ESRF

Experiment title:

Natural Circular Dichroism in the X-ray Region

Experiment number:

CH-42

Beamline:	**Date of Experiment:**			**Date of Report:**
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Report:

The aim of the project was to detect **natural** circular dichroism (CD) in the X-ray region using the unique circularly polarised BL-6A at ESRF.

The choice of compounds for our initial attempt at detecting natural CD was dictated by the following factors:

(i) an accessible p state in the energy range where HELIOS 2 performs at its best (has the highest circular polarisation)
(ii) the samples should be single crystals in order to optimise the magnitude of the (weak) optical activity
(iii) the crystals should be vacuum-stable.

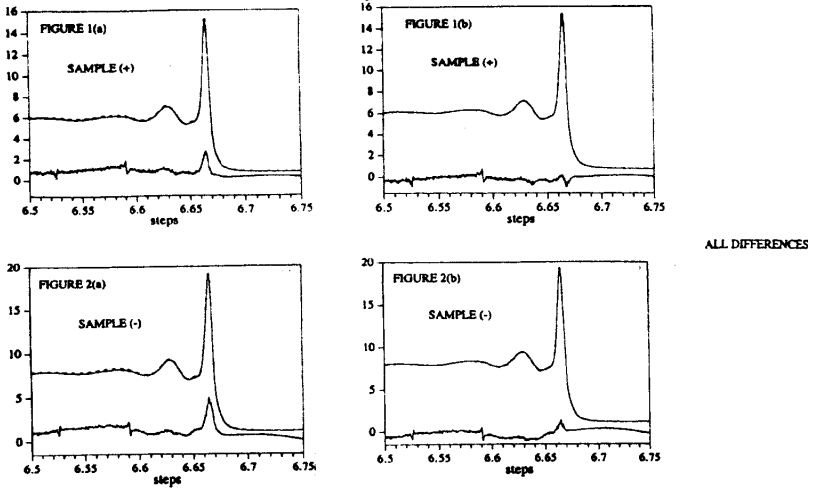
Criterion (i) suggested that Neodymium was an ideal element to study and we chose to examine single crystals of $Na_3Nd(C_4H_4O_5)_3 2NaBF_4 6H_2O$ which crystallise in the enantiomeric space group $R32$ from a racemic aqueous solution by slow evaporation [1]. The neodymium ion lies in a tri-capped trigonal prismatic environment co-ordinated by 6 carboxylate oxygens and 3 ether oxygens. The hexagonal, uniaxial crystals were hand-picked and analysed using a commercial CD spectrometer to determine their chirality.

Two enantiomeric crystals, of dimensions 6x6x2mm, were glued onto a sample holder with their C_3 axis parallel to the light path. Absorption experiments were run and spectra recorded in the fluorescence mode with a single photodiode detector placed at 120 degrees with respect to the beam direction. For each enantiomeric crystal, absorption spectra were obtained with the two hands of circularly polarised light. Spectra using left or right cpl were run close in time to one another in order to minimise the effect of intensity drift of the beam. This was facilitated by the efficient software procedure which allows the phase of the beam to be changed, in order to produce circular and linear polarisations, in a very short time.

Data analysis of single crystal spectra run with circularly polarised radiation at the L_3 excitation edge of Nd shows that there is a circular dichroic response of the crystalline samples. This can be broken down into two effects. The major contribution obtained by simple subtraction has the same sign for the two enantiomeric forms (Figs 1a and 2a), with a dissymmetry factor (AA/A) of around 2 x 10^{-2} and it may be linked to the birefiringeance of the bulk crystals [2] rather than to the enantiomeric form of the molecules.

A minor residual contribution remains at the white line when the raw CD is minimised in the pre-edge and in the NEXAFS regions (in other words far from resonance) (see Figs lb and 2b). This normalisation was performed using a minimal off-set and linear multiplication of the data.

This residual CD has opposite sign for the two enantiomers and a dissymmetry factor of around 5 x 10-3 ;which is close to the predicted value for natural CD. This result is Persistent throughout all the runs.



In the next proposal we will count on improved experimental conditions developed at BL-6A and on newly prepared samples. We will also investigate finely powdered samples of the enantiomeric and racemic forms, which will help us in disentangling the intriguing matter of dichroic effects from enantiomeric crystals.

[1] Fronczek, F. R., Banerjee, A. K., Watkins, S. F., Schwartz, R. W., *Inorg.* Chem. 20 (1981) 2745.

[2] Machavariani, V. Sh., *J. Phys.: Condensed Matter 7 (1995) 5151-53.*