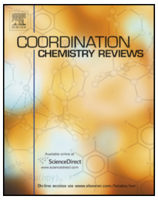
Coordination Chemistry Reviews xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

X-ray magnetic circular dichroism—A versatile tool to study magnetism

Gerrit van der Laan, Adriana I. Figueroa

Magnetic Spectroscopy Group, Diamond Light Source, Harwell Science and Innovation Campus, Didcot OX11 0DE, United Kingdom

Contents

E-mail addresses: gerrit.vanderlaan@diamond.ac.uk (G. van der Laan), adriana.figueroa-garcia@diamond.ac.uk (A.I. Figueroa).

http://dx.doi.org/10.1016/j.ccr.2014.03.018

Please cite this article in press as: G. van der Laan, A.I. Figueroa, Coord. Chem. Rev. (2014), http://dx.doi.org/10.1016/j.ccr.2014.03.018

ARTICLE INFO

Article history:
Received 6 January 2014
Received in revised form 10 March 2014
Accepted 10 March 2014
Available online xxx

Keywords:
X-ray absorption spectroscopy
X-ray magnetic dichroism
Single molecule magnets
Magnetic nanoparticles

ABSTRACT

An overview of different chemical complexes studied by X-ray magnetic circular dichroism (XMCD) is presented. We intend to show to the chemistry community the possibilities of this technique for the characterization of magnetically interesting systems. The versatility of XMCD is demonstrated using a wide variety of representative examples, such as spinels, bionanomagnets, functionalized nanoparticles, metal nanoparticles, (single) molecular magnets, butterfly molecules, photomagnetism, actinide materials, dilute magnetic semiconductors, and exchange spring magnets. The emerging technique of XMCD is shown to be of invaluable use in the design of magnetic particles and materials, and in the investigation of the remarkable diversity of systems that can be obtained and systematically tuned.

1. Introduction

As a complementary method to X-ray diffraction, X-ray absorption spectroscopy (XAS) has become one of the fundamental and most used techniques by the biochemistry and materials science communities to study the local structure and oxidation states in catalysts and other chemical complexes. In coordination chemistry, for instance, it has allowed to study the electronic structure of metal complexes [1], becoming increasingly popular over time. Only recently, X-ray magnetic circular dichroism (XMCD) [1] has found its way into the community, providing detailed information of the electronic and magnetic structure of nanoparticles, molecular materials, and single molecule magnets, organometallic complexes, to only cite some applications.

While X-ray diffraction recently celebrated its centenary, magnetic X-ray dichroism has been around for only a quarter-century. This addition to synchrotron radiation-based techniques was first observed in 1986 [2]; one year after its theoretical prediction [3]. Since then it has emerged as a potent tool for the study of magnetic materials. Today there are state-of-the-art beamlines for XMCD at practically all synchrotron facilities around the world. A recently compiled list counted 55 beamlines for X-ray magnetic spectroscopy [4].

The modern definition of *dichroism* is the polarization dependence of the light absorption by a material. Dichroism occurs when the material's symmetry is broken. Circular dichroism is enabled by breaking either the inversion or the time-reversal symmetry. In non-centrosymmetric crystals the parity-odd symmetry permits natural circular dichroism (NCD). Here, we will only treat the XMCD originating from time-reversal symmetry breaking by a magnetic field.

The XMCD spectrum is obtained as the difference between the two XAS spectra with the circular polarization vector parallel and antiparallel to the external magnetic field. Hence, the technique resemblances the magneto-optical phenomena in the visible region, such as the Faraday effect. Unlike the latter, the XMCD arises from the excitation of a core electron, instead of a valence electron, into the unoccupied conduction states The XMCD originates from electric dipole (or quadruple) transitions—and not from magnetic-dipole transitions, which only give a notoriously weak effect [5]. Except for the K edges, the effect is strong due to the large core spin–orbit coupling.

In a simple picture, XMCD can be described as a two-step process [cf., Fig. 1(a)]. The $2p$ core state of a $3d$ metal is split in a $j = 3/2$ level (L_3 edge) and $j = 1/2$ level (L_2 edge), where spin and orbit are coupled parallel and antiparallel, respectively. In the first step, the emission with the light helicity vector parallel (antiparallel) to the $2p$ orbital moment results in excited electrons of preferred spin up (down) direction. In the second step the excited electron has to find its place in the unoccupied $3d$ valence band, and if there are less spin-up than spin-down *holes* available, the XMCD spectrum has a net negative L_3 and positive L_2 peak. We will refine this picture as we go along, e.g., in a more sophisticated picture, the polarization dependent selection rules give rise to a multiplet structure, which can serve as a fingerprint for the ground state electronic and magnetic structure.

---

[1] Note that in the older literature, XMCD is often denoted as CMXD.

Please cite this article in press as: G. van der Laan, A.I. Figueroa, Coord. Chem. Rev. (2014), http://dx.doi.org/10.1016/j.ccr.2014.03.018