ESRF	**Experiment title:** Influence of polymorphism on electronic diostribution and properties in the solid state	**Experiment number**: 01-02-841
Beamline: BM1A	**Date of experiment**: from: 23.10.08 to: 27.10.08	**Date of report**: 03.03.09
Shifts: 15	**Local contact(s)**: Dmitry CHERNISHOV	*Received at ESRF:*

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Report:

This project was the continuation of proposal CH-2283 that had the aim of investigating the influence of polymorphism on dynamics and electronic properties of a model system relevant to biology (the dipeptide Glycyl-Alanine) in its crystalline state, applying the X-ray constrained wave function technique (XCW).

The XCW method is a relatively new technique for analysing X-ray diffraction experiments, in which the X-ray diffraction data are introduced directly into the calculation of the quantum mechanical molecular wave function in such a way that the latter is constrained to reproduce the X-ray data, at the expense of the smallest possible energy variation. In XCW studies it is vital to account for the effects of thermal motion, including the correlation of atomic motion in the crystal. This information is represented by the 3x3 off-diagonal blocks of the mean square displacement matrix that can be retrieved by analysing with a molecular Einstein model the temperature-dependence of the Anisotropic Dipslacement Parameters obtained in a multi-temperature diffraction experiment.

Glycyl-alanine crystallizes in three polymorphic forms: an orthorhombic (P212121) and a monoclinic (P21) one for the pure enantiomers, and a different monoclinic one (P21/c) for the racemate. The three modifications show different crystal packing. While the orthorhombic form has been investigated with the XCW method based on both neutron and x-rays diffraction data, in experiment CH2283 (ID11) we wanted to study the monoclinic form of the pure enantiomer in the temperature range 10-290K at high resolution. That goal was not achieved, in part because of problems with the crystals but mainly because of major failures of the liquid-helium cryostream (Helijet) used to reach 10K (see exp. Report CH-2283).

In experiment 01-02-841, we wanted to repeat the procedure intended for experiment CH-2283, measuring

the crystal structure of the monoclinic form of the pure enantiomer in the temperature range 10-290K using the Kuma 6-circle diffractometer of BM1A equipped with a CCD detector and the Helijet liquid-helium cryostream.

As soon as we tested the crystals of the pure enantiomer we realized that the few monoclinic crystals that remained from the CH-2283 experiment, had transformed into the orthorhombic form. The new crystallizations trials gave crystals too small to have a sufficient signal on a bending magnet. A test of the crystals of the racemate showed that they were not of good quality and a data collection on those would not have been possible. To our regret, for this experiment we were not able of testing the crystals on a lab x-ray machine because there is nothing like that available at the Grenoble site (neither at the ESRF nor at the ILL) and in an attempt to send the crystals to Milan (I) to have them measured there, they got destroyed.

After the first shift and many crystals screened, we were left with crystals of the already measured orthorhombic form only, and they were not the best crystals we wanted to have either, but at least one big crystal (0.2 x 0.2 x 0.8 mm) gave nice diffraction spots. We decided then to change the aim of the experiemnt and to measure this crystal of the orthorhombic form in the range 80-290K, i.e. with a nitrogen cryostream, in order to investigate whether multi-temperature data in this temperature range would allow to extract information on the region in which the mean square displacements of the atoms change their dependence on temperature from the classical linear limit to the quantum regime. Having already data on this polymorph in the range 10-290K, the new data would have been quite useful for a detailed comparison of the temperature dependence of the ADP's and of the normal mode frequencies and eigenvectors obtained from the Einstein model.

Data collection was performed straigthforwardly at 80, 95, 110, 150, 200, 270K with no major problems. On-line data reduction did not show significant problems either and lead to reasonable agreement factors. A more detailed analysis of the integrated intensities during refinement of the crystal structure showed an unusual behaviour of the weak, high resolution reflections: the observed intensities were much lower than the calculated ones. The following statistic from SHELXL are reported here for the 95K data but are quite similar for the datasets at all temperatures:

Analysis of variance for reflections employed in refinement K = Mean[Fo^2] / Mean[Fc^2] for group

Fc/Fc(max)	0.000	0.017	0.026	0.034	0.043	0.052	0.061	0.075	0.097	0.136	1.000
Number in group	671.	617.	656.	652.	663.	577.	649.	646.	618.	641.	
GooF	0.875	1.122	1.249	1.072	1.168	1.002	1.013	1.113	1.061	1.013	
K	0.727	0.795	0.857	0.933	0.959	0.993	1.024	1.046	1.056	1.042	

Resolution(A)	0.48	0.50	0.52	0.55	0.58	0.61	0.66	0.72	0.83	1.04	inf
Number in group	662.	620.	641.	648.	630.	636.	636.	634.	640.	643.	
GooF	1.256	1.012	0.934	0.883	0.965	1.014	1.140	1.023	1.220	1.208	
K	0.972	1.055	1.080	1.066	1.068	1.011	1.033	1.051	1.017	1.035	
R1	0.129	0.085	0.068	0.059	0.052	0.050	0.047	0.038	0.033	0.033	

As one expects that K becomes >1 for the outer shells in the Fc/Fc_{max} statistic, the low numbers were quite surprising. At the moment we do not have a good explanation for this observation and it seems that the data collected in the experiment preceding ours did not show these features.

In summary: due to failure of our crystals we could not perform the experiment we intended to. For the experiment we did perform we cannot trust the high-resolution intensities that are of major importance for ADP and charge-density analysis.