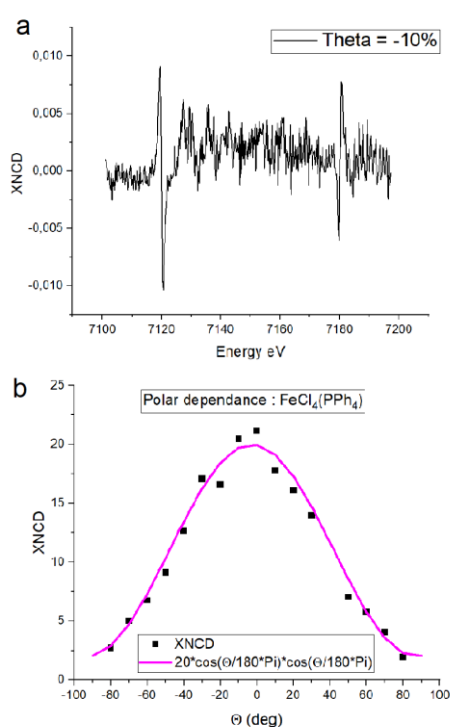


The objective of this beamtime was to record, for the first time, X-ray Natural Circular Dichroism (XNCD) in non-chiral systems.

The symmetry of a crystal is revealed in the symmetry of its properties, and vice versa. Many interesting properties occur only in non-centrosymmetric crystals, such as pyroelectricity, piezoelectricity or optical activity. Regarding the latter, optical activity is seen in enantiomorphous crystals. Enantiomorphism in crystal chemistry refers to a lack of an improper rotation, that is, the absence of  $\bar{1}$ ,  $\bar{2}$  or  $\bar{4}$ , and the generation of right-handed and left-handed crystals. Enantiomorphous crystals belong to one of the 11 crystal classes allowing enantiomorphism and induce the rotation of plane polarized light, an effect called *optical activity*. While enantiomorphism and optical activity are often used interchangeably, they are not identical, as there also exists non-enantiomorphous crystal classes which can show optical activity, namely  $m$ ,  $mm2$ ,  $\bar{4}$  and  $\bar{4}2m$ . Of these,  $m$  and  $mm2$  are polar groups capable of showing pyroelectricity, while  $\bar{4}$  and  $\bar{4}2m$  are non-polar groups capable of showing piezoelectricity and second-harmonic generation, as well as optical activity.



a) Representative XNCD spectrum; b) Angular dependence of the normalized XNCD intensity with respect to  $\theta$ .

Remarkably, three of the selected compounds demonstrated a clear XNCD signal with the proper orientation of the crystal with the incident beam in terms of  $\theta$ , the polar angle, and  $\varphi$ , the azimuthal angle, as laid out in Natoli et al.<sup>1</sup> Figure 1 shows a representative spectrum for  $FeCl_4(PPh_4)$ . According to the symmetry arguments found in this work, the XNCD cross-section of the compounds belonging to the  $I\bar{4}2d$  and  $P\bar{4}2_1m$  groups will have an angular dependence with respect to  $\theta$  and  $\varphi$  of  $\sin^2\theta\cos 2\varphi$ , while the compound belonging to  $I\bar{4}$  will have the more complex dependence  $\alpha.\sin^2\theta\cos 2\varphi + \beta.\sin^2\theta\sin 2\varphi$  ( $\beta$  and  $\alpha$  are given by the electronic structure). We were able to perform a full polar and azimuthal angular dependence with a step of  $10^\circ$  for  $FeCl_4(PPh_4)$ , the first time this has been performed using XNCD, and were able to confirm the agreement with theory. Furthermore, we were able to do partial axial and azimuthal angular dependencies for  $[CuCl_4](tetraethylamine)(tetramethylamine)$  and  $Cu(tetraphenylporphyrin)$ . Interestingly, no XNCD signal was found for  $[MnBr_4](tetraethylamine)(tetramethylamine)$ , even if it is isostructural with  $[CuCl_4](tetraethylamine)(tetramethylamine)$ .

To the best of our knowledge, optical activity has not been measured in crystals belonging to any of the four aforementioned crystal classes, and certainly not with X-rays.

For this work, we synthesized, crystallized and crystallographically indexed the crystals of several different molecules to study during the beamtime. Of these, the following were exposed to X-rays during the beamtime:  $[FeCl_4](PPh_4)$  ( $I\bar{4}$ ),  $Ni(ethylenediamine)_3(I_3)(I)$  ( $I\bar{4}2d$ ),  $Cu(tetraphenylporphyrin)$  ( $I\bar{4}2d$ ),  $[CuCl_4](tetraethylamine)(tetramethylamine)$  ( $P\bar{4}2_1m$ ), and  $[MnBr_4](tetraethylamine)(tetramethylamine)$  ( $P\bar{4}2_1m$ ).  $Ni(ethylenediamine)_3(I_3)(I)$  proved to significantly degrade under the X-rays, and was thus omitted from further study.

Remarkably, three of the selected compounds demonstrated a clear XNCD signal with the proper orientation of the crystal with the incident beam in terms of  $\theta$ , the polar angle, and  $\varphi$ , the azimuthal angle, as laid out in Natoli et al.<sup>1</sup> Figure 1 shows a representative spectrum for  $FeCl_4(PPh_4)$ . According to the symmetry arguments found in this work, the XNCD cross-section of the compounds belonging to the  $I\bar{4}2d$  and  $P\bar{4}2_1m$  groups will have an angular dependence with respect to  $\theta$  and  $\varphi$  of  $\sin^2\theta\cos 2\varphi$ , while the compound belonging to  $I\bar{4}$  will have the more complex dependence  $\alpha.\sin^2\theta\cos 2\varphi + \beta.\sin^2\theta\sin 2\varphi$  ( $\beta$  and  $\alpha$  are given by

1 C. R. Natoli, C. Brouder, Ph. Sainctavit, J. Goulon, C. Goulon-Ginet and A. Rogalev, *Eur. Phys. J. B*, 1998, **4**, 1–11.