Determination of Spin- and Orbital-Moment Anisotropies in Transition Metals by Angle-Dependent X-Ray Magnetic Circular Dichroism

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Angle-dependent x-ray absorption spectroscopy in strong magnetic fields is shown to yield precise site specific information about spin and orbital moments in highly anisotropic $3d$ transition metal systems. A new angle averaging spin sum rule allows for the separate determination of spin and magnetic dipole moments in lower than cubic site symmetry. The microscopic origin of the magnetocrystalline anisotropy can be probed directly through the angular dependence of the orbital moment.

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The understanding of magnetic phenomena in thin transition metal films and multilayers, like giant magnetoresistance [1] and perpendicular magnetic anisotropy [2–4], would be greatly aided by a better knowledge of the microscopic magnetic properties of the materials. Of key importance is the reliable measurement of element specific magnetic spin and orbital moments and their anisotropies. In thin magnetic films, and at interfaces and surfaces, all these properties are expected to significantly differ from those in the bulk [3–5]. In practice, however, the quantitative determination of magnetic moments and their anisotropies is anything but simple.

Over the last few years x-ray magnetic circular dichroism (XMCD) spectroscopy has shown great promise as a quantitative magnetometry tool. In contrast to most other techniques, it offers element and site specificity, and the ability to separate the spin and orbital contributions to the magnetic moment by use of powerful theoretical sum rules derived in an atomic framework [6,7]. The sum rules have been tested by band structure calculations [8,9] and have been verified experimentally for bulk Fe and Co [10]. While the orbital magnetic moment is directly linked to the measured dichroism intensity [6], the determination of the spin moment is complicated by the presence of a correction term, the magnetic dipole moment [7], which is known to be sizable in ultrathin films and at surfaces [9]. So far, the presence of this term has appeared to limit the quantitative sum rule determination of spin moments to crystal sites of cubic symmetry.

The present paper shows that, for $3d$ transition metals, the spin and magnetic dipole contributions to the XMCD spin sum rule can be separately determined, for sites with lower than cubic symmetry, i.e., for all cases with important magnetic dipole contributions to the local magnetic moment. In particular, a new sum rule is derived for the spin moment only, based on the angular average of XMCD intensities in an external magnetic field, oriented along Cartesian axes, sufficiently strong to magnetically saturate the sample along all directions. The angle averaged XMCD spin sum rule holds remarkably well for $3d$ transition metals and offers exciting new capabilities for the study of the anisotropic magnetic properties of ultra thin films, surfaces, and interfaces. The spin and magnetic dipole moments can now be quantitatively determined by sum rule analysis of experimental spectra and compared with moments obtained from electronic structure calculations. By use of the XMCD orbital sum rule, the anisotropy of the orbital magnetic moment can also be determined, and it is directly related to the magnetocrystalline anisotropy. Estimates of the size of the expected anisotropies of spin and orbital moments for ultrathin transition metal films suggest them to be easily observable in a suitable XMCD measurement.

The magnetic properties of the transition metals are determined mainly by d electrons. For the ferromagnets Fe, Co, and Ni the combined $4s$ and $4p$ contribution to the magnetic spin moment is less than 5%, and the orbital magnetic moment is entirely due to $3d$ electrons [11]. In the following we shall rely on a simple single particle picture, using a Slater-Koster d-orbital basis, to convey the physics involved. The theory developed is more general, however, and is tested by numerical multiplet calculations.

The properties of $3d$ electrons are best probed in an x-ray absorption experiment by excitation of $2p$ electrons to unfilled $3d$ states. The resulting integrated "white line" intensities A_{L_3} and A_{L_2} are linked to the number of unoccupied $3d$ states (holes) N in the electronic ground state. The polarization dependent white line intensity for a magnetically random sample [12] with higher than D_{2h} crystal symmetry [13] (z axis along a threefold or higher axis) is given by [14]

$$[A_{L_3} + A_{L_2}]_\alpha = \frac{C}{3} \sum_i N^i \left(1 + \frac{7}{B} Q_\alpha^i\right), \qquad (1)$$

where $\alpha = x, y$, or z, and C is proportional to the square of the radial $p \longrightarrow d$ transition matrix element. Here, N^i is the number of holes per orbital d_i, summed over the Brillouin zone (BZ), so that $N = \sum_i N^i$. It can be shown that $B = -4$ for linearly polarized light (electric field vector $\mathbf{E} \parallel \alpha$), and $B = 8$ for circularly or plane polarized light (x-ray wave vector $\mathbf{k} \parallel \alpha$, $\mathbf{E} \perp \mathbf{k}$).

The polarization dependent correction term $(7C/3B)\sum_i N^i Q_\alpha^i$ to the isotropic intensity $CN/3$ arises from the anisotropy of the d charge density within the atomic sphere. In a band picture, the two terms in Eq. (1) may be thought of as a monopole and quadrupole contribution to the d hole density in the Wigner-Seitz cell [15]. Here $Q_\alpha^i = \langle d_i | Q_{\alpha\alpha} | d_i \rangle$, where $Q_{\alpha\beta} = \delta_{\alpha\beta} - 3r_\alpha r_\beta / r^2$ is the quadrupole tensor with $Q_{\alpha\beta} = Q_{\beta\alpha}$ and $\sum_\alpha Q_{\alpha\alpha} = 0$. The matrix elements $\langle d_i | Q_{\alpha\alpha} | d_i \rangle$ are given in the first column of Fig. 1. The vanishing trace of Q results in the important sum rule for the total intensity

$$\sum_\alpha [A_{L_3} + A_{L_2}]_\alpha = CN \,. \qquad (2)$$

Equation (2) also holds for a single measurement of polycrystalline samples or, for samples with higher than twofold symmetry about z, it applies when $\mathbf{E}$ ($\mathbf{k}$) for linear (circular) polarized light is at the "magic angle" 54.7° from the z axis [13,16].

Carra *et al.* have recently derived a related sum rule for the XMCD intensity [7,14],

$$[\Delta A_{L_3} - 2\Delta A_{L_2}]_\alpha = C/3\hbar(2\langle S_\alpha \rangle + 7\langle T_\alpha \rangle) \,. \qquad (3)$$

Here, ΔA_{L_3} and ΔA_{L_2} are the L_3 and L_2 dichroism intensities measured in a geometry $\mathbf{k}, \mathbf{H}_{\mathrm{ext}} \parallel \alpha$, where $\alpha = x, y$, or z denotes the Cartesian frame. It is assumed that the external magnetic field $\mathbf{H}_{\mathrm{ext}}$ is large enough to magnetically saturate the sample [17]. $\langle S_\alpha \rangle$ and $\langle T_\alpha \rangle$ are the expectation values of the spin operator and the intra-atomic magnetic dipole operator $\mathbf{T} = \mathbf{S} - 3\hat{r}(\hat{r} \cdot \mathbf{S})$ for the spin quantization axis aligned along α. We can write $T_\alpha = \sum_\beta Q_{\alpha\beta} S_\beta$, indicating the coupled charge (Q) and spin (S) components of T.

For $3d$ transition metals the spin-orbit (s.o.) interaction $\xi \mathbf{L} \cdot S$ ($\xi \leq 0.1$ eV) is much smaller than the exchange interaction (band splitting $\Delta_{\mathrm{ex}} \approx 1$ eV) and the crystal potential (characteristic splitting $\Delta_{CF} \approx 1$ eV at Γ in the BZ) and hence can be treated by perturbation theory [3,18]. Such a treatment yields a nearly isotropic spin $\langle S_\alpha \rangle = \langle S \rangle$ when the sample is magnetically saturated along the Cartesian axes by a strong magnetic field [17], the s.o. induced anisotropy being only of second order (about 1%). A perturbative calculation of $\langle T_\alpha \rangle$ yields the approximate result $\langle T_\alpha \rangle \approx \sum_i Q_\alpha^i s^i$ for higher than D_{2h} symmetry [13], where we have expressed $\langle S \rangle = \sum_i s^i$ in terms of its d-orbital projected components s^i. While the above result is exact in the limit of zero s.o. coupling, the neglected s.o. correction terms are of orders $(\xi/\Delta_{CF})^2 \approx 0.01$ (same spin) and $\xi/(\Delta_{\mathrm{ex}} + \Delta_{CF}) < 0.1$ (opposite spin), respectively. In $3d$ transition metals, to a good approximation, $\langle T_\alpha \rangle$ is therefore due to a lower than cubic site symmetry only, and the effect of s.o. coupling on $\langle T_\alpha \rangle$ can be neglected. This result expresses the intuitive picture that, for weak s.o. coupling, the quadrupolar charge distribution $Q_{\alpha\beta}$ remains largely decoupled from, and unaffected by, the magnetic spin orientation S_β. For $3d$ metals, $\langle T_\alpha \rangle$ therefore predominantly reflects a quadrupole term in the anisotropic spin density within the Wigner-Seitz cell [19]. In close analogy to Eq. (1) we obtain

$$[\Delta A_{L_3} - 2\Delta A_{L_2}]_\alpha = \frac{2C}{3\hbar} \sum_i s^i \left(1 + \frac{7}{2} Q_\alpha^i\right) . \qquad (4)$$

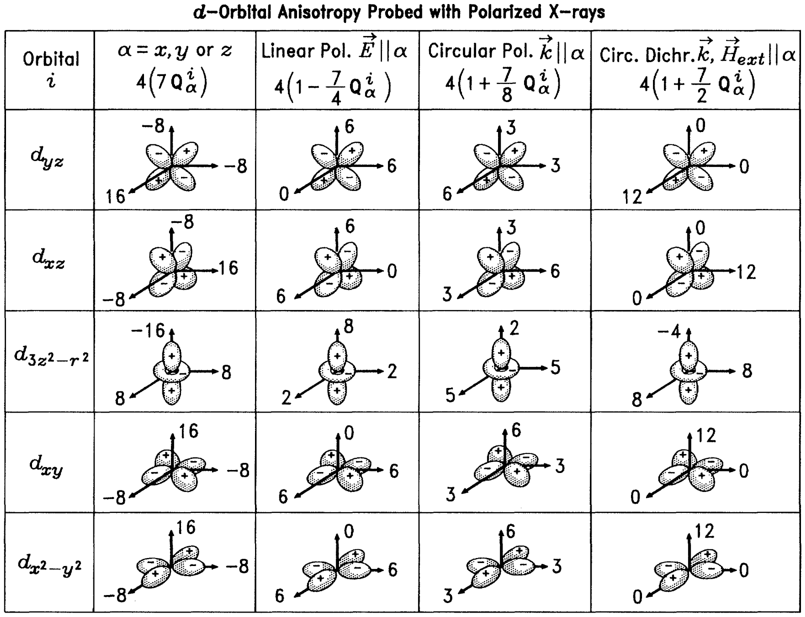

FIG. 1. Calculated matrix elements $\langle d_i | Q_{\alpha\alpha} | d_i \rangle$, ($\alpha = x, y, z$) and polarization factors in Eqs. (1) and (4) for the d orbitals [20]. Factors are given for x-ray absorption experiments with linearly (electric field vector $\mathbf{E} \parallel x, y, z$) and circularly polarized x rays (x-ray wave vector $\mathbf{k} \parallel x, y, z$), and for x-ray circular dichroism studies in an external magnetic field H_{ext} ($\mathbf{k}, \mathbf{H}_{\mathrm{ext}} \parallel x, y, z$). Note $\mathbf{E} \perp \mathbf{k}$.

Similar to Eq. (2), there is a new sum rule which follows from the property $\sum_\alpha \langle T_\alpha \rangle \approx \sum_i s^i \sum_\alpha Q^i_\alpha = 0$. It allows direct determination of $\langle S \rangle$ by averaging measurements along the x, y, and z axes,

$$\sum_\alpha [\Delta A_{L_3} - 2\Delta A_{L_2}]_\alpha = \frac{2C}{\hbar} \langle S \rangle, \tag{5}$$

provided the sample is magnetically saturated. Note that Eq. (5) also holds for polycrystalline samples or for a "magic angle" measurement [13,16].

We have calculated the expectation values Q^i_α ($\alpha = x, y, z$) for the five d orbitals d_i [20], and they are given in Fig. 1, together with the polarization dependent correction terms in Eqs. (1) and (4). It is apparent that, for each orbital, Q^i_α is very anisotropic. The term Q^i_α vanishes when averaged over all directions and over all orbitals d_i. Also, for cubic symmetry the orbitals group into degenerate e_g ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$) and t_{2g} (d_{xy}, d_{yz}, d_{xz}) sets, and Q^i_α vanishes for each set. The correction term is expected to be large in ultrathin films, where the charge density and spin density are not spherically symmetric.

Electronic structure calculations for thin films typically show a larger spin-density [Eq. (4)] than charge-density [Eq. (1)] anisotropy so that, in practice, the measured effect is much larger for the former. For example, Daalderop, Kelly, and Schuurmans [19] have calculated the d-orbital projected moments $m_s(i) = -(2\mu_B/\hbar)s^i$, $m_s(d_{x^2-y^2}) = m_s(d_{xy}) = 0.28\mu_B$, $m_s(d_{xz}) = m_s(d_{yz}) = 0.44\mu_B$, and $m_s(d_{3z^2-r^2}) = 0.43\mu_B$ for a Co monolayer, which yields large correction terms in Eq. (3), $7\langle T_\perp \rangle = 7\langle T_z \rangle = 0.62\hbar$ and $7\langle T_\parallel \rangle = 7(\langle T_x \rangle + \langle T_y \rangle)/2 = -0.31\hbar$, respectively. The same calculation yields an almost isotropic charge density, such that the correction term in Eq. (1) would be immeasurably small. Large values $7\langle T_z \rangle \geq 0.23\hbar$ have also been obtained for Co(0001) and Fe(001) surfaces by Wu and Freeman [9].

We have verified the validity of the sum rule expressed by Eq. (5) by performing atomic multiplet calculations with scalar relativistic corrections [21,22]. Anisotropic embedding was included by use of a crystal electric field, while magnetic exchange was modeled by an external magnetic field coupled to spin only [23]. Thermal averages were determined by applying Boltzmann statistics to the occupation of crystal field split multiplet levels. We chose D_{4h} symmetry with z along the fourfold axis, and cubic and tetragonal crystal field splittings $10Dq$ and $Dt = Ds$, respectively [24].

Results for Co^{2+} in a ($3d^7$) configuration, as a function of Ds and exchange splitting Δ_{ex}, are shown in Table I. While the relative dipolar contribution for a given magnetization direction, e.g., $7\langle T_z \rangle / 2\langle S_z \rangle$, increases substantially with increasing Ds, the angle averaged dipolar contribution $7\langle T_{\mathrm{av}} \rangle / 2\langle S_{\mathrm{av}} \rangle$ decreases strongly. Remarkably, upon angle averaging, the dipolar contribution is smaller in tetragonal than in cubic symmetry. We observe that the angular average of the XMCD spin sum rule effectively cancels the contribution of the magnetic dipole operator when the tetragonal crystal field splitting Ds becomes larger than the spin-orbit splitting ξ.

TABLE I. $\langle S_\alpha \rangle$ and $\langle T_\alpha \rangle$ calculated for $\mathrm{Co}^{2+}(d^7)$ ion for varying tetragonal distortion Ds and exchange splitting Δ_{ex}. We have used a s.o. coupling constant $\xi = 0.066$ eV, a cubic crystal field splitting $10Dq = 1$ eV, temperature $T = 25$ meV, and define $\langle T_{\mathrm{av}} \rangle = (\langle T_x \rangle + \langle T_y \rangle + \langle T_z \rangle)/3$ and $\langle S_{\mathrm{av}} \rangle = (\langle S_x \rangle + \langle S_y \rangle + \langle S_z \rangle)/3$.

Ds (eV)	0	0.075	0.1	0.5	0.5	0.5
Δ_{ex} (eV)	1	1	1	1	0.1	0.01
$\langle S_z \rangle (\hbar)$	−1.498	−1.498	−1.498	−1.498	−1.464	−0.405
$\langle S_{x,y} \rangle (\hbar)$	−1.498	−1.498	−1.498	−1.498	−1.479	−0.506
$\langle T_z \rangle (\hbar)$	0.057	−0.088	−0.139	−0.213	−0.916	−0.053
$\langle T_{x,y} \rangle (\hbar)$	0.057	0.084	0.088	0.104	0.096	0.033
$\langle S_{\mathrm{av}} \rangle (\hbar)$	−1.498	−1.498	−1.498	−1.498	−1.474	−0.472
$\langle T_{\mathrm{av}} \rangle (\hbar)$	0.057	0.026	0.013	−0.002	−0.001	0.004
$7\langle T_z \rangle / 2\langle S_z \rangle$	−0.132	0.207	0.325	0.498	0.469	0.461
$7\langle T_{\mathrm{av}} \rangle / 2\langle S_{\mathrm{av}} \rangle$	−0.132	−0.061	−0.030	0.005	0.002	−0.030

Angle-dependent XMCD spectroscopy also yields valuable information about the origin of the magnetocrystalline anisotropy. For example, in thin films, a perpendicular magnetic anisotropy results when the shape anisotropy, favoring in-plane orientation, is overcome by an anisotropy resulting from the s.o. interaction. Bruno [3] has shown in a perturbation picture that the energy anisotropy due to the spin orbit interaction $\Delta E_{\mathrm{s.o.}}$ is proportional to the anisotropy of the orbital moment $m_0^\gamma = -\langle L_\gamma \rangle \mu_B / \hbar$. As discussed above, the spin moment for $3d$ transition metals remains isotropic to a very good approximation in the presence of s.o. coupling, with an anisotropy of order $(\xi/\Delta_{CF})^2$, only. On the other hand, the anisotropy of the orbital moment is of order ξ/Δ_{CF}, as illustrated in Table II, and hence dominates [25]. It can therefore be viewed as the microscopic origin of the s.o. induced magnetic anisotropy, i.e., of the magnetocrystalline anisotropy. The anisotropy persists even when the states are summed over the BZ, and Bruno [18] has estimated the orbital moment anisotropy for (100) and (111) fcc monolayers of Fe and Co and found large values $m_0^\parallel - m_0^\perp \approx 0.20\mu_B$. From these estimates, we expect that the anisotropy of the orbital moment and its preferred direction should be easily measurable by XMCD.

For samples with uniaxial anisotropy (no in-plane anisotropy), one obtains $\Delta E_{\mathrm{s.o.}} \propto m_0^\perp - m_0^\parallel$, and the angular dependence of the orbital moment can be directly determined by XMCD. For an experimental geometry where $\mathbf{k}$ and $\mathbf{H}_{\mathrm{ext}}$ are at an angle γ with respect to the surface normal and H_{ext} is sufficiently large to magnetically saturate the sample [17], the orbital moment m_0^γ along the field direction can be directly determined by use of the sum rule [6]

$$[\Delta A_{L_3} + \Delta A_{L_2}]_\gamma = -\frac{C}{2\mu_B} m_0^\gamma . \tag{6}$$

TABLE II. Orbital magnetic moment and its anisotropy for the d orbitals [3]. For simplicity we assume that the magnetic exchange splitting is large, and we consider only states of one spin [25]. Band structure and crystal field effects result in d orbitals which are linear combinations of functions $|m_l\rangle$ $(-2 \leq m_l \leq +2)$ [20]. The pure d orbitals used (i.e., at high symmetry points in the BZ) possess no orbital moment. The inclusion of the spin-orbit interaction in lowest order perturbation theory results in anisotropic orbital moments as shown, where $\xi \leq 0.1$ eV is the spin-orbit coupling constant and $\Delta_{ij} \approx 1$ eV is the energy separation (taken positive) of a higher energy state i and a lower state j.

	$\langle L_z \rangle^{\mathrm{so}}$	$\langle L_y \rangle^{\mathrm{so}}$	$\langle L_x \rangle^{\mathrm{so}}$
$\|5\rangle = d_{xz \propto \|1\rangle - \|-1\rangle}$	$\frac{-\xi}{\Delta_{54}}$	$\frac{-\xi}{\Delta_{51}} + \frac{-3\xi}{\Delta_{52}}$	$\frac{-\xi}{\Delta_{53}}$
$\|4\rangle = d_{yz \propto \|1\rangle + \|-1\rangle}$	$\frac{\xi}{\Delta_{54}}$	$\frac{-\xi}{\Delta_{43}}$	$\frac{-\xi}{\Delta_{41}} + \frac{-3\xi}{\Delta_{42}}$
$\|3\rangle = d_{xy \propto \|2\rangle - \|-2\rangle}$	$\frac{-4\xi}{\Delta_{31}}$	$\frac{\xi}{\Delta_{43}}$	$\frac{\xi}{\Delta_{53}}$
$\|2\rangle = d_{3z^2 - r^2 \propto \|0\rangle}$	0	$\frac{3\xi}{\Delta_{52}}$	$\frac{3\xi}{\Delta_{42}}$
$\|1\rangle = d_{x^2 - y^2 \propto \|2\rangle + \|-2\rangle}$	$\frac{4\xi}{\Delta_{31}}$	$\frac{\xi}{\Delta_{51}}$	$\frac{\xi}{\Delta_{41}}$

In case of uniaxial anisotropy, $m_0^{\gamma} = m_0^{\perp} \cos^2\gamma + m_0^{\|} \sin^2\gamma$, such that measurements at two angles are needed to determine $m_0^{\perp} - m_0^{\|}$. The angle-averaged moment $(m_0^{\perp} + 2m_0^{\|})/3$ may be determined in a single magic angle measurement.

It is apparent from Fig. 1 and Table II that the electronic charge-density anisotropy is closely related to the magnetic spin-density and orbital-moment anisotropies. In the presented picture, all three arise from unequal contributions of the d orbitals when the **k**-dependent states are summed over the BZ. Estimates show that the charge-density anisotropy is typically small in transition metal films, but that the two magnetic anisotropies are large and measurable by XMCD. From the above discussion, we expect to find a close relationship between their absolute values and symmetries. This picture is indeed confirmed by recent XMCD measurements on an Au/Co/Au wedge [26].

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[12] For a magnetically random sample the orbital moment is not detected, and linear magnetic dichroism effects are absent.

[13] For higher than D_{2h} symmetry, all cross terms $\langle d_i | Q_{\alpha\alpha} | d_j \rangle$ in the crystal wave functions vanish. This holds even in the presence of s.o. coupling, since it does not mix the two e_g orbitals which give rise to a cross term. Note that the sum rules [Eqs. (2) and (5)] remain valid even for lower crystal symmetry, because the cross terms for Q_{xx} and Q_{yy} cancel.

[14] In a band picture, Eqs. (1)–(6) hold if the radial $p \longrightarrow d$ matrix element does not vary across the d band (in E and **k**).

[15] Note that for K shell absorption ($s \longrightarrow p$ transitions) the angular dependence is more pronounced [e.g., J. Stöhr, *NEXAFS Spectroscopy,* Springer Series in Surface Sciences 25 (Springer, Heidelberg, 1992)].

[16] For higher than twofold symmetry about z, and a geometry where **E** (**k**) for linear (circular) polarized light is at a polar angle ϑ, the correction factor in Eqs. (1) and (4) is given by $Q_{\vartheta} = (\langle Q_{xx} \rangle + \langle Q_{yy} \rangle) \sin^2\vartheta/2 + \langle Q_{zz} \rangle \cos^2 \vartheta$.

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