ESRF	**Experiment title:** **Vibrational entropies of the α-, β- and γ-polymorphs of *p*-dichlorobenzene from atomic displacement parameters measured between 10 and 300 K.**	**Experiment number**: 01-02-624
Beamline: BM01A	**Date of experiment**: from: 30 - OCT - 2003 to: 04 - NOV - 2003	**Date of report**: 24 - FEB - 2004
Shifts: 12	**Local contact(s)**: Dr. Philip PATTISON	*Received at ESRF:*

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Report:

The initial goal of this project was to collect Bragg diffraction data for the α, β and γ-polymorphs of p-dichlorobenzene (DCB) in the temperature range 15 to 230 K, to determine atomic displacement parameters, to obtain rigid-body libration and translation frequencies, their anharmonicities, low frequency deformation motions, and to estimate the corresponding vibrational entropies. Data have been collected at 15, 100, 130, 180 and 230 K with a wavelength of 0.700(1) Å using the Onyx CCD installed very recently on the KUMA 6-circle diffractometer. Due to technical difficulties (summarized below) data could be collected for the α-polymorph only. The first results obtained from these data look promising both in terms of confidence factors (Table 1) and structural parameters (Figure 1).

Determining reliable ADPs requires diffraction data to high resolution, implying data collection at two different positions of the detector (θ=-10° and θ =45°). We found that the total collection time for the two theta settings was about 10 hours per temperature, approximately twice as long as we had planned and too long to complete the initial project. As our experiment was one of the first ones – if not the first one - making use of the Onyx CCD a number of other problems have also been encountered, had to be fixed during the experiment, and resulted in a further cost of time:

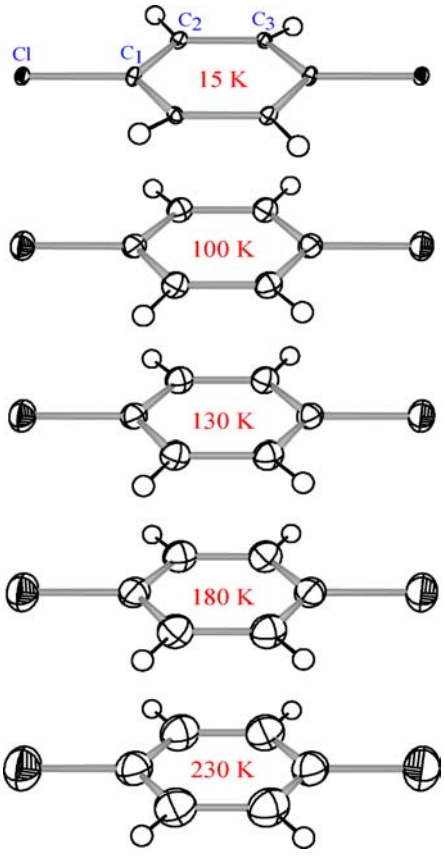
- High parasitic background; reduced to a significant extent by fine tuning the slits of the primary beam.
- Collision of the detector with the Helijet; required re-alignement of the cryostat nozzle. (The risk of collisions should be reduced or even eliminated by providing collision maps).
- Icing problems with the Helijet cryostat; due to icing only a single quadrant of data in the high theta setting of the detector could be collected at 15 K. (Icing should be reduce or eleiminated by installing a suction device removing the cold Helium).

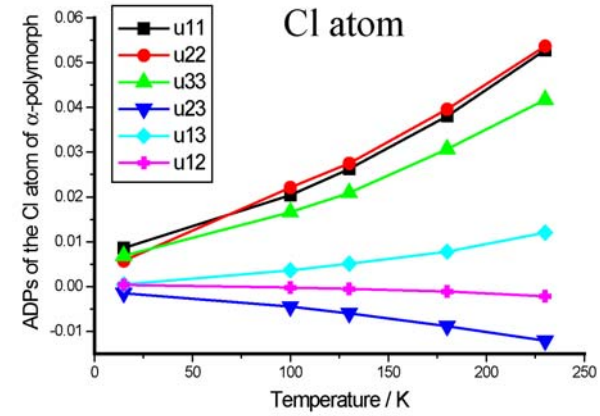
These and other points have already been addressed in a detailed preliminary report sent to P. Pattison. The report also mentions software issues related to the data processing: e.g. the flood field correction for a wave length of 0.7 Å, the gain factor of the CCD detector and the consequent uncertainty in the calculations of sigmas.

On the whole the first results obtained for the α-polymorph look encouraging. The data processing protocol had to be "optimized" within the constraints of the CrysAlis software. Different ways of calculating and substracting the background were tested, and the influence of the box size of integration on confidence factors and structural parameters assessed. After integration the data were corrected for the decay of the synchrotron beam and the anisotropy of the absorption of the sample using Sadabs. In terms of confidence factors the data are decent (Table 1). The results also look promising with respect to the structural parameters (Fig. 1, left). The thermal evolution of the ADPs shows the expected behaviour with anharmonicity, which is visible already at 200 K and is consistent with the fact that the sample sublimes at room temperature (Fig. 1 right). Furthermore, ΔU-values along chemical bonds are small, of the order of 0.0004 Å, as expected from ab inito calculations of the molecular vibrations. For the partial 15 K data ΔU-values are three time larger.

Table 1. Confidence factors obtained for α-DCB.

T/K	15	100	130	180	230
R_{int}	0.019	0.021	0.022	0.029	0.028
R_1	0.040	0.032	0.032	0.037	0.047
wR_2	0.139	0.111	0.116	0.126	0.150
Goof	1.283	1.128	1.129	1.153	1.083





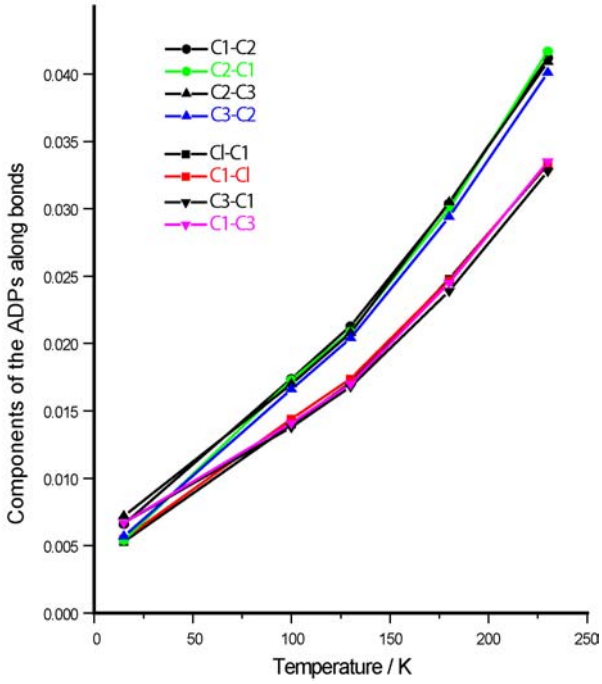


Fig. 1. (left) ORTEP plots of the *p*-dichlorobenzene molecule in the α-polymorph as a function of T; (top right) ADPs of Cl atoms; (bottom right) components of the ADPs along the chemical bonds.