



HAL
open science

Simulation of magnetic circular dichroism in the electron microscope

Stefano Rubino, Peter Schattschneider, Jan Ruzs, Johan Verbeeck, Klaus Leifer

► **To cite this version:**

Stefano Rubino, Peter Schattschneider, Jan Ruzs, Johan Verbeeck, Klaus Leifer. Simulation of magnetic circular dichroism in the electron microscope. *Journal of Physics D: Applied Physics*, 2010, 43 (47), pp.474005. 10.1088/0022-3727/43/47/474005. hal-00570716

HAL Id: hal-00570716

<https://hal.science/hal-00570716>

Submitted on 1 Mar 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Simulation of magnetic circular dichroism in the electron microscope

Stefano Rubino

Dept. of Engineering Sciences, Uppsala University, Box 534, S-75121 Uppsala, Sweden

E-mail: stefanorubino@yahoo.it

Peter Schattschneider

Inst. für Festkörperphysik und Univ. Serviceeinrichtung für Elektronenmikroskopie, Technische Universität Wien, A-1040 Vienna, Austria

Jan Rusz

Dept. of Physics and Astronomy, Uppsala University, Box , S-75121 Uppsala, Sweden

Johan Verbeeck

EMAT, University of Antwerp, B-2020 Antwerpen, Belgium

Klaus Leifer

Dept. of Engineering Sciences, Uppsala University, Box 534, S-75121 Uppsala, Sweden

Abstract. As Electron Energy-Loss Spectroscopy (EELS) and X-ray Absorption Spectroscopy (XAS) probe the same transitions from core-shell states to unoccupied states above the Fermi energy, it should be always possible to apply the two techniques to the same physical phenomena, such as magnetic dichroism, and obtain the same information. Indeed, the similarity in the expression of the electron and x-ray cross-sections had been already exploited to prove the equivalence of X-ray Magnetic Linear Dichroism (XMLD) and anisotropy in EELS, by noting that the polarization vector of a photon plays the same role as the momentum transfer in electron scattering. Recently, the same was proven true for X-ray Magnetic Circular Dichroism (XMCD) by establishing a new TEM technique called EMCD (Electron energy-loss Magnetic Chiral Dichroism) [?], which makes use of special electron scattering conditions to force the absorption of a circularly polarized virtual photon.

The intrinsic advantage of EMCD over XMCD is the high spatial resolution of electron microscopes, which are readily available. Among the particular obstacles in EMCD that do not exist for synchrotron radiation is the notoriously low signal and the very particular scattering conditions necessary to observe a chiral dichroic signal. In spite of that, impressive progress was made in the last years. The signal strength could be considerably increased, and some innovations such as using a convergent beam have been introduced. EMCD has evolved into several techniques, which make full use of the versatility of the TEM and energy filtering, spectroscopy or STEM conditions [?].

1. Introduction

Dichroism is the property of certain materials that their photon absorption spectrum depends on the polarization of the incident radiation. We distinguish between linear and circular dichroism (LD and CD respectively) when the spectral changes arise as a response to a change in the direction of the polarization vector \vec{e} (LD) or a change in the helicity of the exciting radiation (CD). **Magnetic** dichroism is dichroism induced by the presence of a magnetic field (either external or intrinsic magnetization) and can be both linear or circular. In the case of XMCD the absorption cross section of a ferromagnet or a paramagnet in a magnetic field changes when the helicity of a circularly polarized probing photon is reversed relative to the magnetization. This should not be confused with the Faraday effect (a property of all matter) where photons with opposite helicities travel with different speeds in the direction parallel to the magnetic field. The physical origin of XMCD can be explained as follow: the magnetic field \vec{B} creates a difference in the population and availability of states with different spin orientation with respect to \vec{B} . Core shell electrons can be excited to available states above the Fermi energy by using photons of appropriate energy, typically a few hundreds or thousands of eV, depending on the atomic number Z and electronic shell (K, L, M, ...), meaning that x-rays are to be used. If the photoelectron thus emitted has a well defined spin, the probability of transition will be proportional to the corresponding spin-polarized Density of States (DoS). A circularly polarized photon carries a quantum of angular momentum that is absorbed by the photoelectron, resulting in specific selection rules (specifically, $\Delta m = 1$ for positive helicity and $\Delta m = -1$ for negative helicity). This perturbation does not act on the spin space and therefore one would expect that the photoelectron maintains its spin polarization (*i.e.* the absorption does not cause spin flip). This is indeed the case, however spin-orbit coupling complicates the situation as l and s are no longer good quantum numbers and therefore the initial core shell states will be a mixture of $|l, s, m_l, m_s\rangle$ states, meaning that the photoelectron will not be in a well defined spin state. It can be shown that, by calculating the transition probability of each component, the emitted photoelectron is polarized and that its polarization changes when the helicity of the x-rays is changed. For a more rigorous and detailed derivation, see for example ref. [?]. In the following section we will demonstrate how EMCD excites the same transitions as XMCD through the absorption of a virtual circularly polarized photon. Therefore all considerations made in this paragraph can be extended to EMCD. The theoretical prediction that circular magnetic dichroism could be observed by using circularly polarized x-ray photons was made by Erskine and Stern in 1975 [?]. The first experimental observation of the predicted effect was reported twelve years later by G. Schütz [?] studying the XMCD effect on the K edge of Fe. The sum rules, necessary to extract the information about the magnetic moment of the specimen, were derived about five years later [?, ?]. The experimental confirmation of the validity of the sum rules followed shortly thereafter [?]. Around the same years came the realization that XMLD and EELS anisotropy were two facets of the same phenomenon, because of the

similarity between photon polarization \vec{e} and momentum transfer \vec{q} [?].

However, it wasn't until ten years later that the same could be done for XMCD, because it was erroneously presumed that extending such equivalence to circular dichroism would require a beam of spin polarized electrons, which hasn't been developed yet for the TEM. As mentioned before, we need not act on the spin space to obtain a CD signal. Once this was understood, the way for EMCD was opened and rapid progress quickly followed: its theoretical prediction was published in 2003 [?], followed the same year by the first chiral TEM measurement [?] and the definitive experimental confirmation of the effect was made known less than three years later [?]. The sum rules for EMCD [?] were then presented in 2007, as well as a number of adaptations of EMCD to several already well established (S)TEM techniques: LACDIF [?], CBED [?], EFTEM [?], chiral STEM [?], quantitative EMCD [?]. In many cases, this rapid progress was simply a matter of adapting the particular scattering conditions required for EMCD to already existing techniques or theory. In some respects, EMCD measurements could be considered a special case of angular resolved EELS [?, ?, ?].

2. Basis for the equivalence between x-ray absorption and electron scattering

The theoretical framework behind both XMCD and EMCD can be derived from the Fermi Golden Rule applied to electronic transitions between atomic core states $|i\rangle$ and unoccupied free states $|f\rangle$ above the Fermi Energy, be it band states, molecular orbitals or the plane waves of the continuum. This derivation can be found in textbooks on Quantum Mechanics and will not be reproposed here.

It can be shown that the absorption cross-section σ for x-rays is:

$$\sigma \propto \omega \sum_{i,f} |\langle f | \vec{e} \cdot \vec{R} | i \rangle|^2 \delta(E + E_i - E_f) \quad (1)$$

where ω is the angular frequency of the photon, \vec{R} the quantum mechanical position operator and \vec{e} the polarization vector, *i.e.* the direction of the associated oscillating electric field \vec{E} (not to be confused with the energy E).

A similar expression is derived for the Double Differential Scattering Cross-Section for electron diffraction in the plane wave approximation [?, ?, ?]:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{4\gamma^2 k_f}{a_0^2 k_i} \frac{S(\vec{q}, E)}{q^4} \quad (2)$$

with

$$S(\vec{q}, E) = \sum_{i,f} |\langle i | e^{i\vec{q} \cdot \vec{R}} | f \rangle|^2 \delta(E_f - E_i - E) \quad (3)$$

where $\vec{q} = \vec{k}_f - \vec{k}_i$ is the difference (wave vector transfer) between final wave vector \vec{k}_f and initial wave vector \vec{k}_i of the fast electron; $\gamma = 1/\sqrt{1 - v^2/c^2}$ is a relativistic factor and a_0 is the Bohr radius. The $S(\vec{q}, E)$ is the Dynamic Form Factor (DFF) [?]. If we

Table 1. Examples of polarizations and corresponding Jones vectors. For convenience, the identity $i = e^{i\frac{\pi}{2}}$ is used.

Polarization	Jones vector
Linear polarized in the x-direction	(1, 0)
Linear polarized in the y-direction	(0, 1)
Linear polarized at an angle θ from the x-axis	($\cos \theta$, $\sin \theta$)
RCP	(1, i)
LCP	(1, $-i$)

take the first two Taylor components of the exponential term in the matrix element of eq. 2, we obtain the DFF in the so-called *dipole approximation*:

$$e^{i\vec{q}\cdot\vec{R}} = \hat{1} + i\vec{q}\cdot\vec{R} + \dots$$

$$S(\vec{q}, E) = \sum_{i,f} |\langle i|\vec{q}\cdot\vec{R}|f\rangle|^2 \delta(E_f - E_i - E) \quad (4)$$

assuming orthogonality between initial and final states. A comparison with eq. 1 leads to the conclusion that the momentum transfer $h\vec{q}$ in electron scattering is the equivalent of the polarization vector \vec{e} for photons. From the basis of this observation it has been possible to establish a correspondence between x-ray and electron magnetic linear dichroism (respectively XMLD and EMLD), the latter most commonly referred to as *EELS anisotropy* in the TEM community [?, ?].

3. Polarization of photons

The polarization vector \vec{e} can be conveniently described as a two-dimensional complex vector known as *Jones vector*:

$$\vec{e} = a_1 e^{i\theta_1} E_x + a_2 e^{i\theta_2} E_y = e^{i\theta_1} (a_1 E_x + a_2 e^{i\Delta\theta} E_y). \quad (5)$$

Here a_1 and a_2 denote the oscillation amplitudes of the two components of the electric field vector $\vec{E} = (E_x, E_y)$, while θ_1 and θ_2 represent the phases and $\Delta\theta = \theta_2 - \theta_1$ the relative phase. It is clear that the polarization state only depends on the relative phase; moreover, since the polarization is always perpendicular to the direction of propagation, Jones vectors are normally given as two-component vectors, of which the first is real. Some examples are shown in table 1, where right-/left-handed circularly polarized light (RCP/LCP) indicates an electric field rotating clockwise/counterclockwise when looking in the direction of propagation.

In some cases it is more convenient to redefine Jones vectors by expressing the polarization as superposition of RCP and LCP light. In this case, linear polarization forming an angle θ with the x axis (third example in table 1) would be represented as:

$$\vec{e}_\theta = a(\vec{e}_{RCP} + e^{i2\theta}\vec{e}_{LCP}) \quad (6)$$

4. Polarization in electron scattering

From eq. 5 and table 1 it becomes clear then that to obtain circularly polarized excitation in the TEM one has to achieve the following:

$$\vec{q}_{RCP} = q_x + iq_y \quad (7)$$

$$\vec{q}_{LCP} = q_x - iq_y. \quad (8)$$

What is the physical significance of eqs. 7, 8? Whereas eq. 5 is of simple interpretation, the same cannot be said for eqs. 7, 8. We can easily visualize how the electric field \vec{E} associated to a single photon is rotating perpendicular to the direction of propagation. In fact, as \vec{E} is the driving agent for the electronic transition, the same must hold true for a chiral electron scattering excitation [?]. However, for the momentum transfer of a single electron scattering event, different components are scattered in different directions (*i.e.* different points in reciprocal space) and all components are in phase. But this is not what eqs. 7, 8 require. They simply state that the equivalent of the absorption of a RCP/LCP photon will take place when the atom is excited by two momentum transfers perpendicular to each other and dephased by $\pi/2$. These two transfers need not be from the same electron wave, they could come from two beams propagating in two slightly different directions and dephased by $\pi/2$ with respect to each other. If they simultaneously transfer momentum to the atom, the transfers will be dephased by the same amount. If an EELS detector is placed in particular points of the reciprocal space, these two transfers will also be perpendicular to each other, fig. 1.

There are different methods by which one can obtain two coherent electron beams with a specific phase shift in the TEM, however the only one so far successfully employed for EMCD is the so called *intrinsic way*: the specimen itself, when crystalline in nature, acts as beam splitter, phase tuner and target [?, ?, ?]. This method has the drawback of imposing additional requirements on the samples, namely that the area excited or observed be single crystalline. However these requirements become less stringent when using EMCD techniques that probe small areas. When the electron beam enters a crystal, it becomes a coherent superposition of *Bloch waves* having the same periodicity of the crystal (in the approximation that the crystal is infinite in the x and y direction). Each of this Bloch wave can be taken as an electron beam \vec{k}_i (now with $i = 1, 2, \dots$) capable of transferring momentum to the atom by being scattered in the direction \vec{k}_f . This direction can be easily fixed by placing the EELS detector on a specific point in the diffraction plane. In practice, this is accomplished by projecting the diffraction pattern (*i.e.* the back focal plane of the objective lens) onto the spectrometer entrance aperture (SEA) and using the diffraction deflection coils to adjust the position of the SEA with respect to the transmitted beam (fig. 2). If the SEA is placed on the so-called *Thales circle*, *i.e.* the smallest circle in the diffraction plane passing through the two beam directions, the momentum transfers from the two beams will be perpendicular to each other. Two points on such circle have the additional property that they are equidistant

Figure 1. Scattering geometry for the EMCD experiment. Left: two incident plane waves, with wave vectors \vec{k}_1 and \vec{k}_2 , produce each an oscillating electric field (E_1 and E_2 which can be taken as the E_x and E_y of eqs. 5, 7 and 8) at the atom. Middle: an aperture is then placed in the diffraction plane to select the final scattering direction (\vec{k}_f) so that \vec{q}_1 and \vec{q}_2 (and therefore also E_1 and E_2) are perpendicular to each other. Right: when the phase shift between the two incident waves is set to $\pi/2$, their respective wavefronts are displaced in space by a quarter of the wavelength λ and the total electric field at the atomic site is rotating.

from the two beams and they in fact correspond to RCP and LCP excitation (assuming G is dephased by $\pi/2$ with respect to the transmitted beam); they have been named respectively A (or σ^+) and B (or σ^-) in fig. 2. Any other position of the SEA in the diffraction plane would correspond to elliptical polarization; with the particular case of the SEA lying on the q_x axis corresponding to linear polarization. Since any polarization state can be thought as superposition of RCP and LCP (as was shown for example in eq. 6), it follows that the maximum of MCD can be expected for pure RCP or LCP

states, *i.e.* for the two points A and B on the Thales circle. However, this is only valid in the approximation of two plane waves dephased by $\pi/2$. When we generalize to the many beams case and different dephase values, the maximum (and minimum) of the EMCD signal is shown to appear in other regions of the diffraction plane.

Figure 2. In the diffraction plane, two electron plane waves propagating in two slightly different directions \vec{k}_1 and \vec{k}_2 appear as two bright spots here indicated as 000 and G respectively. The size of the spot is directly related to the convergence angle. The direction from 000 to G defines the q_x axis and the systematic row. The 000-G segment is the diameter of the Thales circle. Placing an aperture in the diffraction plane defines \vec{k}_f and the collection angle. If the aperture is placed on the circle at an equal distance from 000 and G, the points A (σ^+) and B (σ^-) are obtained. If G is dephased by $\pi/2$ with respect to 000, these two points correspond to RCP and LCP excitation respectively.

Fig. 2 also shows that a very easy way for switching from RCP to LCP excitation is to simply shift the SEA from A to B. This is an important fact as the EMCD signal is defined as the difference between spectra with opposite helicity and therefore requires the acquisition of two spectra.

5. Bloch waves and the Mixed Dynamic Form Factor

The amplitude and phase of each of the Bloch wave is determined by the boundary conditions, *i.e.* thickness of the crystal and orientation with respect to the incident beam. This information is contained in the *Bloch wave coefficients*, that is, the coefficients of the decomposition of the incident beam into Bloch waves [?]. The Bloch wave decomposition has an infinite number of terms, but truncating to the first few terms is usually a good approximation. It is possible to select an orientation for which the decomposition can be truncated after the first two or three terms. These orientations are called two-beam case or three-beam case (2BC or 3BC respectively). A more general case is the so called *systematic row*, where the decomposition only includes Bloch waves

for reciprocal lattice vectors along a common direction (*i.e.* \mathbf{G} , $-\mathbf{G}$, $2\mathbf{G}$, $-2\mathbf{G}$, etc.). When simulating dynamical diffraction effects, it is sometimes advantageous to limit the diffraction spots \mathbf{G} to the zero order Laue zone (ZOLZ).

If we substitute eqs. 7, 8 in eq. 4 we obtain an interference term proportional to the imaginary part of a generalized DFF, the so called Mixed Dynamic Form Factor (MDFF) $S(\vec{q}, \vec{q}', E)$ [?].

$$S(\vec{q}, \vec{q}', E) = \sum_{i,f} \langle i | \vec{q} \cdot \vec{R} | f \rangle \langle f | \vec{q}' \cdot \vec{R} | i \rangle \delta(E_f - E_i - E) \quad (9)$$

With this substitution eq. 2 can be written as:

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} = \frac{4\gamma^2 k_f}{a_0^2 k_i} \left\{ \frac{S(\vec{q}, E)}{q^4} + \frac{S(\vec{q}', E)}{q'^4} \pm 2\Im \left[\frac{S(\vec{q}, \vec{q}', E)}{q^2 q'^2} \right] \right\}. \quad (10)$$

The sign in front of the interference term depends on the helicity of the excitation (RCP or LCP). In general the two terms will have different, complex amplitudes A_1 and A_2 determined by the Bloch coefficients. In this case we have:

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} = \frac{4\gamma^2 k_f}{a_0^2 k_i} \left(|A_1|^2 \frac{S(\vec{q}, E)}{q^4} + |A_2|^2 \frac{S(\vec{q}', E)}{q'^4} - 2\Re[A_1 A_2^* \frac{S(\vec{q}, \vec{q}', E)}{q^2 q'^2}] \right), \quad (11)$$

which reduces to eq. 10 when we take $A_1 = 1$ and $A_2 = \pm i$. The dichroic signal is obtained as the difference between spectra with opposite polarizations, divided by their sum. The polarization change is usually obtained by switching \vec{q} with \vec{q}' (or equivalently A_1 with A_2).

$$\sigma_{\text{dich}} := \frac{\sigma^+ - \sigma^-}{\sigma^+ + \sigma^-} := \frac{\Delta\sigma}{2\langle\sigma\rangle}. \quad (12)$$

In the case of pure RCP and LCP difference (eq. 10), this gives:

$$\sigma_{\text{dich}} = \frac{2\Im \left[\frac{S(\vec{q}, \vec{q}', E)}{q^2 q'^2} \right]}{\frac{S(\vec{q}, E)}{q^4} + \frac{S(\vec{q}', E)}{q'^4}}, \quad (13)$$

that is, the dichroic signal originates entirely from the imaginary part of the MDFF. In the more general case of (eq. 11), this gives:

$$\sigma_{\text{dich}} = \frac{2\Im[A_1 A_2^*] \Im \left[\frac{S(\vec{q}, \vec{q}', E)}{q^2 q'^2} \right]}{|A_1|^2 \frac{S(\vec{q}, E)}{q^4} + |A_2|^2 \frac{S(\vec{q}', E)}{q'^4} + 2\Re[A_1 A_2^*] \Re \left[\frac{S(\vec{q}, \vec{q}', E)}{q^2 q'^2} \right]}. \quad (14)$$

This means that the absolute difference only depends on the imaginary part of the MDFF, but an incomplete circular polarization gives a lower dichroic signal both because of the prefactor in the nominator and because of the additional term in the denominator. It is useful to stress that the Bloch coefficients determine the intensity

and phase of each Bloch wave in the crystal and even in the favourable case of only two waves with equal intensity and dephased by $\pi/2$ the equivalent polarization could be elliptical if \vec{k}_f is not properly chosen.

Figure 3. Simulation of the imaginary (upper row) and real (lower row) part of the interference term in eq. 10 as function of q_x, q_y (in units of G). Note how the imaginary part is antisymmetric with respect to the q_x axis, whereas the real part is symmetric with respect to both the q_x and q_y axes. The interference term is undetermined at the 0 and G diffraction spots (respectively at 0,0 and 1,0 in units of G).

It can be shown that the real part of the MDFD is proportional to the scalar product of \vec{q} and \vec{q}' , whereas the imaginary part is proportional to their vector product $\vec{q} \times \vec{q}'$ [?]. We can use the dipole approximation to calculate the real and imaginary part of the MDFD in a simple 2BC, where only the direct beam (000) and one diffracted beam (G) are strongly excited. Because of the properties of the vector and scalar products, the imaginary part of the MDFD is simply proportional to q_y , whereas the real part is negative inside the Thales circle (with a minimum at its centre), zero on the circle itself and positive outside. To obtain the real and imaginary part of the interference term in eqs. 10, 11 we just divide by $q^2 q'^2$ and multiply by the eventual Bloch coefficients.

The results are shown in fig. 3. The real part of the interference term has two mirror axes, one along x and one along y . The imaginary part is symmetric by inversion of x but antisymmetric by inversion of y . This antisymmetric behaviour originates from the pseudovectorial nature of the vector product, which changes sign when we switch \vec{q} with \vec{q}' . The dichroic signal can be calculated as well and is shown in fig. 4 together with the signal-to-noise ratio (S/N) that would be expected from just Poissonian noise. Now each point in the plot of σ_{dich} has been obtained by taking the difference (divided by the sum) with the corresponding point having the same q_x coordinate but opposite q_y coordinate. Each pixel of the dichroic map defines a different \vec{k}_f and therefore a different set of \vec{q} and \vec{q}' ; as mentioned before, RCP and LCP excitation can only be achieved at the points A and B of the Thales circle and, in fact, the dichroic signal has a maximum and a minimum at those two points. All other points have elliptical polarization and can be thought as superposition of RCP and LCP, which cancel each other out. When the superposition has equal weights for RCP and LCP (as it is the case for linear polarization along the systematic row, *i.e.* for $q_y = 0$) the dichroic signal is zero.

The situation becomes more complicated if we take into account a more real case where more than two beams are excited. If we take only the difference at the points A and B of the Thales circle, we can plot the intensity of the dichroic signal as function of crystal thickness and orientation in systematic row approximation. The Laue Circle Centre (LCC) is the projection of the centre of the Ewald sphere on the zero order Laue zone and it is used to indicate the fine tilt with respect to a given zone axis [?].

In fig. 5 the simulated dependence of the L_2 peak value of EELS spectra is shown as function of thickness and LCC (in systematic row approximation, *i.e.* only taking into account the beams $(X,0,0)$ of the excited row). In systematic row approximation, the Bloch wave coefficients depend only on the component of LCC along the row, *i.e.* the component perpendicular to the row (y in fig. 5) can be ignored. A remarkable feature is that few plots overlap completely (LCC = $(1,0,0)$ with LCC = $(0,0,0)$ and LCC = $(\frac{1}{4}, 0, 0)$ with LCC = $(\frac{3}{4}, 0, 0)$). This is because the relation between the tilt of the incoming wave and the tilt of the outgoing wave [?] is determined by the detector position D :

$$LCC_{\text{out}} = D - LCC_{\text{in}}. \quad (15)$$

The simulations have been calculated for $D = (1,1,0)$; this means that when LCC for the incoming wave is set to $(1,0,0)$, which corresponds to a two-beam case for $\vec{G} = (2,0,0)$, LCC for the outgoing wave is $(0,1,0)$, which, because of the systematic row approximation, is equivalent to $(0,0,0)$, a three-beam case. Conversely, for $LCC_{\text{in}} = (0,0,0)$ (a three-beam case) $LCC_{\text{out}} = (1,1,0) \rightarrow (1,0,0)$ (a two-beam case). For these particular orientations, the Bloch coefficients for incoming ($C_{\mathbf{g}}^{(j)}$) and outgoing wave ($D_{\mathbf{h}}^{(l)}$) will switch places. More precisely, the two thickness profiles overlap because in

Figure 4. Simulation of the dichroic signal σ_{dich} (upper row) and of the expected signal-to-noise ratio (S/N, lower row, calculated as $\Delta\sigma/\sqrt{2\langle\sigma\rangle}$) in case of Poissonian noise as function of q_x, q_y (in units of G). The maximum and minimum of the dichroic signal are located, as expected, at the point A and B on the Thales circle, however the S/N is quite good all around the Thales circle.

$$\frac{d^2\sigma}{d\Omega dE} = [\dots] \sum_{\substack{jlj'l' \\ \mathbf{g}\mathbf{h}\mathbf{g}'\mathbf{h}'}} C_{\mathbf{0}}^{(j)*} C_{\mathbf{g}}^{(j)} D_{\mathbf{0}}^{(l)} D_{\mathbf{h}}^{(l)*} C_{\mathbf{0}}^{(j')} C_{\mathbf{g}'}^{(j')*} D_{\mathbf{0}}^{(l')} D_{\mathbf{h}'}^{(l')*} \sum_{\mathbf{a}} MDFF(\mathbf{a}) \quad (16)$$

(see also eq. 17 of in [?]) every $C_{\mathbf{g}}^{(j)}$ obtained for a certain LCC'_{in} becomes the $D_{\mathbf{h}}^{(l)}$ for the orientation which has $LCC_{out} = LCC'_{in}$. The symmetry becomes evident in a 3D plot of the dichroic signal as function of both thickness and LCC (fig. 6), where the axis of symmetry is passing through the $LCC = G/4 = (0.5, 0, 0)$, for which $LCC_{out} = LCC_{in} = (0.5, 0, 0)$. The symmetry does not extend to the range $LCC_{in} > G/2$. In these simulations the effect of absorption has not been included, but it should not have a great influence on the dichroic signal as it affects all spectra in the same way, regardless of helicity.

Figure 5. Left: Simulation of the Ni L_2 peak value of EELS spectra (in arbitrary units) as function of the thickness t (in nm) for $\vec{G} = (2, 0, 0)$, 200 kV electron beam and for different values of the LCC. The detector is placed in the σ_+ position of the Thales circle. **Right:** the corresponding dichroic signal for the L_3 edge between positions σ_+ and σ_- . Calculations performed in systematic row and dipole approximations with an *ad hoc* extension [?] of the EMS code [?]. Due to this approximations and for symmetry reasons, some of the plots in both graphs overlap, for example (0,0,0) with (1,0,0) and (0.25,0,0) with (0.75,0,0).

The simulations can be performed without using the dipole approximation to estimate its validity [?]. If we also drop the systematic row approximation we obtain the dichroic maps published, for example, in [?] for Fe.

There is one last consideration that should be discussed in detail: since the electron beam is losing energy there will be momentum transfer in the z direction because $|k_f| < |k_i|$, with k_i (transmitted beam) normally on or very close to the z axis. How does this affect the polarization? In XMCD the spectral differences are proportional to the component of the magnetization that is parallel to the helicity of the excitation. The same is true for EMCD, where the helicity of the excitation is given by the vector product $\vec{q} \times \vec{q}'$. If the momentum transfer does not have a z component, the EMCD helicity will be parallel to z and only out-of-plane magnetization can be detected. However the momentum transfer always has a small z component for the following reasons: i) for inelastic events, the wave vector of the outgoing beam is smaller because of the energy loss. For L edges of transition metals this is in the range $0.01G < q_z < G$. ii) If the G beam is in a higher order Laue zone (HOLZ) \vec{q}' will have a z component equal to G_z . iii) If the excitation error [?] for G is non-zero, the Ewald sphere will not cut the ZOLZ at that particular reflection and the associated \vec{q}' will have a z component (normally a small fraction of G).

If we neglect ii) and iii) (for example, in a 2BC with a G of the ZOLZ) with the detector in $(G/2, G/2, 0)$ we would expect to have a polarization equivalent to RCP.

Figure 6. Dichroic signal at the Ni L₃ edge, 200 kV electron beam for the $\vec{G} = (2, 0, 0)$ systematic row as function of thickness and tilt of the incoming beam. The plot has an horizontal axis of symmetry at LCC=(0.5,0,0).

However, the small $q_z = q'_z \neq 0$ component gives an helicity along $(0, -k, 1)$, meaning that we can detect magnetization in the y direction. With the detector in $(G/2, -G/2, 0)$ and a polarization equivalent to LCP, the helicity is along $(0, -k, -1)$. If the magnetization is along $(0, 1, 0)$ we would not see a change in sign when going from RCP to LCP. This is exemplified in fig. 7, where the dichroic signal is calculated for a 3BC making use of the vertical mirror axis (*i.e.* $\Delta\sigma$ is calculated between point with the same q_y but opposite q_x), no systematic row approximation for the $G=(2,0,0)$ of Fe in the $[0,1,6]$ zone axis for 300 kV accelerating voltage. Since the figure shows dichroic maps in reciprocal space, every pixel in the figure corresponds to a different k_f and therefore to a different set of \vec{q}, \vec{q}' and to a different helicity of the virtual photon absorbed. In fig. 7 the importance

of a $q_z = q'_z \neq 0$ component is evidenced by calculating the same dichroic maps under three different energy losses: the one corresponding to the Fe $L_{2,3}$ edge (708 eV, middle block), a fictitious 3 keV energy loss with a correspondingly large q_z, q'_z component (lower block) and a fictitious map at no energy loss (upper block; here $q_z \cong 0, q'_z \neq 0$ because of HOLZ components and the small excitation error of G). It can be seen that when q_z, q'_z are large because of the energy loss and the effect of the HOLZ reflections can be neglected, the dichroic signal is almost symmetric with respect to the horizontal axis. At the point (1,0,0) the helicity of the virtual photon absorbed points toward (0,1,0) (neglecting the contribution from -G) and at the point (-1,0,0) the helicity of the virtual photon absorbed points toward (0,-1,0) (neglecting the contribution from G) and we mostly detect the y component of the magnetization. The helicity changes little as we move away from the q_x axis until the point where q_y and q_z (and their primed counterparts) have similar magnitudes and the helicity moves from the xy plane toward the z axis. If we move close to the q_y axis the contribution from the G (-G) beam in the opposite half-plane becomes increasingly larger until they cancel each other out. If the Fe $L_{2,3}$ edge were to occur at zero energy loss (upper block) the q_z, q'_z components would be very small and the effect from HOLZ reflections could no longer be neglected.

6. Experimental setups

A detailed description of all possible experimental setups for the detection of EMCD in the TEM goes beyond the purpose of this work. The interested reader can find the relevant information in the following references: general [?, ?], LACDIF [?], CBED [?], EFTEM [?], chiral STEM [?], quantitative EMCD [?]. The important point to remember is that to excite chiral transitions in the TEM with the intrinsic method (sample as beam splitter and phase tuner) one has to either record the entire diffraction plane at different energy losses or place a k_f -defining aperture (the SEA or the objective aperture, for instance) in the diffraction plane and then record spectra or an EFTEM series. Ideally, one would want to record the entire data cube (fig. 8) either in real space for two opposite polarization or in reciprocal space.

The advantage of recording the entire diffraction pattern is that one can easily see where the maximum dichroic signal is located and comparison with calculated dichroic map is rather straightforward [?, ?]. Spectra can be extracted post-acquisition by use of virtual apertures. The disadvantage is that one can either use parallel illumination, but then spatial resolution will be poor (the size of the illuminated area is defined by the selected area apertures and it is in the 100 nm range); or one can use a convergent beam (LACDIF or CBED method) to improve both signal intensity and spatial resolution, but then the beam in the diffraction patterns will become disks (proportionally to the convergence angle) and the dichroic signal will be smeared out. The datacube in reciprocal space could also be acquired by serially recording spectra while shifting the diffraction pattern with respect to the SEA by use of the deflection coils (similar to energy spectroscopic imaging but in TEM diffraction mode). This acquisition method

Figure 8. Each point of the data cube contains information about the number of electrons that have been detected for that particular energy-loss (z-axis) and spatial coordinate (x- and y-axis) for the image mode. If the data cube is collected in diffraction mode, angular and energy information is recorded, with scattering directions k_x and k_y substituting the x- and y-axis. The set need not be "cubic" (and normally is not) as the number of points in the z axis can differ from that in the x or y axis.

hasn't been tried yet as it sacrifices q_x, q_y resolution for a better energy resolution. However for the application of the sum rules [?] only integrals of the spectral lines are used therefore there is no need for a high energy resolution. It is possible to collect just two spectra from two points on opposite sides of a mirror axis if simulations are used to determine beforehand where the maximum dichroic signal would be expected. This is one of the fastest methods to record an EMCD signal.

7. Outlook

XMCD has been used for many years, both in transmission and PEEM mode, to obtain magnetic information from a variety of materials, bulk, surfaces, interfaces and nanoparticles to cite a few [?, ?, ?, ?]. The spatial resolution achieved today is in the 10-50 nm range and measurements can be performed on many beamlines around the

world on a routine basis. The EMCD techniques discussed here offer to be a powerful complement to XMCD, with better bulk sensitivity than PEEM-XMCD and a lateral resolution better than both transmission and PEEM-XMCD. EMCD only requires a simple TEM equipped with a spectrometer, a tool much cheaper and more common and accessible than the extensive (and expensive) dedicated beamlines with hard-to-get beam times. There are however several drawbacks in the use of EMCD compared to XMCD. The requirements on the sample are more demanding, at least in so far as only the EMCD intrinsic way has been developed. Some or all of these requirements could be dropped once alternative ways to set up a chiral excitation in the TEM are established. Similarly to transmission XMCD, the first limitation is on the specimen thickness; since the electron beam has to pass through the sample for its EELS signature to be recorded, the thickness should be of the same order of magnitude (or smaller) as the electron mean free path λ (typically a few hundreds nanometers, depending on the material). However, if plural scattering effects are to be avoided, a thickness of $< 0.5\lambda$ is preferable [?]. A second limitation is on the sample crystallinity. Whereas there is virtual no limitation for XMCD, the polarization of the virtual photon absorbed in EMCD depends on the relative orientation between electron beam and sample; this would seem to indicate that only single crystalline specimens of high quality can be used for EMCD, but this is not necessarily the case. Only the area currently under excitation or observation needs to be a single crystalline and this can be as small as 10 nm or less in most cases, for example when using convergent beam techniques [?, ?, ?] or real-space maps [?]. The robustness of the dichroic signal with respect to convergence and collection angle has been used to improve the signal-to-noise ratio [?], but it also implies its robustness with respect to imperfections in the crystalline structure; the signal is not disrupted but simply somewhat reduced when passing through bent regions or grains with slightly different orientations (quantitative EMCD has been shown in samples with a texture angle of 0.3 degrees [?]). Another limitation is the strong magnetic field (some Teslas) into which the sample is immersed during TEM experiments; this field is easily strong enough to saturate the sample and force its magnetization out of plane and along the optical axis of the microscope. Under these conditions, studies of magnetic domains or remanent magnetization are not possible. One way to overcome this limitation is to use a Lorentz lens which exerts only a very low magnetic field on the specimen [?].

The limit of applicability of the technique itself, *i.e.* the minimum number of magnetic atoms necessary to detect a reasonable signal, is dictated by the elemental signal-to-noise ratio. We need to be able to see changes in the intensity of an elemental edge that are in the 5 – 30% range, meaning that the difference induced by the change of helicity has to be above the noise. Thus, the limit is expected to be, in the best case, roughly one order of magnitude worse than the limit of detectability of that specific element in EELS. This problem is further compounded by the fact that each of the steps of tuning into a core-loss, then choosing an off-beam condition and finally making a difference measurement decreases successively the signal-to-noise ratio and makes the technique experimentally very challenging.

Notwithstanding these limitations, EMCD can be used quantitatively by application of the sum rules to measure the spin and orbital contribution to the magnetization of the sample. It can also be used qualitatively to reveal the presence of out-of-plane magnetization (as was done in [?, ?]) and therefore track magnetic phase transitions or changes induced by external fields.

Actual real space images showing magnetic contrast have not yet been recorded using EMCD and therefore a direct comparison with XMCD sensitivity is not possible. However, the acquisition of EMCD real-space maps [?] and the successful use of a Lorentz lens in EMCD experiments [?] have both been recently achieved and the next challenge would be to combine those to obtain the first EMCD real space image with magnetic contrast. Among the other future challenges that seem to be well within the reach of the technique, we can mention the quantification of magnetic moments of isolated, 3D nanoparticles down to 10 nm and below such as it was done with XMCD in Ref. [?].

Many questions remain still open, about the technique itself and its possible applications; under which conditions could EMCD be extended to polycrystalline or amorphous materials? What are the possibilities of manipulating the sample or its environment, such as temperature, magnetic field, pressure, low-vacuum conditions? How does this information compare with XMCD?

As we write, ideas are slowly being translated into experiments. We hope that this article may inspire our readers into taking part of this task upon themselves and help us expedite the process.

References