



ESRF

	Experiment title: HIGH RESOLUTION X-RAY EMISSION SPECTROSCOPY OF GYROTROPIC CRYSTALS	Experiment number: HE - 217
Beamline: ID12A	Date of experiments: 18 shifts (+ 2 align) Oct. 10-13 1997 + Oct. 15-17 1997 (PSS test on 16/10/97)	Date of report: March 1rst 1998
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1. High resolution fluorescence spectrometer and motivation of the project HE-217 :

As part of the In House Research program of the XAS group, it was decided in 1997 to *duplicate* the high energy resolution fluorescence spectrometer designed by the ESRF-IXS group (F. Sette *et al.*) for Resonant Inelastic X-ray Scattering (RIXS) experiments performed so-far on beamline ID16. Since the spectrometer is the exact replica of the instrument of ID16, the performances are identical but also the limitations, especially for what concerns its operation at low excitation energy. The coordination of this duplication task was assigned to Claudia Dallera who had a postdoctoral fellowship in the XAS - ID12A team but, unfortunately, resigned shortly after she had completed the commissioning of the new spectrometer. We expect the latter instrument to be now operated most of the time on the new beamline ID26 of the XAS group since this beamline is equipped with one of the most intense sources of the ESRF (3 planar undulators which can be optionally phased) and with suitable focusing optics. Nevertheless, the fluorescence spectrometer can be moved to the experimental hutch of beamline ID12A for very specific studies requiring to excite the sample with circularly polarized (CP) light. This was precisely the case of the project HE-217 which was concerned with polarization dependent studies of uniaxial or biaxial gyrotropic crystals.

During the first half of 1997, as part of another ESRF project HE-121, we had produced the very first experimental evidence of X-ray Natural Dichroism (XNCD) in a uniaxial crystal of α -LiIO₃¹. Surprisingly enough, a fairly intense XNCD signal (up to 7% when corrected for the polarization transfer of the monochromator) was detected at the iodine L₁ edge. This signal was assigned to the electric dipole-electric quadrupole interference term (E1.E2) which contributes to the rank-2 *pseudo* deviator part of the optical activity tensor. Our interpretation and the very large magnitude of the effect measured at the iodine L₁ - edge were remarkably confirmed by Multiple Scattering calculations^{1,2}. We found therefore rather attractive to check how far the emission spectra would be affected by the primary XNCD absorption cross sections when the sample is excited near the iodine L₁ edge. This led us to record the first Differential Fluorescence Intensity spectra when the incident light is either left or right circularly polarized.

2. Results :

To get a full picture of the resonant inelastic processes taking place very near an absorption edge, it is very important to produce a 3-dimensional plot of the emitted intensity as a function of both the excitation energy E_X and "fluorescence" energy E_F . Such a plot is reproduced in Fig. 1 : the sample was a single crystal of α -LiIO₃ with its optical axis $\langle 0,0,1 \rangle$ not anymore strictly colinear with the wavevector of the incident photons (k directed along z), but rotated by *ca.* 20° around the vertical axis (x). The energy E_X was tuned near the iodine L_1 edge, the XANES spectrum featuring a very intense white line peaking at 5193 eV, whereas the XNCD cross section is small in the white line but reaches its maximum at a second shape resonance peaking at *ca.* 5207 eV. The emission spectra were recorded near the $L\beta_3$ (L_1 - M_3) fluorescence line peaking at 4313.4 eV. We borrowed from the ESRF IXS group a Si (620) analyzer and caught the Si (311) reflexion (angular asymmetry : 17.55°). At a Bragg angle of *ca.* 61.36°, the energy resolution of the analyzer was typically 0.13 eV, the energy resolution of the incident beam being only *ca.* 0.7 eV. Given the long input (1010 mm) and output (713 mm) arms, this experiment cannot be carried out in air : we had to enclose the whole spectrometer in a plexiglas box kept under an helium flow. We experienced much troubles trying to maintain the partial pressure constant to the desired precision for dichroism experiments. Fig. 2 reproduces the Differential Fluorescence Intensity spectrum recorded at $E_X = 5207$ eV, *i.e.* at the maximum of the XNCD cross section.

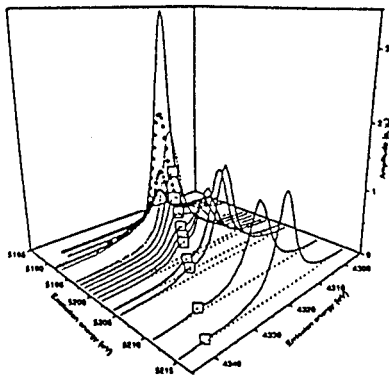


Fig. 1 3D map of the emission intensity near the L_1 edge excitation. Note the presence of a dispersive emission satellite.

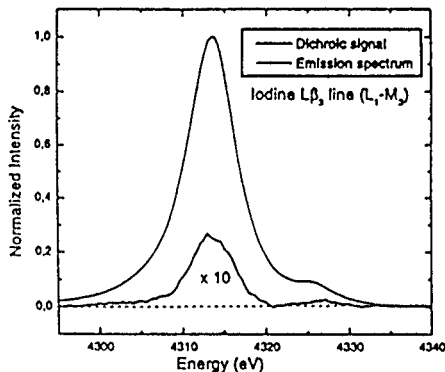


Fig. 2 Differential Fluorescence spectrum recorded at $E_X = 5207$ eV, *i.e.* the maximum of the XNCD cross section

3. Discussion :

Interestingly, Fig.1&2 exhibit a weak satellite featuring an energy dispersive nature which suggest that the primary absorption process may induce a transition to a *bound state* most probably associated with the white line, whereas the $L\beta_3$ fluorescence line is coupled to transitions to the continuum states. The differential spectrum of Fig.2 confirms unambiguously the reality of an intense XNCD : the relative intensity of the differential fluorescence signal agrees quite well with the predicted angular dependence of the XNCD cross section calculated in ². More surprising is the dichroism measured in the satellite³ since we know ¹ that the $E1,E2$ term is weak in the white line. This could be explained by manybody effects involving the outer valence electrons in molecular orbitals, just as in the case of atomic Xe where *multiexcitations* : [$2s, 5p$] → hybridized AO [$6p, 5d$]² were observed 12 eV above the L_1 -edge. Multiexcitations are known to contribute to XMCD spectra and might contribute to XNCD spectra as well ¹. This interpretation will be reconsidered in a subsequent project.

References :

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