First-principles Calculation of the Orbital Magnetic Moment of O and Cr in Half-metallic CrO$_2$

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ABSTRACT

   The electronic and magnetic properties of half-metallic CrO$_2$ have been studied by using the full-potential linearized muffin-tin orbital method within the local spin-density approximation (LSDA)+U approach. It is found that the orbital magnetic moment of Cr atom is quenched while O atom exhibit relatively significant orbital moment in CrO$_2$. For the Hubbard U of 3 eV, LSDA+U gives the orbital moment of -0.051μ_B/atom for Cr and -0.0025μ_B/atom for O, being in good agreement with the experimental orbital moments of -0.05 for Cr and -0.003μ_B/atom for O, respectively. In contrast, LSDA gives the orbital moment of -0.037 for Cr and -0.0011 μ_B/atom for O, being too small as compared with the magnetic circular dichroism measurements. For the larger U considered in this work, both spin and orbital moments almost increase linearly with respect to U.

INTRODUCTION

   CrO$_2$ is a ferromagnetic half-metal with a magnetic moment of 2 μ_B per formula units (fu) [1]. It has been widely used in magnetic recording tapes. In recent years, it attracts substantial interests because of the half-metallic property and the applicable potential for future spintronics. In half-metal CrO$_2$, one spin channel is metallic and the other is insulating, resulting in an unusual transport property of 100 % spin polarization. The Fermi level lies in the partially filled $3d$ band of the majority spin, whereas in the minority spin, the Fermi energy falls in an exchange-split gap between the occupied oxygen $2p$ band and the unoccupied chromium $3d$ band. By the formation of a pseudogap at the Fermi level in the conducting majority spin of the ferromagnetic CrO$_2$, the large density of state at the Fermi energy of the paramagnetic CrO$_2$ is stabilized according to the usual Stoner argument [2]. Since the states involving the conduction and magnetic properties are highly spin-polarized near the Fermi energy, it is therefore interesting to investigate the orbital contributions of the individual atoms to the magnetic moment of CrO$_2$.
   The orbital magnetic moments are usually suppressed in the $3d$ transition metals because of the crystal field in solids. Some $3d$ transition metal oxides exhibit large unquenched orbital magnetic moments. The unquenched orbital moment arises mainly from the spin-orbit interaction in the localized $3d$ orbital where the atomic field is deformed in a relatively slight manner by the crystal field. The strong Coulomb correlations further localize the $3d$ orbitals and suppress the ligand field on the metal atoms. These materials are thus expected to possess larger unquenched orbital moments. It has been found in neutron-diffraction experiment for CoO [3], and in magnetic x-ray scattering experiment for NiO [4] that the unquenched orbital magnetic moments are rather large. Although the calculated orbital moments from the LSDA are usually too small compared with experimental results, the on-site Coulomb energy U in the LSDA+U calculations enhances significantly the orbital moments in both CoO [5] and NiO [6], and gives large orbital moments in agreement with

experimental moments.

Several experimental techniques, such as neutron scattering, magnetic x-ray scattering, and magnetic circular dichroism (MCD) in x-ray absorption spectroscopy (XAS), have been proved to be useful in studying orbital magnetic moments of materials. By using sum rules, MCD in x-ray absorption provides a powerful experimental method to deduce element-specific orbital and spin magnetic moments. Recently, a MCD in soft x-ray absorption spectroscopy experiments for CrO_2 was performed using the elliptically polarized undulator (EPU) beamline of the Synchrotron Radiation Research Center (SRRC) in Taiwan [7]. The results show that the spin moment of O is antiferromagnetically coupled to that of Cr, whereas the orbital moment is ferromagnetically coupled to that of Cr.

The electronic structure of CrO_2 has been calculated self-consistently within the framework of LSDA by several authors. Schwarz [8] predicted firstly for CrO_2 the half-metallic band structure with a spin moment of 2 μ_B/fu by using the augmented spherical wave method. From the ionic viewpoint, 2 μ_B/fu is a nature consequence of Hund's rule for the Cr^{+4} ($3d^2$) ion. They both agree with the experimental moment [1]. Using a plan-wave pseudopotential method, Lewis, *et al.* [2] investigated the energy bands and transport properties. They put CrO_2 into the category of "bad metals" in common with the high-T_c superconductors, the high-T metallic phase of VO_2, and the ferromagnet $SrRuO_3$. In the past decade, the LSDA+U scheme was developed and applied to various transition metal oxides [9]. As compared with the conventional LSDA, the LSDA+U gives rather good results for these strongly correlated systems. Taking the on-site Coulomb energy U into account in LSDA+U, Korotin, *et al.*, [10] explained the conductivity in spite of the large Coulomb interactions, and concluded that CrO_2 is a negative charge transfer gap material which leads to self-doping. The main Cr-$3d$ peak above the Fermi level from the LSDA+U band structure calculations agrees quite well with recent photoemission spectroscopy and specific heat measurements [11]. The LSDA+U model for CrO_2 as a half-metallic ferromagnet with large exchange-splitting energy is further supported by the polarization-dependent x-ray absorption spectroscopy and x-ray magnetic circular dichroism measurements [12]. On the other hand, Mazin, *et al.*, [13] performed all-electron and full-potential band-structure calculations for the transport and optical properties of CrO_2 by using the general potential linearized augmented plan-wave method (LAPW) within the LSDA and also the generalized gradient approximation (GGA). They concluded that strong electron-magnon scattering instead of strong correlation is responsible for renormalizing the electron bands.

METHOD

In this work, the all-electron full-potential linearized muffin-tin orbital (FP-LMTO) method [14] including the spin-orbit interaction were used to perform self-consistent band structure calculations within both the relativistic LSDA and LSDA+U [15] schemes. The Vosko-Wilk-Nusair [16] exchange-correlation potential and the experimental lattice parameters a = 4.419 A, c = 2.912 A, and u = 0.303 [17] of the rutile structure (space group D_{4h}^{14}: $P4_2/mnm$, No. 136) of CrO_2 were used in the calculations. The two chromium atoms are located at the positions (0, 0, 0), and (1/2, 1/2, 1/2), and the four oxygen atoms are at (u, u, 0), (1-u, 1-u, 0), (1/2+u, 1/2-u, 1/2), and (1/2-u, 1/2+u, 1/2). The radii of the muffin-tin spheres used for Cr and O were 2.0 a_0 and 1.5 a_0, respectively. For the valence bands, a triple-κ LMTO basis set expanded in spherical harmonics up to angular momentum l = 6 was used for the

Table I. Calculated spin and orbital magnetic moments (μ_B/atom) and the ratio L/S (%) of Cr and O in CrO_2 from LSDA ($U = 0$) and from the LSDA+U. The exchange parameter $J = 0.87$ eV.

U (eV)	Cr spin	orbital	% L/S	O Spin	orbital	% L/S
0	1.89	-0.037	-2.0	-0.042	-0.0011	2.6
2	1.94	-0.046	-2.4	-0.058	-0.0019	3.2
3	1.99	-0.051	-2.6	-0.079	-0.0025	3.2
4	2.03	-0.056	-2.8	-0.094	-0.0030	3.2
6	2.08	-0.057	-3.2	-0.111	-0.0040	3.6
9	2.12	-0.083	-3.9	-0.124	-0.0047	3.8

charge densities and potentials inside the nonoverlapping muffin-tin spheres. While in the interstitial region, 7558 plane waves with energies up to 111 Ry were employed in the calculations. For the [001] direction of magnetization, the number of k points used in the self-consistent calculations was 126 over the irreducible wedge of the tetragonal Brillouin-zone. For the [100] magnetization, 250 k points were used for the self-consistent calculations of lower symmetry. For simplicity, the spin and orbital magnetic moments will always be referred to [001] direction of magnetization in the rest of this paper unless stated otherwise. To explore the effects of the on-site Coulomb energy U on the electronic structures and the magnetic moments, different U from 2 up to 9 eV were used in the LSDA + U calculations with the exchange interaction parameter $J = 0.87$ eV [10] unchanged.

RESULTS AND DISCUSSION

The calculated spin and orbital magnetic moments and the orbital to spin moment ratio L/S of Cr and O for [001] magnetization are summarized in Table I. The LSDA ($U = 0$) gives spin moments of 1.89 and -0.042 μ_B/atom for Cr and O, respectively. The opposite signs of spin moments between Cr and O indicate charge transfer from the oxygen anion to the chromium cation. The orbital moment of Cr is also antiparallel to the spin moment of Cr, being consistent with Hund's rules for $3d$ shells less than half full. In the meantime, for the O-2p shell that is more than half filled, the orbital moment is consequently parallel to the spin moment. Hence the orbital moment of O is parallel to that of Cr, and the resultant magnetic moments of Cr and O are antiferromagnetically coupled in CrO_2. As usually happened in the LSDA calculations, the obtained orbital moments of -0.037 and -0.0011μ_B/atom for Cr and O, respectively, are both too small as compared with experimental moments [7]. Note that the ratio L/S of oxygen is larger than that of Cr, indicating the relatively significant orbital moment of oxygen in CrO_2 as compared with that in other transition metal oxides. However, we were not aware of any experimental measurements such as magnetic x-ray scattering or neutron scattering on the L/S ratios of CrO_2 during this work.

Also shown in Table I are the spin and orbital magnetic moments from the LSDA+U calculations. The on-site Coulomb energy U further localizes the $3d$ orbital and keeps more spin densities in this orbital. The spin moments of both Cr and O are thus enhanced. For the literature value of $U = 3$ eV and $J = 0.87$ eV [10] considered, the spin moments of Cr and O are raised by an amount of 0.10 and 0.037 μ_B/atom, respectively. Meanwhile, the orbital moments of Cr and O increases dramatically up

Table II. Calculated spin and orbital magnetic moments (μ_B/atom) and the ratio L/S (%) of Cr and O for [001] and [100] magnetization in CrO_2 from LSDA ($U = 0$) and from the LSDA+U ($J = 0.87$ eV).

U (eV)	Cr spin	orbital	% L/S	O Spin	orbital	% L/S
0 [001]	1.89	-0.037	-2.0	-0.042	-0.0011	2.6
0 [100]	1.89	-0.034	-1.8	-0.042	-0.0000	0.0
3 [001]	1.99	-0.051	-2.6	-0.079	-0.0025	3.2
3 [100]	1.99	-0.050	-2.5	-0.079	-0.0004	0.5

to -0.051 and -0.0025 μ_B/atom, respectively. The obtained orbital moments from the LSDA+U are in good agreement with the experimental orbital moments of -0.05 and -0.003 μ_B/atom, respectively [7]. For larger U considered, both spin moments of Cr and O increase more or less linearly with respective to U. Whereas the half-metallic property with a total magnetic moment of 2 μ_B/fu overall remains unchanged. Note that increasing U reduces total charges in the Cr muffin-tin sphere, and increases total charges in the O muffin-tin sphere, indicating increasing ionicity of both Cr and O. Since larger U further localizes the $3d$ electrons and suppresses the octahedral ligand fields on Cr atoms, the orbital moments of Cr and O are raised further by increasing U as shown in the table. Similar trends have been found in CoO [5] and NiO [6]. Nevertheless, the orbital magnetic moment of Cr is found to be quenched in CrO_2, in contrast to the large orbital magnetic moments found in CoO [3] and NiO [4]. In this work, different values of J from 0.3 up to 1.5 eV were also used for $U = 2$, 3, and 4 eV cases. It is found that the spin moments of Cr and O are suppressed by larger values of J, whereas the orbital moments are not sensitive to J.

Table II shows the spin and orbital moment and the L/S ratio of Cr and O in CrO_2 for [001] and [100] directions of magnetization from the LSDA and from the LSDA+U with U =3 eV and J =0.87 eV. The most visible feature is the large anisotropy of the orbital moments of O. In the [100] magnetization, the orbital moment of O is destroyed from the LSDA calculations, while it is strongly suppressed in the LSDA+U approach. Meanwhile, both the LSDA and the LSDA+U give slightly smaller orbital moments for Cr. On the other hand, the anisotropy in spin moments of Cr and O are negligibly small from both the LSDA and the LSDA+U calculations. The anisotropy in orbital magnetic moments indicates that the [001] direction of magnetization, which provides larger orbital moments of Cr and O, would be the easy axis of CrO_2. The smaller anisotropy of the orbital moment of Cr from the LSDA+U calculations also implies that the LSDA+U, rather than the LSDA, might give smaller magnetocrystalline anisotropy energy for CrO_2.

The calculated spin and orbital magnetic moments and the ratio L/S of Cr and O with respect to volume expansion from 0.9 V_0 (experimental volume) to 1.15 V_0 for CrO_2 are listed in Table III. Both the spin and orbital moments of Cr and O increase monotonically with increasing lattice volume. This could be understood as the reduction of the crystal fields and the less hybridizations between Cr-$3d$ and O-$2p$ bands due to lattice expansion. Interestingly, the increasing rate are quite different for spin and orbital moments of Cr and O. As shown in the table, the magnitude of L/S for Cr increases very slowly with increasing V/V_0, whereas that for O decreases significantly. This suppression in L/S of O is due to the rapid growing of spin moment and slow increasing of orbital moment of O with increasing volume, demonstrating a relatively sensitive dependence of spin moment of O on lattice volume. Note that the

Table III. Calculated spin and orbital magnetic moments (μ_B/atom) and the ratio L/S (%) of Cr and O in CrO_2 within the LSDA, with respect to volume expansion (V/V_0).

V/V_0	Cr		%	O		%
	spin	orbital	L/S	Spin	orbital	L/S
0.90	1.80	-0.033	-1.8	-0.010	-0.0009	9.0
0.95	1.85	-0.035	-1.9	-0.025	-0.0010	4.0
1.00	1.89	-0.037	-2.0	-0.042	-0.0011	2.6
1.05	1.94	-0.038	-2.0	-0.059	-0.0012	2.0
1.10	1.99	-0.040	-2.0	-0.078	-0.0013	1.7
1.15	2.04	-0.041	-2.0	-0.099	-0.0015	1.5

spin and orbital moments are both zero in bcc Cr, which reveals that the $3d$ electrons are much more localized in CrO_2 than in Cr metal. However for all the lattice volumes considered, the volumes are not small enough to quench all the moments, and are not large enough to give large orbital moments as that in CoO [5] and in NiO [6].

CONCLUSIONS

In conclusion, we have performed FP-LMTO self-consistent calculations for ferromagnetic half-metal CrO_2 within both the LSDA and the LSDA+U schemes. With spin-orbit coupling included in the self-consistent calculations, the spin and orbital magnetic moments are obtained from both the LSDA and the LSDA+U methods. It is found that the on-site Coulomb interaction U dramatically enhanced the spin and orbital moments. For U =3 eV and J =0.87 eV, the calculated orbital moments of Cr and O are -0.051 and -0.0025 μ_B/atom, respectively, being in good agreement with the experimental moments of -0.05 μ_B/atom for Cr and -0.003 μ_B/atom for O from MCD measurement [7].

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