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Chapter 2.18

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Magnetic X-ray techniques

Gerrit van der Laan*

Diamond Light Source, Harwell Science and Innovation Campus, Didcot OX11 0DE, United Kingdom. *Correspondence e-mail: gerrit.vanderlaan@diamond.ac.uk

The underlying theoretical aspects of X-ray spectroscopies are recapitulated with special emphasis on applications to magnetic systems. Prominence is placed on common conceptual aspects, while highlighting the differences in information that they may offer. X-ray scattering can be used to investigate the electronic and magnetic long-range order in crystals and ordered materials. The crystal symmetry of the sample and the X-ray polarization state have a profound effect on the scattering amplitude of X-ray resonant magnetic scattering (XRMS). Expressions for X-ray magnetic circular and linear dichroism (XMCD and XMLD, respectively) can be derived directly from those for XRMS. The photon-matter interaction for electric and magnetic multipole fields is presented from a general point of view, which reveals the physical implications of the various terms in the cross section for X-ray absorption. X-ray optical activity is due to mixed terms of different multipole rank of the electric and magnetic fields. The different optical effects, such as XMCD, X-ray natural circular dichroism (XNCD) and X-ray magnetic chiral dichroism (XM χ D), can be distinguished by their properties under space inversion and time reversal.

1. Introduction

The theoretical concepts behind magnetic synchrotron techniques are based on quantum mechanics and provide very rich grounds for experimental exploration. The aim of this chapter is to present a general framework that shows the current and future capabilities, although many details are skipped due to page-length considerations. We will first present the general expressions for the scattering amplitude in nonresonant and resonant elastic scattering. From this, expressions for X-ray magnetic circular and linear dichroism (XMCD and XMLD, respectively) are obtained using the optical theorem. Taking crystal-field interaction into account leads to a remarkable result for XMLD.

The advantage of X-ray resonant magnetic scattering (XRMS), compared with other absorption spectroscopies, is that the scattering amplitudes from the various sites interfere coherently, which gives a sensitivity to long-range order. XRMS allows us to investigate the physics of higher order multipoles for the study of strongly correlated electron systems.

We review the interaction of electric and magnetic multipole fields with matter and explain the origin of X-ray optical activity.

Related chapters

Volume I: 2.1, 2.10, 2.12, 2.17, 3.33



- 2. X-ray magnetic scattering
- 2.1. Scattering amplitude

The first magnetic scattering experiment was carried out on NiO under nonresonant conditions (de Bergevin & Brunel, 1981). Subsequent magnetic scattering at resonance (Hannon *et al.*, 1988) showed an enhancement of several orders of magnitude in the scattering amplitude, and also showed a strong dependence on the polarization state of the incident and scattered X-rays. This can be formally taken into account by describing the atomic scattering amplitude as a tensor quantity, instead of a scalar, with consequences for the selection rules of the diffracted intensity. The tensor products associated with the scattering amplitude must belong to the totally symmetric representation of the point group at the resonating ion.

In the scattering process, the incident and scattered photons are characterized by wavevectors **k** and **k'**, unit polarization vectors $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}'$ and energies $\hbar\omega_k$ and $\hbar\omega_{k'}$, respectively. Initially, the electrons are in the ground state $|g\rangle$ with energy E_g . Within the first Born approximation the differential cross section for coherent elastic X-ray scattering ($\omega \equiv \omega_{k'} = \omega_k$) is

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = r_0^2 \left| \sum_j f_j(\boldsymbol{\varepsilon}', \boldsymbol{\varepsilon}, \mathbf{k}', \mathbf{k}, \omega) \exp(i\mathbf{q} \cdot \mathbf{r}_j) \right|^2, \tag{1}$$

where $r_0 = e^2/mc^2$ is the classical electron radius, f_j is the scattering amplitude of the electron at lattice position \mathbf{r}_j and $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ is the scattering vector.

Using the photon-matter interaction Hamiltonian $\mathcal{H}_{in} \propto \mathbf{A}^2 + \mathbf{A} \cdot \mathbf{p}_j + \mathbf{s}_j \cdot \mathbf{H}$ (see also Section 2 of van der Laan & Figueroa, 2024) the scattering amplitude in the Kramers-Heisenberg formalism can be written as (Sakurai, 1985; Blume, 1985)

$$f(\boldsymbol{\varepsilon}', \boldsymbol{\varepsilon}, \mathbf{k}', \mathbf{k}, \omega) = \boldsymbol{\varepsilon}'^* \cdot \langle \mathbf{g} | F(\mathbf{k}', \mathbf{k}, \omega) | \mathbf{g} \rangle \cdot \boldsymbol{\varepsilon}, \qquad (2)$$

with the scattering tensor

$$F(\mathbf{k}', \mathbf{k}, \omega) = -\sum_{j} \exp(i\mathbf{q} \cdot \mathbf{r}_{j}) - \frac{i\hbar\omega}{mc^{2}} \sum_{j} \exp(i\mathbf{q} \cdot \mathbf{r}_{j})$$

$$\times \left(\frac{i\mathbf{q} \times \mathbf{p}_{j}}{\hbar q^{2}} \cdot \mathbf{a} - \mathbf{s}_{j} \cdot \mathbf{b}\right)$$

$$+ \sum_{n} \frac{E_{g} - E_{n}}{m\hbar\omega} \left(\frac{J^{\dagger}(\mathbf{k}')|n\rangle \langle n|J(\mathbf{k})}{E_{g} - E_{n} + \hbar\omega + i\Gamma_{n}/2} - \frac{J(\mathbf{k})|n\rangle \langle n|J^{\dagger}(\mathbf{k}')}{E_{g} - E_{n} - \hbar\omega}\right), \qquad (3)$$

where \mathbf{p}_j and \mathbf{s}_j are the momentum operator and the spin at site j, respectively. Substituting into \mathcal{H}_{int} the magnetic field $\mathbf{H} = -i\mathbf{k} \times \mathbf{A}$ with vector potential $\mathbf{A} = \boldsymbol{\varepsilon} \exp(i\mathbf{k} \cdot \mathbf{r})$, and using $\mathbf{s} \cdot (\mathbf{k} \times \boldsymbol{\varepsilon}) = (\mathbf{k} \times \mathbf{s}) \cdot \boldsymbol{\varepsilon}$, the current operator can be written as $J(\mathbf{k}) = \sum_j \exp(i\mathbf{k} \cdot \mathbf{r}_j)(\mathbf{p}_j - i\hbar\mathbf{k} \times \mathbf{s}_j)$, which reduces to $J_{E1} = \sum_j \mathbf{p}_j$ for electric dipole transitions.

The first term in equation (3) gives the Thomson scattering amplitude f^0 originating from the isotropic charge-density distribution. It also gives incoherent processes, such as nonresonant inelastic scattering (NIXS) and Compton scattering. The magnetic Compton profile, which can be measured with high-energy circularly polarized X-rays (100–200 keV), corresponds to the difference in the one-dimensional projection of the spin-polarized electron momentum density for majority and minority spin bands.

The second term in equation (3) gives the nonresonant X-ray magnetic scattering amplitude, which is due to the orbital and spin magnetic density contributions. The vectors a and **b** contain the coupling between the photon polarization and the scattering vectors. The third term, also known as the anomalous or dispersive term, gives the resonant amplitude, $f^{\text{XRMS}} = f' - if''$, arising from the core-valence transitions. f^{XRMS} probes the intermediate states $|n\rangle$ with energy E_n , selected at the photon energy $\hbar \omega = E_n - E_g$ with a full width Γ_n for the lifetime. The intermediate state in the resonance process enables additional excitation paths that are otherwise not allowed in the direct transition, such as spin-flip transitions and forbidden transitions (see Section 2.3). The resonance term can be ascribed to virtual transitions of an electron from a core state to an unoccupied state above the Fermi level. This is schematically illustrated in Fig. 1(a) for the soft X-ray excitation $3d^n \rightarrow 2p^5 3d^{n+1} \rightarrow 3d^n$ in a magnetic transitionmetal ion.

In contrast to absorption spectroscopies such as X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS), in XRMS the scattering amplitudes from the various sites interfere coherently, which gives a sensitivity to long-range structural, magnetic and multipolar order.

The most important absorption edges for hard XRMS cover the energy range 3.5–15 keV, which includes the 3*d* metal *K* edges, rare-earth *L* edges and actinide *L* edges, with scattering amplitudes of ~0.01–0.1 r_0 . In the soft X-ray region there is a huge enhancement of the resonant amplitude of ~100 r_0 for 3*d* metal *L* edges and rare-earth *M* edges. However, in order to fulfil the scattering condition the X-ray wavelength must be shorter than two times the lattice periodicity of the crystalline



Figure 1

Soft X-ray resonant magnetic scattering. (a) Schematic picture of the resonant scattering process in a 3*d* transition-metal ion, showing the virtual transitions between the 2*p* core level and empty spin-polarized 3*d* states. The core level is split by the strong spin-orbit interaction, which leads to a difference in the electric dipole transition probability for left-and right-circularly polarized X-rays. (*b*, *c*) The real and imaginary parts of the (*b*) charge scattering (f'_c and f''_c) and (*c*) magnetic scattering (f'_m and f''_m) at the Fe $L_{2,3}$ edges of metallic iron.

ordered magnetic structure. The resonant magnetic scattering can be distinguished from the Thomson scattering by tuning on and off the resonance energy.

2.2. The resonant electric multipole amplitude

The next task at hand is to separate the resonant amplitude into the geometric and dynamic factors. We will show this for the electric 2^{L} -pole resonance (EL) in spherical symmetry with current operator $J(\mathbf{k}) = \sum_{j} \mathbf{p}_{j} \exp(i\mathbf{k} \cdot \mathbf{r}_{j})$. The transition operator $\exp(i\mathbf{k} \cdot \mathbf{r}_{j})$ can be expanded in a sum over scalar products of spherical multipole tensors $Y_{\kappa}^{(k)}$ of rank k and components $\kappa = -k, \ldots, k$ as

$$\exp(i\mathbf{k}\cdot\mathbf{r}_j) = 4\pi \sum_{k,\kappa} i^k j_k(qr) Y_{\kappa}^{(k)*}(\hat{\mathbf{k}}) Y_{\kappa}^{(k)}(\hat{\mathbf{r}}_j), \qquad (4)$$

where $j_k(qr)$ is the *k*th-order spherical Bessel function.

We will make use of the standard notation for the tensor product of two spherical tensors $\mathbf{A}^{(k)}$ and $\mathbf{B}^{(k')}$ (Varshalovich *et al.*, 1988),

$$[\mathbf{A}^{(k)}, \mathbf{B}^{(k')}]_{Q}^{(k)} \equiv \sum_{\kappa\kappa'} A^{(k)}_{\kappa} B^{(k')}_{\kappa'} \langle kk'\kappa\kappa' | KQ \rangle,$$
(5)

which defines a spherical tensor of rank *K* and projection *Q*, using Clebsch–Gordan coefficients $\langle kk'\kappa\kappa'|KQ\rangle$. Using this recoupling, the matrix elements for $\mathbf{A} \cdot \mathbf{p}_j = (\varepsilon \cdot \mathbf{p}_j)\exp(i\mathbf{k} \cdot \mathbf{r}_j)$ can be written as a sum of products of a geometric and physical (dynamic) part

$$\langle n | \mathbf{A}(\mathbf{k}, \mathbf{r}_j) \cdot \mathbf{p}_j | \mathbf{g} \rangle \propto \sum_{LM} \left[\boldsymbol{\varepsilon}, Y^{L-1}(\hat{\mathbf{k}}) \right]_M^{(L)} \langle n | J_M^L | \mathbf{g} \rangle,$$
 (6)

where the current operator,

$$J_{M}^{L} = -\frac{4\pi i^{L} k^{L}}{(2L+1)!!} \left(\frac{L+1}{L}\right)^{1/2} \sum_{j} er_{j}^{L} Y_{M}^{L}(\mathbf{r}_{j}),$$
(7)

in the physical part excites an electron from an occupied (core) to an empty (valence) state.

For the electric 2^{L} -pole scattering factor we then obtain the multipole expansion (Luo *et al.*, 1993; Carra & Thole, 1994)

$$f(\omega)_{EL} = 2\lambda \sum_{z=0}^{2L} \sum_{\zeta=-z}^{z} [T_{\zeta}^{(z)}(\boldsymbol{\varepsilon}^{\prime*}, \hat{\mathbf{k}}^{\prime}; \boldsymbol{\varepsilon}, \hat{\mathbf{k}}), \langle \mathbf{g} | F_{\zeta}^{(z)}(\omega) | \mathbf{g} \rangle]_{0}^{(0)}, \quad (8)$$

with physical part

$$F_{\zeta}^{(z)}(\omega) = \sum_{n} \frac{1}{2\lambda} \left(\frac{(J^L)^{\dagger} |n\rangle \langle n|J^L}{E_{g} - E_{n} + \hbar\omega + i\Gamma/2} \right)_{\zeta}^{(z)}$$
(9)

and geometric part

$$T_{\zeta}^{(z)}(\boldsymbol{\varepsilon}^{\prime*}, \hat{\mathbf{k}}^{\prime}; \boldsymbol{\varepsilon}, \hat{\mathbf{k}}) = \frac{2L+1}{L+1} \left[[\boldsymbol{\varepsilon}^{\prime*}, Y^{L-1}(\hat{\mathbf{k}}^{\prime})]^{L}, [\boldsymbol{\varepsilon}, Y^{L-1}(\hat{\mathbf{k}})]^{L} \right]_{\zeta}^{z}.$$
(10)

For the electric-dipole resonance the $\hat{\mathbf{k}}$ dependence disappears and equation (8) reduces to

$$f(\boldsymbol{\varepsilon}', \boldsymbol{\varepsilon}, \omega)_{E1} = 2\lambda \sum_{z=0}^{2} \sum_{\zeta=-z}^{z} \left[\left[\boldsymbol{\varepsilon}'^{*}, \boldsymbol{\varepsilon} \right]_{\zeta}^{(z)}, \langle \mathbf{g} | F_{\zeta}^{(z)}(\omega) | \mathbf{g} \rangle \right]_{0}^{(0)}, \quad (11)$$

containing a scalar $F^{(0)}$, a pseudovector (antisymmetric tensor) $F^{(1)}$ and a symmetric tensor $F^{(2)}$.

In uniaxial symmetry, with **M** along the \hat{z} axis, this leads to the Hannon & Trammel formula (Hannon *et al.*, 1988)

$$F(\boldsymbol{\varepsilon}', \boldsymbol{\varepsilon}, \omega)_{SO_2} \propto \boldsymbol{\varepsilon}'^* \cdot \boldsymbol{\varepsilon} F^{(0)} - i(\boldsymbol{\varepsilon}'^* \times \boldsymbol{\varepsilon}) \cdot \hat{\boldsymbol{z}} F^{(1)} + (\boldsymbol{\varepsilon}'^* \cdot \hat{\boldsymbol{z}})(\boldsymbol{\varepsilon} \cdot \hat{\boldsymbol{z}}) F^{(2)}.$$
(12)

 $F^{(0)}$ gives the charge scattering $f'_c - if''_c$. $F^{(1)}$ gives the magnetic scattering $f'_m - if''_m$, which depends linearly on the magnetization direction and at resonance can become comparable in size to $F^{(0)}$. As an example, Figs. 1(b) and 1(c) shows the charge $(f'_c \text{ and } f''_c)$ and magnetic $(f'_m \text{ and } f''_m)$ scattering at the Fe $L_{2,3}$ edge of metallic iron. $F^{(2)}$ is quadratic in the magnetization direction and is usually much smaller than $F^{(0)}$ and $F^{(1)}$. The resonant amplitudes are complex numbers with strongly energy-dependent phase angles. The real and imaginary parts are related to each other by a Kramers–Kronig transform.

The **q**-dependent scattering intensity is obtained by taking the modulus square of $f(\boldsymbol{\varepsilon}', \boldsymbol{\varepsilon}, \omega)$, which gives the charge scattering, the pure magnetic scattering and the interference term between charge and magnetic scattering (van der Laan, 2008). For instance, the intensity of the pure magnetic scattering in SO_2 symmetry is

$$I_{\text{mag}} = \frac{1}{2} |F_1|^2 P_\sigma |\hat{\mathbf{k}}' \cdot \hat{\mathbf{M}}|^2 + \frac{1}{2} |F_1|^2 P_\pi [|\hat{\mathbf{k}} \cdot \hat{\mathbf{M}}|^2 + |(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{M}}|^2] - |F_1|^2 \operatorname{Re}[(P_2 + iP_3)(\hat{\mathbf{k}}' \cdot \hat{\mathbf{M}}^*)(\hat{\mathbf{k}}' \times \hat{\mathbf{k}}) \cdot \hat{\mathbf{M}}], \quad (13)$$

where $P_{\sigma} = P_0 + P_1$, $P_{\pi} = P_0 - P_1$, P_2 and P_3 represent the Poincaré–Stokes parameters. The equation can be used to determine the polarization dependence of the vector magnetization profile for magnetic multilayers, domain structures, nano-objects, spiral and helical structures, skyrmions *etc.* (Zhang *et al.*, 2017).

2.3. Diffraction conditions

For a collinear structure with all of the magnetization vectors parallel, it follows from equation (1) that the polarization dependence of the coherent scattering is the same as for the single site. This leads to an overlap of the magnetic and charge peaks; therefore, to study ferromagnetic materials the interference between these two contributions has to be used, which shows a change in the scattering signal upon reversal of the sample magnetization. Antiferromagnetically coupled layers and domains as well as spiral structures offer the advantage that the magnetic diffraction peaks are separated from the structural diffraction peaks. Doubling the periodicity in real space gives rise to magnetic peaks with half the structural period in reciprocal space.

The tensorial character of the scattering amplitude allows us to observe otherwise forbidden reflections, for which the crystal structure factor vanishes. The diffracted amplitude generated by the whole crystal is $r_0 \sum_j f_j \exp(i\mathbf{q} \cdot \mathbf{R}_j)$, where *j* runs over all sites. Thus, a necessary condition for reflection is that the total phase factor in the diffracted amplitude does not cancel. If all sites have the same f then we have $f \sum_{i} \exp(i\mathbf{q} \cdot \mathbf{R}_{i})$, which is the result for normal Bragg scattering. This situation changes when the various sites have different orientations (Carra & Thole, 1994). The components of the spherical tensor $T_{\zeta}^{(z)}$ transform under space rotation like spherical harmonics with φ dependence $\exp(i\zeta\varphi)$. An angular rotation of the spherical tensor by $2\pi/n$ gives a phase shift $\exp(2\pi i \zeta/n)$ and thus a scattering factor $f \sum_{i} \exp(2\pi i \zeta / n_i + i \mathbf{q} \cdot \mathbf{R}_i)$. Screw axes and glide planes can give constructive interference. For instance, when **q** is along an *n*-fold screw axis parallel to **c** (*i.e.* with rotation $2\pi/n$ and translation tc/n, the spherical harmonics change by a factor $\exp(2\pi i \zeta/n)$ and the Bragg factor $\exp(i\mathbf{q} \cdot \mathbf{R})$ changes by a phase shift $\exp(i\mathbf{q} \cdot \mathbf{c}t/n)$. Since this factor must reduce to unity, the reflection is only allowed when $\mathbf{q} \cdot \mathbf{c}/2\pi = (nk - \zeta)/t$, where k is an integer.

2.4. Crystal-field symmetry

The Hannon and Trammel equation (equation 12), which has successfully been used in a variety of studies, is restricted to cylindrical symmetry. It does not include crystal-field effects, which become important in localized materials such as oxides. To take these effects into account we have to branch down to the symmetry states of the excited sites. The tensor components in crystal-field symmetry can be obtained using the basis-state transformation $|z\zeta\rangle = \sum_{\Gamma} |z\Gamma\rangle \langle z\Gamma| z\zeta\rangle$, where Γ are the irreps of the point group. However, if **M** or $\boldsymbol{\varepsilon}$ are not along the symmetry directions of the point group then the symmetry of the total system reduces to the trivial group C_1 .

Alternatively, we can use the Cartesian tensor form. For instance, in cubic crystal-field symmetry (O_h) the scalar $F^{(0)}$ has the total symmetric irrep $A_1 = \{1\}$, the pseudovector $F^{(1)}$ has the irrep $T_1 = \{x, y, z\}$ and the symmetric tensor $F^{(2)}$ has the irreps $E = \{z^2 - \frac{1}{3}r^2, x^2 - y^2\}$ and $T_2 = \{xy, yz, zx\}$. Thus, the diagonal matrix elements contain $F_{A_1}^{(0)}$ and $F_E^{(2)}$, while the nondiagonal elements contain $F_{T_1}^{(1)}$ and $F_{T_2}^{(2)}$ with a corresponding symmetry of the magnetization.

Taking $f(\boldsymbol{\varepsilon}', \boldsymbol{\varepsilon}, \omega) = \boldsymbol{\varepsilon}'^* \cdot \mathbf{F}(\hat{\mathbf{M}}, \omega) \cdot \boldsymbol{\varepsilon}$, with unit magnetization vector $\hat{\mathbf{M}} = (m_x, m_y, m_z) = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$ and polarization vector $\boldsymbol{\varepsilon} = (\varepsilon_x, \varepsilon_y, \varepsilon_z)$, the scattering tensor $\mathbf{F}(\hat{\mathbf{M}}, \omega)_{O_h}$ along $C_4 || \langle 001 \rangle$ can be written as (Haverkort *et al.*, 2010; van der Laan, 2013*a*)

$$\begin{array}{ccc} F_{A_{1}}^{(0)} + (m_{x}^{2} - \frac{1}{3})F_{E}^{(2)} & -m_{z}F_{T_{1}}^{(1)} + m_{x}m_{y}F_{T_{2}}^{(2)} & m_{y}F_{T_{1}}^{(1)} + m_{x}m_{z}F_{T_{2}}^{(2)} \\ m_{z}F_{T_{1}}^{(1)} + m_{x}m_{y}F_{T_{2}}^{(2)} & F_{A_{1}}^{(0)} + (m_{y}^{2} - \frac{1}{3})F_{E}^{(2)} & -m_{x}F_{T_{1}}^{(1)} + m_{y}m_{z}F_{T_{2}}^{(2)} \\ -m_{y}F_{T_{1}}^{(1)} + m_{x}m_{z}F_{T_{2}}^{(2)} & m_{x}F_{T_{1}}^{(1)} + m_{y}m_{z}F_{T_{2}}^{(2)} & F_{A_{1}}^{(0)} + (m_{z}^{2} - \frac{1}{3})F_{E}^{(2)} \\ \end{array} \right)$$

$$(14)$$

To include the third-rank tensor $F_{T_1}^{(3)}$, the elements of which are usually small, we can append it to the odd-rank tensor $F_{T_1}^{(1)}$ by the substitution

$$m_i F_{T_1}^{(1)} \Rightarrow m_i F_{T_1}^{(1)} + m_i \left(m_i^2 - \frac{3}{5} \right) F_{T_1}^{(3)} \text{ for } i = \{x, y, z\}.$$
 (15)

2.5. XAS and XMCD

The absorption cross section is obtained by the optical theorem as the imaginary part of the scattering amplitude F in forward direction,

$$\sigma = \frac{4\pi}{|\mathbf{k}|} \operatorname{Im}[\boldsymbol{\varepsilon}^* \cdot F(\mathbf{q} = 0, \hat{\mathbf{M}}, \omega) \cdot \boldsymbol{\varepsilon}].$$
(16)

Thus, the expressions for X-ray absorption are obtained by taking $\boldsymbol{\varepsilon}' = \boldsymbol{\varepsilon}$ in those for the scattering amplitude.

As an example, we give here the scattering amplitude for XMCD in orthorhombic symmetry (D_{2h}) . The tensor $\mathbf{F}^{(1)}$ has elements with irreps $B_1 = \{z\}, B_2 = \{y\}$ and $B_3 = \{x\}$, which gives a directional dependence of $\hat{\mathbf{M}}$ with respect to the crystal frame. The Cartesian scattering tensor along $C_2 \parallel \langle 001 \rangle$ is

$$\mathbf{F}_{D_2}^{(1)}(\hat{\mathbf{M}}) = \begin{vmatrix} 0 & -m_z F_{B_1}^{(1)} & m_y F_{B_2}^{(1)} \\ m_z F_{B_1}^{(1)} & 0 & -m_x F_{B_3}^{(1)} \\ -m_y F_{B_2}^{(1)} & m_x F_{B_3}^{(1)} & 0 \end{vmatrix} \Rightarrow \begin{pmatrix} m_x F_{B_3}^{(1)} \\ m_y F_{B_2}^{(1)} \\ m_z F_{B_1}^{(1)} \end{pmatrix},$$
(17)

where in the right-hand side the antisymmetric tensor is converted by index contraction $[\sum_{jk} \varepsilon^{ijk} a_j b_k \Rightarrow (\mathbf{a} \times \mathbf{b})_i$ with Levi-Civita symbol $\varepsilon^{ijk}]$ into an axial vector. Then, $F_{D_2}^{(1)}(\hat{\mathbf{M}}) = \sum_i P_i m_i F_i^{(1)}$, where $\mathbf{P} = -i(\boldsymbol{\varepsilon}^* \times \boldsymbol{\varepsilon})$ is the helicity vector.

The spin and orbital sum rules for XMCD are treated in van der Laan (2024) and the angular dependence of XMCD in van der Laan & Figueroa (2024). XMCD has become a workhorse technique in physics and materials science with vast applications, and reviews can be found in, for example, Stöhr & Siegmann (2006), van der Laan (2013*b*) and van der Laan & Figueroa (2014).

2.6. XMLD

For cubic crystal-field symmetry the scattering tensor $\mathbf{F}^{(2)}(\hat{\mathbf{M}}, \omega)$, given in equation (14), has diagonal elements with irrep *E* and nondiagonal elements with irrep *T*₂, so that the XMLD depends on the directions of $\boldsymbol{\varepsilon}$ and $\hat{\mathbf{M}}$ with respect to the crystal frame.

For arbitrary directions of $\boldsymbol{\varepsilon}$ and $\hat{\mathbf{M}}$ in cubic crystal-field symmetry the XMLD is a linear combination of two fundamental spectra, which are related to the threefold and fourfold symmetry axes (Arenholz *et al.*, 2006). In this case, the XMLD can be separated into an isotropic and an anisotropic part. The isotropic part is proportional to $2(\boldsymbol{\varepsilon} \cdot \hat{\mathbf{M}})^2 - 1$, which depends only on the included angle and is therefore rotationally invariant. The anisotropic part contains the dependence on the $\boldsymbol{\varepsilon}$ and $\hat{\mathbf{M}}$ directions with respect to the crystal axes. It vanishes in the absence of a crystal field. Notably, there is the curious case of the Ni²⁺ L_2 edge, where the XMLD only has an anisotropic part, and the $F_E^{(2)}$ and $F_{T_2}^{(2)}$ spectra have the same shape but opposite sign. Further details can be found in Haverkort *et al.* (2010) and van der Laan (2013*a*).

In symmetries lower than cubic, there are two distinctly different ways to obtain the XMLD, *i.e.*, by rotating the orientation of either the linear polarization or the magnetization, which give the charge or the magnetic anisotropy, respectively.

3. Electric and magnetic multipole fields

3.1. Multipole expansion

X-ray optical activity arises from the interference between different terms in the multipole expansion of the electromagnetic field. We will follow the derivation of Rose & Brink (1967) and van der Laan (2006) and present relevant results.

The Hamiltonian of a single particle in the presence of a classic electromagnetic field is

$$\mathcal{H} = \frac{1}{2m} \left[\mathbf{p} + \frac{e}{c} \mathbf{A}(\mathbf{r}) \right]^2 + \boldsymbol{\mu} \cdot \mathbf{H}(\mathbf{r}) + e\varphi(\mathbf{r}), \qquad (18)$$

where *e* is the charge and $\mu = g\beta \mathbf{S} = \frac{1}{2}g\beta\sigma$ is the spin magnetic moment of the particle, $\beta = e\hbar/2mc$ is the Bohr magneton, **A** and φ are the vector and scalar electromagnetic potential, respectively, and **r** is the electron position vector. In the following we will use natural units $\hbar = 1$. The gauge condition is taken such that $\varphi = 0$ and we neglect the two-photon process given by the \mathbf{A}^2 term. This leads to a kinetic energy term $\mathcal{H}_0 = \mathbf{p}^2/(2m)$ and an interaction Hamiltonian comprising a charge and spin term,

$$\mathcal{H}_{\rm int} = 2g_l \beta \mathbf{A} \cdot \mathbf{p} + g_s \beta \mathbf{S} \cdot (\mathbf{\nabla} \times \mathbf{A}), \tag{19}$$

where g_l and g_s are the orbital and spin g-factors. The aim is to expand the transverse plane wave **A** in a series of spherical vector fields \mathbf{A}_{LM}^E and \mathbf{A}_{LM}^M , thereby expressing the interaction Hamiltonian in a series of tensor operators \mathbf{T}_{LM}^E and \mathbf{T}_{LM}^M , which are the products of momentum **p** and spin **S** with the fields \mathbf{A}_{LM}^E and \mathbf{A}_{LM}^M .

We define the electric and magnetic multipole fields

$$\mathbf{A}_{LM}^{M} = \frac{1}{\left[L(L+1)\right]^{1/2}} \mathbf{L} \Phi_{LM},$$
(20)

$$\mathbf{A}_{LM}^{E} = \frac{1}{k} \nabla \times \mathbf{A}_{LM}^{M} = \frac{1}{k [L(L+1)]^{1/2}} \nabla \times \mathbf{L} \Phi_{LM}, \qquad (21)$$

where the scalar functions

$$\Phi_{LM} = i^L (2L+1) j_L(kr) C_{LM}(\theta, \varphi), \qquad (22)$$

satisfy the wave equation $\nabla^2 \Phi + k^2 \Phi = 0$ and form a complete set.

The expansion for circularly polarized vector plane waves with component q = 1 (right-handed) and q = -1 (left-handed) can be written as

$$\mathbf{A} = \boldsymbol{\varepsilon}_{q} \exp(i\mathbf{k} \cdot \mathbf{r})$$

$$= -\frac{1}{2^{1/2}} \sum_{LM} (q \mathbf{A}_{LM}^{M} + \mathbf{A}_{LM}^{E}) \mathcal{D}_{Mq}^{L}(R)$$

$$= -\frac{1}{2^{1/2}} \sum_{LM\pi} q^{\pi} \mathbf{A}_{LM}^{\pi} \mathcal{D}_{Mq}^{L}(R), \qquad (23)$$

where $\mathcal{D}_{Mq}^{L}(R)$ is the rotation matrix that takes the *z* axis into the direction of the vector **k**, and the index π in the compact expression runs over $E(\pi = 0)$ and $M(\pi = 1)$. The polarization

vectors are defined as $\boldsymbol{\varepsilon}_{\pm 1} = \mp (\varepsilon_x + i\varepsilon_y)/(2)^{1/2}$ and $\varepsilon_0 = \varepsilon_z$ are co(ntra)variant components: $\varepsilon_q^* = \varepsilon^q = (-)^q \varepsilon_{-q}$.

In the long-wavelength approximation, $kr \ll 1$, the spherical Bessel functions obtain the approximate value $j_L(kr) \approx (kr)^{L}/(2L + 1)!!$, so that the scalar potential Φ_{LM} takes the simplified form $\Phi_{LM} = r^L C_{LM} (ik)^{L}/(2L - 1)!!$. This gives for the interaction Hamiltonian

$$\mathcal{H}_{\text{int}} = -\frac{1}{2^{1/2}} \sum_{LM\pi} \mathcal{D}_{Mq}^{L}(R) [2g_{l}\beta q^{\pi} \mathbf{A}_{LM}^{\pi} \cdot \mathbf{p} + g_{s}\beta q^{\pi} \mathbf{S} \cdot (\mathbf{\nabla} \times \mathbf{A}_{LM}^{\pi})].$$
(24)

The charge and spin interactions of the electric and magnetic multipole fields result in a total of four terms in the interaction Hamiltonian,

$$\mathcal{H}_{\text{int}} = -\sum_{LM} \frac{(ik)^{L}}{(2L-1)!!} \left(\frac{L+1}{2L}\right)^{1/2} \\ \times \mathcal{D}_{Mq}^{L}(R) [Q_{LM} + Q'_{LM} - iq(M_{LM} + M'_{LM})], \quad (25)$$

with the electric (Q) and magnetic (M) multipole operators

$$Q_{LM} = eg_l(\mathbf{r}^L C_{LM}) = -2g_l\beta(i/k)\nabla(\mathbf{r}^L C_{LM}) \cdot \mathbf{p},$$

$$M_{LM} = 2\beta g_l\nabla(\mathbf{r}^L C_{LM}) \cdot \mathbf{L}/(L+1),$$

$$Q'_{LM} = -k\beta g_s \mathbf{L}(\mathbf{r}^L C_{LM}) \cdot \mathbf{S}/(L+1),$$

$$M'_{LM} = \beta g_s\nabla(\mathbf{r}^L C_{LM}) \cdot \mathbf{S},$$
(26)

where the unprimed and primed operators result from the charge and spin interactions, respectively. The Hamiltonian can be cast in a simplified form using the *interaction multipole* operators T_{LM}^{π} , with $\pi = 0$ for E and $\pi = 1$ for M, which are sets of operators all having the same transformation properties,

$$H_{int} = -\sum_{LM\pi} \mathcal{D}_{Mq}^{L}(R) q^{\pi} T_{LM}^{\pi},$$

$$T_{LM}^{E} = \alpha_{L}^{E}(Q_{LM} + Q'_{LM}),$$

$$T_{LM}^{M} = \alpha_{M}^{E}(M_{LM} + M'_{LM}),$$

$$\alpha_{L}^{E} = \frac{(ik)^{L}}{(2L-1)!!} \left(\frac{L+1}{2L}\right)^{1/2} \text{ and } \alpha_{L}^{M} = -i\alpha_{L}^{E}.$$
 (27)

Specifically, for the prefactor we have $\alpha_1^E = ik$, $\alpha_1^M = k$ and $\alpha_2^E = -k^2/2(3)^{1/2}$. We have the parity rules $P\Phi_{LM} = (-)^L \Phi_{LM}$, $PA_{LM}^E = (-)^L A_{LM}^E$ and $PA_{LM}^M = (-)^L A_{LM}^M$. The parity of $\mathbf{A}^E \cdot \mathbf{p}$ and $\mathbf{S} \cdot (\nabla \times \mathbf{A}^E)$ is $(-)^L$, whereas the parity of $\mathbf{A}^M \cdot \mathbf{p}$ and $\mathbf{S} \cdot (\nabla \times \mathbf{A}^M)$ is $(-)^{L+1}$. Therefore, the electric and magnetic 2^L -pole interaction operators T_{LM}^{π} connect states that differ in parity by a factor $(-)^{L+\pi}$. Thus *E*1 has odd parity, while *M*1 and *E*2 have even parity.

Using the expansion for the exponential

$$\exp(i\mathbf{k}\cdot\mathbf{r}) = 1 + i\mathbf{k}\cdot\mathbf{r} - \frac{1}{2}(\mathbf{k}\cdot\mathbf{r})^2 + \cdots, \qquad (28)$$

we can separate $\mathbf{A} \cdot \mathbf{p} = (\boldsymbol{\varepsilon} \cdot \mathbf{p}) \exp(i\mathbf{k} \cdot \mathbf{r})$ into the geometric and dynamic factors given in Table 1, using the tensor product notation defined in equation (5). The prefactor $\alpha_L^{E,M}$ is given in equation (27). The different orders *n* in the expansion are alternatingly imaginary and real. The parity operator gives $P(i, \boldsymbol{\varepsilon}, \mathbf{k}, \mathbf{p}, \mathbf{r}) = (i, -\boldsymbol{\varepsilon}, -\mathbf{k}, -\mathbf{p}, -\mathbf{r})$. The time-reversal operator gives $\theta(i, \boldsymbol{\varepsilon}, \mathbf{k}, \mathbf{p}, \mathbf{r}) = (-i, \boldsymbol{\varepsilon}^*, -\mathbf{k}, -\mathbf{p}, \mathbf{r})$, hence the Table 1

The *n*th-order geometric and dynamic factors in the $(\boldsymbol{\varepsilon} \cdot \mathbf{p})\exp(i\mathbf{k} \cdot \mathbf{r})$ expansion giving the different electric and magnetic multipole terms with rank *L* (*n* is the number of times that **k** appears).

The indicated parity is the same for the geometric and dynamic factor.

n	Term	Geometric factor	Dynamic factor	Parity
0	E1	e ⁽¹⁾	р	-1
1	M1	$[\mathbf{\varepsilon}, \mathbf{k}]^{(1)}$	$[\mathbf{p}, \mathbf{r}]^{(1)}$	+1
	E2	$[\boldsymbol{\varepsilon}, \mathbf{k}]^{(2)}$	$[\mathbf{p}, \mathbf{r}]^{(2)}$	+1
L	ML	$[\boldsymbol{\varepsilon}, \mathbf{k}^{(L)}]^{(L)}$	$[\mathbf{p}, \mathbf{k}^{(L)}]^{(L)}$	$(-)^{L+1}$
	E(L + 1)	$[\boldsymbol{\varepsilon}, \mathbf{k}^{(L)}]^{(L+1)}$	$[\mathbf{p}, \mathbf{k}^{(L)}]^{(L+1)}$	$(-)^{L+1}$

part $i^{L+1}\mathbf{k}^{L}\mathbf{p}$ of the interaction operator T_{LM}^{π} is always time-reversal even.

The zeroth-order contribution (n = 0) gives the E1 term $\varepsilon \cdot \mathbf{p} \propto i\omega \boldsymbol{\varepsilon} \cdot \mathbf{r}$. The geometric factor $\boldsymbol{\varepsilon}$ is parity-odd.

The first-order contribution (n = 1) can be factorized into a geometric factor $[\boldsymbol{\varepsilon}, \mathbf{k}]^{(L)}$ and a dynamic factor $[\mathbf{p}, \mathbf{r}]^{(L)}$, which are both parity-even. For L = 0, the geometric factor vanishes due to transversality, *i.e.* $\boldsymbol{\varepsilon} \cdot \mathbf{k} = 0$. The L = 1 term gives the magnetic dipole contribution (M1) with a geometric factor $[\boldsymbol{\varepsilon}, \mathbf{k}]^{(1)} \propto (\mathbf{k} \times \boldsymbol{\varepsilon})$ and a dynamic factor $[\mathbf{p}, \mathbf{r}]^{(1)} \propto (\mathbf{p} \times \mathbf{r}) \propto \mathbf{L}$. The L = 2 term yields the electric quadrupole contribution (E2) with a dynamic factor $[\mathbf{p}, \mathbf{r}]^{(2)} \propto \mathbf{L}^2 \propto$ the charge quadrupole.

Thus, the leading terms in the transition amplitude can be written as

$$\langle \mathbf{f} | \mathbf{A} \cdot \mathbf{p} | \mathbf{i} \rangle = -\frac{m}{\hbar} (E_{\mathrm{f}} - E_{\mathrm{i}}) \bigg[\langle \mathbf{f} | \boldsymbol{\varepsilon} \cdot \mathbf{r} | \mathbf{i} \rangle + \frac{i}{2} \langle \mathbf{f} | (\boldsymbol{\varepsilon} \cdot \mathbf{r}) (\mathbf{k} \cdot \mathbf{r}) | \mathbf{i} \rangle \bigg] - \langle \mathbf{f} | (\mathbf{k} \times \boldsymbol{\varepsilon}) \cdot (\mathbf{L} + g \mathbf{S}) | \mathbf{i} \rangle, \qquad (29)$$

where the first, second and third terms represent the electric dipole (*E*1), electric quadrupole (*E*2) and magnetic dipole (*M*1) transition amplitudes, respectively. The transition probability of *E*1 is much larger than those of *E*2 and *M*1. The *M*1 operator, with the monopole selection rules $\Delta J \leq 1$, $\Delta L = 0$, $\Delta S = 0$ and $\Delta n = 0$, does not contain a radial variable; therefore, its matrix element vanishes if the radial parts of the initial and final states are orthogonal. The *M*1 transition occurs only at low excitation energies and can be neglected in core-level spectroscopy, since it requires configuration interaction. The explicit angular dependence of the *E*1 and *E*2 transitions can be found in Brouder (1990).

According to Fermi's golden rule in quantum mechanics, the absorption cross section $\sigma(\omega)$ is given by the matrix element product of the interaction between the initial and the final state, summed over final states with the same energy,

$$\sigma(\omega) = \frac{4\pi^2 \hbar \alpha}{m^2 \omega} \sum_{f} \langle \mathbf{i} | \mathcal{H}_{int}^* | \mathbf{f} \rangle \langle \mathbf{f} | \mathcal{H}_{int} | \mathbf{i} \rangle \delta(E_f - E_i - \hbar \omega), \quad (30)$$

which contains interference terms such as E1M1 and E1E2.

3.2. Symmetry of multipole transitions

The ELEL' absorption cross section can be written as

$$\sigma_{ELEL'} = \sum_{b=|L-L'|}^{L+L'} \sum_{\beta=-b}^{b} (-)^{\beta} \sum_{\tau=0,1} \mathbf{T}_{\beta}^{(b,\tau)} \sigma_{-\beta}^{(b,\tau)}, \qquad (31)$$

Table 2 The different optic

The different optical effects.

The phase factors for parity $(-)^{\Pi}$ and time reversal $(-)^{\tau}$ with corresponding multipole transitions. Pure and interference terms of the radiation-matter interaction are parity even and odd, respectively. *M* means sample magnetization (time-reversal odd). The corresponding spectra are the X-ray magnetic linear dichroism (XMLD), X-ray magnetic circular dichroism (XMCD), X-ray natural linear dichroism (XMLD) and nonreciprocal linear dichroism (NRLD).

Parity	Transition	Optical effect	Spectra
+1	+1	E1E1 + E2E2	XAS, XMLD
+1	-1	(E1E1 + E2E2)M	XMCD
-1	+1	E1M1 + E1E2	XNCD
-1	-1	(E1M1 + E1E2)M	NRLD, XΜχD

where the tensors $\mathbf{T}_{\beta}^{(b,\tau)}$ and $\boldsymbol{\sigma}_{-\beta}^{(b,\tau)}$ give the geometric and dynamic factor, respectively, of rank *b* and time-reversal phase factor $(-)^{\tau}$. For the squared matrix elements in equation (30) the geometric factor (*c.f.* Table 1)

$$\mathbf{T}_{\beta}^{(b,\tau)} = \left[\left[\boldsymbol{\varepsilon}^*, \mathbf{k}^{(L-1)} \right]^{(L)}, \left[\boldsymbol{\varepsilon}, \mathbf{k}^{(L'-1)} \right]^{(L')} \right]_{\beta}^{(b,\tau)}$$
(32)

with parity condition $(-)^{\Pi} = (-)^{L+L'}$. The time-reversal symmetry can be even $(\tau = 0)$ or odd $(\tau = 1)$. As $\mathbf{T}_{\beta}^{(b,\tau)}$ in equation (32) does not have a well defined behaviour under time reversal, we recouple it to the form

$$\mathbf{X}_{\beta}^{(b,\tau)} = \left[\left[\boldsymbol{\varepsilon}^*, \, \boldsymbol{\varepsilon} \right]^{(a)}, \, \mathbf{k}^{(N)} \right]_{\beta}^{(b,\tau)}, \tag{33}$$

where N = L + L' - 2 is the number of times that **k** appears in the geometric factor. The tensor **X** has the triangle condition, $|N - a| \le b \le N + a$. The parity condition is $(-)^{\Pi} = (-)^{N}$. The time-reversal condition is

$$(-)^{\tau} = (-)^{a+N} = (-)^{a+\Pi}.$$
 (34)

For a = 0, we have $\boldsymbol{\varepsilon}^* \cdot \boldsymbol{\varepsilon} = 1$ and the geometric factor $\mathbf{k}^{(N)}$ is polarization-independent, so that we obtain $(-)^{\tau} = (-)^{b} = (-)^{N} = (-)^{\Pi}$. Thus, these indices must be either all even or all odd. An even value corresponds to the normal spectrum, while an odd value corresponds to the XM χ D.

For a = 1, we have $(\boldsymbol{\varepsilon}^* \times \boldsymbol{\varepsilon}) \propto i\mathbf{k}$. This gives a *chiral effect*, defined as one in which the intensity contribution is reversed by conjugating the polarization vectors (Stedman, 1990). Since $\mathbf{k} \times \mathbf{k}^{(N)} = 0$ we have $b = N \pm 1$, and using $(-)^{\tau} = (-)^{N+1}$ we obtain $b + \tau$ is even. Equation (34) leads to two different possibilities for the chiral effect. The first is $\Pi = 0$ and $\tau = 1$, which gives magnetic circular dichroism (MCD) with *b* odd and *N* even. The second possibility is $\Pi = 1$ and $\tau = 0$, which gives the natural circular dichroism (NCD) with *b* even and *N* odd (*c.f.* Table 2).

For a = 2 we have $(-)^{\tau} = (-)^{\Pi} = (-)^{N}$, while *b* can have different values. b = 1 contributes to the XM χ D and b = 2 and b = 3 contribute to the XMLD.

In the case that L = L', the parity is even so that $(-)^{\tau} = (-)^{a}$, hence τ is even and odd for even and odd *a*, respectively. In the special case N = 0 (*i.e.* E1E1) we have $\mathbf{T}^{(b,\tau)} = [\boldsymbol{\varepsilon}^*, \boldsymbol{\varepsilon}]^{(a)}$, hence a = b. For the isotropic spectrum (a = 0) the sum rule gives the number of particles *n* (Thole & van der Laan, 1988). For the X-ray magnetic circular dichroism (XMCD; a = 1) the

Table 3 Linear combinations of spectra with reversing helicity vector λ and magnetization *M*.

Spectra	Linear combinations
Sum	$\lambda^{+}M^{+} + \lambda^{+}M^{-} + \lambda^{-}M^{+} + \lambda^{-}M^{-} = (\lambda^{+} + \lambda^{-})(M^{+} + M^{-})$
XNCD	$\lambda^{+}M^{+} + \lambda^{+}M^{-} - \lambda^{-}M^{+} - \lambda^{-}M^{-} = (\lambda^{+} - \lambda^{-})(M^{+} + M^{-})$
XMχD	$\lambda^{+}M^{+} - \lambda^{+}M^{-} + \lambda^{-}M^{+} - \lambda^{-}M^{-} = (\lambda^{+} + \lambda^{-})(M^{+} - M^{-})$
XMCD	$\lambda^+ M^+ - \lambda^+ M^ \lambda^- M^+ + \lambda^- M^- = (\lambda^+ - \lambda^-)(M^+ - M^-)$

sum rule gives the orbital moment **L** (Thole *et al.*, 1992). For the X-ray magnetic linear dichroism (XMLD; a = 2) the sum rule gives the quadrupole moment $Q \propto \mathbf{L}^2$ (Carra *et al.*, 1993; van der Laan, 1999).

All interference terms have N odd, so that $(-)^{\tau} = (-)^{a+1}$, *i.e.* $\tau + a$ is odd, hence τ is even and odd for odd and even a, respectively.

The effective operators which form the sum-rule results can be built from the triad of mutually orthogonal vector operators (Goulon *et al.*, 2003; Carra *et al.*, 2003): $\mathbf{n} = \mathbf{r}/r$, which is a time-even, polar vector, typically associated with the electric dipole moment, the orbital angular momentum \mathbf{L} , which is a time-odd, axial vector, and the toroidal vector $\mathbf{\Omega} = \frac{1}{2}[(\mathbf{n} \times \mathbf{L}) - (\mathbf{L} \times \mathbf{n})] = \frac{1}{2}i[\mathbf{n}, \mathbf{L}^2]$, which is odd with respect to both inversion and time reversal and is proportional to the orbital anapole moment.

The *E*1*E*2 interference has a geometric factor $\mathbf{T}_{\beta}^{(b,\tau)} = [\boldsymbol{\varepsilon}^*, [\boldsymbol{\varepsilon}, \mathbf{k}]^{(2)}]_{\beta}^{(b,\tau)}$ and the multipole selection rules impose a mixing (hybridization) between *l* and *l* + 1 valence levels. The following results have been reported (Goulon *et al.*, 2003; Carra *et al.*, 2003).

The X-ray magnetochiral dichroism (XM χ D) sum rule involves the ground-state expectation value of the toroidal vector $\mathbf{\Omega}^{(1,\tau=1)}$ with a geometric factor $\mathbf{T}_0^{(1,\tau=1)} = -\frac{1}{2} \left(\frac{3}{5}\right)^{1/2} \mathbf{k}$, associated with the Stokes component S_0 .

The XNCD sum rule gives the expectation value of the time-even pseudodeviator $\mathbf{N}^{(2,\tau=0)} = [\mathbf{L}, \mathbf{\Omega}]^{(2)}$ and $\mathbf{T}^{(2,\tau=0)} = \frac{1}{2}(3)^{1/2}[[\boldsymbol{\varepsilon}^*, \boldsymbol{\varepsilon}]^{(1)}, \mathbf{k}]_0^{(2)}$.

For the nonreciprocal XMLD the effective operator must be a time-odd pseudodeviator $\mathbf{W}_{\pm 2}^{(2,\tau=1)} = [\mathbf{L}, \mathbf{n}]^{(2)}$ and $\mathbf{T}_{\pm 2}^{(2,\tau=1)} = \frac{1}{2}[[\boldsymbol{\varepsilon}^*, \boldsymbol{\varepsilon}], \mathbf{k}]_{\pm 2}^{(3)}$.

An effective operator $\Gamma^{(3,\tau=1)} = [[\mathbf{L}, \mathbf{L}]^{(2)}, \mathbf{\Omega}]^{(3)}$ is involved in the sum rules for both XM χ D and nonreciprocal XMLD.

3.3. X-ray optical activity

The results in Section 3.2 permit a simple physical description of the optical effects. Pure transitions must have even parity. The only way of inducing natural (field-independent) optical activity is by interference between multipoles of different order in the *k*-expansion of the photon wavevector. Only the interference of a real and an imaginary term T_{LM}^{π} can lead to odd parity. The *E*1*M*1 interference in the visible region allows the detection of natural circular dichroism and optical rotation, such as in the well known example of a sugar solution. Although in the visible region the *E*2 transitions are negligibly small, their magnitude increases with photon energy, so that for harder X-rays the *E*1*E*2 interference can be observed. We can distinguish the different optical effects by

Table 4	
Character table for the point group $D_2 = C_2 \otimes C_2$	C_2 .

Invariance or reversal with respect to $\{\lambda, M\}$ is indicated by 1 and -1, respectively. *E* is the identity operator. The irreducible representations, with irrep labels A_1 and B_n , correspond to the various spectra. Also note that λ is time-even and parity-odd, while *M* is time-odd and parity-even.

	Ε	М	λ	$M\otimes\lambda$	Spectrum
A_1	1	1	1	1	XAS
B_1	1	1	-1	-1	XNCD
$\dot{B_2}$	1	-1	1	-1	XMχD
$\tilde{B_3}$	1	-1	-1	1	XMCD

their properties under space inversion and time reversal, as given in Table 2.

As a general rule, dichroism can only exist if there is no symmetry that reverses only one measurable observable but leaves the rest of the system unchanged. In the Faraday effect the time-reversal operator reverses both the magnetization and the direction of the light, thereby leaving the total physical system invariant. In natural circular dichroism, the parity operator reverses the rotation angle (screw sense) of both the medium and the light, again leaving the total system invariant. Nonzero effects only show up in crystals that have the appropriate symmetry class. Nonreciprocal optical effects invoke magnetic moments, since they are time non-invariant. They are characterized by a reversal of the phase rotation when the light propagates in the opposite direction, such as in the Faraday rotation in transmission or the Kerr effect in reflection. Magnetic circular dichroism (MCD), the difference in absorption for left- and right-circularly polarized light in the presence of an external magnetic field, also belongs to this category. Nonreciprocal optical effects are not restricted to media that possess a net magnetic moment, such as ferromagnets and ferrimagnets. Magnetoelectric antiferromagnets belong to the special class of magnetic ordered materials where there is no net magnetic moment but, in addition to time reversal, the parity symmetry is also broken, while the combined symmetry operation is conserved. Goulon et al. (2000) reported a nonreciprocal transverse anisotropy in the low-temperature antiferromagnetic insulating phase of a chromium-doped V₂O₃ crystal in which one single antiferromagnetic domain was grown by magnetoelectric annealing.

3.4. A group-theoretical viewpoint

Here, we show how to distinguish experimentally between the different optical effects. Reversing the photon helicity vector λ and the magnetization M gives the spectra shown in Table 3, where the superscripts + and – indicate an alignment along the positive and negative direction. These spectra are symmetric (even) or antisymmetric (odd) in λ and M. Note the difference between this table, where the parity comes from the helicity vector, and Table 2, where even and odd parity is connected to pure and mixed multipole transitions, respectively.

By symmetry, the different spectra correspond to the irreducible representations of the point group $D_2 = C_2 \otimes C_2$, for which the character table is shown in Table 4. Even and odd functions are indicated by 1 and -1, respectively.

international tables

Table 4 shows that the XMCD is the difference between spectra with M and λ parallel and antiparallel, respectively. Therefore, it is odd in both λ and M, but even in $M \otimes \lambda$. The XNCD is the difference between spectra with opposite λ and is independent of M. The XM χ D is the difference between spectra with opposite M and is independent of λ ; hence, it can be measured using linear polarization.

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