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# Chapter 2.17

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# Magnetic ordering and its influence on X-ray spectroscopies

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X-ray absorption (XA) spectroscopy enables us to probe the electronic structure and magnetic ordering in, for example, thin-film systems. The photonmatter interaction contains both nonresonant and resonant terms, but only the latter have a strong sensitivity to the spin and orbital moments of the valence shell. Selection rules in XA provide us with a probe to study the local magnetic ground state. The branching ratio of the spin-orbit split core-level spectra is proportional to the ground-state spin-orbit interaction and can also provide a measure of the spin state. The angular dependence of the X-ray magnetic circular dichroism (XMCD) can be described as a sum over an isotropic and an anisotropic contribution, where the latter is linearly proportional to the axial distortion due to strain. The anisotropic properties of magnetic materials are essential to maintain the preferred magnetization direction. These properties, such as the magnetocrystalline anisotropy energy (MAE), have their origin in the orbital moment anisotropy, which can be studied element-specifically using angular-dependent XMCD. Alternatively, the MAE can also be studied using X-ray magnetic linear dichroism (XMLD).

### 1. Introduction

Much progress has been made since the mid-1980s in the study of magnetic materials using X-ray spectroscopy, an area of research that had previously been the sole domain of neutron scattering. The realization that resonant transitions into the unoccupied valence shell in polarized X-ray absorption and scattering experiments can provide unique element-specific spin and orbital moment information has led to an upturn in theoretical and experimental studies. In this chapter and the next, we will outline some of the many opportunities of magnetic X-ray spectroscopies. In order to fully appreciate the underlying principles we introduce the interaction of photons with matter, as well as resonant processes. The isotropic (i.e. nonpolarized) spectrum gives information about the charge distribution and spin-orbit interaction, but the spin and orbital properties can only properly be probed using circularly polarized X-rays.

Many contemporary and future applications of magnetic materials are linked to their anisotropic magnetic properties, such as the magnetocrystalline anisotropy energy (MAE), perpendicular magnetic anisotropy and interfacial magnetic coupling, which have their origin in the spin–orbit interaction (van der Laan, 1998*a*). It will be shown how the resulting anisotropy in the orbital moment can be probed element-specifically using the angular dependence of the X-ray magnetic circular-dichroism (XMCD) signal.

Related chapters

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#### 2. Photon-matter interaction

In the relativistic photon–matter interaction Hamiltonian,  $\mathcal{H}_{int}$ , the leading terms, which explicitly contain the vector potential **A**, are (Blume, 1985)

$$\mathcal{H}_{\text{int}} = \sum_{n=1}^{N} \left[ \frac{e}{mc} \mathbf{A}(\mathbf{k}, \mathbf{r}_{n}) \cdot \mathbf{p}_{n} + \frac{e^{2}}{2mc} \mathbf{A}^{2}(\mathbf{k}, \mathbf{r}_{n}) + \frac{e\hbar}{2mc} \boldsymbol{\sigma}_{n} \cdot \nabla \times \mathbf{A}(\mathbf{k}, \mathbf{r}_{n}) + \cdots \right],$$
(1)

where  $\mathbf{r}_n$  and  $\mathbf{p}_n$  are the position vector and momentum operator of the *n*th electron, respectively, **k** is the photon wavevector, *e* is the elementary charge, *m* is the electron rest mass and *c* is the speed of light. The first two terms arise from expansion of the kinetic energy operator  $(1/2m)[\mathbf{p} - (e/c)\mathbf{A}]^2$ , while the third term comes from the Dirac equation, where  $\sigma_n$ is the spin-vector operator whose components are the Pauli matrices. For brevity, we will omit the summation over *n* in the following.

The  $\mathbf{A} \cdot \mathbf{p}$  term in  $\mathcal{H}_{int}$  gives the X-ray absorption (XA), resonant elastic X-ray scattering (REXS) and resonant inelastic scattering (RIXS). The  $\mathbf{A}^2$  term gives, apart from the familiar Thomson scattering, the nonresonant inelastic scattering (NIXS) and Compton scattering. The  $\boldsymbol{\sigma} \cdot \nabla \times \mathbf{A} = \boldsymbol{\sigma} \cdot \mathbf{B}$  term gives the magnetic scattering.

#### 3. X-ray absorption

Converting the matrix element to the length form using the equation of motion

$$\mathbf{p} \equiv -i\hbar \nabla = \frac{m}{i\hbar} [\mathbf{r}, \mathcal{H}_0], \qquad (2)$$

where  $\mathcal{H}_0$  is the ground-state Hamiltonian, and expanding the vector potential

$$\mathbf{A}(\mathbf{k},\mathbf{r}) = \boldsymbol{\varepsilon}(\mathbf{k}) \exp(i\mathbf{k}\cdot\mathbf{r}), \qquad (3)$$

where  $\boldsymbol{\varepsilon}(\mathbf{k})$  is the photon polarization vector, gives

$$\langle \mathbf{f} | \mathbf{A} \cdot \mathbf{p} | \mathbf{i} \rangle = \frac{m}{i\hbar} (E_{\mathrm{f}} - E_{\mathrm{i}}) \langle \mathbf{f} | (\boldsymbol{\varepsilon} \cdot \mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) | \mathbf{i} \rangle.$$
 (4)

The lowest order term is the electric dipole transition operator  $\boldsymbol{\varepsilon} \cdot \mathbf{r}$ , which can be written in normalized spherical harmonics as

$$\boldsymbol{\varepsilon} \cdot \mathbf{r} = \sum_{j=x,y,z} \varepsilon_j r_j = r \sum_q C_q^{(1)*}(\boldsymbol{\varepsilon}) \cdot C_q^{(1)}(\hat{\mathbf{r}}), \tag{5}$$

where q = -1, 0, +1 correspond to left-circular, *z*-linear and right-circular photon polarization, respectively.

#### 4. Selection rules

The electron excited from a core level probes the local unoccupied density of states (DOS). The spectral intensity for q-polarized light is given by Fermi's golden rule, in the case of the electric dipole approximation, as

$$I_q(\omega) = |\langle \psi_{\mathbf{f}}(\mathbf{j}'m')|C_q^{(1)}(\hat{\mathbf{r}})|\psi_{\mathbf{i}}(\mathbf{j}m)\rangle|^2 \delta(E_{\mathbf{f}} - E_{\mathbf{i}} - \hbar\omega).$$
(6)

In the presence of a magnetic field the j level is split into m sublevels, and spin-orbit interaction couples the orbital states to the magnetic field. If all directions in space are equivalent, then the atom will be in any of the m levels with equal probability. Therefore, a degenerate, filled state has spherical symmetry, without any spatial orientation. When the symmetry is broken, the state splits into levels with different angular distributions and hence a different polarization dependence. Thus, the energy splitting (*i.e.* symmetry breaking) and the angular or polarization dependence are two different sides of the same coin.

The above can be formalized by considering that the direct product of the irreducible representations,  $\Gamma$ , for the initial and final states and the transition operator must contain the total symmetric representation, *i.e.*  $\Gamma[\psi_{\rm f}(j'm')]^* \times \Gamma(1, q) \times$  $\Gamma[\psi_{\rm i}(jm)] = A_1 + \ldots$ , which in cylindrical symmetry means that -m' + q + m = 0. Thus, conservation of angular momentum gives the selection rule  $\Delta m = m' - m = q$  $(= 0, \pm 1)$ . Hence, from the magnetic ground state *m* only a limited subset of final states can be reached. This means that the spectrum is a fingerprint of the specific ground state with a high sensitivity to crystal-field splitting, spin-orbit interaction, site symmetry and spin configuration. The polarization dependence makes the absorption sensitive to the groundstate magnetic moment. Even with unpolarized light, only a small number of final states can be reached.

The electric dipole operator in equation (6) has spherical components  $rC_0^{(1)}(\hat{\mathbf{r}}) = \hat{\mathbf{z}}$  and  $rC_{\pm 1}^{(1)}(\hat{\mathbf{r}}) = \mp (1/2^{1/2})(\hat{\mathbf{x}} \pm i\hat{\mathbf{y}})$ , resulting in the spectra

$$I_0 = I_z$$
 and  $I_{\pm 1} = \frac{1}{2}(I_x + I_y \mp I_{\text{XMCD}}),$  (7)

in which  $I_{\rm XMCD}$  arises from the imaginary off-diagonal matrix elements, which require complex wavefunctions ( $m \neq 0$ ), where the time-reversal symmetry is broken (Kramers' degeneracy).

By taking linear combinations of the  $I_q$  spectra, the spectral intensity in equation (6) can be separated into a geometrical part and a physical (or dynamic) part, where the latter gives the fundamental spectra

$$I^{0} = I_{-1} + I_{0} + I_{+1}$$
 (isotropic spectrum),  

$$I^{1} = I_{-1} - I_{+1}$$
 (XMCD),  

$$I^{2} = I_{-1} - 2I_{0} + I_{+1}$$
 (XMLD). (8)

Linearly polarized X-rays measure the charge anisotropy and hence give orientational sensitivity (searchlight effect). While circular polarized light can measure the direction of the magnetic moment,  $\langle M \rangle$ , the XMLD is proportional to  $\langle M^2 \rangle$ , which apart from ferromagnets and ferrimagnets can also be used for antiferromagnets, which have no net total magnetic moment.

In the XA measurements the signal is averaged over the probed sample volume. This differs from resonant elastic X-ray scattering (REXS), where the interference between the scattered photon paths gives information on the long-range structural order and, by using polarized light, also the magnetic order. However, in inelastic scattering, such as NIXS and RIXS, the coherence between the scattered photons is lost.

From equation (6) it can be seen that photons only interact with the orbital part of the wavefunction, whereas the spin moment is conserved in the transition. This orbital sensitivity allows the spin and orbital properties of the ground state to be separated, which enables us to study specific orbital effects such as orbital ordering and the Jahn–Teller effect. Using the sum rules (Thole *et al.*, 1992; Carra *et al.*, 1993), the integrated intensities over the spin–orbit split-core manifold give the expectation values of the spin and orbital moments in the ground state.

#### 5. Calculational aspects

Itinerant models for the electronic structure calculation are based on single-particle transitions into the empty DOS. Most *ab initio* methods to calculate the DOS use density-functional theory (DFT) plus a mean-field approximation, and for magnetic materials spin-dependent potentials and spin-orbit interaction have to be taken into account.

DFT calculations can be performed either in real space using multiple scattering (MS) or in reciprocal space using band-structure methods. The ground state in DFT is expressed as a function of the electron density. Its practical application is called the local (spin) density-functional approach (LDA), where the kinetic, nuclear and Hartree potentials are taken into account, with the exchange and correlation effects described by a combined potential. Single-particle calculations (DFT and LDA) give usually good results for the K edges; however, multiplet calculations are needed for transition-



Figure 1

Schematic influence of the various ground-state moments on the isotropic  $L_{2,3}$  XA for an itinerant *d* metal using a one-electron model.

metal L and M edges and lanthanide and actinide L, M, N and O edges.

Due to the strong core-hole interaction in localized materials, the near-edge spectral structure does not display the undistorted unoccupied DOS. The core-hole screening contains a monopole and an angular part. While the direct core-valence Coulomb interaction (*i.e.* the core-hole potential) is well screened in molecules and solids, the higher-order terms (the Slater integrals) are poorly screened, causing a multiplet structure. In this case, a single-particle model will fail and multiplet theory is instead required, which includes the atomic Coulomb and exchange interactions.

The multiplet structure provides a fingerprint for the local ground state, and subtle changes in the magnetic interactions, such as those induced by exchange interaction and spin-orbit interaction, can be distinguished. In the dipole approximation the near-edge spectrum corresponds to resonant transitions, such as  $d^n + \hbar \omega_i \rightarrow p^5 d^{n+1}$  in *d* metals or  $f^n + \hbar \omega_i \rightarrow d^9 f^{n+1}$  in *f* metals. Spectral differences are particularly pronounced when the symmetry of the ground state changes. Crystal- and ligand-field interactions can be included in the multiplet code using group theory. Hybridization and charge-transfer interactions can be taken into account using a model Hamiltonian, similar to the Hubbard–Anderson impurity model.

#### 6. Influence of ground-state moments on XA spectra

#### 6.1. Spectral distribution analysis

Consider a core level with nonzero orbital quantum number  $(l_c \neq 0)$ , which is split by spin-orbit interaction into two levels  $j = l_c \pm s$ . The *j* levels are split into sublevels  $m_j$  due to corevalence exchange interaction, or in the case of a one-electron model an effective field acting on the core level. The core p to valence d transitions in the  $L_{2,3}$  XA can be described using sum rules and moment analysis. The influence of the groundstate moments on the isotropic spectrum is illustrated in Fig. 1 using the one-electron model in an itinerant d metal, under the assumption that *j* is a good quantum number (van der Laan, 1997). The intensity is proportional to the number of d holes,  $n_h$ , giving an integrated signal with statistical ratio  $L_3:L_2 = 2:1$ . The ground-state spin-orbit interaction,  $(l \cdot s)$ , shifts spectral weight from the  $L_2$  to the  $L_3$  edge. For all other ground-state moment contributions the integrated intensity over the separate  $L_3$  and  $L_2$  edges is zero. The orbital moment  $L_z$ , the spin moment  $S_z$  and the magnetic dipole term  $T_z$  =  $\left[\sum_{i} s_{i} - 3\hat{r}_{i}(\hat{r}_{i} \cdot s_{i})\right]_{z}$  shift the spectral weight to lower energy within the  $L_3$  peak, causing an asymmetric line shape. In the  $L_2$  peak the intensity shift is opposite for  $L_z$ . The charge quadrupole moment  $Q_{zz}$  only affects the  $L_3$  edge. The influence of the spin-orbit interaction is discussed in more detail in Section 6.2.

#### 6.2. Branching ratio

The most distinctive feature in the isotropic XA spectra is the branching ratio *B*, which is defined as the fraction of the total transition probability in the  $2p_{3/2}$  manifold. For *d*-metal

# international tables

 $L_{2,3}$  edges, the spin-orbit sum rule can be formulated as (Thole & van der Laan, 1988)

$$B \equiv \frac{I(L_3)}{I(L_3) + I(L_2)} = \frac{2}{3} + \frac{\langle \mathbf{g}|\sum_i l_i \cdot s_i|\mathbf{g}\rangle}{n_h}.$$
 (9)

Hence, *B* is proportional to the ground-state expectation value of the angular part of the spin–orbit interaction  $\langle l \cdot s \rangle$  per *d* hole. Without valence-band spin–orbit interaction  $B = \frac{2}{3}$ , which represents the statistical ratio. When the initial-state crystalfield term is split into sublevels by a spin–orbit interaction that is small compared with the crystal field, each sublevel has a different branching ratio, decreasing with increasing energy.

If the  $p_{3/2}$  and  $p_{1/2}$  manifolds are mixed due to electrostatic core-valence interaction, the core-level angular momentum *j* is no longer a good quantum number. High-spin states will then have a larger branching ratio on average than low-spin states. Due to the selection rule  $\Delta S = 0$  in combination with conservation of angular momentum, a ground state with a higher spin state is then favoured by a transition from a higher core-level *j* state (Thole & van der Laan, 1988).

#### 7. Angular dependence of XMCD

The magnetic anisotropic properties of materials can be studied microscopically and element-specifically using XMCD, which also allows the spin and orbital contributions to the magnetic moment to be separated.

The angular-dependent XMCD can be expressed as a sum over terms that are the product of an energy-dependent spectrum and an angular distribution. Each of these terms must be invariant under all symmetry operations for the site, *i.e.* total symmetric. Since the photon polarization is a vector, there can be no more than three different fundamental XMCD spectra in arbitrary symmetry. For orthorhombic lattice symmetry, for example, any XMCD spectrum can be written as the linear combination,

$$I_{\text{XMCD}} = I_x (\mathbf{P} \cdot \hat{\mathbf{x}}) (\hat{\mathbf{x}} \cdot \hat{\mathbf{M}}) + I_y (\mathbf{P} \cdot \hat{\mathbf{y}}) (\hat{\mathbf{y}} \cdot \hat{\mathbf{M}}) + I_z (\mathbf{P} \cdot \hat{\mathbf{z}}) (\hat{\mathbf{z}} \cdot \hat{\mathbf{M}}),$$
(10)

where  $\mathbf{P} = -i(\boldsymbol{\varepsilon}^* \times \boldsymbol{\varepsilon})$  is the helicity vector,  $\hat{\mathbf{M}}$  is the sample magnetization and  $I_x$ ,  $I_y$  and  $I_z$  are the XMCD spectra for  $\mathbf{P} \parallel \hat{\mathbf{M}}$  along  $\hat{\mathbf{x}}$ ,  $\hat{\mathbf{y}}$  and  $\hat{\mathbf{z}}$ , respectively (van der Laan, 1998b). This means that each XMCD spectrum has a distinct angular dependence, as determined by symmetry.

In axial symmetry  $I_y = I_x$ , and the number of distinct XMCD spectra reduces to two. For small distortions,  $I_z$  will be similar to  $I_x$ , which means that it is advantageous to introduce the isotropic and anisotropic (or quadrupolar) XMCD spectra,  $I_0 = \frac{1}{3}(I_x + I_y + I_z)$  and  $I_2 = \frac{2}{3}I_z - \frac{1}{3}(I_x + I_y)$ , respectively, which have different shapes and  $I_2 \ll I_0$ . The angular-dependent XMCD can be rewritten as

$$\begin{split} I_{\text{XMCD}} &= I_0 \, \mathbf{P} \cdot \hat{\mathbf{M}} + I_2 \bigg[ \frac{3}{2} (\mathbf{P} \cdot \hat{\mathbf{z}}) (\hat{\mathbf{z}} \cdot \hat{\mathbf{M}}) - \frac{1}{2} \, \mathbf{P} \cdot \hat{\mathbf{M}} \bigg] \\ &= I_0 \cos(\gamma - \mu) + I_2 \bigg[ \frac{3}{2} \cos \gamma \cos \mu - \frac{1}{2} \cos(\gamma - \mu) \bigg], \end{split}$$
(11)

1

where  $\gamma$  and  $\mu$  are the angles of **P** and  $\hat{\mathbf{M}}$ , respectively, with the  $\hat{\mathbf{z}}$  axis of the axial symmetry, which is usually the sample surface normal. Equation (11) means that the pure  $I_0$  and  $I_2$  spectra can be measured in selected geometries using

$$I_{\text{XMCD}}(\mathbf{P} \parallel \hat{\mathbf{M}}) = I_0 + I_2 \left(\frac{3}{2}\cos^2 \mu - \frac{1}{2}\right)$$
  
=  $I_z \cos^2 \mu + I_x \sin^2 \mu$ ,  
 $I_{\text{XMCD}}(\mathbf{P} \perp \hat{\mathbf{M}}) = \frac{3}{4} I_2 \sin 2\mu = \frac{1}{2} (I_z - I_x) \sin 2\mu$ . (12)

For  $\gamma = \mu = 54.7^{\circ}$ , we obtain  $I_{\text{XMCD}} = I_0$ . For  $\gamma = 54.7^{\circ}$  and  $\gamma - \mu = 90^{\circ}$ , we obtain  $I_{\text{XMCD}} = I_2/2^{1/2}$ .

The ratio  $I_2:I_0$  gives the amount of distortion of the cubic crystal field by the axial field due to, for example, strain as in the case of MnCr<sub>2</sub>O<sub>4</sub> films (van der Laan *et al.*, 2010). In the next section we will apply this formalism to determine the magnetocrystalline anisotropy using the sum rules.

#### 8. Magnetocrystalline anisotropy energy

The anisotropic magnetic properties, such as the magnetocrystalline anisotropy energy (MAE), easy magnetization direction, magnetostriction and coercivity, all depend on the orbital moment anisotropy, which can be studied elementspecifically using angular-dependent XMCD (Stöhr & König, 1995; van der Laan, 1998a). We limit ourselves here to 3d transition metals. In this case, the spin-orbit constant is small (40-80 meV) compared with the 3d band width of a few eV, so that we can use perturbation theory. Assuming that the majority spin band is completely filled, the MAE will be proportional to the difference between the orbital moments along the easy and hard directions (Bruno, 1989), where the orbital moment is largest along the easy direction. This model was corroborated for a gold/cobalt/gold staircase structure, although a proportionality factor was required to scale the anisotropic part (Weller et al., 1995).

The MAE is defined as  $E(\hat{\mathbf{M}} \perp \hat{\mathbf{z}}) - E(\hat{\mathbf{M}} \parallel \hat{\mathbf{z}})$ , where  $\hat{\mathbf{z}}$  is along the easy direction of magnetization. Sum rules for the electric dipole transition from a core level can measure the orbital moment tensor of the valence shell up to second rank. Therefore, taking a uniaxial symmetry, where the spin  $\mathbf{S} \parallel \mathbf{M}$  makes an angle  $\varphi$  with  $\hat{\mathbf{z}}$ , the orbital moment *L* will be written as a second-rank tensor

$$\langle L(\hat{\mathbf{M}})\rangle = \langle L_{i}\rangle + \langle L_{a}\rangle C_{0}^{(2)}(\hat{\mathbf{M}}), \qquad (13)$$

with reduced spherical harmonic  $C_0^{(2)}(\hat{\mathbf{M}}) = \frac{3}{2}(\hat{\mathbf{M}} \cdot \hat{\mathbf{z}})^2 - \frac{1}{2} = \frac{3}{2}\cos^2 \mu - \frac{1}{2}$  and

$$\langle L_{i} \rangle \equiv \frac{1}{3} [\langle L_{x} \rangle + \langle L_{y} \rangle + \langle L_{z} \rangle],$$
 (14)

$$\langle L_{a} \rangle \equiv \frac{1}{3} [2 \langle L_{z} \rangle - \langle L_{x} \rangle - \langle L_{y} \rangle],$$
 (15)

are the isotropic and anisotropic parts of the orbital moment, respectively. Note that from equation (13),  $\langle L_z \rangle = \langle L_i \rangle + \langle L_a \rangle$ .

Integrating the XMCD spectra in equation (12) and using the orbital sum rule (Thole *et al.*, 1992),

$$\langle L_z \rangle = w_z = \frac{2n_h}{A} \left( \int_{L_3} I_{\text{XMCD}} + \int_{L_2} I_{\text{XMCD}} \right),$$
 (16)

where  $A = \int_{L_3+L_2} I_{iso}$  and  $w_z$  is the measured integrated intensity for  $\mathbf{P} \parallel \hat{\mathbf{M}} \parallel \hat{\mathbf{z}}$ , gives the angular dependence for parallel and transverse geometry as (van der Laan, 1998*b*)

$$w(\mathbf{P} \parallel \hat{\mathbf{M}}) = w_0 + w_2 \left(\frac{3}{2}\cos^2 \mu - \frac{1}{2}\right) = w_z \cos^2 \mu + w_x \sin^2 \mu,$$
  
$$w(\mathbf{P} \perp \hat{\mathbf{M}}) = \frac{3}{4} w_2 \sin 2\mu = \frac{1}{2} (w_z - w_x) \sin 2\mu,$$
 (17)

where  $\mu = \angle (\hat{\mathbf{z}}, \hat{\mathbf{M}})$ ,  $w_0 = \langle L_i \rangle$  and  $w_2 = \langle L_a \rangle$ . This gives the angle from **L** to **M** as

$$\mathcal{L}(\mathbf{L}, \mathbf{M}) = \arctan\left[\frac{3w_2 \sin 2\mu}{4w_0 + w_2(6\cos^2 \mu - 2)}\right]$$
$$\simeq \frac{3}{4} \frac{w_2}{w_0} \sin 2\mu + O\left(\frac{w_2}{w_0}\right)^2.$$
(18)

For small anisotropy, the maximum in the angle  $\angle(\mathbf{L}, \mathbf{M})$  will be near  $\mu = 45^{\circ}$  and proportional to  $w_2/w_0$ .



#### Figure 2

Different geometries for measuring the magnetic anisotropy. The easy axis of magnetization is along z, where the orbital magnetic moment is highest. The spin moment is isotropic. (a) Parallel geometry ( $\mathbf{P} \parallel \mathbf{M}$ ). The anisotropy in the orbital moment is obtained as the difference in the integrated XMCD measured along two different magnetization directions. (b) Transverse geometry ( $\mathbf{P} \perp \mathbf{M}$  and not collinear with a symmetry axis). Competition between spin-orbit coupling and crystal-field interaction gives  $L_{\perp} = \frac{1}{2}(L_z - L_x)\sin 2\gamma$  along **P**. In transverse geometry only a single XMCD measurement is needed, compared with two in parallel geometry.

Table 1

Expectation values of w for  $\mathbf{M} \parallel \mathbf{P}$  and  $\mathbf{M} \perp \mathbf{P}$  at different angles  $\mu$ , together with the directions of L and T with respect to M. It is seen that T rotates from parallel to perpendicular to antiparallel to M.

$\mu = \angle(\mathbf{z}, \mathbf{M}) (^{\circ})$	$w(\mathbf{M} \parallel \mathbf{P})$	$w(\mathbf{M} \perp \mathbf{P})$	$\Delta(\mathbf{L}, \mathbf{M})$	$\angle(\mathbf{T},\mathbf{M})$ (°)
0	$w_0 + w_2$	0	0°	0
45	$w_0 + \frac{1}{4}w_2$	$-\frac{3}{4}w_2$	$\sim \frac{3}{4} (w_2/w_0)$ rad	71.57
54.74	w <sub>0</sub>	$-\frac{1}{2}2^{1/2}w_2$	$\sim \frac{1}{2} 2^{1/2} (w_2/w_0)$ rad	90
90	$w_0 - \frac{1}{2}w_2$	0	0°	180

The angular dependence offers two different ways to measure the magnetic anisotropy, namely in parallel and transverse geometry (Dürr & van der Laan, 1997), which are illustrated in Figs. 2(a) and 2(b), respectively.

The angular dependence of the effective spin moment can be written similarly as

$$\langle S^{\text{eff}}(\hat{\mathbf{M}}) \rangle = \langle S_z \rangle + \frac{7}{2} \langle T_z \rangle C_0^{(2)}(\hat{\mathbf{M}}), \qquad (19)$$

where

$$\langle S_z \rangle \equiv \frac{1}{3} (\langle S_x^{\text{eff}} \rangle + \langle S_y^{\text{eff}} \rangle + \langle S_z^{\text{eff}} \rangle),$$
 (20)

$$\frac{7}{2}\langle T_z \rangle \equiv \frac{1}{3} (2\langle S_z^{\text{eff}} \rangle - \langle S_x^{\text{eff}} \rangle - \langle S_y^{\text{eff}} \rangle), \qquad (21)$$

give the (isotropic) spin moment  $S_z$  and the (anisotropic) magnetic dipole term  $T_z$ , respectively. Note that  $\langle S_z^{\text{eff}} \rangle = \langle S_z \rangle + \frac{7}{2} \langle T_z \rangle$ .

Using the spin sum rule (Carra et al., 1993)

$$\langle S_z^{\text{eff}} \rangle = w_z = \frac{3n_h}{2A} \left( \int_{L_3} I_{\text{XMCD}} - 2 \int_{L_2} I_{\text{XMCD}} \right), \quad (22)$$

we obtain equation (17) again but now with  $w_0 = \langle S_z \rangle$  and  $w_2 = \frac{7}{2} \langle T_z \rangle$ . The angle from **T** to **M** is

$$\angle(\mathbf{T}, \mathbf{M}) = \arctan\left(\frac{3\sin 2\mu}{1 + 3\cos 2\mu}\right).$$
 (23)

Note that  $T_z \propto w_2$  has the properties of a traceless Cartesian tensor. The angular dependence of the various moments is given in Table 1.

Instead of measuring the XMCD with the polarization vector and magnetization direction parallel ( $\mathbf{P} \parallel \mathbf{M}$ ) along the different crystal directions, the MAE can also be obtained from a single XMCD measurement in transverse geometry ( $\mathbf{P} \perp \mathbf{M}$  and not collinear with easy axes; Dürr & van der Laan, 1996). By forcing the electron spins out of the easy direction using an external magnetic field and measuring the perpendicular component of the orbital moment with the polarization vector perpendicular to the magnetization direction it is possible to directly determine the element-specific easy direction of magnetization (see Fig. 2*b*; Dürr *et al.*, 1997).

#### 9. Comparison with XMLD

The MAE can also be obtained from XMLD. Sum rules relate the integrated intensities of the sum and the weighted difference of the XMLD over the  $L_{2,3}$  edges to the charge quadrupole moment and the anisotropic part of the spin-orbit interaction, respectively (van der Laan, 1999).

In 3*d* metals  $H_{\text{soc}} = \zeta \lambda$ , where the radial part  $\zeta$  is scalar (40–80 eV) and the angular part is the operator  $\lambda = l \cdot s$ , and is a small perturbation, so that the MAE can be expressed in terms of the spin–orbit interaction as

$$\Delta E = \frac{1}{2} \zeta \langle \lambda \rangle. \tag{24}$$

Hence, the MAE branching ratio of the XMLD is directly proportional to the MAE.

When all *d* holes have minority spin,  $\langle \lambda \rangle = -\frac{1}{2}\hat{S} \cdot \langle L \rangle$ , we can retrieve Bruno's formula (Bruno, 1989) from equation (24),

$$\Delta E = -\frac{1}{4}\zeta \hat{S} \cdot \langle L \rangle. \tag{25}$$

When there are also d holes with majority spin,

$$\Delta E = -\frac{1}{4}\zeta \hat{S} \cdot (\langle L^{\uparrow} \rangle - \langle L^{\downarrow} \rangle), \qquad (26)$$

where *L* changes sign when *S* is reversed (time-reversal symmetry). In principle,  $\langle L^{\uparrow} \rangle - \langle L^{\downarrow} \rangle$  would be accessible from peak asymmetries. However, the orbital sum rule gives the total projected orbital moment  $\hat{S} \cdot [\langle L^{\uparrow} \rangle + \langle L^{\downarrow} \rangle]$ .

The angular dependence of the spin-orbit interaction is

$$\langle \lambda(\hat{\mathbf{M}}) \rangle = \langle \lambda_i \rangle + \langle \lambda_a \rangle \bigg[ C_0^{(2)}(\hat{\mathbf{M}}) + \frac{3}{5} U^{222}(\hat{\mathbf{z}}, \hat{\mathbf{M}}, \mathbf{P}) \bigg], \quad (27)$$

where

$$\langle \lambda_i \rangle = \frac{1}{3} (\langle l_x s_x \rangle + \langle l_y s_y \rangle + \langle l_z s_z \rangle), \tag{28}$$

$$\langle \lambda_a \rangle = \frac{1}{3} (2 \langle l_x s_x \rangle - \langle l_y s_y \rangle - \langle l_z s_z \rangle).$$
<sup>(29)</sup>

The extra term in equation (27), containing the bipolar spherical harmonic

$$U^{222}(\hat{\mathbf{z}}, \hat{\mathbf{M}}, \mathbf{P}) = \frac{1}{2} \bigg[ 2 - 3(\hat{\mathbf{z}} \cdot \hat{\mathbf{M}})^2 - 3(\mathbf{P} \cdot \hat{\mathbf{M}})^2 - 3(\mathbf{P} \cdot \hat{\mathbf{z}})^2 + 9(\mathbf{P} \cdot \hat{\mathbf{z}})(\hat{\mathbf{z}} \cdot \hat{\mathbf{M}})(\hat{\mathbf{M}} \cdot \mathbf{P}) \bigg], \qquad (30)$$

arises from the linear dichroism (van der Laan, 1999). Using the XMLD rule (van der Laan, 1999) we obtain the angular dependence of the spin–orbit interaction, which can then be used in equation (24) to obtain the MAE.

#### **10. Conclusions**

The photon-matter interaction contains an  $\mathbf{A} \cdot \mathbf{p}$  term which becomes large near the core-to-valence resonances. Selection rules severely curtail the number of allowed transitions, which makes the spectrum a fingerprint for the specific ground state with a high sensitivity to the crystal field, spin-orbit interaction, site symmetry and spin configuration. The polarization dependence makes the absorption sensitive to the groundstate magnetic moment. Even with unpolarized light only a limited number of final states can be reached. The branching ratio of the spin-orbit split core-level spectra is proportional to the ground-state spin-orbit interaction and can furthermore provide a measure for the spin state.

The polarized X-ray absorption signal from a core level to the valence band depends strongly on the directions of the polarized light and the magnetization with respect to the lattice orientation. By including angular-dependent effects we can extend the sum rules which relate the integrated signals over the absorption edges to the expectation values of the spin–orbit coupled ground-state multipole moments. The angular dependence allows us to separate ground-state moments which are indistinguishable in a collinear geometry, such as the spin moment and the magnetic dipole term.

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