

**Experiment title:**

X- RAY NATURAL CIRCULAR DICHROISM IN
GYROTROPIC CRYSTALS AND IN ALIGNED
LIQUID CRYSTALS

**Experiment
number:****HE - 121****Beamline:**

ID12A

Date of experiments: 9 + 9 shifts

1st : Feb. 4-5-6 1997 2nd: April 15-16-17 1997

Date of report:

October 1st 1997

shifts: 18

Local contact(s): **J. GOULON and A. ROGALEV****Received at ESRF:****Names and affiliations of applicants** (* indicates experimentalists):

José GOULON^{1*}, Chantal GOULON-GINET^{1,2*}, Andrei ROGALEV^{1*}, Vincent GOTTE^{1*},
Cécile MALGRANGE^{3*}, Christian BROUDER³, Calogero R. NATOLI⁴

1 ESRF - XAS group, B.P. 220, F-38043, Grenoble Cedex, France

2 Faculté de Pharmacie, Université Joseph Fourier, B.P. 53, F-38041 Grenoble Cedex, France

3 Laboratoire de Minéralogie Cristallographie, Universités Paris VI-VII

4, place Jussieu, Case 115, F-75252, Paris Cedex 05, France

4 Laboratori Nazionali di Frascati, INFN, P.O. Box 13, I-00044 Frascati, Italy

1. Motivations

Our primary goal was to detect X-ray Natural *Circular Dichroism* (X-NCD) in gyrotropic single crystals of *inorganic* chemical species which are, in general, not chiral in non-ordered media. This project was therefore a natural complement to another project (HE-227) concerned also with the detection of X-NCD but in stereogenic organometallic *complexes* in which the absorbing center is itself in a chiral ligand *field*. We were also interested in performing a few preliminary test experiments in order to explore whether or not it might be feasible to detect X-NCD from chiral stereogenic complexes magnetically aligned *in oriented liquid crystals*.

2. First results

Among the 21 non-centrosymmetric crystal classes, only 18 “gyrotropic” classes exhibit a non-zero optical activity tensor. Further classification is possible depending on which are the rotational invariants of the optical activity tensor : only crystal classes compatible with chiral enantiomorphism have a non-zero *pseudo-scalar* part ; a crystal that is pyroelectric has a vector part ; crystals which have a non-zero rank-2 pseudo-deviator part have usually a strong non-linear susceptibility. We have produced the very first unambiguous experimental evidence that the latter crystals are the only ones to exhibit X-NCD. For the sake of simplicity, we selected for a first test a uniaxial single crystal of α -LiIO₃ that is known to exhibit very strong *non-linearities* at optical wavelengths : this crystal is commonly used to frequency double a number of lasers such as [Ti : Sapphire]. Nicely structured X-NCD spectra were recorded at the **L₁ and L_{2,3} edges** of iodine [1]. For illustration, we have reproduced in Fig. 1 the difference spectra [$\sigma^L - \sigma^R$] measured at the L3 edge and which show that the maximum intensity of the effect does not exceed 0.6%. These signals were assigned to the Electric Dipole-Electric Quadrupole (E1.E2) interference terms which do not vanish in gyrotropic crystals but contribute to the pseudo-deviator part of the optical activity tensor. This interpretation is fully supported by TB-LMTO-ASA band structure calculations performed with the code of Andersen and Jepsen [2] : we found a fairly well correlated overlap of [5d,6p] or {5d,4f} DOS.

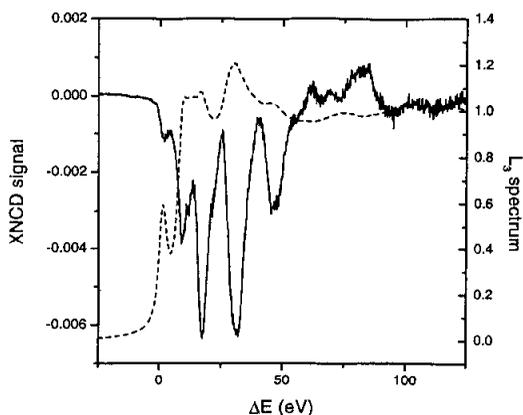


Fig. 1 Normalized X-NCD spectrum [$\sigma^L - \sigma^R$] at the L_3 edge. The Xanes spectrum is also reproduced.

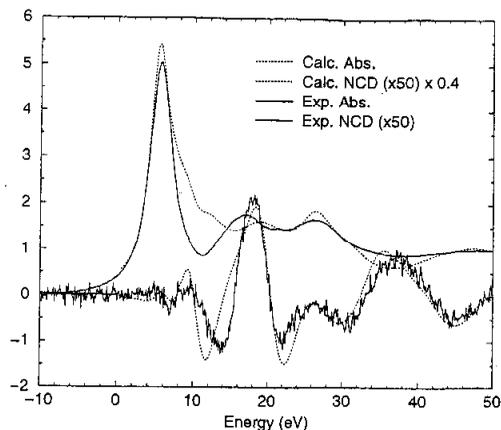


Fig. 2 Comparison of the L_1 Xanes and X-NCD spectra with ab-initio MS calculations using the Andersen/Jepsen potential

3. Refined analyses and new perspectives

An important step towards a quantitative analysis of the X-NCD spectra was the ab-initio calculation of the electric dipole and electric quadrupole matrix elements. This was done in the framework of Multiple Scattering in the *direct* space as opposed to the reciprocal space relevant to band structure calculations. In the case of enantiomorphous crystals like precisely α - LiIO_3 , one might be able to deduce without ambiguity the absolute configuration (R or L) from X-NCD spectra whereas it is well documented that conclusions drawn from CD at optical wavelengths are not reliable. Furthermore, it was realized that edge specific sum rules relate X-NCD spectra to the mixing of odd and even orbitals in the *ground state* [3]: this is of considerable value since the calculation of the intensities of optical transitions in minerals is still in infancy. This is even worse regarding the prediction of the non-linear optical susceptibility of crystals used in non linear optics. On the other hand, as illustrated by Fig. 2, X-NCD spectra can also be analyzed in terms of *multiple scattering* paths of specific symmetry [3], as opposed to the single scattering paths given by EXAFS. It may be worth emphasizing that the X-NCD spectra recorded at the L_2 or L_3 edges look very similar and have the same sign whereas the spectrum recorded at the L_1 edge is different and has the reverted sign. This is contrasting with X-MCD: while spin-orbit interaction is the driving term in X-MCD, this is not the case here. This leaves very little or no space for a contribution of the pseudoscalar $E1.M1$ interference terms which dominate at optical wavelengths but should hardly be detectable in the X-ray range. There is another key difference between X-NCD and X-MCD: whereas X-MCD is most often dominated, at least in the near edge energy range, by *atomic effects*, X-NCD is entirely due to molecular *effects* and calls for refined descriptions of the hybridization of AOs.

In the near future, our efforts will be oriented in two directions: (i) the investigation of biaxial crystals in which strong linear dichroism and birefringence effects swamp completely the X-NCD signal and can lead to erroneous conclusions; (ii) the determination of X-NCD spectra from chiral complexes aligned in liquid crystals. The latter strategy would allow us to extend considerably the field of application of X-NCD since the $E1.E2$ interference term vanishes in non ordered media. Test experiments have confirmed the possibility to align a chiral solute in a liquid crystal but we failed so far to detect any X-NCD spectrum due to the poor stability of the liquid crystal phase under irradiation by the refocused undulator beam.

References:

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