Soft x-ray magnetic circular dichroism study of weakly ferromagnetic Zn$_{1-x}$V$_x$O thin film

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We performed a soft x-ray magnetic circular dichroism (XMCD) study of a Zn$_{1-x}$V$_x$O thin film which showed small ferromagnetic moment. Field and temperature dependences of V 2p XMCD signals indicated the coexistence of Curie-Weiss paramagnetic, antiferromagnetic, and possibly ferromagnetic V ions, quantitatively consistent with the magnetization measurements. We attribute the paramagnetic signal to V ions substituting Zn sites which are somewhat elongated along the c-axis.

Recently, ZnO-based diluted magnetic semiconductors (DMSs) have attracted much interest due to their potentially high Curie temperatures ($T_C$’s) $^2$ aiming at practical applications in spintronics devices $^2$. After the report of high $T_C$ ($\sim$280 K in Zn$_{1-x}$Co$_x$O $^2$), there have been many reports on ZnO-based DMSs showing high $T_C$’s (for recent review, see $^3$). Zn$_{1-x}$V$_x$O (ZVO) thin films prepared by the pulsed laser deposition method under a reduced atmospheric condition showed $T_C$’s above 400 K $^2$. The ferromagnetism in ZVO was reproduced in $^4$, $^5$, $^6$, $^7$, but no ferromagnetic behavior was observed in a recent report $^8$. Thus, the high $T_C$ in ZVO has remained controversial concerning its origin $^9$. In order to exclude possible metal precipitations as an extrinsic origin of ferromagnetism, magnetization measurements or anomalous Hall effect measurements may not be sufficient $^{10}$. In this Letter, we report on a soft x-ray magnetic circular dichroism (XMCD) study of ZVO. XMCD in core-level soft x-ray absorption spectroscopy (XAS) is an element specific probe and is sensitive to the magnetic states of each element. Their line shapes are fingerprints of the electronic structures such as the valence and the crystal field of the magnetic ion, making XMCD a powerful tool to investigate the electronic and magnetic properties of DMSs $^{11, 12, 13, 14, 15, 16, 17}$. 

A thin film of ZVO ($x=0.05$) was epitaxially grown on a ZnO (0001) buffer layer on an Al$_2$O$_3$ (1120) substrate as described elsewhere $^3$. The film size was approximately 5 mm$\times$7 mm with the thickness of 100 nm. XAS and XMCD measurements were performed at BL23-SU of SPring-8 $^1$. The monochromator resolution was $E/\Delta E > 10000$. The photon helicity (>$90\%$ circular polarization within the $ab$-plane) was switched at each photon energy. Magnetic field $H$ was applied parallel and antiparallel to the c-axis. Sample surface was cleaned in situ by Ar-ion sputtering at 1 keV and subsequent annealing up to 200$^\circ$C. We also performed magnetization measurements after the XAS and XMCD measurements using a SQUID magnetometer (MPMS, Quantum Design Co., Ltd).

![Figure 1: (Color online) Results of magnetization measurements on Zn$_{0.95}$V$_{0.05}$O. (a) Magnetization curves at various temperatures. Inset shows a magnified plot near $H = 0$. (b) High-field susceptibility (see, text) vs temperature fit to the Curie-Weiss law (solid curve), $\partial M/\partial H > 2T = NC/(T-\Theta)+\partial M/\partial H_0$, where $\partial M/\partial H_0 = -(1.361\pm0.010) \times 10^{-3}$ emu/T, $NC = (1.30 \pm 0.16) \times 10^{-3}$ emu K/T, and $\Theta = -25.4 \pm 3.6$ K.](http://example.com/figure1.png)

Figure (a) shows magnetization curves of the ZVO film taken at various temperatures. We observed hysteresis loops on a strong diamagnetic background of the substrate and confirmed that the sample was ferromagnetic with $T_C > 200$ K [see inset of Fig. (a)]. The ferromagnetic moment was $\sim 6\times10^{-3} \mu_B$/V ion. In Fig. (b), we have plotted a high-field ($H > 2$ T) magnetic susceptibility, $\partial M/\partial H > 2T$, as a function of $T$, where
$M$ is the magnetization of the sample. $\partial M/\partial H_{H>2T}$ was fitted to the Curie-Weiss (CW) law with an offset, $\partial M/\partial H_{H>2T} = NC/(T-\Theta) + \partial M/\partial H_0$, where $C = (g\mu_B)^2S(S+1)/3k_B$ is the Curie constant, $\Theta$ is the Weiss temperature, $\partial M/\partial H_0$ is a constant, $N$ is the number of magnetic ions in the sample, and $g$ is the $g$-factor. $\partial M/\partial H_0$ contains the diamagnetic and temperature-independent paramagnetic contribution. The excellent fit indicates that the temperature dependence of $\partial M/\partial H_{H>2T}$ is caused by the local magnetic moments with antiferromagnetic correlations. We attribute this CW behavior to those of the V$^{2+}$ ions (described below). Assuming $g = 2$ and $S = 3/2$, one obtains $N = 0.41 \times 10^{15}$, which is estimated to be $\sim 10\%$ of the total V atoms in the sample.

![Figure 2: XAS and XMCD at the V 2p and O 1s absorption edges of ZVO (x = 0.05) recorded at $T = 20$ K and $H = 7$ T.](image)

Figure 2 shows V 2p and O 1s XAS and XMCD taken at $T = 20$ K under $H = 7$ T. The structures around $h\nu = 516$ eV, 524 eV, and $>530$ eV are the V 2p$_{3/2}$, V 2p$_{1/2}$, and O 1s absorption edges, respectively. We note that Ar-ion sputtering have reduced the peak at 518.3 eV (most likely due to contamination in the surface region), although it was not completely removed. The O 1s XAS showed a sharp peak at $h\nu = 537.5$ eV and a plateau at $h\nu \sim 540 - 543$ eV, similar to that of highly oriented ZnO microrod arrays with polarization vector within the ab-plane [19]. This indicates that the c-axis of ZVO was oriented to surface normal. The V 2p XAS and XMCD show multiplet structures, indicating that the doped V atoms were in an oxidized state and not in a metallic state such as metallic clusters. The strongest negative and positive XMCD signals were observed at $h\nu = 515.6$ eV and 517.5 eV, respectively, which were different from the peak positions of $h\nu = 515.9$ eV and 517.3 eV in the V 2p XAS spectrum. This may be explained in a magnetically inhomogeneous picture of the V ions that there exists an XMCD-active minority component whose electronic environment differs from the XMCD-inactive majority component. The energy integral of the V 2p XMCD signal was close to zero (or even slightly negative: see, Fig. 2), indicating that the orbital magnetic moment of the V 3d electrons is quenched from the ionic value [20].

![Figure 3: (Color online) Magnetic field dependence of XMCD at the V 2p absorption edge. (a) Raw spectra taken at $T = 20$ K. Inset shows the normalized spectra. (b) XMCD signal intensity vs magnetic field.](image)

Figure 3 shows V 2p and O 1s XAS and XMCD taken at $T = 20$ K under $H = 7$ T. Since XMCD taken at $\sim 0.1$ T was small on the scale of Fig. 3 (b), we show normalized XMCD in the inset in Fig. 3 (a). Figure 3 (b) shows the XMCD intensity as a function of $H$. The linear increase of the XMCD signal with $H$ indicates that the paramagnetic signal dominates the XMCD signal and that the ferromagnetic component is small, consistent with the magnetization measurements. The line shapes under 2 T and 7 T were nearly identical [inset in Fig. 3 (a)]. The V 2p XMCD signals at 170 K under 2 T was $\sim 30\%$ of that at 20 K under 2 T. This indicates that the paramagnetism observed in the V 2p XMCD signal is mainly reflecting the CW paramagnetism of the V ions. In fact, using $\Theta = 25$ K derived from the magnetization measurements (Fig. 1), the CW susceptibility at 170 K becomes 23% of that at 20 K, which explains most of the XMCD intensity decrease from 20 K to 170 K. The majority of the V ions were presumably strongly coupled antiferromagnetically (Néel temperature $\gtrsim 1000$ K [16]), and hence its contribution to the susceptibility was negligible.

![Figure 4: (Color online) Comparison of V 2p XAS and XMCD with atomic multiplet calculations of V$^{2+}$ ions. $\langle S_z \rangle$ and $\langle L_z \rangle$ (in unit of $\mu_B$) are also shown. Crystal field parameters are schematically shown in the right panel.](image)

In Fig. 4 we show atomic multiplet calculations for V$^{2+}$ under octahedral $(O_h)$, tetrahedral $(T_d)$, and trigonal $(C_{3v})$ symmetries by introducing the crystal field parameters $10Dq$ and $\Delta_t$ (see right panel in Fig. 4). $C_{3v}$
symmetry arises from a slight elongation or contraction of the tetrahedron along the c-axis of ZnO having the wurtzite structure. The orbital and spin magnetic moments, \( \langle L_z \rangle \) and \( \langle S_z \rangle \), are also indicated in the figure. Large \( \langle L_z \rangle \) is present in the case of \( T_d \) or \( C_{3v} \) with \( \Delta_t < 0 \) while those in the case of \( O_h \) or \( S_3 \) with \( \Delta_t > 0 \) are small, because the orbital degeneracy remains for \( T_d \) and \( C_{3v} \) with \( \Delta_t < 0 \) while it is lifted for \( O_h \) and \( S_3 \) with \( \Delta_t > 0 \). Thus, we conclude that the V 2p XMCD came from substitutional \( V^{2+} \) ions under slight elongation of the tetrahedra along the c-axis of ZnO. On the other hand, the experimental V 2p XMCD indicated a quenched \( \langle L_z \rangle \), we could exclude \( T_d \) and \( C_{3v} \) with \( \Delta_t < 0 \). A shoulder structure around \( h\nu \sim 514 eV \) in the XMCD was reproduced in \( C_{3v} \) with \( \Delta_t > 0 \). Therefore, the majority of the V ions were expected to be at the substitutional sites as divalent ions without significant elongation of the tetrahedra (reduced \( \Delta_t \)).

The CW paramagnetic magnetization of the sample at 20 K under 2 T (Fig. 1) could be explained by \( \sim 2 \% \) of the full magnetization of the \( V^{2+} \) ions. This value was in good agreement with the observed V 2p XMCD intensity which was \( \sim 5 \% \) of that of the atomic multiplet calculation (note that the experimental XMCD is magnified by a factor of 20 in Fig. 1). Thus, we could associate the CW paramagnetic behavior in \( \partial M/\partial H_{H>2T} \) to the CW paramagnetic behavior in V 2p XMCD and hence to the substitutional \( V^{2+} \) under slight elongation along the c-axis.

In the previous XMCD study of \( \text{Zn}_1-x\text{Co}_x\text{O} \), the ferromagnetic and paramagnetic Co ions were found to exist in similar electronic environment. Therefore, although not observed in this study, the ferromagnetic V ions may be in a similar environment to that of the paramagnetic V ions identified in this study. It may be possible that subtle environmental differences, e.g., in the nearest neighbor cations and/or neighboring defects determine whether the magnetic ion becomes ferromagnetic or paramagnetic in transition-metal-doped ZnO.

In summary, the field and temperature dependence of the V 2p XMCD of ZVO \((x = 0.05)\) showing small ferromagnetic moment revealed that \( \sim 10 \% \) of the V ions were CW paramagnetic, \( \sim 90 \% \) were presumably strongly coupled antiferromagnetically, and the ferromagnetic component was below the detection limit of XMCD. Elongation along the ZnO c-axis was important in order to explain the XMCD line shape and the quenched orbital magnetic moment of the \( V^{2+} \) CW paramagnetic component. Our study suggests that local lattice distortion and subsequent orbital anisotropy are important in explaining the magnetism of ZnO-based DMSs.

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