Soft x-ray magnetic circular dichroism study of weakly ferromagnetic Zn\textsubscript{1-x}V\textsubscript{2}O thin film

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The authors performed a soft x-ray magnetic circular dichroism (XMCD) study of a Zn\textsubscript{1-x}V\textsubscript{2}O thin film, which showed a small ferromagnetic moment. Field and temperature dependences of V 2p XMCD signals indicated the coexistence of Curie-Weiss paramagnetic and antiferromagnetic V ions, quantitatively consistent with the magnetization measurements. The authors attributed the paramagnetic signal to V ions substituting for Zn sites, which are somewhat elongated along the c axis. A possible formation of ferromagnetically dead layers in the surface region of the film is also discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2431571]

Recently, ZnO-based diluted magnetic semiconductors (DMSs) have attracted much interest due to their potentially high Curie temperatures \(T_C\).\textsuperscript{1} aiming at practical applications in spintronics devices.\textsuperscript{2} After the report of \(T_C \approx 280\) K in Zn\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{2},\textsuperscript{3} there have been many reports on ZnO-based DMSs showing high \(T_C\)’s (for a recent review, see Ref. 4). Zn\textsubscript{1-x}V\textsubscript{2}O (ZVO) thin films prepared by the pulsed laser deposition method under a reduced atmospheric condition showed \(T_C\)’s above 400 K.\textsuperscript{5} The ferromagnetism in ZVO was reproduced in Refs. 6 and 7, but no ferromagnetic behavior was observed in a recent report.\textsuperscript{8} Thus, the high \(T_C\) in ZVO has remained controversial because of its origin.\textsuperscript{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.\textsuperscript{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 for investigating the electronic and magnetic properties of DMSs.\textsuperscript{11-17}

A thin film of ZVO (\(x=0.05\)) was epitaxially grown on a ZnO(0001) buffer layer on an Al\textsubscript{2}O\textsubscript{3}(1120) substrate as described elsewhere.\textsuperscript{5} The film size was approximately \(5 \times 7 \text{ mm}^2\) with the thickness of 100 nm. XAS and XMCD measurements were performed at BL23SU of SPring-8.\textsuperscript{18} The monochromator resolution was \(E/\Delta E > 10,000\), and absorption spectra were recorded in a total electron yield mode. 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 °C, similar to that performed in a photoemission study.\textsuperscript{19} We also performed magnetization measurements after the XAS and XMCD measurements using a semiconductor quantum interference device magnetometer (MPMS, Quantum Design Co., Ltd.).

Figure 1(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. 1(a)]. The ferromagnetic moment was \(\sim 6 \times 10^{-3} \mu_B\) per V ion. In Fig. 1(b), we have plotted a high-field (\(H > 2\) T) magnetic susceptibility, \(\partial M/\partial H_{H=2} - \partial M/\partial H_{H=0}\), as a function of \(T\), where \(M\) is the magnetization of the sample. \(\partial M/\partial H_{H=2}\) was fitted to the Curie-Weiss (CW) law with an offset, \(\partial M/\partial H_{H=2} = NC/(T - \Theta) + \partial M/\partial H_0\), 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 contributions. The excellent fit indicates that the temperature dependence of $\partial M / \partial H_{Z0}$ is caused by the local magnetic moments with antiferromagnetism in the surface region produced the peak at 518.3 eV edges, respectively. We note that Ar-ion sputtering has reduced the total V atoms in the sample.

Figure 2 shows V 2p and O 1s XAS and XMCD taken at $T=20$ K under $H=7$ T. The structures around $h\nu=516, 524,$ 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 has 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 $h\nu\sim540-543$ eV, similar to that of highly oriented ZnO microrod arrays with polarization vector within the $ab$ plane. This indicates that the $c$ axis of ZVO was oriented along the 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 $h\nu=515.6$ and 517.5 eV, respectively, which were different from the peak positions of $h\nu=515.9$ 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.

Figure 3(a) shows the $H$ dependence of V 2p XMCD at 20 K. Since XMCD taken at $\sim0.1$ T was small on the scale of Fig. 3, 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 and 7 T were nearly identical with the magnetization measurements. The line shapes under 2 and 7 T were nearly identical with the magnetization measurements. The line shapes under 2 and 7 T were nearly identical with the magnetization measurements. The line shapes under 2 and 7 T were nearly identical with the magnetization measurements. The line shapes under 2 and 7 T were nearly identical with the magnetization measurements. The line shapes under 2 and 7 T were nearly identical with the magnetization measurements.

In Fig. 4, we show atomic multiplet calculations for V$^{2+}$ (Ref. 25) under octahedral ($O_h$), tetrahedral ($T_d$), and trigonal ($C_{3v}$) symmetries by introducing the crystal field parameters $10Dq$ and $\Delta_i$ (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, $\langle L_s \rangle$ and $\langle S \rangle$, are also indicated in the figure. Large $\langle L_s \rangle$ is present in the case of $T_d$ and $C_{3v}$ with $\Delta_i<0$ while those in the case of $O_h$ and $C_{3v}$ with $\Delta_i>0$ are small, because the orbital degeneracy remains for $T_d$ and $C_{3v}$ with $\Delta_i<0$ while it is lifted for $O_h$ and $C_{3v}$ with $\Delta_i>0$. Since the V 2p XMCD indicated a quenched $\langle L_s \rangle$, we
could exclude $T_d$ and $C_{3v}$ with $\Delta_2 < 0$. A shoulder structure around $h\nu \sim 514$ eV in the XMCD was reproduced in $C_{3v}$ with $\Delta_2 > 0$. 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 XAS line shape resembled the spectra for $T_d$ or $C_{3v}$ with $\Delta_2 < 0$. 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 $\Delta_2$).

The CW paramagnetic magnetization of the sample at 20 K under 2 T (Fig. 1) could be explained by ~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 ~5% of that of the atomic multiplet calculation (note that the experimental XMCD is magnified by a factor of 20 in Fig. 4). Thus, we could associate the CW paramagnetic behavior in $\partial M / \partial H_{C}>2$ T 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 Zn$_{1-x}$Co$_x$O$_2$, the ferromagnetic and paramagnetic Co ions were found to exist in a 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. The subtle environmental differences such as the neighboring cations and defects would be important ingredients that would determine the magnetic character of the transition-metal ions in ZnO. The small (undetectable) ferromagnetic XMCD signals may be due to magnetically dead surface layers as inferred for the cases of Zn$_{1-x}$Co$_x$O$_2$ (Ref. 16) and Ti$_{1-x}$Co$_x$O$_2$. In summary, the field and temperature dependences of the V 2p XMCD of ZVO ($x=0.05$) showing small ferromagnetic moment revealed that ~10% of the V ions were CW paramagnetic, ~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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