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<b>Experiment title:</b> Rochelle Salt - A Redetermination of the Pараelectric and Ferroelectric Crystal Structures		<b>Experiment number:</b> 01-02-231
<b>Beamline:</b> BM01-EH2	<b>Date of experiment:</b> from: 24.11.99 07:00 to: 30.11.99 07:00	<b>Date of report:</b> 18.02.00
<b>Shifts:</b> 18	<b>Local contact(s):</b> K. Knudsen	<i>Received at UNIL:</i>

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**Report:**

In a previous experiment (01-02-194) we have tested a new sample chamber for diffraction work designed to allow control of temperature and humidity of the sample environment. A brief description of this chamber was given in Experiment Report 01-02-194 along with the results from a comparison of various experimental conditions implemented to prevent crystal dehydration or deliquescence. Crystals of many hydrates do show this behaviour, and in our experience with Rochelle salt and other hydrates, loss of water and crystal deterioration is initiated more easily and accelerates under exposure to X-rays. This involves a partial change of structure, a devastating problem for the acquisition of high-quality diffraction data. This problem may be delayed by mounting the crystal in a capillary, which in itself is not desirable.

Rochelle salt (RS) has been the subject of several crystallographic (both X-rays and neutrons) and spectroscopic studies. In the most recent study (Suzuki & Shiozaki, 1996), a very large crystal  $\sim 0.7 \times 0.7 \times 2.0$  mm sealed in a glass capillary was used for the data collection. 2330 intensities were collected for the paraelectric phase at 308K, yielding 1310 unique reflections with  $F > 3\sigma(F)$ . According to the authors their refinement included H atoms, but the report gives only parameters for the non-H atoms. Final crystallographic indices were  $R = 0.0912$  and  $R_w = 0.1297$ . These numbers indicate problems with the data, or the structure model, or both.

In the present work a small irregular crystal of RS with dimensions  $\sim 0.20 \times 0.15 \times 0.09$  mm was mounted on the conical tip of a short, sturdy glass rod and placed on the goniometer head

of the chamber in a humidified  $N_2$ -stream. This crystal was cut from a larger specimen. Radiation with  $\lambda = 0.6001 \text{ \AA}$ , slitted down to a  $0.6 \times 0.6 \text{ mm}^2$  square was used for the experiment. All reflections in the  $2\theta$  range  $3.0 - 56^\circ$  were measured from 2 to 10 times, by repetition or more generally as a symmetry equivalent. In the range  $56 < 2\theta < 100^\circ$  all reflections precalculated to be larger than a certain threshold were collected, a total 586 reflections which include two equivalents. Reflections in the range  $3 < 2\theta < 35^\circ$  were measured both with and without a  $1000 \text{ \mu m}$  Al attenuator foil, to accomplish interscaling and determination of an attenuation factor for the strong reflections. In total 8963 data reflections were measured, the number of unique reflections after merging was 2713, of which 258 had  $F^2 < \sigma(F^2)$  and were assigned weight  $w = 0$ .  $R_{\text{merge}}$  for all reflections was 0.0162, and 0.0159 for reflections with  $w > 0$ . Data were collected at  $308 \pm 0.8 \text{ K}$ .

Throughout the measurement period which lasted for about 90 hrs. full-width at half-maximum (FWHM) values for three test reflections were checked at regular intervals by  $\omega$  scans. The initial values, in the range  $0.0055 - 0.0070^\circ$  did not increase, in fact two reflections showed a small decrease in FWHM. There were no significant changes in the intensity of the three standard reflections, until about 2/3 of the data had been collected, when a slow and uniform decrease took place giving a final 9 % intensity reduction..

A preliminary structure refinement has been carried out with the data, uncorrected for absorption. Refinement was in the mixed mode for ADP, anisotropic  $U_{ij}$  for non-H atoms and isotropic  $U$  for H. Crystallographic indices at convergence were  $R = 0.037$ , and  $R_w = 0.031$ , both based on 2455  $F$ . As expected one of the K atoms and three of the four water molecules show large and very anisotropic displacements. Even so, all H atoms could be refined in position and  $U$ -factor. A consequence of the large anisotropy, an important part of the structural transition, is that these atoms do not comply well with the harmonic description of the displacements, and this is reflected in the final  $R$  values as compared to the  $R_{\text{merge}}$ .

We conclude from this work that the controlled environment in the sample chamber allowed collection of very good data for this compound, there was no clear indication of crystal deterioration. The reduction in the standard intensities towards the end of data collection could be incorporated in the scaling of the data.

In our setting transition to the ferroelectric state requires reduction of the temperature from 308 K to a  $T < T_c^{\text{high}} = 297 \text{ K}$  and the simultaneous application of an electric DC field on the sample. The last part of the experiment period was used to construct a capacitor of suitable form and size and a translation stage to introduce the capacitor in position about the crystal. We were able to carry out a test involving a reduction of  $T$  to 276 K, while maintaining a suitable humidity of the gas stream and applying a DC field of about 210 V/cm on the crystal. This test was in part successful, but showed that some modifications in the equipment and procedures are necessary.

The first day of the period was spent in part on work with the crystal alignment optics on the diffractometer, and in part on tracking the beam which had moved about  $250 \text{ \mu m}$  vertically on the SNBL beamline following a change in operation from  $2 \times 1/3$  fill to 16 bunch mode.