

# Local environment of Mn atoms in IV-VI ferromagnetic semiconductor $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$

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Mn  $L_{2,3}$  x-ray absorption and magnetic circular dichroism study has been performed on IV-VI ferromagnetic semiconductor  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  with different Mn compositions  $x=0.12, 0.32, 0.51,$  and 1. The absorption and dichroism line shapes are found to be almost independent of the Mn composition, suggesting that the local chemical environment of Mn atoms is the same for  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  with the wide range of  $x$ . On the basis of the configuration interaction analysis for a  $\text{MnTe}_6$  cluster, the electronic structure parameters such as the  $p$ - $d$  hybridization and the  $p$ - $d$  exchange constant have been estimated. © 2006 American Institute of Physics.

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## I. INTRODUCTION

Diluted magnetic semiconductors (DMSs) have in recent years attracted considerable attention due to the possibility of spintronic device applications such as spin light-emitting diodes and tunable ferromagnetic devices using carrier-induced ferromagnetic order.<sup>1-6</sup> To understand the mechanism of the ferromagnetism, the electronic structure has been investigated by photoemission spectroscopy and x-ray absorption spectroscopy.<sup>7-9</sup> Information obtained from the spectroscopy provides guiding principles to synthesize new DMSs.<sup>10</sup> The extensive studies are performed on II-VI and III-V DMSs which crystallize in zinc-blende or wurtzite structure with atoms in a tetrahedral coordination. Bearing in mind, however, that a comprehensive understanding of the physics has not yet been achieved, it is important to explore the electronic and magnetic properties of various DMSs.

IV-VI DMS  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  show the carrier-induced ferromagnetic order up to 140 K for  $x=0.51$ .<sup>11</sup> This material offers a good opportunity to study the ferromagnetism because the concentrations of the Mn ion and the hole can be controlled independently,<sup>12</sup> and the solubility limit of Mn into GeTe is relative high ( $x \leq 0.96$ ).<sup>11</sup>  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  differs from the II-VI and III-V DMSs in two important respects: it crystallizes in the rock-salt structure with atoms in an octahedral coordination, and the conduction-band minimum and the

valence-band maximum (VBM) are located at the  $L$  point of the fcc Brillouin zone. In this article, to probe the Mn 3d local electronic structure of  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  with a wide range of Mn compositions, x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) are carried out. In DMSs, the electronic structure of the Mn atom is strongly affected by its neighboring (ligand) atoms because of the highly localized nature of the 3d state. We have, therefore, analyzed the XAS and XMCD spectra using the configuration interaction (CI) cluster-model calculation.

## II. EXPERIMENT

Samples were grown by an ionized cluster beam method onto air-cleaved  $\text{BaF}_2$  (111) substrates using effusion cells of GeTe and MnTe. Details of the growth procedure are presented elsewhere.<sup>13</sup> After the growth of the  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  layer, Au cap layer was *in situ* grown to prevent the oxidation of the surface. The samples studied here consist of a top 2 nm Au layer, a 500 nm thick  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  layer, a 100 nm thick GeTe buffer layer, and a  $\text{BaF}_2$  substrate. The Mn composition  $x$  was determined by the electron probe microanalysis. The crystallinity was checked by x-ray diffraction measurements.

The XAS and XMCD measurements were done at BL-25SU beamline of SPring-8.<sup>14</sup> The beamline provides >95% left- or right-circular polarized light using the twin helical undulator.<sup>15</sup> XAS and XMCD spectra were taken in total

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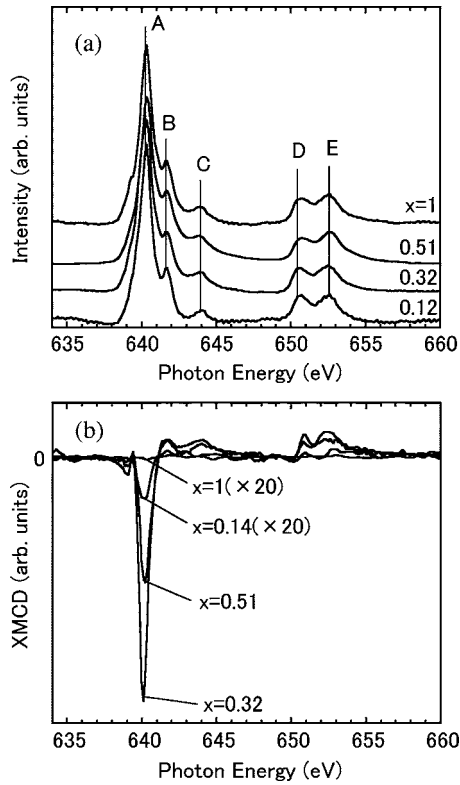


FIG. 1. Mn  $L_{2,3}$  (a) XAS and (b) XMCD spectra for  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  with different Mn compositions at 40 K.

electron yield mode. The XMCD scans were taken in the Faraday geometry by switching helicity (1 Hz) of the circular polarized light at the fixed magnetic field of 1.4 T using a Nd-Fe-B magnet, and then the same procedure was performed at the opposite magnetic field to correct instrumental asymmetry.

### III. RESULTS AND DISCUSSION

Figure 1 shows the Mn  $2p$  XAS and XMCD spectra for  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  with  $x=0.12, 0.32, 0.51,$  and  $1$ . The spectra were taken at temperature of 40 K. Two groups of the peaks shown in the XAS spectra correspond to transitions from the  $2p_{3/2}$  ( $L_3$  edge) and  $2p_{1/2}$  ( $L_2$  edge) states to the Mn  $3d$  state. The contribution from the Au capping layer was subtracted as a linear background. The rich structure observed in all the spectra is indicative of a highly localized state with a  $3d^5$  configuration in the ground state, as reported for various Mn-doped DMSs.<sup>16–19</sup> The peak position of multiplet features (A, B, C, D, and E) is the same for  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  with the wide range of  $x$ , although the intensity of the satellite peak B of the  $L_3$  region is slightly different. The local Mn states could, therefore, be independent of  $x$ . As shown in Fig. 1(b), clear XMCD signals are observed in all the  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  except for  $x=1$  due to the antiferromagnetic nature. The amplitude of XMCD increases rapidly with increasing Mn composition up to  $x=0.32$ , and it then starts to decrease as  $x$  increases further. This behavior is similar to the spontaneous magnetization measured by a superconducting quantum interference device magnetometer.<sup>20</sup> The decrease of the amplitude of XMCD is thus due to the increase of the antiferromagnetic

superexchange interaction between neighboring Mn ions, which suppresses the carrier-induced ferromagnetic order. It should be noted that the shape of XAS spectra is almost unchanged, although the XMCD intensity is drastically changed. This implies that the magnetic order scarcely affects the local environment of the Mn atom: the local environment of the ferromagnetically and antiferromagnetically coupled Mn atoms are the same. In the case of  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ , interstitial Mn ( $\text{Mn}_I$ ) suppresses the ferromagnetism because  $\text{Mn}_I$  not only compensates holes provided by the substitutional Mn ( $\text{Mn}_{\text{sub}}$ ), but  $\text{Mn}_I$  also couples antiferromagnetically to neighboring  $\text{Mn}_{\text{sub}}$ .<sup>21–23</sup> Such a different local situation of the Mn ions, which originates from different As coordination, was detected as a doublet structure of the main  $L_3$  peak in the XAS and XMCD spectra.<sup>24</sup> In the  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  studied here, while the ratio of the ferromagnetically to antiferromagnetically coupled Mn atoms is drastically changed, the shape of the XAS spectra is almost identical. We conclude that the local chemical environment of the Mn atoms is the same for  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  with the wide range of  $x$ .

In order to investigate the Mn  $3d$  electronic structure, the XAS and XMCD spectra are analyzed using the CI theory. The CI calculation is widely used to deduce the electronic parameters such as  $p$ - $d$  charge transfer energy  $\Delta$ , on-site  $3d$  Coulomb interaction energy  $U$ , and  $p$ - $d$  charge transfer energy ( $pd\sigma$ ) in DMSs.<sup>7–10</sup> The  $p$ - $d$  charge transfer energy and the  $d$ - $d$  Coulomb interaction energy are expressed by  $\Delta = E(d^{n+1}L) - E(d^n)$  and  $U = E(d^{n-1}) + E(d^{n+1}) - 2E(d^n)$ , respectively. The  $2p$ - $3d$  Coulomb interaction energy is set to be empirical value of  $1.25U$ . The hybridization between the Mn  $3d$  and ligand  $p$  orbital is expressed in terms of Slater-Koster parameters ( $pd\sigma$ ) and ( $pd\pi$ ), where the relation of  $(pd\sigma)/(pd\pi)$  is fixed to  $-2.17$ . To reproduce the experimental XAS and XMCD spectra, the electronic parameters are adjusted using an octahedral  $\text{MnTe}_6$  cluster model for  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  with  $x=0.32$ . As shown in Fig. 2, the observed peak position and line shape in the experimental spectra are best reproduced for the calculated spectra using  $\Delta=2.5$  eV,  $U=4.0$  eV,  $(pd\sigma)=-0.4$  eV, and  $10Dq=0.4$  eV. From the obtained values, one can estimate the  $p$ - $d$  exchange constant  $N_0\beta$  between the Mn ions and holes at VBM.  $N_0\beta$  is an important role in understanding the strength of ferromagnetic ordering as well as the magneto-optical effects such as giant Faraday rotation in zinc-blende DMSs.<sup>10,24</sup> In the case of rock-salt  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$ , the VBM locates at the  $L$  point and  $N_0\beta$  is thus given by

$$N_0\beta = -\frac{8}{5} \left( \frac{2(pd\pi)^2}{U_{\text{eff}} - \Delta_{\text{eff}}} + \frac{(pd\sigma)^2}{U_{\text{eff}} - \Delta_{\text{eff}} - 10Dq} + \frac{2(pd\pi)^2}{\Delta_{\text{eff}}} + \frac{(pd\sigma)^2}{\Delta_{\text{eff}} + 10Dq} \right)$$

(Ref. 25), where  $U_{\text{eff}}$  and  $\Delta_{\text{eff}}$  are the lowest term of  $U$  and  $\Delta$ , respectively. Here, the magnitude of the local spin  $S$  is assumed to be  $5/2$ .  $N_0\beta$  of  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  is approximately  $-0.2$  eV. The negative  $N_0\beta$  implies that the  $p$ - $d$  exchange interaction is antiferromagnetic. The electronic structure parameters obtained are summarized in Table I and compared

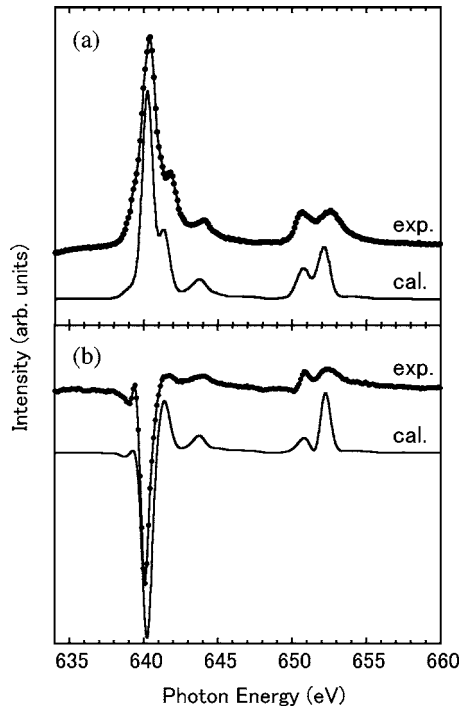


FIG. 2. Comparison of experimental (a) XAS and (b) XMCD spectra with theoretical spectra calculated on the CI analysis using a  $\text{MnTe}_6$  cluster.

with those deduced from XAS measurements for the other DMSs.  $N_0\beta$  of  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  is smaller than the others. The values of  $\Delta$  and  $U$  are the same for  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ , although the value of  $\Delta$  for  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  is larger due to the large electronegativity of the O ion. The origin of smaller  $N_0\beta$  in  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  could, therefore, be due to smaller ( $pd\sigma$ ). This is qualitatively understood in that the bond length of 2.92 Å for  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  is longer than that of 2.59 Å for  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ . The theoretical studies on  $T_C$  of zinc-blende DMSs have suggested that  $N_0\beta$  scales with the bond length between the Mn and ligand atoms.<sup>26</sup> This guideline would also be applied in different symmetry at VBM between IV–VI DMSs and II–VI or III–V DMSs.

#### IV. CONCLUSIONS

We have investigated the local environment of Mn atoms in IV–VI ferromagnetic semiconductor  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  with different Mn compositions  $x=0.12, 0.32, 0.51$ , and 1 using XAS and XMCD measurements and CI analysis. The XAS and XMCD spectra show a characteristic feature of the localized Mn  $3d^5$  ground state. The shapes of the XAS and XMCD spectra are almost identical for the wide range of  $x$ ,

TABLE I. Electronic structure parameters  $U$ ,  $\Delta$ , and ( $pd\sigma$ ) used to calculate the x-ray absorption spectra and the  $p$ - $d$  exchange constant  $N_0\beta$  for Mn-doped DMSs (in eV).

	$\Delta$	$U$	( $pd\sigma$ )	$N_0\beta$	Ref.
$\text{Ge}_{1-x}\text{Mn}_x\text{Te}$	2.5	4.0	-0.4	-0.20	
$\text{Ga}_{1-x}\text{Mn}_x\text{As}$	2.5	4.0	-0.67	-0.34	17
$\text{Zn}_{1-x}\text{Mn}_x\text{O}$	6.5	5.0	-1.6	-3.00	9

indicating that the local environment of the Mn atoms is independent of  $x$ . The CI analysis predicts that  $N_0\beta$  in  $\text{Ge}_{1-x}\text{Mn}_x\text{Te}$  is  $-0.2$  eV and its magnitude is qualitatively understood by the bond length between the Mn and the ligand atoms, that is, the  $p$ - $d$  hybridization strength.

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- <sup>1</sup>S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, *Science* **294**, 1488 (2001).
- <sup>2</sup>R. Fiederling, M. Keim, G. Reuscher, W. Ossau, G. Schmidt, A. Waag, and L. W. Molenkamp, *Nature (London)* **402**, 787 (1999).
- <sup>3</sup>Y. Ohno, D. K. Young, B. Beschoten, F. Matsukura, H. Ohno, and D. D. Awschalom, *Nature (London)* **402**, 790 (1999).
- <sup>4</sup>S. Koshihara, A. Oiwa, M. Hirasawa, S. Katsumoto, Y. Iye, C. Urano, H. Takagi, and H. Munekata, *Phys. Rev. Lett.* **78**, 4617 (1997).
- <sup>5</sup>H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno, and K. Ohtani, *Nature (London)* **408**, 944 (2000).
- <sup>6</sup>D. Chiba, M. Yamanouchi, F. Matsukura, and H. Ohno, *Science* **301**, 943 (2003).
- <sup>7</sup>T. Mizokawa and A. Fujimori, *Phys. Rev. B* **48**, 14150 (1993); **56**, 6669 (1997).
- <sup>8</sup>J. Okabayashi, T. Mizokawa, D. D. Sarma, A. Fujimori, T. Slupinski, A. Oiwa, and H. Munekata, *Phys. Rev. B* **65**, 161203 (2002).
- <sup>9</sup>J. Okabayashi, K. Ono, M. Mizuguchi, M. Oshima, S. S. Gupata, D. D. Sarma, T. Mizokawa, A. Fujimori, M. Yuri, C. T. Chen, T. Fukumura, M. Kawasaki, and H. Koinuma, *J. Appl. Phys.* **95**, 3573 (2004).
- <sup>10</sup>T. Mizokawa, A. Fujimori, J. Okabayashi, and O. Rader, *J. Electron Spectrosc. Relat. Phenom.* **136**, 21 (2004).
- <sup>11</sup>Y. Fukuma, T. Murakami, H. Asada, and T. Koyanagi, *Physica E (Amsterdam)* **10**, 273 (2001).
- <sup>12</sup>Y. Fukuma, H. Asada, M. Arifuku, and T. Koyanagi, *Appl. Phys. Lett.* **80**, 1013 (2002).
- <sup>13</sup>Y. Fukuma, M. Arifuku, H. Asada, and T. Koyanagi, *J. Appl. Phys.* **97**, 073910 (2005).
- <sup>14</sup>Y. Saitoh, H. Kimura, Y. Suzuki, T. Nakatani, T. Matsushita, T. Muro, T. Miyahara, M. Fujisawa, K. Soda, S. Ueda, H. Harada, M. Kotsugi, A. Sekiyama, and S. Suga, *Rev. Sci. Instrum.* **71**, 3254 (2000).
- <sup>15</sup>T. Hara, K. Shirasawa, M. Takeuchi, T. Seike, Y. Saitoh, T. Muro, and H. Kitamura, *Nucl. Instrum. Methods Phys. Res. A* **498**, 496 (2003).
- <sup>16</sup>K. Cho, H. Koh, J. Park, S.-J. Oh, H.-D. Kim, M. Han, C. T. Chen, Y. D. Kim, J.-S. Kim, and B. T. Jonker, *Phys. Rev. B* **63**, 155203 (2001).
- <sup>17</sup>S. Ueda, S. Imada, T. Muro, Y. Saitoh, S. Suga, F. Matsukura, and H. Ohno, *Physica E (Amsterdam)* **10**, 210 (2001).
- <sup>18</sup>K. W. Edmonds, N. R. S. Farley, T. K. Johal, R. P. Campion, B. L. Gallagher, C. T. Foxon, and G. van der Laan, *J. Appl. Phys.* **95**, 7166 (2004).
- <sup>19</sup>P. T. Chiu, B. W. Wessels, D. J. Keavney, and J. W. Freeland, *Appl. Phys. Lett.* **86**, 072505 (2005).
- <sup>20</sup>Y. Fukuma, H. Asada, N. Nishimura, and T. Koyanagi, *J. Appl. Phys.* **93**, 4034 (2003).
- <sup>21</sup>J. Blinowski and P. Kacman, *Phys. Rev. B* **67**, 121204 (2003).
- <sup>22</sup>K. W. Edmonds, P. Boguslawski, K. Y. Wang, R. P. Campion, S. N. Novikov, N. R. S. Farley, B. L. Gallagher, C. T. Foxon, M. Sawicki, T. Dietl, M. B. Nardelli, and J. Bernholc, *Phys. Rev. Lett.* **92**, 037201 (2004).
- <sup>23</sup>J. Masek and F. Maca, *Phys. Rev. B* **69**, 165212 (2004).
- <sup>24</sup>A. Fujimori, J. Okabayashi, Y. Takeda, T. Mizokawa, J. Okamoto, K. Mamiya, Y. Saitoh, Y. Muramatsu, M. Oshima, S. Ohya, and M. Tanaka, *J. Electron Spectrosc. Relat. Phenom.* **144–147**, 701 (2005).
- <sup>25</sup>H. Sato, K. Fujimoto, Y. Fukuma, K. Tsuji, A. Kimura, M. Taniguchi, S. Senba, A. Tanaka, H. Asada, and T. Koyanagi, *J. Electron Spectrosc. Relat. Phenom.* **144–147**, 727 (2005).
- <sup>26</sup>T. Dietl, H. Ohno, and F. Matsukura, *Phys. Rev. B* **63**, 195205 (2001); T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science* **287**, 1019 (2000).