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Review

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

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Contents

Abbreviations: XAS, X-ray absorption spectroscopy; XMCD, X-ray magnetic circular dichroism; CD, circular dichroism; MCD, magnetic circular dichroism; PEEM, photoelectron emission microscopy; lcp, left circularly polarized; rcp, 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; CODH, carbon monoxide dehydrogenase; ACS, acetyl coenzyme-A synthase; ACDS, acetyl coenzyme-A decarbonylase

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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.

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 $\vec{E}_{\mathrm{rcp}}$ for a right circularly polarized photon propagating in the z-direction resembles a right-handed screw (Fig. 1).

$$\vec{E}_{\mathrm{rcp}} = E_0\{\sin[\omega t - kz + \phi_0]\boldsymbol{i} + \cos[\omega t - kz + \phi_0]\boldsymbol{j}\} \quad (1)$$

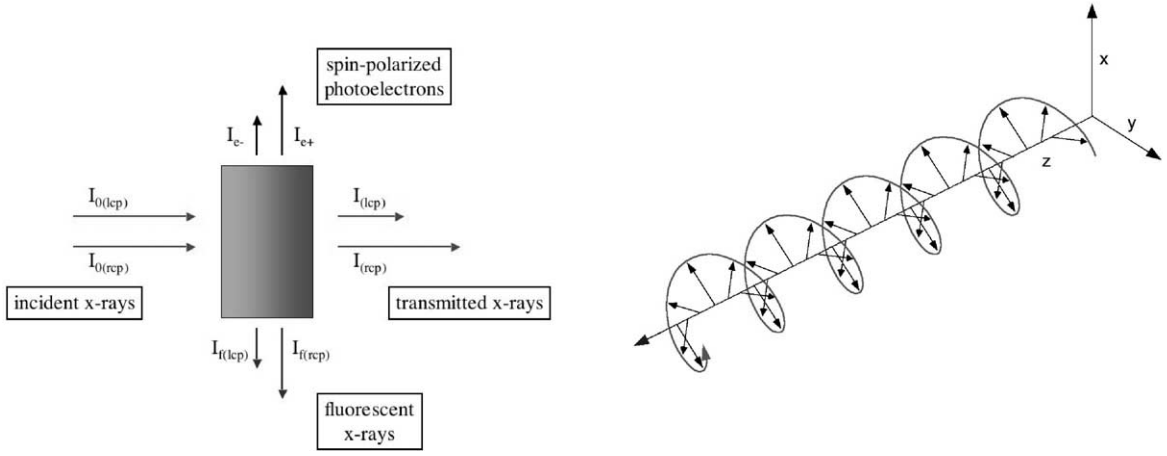

Fig. 1. (Left) Schematic of XMCD experiment. I_0 is incident beam intensity, I is the transmitted intensity while I_f and I_e are the intensities of the emitted fluorescence and photoelectrons respectively. (Right) Illustration of the electric field direction along the propagation axis for right circularly polarized light.