110. **Heat Capacities of Rochelle Salt between 230 and 310 K**

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Rochelle salt (NaKC$_4$H$_4$O$_6$·4H$_2$O) has been known for a long time as the first ferroelectric crystal that was discovered by Valasek in 1920 from its anomalous dielectric properties.\(^1\) This crystal is also one of the few ferroelectrics which exhibit two Curie points. Various properties such as dielectric\(^2\) and piezoelectric\(^3\) constants, spontaneous electric polarization,\(^2\) optical properties,\(^4\) electrocaloric effect,\(^5\) thermal expansion,\(^4\) heat capacity,\(^4\) etc. have been measured. Müller (1940)\(^6\) developed a phenomenological theory\(^10\) to give a comprehensive correlation among these properties. The crystal structure with X-ray diffraction method was first determined by Beevers and Hughes (1941).\(^7\) Based on the atomic arrangements in the crystal theoretical studies from the microscopic point of view have been developed by Mason,\(^8\) Devonshire,\(^9\) and Mitsui.\(^10\) In comparison with the single sublattice model adopted by the two formers Mitsui's theory assumes a two-sublattice model based on the new informations obtained by further X-ray\(^11\) and neutron diffraction\(^12\) studies. Regarding the theory of the heat capacity, there are following two different predictions. One is that the heat capacity anomalies (Δ$C_p$) at the Curie points is to be negative at the lower Curie point and positive at the upper one. This prediction is based mainly on the Ehrenfest relation.\(^13\) The other is that Δ$C_p$ are positive at both of the two Curie points, which is expected from the Müller and the Mitsui theories. Experimental studies of Δ$C_p$ at the Curie points have been carried out by a number of authors, but again the results are not in agreement with one another. In contrast to the other properties which exhibit remarkable changes at the both Curie points, it is certain that enthalpy of transition is very small and barely detectable at both of the Curie points.

The purpose of the present investigation is to determine the accurate values of the heat capacities which hopefully enable us to evaluate Δ$C_p$ at the Curie points and thus discriminate between the single and two sublattice models mentioned above.
A large single crystal of Rochelle salt was grown from an aqueous solution of the reagent-grade sample (Wako Pure Chemical Ind. Ltd.) by slow cooling after seeding. The crystal was then shaped into a cylindrical rod with the diameter 25 mm and the height 40 mm and was enclosed in a vacuum-tight calorimeter cell made of copper. The weight of the sample was 36.1299 g.

The heat capacity measurements were performed with a high-resolution calorimeter. This adiabatic-type calorimeter was equipped with two kinds of thermometer; one is a platinum-resistance thermometer for the absolute measurement within the precision of $1 \times 10^{-5}$ K, and the other is a thermistor-thermometer of which the temperature resolution was within 3 $\mu$K. The inaccuracy of this calorimeter was confirmed to be less than 0.2% at room temperature and the deviations of the heat capacities from a smoothed curve (precision) were less than 0.05%. The heat capacities were measured in

![Fig. 1. Heat capacity vs. temperature curve of Rochelle salt.](image-url)
Fig. 2. Detailed representation of $C_p \sim T$ relationship around the lower Curie point.

Fig. 3. Detailed representation of $C_p \sim T$ relationship around the upper Curie point.
the temperature range of 230–310 K with an ordinary resolution (ΔT ≈ 1–2 K). In the vicinity of each Curie point the measurements were made with higher resolution (ΔT ≈ 0.1 K). Further details for the construction of the whole calorimeter were published elsewhere.¹⁴)

In the first run of the measurements a small peak appeared at ca. 269 K which was due to melting of a surplus water incorporated into the crystal. The sample was taken out from the calorimeter and kept in a closed glass vessel along with a partially dehydrated Rochelle salt for a month. This procedure made the spurious peak much smaller. (The corresponding water-content was estimated to be ca. 1 mg from the peak area.) After this treatment all the measurements were carried out with higher stability than before.

Figure 1 shows our results together with the data by Rusterholz,¹⁵) Hicks and Hooley,¹⁶) and by Wilson.¹⁷) As is evident the results by Rusterholz deviate appreciably from all the others. We can not understand the origin of his large absolute values and the sharp peak at the upper Curie point. All the remaining data are in agreement within the experimental error of about 1%. In Figs. 2 and 3 our data are plotted in an enlarged scale at the neighborhood of each Curie point together with those by other investigators. Among the other data Wilson’s will be the best one which has the precision of about ±0.5%. The latest values by Reese et al.¹⁸) (1972), from which they suggested the first evidence for the negative drop at the lower Curie point, have the scattering (of the data) amounting to about ±1%. Accordingly their conclusion seems to be too hasty. Contrary to their results we have found a real positive value of ΔC_p as is evidently shown in Fig. 2.

As to the upper Curie point (see Fig. 3) we have given also a definite evidence of an upward anomaly (about 0.2%) for the first time. All the detailed numerical values of the present study will be given elsewhere in near future. It should be emphasized here that a solution for such a long-unsolved problem (for about forty years!) on the behavior of heat capacity anomalies required a sophisticated calorimeter which has the high-level precision amounting to at least ±0.05%.

In conclusion we should like to mention that our results favor the latest microscopic theory by Blinc et al.¹⁹) (1972) based on Mitsui’s two sublattice model and also the prediction derived indirectly from the experimental data on electrocaloric effect by Wiseman et al.⁵)

Note added in proof. In Figs. 1, 2 and 3, the data by Wilson¹⁷) and by Reese and May¹⁸) are those read from magnified photocopies
of the figures in their original papers. Reese and May's data were re-scaled so as to make their average value coincide with the present data.

References