ESRF	Experiment title: Natural X-ray circular dichroism of enantiomeric crystals	Experiment number: HE-227
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Report:

During our previous visit [HE022], we established that natural circular dichroism in the X-ray region (XNCD) could be measured with good signal to noise ratio on beamline ID12A. The system chosen on that occasion was the L_3 edge spectra of enantiomeric crystals of $Na_3[Nd(dig)_3].2NaBF_4.6H_2O$. The spectra obtained [l] showed two interesting features (a) a large dichroism (AI/I ~ 10^{-2}) in the pre-edge region corresponding to the quadrupole allowed 2p to 4f transition and (b) XNCD in the XANES region (XanesCD) which we have related to chiral multiple scattering paths.

In this work, we extended the measurements to the K edge of a transition metal complex, $2[Co(en)_3]Cl_3.NaCl.6H_2O$. There were two reasons for choosing this system. Firstly, there is a report by M. Hart et *al.* of ellipticity measurements on randomly oriented powders of this compound. Secondly, the pre-edge feature [1s to 3d(eg)] is clearly visible in the isotropic spectrum some 20 eV to lower energy of the white line. We hoped that the pre-edge XNCD might have a comparable magnitude to that measured at the L_3 edge.

In the event, the XNCD of single crystals of $2[Co(en)_3]Cl_3.NaCl.6H_2O$ proved to be spectacular. The pre-edge transition has an even larger dissymmetry factor than we had anticipated (AI/I -20%) and clear XanesCD is also seen. The enantiomeric crystals have opposite signed XNCD (Fig. 1) and the racemic crystal (spectrum not shown) showed no dichroism. The experiment was greatly assisted by cooling the samples to -8OK using a N_2 gas stream; this minimised sample decomposition and lead to increased signal to noise..

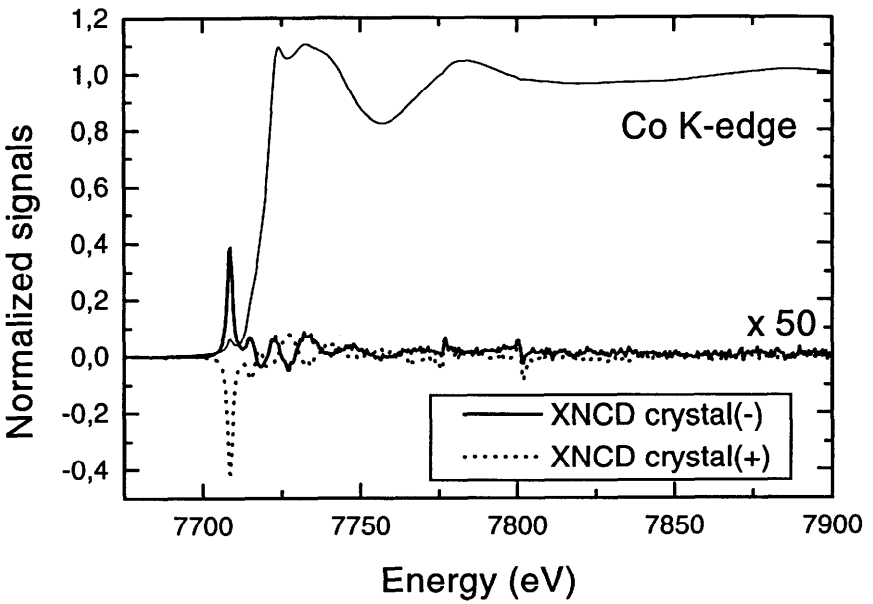

Fig 1: Axial absorption and XNCD spectra of single crystals of $2[Co(en)_3]Cl_3.NaCl.6H_2O$ at 80K

The crystal structure of $2[Co(en)_3]Cl_3.NaCl.6H_2O$ was last obtained in 1956 from 2-D data, we have accordingly redetermined the structure [3] in order to have an accurate structure to use in our calculations, which are in progress. In conclusion, we have established XNCD as a viable technique for the study of local chirality in oriented crystals and potentially in unoriented samples. We have shown that XanesCD uniquely gives direct information on chiral multiple-scattering photoelectron paths and that XNCD of pre-edge features promises to be a sensitive probe of local chirality for metal sites.

References

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[2] D. P. Siddons, M. Hart, Y. Amemiya and J. B. Hastings, Phys. Rev. Lett., (1990) 64,1967.
[3] L. J. Farrugia, R. D. Peacock and B. Stewart, Acta Cryst., to be published.