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1. X-RAY DETECTED MAGNETIC RESONANCE IN PARAMAGNETIC SAMPLES

X-ray Detected Magnetic Resonance (XDMR) is a novel spectroscopy[1] in which ***element selective*** X-ray Magnetic Circular Dichroism (XMCD) is used to probe the resonant precession of the magnetization caused by a strong microwave pump field $\mathbf{h_1}$ perpendicular to the static bias field $\mathbf{H_0}$. As illustrated with Figure 1, two different geometries can be envisaged to probe the precession dynamics.

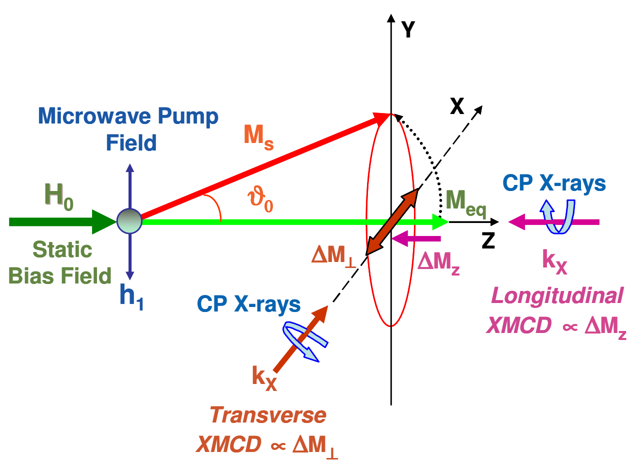

Figure 1

In the *longitudinal* geometry[1], the wavevector $\mathbf{k_x}(\parallel)$ of the incident circularly polarized X-rays is parallel to $\mathbf{H_0}$. The precession induces a steady-state change ΔM_z of the magnetization probed by XMCD. The XDMR signal is then a 2nd order effect proportional the microwave power and that probes how fast the damping torque drives the magnetization $\mathbf{M}$ back to $\mathbf{M_{eq}}$.

In the *transverse* geometry[1], the wavevector $\mathbf{k_x}(\perp)$ of the X-rays is perpendicular to both $\mathbf{H_0}$ and the microwave pump field $\mathbf{h_1}$. XMCD then probes the transverse component of the magnetization $\mathbf{\Delta M_\perp}$ which oscillates at the microwave resonance frequency. The detection of this 1rst order effect, however, requires a very special instrumentation[1].

The aim of this highly challenging project was to explore whether XDMR could be detected in organometallic paramagnets. Recall that all successful XMCD studies on paramagnetic systems were performed so far in a ***strong*** magnetic field ($H_0 \geq 5$T) : *X-ray Detected Electron Paramagnetic Resonance*

(XD_EPR) would then be shifted up to 100 GHz if not in the *sub*-THz range. There are long term projects to extend XDMR towards such high frequencies. In this proposal, we tried to explore whether a weak XD_EPR signal could still be measured in a low field, *i.e.* $H_0 \leq 0.8$T and with a microwave frequency $F \leq 20$ GHz.

2. XMCD MEASUREMENTS ON THE PARAMAGNETIC CYANOMETALATE: $[Re(CN)_7]^{3-}$

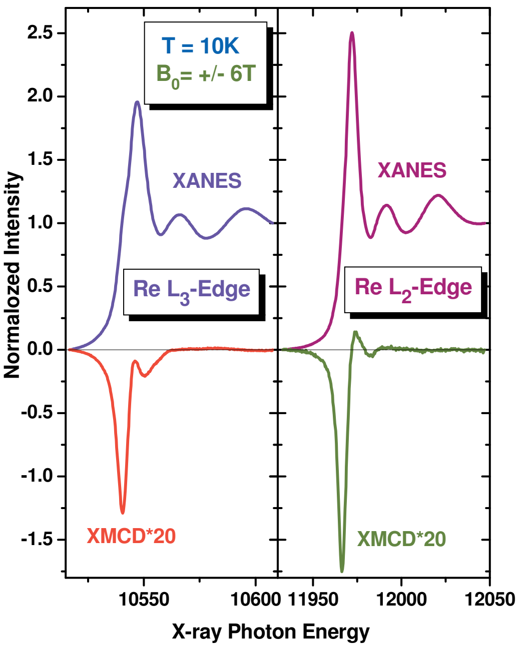

Figure 2

The paramagnetic Re (IV) complex **1** = $(Bu_4N)_3 [Re(CN)_7]$ was prepared at the ICMUB (Dijon) following the synthesis reported by Bennett & Long[2]. The effective magnetic moment (2.02 μ_B at 298K) is consistent with a S = 1/2 complex. The heptacyanometalate anion has D_{5h} symmetry which favours $^2E_1$” as ground term. High quality XMCD spectra were recorded at the Re $L_{2,3}$-edges (Fig. 2). Measurements were carried out at low temperature (T=10K) and in a high magnetic field ($H_0 = \pm 6$T).

It is immediately obvious from *the sign* of the spectra reproduced in Fig. 2 that the L-edge XMCD spectra should be strongly dominated by the contribution of (Van Vleck) ***orbital paramagnetism***. After proper correction of those spectra for fluorescence re-absorption and circular polarization rates, the magneto-optical sum-rules led to the following determination of the effective orbital moment: $\mathbf{L_Z} = 0.11\ \mu_B$, whereas we found a nearly perfect *cancellation of the Spin components* since: $\mathbf{S_Z} - 7\mathbf{T_Z} = \pm 5\ 10^{-4}\ \mu_B$. The sum-rules also yield an approximate value of the number of holes in the projected 5d band: $N_H = 7$. This is the first example where such a cancellation of the Spin components is observed experimentally at L-edges.

3. TENTATIVE DETECTION OF ELECTRON PARAMAGNETIC RESONANCE WITH X-RAYS

The X-band EPR spectrum measured at 20K by Bennett & Long[2] from *undiluted* powder revealed a large g-anisotropy: $g_{//} = 3.66$; $g_{\perp} = 1.59$. The high natural abundancy of the I = 5/2 nuclei, *i.e.* ^{185}Re (0.374) and ^{187}Re (0.672) resulted in resolved sextets. A large anisotropy of the g tensor looks, *a priori*, consistent with the existence of a significant orbital magnetic moment.

Given that our XDMR spectrometer has its highest sensitivity in the X-band, the first challenge for us was to clarify whether we could record the same XMCD spectra as illustrated with Figure 2, but with a much lower bias field, e.g. $H_0 = 0.16$ T since this was the order of magnitude of the resonance field reported by Bennett & Long for the published EPR spectrum. Unfortunately, such low field XMCD measurements turned out to be inconclusive: we ***could not*** reproduce the spectra of Figure 2. Under such unfavourable conditions, it would have been very surprising if the planned XD_EPR experiment had not failed: we nevertheless tried hard but without any success to extract any resonance signal from noise.

There is still a point which would deserve to be clarified: the low field XMCD measurements as well as the negative XD_EPR experiment were not carried out with the same sample as for the high field XMCD measurements of Figure 2: we decided to use a *freshly* prepared sample. Unfortunatly, no beamtime was left available to reproduce the time-consuming high field XMCD measurements with this fresh sample. Another point -which looks also puzzling-, is that we failed to detect any standard X-band EPR spectrum with this fresh sample. We have no clear interpretation as yet for this additional (unexpected) problem.

REFERENCES

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