X-ray Magnetic Circular Dichroism and Photoemission Study of the Diluted Ferromagnetic Semiconductor Zn$_{1-x}$Cr$_x$Te

Yukiaki Ishida$^{1, *}$, Masaki Kobayashi$^1$, Jong-II Hwang$^1$, Yukiharu Takeda$^2$, Shin-ichi Fujimori$^2$, Tetsuo Okane$^2$, Kota Tera$^2$, Yui Saitoh$^2$, Yasuji Muramatsu$^2$, Atsushi Fujimori$^{1, 2}$, Arata Tanaka$^3$, Hidekazu Saito$^4$, and Koji Ando$^4$

$^1$Department of Physics, University of Tokyo, Bunkyo, Tokyo 113-0033, Japan
$^2$Synchrotron Radiation Research Center, Japan Atomic Energy Agency, Sayo, Hyogo 679-5148, Japan
$^3$Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashihiroshima, Hiroshima 739-8530, Japan
$^4$Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

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We have performed X-ray magnetic circular dichroism (XMCD) and valence-band photoemission studies of the diluted ferromagnetic semiconductor Zn$_{1-x}$Cr$_x$Te. XMCD signals due to ferromagnetism and paramagnetism and/or superparamagnetism were observed at the Cr 2p absorption edge. Comparison with atomic multiplet calculations suggests that the magnetically active component of the Cr ion was divalent under the tetrahedral crystal field with tetragonal distortion along the crystalline a-, b-, and c-axes. In the valence-band spectra, spectral weight near the Fermi level was strongly suppressed, suggesting the importance of Jahn–Teller effect and the strong Coulomb interaction between the Cr 3d electrons.

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**D**iluted magnetic semiconductors (DMSs)$^{1, 11}$ showing high ferromagnetic Curie temperatures ($T_C$)’s are considered to be key materials for spintronics.$^3$ Ferromagnetism of II–VI-semiconductor-based DMS Zn$_{1-x}$Cr$_x$Te thin films (x $\lesssim$ 0.2) reported by Saito et al.$^{3, 4}$ has attracted much interest since the T$_C$ was as high as 300 K and the large ferromagnetic sp–d exchange constant was confirmed by magnetic circular dichroism (MCD) measurements in the visible to ultraviolet regions.$^3$ Subsequently, it was reported that control of ferromagnetism is possible through co-doping N or I during the thin film growth.$^{6–8}$

Even though the samples having Cr concentrations beyond the solubility limit (x $\ll$ 0.02) are in a single phase,$^{4, 9}$ it is not clear how homogenous the Cr ions are in terms of their electronic structures, given the observation of ferromagnetic and paramagnetic components coexisting in highly-Cr-doped thin-film samples.$^{10}$ In this paper, we report on soft-X-ray MCD (XMCD) and photoemission spectroscopy (PES) studies on ferromagnetic Zn$_{1-x}$Cr$_x$Te thin films. We observe the coexistence of ferromagnetic and paramagnetic and/or superparamagnetic Cr ions and that both components have similar chemical environment, most likely a Cr$^{3+}$ state subject to Jahn–Teller distortion. This indicates that the magnetism of Cr ions in ZnTe is strongly affected by subtle environmental differences such as nearest neighbor cations or neighboring defects. We also found suppressed spectral weight near the Fermi level ($E_F$), indicating that the origin of ferromagnetism is different from the carrier-induced ferromagnetism of the well-established III–V DMSs.$^{11}$

A 150-nm-thick epitaxial thin film of Zn$_{1-x}$Cr$_x$Te with x = 0.045 was grown on a 120-nm-thick ZnTe layer on a semi-insulating GaAs(001) substrate using the molecular beam epitaxy method.$^{1, 4}$ T$_C$ was estimated to be $\sim$70 K from the magnetization measurements and the Arrot Plot analysis.$^{1, 4, 10}$

The sample surface was capped with a 3-nm-thick ZnTe layer to avoid contamination for the Zn$_{1-x}$Cr$_x$Te layer. Core-level absorption (XAS) spectra were recorded in the total-electron-yield mode at undulator beam line BL23SU of SPring-8.$^{12}$ The degree of circular polarization was higher than 90%. The monochromator resolution was $E/\Delta E$ > 10000. Magnetic fields $H$ up to 7 T were applied parallel and antiparallel to the propagation vector of the incident light and the sample surface. Photon helicity was switched at each photon energy. Valence-band PES measurements were performed at BL-18A of Photon Factory (PF), High Energy Accelerator Research Organization (KEK). An x = 0.043 sample ($T_C$ $\sim$ 70 K) without a capping layer and a ZnTe film were measured. The surface was cleaned by Ar-ion sputtering at 1.0 kV and subsequent annealing at 200°C. Cleanliness of the sample surface was checked by the absence of O 1s core-level PES signal. In order to avoid charging effects, the spectra were taken at room temperature and at $\sim$450 K. The base pressure was $\gtrsim 7.5 \times 10^{-10}$ Torr, and the resolution of the spectrometer (VG CLAM) including temperature broadening was $\sim$200 meV.

Figure 1(a) shows Cr 2p XAS and XMCD spectra taken at $T$ = 20 K and $H$ = 2 T. Here, $\mu^+$ and $\mu^-$ indicate absorption spectra for photon helicity parallel and antiparallel to...
the Cr 3d spin, respectively. The structures around $h\nu = 576$ and $586 \text{ eV}$ are due to absorption from the Cr 2p$_{3/2}$ and Cr 2p$_{1/2}$ core levels, respectively. The XAS and XMCD spectra at the Cr 2p edge show multiplet structures indicating the localized nature of the Cr 3d electrons in a crystal field. The Cr 2p absorption overlaps with the tail of the broad absorption due to Te 3d $\rightarrow$ Te 5p transition. For subsequent comparison of the Cr 2p XAS line shape with atomic multiplet theory, we have removed the Te 3d absorption assuming a polynomial function as shown by dashed curves in Fig. 1(a).

Following the orbital sum rule, the energy integral of the Cr 2p XMCD is proportional to the orbital moment of the Cr 3d electrons, $\langle L_z \rangle$. If the Cr ions are isovalently substituting for Zn and become Cr$^{2+}$ (3d$^4$) under a crystal field of $T_d$ symmetry as shown in the left panel of Fig. 1(b), $\langle L_z \rangle$ becomes negative or the integrated XMCD becomes positive since the filling of the 3d orbital is less than half and there is orbital degrees of freedom in the $t_2$ states. However, as shown in Fig. 1(a), the integral became very small or slightly negative, indicating that $\langle L_z \rangle$ is largely quenched compared with the value of the Cr$^{2+}$ ion in the $T_d$-symmetry crystal field. In fact, Vallin and co-workers have shown in their optical absorption study that dilute Cr ions in bulk ZnTe are subject to Jahn–Teller distortion as shown in the right panel of Fig. 1(b), leading to the lift of the orbital degeneracy and the quenching of $\langle L_z \rangle$.

Figure 2(a) shows $H$ dependence of the Cr 2p XMCD spectra. We could observe dichroism down to $H = 0.1 \text{ T}$, as shown in panels (a) and (b), indicating the presence of substantial residual magnetization of the Cr 3d electrons. The XMCD strength did not saturate even above $H = 2 \text{ T}$ and showed convex behavior as shown in Fig. 2(b). In addition, the XMCD strength remained at temperatures above $T_C$ as shown in Fig. 2(c). These observations indicate the presence of superparamagnetism and/or paramagnetism in the present sample. Please note that the Cr 2p XMCD strength is free from diamagnetism of the substrate.

In the inset of Fig. 2(a), we show XMCD spectra around the Cr 2p$_{3/2}$ peak normalized to the XMCD peak intensity. The normalized XMCD spectra overlap with each other except for a dip structure around $h\nu \sim 578 \text{ eV}$, which is discussed later. This indicates that there was a single chemical environment for the magnetically active Cr ions in Zn$_{1-x}$Cr$_x$Te. This is in line with the unchanged line shapes of the visible to ultraviolet MCD under varying magnetic field.

In Fig. 3, we compare the XAS and XMCD spectra with those calculated using atomic multiplet theory taking into account the Jahn–Teller distortion. The calculated spectra for $T_d$ and $D_{2d}$ symmetries with high-spin configurations are shown in Figs. 3(a) and 3(b), respectively, and the experimental XMCD spectrum is shown in Fig. 3(c). The crystal-field parameters for $D_{2d}$ symmetry, namely, $10Dq = -0.55 \text{ eV}$ and $\Delta_2 = -0.20 \text{ eV}$, and $\Delta_4 = -0.10 \text{ eV}$ have been adopted from ref. 14. In the calculation of the spectra under $D_{2d}$ symmetry, we have assumed that there are equal numbers of tetragonally-distorted Cr sites along the $a$, $b$, and $c$ axes. In fact, the film was relaxed because of the large mismatch in the lattice constant ($a = 6.10 \text{ Å}$ for ZnTe and $a = 5.65 \text{ Å}$ for GaAs) and free from the epitaxial strain from the substrate. Since the line shape of XMCD did not change with $H$ [Fig. 2(a)], we consider that the distribution of the Jahn–Teller distortion axes is isotropic even at high $H$. The overall XAS line shape seems to be well reproduced both for the $D_{2d}$ and $T_d$ symmetries, except for a peak around 578 eV, which may originate from a small amount of other Cr compound(s), as evidenced from the $H$ dependence of the XMCD [Fig. 2(a)]. On the other hand, the XMCD line shape seems to be better reproduced for the $D_{2d}$ symmetry particularly in the Cr 2p$_{3/2}$ absorption region. In Fig. 3, we have also indicated $\langle L_z \rangle$. The experimental $\langle L_z \rangle$ has been calculated using the orbital sum rule. One can see the suppressed $\langle L_z \rangle$ in the case of $D_{2d}$ compared to the case of $T_d$, which is in accord with the observed suppression of the Cr 3d orbital moment (Fig. 1). Thus, we conclude that the XMCD line shape of the magnetically active component are well reproduced if the Jahn–Teller effect is included. The lift of the orbital degeneracy due to Jahn–Teller effect will directly affect the sp–d exchange interaction as studied theoretically in refs. 17–19.

Finally, we show the valence-band PES spectra of Zn$_{1-x}$Cr$_x$Te ($x = 0.043$) and ZnTe thin films in Fig. 4. At
the excitation energy of $h\nu = 48$ eV, the atomic photoionization cross-section of Cr 3d is $\sim 20$ times larger than that of Te 5p. In fact, the intensity of the valence band of Cr-doped ZnTe is $\sim 2$ times higher than the valence-band intensity of ZnTe mainly composed of Te 5p states as shown in the top panel of Fig. 4. By subtracting the spectrum of ZnTe from that of Zn$_{1-x}$Cr$_x$Te ($x = 0.043$), we have deduced the Cr 3d partial density of states (PDOS) as shown in the middle panel of Fig. 4. For comparison, we show the calculated total density of states (DOS) and the Cr 3d PDOS of Zn$_{1-x}$Cr$_x$Te ($x = 0.25$) calculated within the local-spin-density-function approximation in the bottom panel of Fig. 4. One can see a peak at $\sim 1.5$ eV and a broad shoulder centered at $\sim 3$ eV in the experimental Cr 3d PDOS, which can be assigned to nonbonding Cr e and bonding Cr t$_2$ states, and thus agreement between experiment and theory is good on the high binding energy side of the valence band. On the other hand, the spectral weight near $E_F$ was strongly suppressed in the experimental spectra, consistent with the semiconducting transport properties, but deviates from the theoretical Cr 3d PDOS showing finite intensity at $E_F$ due to majority spin states as shown in Fig. 4. If the tetragonal distortion splits the Cr 3d t$_2$ orbitals in the $T_d$ symmetry as suggested from the XMCD study, a gap will open in the Cr 3d t$_2$ impurity band which may explain the suppressed spectral weight near $E_F$, A strong Coulomb interaction between Cr 3d electrons will also suppress the spectral weight at $E_F$. Therefore, it is important to include the distortion effect as well as the strong Coulomb interaction effect to understand the ferromagnetic Zn$_{1-x}$Cr$_x$Te.

In summary, we have detected ferromagnetic and paramagnetic and/or superparamagnetic XMCD signals of the Cr ions in a ferromagnetic Zn$_{1-x}$Cr$_x$Te ($x = 0.045$) thin film, and found that both species have similar electronic environment. Comparison with atomic multiplet calculation indicated that the magnetically-active Cr ions are divalent and substituting the Zn site of the host ZnTe and that the Cr ions were subject to tetragonal distortion due to Jahn–Teller effect as observed in bulk Zn$_{1-x}$Cr$_x$Te. The suppressed spectral weight near $E_F$ in the valence-band spectra was discussed in terms of the distortion effect and the strong Coulomb effect between Cr 3d electrons.

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