

Anisotropy of orbital moments and magnetic dipole term T_z in CrO_2 : An *ab initio* studyMatej Komelj,¹ Claude Ederer,² and Manfred Fähnle^{3,*}¹*Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*²*Materials Research Laboratory, University of California, Santa Barbara, California 93106-5130, USA*³*Max-Planck Institut für Metallforschung, Heisenbergstrasse 3, D-70569 Stuttgart, Germany*

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A systematic study is performed by the *ab initio* density-functional theory of the anisotropy of the orbital moments $\langle l_z \rangle$ and the magnetic dipole term $\langle T_z \rangle$ in bulk CrO_2 . Two different band-structure techniques are used (full potential linearized-augmented-plane-wave method and linear-muffin-tin-orbital method in the atomic-sphere approximation), 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 $\langle l_z \rangle$ and $\langle T_z \rangle$ 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.¹ 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,² as well as from its orbital magnetism^{3,4} which is related to the spin-orbit coupling and the electronic orbital correlation effects. Consequently, there are already several experimental^{3,4} and theoretical⁴⁻⁷ investigations of the orbital moments $\langle l_z \rangle$ 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 Bruno⁸ and later worked out in more detail by van der Laan⁹ 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:

$$\hat{T}_z = \frac{1}{2} [\boldsymbol{\sigma} - 3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \boldsymbol{\sigma})]_z. \quad (1)$$

In Eq. (1) $\hat{\mathbf{r}}$ is the unit vector in the direction of the position vector \mathbf{r} and $\boldsymbol{\sigma}$ 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 $\langle l_z \rangle$ and $\langle T_z \rangle$ is the angle-resolved variant¹⁰ of the x-ray magnetic circular dichroism¹¹ (XMCD) which measures the XMCD spectra for various orientations of the sample magnetization. The orbital moments $\langle l_z \rangle$ then may be determined directly from the application of the XMCD orbital sum rule.¹² In contrast, the application of the spin sum rule¹³ yields a combination of the spin moment $\langle \sigma_z \rangle$ and 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 $\sum_\alpha \langle T_z \rangle_\alpha \approx 0$, where α represents one of the perpendicular directions in which the z axis is oriented. It has been outlined in Ref. 14 that the validity of this relation is not always guaranteed (for the case of CrO_2 see below).

Goering *et al.*³ applied the technique of angle-resolved XMCD to investigate the anisotropy of $\langle l_z \rangle$ and $\langle T_z \rangle$ 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 $2p$ electrons is relatively weak so that the $2p_{1/2}$ and $2p_{3/2}$ levels are not well separated.¹⁵ 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 *et al.*³ 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 analysis¹⁶ (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 $\langle l_z \rangle$ and $\langle T_z \rangle$. 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 ($10^{-4}\mu_B$, see Ref. 17) and comparable to the anisotropy found for extremely thin Co layers.¹⁸ The anisotropy of $\langle T_z \rangle$ 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 ($0.002\mu_B$).¹⁹ 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 superconducting quantum interference device (SQUID) measurement Goering *et al.*³ 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.

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 μ_B , from the LSDA calculations ($U=0$ eV), the LDA+ U calculations for various U , and the LSDA+OP calculations. The values in brackets are from the LMTO-ASA calculations, and all other values are from the FLAPW calculations.

	U (eV)	0	2	3	4	5	LSDA+OP
c axis	$\langle l_z \rangle$	-0.037(-0.055)	-0.053	-0.064(-0.090)	-0.083	-0.117	-0.054
Cr	$\langle \sigma_z \rangle$	1.89 (2.04)	1.97	2.04 (2.03)	2.09	2.12	1.89
	$\langle T_z \rangle$	-0.059(-0.048)	-0.062	-0.066(-0.044)	-0.072	-0.084	-0.061
	$\langle l_z \rangle$	-0.0012(-0.0014)	-0.0019	-0.0025(-0.0018)	-0.0034	-0.0051	-0.0018
O	$\langle \sigma_z \rangle$	-0.046(-0.038)	-0.080	-0.114(-0.036)	-0.131	-0.145	-0.046
	$\langle l_z \rangle$	-0.035(-0.045)	-0.044	-0.051(-0.076)	-0.053	-0.061	-0.049
	$\langle \sigma_z \rangle$	1.89 (2.04)	1.96	2.00 (2.03)	2.10	2.14	1.89
a axis	$\langle T_z \rangle$	0.031 (0.024)	0.040	0.046 (0.022)	0.043	0.043	0.031
	$\langle l_z \rangle$	-0.0001(0.0000)	-0.0001	-0.0008(-.0001)	-0.0000	-0.0002	-0.0003
	$\langle \sigma_z \rangle$	-0.046(-0.038)	-0.077	-0.107(-0.035)	-0.139	-0.155	-0.046
Cr	$ \Delta\langle l_z \rangle $	0.002 (0.010)	0.009	0.013 (0.014)	0.03	0.056	0.005
	$ \Delta\langle T_z \rangle $	0.09 (0.072)	0.102	0.112 (0.066)	0.115	0.127	0.092

The question is whether the extreme anisotropies of $\langle l_z \rangle$ and $\langle T_z \rangle$ found by Goering *et al.*³ are indeed intrinsic properties of bulk CrO₂ with rutile structure. Remember that their measurements were performed on thick layers of CrO₂ on TiO₂. 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 recently³⁰ 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 reanalyzed²⁰ 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 anisotropies of $\langle l_z \rangle$ and $\langle T_z \rangle$ in bulk CrO₂ with rutile structure by calculations based on the *ab initio* density-functional electron theory. In the literature there are already some single results in this direction which, however, are in part contradictory.⁵⁻⁷ We therefore have performed a systematic study, which is based on two different band-structure 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,²¹ which adopts the full-potential linearized-augmented-plane-wave method²² (FLAPW), and the linear-muffin-tin-orbital method in the atomic-sphere approximation²³ (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.²⁴ The electronic orbital correlation effects, which are not included in LSDA, were taken into account by the orbital polarization (OP) term²⁵ or by means of the LDA+ U scheme.^{26,27} 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 fixed² to 0.87 eV, whereas U was an open parameter (the calculated² screened value of U for Cr in CrO₂ is $U=3$ eV). In the literature arguments for and against the use of the LDA+ U method for the case of CrO₂ are given (see, e.g., Ref. 5 and references 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. 28. The magnetization was set along the c or the a axis of the rutile structure. The calculations were performed for the experimental lattice parameters²⁹ $a=0.4419$ nm, $c=0.2912$ nm, and $u=0.303$.

The results are presented in Table I. 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.^{3,4}

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 $-0.05\mu_B$ whose magnitudes are smaller than the experimental values³⁰ 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. 4 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 calculated² 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.⁴ 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. 3. For the magnetization along the a axis (for which there is no FP-LMTO result in Ref. 4) 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.³ 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.*³ 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 calculation⁵ based on the generalized-gradient approximation (GGA) gives an orbital-moment anisotropy of $0.001\mu_B$. A calculation⁷ based on the augmented-spherical-wave method (ASW) and LSDA gave an orbital-moment anisotropy of $0.001\mu_B$. The ASW calculation is very similar to a LMTO-ASA calculation with a additional correction term, the so-called combined-correction term. Our present LMTO-ASA calculation did not include this correction term and therefore may be less accurate than the ASW calculation.] 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 is a factor of about 5 smaller than the value found by a LMTO-ASA calculation by Uspenskii *et al.*⁶). Increasing U beyond $3\mu_B$ enhances the orbital-moment anisotropy to the values comparable to $0.083\mu_B$ discussed by Goering *et al.*,³ but we doubt that such large values of U are physically reasonable for the Cr atom in CrO_2 .

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 ($U \leq 3$ 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 values¹⁹ 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,¹⁴ and they show that the T_z term cannot be neglected in the analysis of the XMCD spectra via the spin sum rule¹³ 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 fact³¹ 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 *et al.*³

Finally, we have checked by the FLAPW method the applicability of the angle-resolved spin sum rule analysis for

the case of CrO_2 . This analysis is appropriate if $7\Sigma_\alpha \langle T_z \rangle_\alpha / \langle \sigma_z \rangle \ll 1$. For $U=3$ eV (0 eV) we find a ratio of 0.09 (0.01).

Based on our values for $|\Delta l_z|$ and $|\Delta T_z|$ we calculated according to Ref. 9 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 data³ discussed above. For the O atom our FLAPW calculation yields for $U=3$ eV a spin moment of about $0.1\mu_B$ which is a factor of 4 smaller than the one obtained by Goering *et al.*³ with their special analysis of the XMCD results. Our FLAPW spin moments for oxygen are a bit larger than those from the FP-LMTO calculation of Ref. 4. Our LMTO-ASA data are even smaller than the FP-LMTO 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.

It should be noted that the very small anisotropy of the spin moment as compared to the anisotropy of the orbital moment is in line with the predictions of a perturbation treatment of the spin-orbit coupling¹⁰ which shows that the anisotropy of the spin moment is of the order $(\xi/\Delta_{CF})^2$ whereas the anisotropy of the orbital moment is of the order ξ/Δ_{CF} . Thereby, the quantity ξ is the spin-orbit parameter and Δ_{CF} is the measure of the strength of the crystal potential, with $\xi \leq 0.1$ eV and $\Delta_{CF} \approx 1$ eV for $3d$ transition metals.

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 the LDA+ U methods. The calculated anisotropies of $\langle l_z \rangle$ ($\langle T_z \rangle$) are very large but still a factor of 5 (2) smaller than those obtained by Goering *et al.*³ from their special type of analysis of XMCD data for thick layers of CrO_2 on TiO_2 . To arrive at such large anisotropies we had to insert values for the parameter U of the LDA+ U method which are considerably larger than 3 eV and which seem to be physically unreasonable. It would be interesting to see how the results for the orbital anisotropy would change when abandoning the mean-field approximation which is adopted in the LDA+ U method for the electronic on-site correlations and performing a calculation within the dynamical mean-field theory.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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