Magnetic circular x-ray dichroism in transverse geometry: Importance of noncollinear ground state moments

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The orbital and spin magnetic moment and the magnetic dipole term of $3d$ transition metals are no longer collinear when the electron spins are forced out of the easy direction by an external magnetic field. This effect provides a simple way to measure with magnetic x-ray dichroism the anisotropy of the orbital magnetic moment and the magnetic dipole term in a geometry where the contribution of the spin magnetic moment disappears, i.e., with the photon helicity vector perpendicular to the magnetization direction. [S0163-1829(96)50526-6]

Recent experimental and theoretical advances have made magnetic circular x-ray dichroism (MCXD) a powerful tool to separate the spin and orbital contributions to the magnetization. Sum rules relate the difference in absorption between left and right circularly polarized x rays, at, say, the $L_{2,3}$ absorption edges of $3d$ transition metals to ground state magnetic moments.[1,2] Its element specificity makes MCXD the only technique to date for studying the magnetic moments of the individual elements in thin films and multilayers composed of different magnetic materials.[3] Such systems are of increasing importance in magneto-optical recording industry due to the variety of novel magnetic properties, such as perpendicular magnetic anisotropy (PMA), enhanced magnetic moments, and giant magnetoresistance. Exchange biasing of a magnetic layer by a ferromagnetic or antiferromagnetic substrate is used to improve device homogeneity required for further miniaturization.[4] Strong exchange coupling between overlayer and substrate can force the overlayer spins out of their easy magnetization direction. A similar situation occurs during measurement of the magnetocrystalline anisotropy (MCA) where the spins are forced out of the easy direction by a strong external magnetic field. In this paper we show that spin alignment along nonsymmetry directions is characterized by noncollinear ground state moments. This requires a far more judicious application of the sum rules to experimental results and leads to interesting new applications which have not been considered in the analysis of MCXD experiments up to now.[5] When the electron spins are forced out of their easy magnetization direction spin-orbit coupling tries to adjust the electron orbitals with respect to the spins. This is partially counteracted by the strong crystalline field in $3d$ transition metals causing a small noncollinear component for the orbital moment and a larger one for the magnetic dipole term, which is the anisotropy of the spin distribution due to the crystalline field. We will propose experiments which allow the determination of the anisotropy in the orbital magnetic moment and the magnetic dipole term using a transverse geometry, with the photon helicity vector perpendicular to the magnetization direction.

The ground state of a magnetic material can be characterized by its moments, such as the spin and orbital magnetic moment, the quadrupole moment, and the magnetic dipole term. These moments have expectation values **S**, **L**, Q, and **T**, which can be obtained for the spin quantization axis along any chosen unit vector $\hat{\mathbf{S}}$. We stress that **S**, **L**, and **T** are vector quantities[6] whereas Q is a traceless tensor of rank 2. In a one-electron picture, the spin moment is determined by the occupation numbers $n_i^{\uparrow(\downarrow)}$ of majority (minority) bands as $\mathbf{S}=\frac{1}{2}\Sigma_i(n_i^{\uparrow}-n_i^{\downarrow})\hat{\mathbf{S}}$ and its magnitude is constant for all directions $\hat{\mathbf{S}}$. The values of $n_i^{\uparrow(\downarrow)}$ depend on the material and band filling and can be estimated from, e.g., a band structure calculation. We limit the following analysis to the case of $3d$ transition metals where the anisotropy of the total energy E and the presence of an orbital magnetic moment are both due to the small $3d$ spin-orbit interaction. The two quantities **T** and the anisotropy $\mathbf{L}^{\mathrm{A}}$ of the orbital moment, i.e., the angular variation of **L**, play a major role in the MCA. When the majority band is full we have approximately

$$E^{\mathrm{MCA}}=-\tfrac{1}{2}\xi\hat{\mathbf{S}}\cdot\mathbf{L}^{\mathrm{A}}+\tfrac{7}{4}\xi^2\hat{\mathbf{S}}\cdot\mathbf{T}\frac{1}{E^{\mathrm{exch}}}, \tag{1}$$

where ξ is the spin-orbit parameter and E^{exch} the effective exchange splitting between majority and minority bands. Equation (1) is equivalent to the one given by Bruno.[7] The relationship of the second term to the quadrupole moment was indicated by Wang *et al.*[8] The quadrupole moment Q, i.e., the anisotropy of the charge distribution of the $3d$ electrons around the atom, is dominated by the crystalline field and we can neglect any spin-orbit induced contributions to **T**, so that

$$\mathbf{T}=\tfrac{1}{2}(\mathsf{Q}^{\downarrow}-\mathsf{Q}^{\uparrow})\hat{\mathbf{S}}. \tag{2}$$

Thus **T** describes the anisotropy in the spin distribution of the $3d$ electrons, and is given by a traceless tensor times $\hat{\mathbf{S}}$.[5] As implicitly given by, e.g., Bruno,[7] the orbital moment of $3d$ ferromagnets in perturbation theory is[9]

$$\mathbf{L}=\mathsf{R}\hat{\mathbf{S}}, \tag{3}$$

where R is a (second rank) tensor. In general the trace of R does not vanish. For C_{2v} and higher symmetry, R is diagonal

TABLE I. Components of the quadrupole moments $\frac{7}{2}\mathbf{q}_i$ for the one-electron $3d$ orbitals along the Cartesian coordinates.

d orbital	x	y	z
$x^2-y^2;xy$	1	1	−2
xz	1	−2	1
yz	−2	1	1
z^2	−1	−1	2

and it is formally possible to make a separation into an isotropic part $\mathsf{R}^{\mathrm{I}}=\frac{1}{3}\mathrm{Tr}(\mathsf{R})\mathbf{I}$, where $\mathbf{I}$ is the unit matrix, and a traceless matrix R^{A} which corresponds to the anisotropy of the orbital moment in Eq. (1), i.e., $\mathbf{L}^{\mathrm{A}}=\mathsf{R}^{\mathrm{A}}\hat{\mathbf{S}}$.[10]

So, for MCA studies it is important to know **S**, **L**, Q, and **T**, especially for thin magnetic films and multilayers where interface effects lead to a strong enhancement of the MCA of one or two orders of magnitude compared to bulk materials. A large class of systems studied are epitaxial face-centered- or body-centered-cubic magnetic films with (100) surface orientations. In the following we will discuss the ground state moments for such a magnetic film which has C_{4v} symmetry and displays PMA. A generalization of the results is straightforward and will be presented elsewhere.[11] From Eqs. (2) and (3) we see that **T** and **L** are completely determined once we know the components of the tensors $\mathsf{Q}^{\uparrow}-\mathsf{Q}^{\downarrow}$ and R. For the symmetry considered here both tensors are diagonal. We can use the one-electron quadrupole moments $\mathbf{q}_i$ listed in Table I for the different $3d$ orbitals to obtain $\mathsf{Q}^{\uparrow(\downarrow)}=\Sigma_i n_i^{\uparrow(\downarrow)}\mathbf{q}_i$. For convenience the z axis is chosen along the surface normal. Even without detailed knowledge of $n_i^{\uparrow(\downarrow)}$ we can draw some important conclusions based on symmetry arguments. In C_{2v} symmetry the $d(x^2-y^2)$ and $d(xy)$ orbitals are degenerate and the traceless $\mathsf{Q}^{\uparrow(\downarrow)}$ has two independent components. In C_{4v} symmetry x and y belong to the same representation making $d(xz)$ and $d(yz)$ degenerate. $\mathbf{q}_i$ is then averaged over x and y axes, so that

$$-\tfrac{1}{2}\,\mathsf{Q}_{zz}^{\uparrow(\downarrow)}=\mathsf{Q}_{yy}^{\uparrow(\downarrow)}=\mathsf{Q}_{xx}^{\uparrow(\downarrow)}, \tag{4}$$

which leaves us with one independent component for $\mathsf{Q}^{\uparrow}-\mathsf{Q}^{\downarrow}$. A similar relation as Eq. (4) holds for R^{A}, and since our system has PMA we get $\mathsf{R}_{zz}^{\mathrm{A}}>\mathsf{R}_{xx}^{\mathrm{A}}$. For a more than half filled $3d$ band the spin-orbit coupling causes a positive value of R^{I}, which is usually larger than $\mathsf{R}_{xx}^{\mathrm{A}}$.

We will discuss the implications by simulating an MCA measurement. An external magnetic field $\mathbf{H}\|\hat{\mathbf{S}}$ strong enough to saturate the sample[12] is used to reorient the electron spins along $\hat{\mathbf{S}}$ in the xz plane. By varying the direction $\hat{\mathbf{S}}$ from perpendicular to completely in plane, the spin moment vector **S** moves along the circle depicted in Fig. 1. According to Eqs. (2) and (3) it follows that **L** and **T** must move on ellipses given by R and $\frac{1}{2}(\mathsf{Q}^{\downarrow}-\mathsf{Q}^{\uparrow})$, as shown in Fig. 1. If we normalize **S**, **L**, and **T** along the x axis then their x components must be the same for any arbitrary direction of $\hat{\mathbf{S}}$. This is indicated in Fig. 1 by drawing a (dashed) line parallel to the z axis through the end point of **S**. The intersections with the R and $\frac{1}{2}(\mathsf{Q}^{\downarrow}-\mathsf{Q}^{\uparrow})$ ellipses gives then the z components of **L** and **T**. Since the spin-orbit interaction makes $\mathbf{L}_x$ positive, **L** will have the same sense of rotation as **S**. Due to Eq.

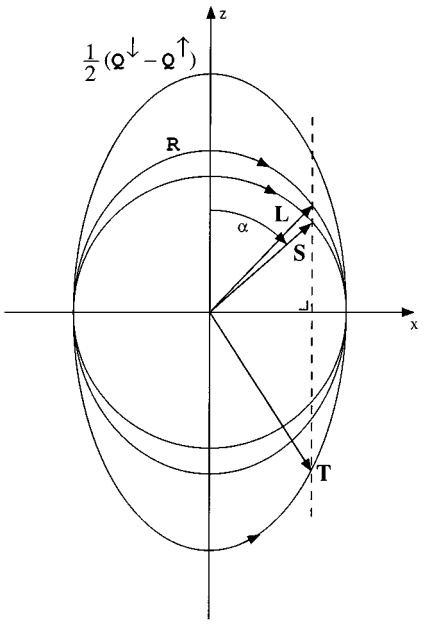

FIG. 1. Construction of $\mathbf{L}=\mathsf{R}\hat{\mathbf{S}}$ and $\mathbf{T}=\frac{1}{2}(\mathsf{Q}^{\downarrow}-\mathsf{Q}^{\uparrow})\hat{\mathbf{S}}$ for given $\hat{\mathbf{S}}$. We assume that the tensors have their main values along the coordinate axes. In, e.g., the xz plane, the tensors are represented by ellipses with the lengths of the main axes given by the corresponding eigenvalues. The abscissae have been normalized to unity. Rotating the external magnetic field moves $\hat{\mathbf{S}}$ on a circle. Its end point is projected, parallel to the z axis, onto the ellipses. Because the x and z eigenvalues of $\frac{1}{2}(\mathsf{Q}^{\downarrow}-\mathsf{Q}^{\uparrow})$ have opposite signs, **T** is obtained by subsequent reflection with respect to the x axis. This causes **T** to move in a sense opposite to $\hat{\mathbf{S}}$.

(4) the two components of **T** have opposite sign and this vector will, therefore, rotate in opposite sense to **S** and **L**. This means that for one particular choice of $\hat{\mathbf{S}}$, the two vectors can even be orthogonal. The physical reason for the occurrence of components of **L** and **T** transversal to **S** is the influence of the crystalline field on both quantities. When the electron spins are rotated out of the easy axis, the crystalline field does not follow and causes, through Q, the large transversal component of **T** in Fig. 1. The effect is smaller for **L** since it is partially aligned with **S** by spin-orbit coupling as described by the isotropic part $\mathbf{L}^{\mathrm{I}}=\mathsf{R}^{\mathrm{I}}\hat{\mathbf{S}}$. However, the electron orbits also have the tendency to stay aligned with the crystal lattice which causes the anisotropic part $\mathbf{L}^{\mathrm{A}}$. Note that in systems with large spin-orbit coupling such as lanthanides and actinides **L** and **T** are always collinear with **S**.

An MCXD measurement of **L**, **S**, and **T** comprises taking the difference in absorption of circularly polarized x rays at the $3d$ metal $L_{2,3}$ edges with the photon helicity aligned parallel and antiparallel to the components of the moments. The projections of the ground state moments onto the direction of the incident light $\hat{\mathbf{P}}$ are obtained from the intensities of difference $\Delta A_{2,3}$ and sum $A_{2,3}$ spectra integrated over the corresponding edges according to the sum rules[1,2] as

$$\hat{\mathbf{P}}\cdot\mathbf{L}=-\frac{4}{3}\,\frac{\Delta A_3+\Delta A_2}{A_3+A_2}\,n_h, \tag{5}$$

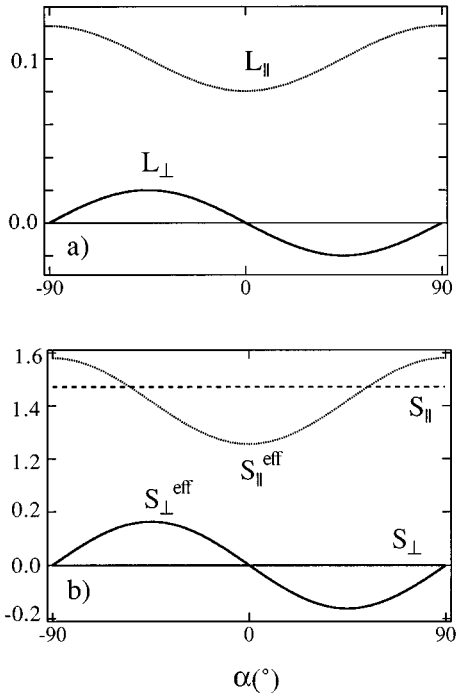

FIG. 2. (a) Orbital **L** and (b) spin **S** and effective spin $\mathbf{S}^{\mathrm{eff}}$ magnetic moments (μ_B) for an ultrathin Fe film grown on a Ag(100) surface (C_{4v} symmetry). Shown are the values as they would be obtained by applying the sum rules of Eqs. (5) and (6) to MCXD data measured for two experimental geometries. In one, the photon incidence direction $\hat{\mathbf{P}}$ is parallel to the applied magnetic field **H** (subscripts $\parallel$; dashed and dotted lines). The other geometry is characterized by $\hat{\mathbf{P}}$ being perpendicular to **H** (subscripts $\perp$; solid lines). All vectors are assumed to be in the xz plane. α is defined in Fig. 1 as the angle between the sample normal and the applied magnetic field. Note that $\mathbf{S}_\parallel^{\mathrm{eff}}=\mathbf{S}_\parallel$ and $\mathbf{L}_\parallel=\mathbf{L}_\parallel^{\mathrm{I}}$ at $\alpha=\pm 54.7°$.

$$\hat{\mathbf{P}}\cdot\mathbf{S}^{\mathrm{eff}}\equiv\hat{\mathbf{P}}\cdot\mathbf{S}+\tfrac{7}{2}\hat{\mathbf{P}}\cdot\mathbf{T}=-\frac{\Delta A_3-2\Delta A_2}{A_3+A_2}n_h, \qquad (6)$$

where n_h is the number of $3d$ holes in the ground state. Experimentally, the simplest way is to maintain the angle between $\hat{\mathbf{P}}$ and **H** fixed and to vary the angle α between **H** and the sample normal by rotating the sample. For clarity we will discuss only two experimental geometries, i.e., $\hat{\mathbf{P}}$ parallel and perpendicular to **H**. Using theoretically predicted values of **S** and **T** (Ref. 13) and an estimate of R (Refs. 7 and 13) for an ultrathin Fe film grown epitaxially on a Ag(100) surface we obtain the curves in Fig. 2 for the photon incidence direction $\hat{\mathbf{P}}$ parallel (dashed and dotted lines) and perpendicular (solid lines) to the applied magnetic field **H**. The components $\mathbf{L}_\parallel$ and $\mathbf{S}_\parallel^{\mathrm{eff}}$ parallel to **H** show a sinusoidal variation with the angle α superimposed on a higher constant offset. For $\mathbf{S}^{\mathrm{eff}}$ the variation is caused by the dipole term, **T**, rotating opposite to **S**, while for **L** it is due to $\mathbf{L}^{\mathrm{A}}$. The constant offsets are due to **S** and $\mathbf{L}^{\mathrm{I}}$ projected onto $\hat{\mathbf{P}}$. It is obvious that in this geometry MCXD measurements at two different angles α should be performed to obtain all components of **L**, **S**, and **T**. If one is only interested in an independent determination of **S**, however, which is desirable in order to establish possible enhancements of the spin moment with increasing film thickness,[14] a single MCXD measurement performed at the ''magic'' angle of $\alpha=54.7°$ would be sufficient. In this geometry the $\mathbf{T}_\parallel$ and $\mathbf{L}_\parallel^{\mathrm{A}}$ components are zero because of Eq. (4) (cf. Fig. 2). The implications of the geometry with $\hat{\mathbf{P}}$ parallel to **H** have been partially discussed by Stöhr and König[5] and first MCXD measurements were reported by Weller *et al.*[15] **T** and $\mathbf{L}^{\mathrm{A}}$ can be obtained from the difference in $\mathbf{S}_\parallel^{\mathrm{eff}}$ and $\mathbf{L}_\parallel$ measured at two different angles α. This induces additional errors due to the subtraction of two values of comparable magnitude, since the MCXD signals at the L_3 edge differ typically by $\sim 30\%$.[15] However, this problem does not occur in the geometry where $\hat{\mathbf{P}}$ is perpendicular to **H**. Here, one directly measures the anisotropy of **L** and $\mathbf{S}^{\mathrm{eff}}$. Since the spin moment is always perpendicular to $\hat{\mathbf{P}}$ in this geometry, we have $\mathbf{S}_\perp^{\mathrm{eff}}=\frac{7}{2}\mathbf{T}_\perp$. Similarly we obtain $\mathbf{L}_\perp=\mathbf{L}_\perp^{\mathrm{A}}$. The maximum effect occurs at an angle $\alpha=45°$ and it is possible to obtain in one single measurement the two main variables in the MCA given by Eq. (1). It is important to note that the angular variation of the magnetic moments shown in Fig. 2 is a consequence of the symmetry of the system and does not depend on the actual magnitude of the moments, i.e., the material properties. In the experiments this will allow an independent determination of the moments, for example as functions of temperature, film thickness, or other parameters, at the ''magic'' angle in a fixed geometry, where the magnetization is perpendicular to the incident photon direction. For systems with C_{2v} symmetry all moment components can be obtained from two transversal measurements in perpendicular planes.[11]

On the basis of Eqs. (2) and (3) we can speculate that noncollinear magnetic moments might be very common at the surfaces of crystalline magnetic materials which usually have a different symmetry than the bulk. This causes enhanced values of the orbital moment as predicted by band structure calculations.[16] But it can also lead to different easy magnetization directions at the surface. A strong exchange interaction between bulk and surface layers, orienting the surface spins can then result in noncollinear surface moments. Experimentally, a separation of surface and bulk signal is difficult and has certainly not been done routinely. A transversal MCXD experiment will provide a more straightforward measurement of the surface magnetic signal when performed in a ''forbidden'' geometry. With $\hat{\mathbf{P}}\perp\mathbf{S}$ the bulk signal is zero since, there, the moments are still collinear.

In conclusion, we have shown a way to extend the sum rule analysis of magnetic ground state moments in magnetic circular x-ray dichroism to systems where the electron spins are not aligned along a high-symmetry crystal direction. Since the ground state moments **L** and **T** have tensor properties, they are then no longer collinear with the spins and can enclose large angles. From symmetry arguments we have shown that there is an optimum experimental geometry which is material independent and allows a separation of these moments.

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[10] The noncollinearity of **L** and **S** is a consequence of the competition between the MCA and the spin-orbit coupling. The MCA tries to orient **L** along the easy axis of magnetization with no preference for parallel or antiparallel direction. Spin-orbit coupling for more than half filled $3d$ shells tries to align **L** parallel to **S**. Thus the projection of **L** onto **S** will be parallel to **S**, but there will also be a component perpendicular to **S** towards the easy axis.

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