Orbital moments of CrO$_2$ and Fe$_3$O$_4$ studied by MCD in soft X-ray absorption

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Abstract

We present studies of orbital magnetic moments of CrO$_2$ and Fe$_3$O$_4$ by measuring magnetic circular dichroism (MCD) in soft X-ray absorption. The results show that Fe$_3$O$_4$ exhibits large orbital moments, as a consequence of the strong Coulomb interactions of Fe 3d electrons. In contrast, orbital moments of Cr in CrO$_2$ are nearly quenched, revealing that Cr 3d electrons are strongly hybridized with O 2p electrons and more delocalized as compared with those of Fe in Fe$_3$O$_4$. Comparing the MCD data with the band structure calculations based on local spin density approximation with on-site Coulomb energy $U$ taken into account, we conclude that to include the on-site Coulomb interactions of 3d electrons is essential for adequately describing the electronic structure of CrO$_2$ and Fe$_3$O$_4$.

Keywords: X-ray absorption; Orbital moments; MCD

1. Introduction

Transition metal oxides, which are interesting for fundamental research and important for technological applications, exhibit anomalous and interesting physical properties [1]. These interesting properties are determined by the coupling between charge, orbital characters and spin of valence electrons, and the lattice degrees of freedom in transition-metal oxides. For instance, magnetic oxides such as Fe$_3$O$_4$, manganites, and CrO$_2$ have drawn much attention because of metal-to-insulator transition, colossal magnetoresistance, and half-metallic behavior. Orbital magnetism is closely related to many novel phenomena, such as magneto-optical effect, magnetostriction, and magnetocrystalline anisotropy. Orbital magnetic moments of 3d transition metals are generally quenched because of crystal field. Some 3d transition metal oxides exhibit large unquenched orbital magnetic moments, which arises mainly from spin-orbit interaction in the localized 3d orbital whereby the atomic field is deformed in a relatively slight manner by the crystal field. In addition, strong Coulomb repulsion of 3d electrons localizes 3d orbitals and reduces the ligand field on the metal atoms, leading to large unquenched orbital moments [2,3]. For instance, results of magnetic X-ray scattering indicate that the orbital magnetic moment of NiO is rather large [4].

Measurements of orbital moments provide us with an opportunity to explore the localized nature of 3d electrons in transition metal oxides [2,3]. Several experimental techniques, such as neutron scattering, magnetic X-ray scattering, and magnetic circular dichroism (MCD) in X-ray absorption spectroscopy (XAS) are useful in studying orbital moments. Element-specific separation of spin and orbital magnetization can be achieved by MCD in X-ray...
applying the MCD sum rules to high resolution and spin magnetic moments of Fe and Co obtained on 2.1. Epitaxial CrO
sections. Measurements are presented in Section 3, followed by the concluding MCD methods and epitaxial growth of CrO2 and section, we briefly describe the experimental methods in- structure calculations based on local spin density approximation performed with correction for saturation effects. We also 
values of orbital magnetic moment. To correct indirect XAS measurements for saturation and self-absorption effects is particularly crucial in measuring orbital moments [11].

Half-metallic oxides such as CrO2 have recently drawn renewed attention due to their interesting magnetic and electrical properties. These properties are potentially important for future spintronics which takes full advantage of electrons’ spins as well as their charge in information circuits. In a half-metallic material [12], one spin channel is conductive, but the other spin channel is insulating. Based on band structure calculations, many materials have been predicted to be half-metallic. However, experiments performed on some predicted half-metals do not show 100% spin polarization of the conduction electrons. One of the main reasons is that electron correlation effects prevent the conduction electrons from being 100% spin polarized. One therefore can measure orbital moments to explore the localized nature of 3d electrons in half-metallic oxides [2,3]. For instance, examining whether orbital moments are quenched is important in revealing the electronic nature of Fe3O4.

In this paper, we present measurements of MCD in soft X-ray absorption to study orbital magnetic moments of CrO2 and Fe3O4. MCD in X-ray absorption spectroscopy were performed with correction for saturation effects. We also compare measurements of orbital moments with band structure calculations based on local spin density approximation with on-site Coulomb energy U taken into account (LDA + U). The rest of this paper is organized as follows. In the next section, we briefly describe the experimental methods including MCD methods and epitaxial growth of CrO2 and Fe3O4 thin films. Results and discussion of MCD measurements are presented in Section 3, followed by the conclusions.

2. Experimental

2.1. Epitaxial CrO2 and Fe3O4 thin films

Epitaxial CrO2 films were grown on TiO2(100) substrates by chemical vapor deposition (CVD) [13]. The substrates were ultrasonically cleaned with acetone, 1,1,1-trichloroethane, 10% hydrofluoric acid and distilled water before air-drying. The deposition was at 400 °C by using CrO3 as the precursor. X-ray diffraction results reveal that CrO2 films are single crystalline and epitaxial; measurements of magneto-optical Kerr effect show a square magnetic hysteresis loop, indicating high magnetic remanence of CrO2 films. Thin films of Fe3O4 were grown on MgO(001) single crystals which provide an ideal template for epitaxial growth. The lattice constant of Fe3O4, 8.396 Å, is close to twice of the MgO lattice constant, 4.211 Å, resulting in an epitaxial growth with a small lattice mismatch. Both the rocksalt structure of MgO and the inverse spinel structure of Fe3O4 are based on a f.c.c. oxygen anion lattice, allowing a continuation of the oxygen sublattice over the MgO/Fe3O4 interface. We achieved to grow epitaxial 100-monolayer (ML) (i.e. 210 Å thick) Fe3O4 thin films with evaporating Fe from an effusion cell at the presence of oxygen. Before film growth, the MgO(100) substrate was cleaved ex situ and annealed at a temperature around 650 °C with an oxygen pressure of 5 × 10−3 Torr for 1–2 h to remove contamination such as hydrocarbons. The cleanliness and the structure of MgO(100) surface were characterized by photoemission and reflection high energy electron diffraction (RHEED), respectively. The growth rate of Fe3O4 thin films was ~1 ML per minute. Structure of the thin films was real-time monitored by RHEED and its thickness was calibrated with the intensity oscillation of the RHEED specular beam, as shown in Fig. 1(a). The results reveal that the growth of Fe3O4 thin films on MgO(001) is in an epitaxial layer-by-layer mode. The film and its epitaxy were fully characterized by X-ray diffraction. The composition of the film was examined by core-level photoemission and X-edge X-ray absorption of Fe; the results are identical to those obtained from Fe3O4 single crystals. In addition, the resistance measurement shown in Fig. 1(b) reveals that our film has a well-defined Verwey transition temperature which is also a good indication of the quality of our Fe3O4 thin films.

2.2. MCD sum rules

The sum rules of MCD in X-ray absorption permit element-selective separation of spin and orbital contributions to the total magnetic moment of materials [5.6.9.8.10]. Calculations on the basis of a tight-binding approximation show that K-edge MCD spectra is generated mainly by the 3d orbital moment on the neighboring sites through the p-d hybridization [14]. MCD spectra of an s-level absorption reflect the p-projected orbital magnetization density of unoccupied states. According to X-ray MCD sum rules, orbital magnetic moments morb in units of μB per atom can be obtained from K-edge XAS and MCD spectra. Sum rules of K-edge absorption relate orbital magnetic moments to K-edge XAS and MCD spectra as
2p states and the photon energy, respectively; \( \sigma \) dipole operator. For cubic materials, \( \langle \sigma \rangle \) denotes the degree of circular polarization of incident photons.

For measuring L-edge XAS of Fe with the TEY method, there exists significant saturation effects. To extract the correct value of orbital moments by applying the sum rules to the MCD data obtained with a TEY measurement, one needs to examine carefully the saturation effects. When saturation occurs, the measured TEY signal is no longer uniformly proportional to the absorption cross section, leading to an inaccurate measurement of orbital magnetic moments [11].

The degree to which saturation occurs in the TEY signal depends on the relative photon penetration depth \( \lambda_e \) and electron sampling depth \( \lambda_e \). The measured absorption signal \( I_{TEY} \) in a TEY measurement is reduced by a correction factor \( f = 1/(1 + \lambda_e/\lambda_s \cos \theta) \), where \( \theta \) is the incidence angle of X-ray with respect to the surface normal [11], i.e., \( I_{TEY} = C f \sigma \), in which \( C \) and \( \sigma \) are a proportion constant and the absorption cross section, respectively. The \( \lambda_e \) of Fe was estimated to be 50 Å, and \( \lambda_e \) at the L3 and L2 edges, respectively, were 170 and 525 Å [21].

To determine the energy-dependent correction factor \( f \) of FeO, we measured the energy-dependent X-ray penetration depth \( \lambda_e \) with a new quasi-transmission technique in XAS. The underlying concept of this technique is shown in Fig. 1 (a) intensity oscillation of RHEED specular beam and (b) temperature dependence of resistance measurement of 100ML FeO thin films grown on MgO[110].
Fig. 2. Schematic diagrams of (a) direct transmission and (b) quasi-transmission for soft X-ray absorption measurements. Filled and open circles shown in the substrate represent the composition atoms Mg and O, respectively. In quasi-transmission, O fluorescence $h\nu'$ from the substrate is detected.

Fig. 3. (a) L$_2$-edge quasi-transmission measurements and (b) average X-ray penetration depth $\lambda_x$ of 80 Å thick pure Fe thin films in the region of the L$_2$-edge absorption, as shown in Fig. 3. A semiconductor fluorescence detector was used to measure the intensity of O K-edge fluorescence. Our measured $\lambda_x$ of Fe thin film is in good agreement with that of previous direct transmission results [9,11]. These test results establish unambiguously that a quasi-transmission measurement is as accurate as a direct transmission measurement in obtaining X-ray penetration depth $\lambda_x$ of Fe.

3. Results and discussion

3.1. Orbital moments of CrO$_2$

Fig. 4 presents the O K-edge XAS and MCD of CrO$_2$ [17]. After correction for the incomplete polarization and the incident angle of soft X-ray, i.e. multiplying $(\sigma_+ - \sigma_-)$ by $1/\cos 45^\circ \times 0.6$ for MCD spectra while keeping XAS=$(\sigma_+ + \sigma_-)$ unchanged, we found that the MCD to XAS ratio at the pre-peak position of O K-edge absorption is 4.1%, which is larger than that, 3%, observed on La$_{1-x}$Sr$_x$MnO$_3$ single crystals [18]. For $q$ and $r$ as the integrated intensities of MCD and XAS spectra across the

![Graph](image-url)
In our MCD measurements on CrO$_2$, saturation effects have been corrected by normalizing the XAS spectra to the normal intensity data. In contrast, our MCD and XAS data do not provide quantitatively information on the spin moment of Cr because one can not uniquely define which part of the spectra belongs to the $L_3$ or the $L_2$ edges. This is due to the large multiplet splitting in the XAS final states relative to the Cr 2p core-level spin-orbit splitting. Nevertheless, the integration spectrum of our MCD data indicates that the orbital moment of Cr is opposite to its spin moment [17].

MCD measurements presented above, nevertheless, provide valuable qualitative information on element specific orbital magnetic moment. Our measurements reveal that Cr orbital moments of CrO$_2$ is opposite to its spin moment, but parallel aligned to O orbital moment. We found that the measured Cr orbital moment of $-(0.06 \pm 0.02)\mu_B$ is consistent with those of LDA $+ U$ calculations with $U = 3$–4eV [17,19].

### 3.2. Orbital moments of Fe$_3$O$_4$

Fig 6 shows Fe $L_{2,3}$-edge XAS and MCD spectra of Fe$_3$O$_4$ thin films obtained with TEY measurements. Before obtaining the orbital moments, we first discuss the multiplet structure of the spectra. The 2p XAS spectrum reflects directly the nature of the 3d electronic ground state. The local ground state of Fe ions is a mixture of configurations $3d^{5}$, $3d^{6-1}L$, and $3d^{n-1}L^2$ with $n = 5$ and 6 for Fe$^{3+}$ and Fe$^{2+}$ ions, respectively, where $L$ denotes a ligand hole. The final state in $L$-edge absorption is predominantly a mixture of configurations $2p3d^{n-1}$ and $2p5d^{n-2}L$. The $2p3d^{n-1}$ configuration exhibits multiplet structure as a consequence of the $2p$-$3d$ exchange interaction, whereas

![Fig. 5. Cr $L_2$-edge XAS and MCD spectra of Cr in CrO$_2$ (after [17]). Top: XAS spectra with incident photons of different spin directions; middle: XAS integration spectra with an arc tangent-like edge-jump function of background (thin broken line); bottom: MCD and MCD integration spectra. The descriptions of the figure correspond to those of Fig. 4.](image)

![Fig. 6. Fe $L_{2,3}$-edge XAS and MCD spectra of Fe$_3$O$_4$ thin films obtained with TEY measurements. $\sigma_+$ and $\sigma_-$ are defined in the text.](image)
a broad band feature exists in the configuration $2p_{\text{hy}1/2}\rightarrow L_{1,3}$ resulting from the band-like character of the $L_3$ absorption. The MCD measurements suggest that the leading edge of the $L_3$ absorption (i.e. at photon energy 707.5 eV) with a negative MCD peak results mainly from 2p→3d transition in the B-site Fe$^{2+}$ ions. Another negative MCD peak at photon energy 709.4 eV is derived predominately from the A-site Fe$^{3+}$ ions. The energy difference between these two MCD peaks is $\sim (U_{\text{dc}} - U_{\text{dd}})$, where $U_{\text{dc}}$ and $U_{\text{dd}}$ are the Coulomb interaction energies between 3d electrons and 2p core holes, respectively. In addition, the positive MCD peak at photon energy 708.6 eV predominantly results from the A-site Fe$^{3+}$ ions.

To extract the correct value of orbital moments by applying the sum rules to these MCD data, we have obtained the correction factor for saturation effects of Fe L-edge XAS measurements by the measuring X-ray absorption length. We calculated the occupation probabilities of down-spin 3d electrons of high-spin Fe$^{2+}$ ions. We found that oxygen atoms in an octahedral crystal field with the spin-orbit interaction, but without the crystal field and the hybridization between Fe 3d and O 2p, the orbital moment of Fe$^{2+}$ ions maximizes, i.e., $m_{\text{orb}} = 3\mu_B$ as expected from the Hund’s coupling. If the the crystal field and the hybridization are included, the dominant down-spin $t_2g$ state of Fe$^{2+}$ is $1/\sqrt{2}(d_{xy} + d_{yz})$, leading to an orbital moment of $1\mu_B$ [22], i.e., average 0.5$\mu_B$ per B-site Fe atom in Fe$\text{O}_4$. Our MCD measurements thus indicate that 3d electrons of B-site Fe in Fe$\text{O}_4$ are with a strong localized nature even at temperature above the Verwey transition.  

4. Conclusions

We have studied orbital magnetic moments of CrO$_2$ and Fe$\text{O}_4$ by measuring MCD in soft X-ray absorption. The results show that orbital moments of Cr in CrO$_2$ are nearly quenched, revealing that Cr 3d electrons are strongly hybridized with O 2p electrons and more delocalized as compared with those of Fe in Fe$\text{O}_4$. We found that oxygen atoms in CrO$_2$ exhibit a significant orbital magnetic moment compared to those of other oxides. Orbital moments of O in
CrO$_2$ are parallel coupled to that of Cr, while the spin moments are anti-parallel coupled. In addition, the magnitudes of spin and orbital moments of Cr are enhanced as on-site Cr 3d–3d Coulomb interaction increases. We also found that Fe$_3$O$_4$ exhibits large orbital moments, in contrast to nearly quenched orbital moments of Cr in CrO$_2$. Large orbital polarization of Fe in Fe$_3$O$_4$ caused by on-site Coulomb interactions of 3d electrons results in unquenched orbital moments of Fe$_3$O$_4$. As compared with LDA + $U$ calculations, our results indicate that one has to properly include on-site Coulomb interactions of 3d electrons in CrO$_2$ and Fe$_3$O$_4$ in order to describe their electronic structure adequately.

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References