SNBL	**Experiment title:** Rochelle Salt - A Reinvestigation of the Paraelectric and Ferroelectric Crystal Structures.	**Experiment number:** 01-02-194
Beamline: BM01-EH2	**Date of experiment:** from: 05.05.99 07:00 to: 11.05.99 07:00	**Date of report:** 27.09.99
Shifts: 18	**Local contact(s):** K. Knudsen	*Received at UNIL:*

Names and affiliations of applicants (* indicates experimentalists):

F. Mo*, R.H. Mathiesen*
Department of Physics, NTNU, N-7491 Trondheim, NORWAY

Report:

The purpose of this experiment was threefold: a) to test out a new sample chamber designed to maintain a constant temperature in the range about –10 to +50°C, b) to examine various experimental conditions preventing crystal dehydration or deliquescence, and c) to collect diffraction data for the paraelectric phase of Rochelle salt at T = 308K (35°C).

I. The sample chamber. The base of the chamber is screwed directly onto the locking ring of the goniometer head. Heating/cooling is provided by Peltier elements arranged in an annular ring about the base. Dry N_2 gas is heated/cooled as it diffuses through the thermal source and flows upward along the solid crystal mount which is surrounded by a conical Kapton shield. The gas leaves the cone through its open tip. Thermal exchange of the Peltier with the exterior is effected through a ruff of Al ribs. The temperature on the crystal is monitored by thermocouples fixed to the crystal mount and can be easily adjusted. This device worked very satisfactorily and reliably. Neither the chamber mount, nor the gentle flow of N_2 gas created detectable instabilities or vibrations of the crystal as could be ascertained from ω-scans of very narrow peaks.

The only problem we experienced was associated with the gas hose and the electric leads to the sample chamber. As the present software allows several consecutive full rotations of the phi head the connecting hose and leads were twisted, and in one case the hose knocked down the crystal during data collection. For the remaining part of the work it was necessary to select

appropriate sequences of reflection measurements and attend the operation to avoid further accidents. The problem is easily rectified by introducing suitable modifications in the diffractometer software. We have suggested a possible solution.

II. The crystals. Rochelle salt is the tetrahydrate of the NaK salt of tartaric acid. Large and nearly perfect crystals can be grown from water solution. Samples of suitable size were obtained by cutting them from larger crystals. Cutting of the hard crystals frequently introduces defects, as evidenced by broadened and split reflections. Only about one out of 3 cut samples were of good quality for data collection.

Rochelle salt effloresces on exposure to a warm and dry environment, at 100°C it loses 3 H_2O. The loss of water is accompanied by the gradual development of a white crust on the crystal. Our experiments indicate that dehydration is initiated more easily and accellerates under exposure to X-rays. This is a serious problem which involves a partial change of structure. Apparently it has not been solved satisfactory in previous work. Therefore, one important aim of the present study was to try out various experimental conditions preventing or slowing down dehydration. An uncoated crystal in a dry N_2 atmosphere at 35°C and exposed to X-rays for about 1 hr turned into a white opaque lump in about 20 hrs without radiation. (This unplanned break was caused by a PEP interface problem). Coating the crystal sample with an inert oil improved its life time significantly, to about 3 days, however, with a gradual and increasing degradation during the last 15 hrs. The best result was obtained with a N_2 stream partially saturated with H_2O. An uncoated crystal was kept in a humid N_2 atmosphere and exposed to X-rays for about 7 hrs. At the end of a subsequent period of 6 hrs the profiles of a test reflection remained unchanged, FWHM 0.0013 °, and there were no visible changes on the crystal. Even if the last experiment had to be aborted at the end of our allocated beamtime it indicates strongly that the most efficient protection against dehydration involves exposure of the sample to a properly humidified environment.

III. Intensity data. Two shells of data were collected with the oil-coated crystal, and λ = 0.5990 Å. A low-resolution shell, $2\theta \in [1.5, 17.5°]$, was covered by measuring two sets of symmetry-equivalent reflections. In addition two partial sets in this 2θ-range were measured twice. From a total 1717 data reflections, 704 unique data were obtained, and R_{merge} = 0.0144 (all reflections). Data were also collected in a second shell, $2\theta \in [17.0, 26.0°]$. Due to an increasing degradation of the crystal during the last 15 hrs of data collection only one unique set of data could be used, and this set is of inferior quality.

Merging all data from the two shells, including some 60 reflections in the overlap band at $2\theta \in [17.0, 17.5°]$, gave 2026 unique reflections and an R_{merge} = 0.015. A subsequent test refinement with Xtal3.5, converged at R(F) = 0.056 and GOF = 5.91. Final ADP values for three water O atoms and one K atom were strongly anisotropic indicating an inadequacy of the structure model, possibly also involving partial disorder.

Nevertheless, it appears that the test data collected in this run is of better quality than data of Rochelle salt collected in previous work. A weakness of our data is the lack of equivalents at higher resolution, and the fact that this data presumably is affected by crystal deterioration.