orbitals is very strong in these materials. Hybridization effects on XAS spectra are also investigated varying ligand ions of Mn DMS's, and the change of the spectral shape is well explained by the cluster model with CI. These results indicate that the inclu-

sion of the CI in the model calculation is required to describe the transition metal $L_{2,3}$ -edge XAS spectrum of a 3d transition metal compound where the TM-3d orbital strongly hybridizes with the ligand- p orbital.

ACKNOWLEDGMENTS

This work was supported by the Korean Science and Engineering Foundation (KOSEF) through the Center for Strongly Correlated Materials Research (CSCMR) at Seoul

National University (2000), and Grant No. KOSEF 951-0209-014-1. J.-S. Kim acknowledges the support from Atomic Scale Surface Science Research Center (ASSRC) at Yonsei University. The work was also supported by BK21 project of Ministry of Education, Korea (POSTECH, and Kyung Hee U.). The National Synchrotron Light Source, Brookhaven National Laboratory, at which the XAS data were obtained, was supported by the U.S. Department of Energy. We also thank Professor M. Taniguchi of Hiroshima University, Japan, for providing a $\text{Zn}_{0.4}\text{Mn}_{0.6}\text{Te}$ single crystal.

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