Prolegomena to Magnetic Circular Dichroism in X-ray Absorption Spectroscopy

Christian Brouder
Laboratoire de minéralogie cristallographie
Universités Paris 6, Paris 7, Case 115, 4 Place Jussieu
75252 Paris Cedex05
and
Jean-Paul Kappler
IPCMS-GEMME, 23, rue du Loess, 67037 Strasbourg

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Résumé : This chapter gives an overview of the magnetic circular dichroism in x-ray absorption spectroscopy. After a historical introduction, we review the dependence of MCD as a function of temperature, external magnetic field, detection method, etc.

1 Introduction

This article is a short overview of the results concerning magnetic circular dichroism in x-ray absorption spectroscopy. The subject is now exploding, and the relevant literature is scattered in many journals, books and conference proceedings. More detailed introductory presentations can be found in Refs.[1, 2, 3, 4, 5, 6]. Furthermore, this review is restricted to x-ray absorption spectroscopy, although circular dichroism was observed in many other core spectroscopies (see Ref. [7] for a recent overview).

To give an idea of the present status of this subject, we can observe that a total of 1243 experimental spectra and 501 calculations were published (including publication multiplicity: the K-edge of iron was published 47 times). MCD was measured at 79 edges of 32 elements for a total of 451 different spectra.

We start with some historical details and the description of our convention. Then comes an experimental part, followed by some remarks on questions relevant to XMCD (detection method, quadrupole transitions, normalisation of experimental spectra, angular dependence, temperature dependence, field dependence). The theoretical aspects are developed in other chapters and will not be touched upon here.

1.1 History

The influence of magnetism on x-ray absorption spectra was very early sought for and experimentally investigated. To cite just a few examples, Chapman in 1913 [8], Forman in 1914 and 1916 [9, 10], Kurylenko in 1940 [11] tried to measure (with or without alleged success) the influence of the magnetic state of an iron foil on its absorption spectrum. The first serious approach to the problem was made by Bennett, Erskine and Stern [12, 13] who calculated MCD at the M_{23} edges of nickel using a band-structure formalism. Other people have considered the action of the magnetic state on XAFS. In 1980, Rothberg [14] discussed spin-dependent EXAFS, but the physical mechanism he describes is not clear. In 1983, Schütz and coll. [15] measured the "spin-dependent contribution to the photoabsorption in iron", but their set-up was not sensitive enough to find an effect at the available energies. In 1984, Keller and Stern [16] measured magnetic absorption at the Gd L_3-edge of $Gd_{18}Fe_{82}$ amorphous alloy. Although they claim to have a sensitivity of 0.2%, they failed to observe MCD (Kobayashi et al. [17, 18] observed a MCD effect with an intensity of 2% on a similar sample). In 1985, Thole and coll. [19] made an atomic calculation of linear magnetic dichroism at the M_5-edge of Dy. This effect was observed at the M_5-edge of Tb in $Tb_3Fe_5O_{12}$ by van der Laan and coll. [20]. In 1986, Baryshevskii and coll. [21] calculated atomic paramagnetic XMCD, but they assumed to be far from the absorption edges, which makes their results doubtful. XMCD was finally observed for the first time by Schütz and coll. [22] in 1987.

1.2 Conventions

Various names were proposed to call MCD in the x-ray range. The Dutch group proposed magnetic x-ray dichroism (MXD) because x-ray dichroism was already used to describe angular effects in non-cubic crystals. The German group chose spin-dependent absorption spectroscopy (SPAS), then other names were used. Counting the number of publication using each name, we obtained the following list : XMCD (and variants, such as x-ray MCD) : 46, CMXD : 40, MCXD : 26, SPAS or SPASS (an acronym which is funny in German) 15, MXCD : 7, Magnetic XANES : 3, XCMD : 1. Recently, it appears that more and more authors choose to include this phenomenon into the general class of magnetic circular dichroism and use X-ray MCD or XMCD. We shall also use this last name.

Concerning the polarisation, two definitions are standard. We use the convention of optics [23], and call left-circularly polarised an x-ray with a polarisation vector $\hat{\epsilon}^+$ such that $\hat{\epsilon}^+.\mathbf{r} = -(x + iy)/\sqrt{2}$ for an x-ray propagating along Oz [24]. According to this convention, x-rays emitted from a bending magnet are left-circularly polarized when the charges (electrons or positrons) seem to turn left (counterclockwise) from the point of view of the sample [25]. Left-circularly polarised x-rays correspond to a $+\hbar$ helicity (or photon "spin"). The opposite convention for left and right is used by particle physicists [26] and in many XMCD articles. Notice that the helicity convention is unambiguous.

A further source of confusion comes from the fact that, in some papers, initial and final states are inverted. This has the consequence of changing the sign of the dichroic effect. The correct formula for x-ray absorption cross-section is:

$$\sigma(\hat{\epsilon}) = 4\pi^2\alpha_0\hbar\omega \sum_f |\langle f|\hat{\epsilon}.\mathbf{r}|i\rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

i.e. the initial state is on the right and the final state on the left.

As explained in detail in the next section, some confusion can also be observed in the convention used in experimental spectra.

In this article, we assume that circular dichroism is entirely of magnetic origin. Natural magnetic dichroism in the x-ray range was calculated to be very small [27, 28], although probably measurable at low energy (e.g. K-edge of carbon) with present day synchrotron radiation sources. Experimentally, the search for natural magnetic dichroism in a stereogenic Ti complex did not meet clear success [28].

2 Review of experimental results

There exists now quite a few beam lines over the world were XMCD experiments are possible. Experimental XMCD spectra are presented in various ways. The measurement is defined when the direction of the magnetic field with respect to the x-ray beam wavevector and the type of circularly polarisation are specified. Let $\sigma^+(B)$ $(\sigma^+(-B))$ be the spectrum measured with positive helicity x-rays and with the external magnetic field parallel (antiparallel) to the x-ray beam direction. After some fluctuation, the convention used for experimental XMCD spectra is the difference between spectra for right minus left polarisations, when the magnetic field is along the x-ray wavevector (see Ref.[5] for details):

$$\begin{aligned}
\sigma_{MCD} &= \sigma^+(-B) - \sigma^+(B) \\
&= \sigma^+(-B) - \sigma^-(-B) \\
&= \sigma^-(B) - \sigma^-(-B) \\
&= \sigma^-(B) - \sigma^+(B).
\end{aligned}$$

These equations used the identity $\sigma^+(B) = \sigma^-(-B)$, which means that one obtains the same spectrum when reversing the external magnetic field and the circular polarisation. This statement is proved in Appendix and was checked experimentally [29, 30, 31, 32, 33, 34]. However, some difference between the two methods were observed for $TbNi_2Co_3$ [35] because of the hysteresis properties of this compound.

When comparing experimental spectra, the reader should pay attention to the fact that the plotted spectra can be σ_{MCD}, $\sigma_{MCD}/2$ or $\sigma_{MCD}/(\sigma^+ + \sigma^-)$, as well as to possible normalisation factors (degree of circular polarisation, "polarisation of the photoelectron", incomplete saturation of magnetic moment, angle between magnetic moment and x-rays).

Most experiments were carried out on ferro- or ferri-magnetic materials, although some paramagnets, such as Ho_2O_3 [36], various forms of pyrococcus furiosus rubredoxin [37], ferredoxin [38], Cu(II) plastocyanin [39] and an Fe complex [40] were also measured.

The detection method is relevant because it is not clear when different detection methods give the same MCD spectra. For instance, it was shown that spectra obtained by fluorescence and transmission are different for nickel [41], sulfur [42], cobalt [43], dysprosium [44], manganese [45] and copper [46], and that MCD at the K-edge without spin-orbit coupling on the photoelectron is possible in fluorescence detection [47, 48] and not in absorption [49]. The role of Coster-Kronig transitions in fluorescence detection was stressed in Ref. [50]. The normalisation method is relevant because, in the hard x-ray range, Schütz' team has presented MCD spectra as a ratio. This normalisation method, which was only scarcely followed, makes it difficult to compare with experimental spectra normalised differently.

2.1 The detection method

Various methods are used to measure XMCD.

2.1.1 Transmission mode detection

The most direct measurement of the absorption cross-section is through the detection of the photon flux before and after the sample. This is usually used in hard x-rays and sometimes also in soft x-rays. In principle, transmission is the most reliable detection method, although the strong absorption of soft x-rays makes it experimentally difficult at low energy. Its use, below 1000 eV, is only limited by the possibility to prepare transparent thin films : for example about 200Å thickness for Fe-L2,3 edges experiments. A few experiments were carried out, especially at the L2,3 of 3d metals [51, 52, 53, 54] and at the Ce-M4,5 edges [55] which give results very similar to sample current detection. This identity is due to the fact that, in the soft x-ray range, almost all the decay channels are non-radiative [43]. The major advantage of this technique is the insensitivity of the surface effects. The detectors used are either ionisation chambers in hard x-rays or sensitive photodiodes in soft x-rays.

2.1.2 Electron yield detection

The first quantitative analysis of Total Electron Yield (TEY), Gudat and Kuntz [56], demonstrates that the TEY is proportional to the absorption coefficient as long as the absorption length of the incoming photons is much larger than the average escape depth of the photoelectron. More recently, Stöhr [57] has proposed a simple model which takes into account all the various complicated electron scattering processes. It is demonstrated that the primary electrons generated inside the sample is given by $\hbar\omega\sigma(\omega)ML$ where M is material constant describing the conversion efficiency into low-energy electrons and L the effective electron escape depth, to first order independent of the photon energy and estimated to be about 50Åin the 300-1500eV energy range.

According to [29], sample current and total electron yield $Y(\omega)$ are not strictly proportional to the absorption cross-section, even when normalized to the incident photon flux. They use the approximate expression $Y(\omega) \propto \hbar\omega\sigma(\omega)$. Moreover, the probing depth of secondary electrons is estimated to be around 20Å[29, 58], which makes sample current and total electron yield strongly surface sensitive. Note that these two techniques were observed to give equivalent results for nickel [59]. Saturation effects must be taken into account when the sample is measured at glancing angles [60, 29, 61]. When these effects are properly considered, total yield and transmission detection seem to give the same spectra, although additional phenomena, such as spin-dependent electron mean free path [62, 63], could modify this conclusion. O'Brien and Tonner [29] have also tested the applicability of the dichroism sum rules to XMCD measured by TEY. It was observed by Vogel and coll. [59] that total electron yield and sample current detection give identical spectra. Partial electron yield might introduce further non-linearities because it selects a specific range of decay channels.

The TEY signal can be collected by :

- either a channeltron or spiraltron electron multiplier, which should be located near the sample and excluded the presence of static magnetic field ,

- or by the measure of the sample drain current with the help of an electrometer (in the 10^{-12}A range). In this situation the sample must be electrically isolated ($R_{\text{sample}} >$ TΩ), which requests low level DC measurement instruments. The theoretical limit of sensitivity is determined by the ideal noise generated by the resistance involved in the circuit and then need the choose of the best insulators. Sapphire is one of the best insulators with very little charges generated in when stressed mechanically. Its use is also recommended in the case of cooling sample. However its cost and the difficulty to machine and form restrict its use,

- or by collecting the photoelectrons from a high-voltage (around 200V) grids located near the sample.

2.1.3 Fluorescence detection

The fluorescence yield (FY) is especially useful in the investigation of dilute samples and thin layers; in these cases the FY signal is directly proportional to the absorption coefficient and not surface sensitive. For concentrated bulk samples the FY signal can exhibit strong non-linearities improperly called "self absorption effects" [64]. The non proportionality is known for a long time (see [42, 65] and references therein) and was observed for XMCD at the L-edges of transition metals [66]. Moreover, strong saturation effect was observed at the L-edges of Fe [67]. That does not condemn this measurement technique because fluorescence detected spectra can be calculated [41], when the geometry of the detector (position with respect to the incident beam, accepting angle) is known. Saturation effects can also be estimated [67]. In the case of U-$M_{4,5}$ the FY single lines observed can be corrected in a straightforward manner by comparison with the TEY spectra, considering the line intensity as a free adjusting parameter [68]. Gas proportional counters or Si photodiode detectors [69] can be used to detect the FY signal; mounted at different angles of view with respect to the sample surface, they permit to increase the solid angle of fluorescence photon collection and then to monitor the possible geometry dependent self absorption effects.

2.2 The normalisation of experimental spectra

As the XMCD signal results from a difference, the normalisation of the experimental spectra taken for two different polarisations or magnetic fields is a difficult problem. For metallic samples of transition metals one can normalise the spectra so that they match before and after the absorption edges. In the case of rare earths and transition metals, the background can be very small and this normalisation process is difficult to use. Moreover, the normalisation depends of the detection modes. For example, in the case of TEY in principle the magnetic field inversion does not introduce any asymmetry in the trajectory of the photoelectron, especially when this inversion results of a current inversion. However, non perfect symmetric positions of the beam and the sample lead to different efficiency factors of the sample current detector in function of the direction of the magnetic field. Then, the only possible correction corresponds to a normalisation coefficient between the two spectra. The knowledge of the isotropic absorption spectrum is of prime importance in XMCD analysis, especially for the sum rules application. This spectrum $\sigma_0(\omega)$ can be obtained by measuring: $\sigma^+(\omega)$ or $\sigma^-(\omega)$ at B=0, where $\sigma^+(\omega)$ ($\sigma^-(\omega)$) are the absorption spectrum for left (right) circularly polarised x-rays; this is strictly true if remanent effects are negligible, $\sigma(\omega)$ in linearly polarised light, on powder and polycrystalline sample, $\sigma(\omega)$ far away the T_C temperature, $\sigma_0(\omega) = [\sigma^+(\omega) + \sigma^+(\omega)]/2$, in the case of d systems, as discussed in the following. Note that in the case of highly localised systems (4f) where the dichroic effect can be reasonably obtained by a local atomic model, this relation is not valid [70]. In some cases, the spectrum is identical when the sample is rotated around the magnetic field axis and the x-ray axis (e.g. when the sample is a powder or a polycrystal and the applied magnetic field is parallel to the x-rays). In this case, it can be shown that $\sigma_0 = (\sigma^+ + \sigma^-)/2$ [71]. This relation is valid also when the x-rays are elliptically polarised, as well as partly unpolarised. This relation between three spectra is a strong constraint that enables us to check that normalisation is correct. A possible difficulty in applying this formula comes from the fact that, when the slits opening is too large, the apparent resolution can be different in the orbit plane and out of it, for beging magnets or asymmetric wiggler. This is because the distribution of photon intensity out of the plane can act as an effective slit smaller than the real one. To avoid this effect one must work with slits such as the photon intensity does not vary much over the slit heighth.

2.3 Magnetic field

The choice of the magnetic field mode depends on the nature of the experiments. Measurements can be made either in remanence mode or with an applied external field. The first mode enables to use electron detection, concerns only a few cases of high remanent materials, as thin films of 3d metals. In the general cases the magnetic field is created by a current either in resistive coils (0.1T), in electromagnet (2T) or in superconducting coils (7T). For the most part, in the experimental set-up the direction of the applied field corresponds to the x-ray propagation direction. The experimental environment (UHV, low temperature, pressure) affects the choice of the magnetic field system. The ideal solution for the majority of experiments is to reverse the magnetic field at each photon energy step, but this imposes only a moderate magnetic field. As explained in [2], this procedure gets rid of constant measurement drifts and leads to signal to noise ratio better than 10^4 in transmission mode. In the sample current mode the application of an external magnetic field increases the measured current and then improves the signal to noise ratio.

2.4 External field dependence

The variation of XMCD with external magnetic field intensity has been measured in various ways. In the first method, an XMCD spectrum is measured for various applied fields. This was used for Ni(110) [59] and Fe/Gd multilayers [72, 73] and for intermetallic rare earth compounds [70]. In the second method, called “Element Specific Magnetic Hysteresis” (ESMH) by his inventors, x-ray absorption is measured at a fixed energy where MCD signal is strong, and the absorption coefficient as a function of the applied magnetic field is measured. It was used for Co/Cu/Fe [74, 51], for Ni(110) [59] and for Fe(001) [75]. In the third method, the monochromator is also set to a fixed energy, but a small oscillating magnetic field is used and magnetic susceptibility is measured by lock-in detection. It was used for Co/Cu(100) [76], Ni/Cu(100) [77, 78], Co/Ni/Cu [78] and Gd/W [78]. No change in the MCD spectral shape with external magnetic field intensity was ever observed.

2.5 Angular dependence

Angular dependence of XMCD was investigated in the atomic model by Altarelli [79, 80]. In practice, there are two kinds of angular dependence for XMCD. Either the magnetic field is fixed with respect to the rotated sample, or the magnetic field is fixed with respect to the incident beam and only the sample rotates. In the first case, general arguments can be invoked to investigate the angular dependence. Writing $\sigma = \sum \epsilon_i^* \epsilon_j \sigma_{ij}$ and assuming that the magnetic field is along a symmetry axis of order greater than 2 (taken as the z-axis) one obtains:

$$\underline{\sigma} = \begin{bmatrix} \sigma_{xx} & i\sigma_{xy} & 0 \\ -i\sigma_{xy} & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{bmatrix}$$

where all quantities are real, σ_{xx} and σ_{zz} are even functions of B and σ_{xy} is an odd function of B. Then $\sigma^+ - \sigma^- = -2\sigma_{xy}\cos\theta$ (where θ is the angle between the x-ray and the magnetic field, i.e. the z-axis). It was shown in Ref.[81] that this $\cos\theta$ angular dependence of XMCD spectra is true for all point groups except C_1 and C_i (it should be noticed that the invariance point group in question includes the magnetic field, so that one has a C_1 or C_i symmetry group when the magnetic field is not aligned with a symmetry axis of the sample). This first angular dependence was observed on Fe [29], Co [29, 61] and during the search for quadrupole transitions (see section 2.7).

The second angular dependence would measure the magnetic anisotropy of the sample. In $M_{IV,V}$ of rare earths the shape of XMCD does not change with orientation (only its intensity). The same was found for octahedral molecular Ni [82]. This change of shape with magnetic field direction was investigated within the tight-binding approach for Nickel and found to be small [83].

2.6 Temperature dependence

An obvious dependence of XMCD on temperature comes from the temperature dependence of the magnetic moment. Assuming a proportionality between XMCD and some local magnetic moment, the shape of the spectrum does not change and its intensity is multiplied by a temperature dependent factor. This was observed in Nd/Fe multilayers [84, 2], $Gd_3Fe_5O_{12}$ [85], $CeFe_2$ [86], Fe/Cu(001) [87], Ni/Cu(001) [88, 89], Co/Cu(001) [76], $Fe_{73.6}Ni_{28.4}$ [90], $HoCo_2$ [91], Fe/Gd multilayers [72, 92], Fe/Ho multilayers [93], $Ce(Fe_{0.8}Co_{0.2})_2$ [86], Gd [94], in $Er_2Fe_{14}B$ [95], in $Nd_2Fe_{14}B$ [95, 96], in $TbNi_5$ [97], in $Tb(Ni_{0.4}Co_{0.6})_5$ [97].

However, it was also observed that the shape of XMCD spectra can change with temperature. In $Fe_{72}Pt_{28}$ [98], this was attributed to a spin transition, in $YbFe_2$ [99] and $ErFe_2$ [100] this is due to quadrupole transitions.

The temperature dependence of XMCD was also calculated within the atomic multiplet approach in Ref.[101].

2.7 Quadrupole transitions

Carra and Altarelli pointed out that electric quadrupole transitions might be sizeable in the MCD $L_{II,III}$ spectra of rare earths [102]. Further calculations confirmed the relevance of quadrupole transitions [103]. However, the angular dependence characteristic of quadrupole transitions was not observed for a long time. Evidence for a quadrupole contribution was finally found in [104, 105], indirect evidence was found by Krisch et al. [106].

3 Appendix

In this appendix, we would like to give a proof of the frequently alleged statement that inverting the external magnetic field and the circular polarisation gives the same spectrum. This result is a consequence of the time reversal symmetry of the operators and states involved in the problem. A hand-waving argument runs as follows. A magnetic field can be considered as a rotating current. I know that my global system (sample, external magnetic field and x-ray source) is time-reversal symmetric. When reversing time, the current loop goes the other way round, which reverses the magnetic field, and the x-ray polarisation vector as well. Therefore, time-reversal inverts magnetic field and polarisation direction without changing the measured spectrum. This yields $\sigma^+(B) = \sigma^-(-B)$ and $\sigma^+(-B) = \sigma^-(B)$, which are the required relations.

A more formal argument runs as follows [71]. The total system Hamiltonian, including external magnetic field, is time reversal invariant. Therefore, if $\psi(\mathbf{r};\mathbf{B})$ is an eigenstate of the system with external field $\mathbf{B}$, then the time-reversed state $\psi'(\mathbf{r};\mathbf{B}) = \psi^*(\mathbf{r};-\mathbf{B})$ is again an eigenstate of the same system [107]. Writing:

$$\sigma(\hat{\epsilon},\mathbf{B}) = \int f^*(\mathbf{B})\hat{\epsilon}.\mathbf{r}i(\mathbf{B}) \int f(\mathbf{B})\hat{\epsilon}^*.\mathbf{r}i^*(-\mathbf{B})$$

and using the identity between eigenstates, we obtain

$$\sigma(\hat{\epsilon},\mathbf{B}) = \int f(-\mathbf{B})\hat{\epsilon}.\mathbf{r}i^*(-\mathbf{B}) \int f^*(-\mathbf{B})\hat{\epsilon}^*.\mathbf{r}i(\mathbf{B}).$$

which yields:$\sigma(\hat{\epsilon},\mathbf{B}) = \sigma(\hat{\epsilon}^*,-\mathbf{B})$, the required relation. This reasoning was made in a non-relativistic framework, but can be carried out along the same line with Dirac spinors, using the time-reversal symmetry: $\psi'(\mathbf{r};\mathbf{B}) = \beta\psi^*(\mathbf{r};-\mathbf{B})$.

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