Review

X-ray magnetic circular dichroism—a high energy probe of magnetic properties

Tobias Funk a, Aniruddha Deb b, Simon J. George b,*, Hongxin Wang b, Stephen P. Cramer b,a

a Department of Applied Science, University of California, Davis, California 95616, USA
b Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

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Abstract

The XMCD effect and its family of related techniques (XAS, PEEM) have revolutionized the probe of magnetic properties. In this review, we shall focus on the application of XMCD to condensed matter and materials science. The contents of this review are organized into five major sections: (1) Introduction, (2) Experimental considerations, (3) Simplified theory, (4) Chemical and materials science applications of XMCD, and (5) Summary—a dose of reality.

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Abbreviations: XAS, X-ray absorption spectroscopy; XMCD, X-ray magnetic circular dichroism; CD, circular dichroism; MCD, magnetic circular dichroism; PEEM, photoelectron emission microscopy; kp, left circularly polarized; rp, right circularly polarized; ALS, advanced light source; APS, advanced photon source; ESRF, European Synchrotron Radiation Facility; NSLS, national synchrotron light source; EPU, elliptically polarizing undulator; AW, asymmetric wiggler; HU, helical undulator; EW, elliptical wiggler; LMFT, ligand field multiplet theory; DFT, density functional theory; COOHL, carbon monoxide dehydrogenase; ACS, acetyl coenzyme-A synthase; ACDS, acetyl coenzyme-A decarboxylase

* Corresponding author. Tel.: +1 510 486 6094; fax: +1 510 486 5664.
E-mail address: SGeorge@lbl.gov (S.J. George).

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Abstract

X-ray magnetic circular dichroism (XMCD) spectroscopy is a powerful emerging technique that measures difference in absorption of left- and right-circularly polarized X-rays by a magnetized sample, often at cryogenic temperatures. It is already well established in magnetic materials science, and it is likely to become a significant tool for the inorganic and bioinorganic communities. As with all X-ray spectroscopies, XMCD has the advantage of being element specific. Interpretation of the spectra can: provide quantitative information about the distribution of spin and orbital angular momenta from simple “sum rules”; determine spin orientations from the sign of the XMCD signal; infer spin states from magnetization curves; and separate magnetic and non-magnetic components in heterogeneous samples. With new synchrotron radiation sources and improved end stations, XMCD measurements on dilute samples such as metals in enzymes, are becoming more routine. This review first details the technology currently available for XMCD measurements and outlines the theory underlying interpretation of the spectra. It then illustrates the strengths of the XMCD technique using examples taken from bioinorganic chemistry and materials science. In this way, we aim to encourage chemists, materials scientists, and biologists to consider XMCD spectroscopy as an approach to understanding the electronic and magnetic structure of their samples.

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Keywords: X-ray magnetic circular dichroism; Circular dichroism; Magnetization; Absorption-fine-structure; Spin sum-rule; Branching ratio; Ground-state; Crystal-field; Dipole term; Spectroscopy; Spectra; Transition-metal compounds; Metalloproteins; Metalloenzymes

1. Introduction

1.1. The XMCD effect

X-ray magnetic circular dichroism (XMCD) is the difference in absorption of left- and right-circularly polarized X-rays by a magnetized sample (Fig. 1) [1]. Although MCD with X-rays is only about 15 years old, the physics is essentially the same as for the UV–vis MCD that has been known since 1897 [2]. For (bio)inorganic chemists and materials scientists, XMCD has the advantage of elemental specificity that comes with all core electron spectroscopies. Thanks to simple sum rules, XMCD can also provide quantitative information about the distribution of spin and orbital angular momenta. Other strengths include the capacity to determine spin orientations from the sign of the XMCD signal, to infer spin states from magnetization curves, and the ability to separate magnetic and non-magnetic components in heterogeneous samples. With new synchrotron radiation sources and improved end stations, XMCD measurements on biological samples are, if not routine, at least no longer heroic.

One goal of this review is to encourage chemists, materials scientists, and biologists to consider XMCD as an approach to understanding the electronic and magnetic structure of their samples.

1.2. Circular polarization

A circularly polarized X-ray has oscillating electric and magnetic fields that are 90° out of phase with each other. We use the convention of Born and Wolfe [3], in which the instantaneous electric field \( \vec{E}_{\text{rcp}} \) for a right circularly polarized photon propagating in the \( z \)-direction resembles a right-handed screw (Fig. 1).

\[
\vec{E}_{\text{rcp}} = E_0 \left[ \sin(\omega t - k z + \phi_0) \hat{i} + \cos(\omega t - k z + \phi_0) \hat{j} \right]
\] (1)

Fig. 1. (Left) Schematic of XMCD experiment. \( I_0 \) is incident beam intensity, \( I_t \) is the transmitted intensity while \( I_f \) and \( I_e \) are the intensities of the emitted fluorescence and photoelectrons respectively. (Right) Illustration of the electric field direction along the propagation axis for right circularly polarized light.
In this equation, $\omega$ is the angular frequency, $\omega = 2\pi \nu$, $k$ is the wave number, $k = \frac{2\pi}{\lambda}$, where $\lambda$ is the wavelength, $\phi_0$ is an arbitrary phase shift, and $i$ and $j$ are unit vectors along the $x$ and $y$ axes, respectively. With the above definition, it turns out that left circularly polarized photons carry $\hbar$ angular momentum. Beth [4] observed the predicted torque on a macroscopic target in a torsion pendulum experiment in 1936.

Although the Born and Wolf convention is standard for optics and chemistry literature, most physics literature uses the opposite definition, and one should check how the polarization is defined if the sign of the MCD effect is to be meaningful. The papers of deGroot and Brouder generally use the Born and Wolfe convention, while those of Thole, van der Laan, and Carra use the physics or ‘Feynman’ definition [5]. The pitfalls of describing circular polarization have been cogently described by Kliger et al. [6].

1.3. Some history

The existence of polarized light has been known since at least 1690, when Huygens [7] discovered that either of the two light rays refracted by a calcite crystal could be extinguished by rotation of a second ‘analyzer’ crystal. More than a century later (1808), Mauus observed that sunlight reflected from a window pane had similar properties, and by analogy with magnetic bodies, he called this light ‘polarized’ [8]. Although these early observations were first interpreted in terms of Newton’s ‘corpuscular’ theory [9], by the 1820s Fresnel had developed a mathematical description for polarized light in terms of two perpendicular transverse waves [10]. In 1846, Faraday demonstrated rotation of the plane of polarization induced by a magnetic field [11,12]; this ‘Faraday effect’ or ‘magnetic-optical rotation’ is the result of circular birefringence—a difference in the real part of the complex index of refraction $\hat{n}$ for left and right circular polarization. Prompted in part by these results, the theoretical work of Maxwell completed the picture of light as an electromagnetic wave [13].

The first demonstration of a magnetically induced difference in absorption (the imaginary part of $\hat{n}$) came with the Nobel prize-winning work of Zeeman. After first observing both linear and magnetic circular dichroism in the sodium D emission lines in a magnetic field [14], he reversed the experiment and observed MCD effects on the D absorption lines of Na vapor [2].

Shortly after the discovery of X-rays by Röntgen in 1895 [15], attempts were made to observe magnetic effects on X-ray spectra [16,17]. However, a successful experiment would have to wait another 80 years. The modern history of XMCD begins with Erskine and Stern [18] predicting a magneto-optical Kerr effect (MOKE) for ferromagnetic Ni at the M$_2,3$-edge ($3p \rightarrow 3d$). Subsequent attempts to see XMCD in a GdFe alloy at the Gd L$_{3,2}$-edge were unsuccessful [19]. A year later, Thole et al. [20] predicted strong XMCD and X-ray magnetic linear dichroism (XMLD) in the M$_{4,5}$ ($3d \rightarrow 4f$)-edges of rare-earths, and the latter was reported in 1986 [21]. The XMCD effect was finally observed at the K-edge of metallic Fe by Schütz et al. [22] in 1987 (Fig. 2). A much stronger soft X-ray MCD at the Ni L$_{2,3}$-edge was reported in 1990 (Fig. 2) [23]. Our group reported the first XMCD for a paramagnetic metalloprotein in 1993 [24]. Since then, the growth of XMCD for materials science applications has been explosive [25], leading to more than 1000 papers over the past decade.

2. Experimental considerations

Key ingredients for an XMCD measurement are: (1) a source of circularly polarized X-rays, (2) a monochromator and optics (a ‘beamlime’), (3) a means for producing a
magnetized sample, and (4) an X-ray absorption detection system. The latter two are considered the ‘endstation’.

2.1. Sources of circularly polarized X-rays

Before the introduction of synchrotron radiation facilities, sources of circularly polarized high energy photons were exotic, such as magnetically oriented radioactive nuclei [26,27] and astronomical synchrotron radiation [28]. Although the concepts behind X-ray circular polarizers had been demonstrated with Cu Kα radiation [29], the resultant beams were not bright enough (∼15 photons/s) for practical applications.

The frustration of pre-synchrotron X-ray physicists can be heard in the comments of Skalicky and Malgrange, "in principle therefore all polarization experiments which are possible with visible light can be performed with X-rays (but)... it is in practice difficult to obtain sufficient intensity [30]."

2.1.1. Bend magnets

The bend magnets associated with particle storage rings are the simplest sources of circular polarization. By viewing the particle beam off-axis, one observes a charge accelerated in an elliptical orbit, while viewing the beam on-axis reveals only a horizontal component to the acceleration (Fig. 3). Thus, the synchrotron radiation emitted from bend magnets is highly polarized—ranging from pure linear polarization in the plane of the orbit to nearly circular far out of the plane. Borrowing from Kim [31], the relative amplitudes of the horizontal and vertical electric field components (\(E_x\) and \(E_y\)) are given by (Fig. 3):

\[
\begin{pmatrix}
E_x \\
E_y
\end{pmatrix} = \frac{K_{1/3}(\eta)}{\sqrt{1 + (\gamma y)^2}} \begin{pmatrix} \frac{K_{2/3}(\eta)}{(\eta)^{1/3}} \\
(\gamma y)^{1/3}
\end{pmatrix}
\]

where \(K_{1/3}\) and \(K_{2/3}\) are modified Bessel functions, \(y\) is the ratio of photon energy to the critical energy, \(\gamma\) is the ratio of the electron energy to its rest mass energy, and \(\eta = (y/2) [ 1 + (\gamma y)^2 ]^{3/2}\). Defining \(r\) as the ratio of the minor to major axes of the polarization ellipse, given by \(r = E_y/E_x\), yields the degree of circular polarization \(P_c\) (defined as \(P_3\) by Kim):

\[P_c = \frac{2r}{1 + r^2}\]

Although bend magnets can provide any desired degree of polarization, this comes at a price—the flux falls dramatically as \(\psi\) increases. The strongest XMCD is obtained with
pure circular polarization, but as $P_c \rightarrow 1$, $I \rightarrow 0$. One therefore has to make a tradeoff between flux and polarization. A figure of merit for most XMCD experiments is $P^2 I$, and the angle for optimal $P^2 I$ depends on the photon energy and the critical energy of the ring (Fig. 3). Apart from limited $P_c$, other drawbacks of bend magnets are modest brightness and the emission of lcp and rcp in different directions. Better XMCD measurements can be done with insertion device beamlines.

2.1.2. Insertion devices

Insertion devices are magnetic structures ‘inserted’ into straight sections of a storage ring lattice to produce synchrotron radiation with special characteristics. Table 1 lists a variety of the insertion device beamlines available at synchrotron facilities worldwide. One clever approach proposed by Goulon et al. [32] and others [33] is the ‘asymmetric wiggler’. In this device, a strong magnetic field bends the charged particle sharply in one direction, and subsequently a pair of weaker magnetic regions brings the particle back in the opposite direction (Fig. 4). The result is an emission pattern with strong circular polarization at high energies. In the related ‘elliptical wiggler’ [34], the field is arranged to produce an orbit that spirals around the central axis in an elliptical manner (Fig. 4). This source can be considered as an array of tilted bend magnets arranged to produce the same polarization along the wiggler axis. Other devices, such as helical undulators and crossed undulators (Fig. 4) are also in use [35,36].

The elliptical undulator (EPU) is one of the most successful devices for the production of circularly polarized synchrotron radiation. In an EPU, the magnetic field vector rotates as a particle passes through the device, causing the particle to spiral about a central axis. Both electromagnetic and permanent magnet versions have been developed (Fig. 4). Permanent magnet EPUs consist of four banks of magnets—two on top and two below (Fig. 4). The peak energy of the undulator output is changed by varying the vertical separation between the magnet assemblies, a so-called ‘gap scan’, while the polarization is varied by changing the relative positions (phases) of adjacent rows of magnets—a ‘row scan’. In the case of the EPU on ALS beamline 4.0.2, the polarization can be changed from left to right circular polarization in a few seconds, and the peak energy can be varied as quickly as the monochromator scans [37].

2.1.3. Soft X-ray beamlines

In the soft X-ray region, beamlines use grazing incidence mirrors and gratings. In these geometries, the source polarization is almost completely preserved as it passes through the optics. For example, ALS beamline 4.0.2 employs an initial horizontally deflecting toroid (M1) at $2^\circ$, a plane pre-mirror (M3) at $\sim 3^\circ$, a plane grating at variable glancing angle, a cylindrical magnifying mirror (M4) at $\sim 1^\circ$, and a final refocusing mirror (M5) at $\sim 1^\circ$ (Fig. 5). This beamline provides $\sim 10^{11}$ photons/s between 50 and 2000 eV with $\Delta E/E \sim 20,000$ at the lower energy [37].

2.1.4. Hard X-ray beamlines and quarter wave plates

Hard X-ray applications could employ the same sources of circular polarization, but crystal monochromators are generally used in this region, and the effect of the crystal optics on the beam polarization can be considerable. A well-known property for visible light reflection is the so-called ‘Brewster angle’—the angle of incidence at which the electric field in the plane of incidence ($\sigma$ component) of a reflected beam is totally suppressed. This results in pure linear polarization along the out-of-plane or $\pi$ direction. The same phenomenon can occur with Bragg reflection from crystals. Despite

Table 1

<table>
<thead>
<tr>
<th>Storage ring facility</th>
<th>Beamline</th>
<th>CP X-ray source</th>
<th>Energy range</th>
<th>Endstation(s) magnet/cryostat</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALS, Berkeley, CA, USA</td>
<td>4.0.2</td>
<td>EPU</td>
<td>50-1000 eV</td>
<td>6 T, 0.5 K, 2 T, 0.1 K</td>
</tr>
<tr>
<td>APS, Argonne, IL, USA</td>
<td>4-ID-D</td>
<td>Undulator with phase retarder</td>
<td>3–50 keV</td>
<td></td>
</tr>
<tr>
<td>APS, Argonne, IL, USA</td>
<td>4-ID-C</td>
<td>EPU</td>
<td>0.5-2.8 keV</td>
<td></td>
</tr>
<tr>
<td>DELTA, Dortmund, Germany</td>
<td>SD08</td>
<td>Superconducting AW</td>
<td>$\sim 3.22$ keV</td>
<td></td>
</tr>
<tr>
<td>DELTA, Dortmund, Germany</td>
<td>SD12A</td>
<td>Twin EPU</td>
<td>0.5-1.6 keV</td>
<td>7 T, 1.5 K</td>
</tr>
<tr>
<td>ELETTRA, Trieste, Italy</td>
<td>E2.1A</td>
<td>Twin HU</td>
<td>$\sim 3.22$ keV</td>
<td>7 T, 1.5 K</td>
</tr>
<tr>
<td>ELETTRA, Trieste, Italy</td>
<td>E2.2 (BACH)</td>
<td>Twin EPU</td>
<td>0.35–1.66 keV</td>
<td>7 T, 27 K</td>
</tr>
<tr>
<td>LNLS/ESRF, Gouvay, France</td>
<td>S123</td>
<td>AW</td>
<td>100–1000 eV</td>
<td>7 T, 20 K</td>
</tr>
<tr>
<td>SPring-8, Hyogo, Japan</td>
<td>U4B</td>
<td>Bend magnet</td>
<td>20–1200 eV</td>
<td>5 T, 5 K</td>
</tr>
<tr>
<td>SPring-8, Hyogo, Japan</td>
<td>BL08W</td>
<td>EW</td>
<td>70–3000 eV</td>
<td>3 T, 10 K</td>
</tr>
<tr>
<td>SPring-8, Hyogo, Japan</td>
<td>BL25SU</td>
<td>Twin HU</td>
<td>0.22–2 keV</td>
<td>4.7 T permanent</td>
</tr>
<tr>
<td>SPring-8, Hyogo, Japan</td>
<td>BL10XU</td>
<td>Undulator with phase retarder</td>
<td>5–37 keV</td>
<td>10 T, 1.7 K</td>
</tr>
<tr>
<td>SRS, Daresbury, UK</td>
<td>1.1</td>
<td>Bend magnet</td>
<td>200–1000 eV</td>
<td>5 T, 1.6 K</td>
</tr>
<tr>
<td>SSO, Stanford, USA</td>
<td>8-2</td>
<td>Bend magnet</td>
<td>80–1200 eV</td>
<td></td>
</tr>
<tr>
<td>SSO, Stanford, USA</td>
<td>5-2</td>
<td>EPU</td>
<td>10–1200 eV</td>
<td></td>
</tr>
</tbody>
</table>

AW: asymmetric wiggler; HU: helical undulator; EW: elliptical wiggler; EPU: elliptically polarizing undulator.
perfect circular polarization from a hard X-ray EPU, the crystal optics could degrade the degree of circular polarization and in some cases produce pure horizontal polarization! (For X-rays the Brewster angle is close to 45°, and for diffraction near normal or glancing incidence, the loss of circular polarization is not significant.)

The solution is the same approach used with UV–vis MCD experiments—start with linear polarization and
convert to circular polarization with a retarder, commonly a quarter wave plate. X-ray quarter wave plates exploit the birefringence of crystals for \( \sigma \) and \( \pi \) electric field components for geometries on or close to diffraction conditions. Although early work emphasized on-reflection Bragg or Laue geometries [29,30,38–40], the most popular X-ray quarter wave plates operate in the off-Bragg transmission geometry. In this case, the crystal is adjusted to one of the wings of the Bragg reflection, at an angular deviation \( \Delta \theta \) from the center of the rocking curve for Bragg angle \( \theta_B \). The crystal planes are placed at a 45° angle to the incident polarization direction, to allow equal intensity for \( \sigma \) and \( \pi \) components of the electric field. The phase shift \( \Delta \phi \), for a sufficiently large \( \Delta \theta \), depends on the difference in indices of refraction (\( n_\sigma - n_\pi \)), as well as the beam path \( t \) and wavelength \( \lambda \), and is given by [41]:

\[
\Delta \phi = \frac{2 \pi}{\lambda} (n_\sigma - n_\pi) t
\]

\[
= \left[ \frac{r_e^2 F_h F_{\bar{h}} \lambda^2}{2 \pi V^2} \sin 2\theta_B \right] t = A \cdot \frac{t}{\Delta \theta}
\]

\[ (3) \]

\( F_h \) and \( F_{\bar{h}} \) are structure factors for \( h \) and \( \bar{h} \) reflections, \( r_e \) is the classical electron radius, and \( V \) is the unit cell volume.
By rocking a low-Z crystal such as diamond [42], Be [41], or LiF [43], from one side of the Bragg reflection to another, the polarization can be switched from lcp to rcp, with a $P_c > 90\%$. APS 4-ID-D is one beamline that uses such quarter wave plates (Fig. 6) [44].

2.2. Magnetic field and temperature control

The simplest samples for XMCD experiments are permanent magnets, such as the domains in disk storage devices. These samples can be magnetized separately from the XMCD measurement. For example, Stöhr et al. [45] have used the XMCD effect to image magnetic domains in disk storage devices. Other groups have magnetized thin film samples in situ with a pulsed magnetic field, which is then turned off during the experiment [46,47]. Ferromagnets are also easy to study, since only a small field need be applied. For example, the early measurements of Chen and co-workers used an external cylindrical permanent magnet in close proximity to the Ni foil. The field was switched by manually reversing the external magnet [23]. NdFeB alloy permanent magnets are still used in some experiments to polarize the sample. Electromagnets make this process easier to automate, and several groups have used them in a variety of ways [48]. For example, Arenalho has recently built an eight-pole system that, in combination with a sample manipulator that allows 180° polar and 360° azimuthal rotation of the sample, permits any geometry of magnetic field, sample surface, and incident photon direction (Fig. 7).

Superconducting magnets are required to achieve the highest magnetic fields. Our group employs two different split coil designs. In one instrument, a 6 T split coil is used, with a transverse gap between the coils [24,49]. This device has the advantage that full magnetization of the sample is achieved at 2–3 K, which is readily achieved with pumped $^4$He cryostats. A temperature of $\sim$0.5 K can be reached by using a $^4$He insert (Fig. 7) [50]. It has two limitations. First, the small gap limits the size of the Ge detector that can be introduced between the coils; hence we lose some solid angle of fluorescence collection. More important, the relatively large (31 H) inductance limits the rate at which the magnetic field can be reversed. However, because of its relative ease of use, this machine remains the workhorse of our XMCD measurements.

Another, more recent, instrument employs a $^3$He–$^4$He dilution refrigerator, a split-coil 2 T superconducting magnet system, and a 30-element windowless Ge fluorescence detector [51]. This device has a larger gap (8.25 cm), allowing insertion of the 30-element Ge detector close to the sample. It also has a low inductance winding (1.3 H), allowing field sweeps from +2 T to −2 T in $\sim$10 s. Several layers of thermal shielding allow temperatures below 0.5 K to be reached routinely (Fig. 7); in principle, 0.1 K should be possible.

2.3. Detection methods

Since XMCD is essentially a measurement of relative absorption coefficients, all of the methods used for conventional XAS can in principle be applied (Fig. 1). In practice, the three most important modes are transmission, fluorescence, and electron yield. As discussed long ago by Lee et al. [52], the preferred mode depends on the concentration and spatial distribution of the element under investigation, as well as the fluorescence yield and the matrix absorption coefficient. Since all of the factors involved in optimizing hard X-ray absorption measurements are well known, we will concentrate on the special requirements for MCD with soft X-rays.
2.3.1. Transmission

Transmission is the simplest measurement, and it should be used whenever possible. The beam intensity before the sample ($I_0$) is often measured using the electron yield or photocurrent from a partially transmitting metal grid. The intensity after the sample ($I$) can be measured using a second grid, a solid metal plate, or a Si photodiode. Chen and coworkers have done careful transmission measurements...
of the XMCD of thin metal foils to check the accuracy of the sum rules [53], and with these samples transmission works beautifully. Unfortunately, in the soft X-ray region it is difficult to prepare coordination complexes as homogeneous, pinhole-free samples with the required sub-micron thickness. As discussed by Stern and Kim [54] and Goulon et al. [55], thick or porous samples will have suppressed absorption features due to ‘leakage’ effects, and consequently diminished XMCD amplitudes, especially if harmonics are present in the incident beam. Since the particle size of most samples is often greater than the \(1/e\) (<1 \(\mu\)m) path-length, diluting the sample in a low-Z powder or null is of no use.

2.3.2. Electron yield

For concentrated inorganic samples, electron-based detection methods are preferred. One can either measure the electron yield directly with a channeltron electron multiplier (CEM), or indirectly as the ‘photocurrent’ of electrons flowing to the sample from ground. Since electrons are only emitted from approximately the first 25–50 Å of a sample, these approaches are very sensitive to oxidation or other surface reactivity. For very high cross sections, they can also suffer from saturation effects [56]. A problem for inorganic chemists is that many coordination complexes are poor conductors at the \(\sim 4\) K temperature required for XMCD of paramagnets. To some extent, this can be overcome by: (1) making very thin samples, (2) using a high collection voltage, (3) embedding the sample in a metallic grid, (4) pressing the sample particles into an indium foil, or (5) mixing the sample with a good conductor (Ag or graphite dust). The one generalization we can make from past experience is that every sample is different.

Apart from S/N issues, electron methods may suffer from artifacts if magnetic field switching is used to measure the XMCD effect. The trajectories of emitted photoelectrons will depend not only on their initial velocity, the applied voltage, and the geometry of the collector placement, but also on the magnetic field. The apparent absorption cross section will vary if changing the field affects the fraction of photoelectrons that are accepted. Thus, electron-based XMCD measurements are best done with variable photon polarization.

2.3.3. Fluorescence yield

Fluorescence yield might seem immune from magnetic field artifacts, since the magnetic field will not affect the photons once emitted. However, most detectors convert X-rays into electrons, hence the detector resolution or gain can be influenced by a strong field. The potential detector sensitivity needs to be checked before varying the magnetic field for XMCD measurements or magnetization curves. As pointed out by de Groot et al. [57,58] and others [59], the fluorescence-detected excitation spectrum is not necessarily the same as the absorption spectrum, because the fluorescence yield can vary for different excited states. In extreme cases, a line can even be missing from the excitation spectrum (Fig. 8) [59]. However, as noted by van Veenendaal et al. [60,61], the effect is not usually that severe for XMCD. They point out that, ‘although in principle fluorescence yield is unequal to X-ray absorption, in the presence of a crystal field or of strong core-hole spin-orbit coupling fluorescence yield can be used to obtain ground state expectation values of \(L_z\) and \(S_z\) (vide infra) [60]. It is presumably even less important for magnetization curves, where one only needs proportionality at a single point in the spectrum. From an experimentalist’s point of view, a fluorescence-detected spectrum with known limitations is better than no spectrum at all.

Finally, it should be noted that even polarization-switched measurements suffer from potential artifacts. If the effective source point for left- and right-circularly polarized beams is slightly different, this can transform into an energy difference between the two beams at a given monochromator position. The slight mismatch will result in a derivative shaped contribution to the spectrum that is stronger for sharper features. Since this effect is independent of the applied field, one should check that there is indeed no XMCD effect in the absence of sample magnetization. (This presumes there is no ‘natural’ CD effect, but that is another story [62,63].)
3. Simplified theory

A full description of the XMCD effect for a transition metal complex with multiple d-vacancies requires a sophisticated computer program, and even then, the models are only approximations. A simple approach, the ‘one-electron picture’, is commonly applied to metallic samples, while the more complex ‘ligand field multiplet approach’ includes Coulomb and exchange integrals and is more often used for transition metal complexes. Below we compare the predictions of both pictures. It should be noted that the ligand field multiplet model reduces to the one-electron approach in the limit where the Coulomb and exchange integrals are zero.

3.1. One-electron theory

A large fraction of the XMCD literature, especially papers involving magnetic thin film and metallic samples, uses the one-electron model along with a two-step approach to XAS [64]. In this picture, the first step is to write the one-electron model along with a two-step approach to the one-electron model. The next step is to find expressions for the cross sections for transitions to various states with d symmetry. Stohr and Wu [64] write these, citing Bethe and Salpeter [65], as:

\[ n', l + 1, m_l + 1 | P_{l}^{(1)}(n, l, m_l) \]

and

\[ (l + m_l + 1) (l + m_l + 1) \]

where

\[ P_{l}^{(1)} = \frac{1}{\sqrt{2}} (x + iy) \]

and

\[ P_{l}^{(1)} = \frac{1}{\sqrt{2}} (x - iy) \]

Finally, the XMCD effect, for transitions solely to spin-down orbitals, is given by \( \Delta I = I^+ - I^- \). For the L3-edge, \( \Delta I_{L3} = -(2/9)R^2 \), while at the L2-edge, \( \Delta I_{L2} = +(2/9)R^2 \). The key result from these calculations is that with lcp (using our ‘optical’ definition), at the L3-edge the atom preferentially (5/8 of the time) emits spin-up electrons, while at the L2-edge the atom preferentially (3/4 of the time) emits spin-down electrons (Fig. 9). This can be measured directly with spin-polarized circular dichroic photoemission [66,67].

The one-electron model can also be used to explain the spin polarization of K-edges. In these cases, spin-orbit coupling of the final state p-electron is invoked [22,68]. However, as noted by Broder and Hikam [69], at K-edges the relative amounts of spin-up and spin-down states depend on the absorbing atom, the neighboring atoms, and the energy above threshold. Because spin-orbit coupling is much weaker, the degree of spin-polarization is typically 1% or less.

3.1.1. Band theory and XANES XMCD

Once the spin polarization of the ‘emitted’ electron is established, the one-electron model can be used to explain XMCD effects in both the XANES and EXAFS regions. In the two-step model, the p1/2 and p3/2 shells are viewed as spin-polarized sources, and vacant spin-up and spin-down 3d bands are viewed as spin-sensitive ‘detectors’. For example,
have been calculated for 3d1 through 3d9 systems with a consequence of angular momentum selection rules. Spectra in this approach, the XMCD effect emerges naturally as a mixed and split by the symmetry of the ligand field [73–77].

3.2. Ligand field multiplet theory (LFMT)

The EXAFS region is also sensitive to the spin polarization of emitted electrons—scattering by magnetic neighbors depends on the photoelectron polarization. When the neighboring atom is spin polarized, there will be an exchange contribution in addition to the Coulomb scattering potential. This will modify both the amplitude f_0(σ, k) and phase shift φ_0(σ, k) for electron backscattering, so that the traditional formula for EXAFS for a single absorber-scatter interaction requires modification. Schütz and coworkers proposed addition of corrective terms f_1(σ, k) and φ_1(σ, k) for the magnetic backscattering amplitude and phase shift, scaled by the degree of photoelectron polarization σ_z [68]:

\[ y(k) = \frac{e^{-2\pi^2 f_1(σ_z,k)} \cdot |f(σ,k)| \sin[2kR + φ(k)]} {kR^2} \]  

(8)

where

f_0(σ,k) = f_0(σ,k) ± (σ_z f_1(σ,k)) and φ_0(k) = φ_0(k) ± σ_z φ_1(k)  

(9)

The other terms have their conventional meaning: R is the absorber-scatterer distance, σ is the rms variation in R, k is the photoelectron wave number, and λ is its mean free path.

3.2. Ligand field multiplet theory (LFMT)

Ligand field multiplet theory is a multi-electron viewpoint that describes the initial and final states as multiplets that are mixed and split by the symmetry of the ligand field [73–77]. In this approach, the XMCD effect emerges naturally as a consequence of angular momentum selection rules. Spectra have been calculated for 3d1 through 3d9 systems with a range of crystal field and spin-orbital coupling strengths [78,79], so for many inorganic systems one can check beforehand to see if XMCD will be useful. Before discussing this in detail, it is worth illustrating the differences between one electron and multiplet approaches using the same (assuming no orbital angular momentum) if only spin down states are available, then the ‘asymmetry’, (σ− − σ+)|(σ− + σ+) at the L_2-edge should be a 50% effect, twice as large as at the L_1-edge (opposite in sign). The simplest case, the rigid band ‘Stoner model’, is illustrated in Fig. 9.

In a more sophisticated analysis, multiple scattering calculations using FEFF8 source code reproduced most of the Ni metal L_2 XMCD, including a controversial satellite 6 eV above the main resonance [70]. The latter peak was missing using a 13-atom cluster, but appeared in the 50-atom calculation. A lower energy feature at 3 eV was assigned to many body effects. The authors point out that no approach yet captures all the physics in the XMCD effect. We note that an alternative approach using the configuration interaction model can also reproduce both the 6 eV XAS satellite and the 3 eV XMCD feature [71,72].

3.2.1. Scattering theory and EXAFS XMCD

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The other terms have their conventional meaning: R is the absorber-scatterer distance, σ is the rms variation in R, k is the photoelectron wave number, and λ is its mean free path.
the $2p^3 3d^0 \rightarrow 2p^3 3d^0$ transition seen with Cu(II) and Ni(II) complexes, as explicated in a classic paper by van der Laan and Thole [79]. They begin by writing the initial and final states of an atom in a magnetic field as $|\mu J M\rangle$ and $|\mu' J' M'\rangle$, where $J$ and $M$ are the total angular momentum and magnetic moment respectively, and $\alpha$ designates all other quantum numbers. They note that the temperature-dependent line strength is given by:

$$\langle \alpha J' \rangle = |\langle \alpha | C^{\dagger} | J \rangle|^2 \tag{10}$$

where the last factor is the line strength of the $|J \rightarrow J'\rangle$ transition, and the geometric factor $\langle \alpha J' \rangle$ distributes this intensity over the different $M \rightarrow M'$ transitions:

$$\langle \alpha J' \rangle = \sum_{M} \left( \begin{array}{ccc} J & 1 & J' \\ M & q & M' \end{array} \right)^2 e^{-\frac{2\mu\mu'}{kT}} \tag{11}$$

In the last equation, $\theta$ is the reduced temperature, $T = kT/\mu g\beta H$, and the squared term in the summation is a ‘$3j$ symbol’ [82]. Once the wave function is described in terms of $J$ and $\mu$, the $T = 0$ XMCD intensities derive from the angular momentum algebra contained in the $3j$ symbol.

Life is simple in spherical symmetry. The initial $d^0 3d$ term is split by spin-orbit coupling into $1D_{3/2}$ and $2D_{3/2}$ levels by the 3d spin-orbit interaction, and in a magnetic field, the latter is split by the Zeeman effect into six distinct states. At $T = 0$, there is only one allowed transition, $1D_{3/2} (M_J = -3/2) \rightarrow 2D_{3/2} (M_J = -3/2)$, thus $\Delta M_J = q = +1$. This corresponds with absorption of lcp X-rays with our optical definition (Fig. 11).

Of more interest to chemists is the effect of a ligand field on the energies and intensities of different transitions. For example, for Cu$^{2+}$ in $D_4h$ symmetry, the wave function can have $B_1$, $A_1$, $B_2$, and $E$ irreducible representations [83]. Further splitting by spin-orbit coupling and a magnetic field along the $c$-axis axis yields a $\Gamma_1^\prime$ ground state that is a mixture of $|5/2, 2/2\rangle$, $|5/2, -2/2\rangle$, and $|3/2, 3/2\rangle$ levels [79]. When the spin-orbit splitting is small compared to crystal field splittings, first order perturbation theory gives the ground state wave function as [79]:

$$|\Gamma_1\rangle = |B_1\rangle + \zeta_d |\Delta(B_2)\rangle (B_2) + (1/\sqrt{2}) \zeta_e |\Delta(E)\rangle (E) \tag{12}$$

To give the reader the flavor of the information content of these spectra, the results of the van der Laan and Thole analysis are reproduced in Table 3. Note the major difference between LFMT and ‘two-step’ predictions. In the absence of ground state spin orbit coupling, LFMT predicts a branching ratio of 1 for $q = -1$ (a 100% XMCD effect at the L2-edge).

In contrast, we have seen that one-electron theory predicts at most a 50% asymmetry.

The complexity of XMCD spectra increases rapidly as:

(a) the number of d-electrons near a half-filled shell, (b) charge-transfer effects require inclusion of multiple configurations, (c) lower symmetry requires inclusion of orientation dependence, and (d) zero field splittings (which arise from 3d spin-orbit coupling effects) complicate the magnetic field dependence. Since this is a primer and not an encyclopedia, we merely mention potential complications and point the interested reader toward the relevant literature.

First of all, the calculations become more complex towards the middle of the transition series. As noted by deGroot, there are 1512 possible final states for a $2p^3 3d^0$ final state (for example, a Mn$^{3+}$ initial state) [84]. Furthermore, in lower symmetry structures, additional parameters (Ds, Dd) are required to describe the ligand field, and the potential for artificially good simulations rises proportionally.

Van der Laan [85] has pointed out that in C$_4$ symmetry, the XMCD is a sum over three fundamental spectra, and that measurements in four different geometries are required. Van Elp and Searle [86] have discussed how the XMCD can vary dramatically for different molecular orientations with respect to the magnetic field, especially when there is a zero field splitting comparable or larger than the applied Zeeman splitting. Finally, if charge transfer is significant between the metal ion and the ligands, then two or more configurations (e.g. 3d$^2$, 3d$^{10}$) may be required to describe the electronic structure of both the initial and final states. Configuration interaction will add additional free parameters to the spectroscopic model. Given the potential complications to spectral simulation, it is fortunate that an alternate approach exists that requires far fewer assumptions—sum rule analysis.

3.3. Sum rule analysis

Sum rules are equations based on integrated spectra, and they allow derivation of valuable information without resort to laborious simulation techniques [87,88]. For example, most chemists are familiar with the Kuhn–Thomas sum rule, which states that the sum of oscillator strengths $f_{\omega}$ is equal to the number of electrons $N_e$ [89]:

$$\sum_{\nu} f_{\omega} = N_e \tag{13}$$

The first X-ray sum rule to consider states that the integrated intensity over particular absorption edges reflects the number of empty states with the appropriate symmetry for the transition [90]:

$$\int \mu_{\nu} \mu_{\nu+1} \mu_{\nu-1} d\omega \propto \frac{\Delta + 2 - n}{2\Gamma + 1} \mu_\nu^2 \tag{14}$$

Table 3: Line strength and branching ratio for $d^0$ system with $\Gamma_3$ character in C$_4$ symmetry

<table>
<thead>
<tr>
<th>Dipole excitation</th>
<th>Line strength ($P$)</th>
<th>Branching ratio ($B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotopic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q = +1$</td>
<td>$</td>
<td>1 - 2q/\Delta(E)</td>
</tr>
<tr>
<td>$q = -1$</td>
<td>$</td>
<td>1 + 2q/\Delta(E)</td>
</tr>
<tr>
<td>$q = 0$</td>
<td>$(\mu_{Aq})^2/20$</td>
<td>1</td>
</tr>
</tbody>
</table>
For transition metal L$_{2,3}$-edges, which have an initial 2p level, the transitions are primarily to states of 3d-symmetry, since the 2p → 4s transitions are ~20-fold weaker than the 2p → 3d transitions [1]. The decrease in the number of d-vacancies across the first transition series is nicely illustrated by comparing the white line intensities of the pure metals (Fig. 12) [56]. We have used this sum rule to quantify the amount of electron density transferred from copper to its ligands in blue copper proteins [91] and the CuA site, as well as the number of 3d vacancies in compounds with different Ni oxidation states [92].

For XMCD, the most important sum rules involve projections of the spin (S) and orbital (L) angular momentum of the absorbing species. In general terms:

\[
\delta = \frac{\int_{J_{+, \cdots}} (\mu_{1} - \mu_{-}) \, d\omega - \frac{1}{2} \int_{J_{-, \cdots}} (\mu_{1} - \mu_{-}) \, d\omega}{\int_{J_{+, \cdots}} (\mu_{0} + \mu_{1} + \mu_{-}) \, d\omega}
\]

and

\[
\rho = \frac{\int_{J_{+, \cdots}} (\mu_{1} - \mu_{-}) \, d\omega}{\int_{J_{+, \cdots}} (\mu_{0} + \mu_{1} + \mu_{-}) \, d\omega}
\]

where $J_{+, \cdots}$ and $J_{-, \cdots}$ represent the transitions involved, and $\mu_{0}$, $\mu_{1}$, and $\mu_{-}$ are the magnetic moments associated with the states involved in the transitions. The factors $S_{\parallel}$ and $L_{\parallel}$ represent the parallel components of the spin and orbital angular momenta, respectively.

\[
\begin{align*}
\delta & = \frac{\int_{J_{+, \cdots}} (\mu_{1} - \mu_{-}) \, d\omega - \frac{1}{2} \int_{J_{-, \cdots}} (\mu_{1} - \mu_{-}) \, d\omega}{\int_{J_{+, \cdots}} (\mu_{0} + \mu_{1} + \mu_{-}) \, d\omega} \\
\rho & = \frac{\int_{J_{+, \cdots}} (\mu_{1} - \mu_{-}) \, d\omega}{\int_{J_{+, \cdots}} (\mu_{0} + \mu_{1} + \mu_{-}) \, d\omega}
\end{align*}
\]
Stöhr and König have shown that $\langle T_z \rangle$ angular averages to zero in 'powder' samples [93], so the last term in Eq. (15) can often be omitted. The quantities involved in sum rule analysis are illustrated graphically in Fig. 12.

Using these A, B, and C to represent the appropriate integrals (Fig. 12), neglecting the $\langle T_z \rangle$ term, and assuming that $\mu_0 = (\mu_1 + \mu_{-1})/2$ [94], yields the following simple expressions for the sum rules.

$$\langle L_z \rangle = \frac{2(A + B)}{3C} n_h,$$

$$\langle S_z \rangle = \frac{A - 2B}{2C} n_h$$ (17)

The sum rules have been tested by comparison with experimental measurements [53,56] and theoretical calculations [95,96]; they are generally thought to be accurate within about 10%. One possible source of error is found for the early transition metals, such as Cr, where the multiplet effects are larger than the 2p spin-orbit coupling and hence the L$_2$ and L$_3$-edges cannot be separated. Sainctavit et al. [97] have done analytical calculations for Cu(II) in an octahedral ligand field that address the sum rule assumptions. They found that at low temperature, the $\langle T_z \rangle$ term makes a large contribution to the spin sum rule and cannot be ignored. Others have shown that $\langle T_z \rangle$ can also be significant for other first transition metals, especially at lower symmetry surface sites [98].

4. Chemical and materials science applications of XMCD

There is now a very large literature of XMCD applications, the majority of which involve the characterization of magnetic materials. In a brief review, it is impossible to cover all of this literature, so below we simply illustrate some of the bioinorganic applications and highlight how XMCD is being used in materials science. Note that all of the (bio)inorganic XMCD examples arise from paramagnetic properties, and measurement of these spectra require liquid helium temperatures and magnetic fields of several Tesla. In contrast, many of the materials science examples involve ferromagnetic samples that are magnetized by much smaller fields and which can be measured at much higher temperatures. In both cases, however, the key spectroscopic advantages of XMCD are much the same.

4.1. Element specific detection of magnetic moments

A simple example of a bioinorganic application of XMCD involves the Ni derivative of the 'blue' Cu protein *Pseudomonas aeruginosa* azurin (NiAz) [99,100], a system we have studied in collaboration with Gray and co-workers [101]. Ni azurin can potentially serve as a model for more complex Ni sites such as those observed in H$_2$ases [NiFe], CODH C, and ACS A-clusters [102,103]. The Ni L-edge XMCD clearly shows the Ni(II) center is paramagnetic (Fig. 13); the spectra and simulations indicate that the Ni has a high-spin, triplet, ground state. The XAS and XMCD spectra have been calculated using the 3d orbital splitting pattern obtained from density functional theory (DFT) calculations as the basis for ligand field multiplet simulations (Fig. 13). Similar L-edge and XMCD studies have also provided evidence for high spin Ni(II) in NiFe H$_2$ases [104] and in certain forms of the C-clusters [105] and A-clusters [106].

Ni L-edge XMCD is playing a useful role in investigating the magnetic properties of transition metal rare-earth alloys and compounds. For example, it has been used to site-selectively monitor the Ni magnetic moment in RNi$_2$, where R is a rare-earth element. Normally, the Ni moment disappears as the rare-earth (R) content increases up to the Laves phase. Recently, XMCD has shown that the Ni site in GdNi$_2$ retains an intrinsic magnetic moment even in Laves phase concentrations. Its antiparallel alignment with the Gd moment can also be observed from the M$_4$-edge XMCD (Fig. 14) [107]. This is discussed in the magnetic coupling section below.

XMCD also occurs at transition metal K-edges, although the dichroism is significantly weaker than at L- and M-edges. For example, in rare-earth transition metal alloys of Ho$_4$Fe$_{23}$ and Y$_6$Fe$_{23}$, the structure and intensity
of Fe K-edge XMCD signals have been directly related to the Fe(4p,3d)-Ho(5d)/Y(5d) hybridized bands [108]. The shape of the Fe K-edge XMCD spectra of Y₆Fe₂₃ (Fig. 14) closely resembles that of Fe metal (not shown). In contrast, the Fe K-edge XMCD for the Ho alloy shows significant differences, with an additional positive feature observed at about 7.118 keV. This has been attributed as an effect due to Ho, implying stronger Fe–Ho hybridization than in the Fe–Y case.

Another example of Fe K-edge XMCD involves H₂ absorption by intermetallic R₂Fe₁₄B materials. These experiments are driven by interest in permanent magnet technology [109] and aim to distinguish the effects of hydrogen on the iron sublattice magnetism from the effects on the rare-earth element. Fe K-edge XMCD spectra on Nd₂Fe₁₄BHₓ and Y₂Fe₁₄BHₓ, show that increasing interstitial hydrogen content in the Y–Fe intermetallic has little effect on the Fe magnetic moment (Fig. 15). In contrast, the difference XMCD signal increases with hydrogen content for the Nd–Fe material, showing that the Nd contribution to the Fe magnetism decreases with the increase in hydrogen content.

---

Fig. 13. (Left) Model of Ni₄Ni and orbitals involved in L-edge XMCD. (Right) XMCD data for Ni₄Ni at 6 T and 2 K. (a) Zero-field XAS spectrum. (b) rcp (----) and lcp (—) XAS spectra. (c) XMCD spectrum. (d) Calculated XMCD. The L₃ centroid energy is 853.1(1) eV; the branching ratio is 0.722(4); and the magnetic moment is calculated to be 1.9(4)µB.

Fig. 14. (Left) Ni 2p → 3d XAS and XMCD spectra of GdNi₂, at a temperature of 25 K. (Center) Corresponding Gd 4d → 4f XAS-MCD spectra. The inset shows the theoretical XAS and XMCD spectra [107]. Reprinted with permission from [107]. Copyright (2003), by the American Physical Society. (Right) Fe K-edge XMCD spectra of Ho₆Fe₂₃ and Y₆Fe₂₃ alloys at room temperature. Reprinted with permission from [108]. Copyright (2000), American Institute of Physics.
A recent XAS/XMCD study of CeRu$_2$Si$_2$ [110] nicely illustrates magnetic effects at rare-earth L-edges. CeRu$_2$Si$_2$ is a typical ‘heavy fermion’ (HF) compound with an electronic specific-heat coefficient $\nu = 350 \text{ mJ/K}^2 \text{ mol}$ below $T_K = 20 \text{ K}$ [111]. This compound is reported to show a metamagnetic transition into a ferromagnetically ordered state induced by the magnetic field at 7.8 T below a temperature of 10 K [112]. Although such behavior among heavy-fermion systems is an important topic, this property in these systems is still not completely understood.

Honma and coworkers used Ce L$_2$-edge XMCD (2p $\rightarrow$ 5d transitions) to characterize unoccupied Ce 5d electronic states in CeRu$_2$Si$_2$ [110]. The Ce L$_2$-edge XAS (Fig. 16) of the trivalent CuRu$_2$Si$_2$ and CuRu$_2$Ge$_2$ systems exhibits a strong peak A arising from 2p $\rightarrow$ 5d electric dipole transitions with 4f$^1$ configuration and a weak shoulder B attributed to the 4f$^0$ configuration [113]. A similar double peak structure A$'$ and B$'$ is observed in the tetravalent CeO$_2$ system. The XMCD (Fig. 16) shows a change around the white line qualitatively suggesting the decreasing c–f hybridization in CeRu$_2$Si$_2$ and that the 4f states are almost localized states of Ce$^{3+}$ (4f$^1$) similar to the CeRe$_2$Ge$_2$ system.

The Ce L$_2$ and L$_3$ XAS/MCD of CeRu$_2$Si$_2$ measured at magnetic fields lower and higher than the metamagnetic crossover field $H_c$ (Fig. 16), showed an enhancement of the ‘white line’ of the Ce L$_2$-edge above the phase transition, suggesting weaker c–f hybridization and stronger localization of the 4f states in the ferromagnetic phase. Notice that even though the XMCD effect at these hard X-ray edges was less than 1%, an excellent signal-to-noise ratio was possible.

### 4.2 Deciphering mixtures

XMCD provides an extra tool for separating magnetic and non-magnetic components in an X-ray spectrum, as well as for distinguishing components with different magnetic moments. Real world samples are often inhomogeneous. In some spectroscopies, such as EPR, this is not a major problem—non-magnetic components do not give a signal, and overlapping spectra can be separated by exploiting different power saturation curves or by other methods. Inhomogeneity is more of a problem for conventional X-ray spectroscopy, where chemical shifts are relatively small compared to natural line widths and here XMCD can make real contributions.

For example, in collaboration with David Grahame, we have studied the β$^*$-subunit ‘A-cluster’ Ni site of M. thermophila ACDS protein [114]. This cluster is closely related to the active site for acetyl-CoA synthesis in the α-subunit of carbon monoxide dehydrogenase/acetyl-CoA synthase (CODH/ACS) from C. thermocaceticum, where the first crystal structure revealed a unique Ni-Cu-Fe$_4$S$_4$ cluster (Fig. 17) [115]. A later structure found both Ni-Zn-Fe$_4$S$_4$ and Ni-Ni-Fe$_4$S$_4$ clusters in the same crystal [116], and it is now generally accepted that the Ni-Ni species is the active catalytic form [117].

Both high spin (paramagnetic) and low-spin (diamagnetic) Ni$^{II}$ have been proposed as constituents of various Ni enzymes [105,118]. When we examined the Ni L-edge spectrum of one particular sample, we observed a complex spectrum with at least three bands (Fig. 17) [106]. The XMCD spectrum showed that the low and high energy features were magnetic, and most likely represented two components of a single high-spin Ni$^{II}$ spectrum. The central peak did not show an XMCD effect and most likely represented low-spin Ni$^{II}$. Since Ni presumably occupies both ‘external’ sites in this particular protein, our working hypothesis is that the low-spin Ni occupies the more square planar ‘M$_6$’ site, while the high-spin Ni occupies the more tetrahedral ‘M$_4$ site’ [106]. The observed heterogeneity...
Fig. 16. (Upper panel) (a) Ce L₂-edge spectra for CeRu₂Si₂, trivalent CeRu₂Ge₂, and tetravalent CeO₂. Note the absorption-edge energy shift from CeRu₂Ge₂ to CeO₂ arises from the difference in Ce oxidation states. (b) The observed Ce L₂-edge XAS spectra at different fields of 6 T (60 kOe), 10 T (100 kOe), and zero field for CeRu₂Si₂. (Lower panel) XAS at zero field and MCD spectra at: (a) Ce L₂-edge and (b) Ce L₃-edge. Reprinted with permission from [110]. Copyright (2003), Institute of Physics.

would be hard to infer from the K-edge XANES or EXAFS alone.

4.3. Magnetic coupling

Since the sign of the XMCD effect reveals the net spin orientation for a given element or oxidation state, this technique can probe the interaction between different species in magnetically coupled systems. The easiest cases to study are interactions between different elements, because the edges are usually well separated in energy. The first such application was a temperature dependent XMCD study of Fe₃Gd₃O₁₂ [119]. At room temperature, the primary Fe XMCD signal was negative, while the Gd signal was positive. This indicated that the bulk magnetic moment was dominated by the contribution from the Fe spins, and that the Gd was antiferromagnetically coupled to the Fe. At low temperature, the Gd M₃-edge showed a strong

Fig. 17. (Left) The structure of the Ni-Cu form of the A-cluster [115]. The β*-subunit presumably has Ni in both proximal and distal sites. (Middle) Ni L absorption spectrum for the β*-subunit "A-cluster" of M. thermophila ACDS protein. (Right) 6 T, 2 K XMCD spectrum for the same sample. Arrows indicate the bands discussed in text.
negative XMCD, indicating that the Gd moment became the dominant factor, while positive Fe $L_3$-edge XMCD again indicated antiferromagnetic coupling (Fig. 18).

In collaboration with the Solomon and Karlin groups, we have used XMCD to observe antiferromagnetic coupling between Fe and Cu in Karlin’s [(F8 -TPP)Fe(III)−Cu(II)] complex (Fig. 19). This is an $S = 2$ system with antiferromagnetic coupling between $S = 5/2$ high-spin Fe(III) and $S = 1/2$ Cu(II). As expected, the Fe and Cu XMCD are of opposite sign.

XMCD analysis can also be used to study the magnetic coupling in mixed valence of the same element, provided there is a useful chemical shift between different oxidation states. Our long-term goal is to use XMCD for interpreting the spectra of complex clusters, such as the Mn center in nitrogenase [120] and the oxygen-evolving complex (OEC) of photosystem II [121]. As a model for the latter problem, we studied the C15-carboxylate derivative of a weakly coupled Fe(II)Fe(III) system [Fe$_2$(III,II)(btmp)($\mu$-O$_2$CC$_2$H$_5$)$_2$][BPh$_4$]$_2$ (Fig. 21) [126]. In a 6 T field, both Mn(III) and Mn(IV) complexes were simulated using ligand field multiplet calculations with a single configuration and reduced Slater integrals.

XMCD powder spectra reflect an average of absorption cross sections over particular molecular orientations with respect to the magnetic field, and in principle a simulation should include these effects (much as is done in EPR simulations). However, the authors employ an approximate integration procedure developed by Ayant et al. [125], in which a powder spectrum is simulated by a sum over special orientations. The Mn(III) spectra were calculated in $D_4h$ symmetry. This is an $S = 10$ antiferromagnetically coupled Mn(III)$_8$Mn(IV)$_4$ cluster from the same system, Mn$_{12}$-ac [123]. This paper illustrates both the valuable information content in XMCD of mixed-valence complexes as well as the complex analysis required for quantitative interpretation of these spectra. (A paper primarily concerned with sum rule analysis of Mn12 has also appeared [124].) The authors recorded XMCD at 1.5 K in a 4 T field using photocurrent yield detection and an asymmetric wig- gler as a ∼60% polarized source. To assist in the interpretation, they also recorded XMCD of representative mononuclear Mn(III) and Mn(IV) complexes. These spectra were simulated using ligand field multiplet calculations with a single configuration and reduced Slater integrals.

One of the most interesting results from the model calculations was the highly anisotropic magnetic properties for the Mn(III) complex, for which a 4 T $\beta$ field parallel to the 'hard' $xy$ plane was insufficient to force magnetization of the complex (Fig. 20). In contrast, the magnetic properties and XMCD of the Mn(IV) complex were nearly isotropic (Fig. 20).

Turning to the Mn$_{12}$-ac, the calculations were done by assuming that all of the Mn(III)$_8$C$_4$ axes were parallel to each other, and then calculating a powder average. The Mn(IV) contribution was treated by assuming a single $S = 1/2$ system antiparallel to the magnetic moment of the Mn(III) ions, yielding a factor of $-1/2$ compared to the mononuclear XMCD. The general success of this model can be seen in the reasonably good agreement between experimental and calculated XMCD (Fig. 20).

We have observed even more complex XMCD in the weakly coupled Fe(II)Fe(III) system [Fe$_2$(III,II)(btmp)($\mu$-O$_2$CC$_2$H$_5$)$_2$][BPh$_4$]$_2$ (Fig. 21) [126]. In a 6 T field, both Fe(III) and XMCD of the Mn(III) spectra were calculated in $D_4h$ symmetry to account for the large Jahn–Teller distortion, while the Mn(IV) spectra were simulated under $O_h$ symmetry. This lead to the following particular summations:

\[
\sigma_{\text{Mn(III)}}^{(l(r))} = \frac{1}{4} (\sigma_{\text{Mn(III)}}^{(001)B} + \sigma_{\text{Mn(III)}}^{(010)B} + \sigma_{\text{Mn(III)}}^{(100)B})
\]

\[
\sigma_{\text{Mn(IV)}}^{(l(r))} = \frac{1}{4} (\sigma_{\text{Mn(IV)}}^{(001)B} + \sigma_{\text{Mn(IV)}}^{(010)B} + \sigma_{\text{Mn(IV)}}^{(100)B})
\]

\[
\sigma_{\text{Mn(III)}}^{(l(r))} + \sigma_{\text{Mn(IV)}}^{(l(r))} = \frac{1}{4} (\sigma_{\text{Mn(III)}}^{(001)B} + \sigma_{\text{Mn(III)}}^{(010)B} + \sigma_{\text{Mn(III)}}^{(100)B}) + \frac{1}{4} (\sigma_{\text{Mn(IV)}}^{(001)B} + \sigma_{\text{Mn(IV)}}^{(010)B} + \sigma_{\text{Mn(IV)}}^{(100)B})
\]

One of the most interesting results from the model calculations was the highly anisotropic magnetic properties for the Mn(III) complex, for which a 4 T $\beta$ field parallel to the 'hard' $xy$ plane was insufficient to force magnetization of the complex (Fig. 20). In contrast, the magnetic properties and XMCD of the Mn(IV) complex were nearly isotropic (Fig. 20). The Mn(III) spectra were calculated in $D_4h$ symmetry. This is an $S = 10$ antiferromagnetically coupled Mn(III)$_8$Mn(IV)$_4$ cluster from the XMCD alone.
signals are negative, indicating that the spins are mostly parallel and that the Zeeman interaction overwhelms the zero field splittings D and the exchange interaction $J_{AB}$. The observed XMCD was $\sim 34\%$ of the effect expected for two independent and totally oriented Fe(II) and Fe(III) ions, indicating that the temperature and field were not sufficient to achieve total spin alignment. In a weaker 1 T field, the Fe(II) XMCD became quite weak. There is a competition between the different terms in the spin Hamiltonian, but neglecting zero field splittings, the antiferromagnetically

Fig. 20. (Left) Mn(III), (middle) Mn(IV), and (right) Mn-12 XMCD. Reprinted with permission from [123]. Copyright (2003), American Physical Society.
coupled Fe(II) should eventually have a positive XMCD at a sufficiently weak magnetic field. One of the most intractable systems we have encountered is the relatively ‘simple’ $S=\frac{1}{2}$ Fe(II)Fe(III) site encountered in reduced 2Fe ferredoxins. Naïve subtraction of a reduced $(S=2)$ Fe(II) rubredoxin (Rd) XMCD from the oxidized $S=\frac{5}{2}$ Fe(III) Rd spectrum yields a bipolar spectrum distinctly different from the experimental spectrum (Fig. 21). At least two factors complicate the naïve analysis. First, Mössbauer data show that the covalency of Fe in the binuclear site is such that chemical shifts between the ferrous and ferric site are significantly reduced from the 1.4 eV values observed in mononuclear Rd centers. Assuming a direct proportionality between isomer shift and L-edge shift, only $\sim 0.5$ eV is expected. Second, one must consider the spectra from all the possible $M_s$ states that give rise to the total $S=\frac{1}{2}$. Not only is there a $M_{\text{Fe(II)}}=\frac{5}{2}+M_{\text{Fe(III)}}=-2$ contribution, but there are four other combinations $(3/2,-1; 1/2,0; -1/2,1; -3/2,2)$ weighted in proportion to their Clebsch–Gordon coefficients \[127\].

A curious coupling example from materials science is in the non-oxidic colossal magnetoresistance (CMR) spinel $\text{Fe}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{S}_4$, which exhibits very large negative magnetoresistance even at room temperature \[128\]. In this compound, L-edge XAS reveals that Fe is formally in the ferric state, Cr is trivalent and the Cu site is Cu(II). However, while XMCD reveals antiferromagnetic coupling between Fe and Cr as the XMCD signs are opposite, the XMCD at the Cu L-edge revealed that any magnetic moment at the Cu sites is very small if not zero ($<0.20\mu_B$) (Fig. 22).

4.4. Magnetic moments from sum rule analysis

Element specific magnetic spin moments have been one of the major applications of XMCD. Thanks to the ‘charge’, ‘spin’ and ‘orbital sum rules’ discussed above, simple integration of properly normalized spectra can reveal the number of vacancies and the magnetic moments. The first bioinorganic application of XMCD sum rule analysis involved the ‘blue Cu’ site in plastocyanin (Fig. 23). XMCD sum rule analysis has also been applied to Ni(II) sites in Ni-doped MgO (Fig. 23). For the plastocyanin work, application of the orbital sum rule yielded a Cu 3d specific $\langle L_z \rangle$ of $\sim 0.07\hbar$ and $\langle S_z \rangle$ of $\sim 0.18\hbar$ per Cu, both within 15% of values derived from SCF-Xo-SW calculations \[129\].
4.5. Element-specific magnetization curves

The field and temperature dependence of the XMCD effect yield information about the magnetization of a sample that can be interpreted independently of one-electron or LFMFT models. The advantage of X-rays over optical techniques such as the Kerr effect is that each element can be probed separately. An important technological application has been the study of the magnetization of different elements in magnetic multilayers, such as the ‘spin-valve’ heads used in modern high-density read heads [130]. These devices employ the giant magnetoresistance (GMR) effect to produce a large change in electrical current from a small change in applied field, thus allowing higher density information storage. We remind the reader that the magnetization of ferromagnetic samples can depend not only on temperature and the current applied field \(\vec{H}\), but also on the previous values of \(\vec{H}\); in other words, samples can exhibit ‘hysteresis’ [131].

For example, scientists at ESRF have studied a model trilayer system consisting of a (soft) 50 Å Ni\(_{80}\)Fe\(_{20}\) layer, a variable thickness metallic Cu spacer, and a (hard) 50 Å Co layer, using fluorescence detected XMCD at the Ni and Co L\(_3\)-edges. With a thin (60 Å) Cu spacer and a slowly changing applied field, both Ni and Co reverse magnetization with the same coercive field, showing that the layers are strongly ferromagnetically coupled. With a thicker (100 Å)
Cu spacer, the Ni$_{80}$Fe$_{20}$ layer requires a much smaller coercive field—the magnetic layers have become decoupled. By employing a pump-probe technique, the authors were able to observe the dynamics of the magnetization process on a nanosecond time scale [132].

For the paramagnets of interest in (bio)inorganic chemistry, the simplest model for the magnetization of $N$ interacting atoms in volume $V$ is given by $M = M_0 B(x, J)$, where $M_0$ is the saturation magnetization, $x = (gJ\mu_B H)/(kT)$ and $B(x, J)$ is the Brillouin function:

$$B(x, J) = \frac{2J + 1}{2J} \coth \left( \frac{2J + 1}{2J} x \right) - \frac{1}{2J} \coth \left( \frac{1}{2J} x \right)$$

which reduces to $\text{XMCD} \sim \tanh[(gJ\mu_B H)/(kT)]$ for $S = 1/2$ systems with no orbital moment [131]. The curves in Fig. 19 and Fig. 24 illustrate the potential of XMCD magnetization curves as a characterization tool separate from sum rule analysis and multiplet simulations. Magnetization curves should be especially useful for the analysis of mixtures, where different uncoupled species might magnetize at different rates.

Of course, as noted by Pavel and Solomon [133], systems with zero field splittings such as Fe(II) can exhibit far more complex magnetization curves. Only recently has the quality of magnetization curves improved enough to warrant a more sophisticated analysis.

### 4.6. Element specific magnetic microscopy

All of the strengths of XMCD can in principle be combined with spatially resolving instruments to obtain element-specific images of magnetic properties [45,112,134]. These microscopes can generally be divided into three types: (a) scanning instruments, in which a focused X-ray spot is raster-scanned across the sample and the transmission or secondary yield of fluorescence or photoelectrons is recorded, (b) imaging transmission microscopes, that operate in a mode similar to transmission light microscopes, with the condenser and analyzer lenses replaced by zone plates for the X-ray region, and (c) photoelectron microscopes, in which the photoelectron yield from different regions of the sample is imaged through electron microscope optics (Fig. 25).
XMCD–photoemission electron microscopy (XMCD–
PEEM) is a powerful tool to examine element-specific mag-
etism. For example, in the search for new materials for use
in ‘spintronics’ applications, ‘half-metallic ferromagnets’
(HFM) are among the desirable targets. These materials
have one spin channel (up or down spin) that is metal-
lic, while the other spin channel has a gap at the Fermi
level. This causes complete polarization of the conducting
electrons. Recent calculations predicted that the Heusler
compound Co$_2$Cr$_{0.6}$Fe$_{0.4}$Al, an electron-doped derivative
of Co$_2$CrAl, would exhibit a total spin polarization at the
Fermi level and a large magnetoresistance effect [135]. This
is demonstrated by XMCD–PEEM imaging at the Co and
Fe $L_3$-edges (Fig. 26). Dark and bright areas represent the
induced micron-sized domains with magnetization opposite
and parallel to the projection of the photon respectively.
The similarity in the contrast of the Co and Fe images
demonstrates ferromagnetic coupling, for antiferromagnetic
coupling the images would be inverted.

For the study of multilayered magnetic materials, XMCD
can be coupled with depth-resolving techniques to resolve
magnetic structure beneath the surface. These use, for ex-
ample, X-ray standing waves [136] or alternatively exploit the
narrow escape depth of the photoelectron (Fig. 27) [137].
This latter approach has been applied to ultra-thin films of
Fe grown on Cu(100), allowing the magnetic moment of
individual layers to be determined. In case of a 4 mul-
ti-layer (ML) film, the XMCD for each of the layers were es-
tially identical (Fig. 27). On the other hand, the XMCD
signal for the top 2 layers of a 8 ML film (Fig. 27) shows
significant dichroism, while the inner 6 layers showed little
XMCD [137]. This shows that while the 4 ML films is uni-
formly magnetized, the surface region of the 8 ML film is
ferromagnetically coupled while the inner region does not
possess any average magnetization.

Fig. 26. (Left) XMCD–PEEM images over 9.3 $\times$ 8.3 $\mu$m$^2$ region using
(a) Fe and (b) Co $L_3$-edges. These illustrate the micromagnetic domains
that are prevalent in Co$_2$Cr$_{0.6}$Fe$_{0.4}$Al. Magnetic domains that are opposite
or parallel to the direction of the photon beam appear dark and light
respectively. (Right) The upper and the lower panel show the Cr Fe and Co
$2p$ XAS and MCD spectra are shown for the quenched Co$_2$Cr$_{0.6}$Fe$_{0.4}$Al
system. Reprinted with permission from [135]. Copyright (2003), Institute
of Physics.
Fig. 27. (Left) Schematic diagram of depth-resolved XMCD measurements of magnetic multilayers. By moving the sample along the incident beam axis, the electron detection angle $\theta_d$ can be altered, thus decreasing the electron escape depth. Spectra were measured at 110 K; samples were magnetized prior to measurement. (Center) Fe L-edge absorption and XMCD spectra for each layer of a 4 ML Fe film. (Right) Fe L-edge absorption and XMCD spectra (dotted line) for surface two layers and inner six-layer thick region for a 8 ML Fe film. Reprinted with permission from [137]. Copyright (2003), Institute of Physics.

4.7. Electronic structure

In UV–vis spectroscopy, MCD is often used to bring out detail in absorption spectra that are otherwise broad and featureless. L-edge XMCD can be used in the same manner. For example, the L-edge spectra of V(II) and V(III) complexes are relatively uninformative, and can be modeled by a wide set of ligand field parameters. In contrast, the XMCD spectra contain a wealth of structure that puts additional constraints on any LFMT simulation (Fig. 28).

XMCD can also help to distinguish $p \rightarrow d$ transitions from those that are primarily charge transfer in nature. In Fig. 28, we show some recent XMCD spectra for a Ni(II) complex from Charles Riordan’s lab. As expected for a $d^9$ system,
there is a strong signal at the L$_3$-edge, and the XMCD approaches a 100% effect at the L$_2$-edge. In contrast, a feature near 856 eV has almost no dichroism. We attribute the latter to a charge transfer transition to an empty $n^\pi$ orbital. DFT calculations are being done in collaboration with Jorge Rodrigues to quantify these assignments (Fig. 28).

5. Summary—a dose of reality

Few would argue that XMCD spectra, in principle, contain a wealth of information. As circularly polarized beamlines proliferate worldwide, access to and conduct of these measurements should become significantly easier. In ideal cases, XMCD should be able to reveal: (a) the distribution of spin and orbital angular momentum in transition metal complexes (from sum rule analysis), (b) the strength of magnetic coupling between different centers (from the field dependence), and (c) the total magnetic moment (from the magnetization curve). In practice, intelligent use of the technique requires some caution—caveat emptor.

For example, for systems more complicated than d$^9$ ions, the XMCD effect at a given edge is often bipolar or even more complex (see the calculations of van der Laan and Thole [76] and witness the detailed analyses of an Mn$_2$ cluster discussed above). For the analysis of coupled systems, one is often faced with the question—is the XMCD bipolar because of antiferromagnetically coupled ions, or because of side lobes in a single component spectrum? In the extreme cases of Fe–S clusters, it seems that individual features can completely overlap, leaving a relatively featureless XMCD spectrum.