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-1834
Beamline: ID11	**Date of experiment**: from: 13th Dec. 2004 at 08h00 to: 19th Dec. 2004 at 08h00	**Date of report**: 18/08/2005
Shifts: 18	**Local contact(s)**: Silvia Chiara Capelli	*Received at ESRF:*

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Report:

The project aims 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, to determine atomic displacement parameters (ADPs), to obtain rigid-body libration and translation frequencies, their anharmonicities, low frequency deformation motions, and to estimate the corresponding vibrational entropies. Data for the α-polymorph have already been collected to 0.5 Å resolution at 15, 100, 130, 180 and 230 K at the SNBL with a wavelength of 0.700(1) Å using the ONYX CCD installed on the KUMA 6-circle diffractometer (experiment number SNBL 01-02-624). The present experiment has been conducted on the β-polymorph to 0.42 Å resolution at 10, 100, 130, 180 and 230 K at the ID11 beamline with a wavelength of 0.3112(1) Å using the SMART CCD. The data were processed with SAINT, SADABS and refined with SHELXL-97, yielding $R_{int} \leq 3.5\%$ and $R_1 \leq 4.4\%$, Table 1. The ADPs as a function of temperature are displayed in Fig. 1. Further refinements with a multipole atom model performed with XD provide $R_1 \leq 2.5\%$ (Table 1). Difference densities indicate that most of the valency density has been separated from the spherical core density. The ADPs are slightly changed for the Cl-atom and are smaller (U^{22}, U^{33}) and larger (U^{11}) up to 6 s.u. for the C-atoms (Fig. 2).

Table 1. Statistics of the β-*p*-DCB data;
sph = spherical refinement, *mul* = multipole refinement.

T/K	10	100	130	180	230
R_{int}	0.0272	0.0299	0.0345	0.0277	0.0249
R_1_*sph*	0.0167	0.0180	0.0213	0.0332	0.0439
R_1_*mul*	0.0134	0.0117	0.0141	0.0217	0.0250

The ADPs derived from multipole refinements were then used for normal mode analysis with NKA [2] to determine average translation and libration frequencies of the β-polymorph as had been done for the α-polymorph. These six frequencies, combined with intramolecular vibration frequencies from high-level DFT calculations were used together with Einstein and Debye models of heat capacity to calculate C_v as illustrated in Fig. 3. The concurrent analysis of multi-temperature ADPs provides C_v in fair agreement with C_p from calorimetric measurements [3] (Fig. 3).

In addition, two data sets of the α-polymorph at 10 and 130 K have also been collected. It is found that the ADPs at 130 K on BM1A and ID11 are differerent by 5–30 s.u. Therefore we have proposed to remeasure diffraction data for the α-polymorph in the temperature range 10–230 K at both SNBL and ID11 with the aim of establishing a protocol providing comparable ADPs from the two different installations (experiment number CH-2065).

Several problems occurred during the experiment resulting in unnecessary loss of beamtime.

- The experimental set-up of the detector, beam and N_2 cryostream system took about 3.5 shifts.
- The N_2 cryostream (ID11, Series 600) and HeliJet did not perform to standard at all. Icing was a recurrent problem. De-icing always introduced a shift in the orientation matrix of the crystal.
- Communication with the detector and goniometer controller was lost several times. This required total restart of the system (including turning off the detector cooling).

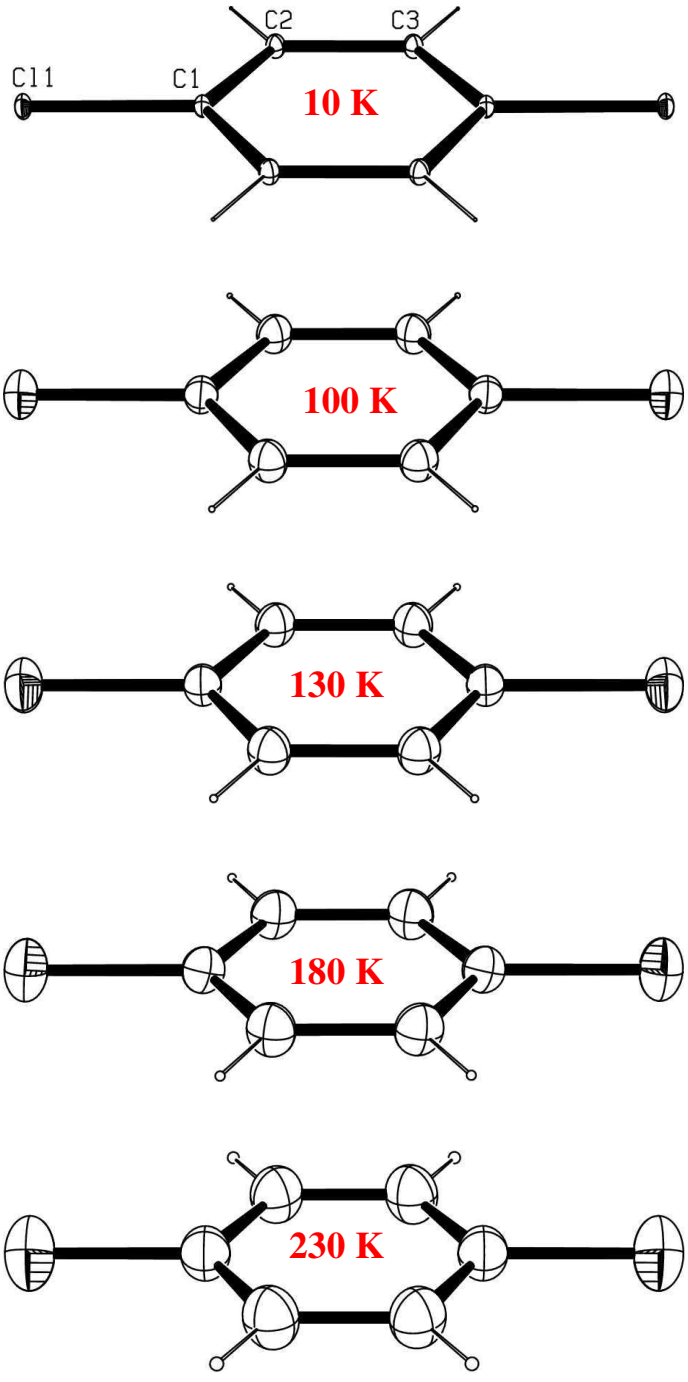

Fig. 1. Ortep (50% probability) plots of β-*p*-DCB.

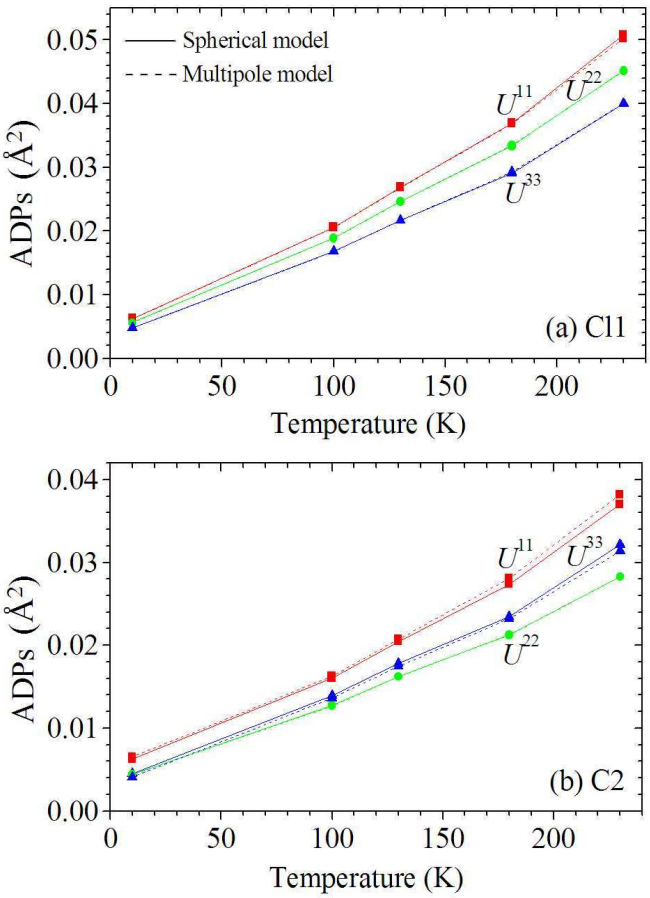

Fig. 2. ADPs of β-*p*-DCB as a function of temperature, (a) Cl1 and (b) C2.

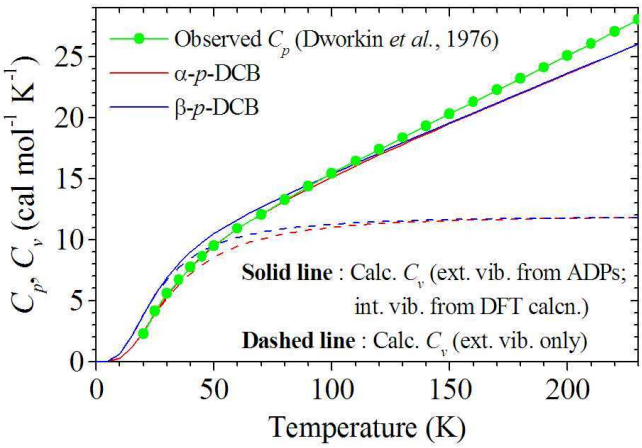

Fig. 3 Molar heat capacity of *p*-DCB.

References

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

[2] H.B. Bürgi, S.C. Capelli, H. Birkedal, *Acta Cryst*. **A56** (2000) 425–435.

[3] A. Dworkin, P. Figuière, M. Ghelfenstein, H. Szwarc, *J. Chem. Thermodyn.* **8** (1976) 835–844.