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Determination of the element-specific magnetic anisotropy in thin films and surfaces

Gerrit van der Laan

Magnetic Spectroscopy Group, Daresbury Laboratory, Warrington WA4 4AD, UK

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Abstract

We discuss the various element-specific methods to obtain the magnetocrystalline anisotropy energy (MAE) of thin films, multilayers and surfaces. X-ray magnetic circular dichroism has recently emerged as a routine method, where the orbital magnetic moment of 3d transition metals can be determined using the sum rule for the $L_{2,3}$ absorption spectra. The obtained orbital moment can be related to the MAE using Bruno's model, which is only valid under the assumption that the majority-spin subband is completely filled. This limitation can be avoided by employing x-ray magnetic linear dichroism (XMLD). The XMLD branching ratio is proportional to the anisotropy in the spin–orbit interaction, which, in second-order perturbation, can be related to the MAE. We present an expression for the angular dependence of the sum rules, which can be used to determine the magnetic anisotropy from the linear dichroism for a system with arbitrary point-group symmetry.

1. Introduction

Magnetic monolayers and multilayers exhibit a rich variety of unusual magnetic properties arising from their reduced dimensionality. The ability to grow epitaxial thin films has led to materials with novel magnetic properties, such as perpendicular magnetic anisotropy (PMA), giant magnetoresistance and exchange biasing. The preferred orientation of the magnetization is determined by the magnetocrystalline anisotropy energy (MAE), which is the change in the free energy for a crystal upon rotation of the magnetization. In thin films, multilayers and at surfaces, the MAE differs often strongly from the bulk value due to symmetry breaking of the lattice. It is possible to manipulate the magnetic anisotropy by varying the individual layer thickness and an appropriate choice of the elements. The driving force behind this research has been the ability to grow ultra-thin films with PMA, which is particularly appealing for the magnetic recording industry by offering increased storage density.

Thin films of only a few monolayers in heterogeneous systems require ultra-sensitive and element-selective magnetic probes. Separation of the magnetic moment into spin and orbital parts will be required to study the influence of the crystalline field on the magnetic anisotropy.

So far, x-ray magnetic circular dichroism (XMCD), which measures the difference between the x-ray absorption with light helicity vector parallel and antiparallel to the magnetization direction, has been the sole technique able to determine the orbital moments in an element-specific manner. We shall briefly discuss how one can obtain the MAE from the XMCD and what are the limitations. This procedure has gained widespread popularity, not least because the sum rules give the spin and orbital moments in a quantitative and straightforward manner [1–6]. Recently, an alternative method using the linear counterpart of XMCD was proposed based on x-ray magnetic linear dichroism (XMLD) [7]. Although XMLD is considered to be less straightforward than XMCD [8, 9], a new sum rule has designated it as an element-specific probe of the spin–orbit anisotropy, which is directly proportional to the MAE [7]. This quantity can be extracted from the branching ratio of the $L_{2,3}$ x-ray absorption spectra (XAS) due to the fact that the strong core–hole spin–orbit interaction in the final state acts as a magnifying glass for the small valence-band spin–orbit interaction [10–12]. Its anisotropy can be determined by rotating either the applied magnetic field or the linear polarization of the x-rays with respect to the easy axis of magnetization [7].

The outline of the paper is as follows. In section 2 we discuss the capability of XMCD to determine the MAE. In the next sections we discuss in detail how to extract the anisotropic spin–orbit interaction from the integrated XMLD signal using the sum rule. The isotropic spin–orbit interaction and the isotropic x-ray absorption are discussed in section 3. Section 4 gives some general definitions concerning the polarized spectra and the ground state tensors needed for the discussion that follows. In section 5 we treat the angular dependence of the XMLD in spherical symmetry. This is generalized to arbitrary point group symmetry in section 6. The latter, slightly more complicated approach, allows us to determine the MAE for any symmetry. A specific example will be given in section 7 for a system with D_2 symmetry. Conclusions are drawn in section 8.

2. X-ray magnetic circular dichroism

The use of XMCD to determine the element-specific orbital magnetization has been perceived as a breakthrough in the quantitative assessment of the MAE [4, 5]. This procedure requires two steps.

In the first step, the orbital magnetization sum rule is evoked [1]

$$\frac{\hat{\boldsymbol{P}}\cdot\boldsymbol{L}}{n_h} \approx -\frac{4}{3}\frac{\rho_1-\rho_{-1}}{\rho_1+\rho_{-1}} \tag{1}$$

where $\hat{\boldsymbol{P}}$ is the light helicity vector, $\boldsymbol{L}$ is the expectation value of the orbital moment, n_h is the number of 3d holes and ρ_1 and ρ_{-1} are the integrated intensities of the $L_{2,3}$ absorption signal recorded with right and left circular polarization, respectively. Equation (1) states that the projected orbital moment per hole is proportional to the normalized XMCD signal. Although this equation requires several assumptions [13], it is generally assumed that the orbital polarization can be obtained within an accuracy of $\sim$10%. The normalization of the sum spectrum contributes to most of the uncertainty due to the background correction together with the choice of the energy cut-off. Furthermore, when the applied magnetic field is not along one of the crystalline axes, the spin and orbital moment will be non-collinear, resulting in an apparently smaller orbital moment [5, 14–16].

In the second step of the procedure, the orbital moment—deduced from the sum rule—is related to the MAE using Bruno's model [17]. The second-order change in the energy due to a magnetization along the unit vector of the spin magnetic moment, $\hat{\boldsymbol{S}} = 2\boldsymbol{S}$, in 3d transition metals is

$$E(\hat{\boldsymbol{S}}) = -\tfrac{1}{4}C\zeta\,\hat{\boldsymbol{S}}\cdot\langle\boldsymbol{L}\rangle \tag{2}$$

where ζ is the radial part of the 3d spin–orbit interaction and C is a proportionality constant [5, 18]. Equation (2) assumes the absence of holes in the majority band and neglects spin-flip transitions. This limitation is circumvented by writing the magnetic energy as a perturbation of the angular part of the spin–orbit interaction, $\frac{1}{2}\boldsymbol{L}\cdot\hat{\boldsymbol{S}}$,

$$E(\hat{\boldsymbol{S}}) = -\tfrac{1}{4}C\zeta\langle\boldsymbol{L}\cdot\hat{\boldsymbol{S}}\rangle \approx -\tfrac{1}{4}C\zeta\,\hat{\boldsymbol{S}}\cdot[\langle\boldsymbol{L}^{\downarrow}\rangle - \langle\boldsymbol{L}^{\uparrow}\rangle] = -\tfrac{1}{4}C\zeta\,\hat{\boldsymbol{S}}\cdot[\langle\boldsymbol{L}\rangle - 2\langle\boldsymbol{L}^{\uparrow}\rangle] \tag{3}$$

where $\langle\boldsymbol{L}^{\uparrow(\downarrow)}\rangle$ is the expectation value of the majority (minority) spin subband. Comparison of equations (2) and (3) shows that in Bruno's model it is assumed that $\langle\boldsymbol{L}^{\uparrow}\rangle = 0$. This requires that the majority spin band is completely filled, which is usually not the case. The XMCD sum rule provides only the total orbital moment, $\langle\boldsymbol{L}\rangle = \langle\boldsymbol{L}^{\downarrow}\rangle + \langle\boldsymbol{L}^{\uparrow}\rangle$. Precise values of the separate subband orbital moments are difficult to establish and depend in a subtle way on the details of the band structure [19]. Moreover, $\langle\boldsymbol{L}\cdot\hat{\boldsymbol{S}}\rangle$ includes also non-diagonal terms, $\frac{1}{2}(L_+S_- + L_-S_+)$, which give rise to a spin-flip contribution in the magnetic energy [20]. The latter can be expressed as a contribution of the magnetic dipole term, $\langle\boldsymbol{T}\rangle$ [20].

The MAE can be measured as

$$\Delta E \equiv E(\hat{\boldsymbol{M}} \perp \hat{\varepsilon}) - E(\hat{\boldsymbol{M}} \parallel \hat{\varepsilon}) \tag{4}$$

where $\hat{\boldsymbol{M}}$ is the magnetization direction and $\hat{\varepsilon}$ the easy direction of magnetization.

An interesting variation of the above method is to replace the first step by *transverse* XMCD. In this case the anisotropy in the orbital moment can be determined in a single geometry instead of taking the difference between two geometries with perpendicular magnetization directions as given in equation (4). This is done using the so-called forbidden geometry, i.e. by taking the direction of the circularly polarized beam perpendicular to the magnetization direction, which should be along a non-symmetry direction of the sample. Then the direction of the orbital moment is settled by the competition between the crystal–field interaction and the spin–orbit coupling [14,21]. The spin–orbit coupling tries to align $\boldsymbol{L}$ parallel to $\boldsymbol{S}$, whereas the crystal field prefers an alignment of $\boldsymbol{L}$ along the easy direction of magnetization, which is along a principal axis of the lattice. Consequently, $\boldsymbol{L}$ is no longer collinear with $\boldsymbol{S}$ but has a small component perpendicular to $\boldsymbol{S}$. This component is parallel to the beam direction, and hence the sum rule provides a direct determination of the anisotropy in $\boldsymbol{L}$.

3. Isotropic spin–orbit interaction

The above considerations, and especially equation (3), suggest that it is more advantageous to obtain the MAE directly from the anisotropy in the spin–orbit interaction, $\langle L\cdot S\rangle$. Already in 1988, Thole and van der Laan [10–12] demonstrated that the spin–orbit interaction can be obtained from the branching ratio of the spin–orbit split core level in the isotropic x-ray absorption spectrum. More recently it was shown that the isotropic signal also contains a contribution of the anisotropy in the spin–orbit interaction [7]. The operator $\langle L\cdot S\rangle$ is a scalar in the total angular momentum, j; however, it is a vector property in the orbital and spin magnetic moments. This means that although the expectation value is independent of the reference frame, i.e. the $\hat{\boldsymbol{Z}}$-direction, it depends on the magnetization direction, $\hat{\boldsymbol{M}}$.

Assume, for a 3d transition metal system, a model Hamiltonian

$$H = V_{\mathrm{cf}}(\hat{\varepsilon}) + \zeta\,\boldsymbol{L}\cdot\boldsymbol{S} + \boldsymbol{S}(\hat{\boldsymbol{M}}) \tag{5}$$

with $V_{\mathrm{cf}} \gg \zeta \gg M$. A crystal field, V_{cf}, with cylinder symmetry (SO_2) is along the direction of the easy axis of magnetization, $\hat{\varepsilon}$. The magnetization, $\hat{\boldsymbol{M}}$, is along the polar angle $\vartheta = \angle(\hat{\varepsilon}\cdot\hat{\boldsymbol{M}})$. The crystal field does not act on the spin, so that the spin moment, $\boldsymbol{S}$, is

isotropic, having its direction along $\hat{\boldsymbol{M}}$. Since the crystal field acts only on the orbital part of the wavefunction, the orbital moment is given by a tensor relation $\boldsymbol{L} = \boldsymbol{R} \cdot \hat{\boldsymbol{S}}$, so that

$$\langle L(\vartheta) \rangle = \langle R_z \rangle \cos^2 \vartheta + \langle R_x \rangle \sin^2 \vartheta \tag{6}$$

where $\langle R_k \rangle$ are Cartesian tensor components. The physical interpretation is as follows. The spin–orbit interaction and the crystalline field are trying to align $\boldsymbol{L}$ parallel to $\boldsymbol{S}$ and parallel to $\hat{\varepsilon}$, respectively. The result is that $\boldsymbol{L}$ will be directed somewhere between these two directions depending on the relative strength of both interactions. Along the high-symmetry directions, $\boldsymbol{L}$ and $\boldsymbol{S}$ will be parallel. The expectation values of the orbital moment will be different along the different high-symmetry directions, z and x, where the minimal value is found along $\hat{\varepsilon}$.

The SO_2 symmetry permits one monopole and one quadrupole moment. Hence, we can define the isotropic and anisotropic part as

$$\langle R^0 \rangle \equiv \tfrac{1}{3}[\langle R_x \rangle + \langle R_y \rangle + \langle R_z \rangle] \tag{7}$$

$$\langle R^2_0 \rangle \equiv \tfrac{1}{3}[2\langle R_z \rangle - \langle R_x \rangle - \langle R_y \rangle] \tag{8}$$

which transform equation (6) to

$$\langle L(\hat{\boldsymbol{M}}) \rangle = \langle R^0 \rangle + \langle R^2_0 \rangle C^2_0(\hat{\boldsymbol{M}}) \tag{9}$$

where $C^2_0(\hat{\boldsymbol{M}}) = \frac{3}{2}\cos^2 \vartheta - \frac{1}{2}$. The superscripts give the multipole moments; the subscripts give its components. The isotropic value of $\langle L \rangle$ is obtained at the magic angle, where C^2_0 vanishes, i.e. at $\vartheta = 54.74^\circ$.

Similarly, we can write the expectation value of the angular part of the spin–orbit interaction, $L \cdot S$, with $\hat{\boldsymbol{S}} \| \hat{\boldsymbol{M}}$ along ϑ, as

$$\langle L \cdot S(\hat{\boldsymbol{M}}) \rangle = \langle \lambda_z \rangle \cos^2 \vartheta + \langle \lambda_x \rangle \sin^2 \vartheta = \langle \lambda^0 \rangle + \langle \lambda^2_0 \rangle C^2_0(\hat{\boldsymbol{M}}) \tag{10}$$

where the spin–orbit interaction has been separated into an isotropic and an anisotropic contribution

$$\langle \lambda^0 \rangle \equiv \tfrac{1}{3}[\langle \lambda_x \rangle + \langle \lambda_y \rangle + \langle \lambda_z \rangle] \tag{11}$$

$$\langle \lambda^2_0 \rangle \equiv \tfrac{1}{3}[2\langle \lambda_z \rangle - \langle \lambda_x \rangle - \langle \lambda_y \rangle]. \tag{12}$$

The spectral intensities can be obtained by using the sum rules. For the isotropic $L_{2,3}$ spectrum of a 3d transition metal [10–12]

$$\frac{\delta^0}{\rho^0} \equiv \frac{A_{L_3} - 2A_{L_2}}{A_{L_3} + A_{L_2}} = \frac{\langle L \cdot S(\hat{\boldsymbol{M}}) \rangle}{n_h} = \frac{\langle \lambda^0 \rangle + \langle \lambda^2_0 \rangle C^2_0(\hat{\boldsymbol{M}})}{n_h} \tag{13}$$

where $A_{L_{2,3}}$ is the integrated signal over the $L_{2,3}$ edge and n_h is the number of d holes. Equation (13) shows that we can obtain the anisotropy in the spin–orbit interaction by rotating $\hat{\boldsymbol{M}}$, while the signal remains unchanged for rotation of $\hat{\boldsymbol{P}}$. Thus contrary to common belief, the isotropic spectrum depends on $\hat{\boldsymbol{M}}$.

It is difficult—if not impossible—to produce isotropic light. Synchrotron radiation is linearly polarized in the plane of the storage ring. The linear polarized signal contains an addition term, δ^2_0, proportional to the linear dichroism,

$$\frac{\delta_0}{\rho_0} = \frac{\delta^0(\hat{\boldsymbol{M}}) - \delta^2_0(\hat{\boldsymbol{M}}, \hat{\boldsymbol{P}})}{n_h - q_z C^2_0(\hat{\boldsymbol{P}})} \tag{14}$$

where q_z is the quadrupole moment of the 3d holes.

$$\text{For} \quad \hat{\boldsymbol{M}} \| \hat{\varepsilon} : \delta^2_0(\hat{\boldsymbol{P}}) = \tfrac{3}{5}\langle \lambda^2_0 \rangle C^2_0(\hat{\boldsymbol{P}}) + \cdots. \tag{15}$$

$$\text{For} \quad \hat{\boldsymbol{P}} \| \hat{\varepsilon} : \delta^2_0(\hat{\boldsymbol{M}}) = -\tfrac{2}{5}\langle \lambda^2_0 \rangle C^2_0(\hat{\boldsymbol{M}}) + \cdots. \tag{16}$$

These equations will be developed in section 5.

4. Some general definitions

In preparation for the next sections we recall here the relevant definitions of the fundamental spectra, their integrated intensities; the ground-state tensors and the relating sum rules. We also show how the spin–orbit tensors can be split into an isotropic and an anisotropic part.

Electric-dipole transitions give the isotropic spectrum, XMCD and XMLD as

$$I^0 \equiv I_1 + I_0 + I_{-1} \tag{17}$$

$$I_0^1 \equiv I_1 - I_{-1} \tag{18}$$

$$I_0^2 \equiv I_1 - 2I_0 + I_{-1} \tag{19}$$

respectively. The spectra I_ζ^z have multipole moment z and component ζ (similar to the spherical harmonics, Y_ζ^z). Conversely we obtain

$$I_0 = \tfrac{1}{3}I^0 - \tfrac{1}{3}I_0^2 \tag{20}$$

$$I_{\pm1} = \tfrac{1}{3}I^0 \pm \tfrac{1}{2}I_0^1 + \tfrac{1}{6}I_0^2 \tag{21}$$

which gives a perpendicular component

$$I_\perp \equiv \tfrac{1}{2}(I_1 + I_{-1}) = \tfrac{1}{3}I^0 + \tfrac{1}{6}I_0^2. \tag{22}$$

In spherical symmetry each I^z has $2z+1$ components with $\zeta = -z, \ldots, z$,

$$I_\zeta^z \equiv n_{1z}^{-1} \sum_{qq'=-1}^{1} (-)^{1-q} \begin{pmatrix} 1 & z & 1 \\ -q & \zeta & q' \end{pmatrix} I_{qq'} \tag{23}$$

where $n_{1z} = \begin{pmatrix} 1 & z & 1 \\ -1 & 0 & 1 \end{pmatrix}$ is a normalization factor and $I_{qq'}$ correspond to the elements of a density matrix. The equation can be transformed to that for any point group (cf equation (64)) in which case off-diagonal elements ($q \neq q'$) might be non-zero. In SO_2 symmetry, $\zeta = 0$, so that $q = q'$, and the matrix becomes diagonal in q, which is the natural quantum number of SO_2. It is useful to realize that the I_q are not components of a vector, but that they represent (eigen-) values for light with polarization q.

For a given XAS spectrum we define the total intensity, ρ, integrated over the spin–orbit-split core levels, $j_\pm = c \pm \frac{1}{2}$, and the weighted difference intensity, δ, as

$$\rho = I_{j_+} + I_{j_-} \tag{24}$$

$$\delta = I_{j_+} - \frac{c+1}{c} I_{j_-}. \tag{25}$$

The integrated signals of an I^z spectrum give information about ground-state tensors $\langle \underline{w}^{xyz} \rangle$ that have the same multipole moment z. Moments with even x describe the shape of the charge distribution and those with odd x describe the orbital motion. The underscore signifies that the expectation value is not over the electrons but over the holes, as required for XAS, which probes the unoccupied valence states. $y = 0$ and 1 signify the absence and presence, respectively, of the spin magnetic moment coupled in the total magnetic moment. Except for $\underline{w}^{011} = 2S_z$, all tensors with $y = 1$ will contribute to the magnetic anisotropy. The integrated quantities ρ^z and δ^z are completely determined by a purely orbital tensor $\underline{w}^{z0z}$, and two tensors with the spin coupled into the total moment, $\underline{w}^{(z-1)1z}$ and $\underline{w}^{(z+1)1z}$, respectively. For the dipole transitions $c \to l$ with $l = c + 1$, such as s $\to$ p, p $\to$ d and d $\to$ f, the integrated signals can be expressed as [6]

$$\rho_\zeta^z = \langle \underline{w}_\zeta^{z0z} \rangle \tag{26}$$

$$\delta_\zeta^z = \frac{z}{2z+1} \langle \underline{w}_\zeta^{(z-1)1z} \rangle + \frac{z+1}{2z+1} \langle \underline{w}_\zeta^{(z+1)1z} \rangle. \tag{27}$$

Therefore, the signal, ρ, is connected to the charge anisotropy. For electric-dipole transitions in SO_2 symmetry we obtain using equations (20) and (26)

$$\rho_0 = \tfrac{1}{3}\langle \underline{w}^{000}\rangle - \tfrac{1}{3}\langle \underline{w}_0^{202}\rangle \tag{28}$$

where

$$\langle \underline{w}^{000}\rangle = n_h \tag{29}$$

$$\langle \underline{w}_0^{202}\rangle = \frac{1}{l(2l-1)}\big[3\langle l_z^2\rangle - l^2\big] \equiv q_z \tag{30}$$

give the number of holes and the charge quadrupole moment, respectively. Likewise

$$\delta_0 = \tfrac{1}{3}\langle \underline{w}_0^{110}\rangle - \tfrac{1}{3}\big[\tfrac{2}{5}\langle \underline{w}_0^{112}\rangle + \tfrac{3}{5}\langle \underline{w}_0^{312}\rangle\big]. \tag{31}$$

The spin–orbit interaction, $\langle \underline{w}_0^{110}\rangle$, can be separated into an isotropic and an anisotropic part

$$\langle \underline{w}_0^{110}\rangle = \langle \underline{w}^{110(t=0)}\rangle + \langle \underline{w}_0^{110(t=2)}\rangle \tag{32}$$

$$\langle \underline{w}^{110(t=0)}\rangle = \tfrac{1}{3}\big[\langle \lambda_1\rangle + \langle \lambda_0\rangle + \langle \lambda_{-1}\rangle\big] \equiv \langle \lambda^0\rangle \tag{33}$$

$$\langle \underline{w}_0^{110(t=2)}\rangle = \tfrac{1}{3}\big[2\langle \lambda_0\rangle - \langle \lambda_1\rangle - \langle \lambda_{-1}\rangle\big] \equiv \langle \lambda_0^2\rangle \tag{34}$$

$$\langle \underline{w}_0^{110}\rangle = (ls)^{-1}\langle L_z S_z\rangle = \langle \lambda_0\rangle = \langle \lambda^0\rangle + \langle \lambda_0^2\rangle \tag{35}$$

where $\langle \lambda_k\rangle \equiv (ls)^{-1}\langle L_k S_k\rangle$.

The anisotropic spin–orbit tensor, $\underline{w}^{112}$, contains no isotropic part. Using $(ls)^{-1}\langle L\cdot S\rangle = 3\langle \lambda^0\rangle$ we obtain from its definition [6, 22]

$$\langle \underline{w}_0^{112}\rangle \equiv \frac{3}{2ls}\left[\langle L_z S_z\rangle - \frac{1}{3}\langle L\cdot S\rangle\right] = \frac{3}{2}\langle \lambda_0^2\rangle. \tag{36}$$

5. Angular dependence

We shall give angular relations for the sum rules relating the charge density and the spin–orbit interaction with the integrated signals. The angular dependence can be expressed in the normalized spherical harmonics in polar angles

$$C_\zeta^z(\vartheta,\varphi) \equiv \left(\frac{4\pi}{2z+1}\right)^{1/2} Y_\zeta^z(\vartheta,\varphi). \tag{37}$$

The angular dependence can be rather complicated if both $\hat{\boldsymbol{P}}$ and $\hat{\boldsymbol{M}}$ are rotated. Here, we shall discuss two simple ways to measure the XMLD, namely the following.

(i) *Linear dichroism (LD).* Rotation of $\hat{\boldsymbol{P}}$ while keeping $\hat{\varepsilon}\|\hat{\boldsymbol{M}}$. For LD we shall denote the multipoles by z and its components by ζ. Normally in the literature, the sum rules are given in this geometry [1–5].

(ii) *Magnetic dichroism (MD).* Rotation of $\hat{\boldsymbol{M}}$ while keeping $\hat{\varepsilon}\|\hat{\boldsymbol{P}}$. For MD we shall denote the multipoles by t and its components by τ.

For case (i) we obtain using equations (26) and (20)

$$\rho^{z=0} = \langle \underline{w}^{000}\rangle \tag{38}$$

$$\rho_\zeta^{z=2} = \langle \underline{w}_\zeta^{202}\rangle \tag{39}$$

$$\rho_0 = \tfrac{1}{3}\big[\langle \underline{w}^{000}\rangle - \langle \underline{w}_0^{202}\rangle\big]. \tag{40}$$

The $\boldsymbol{P}$ dependence should therefore satisfy

$$\rho(\hat{\boldsymbol{P}}) = \tfrac{1}{3}\big[\langle \underline{w}^{000}(\hat{\boldsymbol{P}})\rangle - \langle \underline{w}^{202}(\hat{\boldsymbol{P}})\rangle\big]. \tag{41}$$

Substitution of the $\boldsymbol{P}$ dependence of the charge tensors

$$\langle \underline{w}^{z0z}(\hat{\boldsymbol{P}})\rangle = \sum_{\zeta} \langle \underline{w}_{\zeta}^{z0z}\rangle C_{\zeta}^{z}(\hat{\boldsymbol{P}}) \tag{42}$$

gives

$$\rho(\hat{\boldsymbol{P}}) = \tfrac{1}{3}\left[\langle \underline{w}^{000}\rangle C^{0}(\hat{\boldsymbol{P}}) - \sum_{\zeta} \langle \underline{w}_{\zeta}^{202}\rangle C_{\zeta}^{2}(\hat{\boldsymbol{P}})\right]. \tag{43}$$

Substitution of equations (38) and (39) into (43) gives

$$\rho(\hat{\boldsymbol{P}}) = \tfrac{1}{3}\left[\rho^{z=0} C^{0}(\hat{\boldsymbol{P}}) - \sum_{\zeta} \rho_{\zeta}^{z=2} C_{\zeta}^{2}(\hat{\boldsymbol{P}})\right] \tag{44}$$

which suggests that ρ_{ζ}^{z} corresponds to that part of $\rho(\hat{\boldsymbol{P}})$ which has an angular dependence $C_{\zeta}^{z}(\hat{\boldsymbol{P}})$. We can now use this observation to find the magnetic dichroism of case (ii), since a similar condition as equation (41) should also apply for $\hat{\boldsymbol{M}}$, hence it provides a way of normalization.

$$\rho(\hat{\boldsymbol{M}}) = \tfrac{1}{3}\left[\langle \underline{w}^{000}(\hat{\boldsymbol{M}})\rangle - \langle \underline{w}^{202}(\hat{\boldsymbol{M}})\rangle\right] \tag{45}$$

together with the $\hat{\boldsymbol{M}}$ dependence of the charge tensors

$$\langle \underline{w}_{0}^{z0z}(\hat{\boldsymbol{M}})\rangle = \langle \underline{w}_{0}^{z0z}\rangle = \langle \underline{w}_{0}^{z0z}\rangle C^{0}(\hat{\boldsymbol{M}}) \tag{46}$$

gives

$$\rho(\hat{\boldsymbol{M}}) = \tfrac{1}{3}\left[\langle \underline{w}^{000}\rangle - \langle \underline{w}_{0}^{202}\rangle\right] C^{0}(\hat{\boldsymbol{M}}) \tag{47}$$

so that

$$\rho^{t=0} = \langle \underline{w}^{000}\rangle - \langle \underline{w}_{0}^{202}\rangle \tag{48}$$

$$\rho_{\tau}^{t=2} = 0. \tag{49}$$

Since $\rho(\hat{\boldsymbol{P}}) = \rho(\hat{\boldsymbol{M}})$ for $\hat{\boldsymbol{M}} \| \hat{\boldsymbol{P}} \| \hat{\varepsilon}$ we obtain with equations (38), (39), (48) and (49) the sum rules for $\zeta = \tau = 0$

$$\rho^{z=0} - \rho_{0}^{z=2} = \rho^{t=0} - \rho_{0}^{t=2} = 3\rho_{0} = \langle \underline{w}^{000}\rangle - \langle \underline{w}_{0}^{202}\rangle \tag{50}$$

$$\rho^{z=0} - \rho^{t=0} = \rho_{0}^{z=2} - \rho_{0}^{t=2} = \langle \underline{w}_{0}^{202}\rangle. \tag{51}$$

The methodology used to derive the angular dependence of charge anisotropy and its sum rule can be applied to the magnetic anisotropy, which is obtained from the weighted difference signal, δ.

$$\delta(\hat{\boldsymbol{P}}) = \tfrac{1}{3}\left[\delta^{z=0} C^{0}(\hat{\boldsymbol{P}}) - \sum_{z} \delta_{\zeta}^{z=2} C_{\zeta}^{2}(\hat{\boldsymbol{P}})\right] \tag{52}$$

or if $\hat{\boldsymbol{M}}$ is rotated then $(\hat{\boldsymbol{P}}, z, \zeta)$ is replaced with $(\hat{\boldsymbol{M}}, t, \tau)$. Using the sum rule results from equation (27) we have

$$\delta^{z=0} = \langle \underline{w}^{110}\rangle = \langle \lambda^{0}\rangle + \langle \lambda_{0}^{2}\rangle \tag{53}$$

$$\delta_{\zeta}^{z=2} = \tfrac{2}{5}\langle \underline{w}_{\zeta}^{112}\rangle + \tfrac{3}{5}\langle \underline{w}_{\zeta}^{312}\rangle = \tfrac{3}{5}\langle \lambda_{\zeta}^{2}\rangle + \tfrac{3}{5}\langle \underline{w}_{\zeta}^{312}\rangle \tag{54}$$

so that

$$\delta(\hat{\boldsymbol{P}}) = \tfrac{1}{3}\left[\langle \lambda^{0}\rangle + \langle \lambda_{0}^{2}\rangle\right] - \tfrac{1}{3}\sum_{\zeta}\left[\tfrac{3}{5}\langle \lambda_{\zeta}^{2}\rangle + \tfrac{3}{5}\langle \underline{w}_{\zeta}^{312}\rangle\right] C_{\zeta}^{2}(\hat{\boldsymbol{P}}). \tag{55}$$

For rotation of $\hat{\boldsymbol{M}}$ we have

$$\delta(\hat{\boldsymbol{M}}) = \tfrac{1}{3}\langle \underline{w}^{110}(\hat{\boldsymbol{M}})\rangle - \tfrac{1}{3}\big[\tfrac{2}{5}\langle \underline{w}^{112}(\hat{\boldsymbol{M}})\rangle + \tfrac{3}{5}\langle \underline{w}^{312}(\hat{\boldsymbol{M}})\rangle\big]. \tag{56}$$

Using the angular dependence of the tensors [7, 23]

$$\langle \underline{w}^{110}(\hat{\boldsymbol{M}})\rangle = \langle\lambda^0\rangle C^0(\hat{\boldsymbol{M}}) + \sum_\tau \langle\lambda^2_\tau\rangle C^2_\tau(\hat{\boldsymbol{M}}) \tag{57}$$

$$\langle \underline{w}^{112}(\hat{\boldsymbol{M}})\rangle = \tfrac{3}{2}\sum_\tau \langle\lambda^2_\tau\rangle C^2_\tau(\hat{\boldsymbol{M}}) \tag{58}$$

$$\langle \underline{w}^{312}(\hat{\boldsymbol{M}})\rangle = \sum_\tau \langle \underline{w}^{312}_\tau\rangle C^2_\tau(\hat{\boldsymbol{M}}) \tag{59}$$

we obtain

$$\delta(\hat{\boldsymbol{M}}) = \tfrac{1}{3}\langle\lambda^0\rangle C^0(\hat{\boldsymbol{M}}) - \tfrac{1}{3}\sum_\tau \big[\big(\tfrac{3}{5}-1\big)\langle\lambda^2_\tau\rangle + \tfrac{3}{5}\langle \underline{w}^{312}_\tau\rangle\big] C^2_\tau(\hat{\boldsymbol{M}}) \tag{60}$$

from which we deduce that

$$\delta^{t=0} = \langle\lambda^0\rangle \tag{61}$$

$$\delta^{t=2}_\tau = -\tfrac{2}{5}\langle\lambda^2_\tau\rangle + \tfrac{3}{5}\langle \underline{w}^{312}_\tau\rangle. \tag{62}$$

It can be verified that the sum rules for $\zeta = \tau = 0$ are

$$\delta^{z=0} - \delta^{z=2}_0 = \delta^{t=0} - \delta^{t=2}_0 = 3\delta_0 = \langle\lambda^0\rangle + \tfrac{2}{5}\langle\lambda^2_0\rangle - \tfrac{3}{5}\langle \underline{w}^{312}_0\rangle \tag{63}$$

$$\delta^{z=0} - \delta^{t=0} = \delta^{z=2}_0 - \delta^{t=2}_0 = \langle\lambda^2_0\rangle \tag{64}$$

which clearly brings out the difference between LD and MD.

6. Point group symmetry

The previous section treated spherical symmetry. SO_2 symmetry is obtained using the group theoretical branching $(z)SO_3 \supset (\mathbf{0})SO_2$, where $\zeta = \tau = 0$ is the only total-symmetric representation. This means that the sum rules in equations (50), (51), (63) and (64) provide the complete information. However, in an arbitrary point group symmetry G there can be more than one total-symmetric representation, as will be the subject of this section.

In principle, the tensors can be developed directly in the desired point group symmetry. Using the notation of Butler [24, 25], equation (23) generalizes to

$$I^z_{\Gamma\gamma_0} = n^{-1}_{1z} \sum_{\Gamma_1\gamma_1\kappa_1,\Gamma_2\gamma_2\kappa_2} \begin{pmatrix} 1 \\ \Gamma_1 \\ \gamma_1 \\ \kappa_1 \end{pmatrix} \begin{pmatrix} 1 & z & 1 \\ \Gamma^*_1 & \Gamma & \Gamma_2 \\ \gamma^*_1 & \gamma & \gamma_2 \\ \kappa^*_1 & 0 & \kappa_2 \end{pmatrix} I_{\Gamma_1\gamma_1\kappa_1,\Gamma_2\gamma_2\kappa_2}. \tag{65}$$

Even though $\kappa_1 = \kappa_2$, this can yield non-diagonal matrix elements $\Gamma_1\gamma_1 \neq \Gamma_2\gamma_2$. Although equation (65) is of great benefit in computer programs [24, 26], it does not provide much insight. We shall therefore not use the $3jm$ symbol here, but adopt a simpler approach.

We transform the functions of SO_3 symmetry, i.e. the spherical harmonics $|z\xi\rangle$, into the 'crystal field' functions $|z\Gamma\gamma\rangle$ of the point group symmetry G,

$$|z\Gamma\gamma\rangle = \sum_\zeta |z\zeta\rangle\langle z\zeta|z\Gamma\gamma\rangle \tag{66}$$

where Γ is a representation of G and γ is a subspecies label needed when Γ is degenerate. The rotational dependence of an arbitrary physical property, I^z, can be written as

$$I^z(\hat{\boldsymbol{R}}) \equiv \sum_\zeta I^z_\zeta C^z_\zeta(\hat{\boldsymbol{R}}) = \sum_{\Gamma\gamma\zeta} I^z_\zeta \langle z\zeta|z\Gamma\gamma\rangle\langle z\Gamma\gamma|z\zeta'\rangle C^z_{\zeta'}(\hat{\boldsymbol{R}}). \tag{67}$$

Defining

$$I^z_{\Gamma\gamma} \equiv \sum_\zeta I^z_\zeta \langle z\zeta | z\Gamma\gamma \rangle \tag{68}$$

$$C^z_{\Gamma\gamma}(\hat{\boldsymbol{R}}) \equiv \sum_\zeta C^z_\zeta(\hat{\boldsymbol{R}}) \langle z\Gamma\gamma | z\zeta \rangle \tag{69}$$

we obtain

$$I^z(\hat{\boldsymbol{R}}) = \sum_{\Gamma\gamma} I^z_{\Gamma\gamma} C^z_{\Gamma\gamma}(\hat{\boldsymbol{R}}) \tag{70}$$

so that the angular dependence of the tensors with even z can be written

$$\left\langle \underline{w}^{xyz}(\hat{\boldsymbol{P}}) \right\rangle = \sum_{\Gamma\gamma} \langle \underline{w}^{xyz}_{\Gamma\gamma} \rangle C^z_{\Gamma\gamma}(\hat{\boldsymbol{P}}) \tag{71}$$

$$\left\langle \underline{w}^{110}(\hat{\boldsymbol{M}}) \right\rangle = \langle \lambda^0 \rangle + \sum_{\Gamma\gamma} \langle \lambda^2_{\Gamma\gamma} \rangle C^2_{\Gamma\gamma}(\hat{\boldsymbol{M}}) \tag{72}$$

$$\left\langle \underline{w}^{112}(\hat{\boldsymbol{M}}) \right\rangle = \tfrac{3}{2} \sum_{\Gamma\gamma} \langle \lambda^2_{\Gamma\gamma} \rangle C^2_{\Gamma\gamma}(\hat{\boldsymbol{M}}) \tag{73}$$

$$\left\langle \underline{w}^{312}(\hat{\boldsymbol{M}}) \right\rangle = \sum_{\Gamma\gamma} \left\langle \underline{w}^{312}_{\Gamma\gamma} \right\rangle C^2_{\Gamma\gamma}(\hat{\boldsymbol{M}}). \tag{74}$$

Following the procedure from section 5 the resulting angular dependence is

$$\delta(\hat{\boldsymbol{P}}) = \tfrac{1}{3}[\langle \lambda^0 \rangle + \langle \lambda^2_0 \rangle] - \tfrac{1}{3} \sum_{\Gamma\gamma} \left[\tfrac{3}{5} \langle \lambda^2_{\Gamma\gamma} \rangle + \tfrac{3}{5} \left\langle \underline{w}^{312}_{\Gamma\gamma} \right\rangle \right] C^2_{\Gamma\gamma}(\hat{\boldsymbol{P}}) \tag{75}$$

$$\delta(\hat{\boldsymbol{M}}) = \tfrac{1}{3} \langle \lambda^0 \rangle - \tfrac{1}{3} \sum_{\Gamma\gamma} \left[-\tfrac{2}{5} \langle \lambda^2_{\Gamma\gamma} \rangle + \tfrac{3}{5} \left\langle \underline{w}^{312}_{\Gamma\gamma} \right\rangle \right] C^2_{\Gamma\gamma}(\hat{\boldsymbol{M}}) \tag{76}$$

from which we deduce that

$$\delta^{z=0} = \langle \lambda^0 \rangle + \langle \lambda^2_0 \rangle \tag{77}$$

$$\delta^{z=2}_{\Gamma\gamma} = \tfrac{3}{5} \langle \lambda^2_{\Gamma\gamma} \rangle + \tfrac{3}{5} \left\langle \underline{w}^{312}_{\Gamma\gamma} \right\rangle \tag{78}$$

$$\delta^{t=0} = \langle \lambda^0 \rangle \tag{79}$$

$$\delta^{t=2}_{\Gamma\gamma} = -\tfrac{2}{5} \langle \lambda^2_{\Gamma\gamma} \rangle + \tfrac{3}{5} \left\langle \underline{w}^{312}_{\Gamma\gamma} \right\rangle. \tag{80}$$

7. Example

An illustration will make the treatment in the previous section clearer. We develop the physical properties in the group chain $SO_3 \supset O \supset D_4 \supset D_2 \supset C_2 \supset C_1$ and use the notation of Butler [24]. The alternative Mulliken notation and the relations to the $|lm\rangle$ functions are given in table 1. First we should establish the coordinate axes. In the usual convention of the normalized spherical harmonics

$$C^1_{\pm 1} = \mp \frac{1}{\sqrt{2}} (x \pm \mathrm{i}y) \tag{81}$$

and defining the real functions

$$C^l_{mc} \equiv \frac{1}{\sqrt{2}} [(-1)^m C^l_m + C^l_{-m}] \tag{82}$$

$$C^l_{ms} \equiv \frac{-\mathrm{i}}{\sqrt{2}} [(-1)^m C^l_m - C^l_{-m}] \tag{83}$$

Table 1. The relation between the partners $|z\Gamma\gamma\rangle$ in the group chain $SO_3 \supset O \supset D_4 \supset D_2 \supset C_2 \supset C_1$ given both in Mulliken and Butler notation [24] and the partners $|zm\rangle$ in the chain $SO_3 \supset SO_2(\supset C_1)$ for $z = 0, 1, 2$.

$\|0A_1A_1A_1\Gamma_1\Gamma_1\rangle = \|000000\rangle = \|00\rangle$
$\|1T_1A_2B_1\Gamma_1\Gamma_1\rangle = \|11\tilde{0}\tilde{0}00\rangle = \|10\rangle$
$\|1T_1EB_2\Gamma_2\Gamma_1\rangle = \|111110\rangle = \frac{-1}{\sqrt{2}}[\|11\rangle + \|1\,{-1}\rangle]$
$\|1T_1EB_3\Gamma_2\Gamma_1\rangle = \|111\tilde{1}10\rangle = \frac{1}{\sqrt{2}}[\|11\rangle - \|1\,{-1}\rangle]$
$\|2EA_1A_1\Gamma_1\Gamma_1\rangle = \|220000\rangle = -\|20\rangle$
$\|2EB_2B_1\Gamma_1\Gamma_1\rangle = \|222000\rangle = \frac{1}{\sqrt{2}}[\|22\rangle + \|2\,{-2}\rangle]$
$\|2T_2EB_2\Gamma_2\Gamma_1\rangle = \|2\tilde{1}1110\rangle = \frac{1}{\sqrt{2}}[-\|21\rangle + \|2\,{-1}\rangle]$
$\|2T_2EB_3\Gamma_2\Gamma_1\rangle = \|2\tilde{1}1\tilde{1}10\rangle = \frac{1}{\sqrt{2}}[\|21\rangle + \|2\,{-1}\rangle]$
$\|2T_2B_2B_1\Gamma_1\Gamma_1\rangle = \|2\tilde{1}\tilde{2}\tilde{0}10\rangle = \frac{1}{\sqrt{2}}[\|22\rangle - \|2\,{-2}\rangle]$

i.e. $C_{1c} = x$ and $C_{1s} = y$, we can transform with the use of table 1 the $C^1_{\Gamma\gamma}$ in normalized spherical harmonics, C^l_m, spherical coordinates $\{\vartheta, \varphi\}$ and Cartesian coordinates $\{x, y, z\}$, respectively

$$C^1_{1\tilde{0}\tilde{0}00} = C^1_0 = \cos\vartheta = z \tag{84}$$

$$C^1_{11110} = \frac{-1}{\sqrt{2}}(C^1_1 + C^1_{-1}) \equiv \mathrm{i}C^1_{1s} = \mathrm{i}\sin\vartheta\sin\varphi = \mathrm{i}y \tag{85}$$

$$C^1_{11\tilde{1}10} = \frac{1}{\sqrt{2}}(C^1_1 - C^1_{-1}) \equiv -C^1_{1c} = -\sin\vartheta\cos\varphi = -x. \tag{86}$$

We now consider the $z = 0$ and 2 functions, as they might appear in the anisotropy. For the angular functions we have the isotropic part

$$C^0_{00000} = C^0 = 1 \tag{87}$$

together with the five branches from $(\mathbf{2})SO_3$ to the total symmetric representation $(\mathbf{0})C_1$, where $C^2_{\Gamma\gamma}$ transforms as

$$C^2_{20000} = -C^2_0 = -\tfrac{1}{2}(3\cos^2\vartheta - 1) = -\tfrac{1}{2}(3z^2 - 1) \tag{88}$$

$$C^2_{22000} = \frac{1}{\sqrt{2}}(C^2_2 + C^2_{-2}) \equiv C^2_{2c} = \tfrac{1}{2}\sqrt{3}\sin^2\vartheta\cos 2\varphi = \tfrac{1}{4}\sqrt{3}(x^2 - y^2) \tag{89}$$

$$C^2_{\tilde{1}1110} = \frac{1}{\sqrt{2}}(-C^2_1 + C^2_{-1}) \equiv C^2_{1c} = \sqrt{3}\sin\vartheta\cos\vartheta\cos\varphi = \sqrt{3}zx \tag{90}$$

$$C^2_{\tilde{1}1\tilde{1}10} = \frac{1}{\sqrt{2}}(C^2_1 + C^2_{-1}) \equiv -\mathrm{i}C^2_{1s} = -\mathrm{i}\sqrt{3}\sin\vartheta\cos\vartheta\sin\varphi = -\mathrm{i}\sqrt{3}zy \tag{91}$$

$$C^2_{\tilde{1}\tilde{2}\tilde{0}00} = \frac{1}{\sqrt{2}}(C^2_2 - C^2_{-2}) \equiv \mathrm{i}C^2_{2s} = \frac{\mathrm{i}}{2}\sqrt{3}\sin^2\vartheta\sin 2\varphi = \mathrm{i}\sqrt{3}xy. \tag{92}$$

The relevant tensors are obtained by looking for all branchings that produce the total symmetric representation in the point group of consideration. In all point groups one component is needed to give the isotropic moment. Furthermore, in all groups the angular dependence of the orbital moment is $C^1_0 = \cos\vartheta = z$. This is true also in C_1 symmetry if we rotate the $\hat{\boldsymbol{Z}}$-axis along the orbital moment, in which case C^1_{11110} and $C^1_{11\tilde{1}10}$ are zero. Thus these components of $z = 1$ give the direction of the orbital moment.

In SO_2, D_4 and D_3 symmetry the quadrupole moment is determined by one component. In D_2 symmetry two extra components are needed to characterize the quadrupole moment. An additional two components in C_1 are needed to determine the orientation of the axis.

We shall treat here the case of D_2 symmetry. The total-symmetric representation $(\mathbf{0})D_2$ gives the non-zero quadrupole moments

$$\langle w^0_{00000}\rangle = \langle w^0\rangle \tag{93}$$

$$\langle w^2_{20000}\rangle = -\langle w^2_0\rangle \tag{94}$$

$$\langle w^2_{22000}\rangle = \frac{1}{\sqrt{2}}[\langle w^2_2\rangle + \langle w^2_{-2}\rangle] \equiv \langle w^2_{2c}\rangle. \tag{95}$$

Note that the sign convention [23] has no consequence for the physics, for example

$$\langle w^2_{20000}\rangle C^2_{20000} = \langle w^2_0\rangle C^2_0. \tag{96}$$

First, we work out the Cartesian tensor for the orbital moment introduced in section 3.

$$\langle L(\hat{\boldsymbol{M}})\rangle = \sum_{b=0,2}\sum_{\beta=-b}^{b}\langle R^b_\beta\rangle C^b_\beta(\hat{\boldsymbol{M}}) = \langle R^0\rangle + \langle R^2_0\rangle C^2_0(\hat{\boldsymbol{M}}) + \langle R^2_{2c}\rangle C^2_{2c}(\hat{\boldsymbol{M}}) \tag{97}$$

$$\langle R^0\rangle = \tfrac{1}{3}[\langle R_x\rangle + \langle R_y\rangle + \langle R_z\rangle] \tag{98}$$

$$\langle R^2_0\rangle = \tfrac{1}{3}[2\langle R_z\rangle - \langle R_x\rangle - \langle R_y\rangle] \tag{99}$$

$$\langle R^2_{2c}\rangle = \tfrac{1}{2}[\langle R_x\rangle - \langle R_y\rangle] \tag{100}$$

or conversely,

$$\langle R_z\rangle = \langle R^0\rangle - \langle R^2_0\rangle \tag{101}$$

$$\langle R_x\rangle = \langle R^0\rangle + \tfrac{1}{2}\langle R^2_0\rangle + \langle R^2_{2c}\rangle \tag{102}$$

$$\langle R_y\rangle = \langle R^0\rangle + \tfrac{1}{2}\langle R^2_0\rangle - \langle R^2_{2c}\rangle. \tag{103}$$

By taking $\langle R^2_{2c}\rangle = 0$, i.e. $\langle R_x\rangle = \langle R_y\rangle$, we retrieve the result for SO_2 symmetry in section 3.

Similarly, the XMLD signals give the magnetic anisotropy

$$\delta^{z=2}_\zeta = \tfrac{3}{5}\langle\lambda^2_\zeta\rangle + \tfrac{3}{5}\langle\underline{w}^{312}_\zeta\rangle \tag{104}$$

$$\delta^{t=2}_\tau = -\tfrac{2}{5}\langle\lambda^2_\tau\rangle + \tfrac{3}{5}\langle\underline{w}^{312}_\tau\rangle \tag{105}$$

with $\zeta = \{0, 2c\}$ and $\tau = \{0, 2c\}$, where

$$\lambda^0_0 = \tfrac{1}{3}(\lambda_x + \lambda_y + \lambda_z) \tag{106}$$

$$\lambda^2_0 = \tfrac{1}{3}(2\lambda_z - \lambda_x - \lambda_y) \tag{107}$$

$$\lambda^2_{2c} = \tfrac{1}{2}(\lambda_x - \lambda_y). \tag{108}$$

At an arbitrary direction we shall measure a mixture of these signals

$$\begin{aligned}3\delta(\hat{\boldsymbol{P}}) &= \delta^0 - \delta^2_0 C^2_0(\hat{\boldsymbol{P}}) - \delta^2_{2c}C^2_{2c}(\hat{\boldsymbol{P}})\\ &= \langle\lambda^0\rangle + \langle\lambda^2_0\rangle + \big[-\tfrac{3}{5}\langle\lambda^2_0\rangle - \tfrac{3}{5}\langle\underline{w}^{312}_0\rangle\big]C^2_0(\hat{\boldsymbol{P}}) + \big[-\tfrac{3}{5}\langle\lambda^2_{2c}\rangle - \tfrac{3}{5}\langle\underline{w}^{312}_{2c}\rangle\big]C^2_{2c}(\hat{\boldsymbol{P}})\end{aligned} \tag{109}$$

$$\begin{aligned}3\delta(\hat{\boldsymbol{M}}) &= \delta^0 - \delta^2_0 C^2_0(\hat{\boldsymbol{M}}) - \delta^2_{2c}C^2_{2c}(\hat{\boldsymbol{M}})\\ &= \langle\lambda^0\rangle + \big[\tfrac{2}{5}\langle\lambda^2_0\rangle - \tfrac{3}{5}\langle\underline{w}^{312}_0\rangle\big]C^2_0(\hat{\boldsymbol{M}}) + \big[\tfrac{2}{5}\langle\lambda^2_{2c}\rangle - \tfrac{3}{5}\langle\underline{w}^{312}_{2c}\rangle\big]C^2_{2c}(\hat{\boldsymbol{M}}).\end{aligned} \tag{110}$$

Using

$$C^2_0(\hat{\boldsymbol{Z}}) = 1; \qquad C^2_0(\hat{\boldsymbol{X}}) = C^2_0(\hat{\boldsymbol{Y}}) = -\tfrac{1}{2}; \qquad C^2_{2c}(\hat{\boldsymbol{Z}}) = 0;$$
$$C^2_{2c}((\hat{\boldsymbol{X}} \pm \hat{\boldsymbol{Y}})/\sqrt{2}) = \pm\tfrac{1}{2}\sqrt{3}$$

we obtain for the three different geometries

$$3\delta(\varepsilon_z M_z P_z) = \langle\lambda^0\rangle + \tfrac{2}{5}\langle\lambda^2_0\rangle - \tfrac{3}{5}\langle\underline{w}^{312}_0\rangle \tag{111}$$

$$3\delta(\varepsilon_z M_z P_{x,y}) = \langle\lambda^0\rangle + \tfrac{13}{10}\langle\lambda^2_0\rangle + \tfrac{3}{10}\langle\underline{w}^{312}_0\rangle \pm \tfrac{3}{10}\sqrt{3}\langle\lambda^2_{2c}\rangle \mp \tfrac{3}{10}\sqrt{3}\langle\underline{w}^{312}_{2c}\rangle \tag{112}$$

$$3\delta(\varepsilon_z M_{x,y} P_z) = \langle\lambda^0\rangle - \tfrac{1}{5}\langle\lambda^2_0\rangle + \tfrac{3}{10}\langle\underline{w}^{312}_0\rangle \pm \tfrac{1}{5}\sqrt{3}\langle\lambda^2_{2c}\rangle \mp \tfrac{3}{10}\sqrt{3}\langle\underline{w}^{312}_{2c}\rangle \tag{113}$$

with difference spectra

$$3\delta(\varepsilon_z M_z P_z) - 3\delta(\varepsilon_z M_z P_{x,y}) = -\tfrac{9}{10}\langle\lambda_0^2\rangle - \tfrac{9}{10}\langle\underline{w}_0^{312}\rangle \pm \tfrac{3}{10}\sqrt{3}\langle\lambda_{2c}^2\rangle \pm \tfrac{3}{10}\sqrt{3}\langle\underline{w}_{2c}^{312}\rangle \quad (114)$$

$$3\delta(\varepsilon_z M_z P_z) - 3\delta(\varepsilon_z M_{x,y} P_z) = \tfrac{3}{5}\langle\lambda_0^2\rangle - \tfrac{9}{10}\langle\underline{w}_0^{312}\rangle \mp \tfrac{1}{5}\sqrt{3}\langle\lambda_{2c}^2\rangle \pm \tfrac{3}{10}\sqrt{3}\langle\underline{w}_{2c}^{312}\rangle. \quad (115)$$

Of course, these results could also have been obtained directly by substituting equations (54) and (61) into

$$3\delta(\varepsilon_z M_z P_z) - 3\delta(\varepsilon_z M_z P_{x,y}) = -\tfrac{3}{2}\delta_0^{z=2} \pm \tfrac{1}{2}\sqrt{3}\delta_{2c}^{z=2} \quad (116)$$

$$3\delta(\varepsilon_z M_z P_z) - 3\delta(\varepsilon_z M_{x,y} P_z) = -\tfrac{3}{2}\delta_0^{t=2} \pm \tfrac{1}{2}\sqrt{3}\delta_{2c}^{t=2}. \quad (117)$$

8. Conclusions

We have shown that the spin–orbit interaction, $\langle\underline{w}^{110}\rangle$, is a tensor with the same properties as the MAE. This provides the possibility to measure the angular dependence of the spin–orbit interaction, and hence the MAE, by forcing $\hat{M}$ out of its easy direction of magnetization. Such a measurement could already be done with isotropic light, if it was available to the experimentalist. With linear polarized light there is an additional contribution due to the anisotropic spin–orbit tensor, $\langle\underline{w}^{112}\rangle$.

We have discussed the different methods to obtain the element-specific MAE of magnetic thin films and surfaces. Although XMCD has become a routine method, it suffers from the shortcoming that it does not supply the orbital magnetization of the majority spin subband. This drawback is absent in XMLD, which makes the latter a very promising technique. Recently, Dhesi *et al* [18] obtained experimental confirmation for the proportionality between the XMLD branching ratio and the MAE. The anisotropy of the in-plane spin–orbit interaction, $\langle\lambda_{2c}^2\rangle$, in vicinal Co films with varying step densities was measured using XMLD. A linear increase in $\langle\lambda_{2c}^2\rangle$ with Co step density was determined using the sum rule. The proof of the XMLD sum rule was enabled by the large sensitivity of $\langle\lambda_{2c}^2\rangle$ to the MAE. Interestingly, a similar prefactor C arises in XMLD as appears in XMCD. This indicates that high-energy spectroscopies of the MAE must differ from low-energy macroscopic techniques. Given that XMCD has already allowed the characterization of many interesting ferromagnetic systems, XMLD can make an even greater impact since it measures directly the origin of the MAE, the spin–orbit anisotropy, and is sensitive to antiferromagnetism.

Currently XMLD, as a prototype experiment, belongs to the realm of physics. To a lesser extent, this is also true for XMCD. However, there is a large number of dedicated insertion-device beamlines being built or projected at third-generation synchrotron radiation facilities. These beamlines will make techniques such as XMCD and XMLD more accessible to non-experts and will greatly extend the scope of these techniques.

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