Strong Anisotropy of Projected 3d Moments in Epitaxial CrO₂ Films

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Soft x-ray magnetic circular dichroism (XMCD) spectra have been investigated for different crystallographic projections of CrO₂. Strong anisotropic orbital Cr 3d contributions and a change of sign of the XMCD signal is observed and attributed to t_{2g} majority states near the Fermi level. Additionally, moment analysis exhibits anisotropic behavior in the projected spin contributions of CrO₂ assigned to a strong magnetic dipole term T_z , consistent with an intrinsic magnetic easy axis behavior along the CrO₂ [001] axis. A reduced projected isotropic Cr 3d spin moment has been interpreted in terms of hybridization with oxygen.

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In the past few years, CrO₂ has attracted revived interest due to its remarkably high spin polarization at the Fermi energy, theoretically predicted to be 100% [1–4] and recently verified by superconducting tunneling spectroscopy at $T = 18$ K [5,6] and spin-polarized photoemission spectroscopy at $T = 293$ K [7]. The reason for this revival is mainly related to promising future applications such as magnetic tunneling and spin injection devices on the basis of CrO₂ electrodes [8]. The oxygen mediated coupling and its half metallic nature are a challenging problem for theoretical investigations, originated by the presence of oxygen hybridization, double exchange, self-doping, and correlation effects [2]. The quantitative influence of orbital moments [9], inner 3d shell spin-orbit coupling, and the magnetic dipole term T_z [10] to the magnetocrystalline anisotropy (MCA) is still unknown but of importance for the understanding of the magnetic properties of CrO₂. Recent theoretical orbital momentum calculations of CrO₂ have been published with contradictory results: Vanishing [11] as well as nonvanishing orbital moments [12] have been predicted.

CrO₂ is metastable at room temperature, which is a severe problem for surface sensitive spectroscopic investigations [13]. Nevertheless, high quality epitaxially grown thin film samples of CrO₂ can be prepared [14], which exhibit anisotropic electronic transport properties and a magnetic easy axis along the CrO₂ [001]-direction [15]. Stagarescu *et al.* recently performed oxygen K -edge x-ray absorption spectroscopy (XAS) on an epitaxially grown CrO₂ thin film with nearly no Cr₂O₃ contributions [16], which clearly shows anisotropic behavior and gives information about the orbital character of the O 2p-like states near the Fermi level.

CrO₂ crystallizes in a rutile structure with two equivalent a axes (0.4421 nm) and a shorter c axis (0.2916 nm) [17]. CrO₂ films investigated have been epitaxially grown on isostructural TiO₂ substrates by a chemical vapor deposition technique [18] with a resulting sample thickness of

approximately 100 nm. CrO₂ films show a (100) orientation and have a Curie temperature of 385 K. Further details of the sample growth and characterization have been discussed elsewhere [14].

All spectra were recorded in total electron yield mode at the bending-magnet beam line PM I at BESSY II with an energy resolution $E/\Delta E = 2000$ in an applied magnetic field of ± 5 kOe (flipped at each data point). The degree of circular polarization was 95%. All spectra have been measured at 80 K. Spectra are carefully background subtracted and edge normalized using the same background and normalization factor for parallel and antiparallel orientation of the photon beam k vector with respect to the sample magnetization. Further details of the experimental setup and data analysis have been published elsewhere [19]. The experimental geometry is schematically shown in the inset of Fig. 1a. X-ray magnetic circular dichroism (XMCD) spectra were taken at fixed grazing incidence ($\phi = 60^\circ$) and the sample was rotated by the angle ϑ around the surface normal.

Figure 1a shows normalized XAS spectra for $\vartheta = 7^\circ$ and Fig. 1b shows the corresponding XMCD signals for nearly a axis (7°), c axis (86°) and intermediate (40°) projected azimuthal sample orientations. Compared to other 3d metal XMCD spectra [20–22], very strong and pronounced changes as a function of the azimuthal angle ϑ are present. For c -axis enhanced projection ($\vartheta = 86^\circ$) a direct observable change of sign at 587 eV is present. The negative XMCD intensity suggests a strong increase of the projected orbital moment for increased c -axis projections. In contrast only very small changes in the averaged Cr $L_{2,3}$ XAS are present and therefore not shown. We have measured ϑ at seven different angles, partially omitted in Fig. 1 for enhanced clarity but considered in the following data analysis. In order to prove that all spectral variations are related to crystallographic projections, we have performed two different series of XMCD spectra with fixed azimuthal angles and corresponding rotations around the

FIG. 1. (a) CrO₂ XAS for parallel and antiparallel alignment of the photon beam to the sample magnetization; the inset shows the experimental geometry of the crystallographic axes of the sample relative to the incoming photon beam. (b) XMCD signal at 5 kOe applied magnetic field for three different azimuthal angles θ and fixed $\phi = 60^\circ$; the inset shows *in situ* Cr 3d related XMCD magnetization loops for enhanced *a*- and *c*-axes projections.

in-plane *c* and *a* axes perpendicularly aligned to the photon $\vec{k}$ vector. For the *c*-axis rotation the photon $\vec{k}$ vector lies in the crystallographic *a*-*a* plane, and no changes in the XMCD spectra have been observed. While the other scans with a rotation around the in-plane *a*-axis, the photon $\vec{k}$ vector varies from *c*-axis to *a*-axis projection similar to the grazing incidence azimuthal scans shown in Fig. 1b, leading to the same changes in the XMCD spectra. In addition, *in situ* element specific magnetization curves have been measured at each θ , which are shown in the inset of Fig. 1b [23]. From these hysteresis loops (confirmed by SQUID data) we have extracted the uniaxial anisotropy energy $K_1 = (5.8 \pm 0.5) \times 10^4 \frac{\text{J}}{\text{m}^3}$ [24], demonstrating a magnetic easy axis along the crystallographic *c* axis [15].

For a detailed analysis of the experimental data we have reproduced a recent local spin density approximation including the Hubbard *U* (LSDA + *U*) calculation [2]. Figure 2 shows the spin-up and spin-down density of states (DOS) for Cr 3*d* and O 2*p* states. Two general features are directly observable, a narrow (1 eV wide) fully spin-polarized unoccupied band feature at 0.5 eV above the Fermi level and a broader feature 3 eV above. The first one has been identified as unoccupied majority t_{2g} states

FIG. 2. Total density of states for Cr *d* (solid line) and O *p* (dotted line) like states reproduced from Korotin *et al.* [2]. The inset shows the corresponding spin-polarized DOS.

while the one at higher energy is a mixture of e_g -majority and t_{2g}/e_g -minority states. For the interpretation of the angular dependent XMCD spectra we take the CrO₂ band structure into account as a simple superposition of three sets of ground-state moments, similar to previously published data of textured CrO₂ films [25]. Conventional sum rule analysis [26,27] can unambiguously yield to the total projected 3*d* orbital moment but not to the Cr 3*d* spin moment, which is related to the small 2*p* spin-orbit splitting ($E_{SO} = 9.3$ eV [28]). Therefore, XMCD data has been fitted with a procedure originally used to understand the fundamental XMCD spectra of the pure metal 3*d* series as a superposition of so-called ground-state moments $\langle w^{xyz} \rangle$ introduced by van der Laan [29]. Those moments represent several contributions to the $2p \rightarrow 3d$ XMCD signal. For example, the moments $\langle w^{000} \rangle = n_h$, $\langle w^{101} \rangle = L_z/2$, $\langle w^{011} \rangle = 2S_z$, $\langle w^{110} \rangle = -\sum_i l_i \cdot s_i$, and $\langle w^{211} \rangle = 7T_z/2$ correspond to the number of holes in the 3*d* band, orbital moment, spin moment, spin-orbit coupling, and the magnetic dipole term, respectively. This method has been experimentally proven for iron garnets [30] and light transition metals [31].

By applying this fitting procedure the spectral overlap of L_3 and L_2 edges can be separated, but possible quantum mechanical mixtures of $J = 3/2$ and $1/2$ contributions [32] will not be considered. Figure 3 shows the intermediate spectrum at $\theta = 40^\circ$ (open circles) and a moment fit (solid line) using a sum over three different sets at energies $E_1 = 577.0$ eV (dotted line), $E_2 = 580.5$ eV (dashed line), and $E_3 = 587.0$ eV (dot-dashed line). Energy positions for the corresponding L_3 and L_2 centers of gravity are indicated by vertical lines. To reduce the number of free parameters the sum over all orbital contributions has been set to the sum rule determined value. Peak width and broadening have been held fixed for all fitted XMCD spectra. The small third energy feature (E_3) could be interpreted in terms of magnetic extended x-ray absorption fine

FIG. 3. Experimental XMCD data at $\vartheta = 40^\circ$ (open circles) and a moment fit (solid line) for three different fit energies $E_1 = 577.0$ eV (dotted line), $E_2 = 580.5$ eV (dashed line), and $E_3 = 587.0$ eV (dot-dashed line).

structure (EXAFS), therefore, only fitted with pure spin contributions [33].

All spectral features could be reproduced nearly perfectly by this fitting procedure. Fit results are presented in Fig. 4. Data points in the polar plot were mirrored at the horizontal and vertical axes to complete a full polar diagram. Figure 4a shows the absolute angular dependency of the total spin moment and extracted orbital contributions for the two different energy regions, and Fig. 4b (Fig. 4c) exhibits spin (orbital) projections.

In Fig. 4b the spin part exhibits a pronounced angular dependency with the same tendency at E_1 and E_2 and nearly constant at E_3 . We attribute this angular dependency to a very strong magnetic dipole term T_z corresponding to a quadrupolar spin distribution at the Cr site [10,20]. The observed T_z related “spin” anisotropy is extremely high compared to previously published experimental [22] and theoretical [32] results. Using the angular dependent sum rule for T_z of Stöhr and König [20], magnetic dipole term contributions and a uniform Cr 3d spin moment of $1.20\mu_B$ can be separated. Assuming a simplified hybridization picture, an oxygen and chromium related number of electrons have been integrated from -1.3 to 0.0 eV in the primarily Cr 3d related occupied DOS (see inset of Fig. 2) [2]. The numbers of occupied electrons have been extracted to $n_{3d} = 1.38$ and $n_{2p} = 0.32$, which gives 2.02 electrons in the Cr3d-O2p valence band and an effective correction factor of $(n_{3d} + 2n_{2p})/n_{3d} = 1.46$. Including a temperature extrapolation (to 0 K) ground-state correction factor of 1.05, related to SQUID data (not shown), gives a total spin moment of $(1.9 \pm 0.1)\mu_B$, which can be theoretically expected for a $3d^2$ [1–4] configuration and is in agreement with experimental values [34]. This is strong evidence that hybridization is the dominating effect of the XMCD related spin reduction and is not due to the small L_2 and L_3 separation with corresponding mixing effects.

Fitted orbital projections (Fig. 4c) show maximum values at $\vartheta = 90^\circ$. The total change by a rotation of 90°

FIG. 4. (a) Fit results for the absolute changes in the spin (solid diamonds; divided by 10) and orbital projections (open squares and circles). Fit results for the (b) spin and (c) orbital projections of Cr 3d electrons by variation of the azimuthal angle ϑ .

is $\Delta L_{\text{sum}} = (0.065 \pm 0.005)\mu_B$ while the shift for each part is $\Delta L_1 = (0.167 \pm 0.008)\mu_B$ and $\Delta L_2 = (-0.102 \pm 0.005)\mu_B$. Therefore, the observed changes of the narrow part of the unoccupied DOS near the Fermi level dominate the angular dependency. The observed total change of the orbital moment is comparable to the calculations of Uspenskii *et al.* [12]. A similar behavior for the two energy regions with opposite sign has been observed in the O K-edge XMCD of CrO_2 , which only reflects O 2p orbital contributions [35]. This strongly supports the Cr 3d- O 2p-hybridization model and that the Cr 3d XMCD spectral expansion in terms of ground-state moments is appropriate for CrO_2 . Bruno’s model of magnetocrystalline anisotropy [9], which is a second order perturbation approach for a filled majority spin system, is not applicable for a less than half filled

3d shell. Van der Laan recently modified the Bruno model [10], by taking into account orbital contributions of majority spin-up and minority spin-down electrons separately. In addition a new origin for MCA has been proposed, related to the magnetic dipole term $\langle \mathbf{T} \rangle$ [10]. The relevant equation (28) from Ref. [10] is $\delta E \approx -\frac{1}{4} \cdot \xi \hat{\mathbf{S}} \cdot [\langle \mathbf{L}^\downarrow \rangle - \langle \mathbf{L}^\uparrow \rangle] + \frac{\xi^2}{\Delta E_{\text{ex}}} \frac{21}{2} \hat{\mathbf{S}} \cdot \langle \mathbf{T} \rangle$, neglecting the squared diagonal spin-orbit interaction. In the case of CrO_2 the minority band is empty, the orbital part of the minority band ($\downarrow$) vanishes, and the MCA reduces to

$$\delta E \approx \frac{\xi}{4} \cdot \hat{\mathbf{S}} \cdot \langle \mathbf{L}^\uparrow \rangle + \frac{\xi^2}{\Delta E_{\text{ex}}} \frac{21}{2} \cdot \hat{\mathbf{S}} \cdot \langle \mathbf{T} \rangle. \quad (1)$$

Correcting for finite $\phi = 60^\circ$ and using the $\langle \mathbf{T} \rangle$ sum rule [20,25] we obtain from the experiment $\Delta(7\langle \mathbf{T} \rangle) = -1.5$, $\Delta\langle \mathbf{L} \rangle = 0.083$, $\langle \mathbf{S} \rangle = 0.6$. From the LSDA + U calculation [2] an averaged exchange energy $\Delta E_{\text{ex}} = 3$ eV is extracted. With the hysteresis-derived uniaxial anisotropy energy $K_1 = (5.8 \pm 0.5) \times 10^4 \frac{\text{J}}{\text{m}^3}$ we can calculate a spin-orbit coupling energy of $\xi = 28.2$ meV from Eq. (1), comparable to theoretical values for light transition metal ions [36]. The orbital term favors an *a-a*-plane easy axis behavior while the dipole term favors the *c* axis. Both MCA contributions nearly cancel each other, but the dipole term dominates. The observed reorientation transition for ultrathin CrO_2 films [15] could be interpreted by lattice mismatch induced changes in the delicate balance between orbital and dipole terms.

Because of the film thickness of approximately 100 nm and a surface sensitivity of the total electron yield (about 1.5–3.0 nm), it has been assumed that the surface is quite unstrained and the observed changes are related to intrinsic properties of CrO_2 [15]. For the presented data it can be excluded that self-absorption is a possible origin for the observed behavior in the projected spin and orbital moments (constant angle of incidence). Details of self-absorption effects and relations to cluster CI calculations have been discussed elsewhere [25].

In conclusion, an unexpected strong anisotropic behavior of the Cr $L_{2,3}$ XMCD spectra has been observed. Using moment analysis, and taking into account band-structure-calculated energy positions and linewidths, leads to a quantitative and qualitative description of XMCD spectra. On the basis of this analysis a consistent description of the absolute spin value in terms of hybridization has been discussed. This is strong evidence that recent band-structure calculations are an appropriate description of CrO_2 ground-state properties. The application of sum rules in conjunction with moment analysis gives reasonable absolute values for light transition metal ions. The intrinsic magnetic easy axis behavior of CrO_2 along the *c* axis could be quantitatively described by a superposition of orbital and dipole term contributions.

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