ESRF	**Experiment title:** Dynamic and thermodynamic properties of glycine polymorphs from simultaneous analysis of multi-temperature diffraction data	**Experiment number**: 01-02 894
Beamline: BM01A	**Date of experiment**: from: 23th June 2010 at 08h00 to: 29th June 2010 at 08h00	**Date of report**: 28/02/2011
Shifts: 9	**Local contact(s)**: Dmitry Chernyshov	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Thammarat Aree*, Chulalongkorn University, Thailand.

Karl W. Törnroos*, University of Bergen, Norway.

Hans-Beat Bürgi*, University of Bern, Switzerland.

Dmitry Chernyshov*, ESRF, France.

Report:

The research project has a three-fold aim: i) measuring accurate atomic displacement parameters (ADPs) of glycine polymorphs (α, β and γ) from 10 to 298 K, ii) investigating the dynamical properties of glycine molecules in the crystals, and iii) determining the thermodynamic parameters (specific heat and entropy).

Synchrotron data of the α- and β-glycine polymorphs were collected to 0.5 Å resolution at 80, 90, 100, 130, 190, 250 and 300 K on beamline BM01A with a wavelength of 0.70128 Å, using an ONYX KUMA CCD, 6-circle diffractometer. Data were processed with CRYSALIS, giving completeness = 98–99%, redundancy = 3.7–4.7, R_{int} = 0.025–0.061, and the structures were refined with SHELXL-97, yielding R_1 = 0.031–0.050, $|\Delta\rho|$ = 0.18–0.63 e Å^{-3}, EXTI = 0.000–0.074 (Table 1). In the overall statistics, the data are of good quality, except for the residual electron density peaks observed on the atoms in addition to those expected on the bonds (Fig. 1). The ADPs of α-glycine obtained with data measured on beamline BM01A are larger than those found with data from other sources and the EXTI parameters are unexpectedly large. The ADPs of β-glycine at 80–100 K show small deviations from the smooth curve; the EXTI parameters equal zero as expected (Fig. 2a,b and Table 1).

The normal mode analysis [1] of all the data available is on going. The preliminary analysis using a rigid body model of motion gives external vibration frequencies in fair agreement with the spectroscopic data for the α-form: 63.1, 76.5, 83.3, 115, 134 cm^{-1} vs. 52, 73, 109, 162, 190 cm^{-1} [2]. The external vibration frequencies of the β-form are 67.8, 71.0, 82.5, 149, 239 cm^{-1}; the experimental data are not available for comparison. The external frequencies from the ADP analysis together with the internal frequencies from high-level ab initio calculations will be used to estimate the thermodynamic parameters.

Table 1. Data statistics of α- and β-glycine from beamline BM01A

T (K)	Compl	Redund	R_{int}	Reflns All/Obs	R_1	Δρ (e Å^{-3})	Δρ positions	EXTI
80	98.6	4.68	0.042	2554/2190	0.050	0.62/–0.39	@ bonds & atoms	0.01782
90	98.1	4.57	0.061	2538/1832	0.044	0.50/–0.34	@ bonds & atoms	0.02137
100	98.8	8.79	0.051	2560/2075	0.041	0.53/–0.38	@ bonds & atoms	0.00131
130	98.1	4.60	0.044	2546/1768	0.039	0.47/–0.33	@ bonds & atoms	0.02512
190	98.1	4.62	0.041	2556/1620	0.041	0.49/–0.33	@ bonds & atoms	0.02839
250	97.9	4.64	0.034	2563/1500	0.042	0.40/–0.31	@ bonds & atoms	0.07434
300	98.0	4.64	0.032	2572/1438	0.042	0.42/–0.30	@ bonds & atoms	0.06930
80	98.6	3.67	0.033	1365/1227	0.032	0.51/–0.26	@ bonds & atoms	0.00000
90	98.5	4.36	0.031	1364/1255	0.031	0.48/–0.26	@ bonds & atoms	0.00000
100	98.6	4.30	0.039	1367/1286	0.041	0.63/–0.44	@ bonds & atoms	0.00000
130	98.5	4.36	0.035	1368/1221	0.033	0.42/–0.25	@ bonds & atoms	0.00000
190	98.6	4.36	0.029	1374/1196	0.036	0.45/–0.24	@ bonds & atoms	0.00000
250	98.6	4.37	0.026	1385/1187	0.035	0.40/–0.22	@ bonds & atoms	0.00000
300	98.8	4.37	0.025	1400/1186	0.036	0.37/–0.18	@ bonds & atoms	0.00000

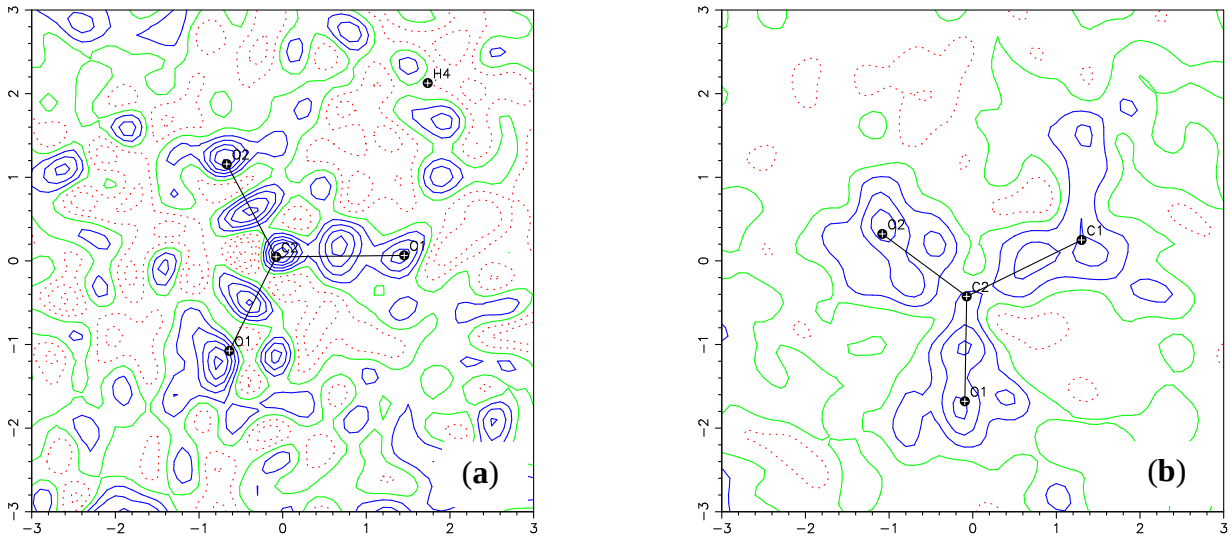

Fig. 1. Residual density maps of (a) α- glycine and (b) β-glycine data at 300 K from beamline BM01A.

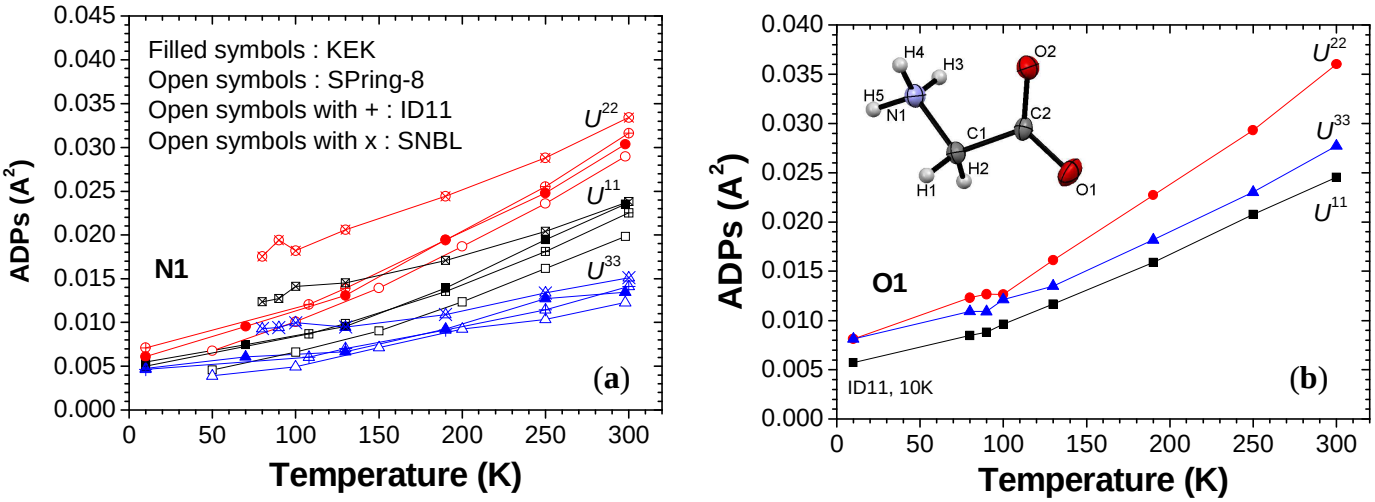

Fig. 2. Variable temperature ADPs for (a) N1 of α-glycine and (b) O1 of β-glycine from beamline BM01A in comparison with other sources. Note the β-glycine 10 K data from ID11. Standard deviations are 2×10^{-4} Å^2.

References:

[1] Bürgi, H.B.; Capelli, S.C. *Acta Cryst*. **2000**, *A56*, 403–412.

[2] Machida, K.; Kagayama, A.; Saito, Y.; Kuroda, Y.; Uno, T. *Spectrochim. Acta* **1977**, *33A*, 569–574.