Anisotropy of the orbital moments and the magnetic dipole term $T_z$ in CrO$_2$: An \textit{ab-initio} study

Matej Komelj,$^1$ Claude Ederer,$^2$ and Manfred Fähnle$^{3,5}$

$^1$Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia
$^2$Materials Research Laboratory, University of California, Santa Barbara, CA 93106-5130, U.S.A.
$^3$Max-Planck Institut für Metallforschung, Heisenbergstr. 3, D-70569 Stuttgart, Germany

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A systematic study is performed by the \textit{ab-initio} density functional theory of the anisotropy of the orbital moments ($l_z$) and the magnetic dipole term ($T_z$) in bulk CrO$_2$. Two different band-structure techniques are used (FLAPW and LMTO-ASA), and the electronic correlations are treated by the local-spin-density approximation (LSDA), the LSDA+orbital polarization method, and the LSDA+U method. The calculated anisotropies of ($l_z$) and ($T_z$) are very large compared to Fe, Ni and Co but still a factor of 5 and 2 smaller than the anisotropies obtained from a recently suggested analysis of the X-ray magnetic circular dichroism spectra for a thick layer of CrO$_2$.

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Recent research within the fields of magnetic tunneling and spin injection involves CrO$_2$ as a promising material for electrodes. Besides its potential importance for applications, this material also exhibits interesting physics originating from its half metallic nature and consequently the ferromagnetism due to the double-exchange coupling, as well as from its orbital magnetism which is related to the spin-orbit coupling and the electronic orbital correlation effects. Consequently, there are already several experimental\cite{1} and theoretical\cite{2,3,4,5,6} investigations of the orbital moments ($l_z$) in CrO$_2$.

However, much less information is available on the anisotropy of the orbital moments, i.e., on its dependence of the orientation of the sample magnetization (in the following the $z$ axis of the external coordinate system is always chosen to be parallel to the magnetization direction). It has been pointed out first by Bruno\cite{7} and later worked out in more detail by van der Laan\cite{8} that the anisotropy of the orbital moment is closely related to the magnetocrystalline anisotropy energy. Furthermore, van der Laan has shown that there is an additional contribution to the anisotropy energy arising from the anisotropy of the magnetic dipole term $T_z$, which is the expectation value of the magnetic dipole operator:

$$T_z = \frac{1}{2} \langle \sigma - 3\hat{r}(\hat{r} \cdot \sigma) \rangle_z,$$ \hfill (1)

In eq.(1) $\hat{r}$ is the unit vector in the direction of the position vector $r$, and $\sigma$ is the vector of the Pauli matrices. In fact, it turns out (see below) that for CrO$_2$ the two contributions are very large and of similar magnitudes but opposite in sign.

A suitable method to investigate the anisotropy of ($l_z$) and ($T_z$) is the angle-resolved variant\cite{9} of the X-ray magnetic circular dichroism (XMCD) which measures the XMCD spectra for various orientations of the sample magnetization. The orbital moments ($l_z$) then may be determined directly from the application of the XMCD orbital sum rule\cite{10}. In contrast, the application of the spin sum rule\cite{11} yields a combination of the spin moment $\langle \sigma_z \rangle$ and of the $\langle T_z \rangle$ term. A separation of these two contributions is possible by applying the spin sum rule to XMCD spectra for various orientations of the sample magnetization. A precondition of the use of this method is that $\sum_l (T_z)_l \approx 0$, where $\alpha$ represents one of the perpendicular directions in which the $z$ axis is oriented. It has been outlined in Ref.\cite{12} that the validity of this relation is not always guaranteed (for the case of CrO$_2$ see below).

Goering \textit{et al.}\cite{13} applied the technique of angle-resolved XMCD to investigate the anisotropy of ($l_z$) and ($T_z$) for the Cr atom in a thick layer of CrO$_2$ on a TiO$_2$ substrate (which is required to stabilize the rutile structure). For CrO$_2$ the analysis of the XMCD spectra of the $L_2$ and $L_3$ edges of the Cr atom (corresponding to the $2p_{1/2} \rightarrow 3d$ and $2p_{3/2} \rightarrow 3d$ transitions) is more difficult because the spin-orbit coupling of the Cr 2$p$ electrons is relatively weak so that the $2p_{1/2}$ and $2p_{3/2}$ levels are not well separated\cite{13}. The subdivision of the XMCD spectra into the $L_2$ and $L_3$ contributions (which is required for an application of the spin sum rule) is therefore highly problematic due to a possible quantum-mechanical mixture of the $2p_{1/2}$ and $2p_{3/2}$ levels and/or due to a strong overlap of the two contributions on the energy scale. In their original analysis Goering \textit{et al.}\cite{13} neglected the quantum-mechanical mixture. Furthermore, they separated the $L_2$ and $L_3$ contributions by an empirical (and theoretical not yet justified) extension of the van der Laan’s method of the moment analysis\cite{13} (which was proposed for systems with very small crystal-field splitting of the valence states) to situations with large band splitting. Based on these two assumptions, they found extremely large anisotropies of ($l_z$) and ($T_z$). For instance, the difference in the orbital moment for the magnetization along the $c$ axis and along the $a$ axis of the rutile structure was 0.083 $\mu_B$, which is extremely large compared to bulk materials with cubic symmetry ($10^{-3} \mu_B$, see Ref.\cite{14}) and comparable to the anisotropy found for extremely thin Co layers\cite{15}. The anisotropy of ($T_z$) appeared to be...
about 0.2 $\mu_B$, two orders of magnitude larger than the absolute value of $\langle T_z \rangle$ in Fe (0.004 $\mu_B$), Ni ($-0.004 \mu_B$) and Co (0.002 $\mu_B$). For the true spin moment of the Cr atom a value of 1.2 $\mu_B$ was obtained. To explain the magnetic moment of about 2 $\mu_B$ per unit cell which was obtained by a SQUID measurement Goering et al. assumed a very large spin moment of about 0.4 $\mu_B$ per O atom which they tried to explain in terms of a hybridization between chromium and oxygen.

The question is whether the extreme anisotropies of $\langle l_z \rangle$ and $\langle T_z \rangle$ found by Goering et al. are indeed intrinsic properties of bulk CrO$_2$ with rutile structure. Remember that their measurements were performed on thick layers of CrO$_2$ on TiO$_2$. So far there is only very little information on the structure of this layer, i.e., on possible oxygen deficiencies. Furthermore, it is not known how the two basic assumptions for the application of the spin sum rule (see above) affect the results for $\langle T_z \rangle$ and for the true spin moment $\langle \sigma_z \rangle$. Indeed, most recently an empirical method has been developed to take into account approximately the effect of mixing of the $p_{1/2}$ and $p_{3/2}$ core states for the analysis of the XMCD spectra by the spin sum rule. The data of Goering et al. were reanalyzed by this method, yielding a Cr moment that agreed reasonably well with the Cr moment suggested by the SQUID measurements after neglecting the O moment, but the anisotropy of the $\langle T_z \rangle$ remained to be very large when obtained by the help of the above discussed moment analysis.

In the present paper we investigate theoretically the anisotropy of $\langle l_z \rangle$ and $\langle T_z \rangle$ in bulk CrO$_2$ with rutile structure by calculations based on the ab-initio density functional theory. In the literature there are already some single results in this direction which – however – are in part contradictory. We therefore have performed a systematic study, which is based on two different bandstructure techniques and which takes a special care of the electronic orbital correlation effects (again by two different methods) which are not included in the commonly used local-spin-density approximation (LSDA) of the density functional theory.

We performed comparative calculations by two different band structure methods, the Wien97 code, which adopts the full-potential linearized-augmented-plane-wave method (FLAPW) and the linear-muffin-tin-orbital method in the atomic-sphere approximation (LMTO-ASA). Whereas in the first method the effective crystal potential is treated exactly, it is spherically averaged in each atomic sphere after each iteration step of the self-consistency cycle in the LMTO-ASA method. The exchange-correlation potential was calculated in LSDA. The electronic orbital correlation effects, which are not included in LSDA, were taken into account by the OP term or by means of the LDA+$U$ scheme. For $U = 0$, the LDA+$U$ calculation is equivalent to a LSDA calculation. In the case of $U \neq 0$ the exchange-interaction parameter $J$, which appears in the LDA+$U$ scheme in addition to the parameter $U$, was fixed to 0.87 eV, whereas $U$ was an open parameter (the calculated screened value of $U$ for Cr in CrO$_2$ is $U = 3$ eV). In the literature arguments for and against the use of the LDA+$U$ method for the case of CrO$_2$ are given (see, e.g., Ref. and Refs. therein). Therefore we performed a comparative study based on various calculational schemes for the electronic correlations. The spin-orbit coupling, OP term and LDA+$U$ scheme were implemented in the LMTO code in Ref. The magnetization was set along the c or the a axis of the rutile structure. The calculations were performed for the experimental lattice parameter $a = 0.4419$ nm, $c = 0.2912$ nm and $u = 0.303$.

The results are presented in Table 1. Hund’s third rule is obeyed for both magnetization directions at any value of $U$ because the orbital moments are always antiparallel (parallel) to the spin moments at the Cr(O) sites, in agreement with the experimental observations.

We first discuss the orbital moments. From the LSDA calculation, the LSDA+OP calculation and for the LDA+$U$ calculation with $U \leq 3$ eV we find Cr orbital moments of about $-0.05 \mu_B$ which magnitudes are smaller than the experimental values for Fe (0.086 $\mu_B$) and Co (0.153 $\mu_B$). For the magnetization along the c axis our FLAPW calculation with $U = 3$ eV yields orbital moments of $-0.064 \mu_B$ and $-0.0025 \mu_B$ at Cr and O sites, in a very good agreement with the XMCD results of Ref. which give $-(0.06 \pm 0.02) \mu_B$ and $-(0.003 \pm 0.001) \mu_B$, respectively. We take this as a hint that $U = 3$ eV (which is also the calculated value for the screened $U$) is a good choice. This is further underpinned by the fact that our LSDA+OP calculation yields very similar results for the orbital moments of chromium and oxygen as the LDA+$U$ calculation for $U$ between 2 and 3 eV. For $U \leq 3$ eV our FLAPW results for the Cr (O) orbital moment agree very well (perfectly) with those of a full-potential LMTO (FP-LMTO) calculation. The probably less-accurate LMTO-ASA calculation yields larger Cr orbital moments than the FLAPW calculation. For $U = 3$ eV the LMTO calculation gives a value of $-0.090 \mu_B$ for the c-axis orientation which agrees very well with the XMCD result of Ref. For the magnetization along the a axis (for which there is no FP-LMTO result in Ref. both our FLAPW and our LMTO-ASA calculations yield smaller orbital moments than those for the c-axis orientation, in agreement with the XMCD results. The difference $|\Delta(\langle l_z \rangle)| = |\langle l_z \rangle_{c \text{ axis}} - \langle l_z \rangle_{a \text{ axis}}|$ is about 0.015 $\mu_B$ at $U = 3$ eV, which is indeed very large in comparison to the orbital-moment anisotropy of cubic bulk materials ($10^{-4} \mu_B$), but still a factor of about 5 smaller than the orbital-moment anisotropy of CrO$_2$ discussed by Goering et al. in the FLAPW calculation the value of $|\Delta(\langle l_z \rangle)|$ decreases drastically when reducing $U$ and it amounts to 0.002 $\mu_B$ for the LSDA calculation (the FLAPW calculation based on the generalized-gradient approximation (GGA) gives an orbital moment anisotropy of 0.001 $\mu_B$). In the LMTO-ASA calculation the reduction with decreasing $U$ is less dramatic: for $U = 0$ eV we find $|\Delta(\langle l_z \rangle)| = 0.01 \mu_B$ (which
are a bit smaller which results from the fact that the
spin and charge densities are calculated in each atomic sphere. The anisotropy
of the orbital moment
\( \sum \langle \sigma_l^z \rangle \) in CrO
\( \langle l_z \rangle \) is very large, about 0.1 \( \mu_B \), in the FLAPW calculation but still a factor of 3 smaller than the one discussed by Goering
\( \langle T_z \rangle \) of the magnetic dipole term
\( \langle T_z \rangle \) at the Cr atom depends only slightly on the way we take into account the correlation-effects. The LSDA, LSDA+OP and LDA+U
\( U \leq 3 \text{ eV} \) calculations with the FLAPW method yield values of about \(-0.06 \mu_B \) (+0.04 \( \mu_B \)) for the c-axis (a-axis) orientation. These values are large compared to the LSDA values for Fe (0.004 \( \mu_B \)), Ni (0.004 \( \mu_B \)) and Co (0.002 \( \mu_B \)) and they arise from a large crystal-field anisotropy. Such large values usually appear in systems with strongly reduced dimensionality, and they show that the \( T_z \)-term cannot be neglected in the analysis of the XMCD spectra via the spin sum rule\(^{13}\) when one wants to arrive at realistic values for the true spin moment. The \( \langle T_z \rangle \) values from the LMTO-ASA calculation are a bit smaller which results from the fact\(^{13}\) that in this method the spin and charge densities are calculated for an effective potential, which is spherically averaged in each atomic sphere. The anisotropy \( \Delta \langle T_z \rangle \) is very large, about 0.1 \( \mu_B \), in the FLAPW calculation but still a factor of 3 smaller than the one discussed by Goering
\( \langle T_z \rangle \) values. This probably results from the fact that sizes of the spheres over which the spin density is integrated are different in various calculations. The atomic sphere in the LMTO-ASA calculation is larger than the muffin-tin spheres in the FP-LMTO and FLAPW calculations and probably contains already a part of the Cr spin-density, which has an opposite sign.

To conclude, we performed a systematic investigation by the FLAPW and the LMTO-ASA methods for the anisotropies of the orbital moment \( \langle l_z \rangle \) and the magnetic dipole term \( \langle T_z \rangle \) in CrO\(_2\). The electronic correlation effects were taken into account by three different methods, the LSDA, LSDA+OP and LDA+U method. The calculated anisotropies \( \langle l_z \rangle \) and \( \langle T_z \rangle \) are very large but still a factor of 5 (2) smaller than those obtained by Goering
\( \langle l_z \rangle \) calculated according to Ref.\(^6\) the respective contributions to the magnetocrystalline anisotropy energy. They appear to be very large, of the same order of magnitude but opposite in sign. Because small uncertainties in either of the two contributions induce very large errors for the magnetocrystalline anisotropy, it does not make sense to calculate the latter quantity from our data.

Finally, we consider the results for the spin moments. In all our different types of calculations we find a Cr spin moment which is only very slightly anisotropic and which exhibits a magnitude of about 2 \( \mu_B \), the value predicted by Hund’s first rule for the case of a Cr\(^{3+}\) ion but considerably larger than the value of 1.2 \( \mu_B \) found by the special type of analysis of the XMCD data\(^6\) discussed above. For the O atom our FLAPW calculation yields for \( U = 3 \text{ eV} \) a spin moment of about 0.1 \( \mu_B \) which is a factor of 4 smaller than the one obtained by Goering
\( \langle l_z \rangle \) and \( \langle T_z \rangle \) values. This probably results from the fact that sizes of the spheres over which the spin density is integrated are different in various calculations. The atomic sphere in the LMTO-ASA calculation is larger than the muffin-tin spheres in the FP-LMTO and FLAPW calculations and probably contains already a part of the Cr spin-density, which has an opposite sign.

Table I: The calculated values of \( \langle l_z \rangle \), \( \langle \sigma_z \rangle \), \( \langle T_z \rangle \) and the anisotropies \( \Delta \langle l_z \rangle \) and \( \Delta \langle T_z \rangle \), all in \( \mu_B \), from the LSDF calculations (\( U = 0 \text{ eV} \)), the LDA+U calculations for various \( U \) and for the LSDA+OP calculations. The values in brackets are from the FLAPW calculations.
sonable. The only chance to arrive at larger anisotropies might be to abandon the mean-field approximation which is adopted in the LDA+$U$ method for the electronic on-site correlations and to perform a calculation within the dynamical mean field theory (DMFT)\textsuperscript{32}.

On the experimental side, more investigations are required on the real structure of the considered layers as well as on the way how to analyze the XMCD spectra which arise from energetically very close core levels.

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\textsuperscript{*} Electronic address: faehnle@mf.mpg.de