ESRF	**Experiment title:** **Influence of polymorphism on Atomic Displacement Parameters and Charge Density**	**Experiment number**: CH-2283
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Shifts: 12	**Local contact(s)**: Gavin Vaughan	*Received at ESRF:*

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The aim of this experiment was to investigate to wich extent the dynamic and electronic properties of the di-peptide Glycyl-L-Alanine depend on its polymorphic form. Optical antipodes of Gly-Ala crystallize as two polymorphs: an orthorhombic form ($P2_12_12_1$) [1] and a more recently determined monoclinic one ($P2_1$) [2], while the racemate adopts another monoclinic arrangement ($P2_1/c$) [3]. X-ray and neutron data for the orthorhombic form of Gly-L-Ala had already been collected, therefore in this experiment we wanted to measure the monoclinic form of the enantiomer and of the racemate.

Data were collected with the Bruker SMART CCD in the first hutch of ID11, equipped with the helium-cryostream "Helijet" for reaching 10K, and subsequently with the usual nitrogen cryostream to reach temperatures in the range 90 to 295K. The beam was focussed with focusing lenses to a size of ~ 50 x 130 microns.

We decided to start the experiment with the very low temperature measurements, therefore setting up the Helijet and programming the controller to reach 10K. A problem arose almost immediately after the temperature was stable at 10K: ice was growing directly on the nozzle of the Helijet, at the level of the inner shield flow. We tried to remove the ice by blowing ethanol vapour onto the nozzle but within 10 minutes the ice was back. Mechanical removal of the ice gave us 20 minutes free of ice, just enough time to test the diffraction of our crystals. However, before starting a data collection, we had to warm up the Helijet to room temperature, dry out all parts by flushing them with helium gas and start again. Unfortunately, the situation did not improve much: ice was still growing although at a lower rate.

We also faced some difficulties related to both the size and the stability of the crystals. Crystallization of the monoclinic form of the pure enantiomer in multi-well plates gave very tiny needle-like crystals (size about 5 to 40 microns min to max dimensions) many of which showed double spots in the diffraction pattern, indicating twinning. In addition such small crystals vibrate in the flow of the helium cold stream, requiring a mounting with a large amount of glue that increased the background noise. Moreover, some of them showed a very rapid decay under the beam, such that after 40 frames, i.e. about 4 minutes exposure time and 12°

rotation, we did not have enough intensity left to continue the data collection. This phenomenon was not observed before, neither for the orthorhombic form measured under similar conditions at ID11 nor for the monoclinic form measured in the home lab and we do not know whether to invoke beam damage (even though the energy we were using, 39 keV, should not be so critical) or a drift of the beam during the data collection.

After destroying many crystals of the chiral form and after three restarts of the Helijet necessary to get rid of ice, we decided to test the stability of the gly-ala racemate under the same conditions. We were able to measure 200 frames (exposure time 2s and rotation 0.3°) before the crystal was once more completely covered with ice (see fig. 1: a view of the crystal as seen through the microscope on the Bruker showing that ice crystals have covered the crystal completely.

Fig.1

We noticed also that the air conditioning in the experimental hutch was malfunctioning, creating quite a warm and humid atmosphere inside the hutch, not the best ambient condition to have the Helijet working properly.

At this point we decided to check with the help of an aspartame crystal for how long we could run the Helijet before the ice was growing on the crystal. The test showed ice rings in the diffraction pattern after 1 hour. With an exposure time of 1s and a $\Delta\Phi$ of 0.3° we could thus collect 180° of data about the Φ axes, but at only one ω position. Because the small Gly-Ala crystals were requiring at least 2s of exposure time, we decided to give up the low temperature measurements with the Helijet and we mounted the nitrogen cryostream in order to have enough time to collect at least 3 or 4 data sets at different temperatures in the range 95 to 280 K.

The nitrogen cryostream reached 95 K only by playing with the setting of the evaporation temperature and once the temperature was reached and after the data collection was started on the monoclinic form of the racemate, the nozzle spewed drops of liquid nitrogen which killed the crystal. Data collection had to be restarted at 100K with a new crystal. (This cryostream has been working in the past at 95K without spitting liquid nitrogen, it may be time for a checkup of the instrument?). We were able to collect data on the racemate crystal at another 2 temperatures: 180 and 280K, with the troublesome aspect that half of the 280K datacollection was empty because the front end closed (automatic mode ended), and we had to remeasure it.

Five fast data collections were measured in the remaining time on two backup projects with the nitrogen cooling system: aspartame (that turned out to be a different compound from that expected) and [2,4,6-tris(4-iodophenoxy)-1,3,5-triazine]·C60.

At the end of 12 strenuous shifts we could take home 8 more or less complete data sets in the range 100 to 280 K and some bits and pieces of other measurements done at 10K. Unfortunately, we could obtain partial data for only one of the modifications we wanted to study and a few other data on backup projects. The helium temperature dataset, the one to give us info on the behaviour in the quantum regime of the Anisotropic Displacement Parameters, is still missing for both chiral and racemic Gly-Ala due to serious icing problems on the nozzle of the Helijet.

Although we took home some data from our visit to ID11, we cannot call this a successful experiment. It is discouraging to see that of the many times we tried to use the Helijet, it has never beeing working more then 20 minutes before icing, and we suggest that such complex equipment undergoes a full testing session in the lab before being given to the users for their experiment (users cannot be the Guinea-pigs in every single experiment!).

[1] A.H.-J. Wang & I.C. Paul, *Cryst. Struct. Comm.* **8(2)**, 269, 1979.

[2] Unit cell measurement: T.C. Tranter, *Acta Cryst.* **6**, 805, 1953. Structure determination: H.B. Bürgi, S.C. Capelli, G. Labat, P. Venugopalan, unpublished results.

[3] Unit cell measurement: J.E. Leonard & R.A. Pasternak, *Acta Cryst.* **5**, 150, 1952. Structure determination: W.F. Paton & I.C. Paul, *Cryst. Struct. Comm.* **8(2)**, 275, 1979.