| ESRF | **Experiment title:** X-RAY NATURAL CIRCULAR DICHROISM OF GYROTROPIC CRYSTALS *II. CASE OF BIAXIAL CRYSTALS* | **Experiment number:** HE-331 |
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| **Beamline:** ID12-A | **Date of experiment:** 1) from: **Feb. 04th** *98* **to** Feb. 07" 98 2) from: April 8th 98 **to** April 10th 98 | **Date of report:** **1rst Sept 1998** |
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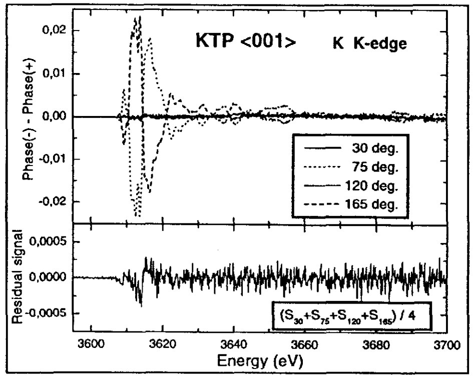
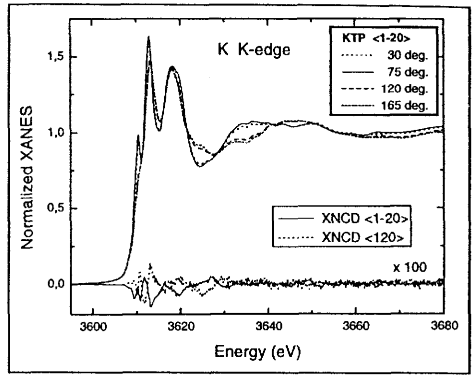
In an earlier project (HE-121), we have produced the very first experimental evidence of X-ray Natural Circular Dichroism (XNCD) in a gyrotropic single crystal: the crystal selected for this very first experiment was a uniuxial crystal of a-LiI03 the optical axis of which was aligned with the direction of the incident X-ray beam[1,2]. The present project is concerned with another gyrotropic crystal : Potassium Titanyl phosphate ("KTP") which belongs to the crystal ***class mm2.*** Such crystals are ***biaxial*** and ***non-enantiomorphous*** with the following implications [3]: (1) the Optical Activity tensor has no pseudoscalar part even ***at optical wavelengths;*** (2) there is no Optical Activity, and for what concerns our experiment no XNCD in the direction of the optical axes. Concretely, one should not detect any XNCD in the direction of the c axis [0,0,1] of KTP whereas the signal should be maximum but with reverse signs along the diad directions perpendicular to c: since a ≈ 2b in the particular case of KTP, the maximum XNCD signal is thus expected along the orthogonal directions [1,2,0] and [1,-2,0] but with opposed signs.

There is a major complication arising from the strong X-ray Natural Linear Dichroism (XNLD) that is expected in planes perpendicular to the directions [0,0,1], [1,2,0] and [1,-2,0] because the crystal is biaxial. Even though the helical undulator source has a high Stokes-Poincaré circular polarization rate $P_3$, we confirmed experimentally that the tiny XNCD signal is systematically swamped by **the** large XNLD signal: this is because the source has always a small Stokes-Poincaré component $P_2$ which couples to the polarization component $P_3$ through the polarization transfer function of the Bragg monochromator with the practical consequence that, on reversing the helicity of the photons produced **by Helios-II,** one will induce at the sample the correlated changes of polarization $\Delta P_3 + \Delta P_2$ which result in the simultaneous observation of XNCD and XNLD [1,3,4,5]

One major success of project **HE-331** was to show that it is possible to disentangle the respective contributions of XNCD and XNLD from their different angular dependences when the crystal is rotated around the direction of the incident X-ray beam. This requires very high quality data and the price to be paid is that several shifts are needed to extract the XNCD and XNLD spectra at one single edge for one crystal orientation. One becomes indeed far more sensible to long term instabilities of the source. The quality of the results is nevertheless quite satisfactory as illustrated by Fig. (I), (2a) and (2b). We were able to confirm that the XNCD signal is very low along the c axis with a residual signal less than 0.04% whereas the gyrotropic XNCD signals (0.3%) are well reversed along the [1,2,0] and [1,-2,0] directions.




extracted along the c axis [0,0,1] of KTP.

**Fig. 2a:** Angular dependence of the K-edge XANES and extracted XNCD for the orthogonal directions of the incident beam [ 1,2,0] and [ 1,-2,0].

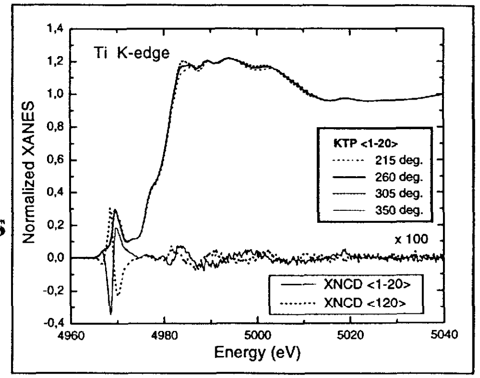



**Fig. 2b:** Angular dependence of the Ti-edge XANES and extracted XNCD for the orthogonal directions of the incident beam [1,2,0] and [1,-2,0].

Preliminary *ab initio* simulations of XNCD spectra agree rather well with our experiments and there is no indication that non gyrotropic 2nd order terms [5] could have a significant contribution. Our results support the view that K as well as Ti contribute to the high non-linear optical susceptibility of KTP [4].

**References:**


[1] J. Goulon, Ch. Goulon-Ginet, A. Rogalev, V. Gotte, C. Malgrange, Ch. Brouder and C.R. Natoli J. Chem. Phys. **108, (1998), 6394-6403**
[2] C.R. Natoli, Ch. Brouder, Ph. Sainctavit, J. Goulon, C. Goulon-Ginet and A. Rogalev, Eur. Phys. J., B4, (1998), 1-11
[3] J. Goulon, C. Goulon-Ginet, A. Rogalev, V. Gotte, C. Malgrange and Ch. Brouder Proc. of the 7th Int. Conf. ***Bianisotropics-98*** **(1998)** pp. 53-56; Proc. of the Int. Conf. ***XAFS-10*** (1999)
[4] J. Goulon, C. Goulon-Ginet, A. Rogalev, V. Gotte, Ch. Brouder and C. Malgrange (in preparation)
[5] J. Goulon, C. Goulon-Ginet, A. Rogalev, V. Gotte, Ch. Brouder and C. Malgrange *Subm. to* J. Opt. Soc. Am. B