Robust Room-temperature Magnetism of (110) CrO2 Thin Films

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Deposited 07/16/2019

Citation of published version:
Robust room-temperature magnetism of (110) CrO$_2$ thin films

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(Received 26 October 2009; published 14 December 2009)

We have used x-ray magnetic circular dichroism (XMCD) and ab initio electronic-structure calculation techniques to investigate the magnetic properties of high-quality epitaxial (110) and (100) CrO$_2$ thin films. A relatively larger XMCD was observed on the Cr $L_{2,3}$ edge of (110)-oriented CrO$_2$ films compared to (100)-oriented CrO$_2$ films at room temperature. Analysis of our data with conventional sum rules for 3$d$ elements shows a nearly 50% higher spin moment on (110) films compared to (100) orientation, consistent with bulk magnetometry measurements. The orbital moment is found to be similar for both orientations. Robust magnetism is attributed to increased collinearity of Cr spins in strain-free (110) films as compared to strained (100) films. Zero-temperature density-functional calculations show opposing trends in nearest-neighbor and next-nearest-neighbor exchange interactions between relaxed and strained CrO$_2$.

DOI: 10.1103/PhysRevB.80.212405

CrO$_2$ is a well-established half metal. Point-contact Andreev reflection$^{1-4}$ and Meservey-Tedrow spin-polarized tunneling measurements$^5$ on CrO$_2$ have recorded spin-polarization values as high as 98%. Half metallicity makes CrO$_2$ one of the most attractive candidates for spin-electronic devices since very large tunnel or giant magnetoresistance can, in principle, be obtained with CrO$_2$-based devices. Other properties of CrO$_2$ include its selective growth on pat-terned TiO$_2$ substrates,$^6$ columnar growth on Al$_2$O$_3$ substrates,$^6$ growth for thicknesses as low as a few tens of nanometers$^10$ and no easy-axis variation with temperature—pointing to their substantially different material properties.

In this paper we investigate the surface magnetic properties of (110) and (100) CrO$_2$ thin films using the element-specific and surface/interface sensitive x-ray magnetic circular dichroism (XMCD) technique. (110)-oriented CrO$_2$ films show substantially stronger XMCD than (100) films at room temperature which we quantify using the XMCD sum rules.$^{11}$ We find the room-temperature magnetism of (100) films to be significantly suppressed—almost 50% lower compared to (110) films. This result is supported by temperature-dependent bulk magnetization measurements. Orbital moments, on the other hand, show no substantial difference between the two orientations. We have also performed ab initio calculations to investigate the effect of strain on exchange interactions of CrO$_2$.

For our experiment, CrO$_2$ samples of both (100) and (110) orientations were deposited on TiO$_2$ substrates of the same respective orientations by a standard chemical vapor deposition technique using a solid CrO$_3$ precursor.$^{12}$ Growth details

FIG. 1. (Color online) Rutile structure of (100)- and (110)-oriented CrO$_2$ films are shown in (a) and (b), respectively, on TiO$_2$ substrates of respective orientations. Unlabeled spheres indicate the O$^{2-}$ ions on both structures. Out-of-plane directions on (100) and (110) films are (001) and (110), respectively, as shown in the figure. In the (100) structures, compressive strain along out-of-plane direction and tensile strain along in-plane directions are schematically shown while the (110) structure remains strain free.
FIG. 2. (Color online) Photon-energy scan on Cr $L_{2,3}$ edges (600–565 eV), showing strong polarization-dependent x-ray absorption. We observed Cr $L_2$ and $L_3$ peaks at 585 and 577 eV, respectively, within the resolution of the instrument (±0.25 eV) for both (100) and (110) oriented films. XAS data are normalized for comparison between the spectra of (100) and (110) oriented films.

are reported in a previous publication. All films had thicknesses of ~45 nm, accurately measured by grazing incidence x-ray reflectivity using a Philips X’pert Diffractometer. Atomic force microscopy performed on as-grown samples shows our films to be extremely flat, with rms roughness of less than 1.0 nm (figure not shown). XMCD experiments were carried out on port 123, 10 m toroidal grating monochromator at the Synchrotron Radiation Center (SRC) at the University of Wisconsin, Madison. In the XMCD setup, polarized soft x rays (~85% polarization) were incident at an angle of 45° ± 5° relative to the sample surface, parallel to the $c$ axis of CrO$_2$, and all spectra were collected by the total electron yield method at room temperature with an energy resolution of 0.25 eV. The photon helicity was fixed and the film magnetization was switched by applying a ±1400 Oe magnetic field along the easy “c” axis to obtain the XMCD spectra. An average of at least five spectra is reported here. The effect of strain on the exchange energy of CrO$_2$ was evaluated by performing first-principles calculations within density-functional theory and the generalized gradient approximation (GGA) (Ref. 14) using the Vienna ab initio simulation package (VASP) (Refs. 15–18) and pseudopotentials generated by Kresse and Joubert. For structural-relaxation and constrained-field calculations (explained later), a $9 \times 5 \times 15$ Monkhorst-Pack $k$-point mesh was used for the supercell with cells stacked along the $b$ axis, and a $9 \times 9 \times 7$ mesh was used for the supercell aligned along the $c$ axis. Forces were relaxed to less than (0.01 eV/Å) and an energy cutoff of 500 eV was used for the plane-wave expansion of the projector augmented wave.

In Fig. 2 we show the normalized x-ray absorption (XAS) spectra of (110) and (100) CrO$_2$ films on Cr $L_{2,3}$ edges after saturating the films in opposite directions with fixed photon helicity (indicated by $\mu_+$ and $\mu_-$). We also obtained XAS spectra on the O-K edge, scanning the beam energy from 550 to 515 eV. However, no unambiguous XMCD was observed from the O-K edge at room temperature. Therefore, in our analysis we have neglected any spin and orbital contribution coming from the O$^{2-}$ ions in CrO$_2$. In Fig. 3(a), we plot the XMCD spectra which is obtained by subtracting the two XAS spectra obtained at opposite sample magnetizations. The (110)-oriented films show a larger XMCD signal than (100) films, as evidenced by the stronger peaks at the $L_3$ edge. The XMCD line shapes are nearly identical and agree well with previous results obtained on (100)-oriented films near room temperature. Quantitative analysis using the sum rules for 3$d$ elements is somewhat complicated for transition-metal oxides in general and for CrO$_2$ in particular. Two main issues are relevant in the case of CrO$_2$. The first arises from the weak spin-orbit splitting of the Cr 2$p$ levels and the second from the distorted oxygen octahedra around the central Cr$^{4+}$ ion. Weak spin-orbit coupling leads to substantial ‘spectral overlap,” meaning that the 2$p_{3/2}$−3$d$ transitions lie very close in energy. This overlap has been estimated to give 5–15 % error in the sum rules. Additionally, and more importantly, the x-ray absorption is not from pure $p_{3/2}$ or $p_{1/2}$ states but rather from a quantum-mechanical superposition of both. This is commonly referred to as $jj$ mixing. To take into account this mixture, correction factors have been evaluated for some systems and estimated to be approximately 2.0 for bulk Cr and we use this value in our estimates. Complications from the distorted CrO$_2$ octahedra result in a substantial contribution to the dipole-moment term, represented by $T_z$ in the spin sum rule. This $T_z$ term for CrO$_2$ has been reported to be much larger than that for 3$d$ metals such as Fe, Co, and anisotropic. In our calculations, for a lack of proper understanding and available data, we do not correct for the $T_z$ value and further assume the $T_z$ value to be the same for (100) and (110) orientations as the $c/a$ ratio values are found to be 0.669 for strained (100) structure and 0.659 for the strain-free (110) structure suggesting a small tetragonal distortion due to strain in (100) structure. The orbital moment, on the other hand, does not depend on the $T_z$ term explicitly and can be estimated directly using the sum rules.

Knowing these limitations, we analyzed our data using the XMCD sum rules for 3$d$ elements. To be more specific, we evaluated the XMCD integral over the $L_3$ edge ($p$), the
FIG. 4. (Color online) Normalized magnetic moments of (100) and (110) CrO$_2$ films plotted vs temperature in steps of 10 K. Data from 10 to 350 K were taken in SQUID and from 300 to 425 K were taken using a VSM. No offset in moment was found between SQUID and VSM data. Moment values are estimated to be correct within less than 2% of their measured value at all temperatures and temperature was stable within 0.2 K. The $T_c$ for (100) and (110) CrO$_2$ films are found to be 385 and 393 K, respectively. Considering the fluctuations near $T_c$, the error in $T_c$ can be estimated to be $\pm 5$ K.

Combined integral over $L_3$ and $L_2$ edges ($q$), and separately the background corrected XAS spectra over the $L_3$ and $L_2$ edges ($r$). We use $N_{\text{SS}}$=8.0 for Cr$^{4+}$, and knowing these values the sum rules take a simpler form: $m_s+7T_2$=2(4$q$−6$p$)/$r$ and $m_s$=−8$q$/$3r$. In Fig. 3(b), we plot the sum integrals $p$ and $q$ vs energy (r not shown). We find the orbital moment to be virtually identical for both (100) and (110) orientations, approximately −0.030±0.005$\mu_B$. This value agrees reasonably well with LDA+U calculations of Komelj et al. (0.037$\mu_B$) but is slightly lower than experimental reports of Goering et al. (0.062$\mu_B$) and Huang et al. (0.051$\mu_B$). The spin moments were found to be (1.2±0.2)$\mu_B$ and (1.8±0.3)$\mu_B$ for (100) and (110) orientations, respectively. Since these measurements are at room temperature, we expect the moment values to be less than 2.0$\mu_B$ per Cr, the experimental and theoretical bulk moment at low temperature, consistent with a 3d$^2$ electronic configurations for Cr$^{4+}$ ion.

We therefore find the (110) spin moment to be nearly 50% higher than (100) orientation at room temperature. This is consistent with bulk magnetic measurements shown in Fig. 4 measured using a Quantum Design superconducting quantum interference device (SQUID) system and vibrating sample magnetometer (VSM). Temperature scans of the magnetic moment for both films are shown in Fig. 4. Magnetization for both films at 10 K is found to be $\sim 6.5 \times 10^5$ A/m which is in agreement with previous reported magnetization values at low temperature. However, the magnetic moment decays faster in case of (100) CrO$_2$ films which are about 25% lower than (110) CrO$_2$ films at room temperature though SQUID and VSM measure the total magnetic moment of the film while XMCD gives surface magnetic moment. Given the 10–15 % error in moment estimation with XMCD, the difference in moment between (100) and (110) CrO$_2$ films at room temperature obtained by SQUID is in good agreement with the difference calculated from XMCD analysis. We believe this is an intrinsic property of our high-quality CrO$_2$ thin films, and a direct manifestation of the different effects of strain in the two orientations. As supporting evidence, Fig. 4, the Curie temperature ($T_c$) for (100) CrO$_2$ was found to be slightly lower than that of (110) CrO$_2$. It is known that $T_c$ can be suppressed due to strain$^{25}$ in a film.

In order to understand the experimental results, we performed first-principles calculations of the electronic structures of unstrained and strained CrO$_2$ using density-functional theory$^{13}$ in the GGA (Ref. 14) as implemented in the vasp code. To model the strained cell, the in-plane lattice constant values ($a$ and $c$) of TiO$_2$ and the experimental out-of-plane value ($b$ axis) of CrO$_2$ from Ref. 10 were used. The internal coordinates of the ions were relaxed starting from the GGA-relaxed CrO$_2$ value for this calculation. This strained structure was found to be half metallic (online information) with a zero-temperature moment of 2$\mu_B$/f.u.—consistent with a Cr$^{4+}$ configuration and similar to bulk CrO$_2$ calculations. The density of states analysis showed an overall slight upward shift for the Cr 3d and O 2p bands (online information), consistent with the higher electronic energy of this structure (online information). Next we evaluated the nearest-neighbor exchange constant ($J_1$) along the body-diagonal (111) direction and the next-nearest-neighbor exchange constants ($J_2$) along c (001) and b (010) directions of the CrO$_2$ cell. For reference, along with the strained cell, we have also calculated the exchange constants for the GGA-relaxed configuration and the experimental bulk structure (results summarized in Table I). To accomplish this calculation, a series of constrained-field calculations were performed within an internally relaxed 12-atom supercell using the method outlined in Ref. 26. In short, the total electronic energy was calculated with the magnetic moment of selected Cr ions rotated up to 60° (noncollinear configuration), and the energy vs angle data fitted to a Heisenberg model to determine the exchange constants. This analysis showed two contrasting trends. We found a small reduction

<table>
<thead>
<tr>
<th>Structure</th>
<th>Lattice constants (Å)</th>
<th>Volume (Å$^3$)</th>
<th>$J_1$ (111) (meV)</th>
<th>$J_2$ (010) (meV)</th>
<th>$J_2$ (001) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt. Bulk</td>
<td>$a=b=4.421$, $c=2.916$</td>
<td>56.994</td>
<td>23.2</td>
<td>−11.8</td>
<td>33.8</td>
</tr>
<tr>
<td>GGA Bulk</td>
<td>$a=4.451$, $b=4.448$, $c=2.923$ (+0.67%, +0.60%, +0.24%)</td>
<td>57.869</td>
<td>22.9</td>
<td>−10.4</td>
<td>35.8</td>
</tr>
<tr>
<td>Expt. Strained</td>
<td>$a=4.584$, $b=4.377$, $c=2.958$ (+3.69%, −1.00%, +1.44%)</td>
<td>59.349</td>
<td>22.5</td>
<td>−8.1</td>
<td>40.1</td>
</tr>
</tbody>
</table>
in $J_1$ in the strained cell (22.5 meV) compared to the GGA-relaxed (22.9 meV) and the experimental-relaxed (23.2 meV) configurations. This is consistent with the picture that the distance between the body-center and corner Cr ions increases in the strained cell. But we also observe a substantial increase in $J_2$ both along (001) and (010) directions as outlined in Table I. Overall this latter effect dominated the total exchange energy. Therefore, our zero-temperature calculations indicate that the Curie temperature of the strained cell should be higher than either the GGA relaxed or the experimental bulk structure—in contradiction to experimental results. The increase in $J_2$ along the c direction is particularly striking. The physical reason for such a behavior is not understood at this moment and shall be a subject of future investigation. It should be emphasized that the theoretical calculations are at zero temperature whereas the theoretical calculations are at zero temperature whereas the experimental deviation in the magnetization between strained and strain-free CrO$_2$ are pronounced near room temperature. Second, it is plausible that $J_1$ and $J_2$ have different temperature dependence with $J_1$ dominating $J_2$ as we approach the Curie temperature. Also it should be pointed out that for our 0 K calculations we have used the available room-temperature lattice-constant values. Additionally, during the course of our calculation we found the exchange energy to extremely sensitive to the nearest neighbor exchange. Therefore, we speculate that the discrepancy between theory and experiment could originate from one or all of the above-mentioned possibilities.

In conclusion, we carried out XMCD measurements on CrO$_2$ thin films of (100) and (110) orientations at room temperature and analyzed the data using XMCD sum rules. Spin moments were found to be almost 50% higher for (110)-oriented films compared to (100)-oriented films. Temperature-dependent bulk magnetometry measurements revealed a similar trend with (100) films also exhibiting a slightly lower Curie temperature. We attribute these effects to the intrinsically different growth modes of (100) and (110) films on TiO$_2$ substrates; (100) films grow strained while (110) films grow strain free. Orbital moments were found to be the same for both orientations. Zero-temperature calculations of the nearest- and next-nearest-neighbor exchange constants using density-functional methods were found to be extremely sensitive to the lattice parameters. For the relaxed and the strained structures that were considered, an overall decrease in exchange energy originating from strong next-nearest interactions was found in the strained cell, masking a small reduction in nearest-neighbor exchange.

The authors gratefully acknowledge Mary Severson and Mark Bissen for helping with beam line and troubleshooting during experiment. Authors also gratefully thank E. Goering of Max-Plank-Institute für Metallforschung, Stuttgart, Germany for fruitful suggestions and discussions. Hideo Sato’s help with detailed x-ray analysis of our samples and Gihan Kwon’s help with data analysis are also gratefully appreciated. This work is based in part upon research conducted at the Synchrotron Radiation Center, University of Wisconsin-Madison, which is supported by the National Science Foundation under Award No. DMR-0537588. This work has been supported by funding from NSF under Grant No. DMR-0706280.