

Magnetic Circular Dichroism

Principle:

Amongst the existing techniques for characterizing electronic structure and magnetic interactions, L edge X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) are receiving an increasing interest Motivated by several reasons:

- i) **The elemental and orbital selectivity of XAS and its sensitivity to the oxidation state,**
- ii) **The strong interaction of x-ray with matter which provides sensitivity down to one monolayer and**
- iii) **The fact that XMCD enables investigation of previously inaccessible magnetic properties such as orbital and spin contributions to the magnetic moment on specific shell and site, especially in the case of 3d systems, since $2p_{1/2,3/2}$ 3d transitions (L_{2,3}-edges) give direct information on the 3d band responsible for magnetism.**

XMCD is defined as the difference between the absorption of right- and left-handed circularly polarised light, when the applied magnetic field (which determines, in general, the direction of the magnetisation M_z) is parallel to the incident X-ray wave-vector. If we define I_{L_2} and I_{L_3} as the dichroic intensities involving electronic excitation from the $2p_{1/2}$ and $2p_{3/2}$ sub-levels respectively, the combination $(I_{L_2} + I_{L_3})$ will account for orbital polarization only and $(I_{L_2} - I_{L_3})$ will give a direct measure of the spin polarisation: these are the so-called “**sum rules**”

The sole condition for observing a dichroic effect is a **nonzero M_z projection**.

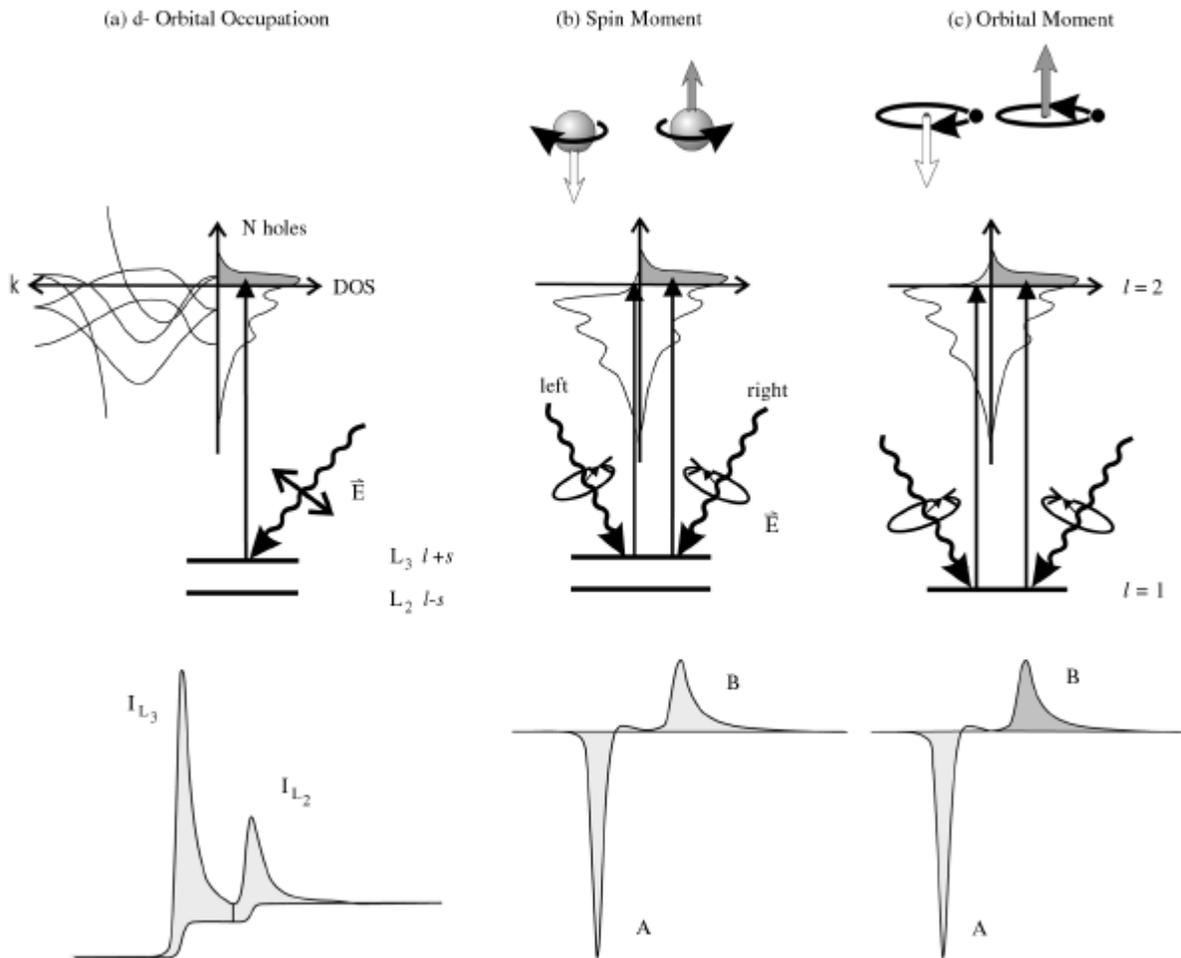
The properties of 3d electrons are best probed in an X ray absorption experiment by excitation of 2p core electrons to the unfilled 3d states as illustrated by a 2 step model picture. In principle, L edge X ray absorption spectra contain contributions from both $p \rightarrow d$ and $p \rightarrow s$ transitions but in practice the $p \rightarrow d$ channel dominates by a factor >20 . The sum of white line intensities, denoted I_{L_3} and I_{L_2} , respectively, is directly proportional to the number of d holes. This correlation follows from one of the sum rules. The use of circularly polarized X rays opens the door for magnetic studies. The underlying picture is most easily understood in the following 2 step picture.

In the first step, the right or left circularly polarized photons transfer their angular momentum, \hbar and $-\hbar$, respectively, to the excited photoelectron. If the photoelectron originates from a spin orbit split level, e.g. the $p_{3/2}$ (L₃ edge), the angular momentum of the photon can be transferred in part to

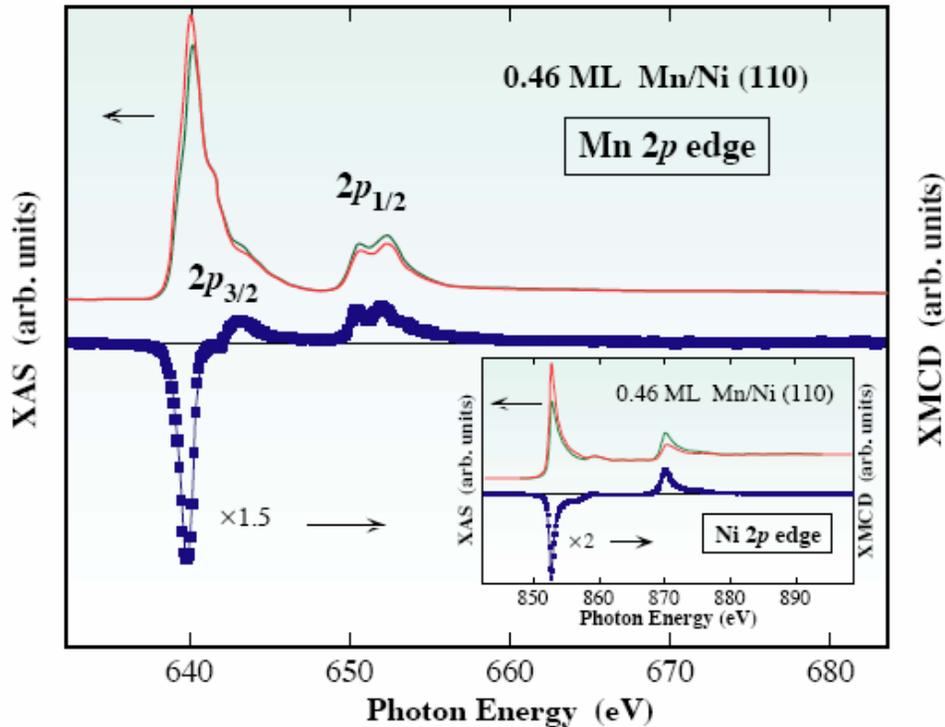
the spin through spin orbit coupling. Right circularly polarized photons transfer the opposite momentum to the electron than left circularly polarized photons, and hence photoelectrons with opposite spins are created in the two cases. Since the $p_{3/2}(L_3)$ and $p_{1/2}$ levels have the opposite spin orbit coupling ($L+s$ and $L-s$ respectively), the spin polarization will be in the opposite at the two edges. In the first (absorption) step, 'spin up' and 'spin down' are defined according to the helicity or photon spin, which is respectively parallel (right) or antiparallel (left) to the X-ray propagation direction .

The magnetic properties enter in the second step. Here the spin orbit valence shell acts as a detector for the spin of the excited photoelectron. The quantization axis of the detector is given by the magnetization direction which for maximum dichroism effect, needs to be aligned with the photon spin direction. As illustrated in the figure we shall denote the white line intensities recorded with right and left circularly polarization, i.e. the XMCD intensities, as $A(L_3 \text{ edge})$ and $B(L_2 \text{ edge})$, respectively. The A and B edges have opposite sign reflecting the opposite spin-orbit coupling of the $P_{3/2}$ and $P_{1/2}$ levels. According to the sum rule the spin moment is quantitatively linked to the measured intensity $A-2B$.

Similarly if the d valence shell possesses an orbital moment, it will act as a detector for the excited photoelectron. By summing over L_3 i.e. $(l+s)$ and $(l-s)$, intensities it is apparent that the spin s is eliminated and one measures the orbital moment of the valence shell, as shown. This is expressed by the sum rule which links the orbital moment in the d shell to the dichroism intensity $A+B$.



Soft X-ray magnetic circular dichroism (XMCD) in core level absorption spectra provides us with useful information related to the electronic states of the magnetic materials. It is noted that the XMCD not only gives us element specific magnetic moments, but also tells us how much an orbital (spin) magnetic moment contributes to their total magnetic moments. The following figure shows an example of a sub monolayer Mn grown on Ni (110) substrate. One finds a clear XMCD of Mn and Ni 2p edges, and the polarities of the XMCD signals are same for both Mn and Ni 2p edges, meaning that the directions of the magnetic moments are parallel between the Mn and the substrate Ni. Thus one can surely obtain the element specific information of the magnetic moments by conducting core excited XMCD experiments.



This technique is very useful for studying isolated paramagnetic ions or atoms and complex molecules. By lowering the sample temperature it is possible to obtain an almost complete magnetisation of the **paramagnetic ion or atom with an external magnetic field of a few teslas**. For a given J state, it is worth pointing out that the shape of the XMCD spectrum is independent of the temperature and applied magnetic field. By simulation of the experimental spectra with Ligand Field Multiplet (LFM) calculations the crystal field, spin orbit coupling parameters and magnetic exchange energy can be extracted, giving a precise description of the ground state of the absorbing atoms.

For example this study presents XMCD results recently obtained at the BACH beam line on two VO^{2+} compounds: a vanadyl-*bis*-enaminoketone complex and vanadyl sulfate $\text{VO}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$. These are the first vanadium $L_{2,3}$ edges experiments performed on oxovanadium, and the first observation, on a paramagnetic system, of the magnetic polarisation of the $2p$ orbitals of the oxygen and nitrogen atoms. Vanadium lends itself to a very rich chemistry as it can be found in oxidation numbers between -1 and +5, the +4 state being the most frequent, with the oxovanadium ion VO_2^+ (or vanadyl) dominating the vanadium(IV) chemistry. In most cases the geometry is square pyramidal, with four ligands forming the base and the $\text{V}=\text{O}$ at the top, oxygen extending outwards. The pyramid can be distorted if the four atoms at the base are not identical like in this compound. The $\text{V}=\text{O}$ bond is very strong, possibly having a triple bond character and in many oxovanadyl complexes the $\text{V}=\text{O}$ units are stacked to form $\text{V}=\text{O} \dots \text{V}=\text{O}$ chains giving rise to original properties such as

ferroelectricity. Coordination of VO with different ligands leads to numerous compounds displaying various magnetic properties like ferromagnetism in dinuclear complexes bridged with pyrimidine or spin frustration and antisymmetric exchange in giant clusters embedding vanadium and Mo. This study has been performed on a vanadyl *bis*-enaminoketone complex in which the V atom is a chiral center contrary to other vanadium complexes whose structure is symmetrical, like in vanadyl sulfate. This particular compound only has weak antiferromagnetic interactions in the bulk (powder) and the molecules do not seem to form the aforementioned chains. The interplay between chirality and magnetism is currently an active field of research and this is one of the examples.

The sample is in a magnetic field (up to 7T) and irradiated with circularly polarised photons, using a cryostat allowing sample temperatures down to ca. 2 K equipped with a superconducting magnet.

The spectra are recorded in the Total Electron Yield (TEY) mode by measuring the drain current of the electrically isolated sample. The XMCD measurements have been taken on samples prepared with the Langmuir-Blodgett technique and consisted of ca. 100 monomolecular layers deposited on crystalline silicon. Each layer is 30 Å thick, with a molecule, *i.e.* one vanadium atom, every 50 Å. In the case of $L_{2,3}$ absorption edges of 3d transition metals, it is well known that the TEY detection is characterised by a probing depth lower than 50Å and that the number of electrons that reach the surface decays exponentially as a function of the depth of the photon absorption.

Now as the orbital momentum is proportional to the total integrated intensity of the dichroic spectrum, if μ^+ , μ^- and μ will be the absorption coefficient for right, left handed polarized light and linear polarization parallel to the quantization axis then L_z is coming about 0.06 and S_z is coming about -0.5 respectively. From the projection theorem the atomic values are coming around $L_z = -1.8$ and $S_z = 0.3$. The strong reduction is due to the strong axial ligand field on the V atom, as is usually observed in polyatomic structure. When the incident angle of the photon varies from 0 to 60 degree the observed values are **0.06 to 0.11**.

It should be emphasized that L_z is always negative in contradiction with the expected L-S coupling. This could be due to the idiosyncrasy of the V=O bonding, which produces huge charge transfer.

Comparison with the reference V^{4+} compound **VO(SO₄)₂·5H₂O** shows that almost the same shape of the dichroic signal is observed in both V compounds, but with more intense dichroic structure in the low energy side of the L3 edge for the reference system.

A magnetic signal is also observed in the VO^{2+} complex at the **N-K edge** (not presented here). Here the shape does not resemble the standard 3d-K edge and indeed, to the two main peaks of the N-K absorption correspond two sets of dichroic structures, as it has recently been observed in metallic

Cyanide complexes [13]. In order to take benefit of these new magnetic sources of information, some technical difficulties, as the contamination of the surface sample by molecular N₂, should be overcome. Moreover, as the amplitude of

these magnetic responses in these paramagnetic systems are inversely proportional to the temperature, XMCD studies at very low temperature are necessary.

The XMCD analysis reveals an almost quenched orbital momentum for the VO₂₊ ions in oxovanadyl bis-enaminoketone complex and a non saturation of the spin component as compared to VOSO₄, taken as a reference. The first observation by these XMCD measurements of the magnetic polarisation of the 2p orbitals of the nitrogen and oxygen atoms in such paramagnetic systems brings the proof, if needed, that this technique is a powerful tool for all the studies pertaining to molecular magnetism. Sensitivity is now high enough for submonolayers to be investigated, even with spin densities as low as 1 μB per nm².

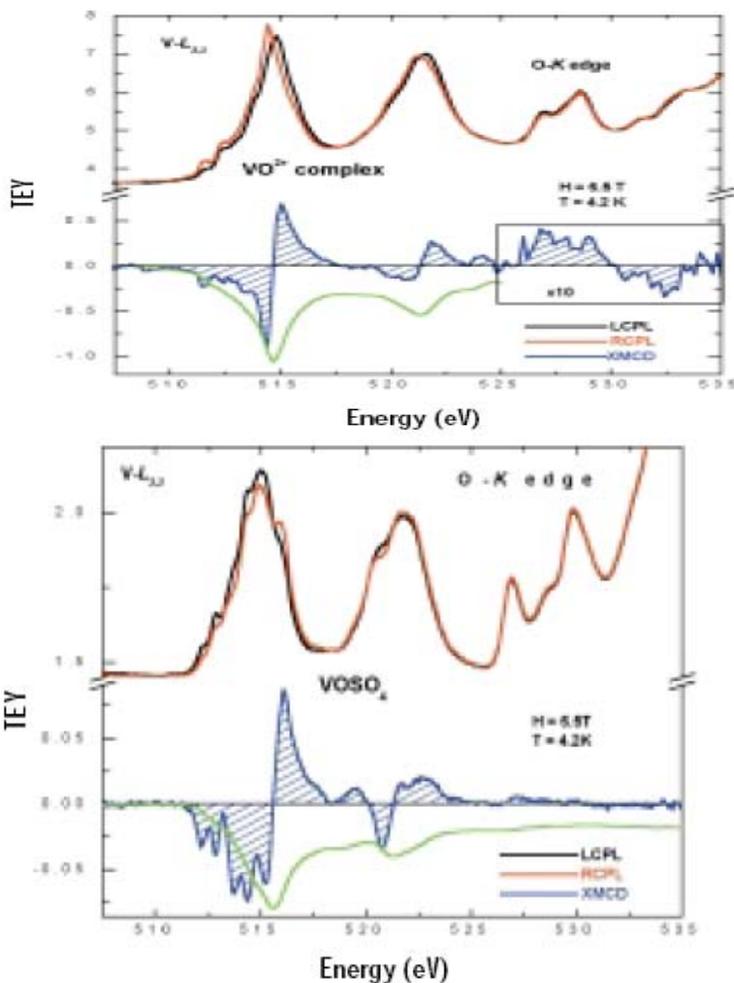


Fig 1 V-L_{2,3} and O-K edges (the two spectra correspond to the absorption of right-and left-handed circularly polarised light, respectively) and XMCD of oxovanadyl bisenaminoketone complex, at T=4.2K and H=6.5T. The enlarged (x10) TEY scale illustrates magnetic polarization of the oxygen atoms. The green line represents the integral of the XMCD signal.

Fig 2 V-L_{2,3} and O-K edges (the two spectra correspond to the absorption of right-and left-handed circularly polarised light, respectively) and XMCD of VO(SO₄)₂·5H₂O, at T=4.2K and H=6.5T. The green line represents the integral of the XMCD signal.

Soft x-ray magnetic circular dichroism: A probe for studying paramagnetic bioinorganic systems

Soft x-ray magnetic circular dichroism demonstrates enormous potential as a probe for studying paramagnetic systems. In this experiment it is used to study a paramagnetic bioinorganic system (*Pyrococcus furiosus* rubredoxin). For this Fe(III) rubredoxin protein the observed dichroism effect was strong (30%) and, in general, in agreement with the calculation. The method is element and oxidation state - specific, and the data can be interpreted by established theoretical procedures.

The availability of high flux and resolution and a high degree of linear or circular polarization from synchrotron radiation beamlines in the energy range (200-1500 eV) has made possible the investigation of the magnetic and electronic structure of 3d transition metal by XMCD. The technique is element specific and only sensitive to the paramagnetic center (a diamagnetic component will not show an effect) of the metalloprotein or inorganic material, thereby increasing the specificity of L edge spectroscopy for complex systems. The orientation of the magnetic moment of a dilute paramagnetic ion requires a strong magnetic field (on the order of several Teslas) and low temperatures, and fluorescence detection is needed to measure the absorption. The origin of the magnetic dichroism in 3d transition metal $L_{2,3}$ edges ($2p \rightarrow 3d$ transitions) relies on the nonuniform occupation of the Zeeman-split levels in the initial state, and the effect is a consequence of the selection rules for electric dipole ($\Delta J = -1, 0, +1$) transitions from the ground state to the final states. For a purely atomic Fe^{3+} high-spin d^5 configuration, the ground state is 6S , with $L = 0$, $S = 5/2$, and $J = 5/2$. In an applied magnetic field, the ground state is split into six Zeeman levels, for which at $T = 0K$ only the lowest level with $M_J = -5/2$ is occupied. The selection rules for right ($\Delta M_J = -1$) and left ($\Delta M_J = +1$) circularly polarized light allow for right circular polarization only transitions to $J' = 7/2$ final states, since these are the only ones that contain the $M_J = -7/2$ sublevel (see Fig.1). Excitation with left circularly polarized light is allowed to $J' = 7/2, 5/2$, and $3/2$ final states.

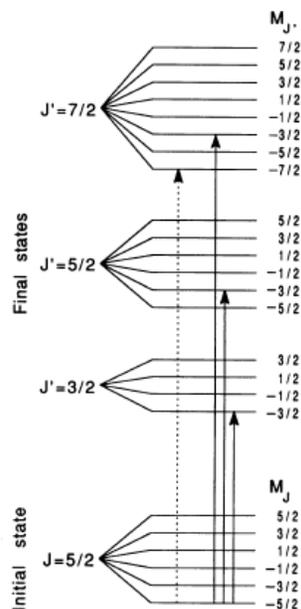


Fig. Soft x-ray magnetic circular dichroism transitions for an atomic d^5 configuration. The dashed line is for right circularly polarized light, and the solid line is for left circularly polarized light.

Experimental procedure: The Fe L edges of the protein is measured, using circularly polarized synchrotron radiation (soft x-ray beams of left and right helicity from double-headed Dragon Beamline is used, the polarization of these beams was set to around 80% for the measurements), a split-coil superconducting magnet, low sample temperatures, and fluorescence detection. The spectra for the left and the right circularly polarized light were measured almost simultaneously. Besides the direction of the magnetic field, also left and right polarization are switched by interchanging both mirrors of the double-headed Dragon beamline. In this experiment magnetic fields of 4T is used and temperature is maintained to as low as 1.5K. By using fluorescence detection, the Fe L edge fluorescence is electronically resolved from the large, mainly oxygen K_{α} background, improving the base-line stability and signal-to-noise ratio. We moved to a new part of the sample before each data set was taken, to minimize the absorption intensity from photoreduced rubredoxin. After each dichroism experiment, zero field scans were taken for both beams with left and right polarization for calibration purposes.

Results:

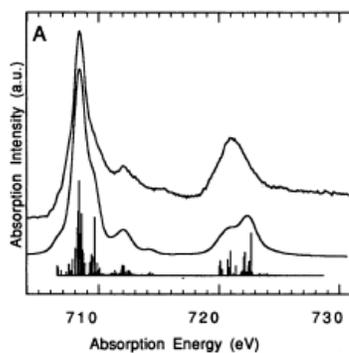
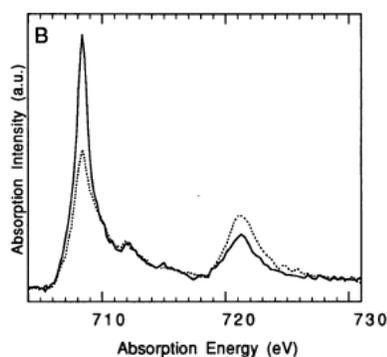


FIG. (A) Isotropic spectrum (upper trace) of the oxidized form of *Pyrococcus furiosus* rubredoxin, together with the ligand field atomic multiplet calculation (lower trace).



Fig(B) The right (solid line) and left (dashed line) circular polarized spectra.

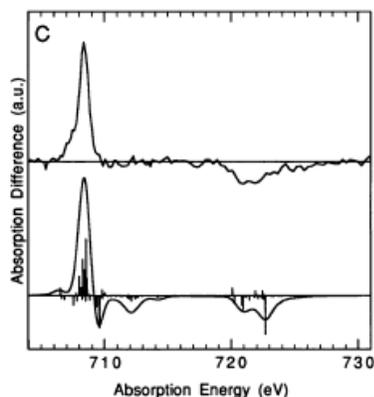


Fig (C) The experimental (upper trace) soft x-ray magnetic circular dichroism spectrum (right minus left circularly polarized light) and the calculated spectrum (lower trace). The "sticks" shown in A and C determine the strength of the individual calculated transitions before line width broadening.

A strong soft x-ray magnetic circular dichroism effect is observed as shown in Fig.2. A very sharply peaked 30% effect [as defined by $I(L-R)/(L+R)$, where L = left and R = right circular polarizations] at the L_3 edge and a rather broad negative structure at the L_2 edge. The experimental dichroism intensity at 707 eV

is a result of some reduced Fe^{2+} present in the sample, as this shoulder increased during prolonged experiments. The position of the reduced peak corresponds exactly to that observed in an earlier study of reduced and oxidized rubredoxin. A Td field was used to represent the local Fe^{3+} rubredoxin environment, and the magnetic field reduces this symmetry to S_4 . Although there is reasonable agreement between the calculation and the isotropic spectrum, as shown in Fig (A), the measured absorption around 712 eV is stronger than calculated because transitions to $2p^5 3d^7 \underline{L}$ final states (where \underline{L} stands for a ligand hole) have not been considered in the calculations.

In conclusion, the dichroism effect observed for rubredoxin is in general agreement with the calculation. Comparison of observed dichroism effects with calculations allows analysis of the orientation of the magnetic moment. Sensitivity of the technique can be increased significantly when synchrotron radiation sources with specialized insertion devices for circular polarization and an increased photon flux and stability will become operational. L edge soft x-ray magnetic circular dichroism studies of paramagnetic clusters in dilute metalloproteins, along with temperature- and magnetic field dependent experiments are feasible. Soft x-ray magnetic circular dichroism, with its sensitivity to relative magnetic orientations of different species and with its straightforward theoretical interpretation, is a promising new probe for bioinorganic and other paramagnetic systems.

Reference:

- [1] W. Grange, J.P. Kappler and M. Maret, *Magnetism: Molecule to Materials, Models and experiments*, 211.
Edited by J.S. Miller and M. Drillon, Wiley-VCH, (2001)
- [2] B.T. Thole, P. Carra, F. Sette and G. van der Laan, *Phys. Rev. Lett.*, 68, 1943, (1992)
- [3] T. Ishida *et al.*, *Inorg. Chem.*, 40, 7059, (2001)
- [4] D. Gatteschi *et al.*, *Inorg. Chem.*, 35, 1926, (1996)
- [5] A. Krowczynski, J. Szydłowska and E. Gorecka, *Liqu. Cryst.*, 26, 685, (1999)
- [6] Minguet *et al.*, *Angew. Chem. Int. Ed.*, 41, 4, 586, (2002)
- [7] J.-L. Gallani *et al.*, *Langmuir*, 17, 1104, (2001)
- [8] Ph. Saintavit and J.-P. Kappler, *Magnetism and Synchrotron Radiation*, Eds. E. Beaurepaire, F. Scheurer, G. Krill and J.P. Kappler, 235, Springer Verlag (2001)
- [9] A. Ulman, *Ultrathin Organic Films*, Academic Press, San Diego (1991)
- [10] R. Nakajima *et al.*, *Phys. Rev. B*, 59, 6421, (1999)
- [11] A. Schertz *et al.*, *J. Appl. Phys.*, 91, 8760, (2002)
- [12] F. de Groot, *et al.*, *Phys. Rev. B*, 40, 5715 (1989)

