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**: CH-1916
Beamline: ID11	**Date of experiment**: from: 21st Jul. 2005 at 08h00 to: 26th Jul. 2005 at 08h00	**Date of report**: 06/12/2005
Shifts: 18	**Local contact(s)**: Silvia Chiara Capelli	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Summary: the data collected for the α- and β-form in July 2005 are of most doubtful quality and insufficient to reach the aim of this experiment, namely to determine reliable ADPs as a function of temperature.

Report:

The project was aimed at collecting Bragg diffraction data for the α, β and γ-polymorphs of *p*-dichlorobenzene (*p*-DCB) [1] in the temperature range 10–230 K, in order to determine atomic displacement parameters (ADPs), to obtain rigid-body libration and translation frequencies with their anharmonicities, and to estimate the corresponding vibrational entropies. Data have been collected on the α- and β-phases to 0.42 Å resolution with a wavelength of 0.31853(1) Å using the SMART CCD. They were processed with SAINT, and SADABS and refined with SHELXL-97. The results have been compared with those from earlier experiments conducted under comparable conditions for the α-polymorph (0.5 Å resolution, wavelength 0.700(1) Å, ONYX CCD, KUMA 6-circle diffractometer, experiment SNBL 01-02-624) and the β-polymorph (0.42 Å resolution, wavelength 0.3112(1) Å, SMART CCD at beamline ID11, experiment CH-1834). Data statistics of the present and previous (*italics*) experiments are compared in Tables 1 and 2; the temperature evolution of unit cell volumes is compared in Figs. 1 and 2, that of the ADPs in Fig.3.

Table 1. Statistics of DCB α-polymorph data.

T/K	10	100	130	180	230
%Compl	98.6 *NA*	99.5 *79.3*	99.9 *78.8*	99.7 *79.4*	99.7 *93.3*
Redund	6.0 *NA*	6.6 *3.4*	6.6 *2.9*	6.6 *2.7*	6.3 *2.3*
R_{int}	0.066 *NA*	0.073 *NA*	0.079 *NA*	0.078 *NA*	0.080 *NA*
R_1	0.065 *NA*	0.087 *0.028*	0.088 *0.030*	0.080 *0.041*	0.070 *0.059*

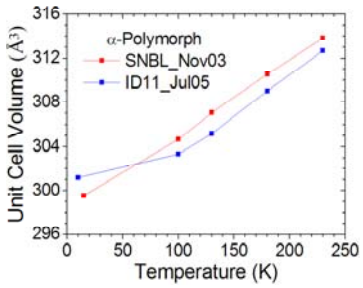

Fig. 1. Unit cell volume as a function of temperature for the α-polymorph from data collected at the SNBL and ID11 beamlines.

Table 2. Statistics of DCB β-polymorph data.

T/K	10	100	130	180	230
%Compl	88.9 *89.7*	90.7 *91.1*	88.8 *91.6*	88.7 *92.3*	88.7 *92.1*
Redund	3.2 *4.4*	3.6 *7.2*	3.8 *7.3*	3.5 *7.3*	3.5 *7.4*
R_{int}	0.046 *0.027*	0.038 *0.029*	0.036 *0.035*	0.042 *0.027*	0.038 *0.023*
R_1	0.071 *0.026*	0.027 *0.018*	0.030 *0.021*	0.035 *0.029*	0.041 *0.035*

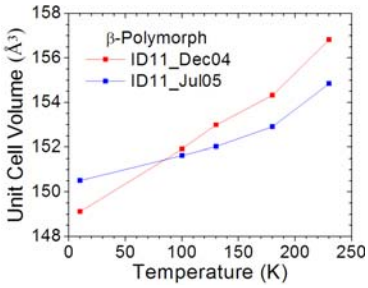

Fig. 2. Unit cell volume as a function of temperature for the β-polymorph from two data sets collected at the ID11 beamline.

It is clearly seen from the unit cell volumes and from the ADPs, that different data sets obtained under the same conditions from different beamlines (α–polymorph) or from the same beamline (β–polymorph) do not agree. Data from the present experiment for the α-form show a high R_{int}, 6.5–8.8% (Tables 1, 2). Inspection of the I/σ(I) values of Jul05 in the low, medium and high resolution ranges of the β-form data at 230 K (Fig. 4), where the differences in ADPs are maximal, shows that the ratios in all resolution shells are 3–10 times lower than those of Dec04. In addition, the Jul05 data cluster at high I/σ(I) into six, four and one groups for low, medium and high resolution, respectively (Fig. 4). Careful analysis of raw and scaled multiple measurements of the same or of equivalent reflections revealed that intensities measured during the Jul05 campaign diverged by up to 100%. As a result SADABS increased σ(I) through an unusually large g-factor. In spite of many tests and checks the reason for this behaviour could not be uncovered. We acknowledge intense support by our local contact both during the experiment and afterwards when we tried to identify the problem with the data, but we should also reiterate here an observation communicated already during the experiment: nearly every frame was retaken irrespective of crystal size or primary beam intensity, and even in the absence of any x-ray beam!

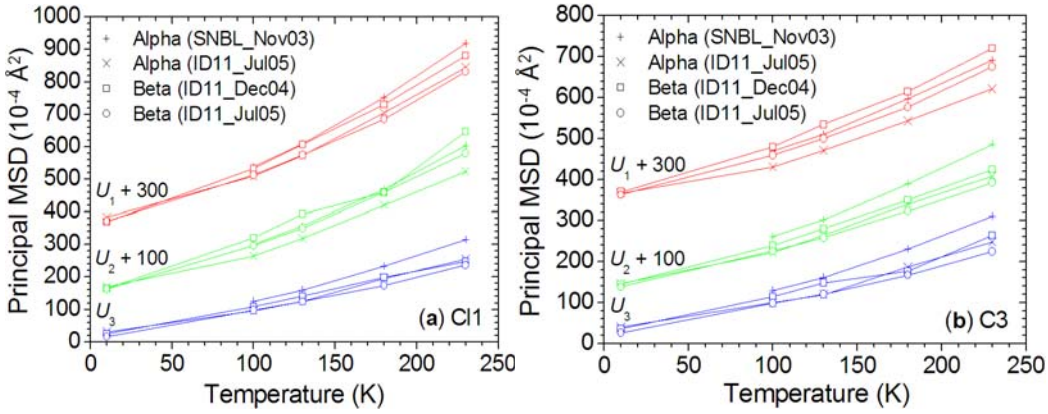

Fig. 3. ADPs of (a) Cl1 and (b) C3 atoms for α- and β-polymorphs from various experiments.

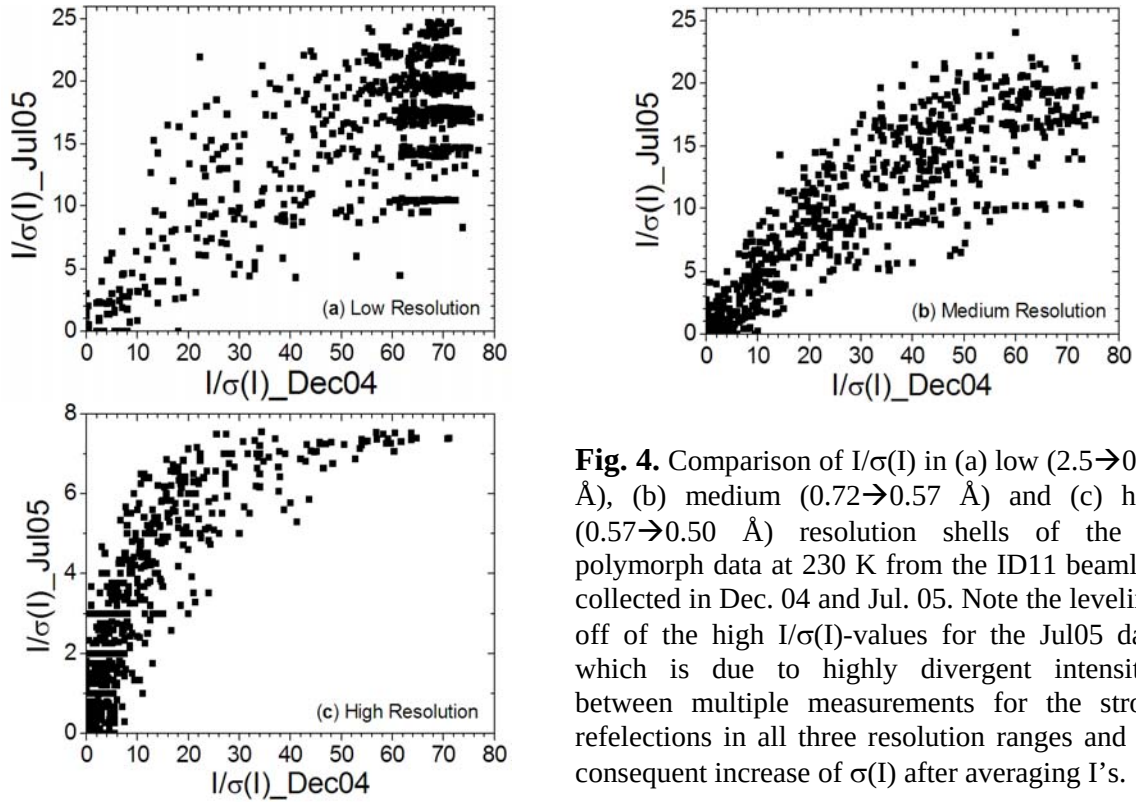

Fig. 4. Comparison of I/σ(I) in (a) low (2.5→0.72 Å), (b) medium (0.72→0.57 Å) and (c) high (0.57→0.50 Å) resolution shells of the β-polymorph data at 230 K from the ID11 beamline collected in Dec. 04 and Jul. 05. Note the leveling-off of the high I/σ(I)-values for the Jul05 data, which is due to highly divergent intensities between multiple measurements for the strong refelections in all three resolution ranges and the consequent increase of σ(I) after averaging I's.

Reference:

1. G.L. Wheeler, S.D. Colson, *J. Chem. Phys*. **65** (1979) 1227–1235.