ESRF	**Experiment title:** Development of a Gas Flow Thermostat Sample Cell with Control of Relative Humidity and Equipment for the	**Experiment number**: 01-02-343
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Report:

A major purpose of this work is to obtain experience with and develop further a gas-flow thermostat sample cell including control of relative humidity and equipment for applying an electric DC field to the sample. The cell is to be used for diffraction studies of crystalline compounds, notably hydrates, that are unstable and may denature easily upon exposure to changes in temperature and/or relative humidity, in particular crystals with a structural phase transition that is induced or facilitated by an electric DC field.

Rochelle salt (RS), $NaKC_4H_4O_6 \cdot 4H_2O$, a well-known ferroic compound with two structural phase transitions involving water molecules, has been selected for the study. RS is paraelectric at $T > T_c^{high} = 297$ K and at $T < T_c^{low} = 255$ K, and is ferroelectric in the range $T_c^{high} > T > T_c^{low}$. Excellent data have been collected previously for the paraelectric crystal at 308 K and used for structure refinement, *cf.* Experiment Report 01-02-231. A further aim of the present experiment was to complete the structural investigation of RS by collecting diffraction data near 273 K for the ferroelectric phase.

The sample cell: Before the experiment started the operation of the Peltier element of the sample cell was checked over the temperature range 35 - 0 ^oC (308 - 273 K) and the proper relative flows of dry and moist N_2 gas were calibrated in this range in order to maintain the desired relative humidity (RH). This test was required because of changes in the experiment conditions on the site as compared to the home lab, and was particularly important at the lowest temperatures where there is a rather narrow range in RH between freezing and deposition of ice in the Peltier element on one side

and dehydration of the sample on the other. As a result of these tests, the sample cell was modified to improve the thermal insulation, yielding a $\Delta T \sim 5.5\ ^{o}C$ between the Peltier element and the sample position, for a sample temperature of 3 ^{o}C.

For the experiment a single crystal of RS was first heated up to 35 ^{o}C in order to centre and orient it in the pararaelectric phase. The temperature was then reduced through the transition T_c^{high} and further down to 3 ^{o}C. At 25 ^{o}C a DC field of 100 V , yielding a field strength of about 400 V/cm, was applied to the crystal in a direction about 35^{o} off the polar axis ***a***. This field was maintained through T_c^{high} and reduced to zero at about 17 ^{o}C. We observe that the intensity peaks remained unsplit after the transition. Throughout the subsequent recentring of the crystal and data collection the temperature was kept within the range 2.5 - 3.0 ^{o}C; two or three excursions up to about 3.4 ^{o}C were easily reversed by increasing slightly the power to the Peltier elements. The RH was controlled in a relatively narrow range.

The performance of the cell is deemed highly satisfactory, and we conclude that this part of the project has been successful.

Data collection and preliminary merging: Several small single crystals selected from a freshly prepared crop of RS were examined first. Single crystals of natural habit are preferable because they enable easy alignment of the crystal prior to the application of the DC field. Unfortunately, all specimens that were examined showed slightly split or deformed reflections and were discarded. Samples cut from larger single crystals were more often of good quality. The specimen selected for data acquisition was cut from a large single crystal grown in 1999, typical FWHM values from ω scans were ~ 0.01^{o}.

About 12.700 reflections were collected with λ = 0.6042 Å. This number includes remeasurements and equivalents, but not the measured standard reflections. It became clear that the transition from paraelectric (orthorhombic cell, $P2_12_12$) to ferroelectric phase (monoclinic cell $P2_111$ with $\alpha \sim 90.05^{o}$) had not proceeded as expected, at best only in part. Preliminary merging of the data was carried out based on different models: monoclinic symmetry, orthorhombic symmetry, with and without Friedel pairs. The merging was made in a straightforward manner, without examination of possible discontinuities or other anomalies in the standard reflection curves signalling a 'bad' sequence of data. Some results are given

'Raw' merging	R_{merge}
Monoclinic symmetry w/Friedel pairs	0.0244
Monoclinic symmetry wo Friedel pairs	0.0231
Only remeasurements w/Friedel pairs	0.0247
Orthorhombic symmetry w/Friedel pairs	0.0277

The results give a slight preference to monoclinic symmetry, however, as stated above, the transition is far from complete and the ferroelectric phase has not been obtained. Careful merging of the data and structure refinements of both symmetry models are necessary to describe the structure at 3 ^{o}C.

Problems with the KUMA software and hardware have been discussed briefly in a report of 02.06.02. At the time of this experiment centring was still a very time-consuming operation, involving frequent 'loss' of reflections in auto-mode centring, in particular when using relatively wide slits, *e.g.* 5.0 x 5.0 mm, as is necessary in the early stages. The precision obtained for the orientation matrix is less than adequate, and does not allow a reliable discrimination between orthorhombic and monoclinic symmetry in the case of RS. In the present case, the refined angle α did not differ significantly from 90^{o}.