

A. A. Volkov, G. V. Kozlov, E. B. Kryukova, and A. A. Sobyenin. *New results on the dynamics of Rochelle salt crystals (a system with a "double" critical point)*. Rochelle salt crystals (RS) occupy a special place among other ferroelectrics because of a number of unique properties. First of all, the ferroelectric phase exists in them only for a narrow temperature interval between two Curie points  $T_1 = 255$  K and  $T_2 = 297$  K.<sup>1</sup> At the points  $T_1$  and  $T_2$  one can observe sharp anomalies of dielectric permittivity, however, in none of the three phases does the behavior follow the Curie-Weiss law ( $\epsilon \sim |T - T_c|^{-1}$ ), which is followed well by other ferroelectrics. Also unusual (three orders of magnitude below "normal" values) are the magnitudes of jumps in heat capacity at the Curie points and the character of heat capacity temperature dependence in the ferroelectric phase.<sup>2</sup> The anomalies of elastic, piezoelectric and optical properties of the crystal are sharply different from the "usual" anomalies. The most surprising, however, are the special features of the ferroelectric dynamics of the crystal. A study of the soft mode done by the method of backward-wave submillimeter-spectroscopy,<sup>3-5</sup> has shown that the temperature dependence of the critical relaxation frequency  $1/2\pi\tau$  of Rochelle salt is completely different from the linear dependence observed in all other crystals with relaxation dynamics. It was found that in the low-temperature phase the temperature dependence follows a cubic law

$$\frac{1}{2\pi\tau} \sim (T_0 - T)^3, \quad (1)$$

where  $T_0$  coincides not with the Curie point  $T_1$ , but with the center of the ferroelectric phase  $T_0 \approx (T_1 + T_2)/2$ .

Such unusual static and dynamic properties of RS crystals cannot be explained within the framework of the traditional approach, which utilizes the expansion of the thermodynamic potential of the system in a power series of the polarization  $P$

$$\Phi = \Phi_0 + \frac{A}{2} P^2 + \frac{B}{4} P^4 + \dots \quad (2)$$

separately near each of the phase transitions being considered. Central for the development of a new approach were the above-mentioned results on the ferroelectric dynamics of RS<sup>3-5</sup> which demonstrated the essentially nonlinear behavior of the coefficient  $A(T) \sim 1/2\pi\tau$  in RS. It is this behavior and the fact that the temperature singled out in dynamic experiments is not the critical ( $T_1$ ), but the average temperature  $T_0 \approx (T_1 + T_2)/2$ , has led us to abandon the usual assumption of a linear temperature dependence of the coefficient  $A$  and to start searching for other forms of approximating it.

For this purpose we have analyzed the data available in the literature on the temperature dependence of the static dielectric susceptibility  $\chi = (\epsilon - 1)/4\pi$  and have discov-

ered that in a very broad temperature interval ( $80 < T < 330$  K), including both phase transitions, the data can be described by the expression (Fig. 1)

$$\frac{1}{\chi} = A = -0,04962 + 8,762 t^2 - 10,50 t^3 + 24,50 t^4, \quad (3)$$

where  $t = (T - T_0)/T_0$ , and  $T_0 = 275$  K corresponds to the minimum of  $A(T)$ . In this expansion that does not contain a linear term the major contribution to  $A(T)$  near  $T_0$  is given by the term quadratic in the temperature, and with a large deviation from  $T_0$  the higher order terms begin to play a larger role. It is interesting to note that an indication of a parabolic character of the temperature dependence of the coefficient  $A$  in the ferroelectric phase was also obtained forty years ago from studies of dielectric susceptibility  $\chi^{c1}$  of a clamped RS crystal (i.e., in the absence of a piezoeffect).<sup>6</sup> It was shown that the dependence  $1/\chi^{c1}$  does not have singularities at the points  $T_1$  and  $T_2$  and becomes zero (as well as the frequency of the soft mode (1)) at  $T_0 \approx (T_1 + T_2)/2$ . Unfortunately, neither these experimental results nor the direct indication<sup>10</sup> of a nonmonotonic dependence of the coefficient  $A$  in RS have attracted proper attention subsequently.

Using a thermodynamic potential with a parabolic dependence of  $A(T)$ , we were able to obtain a unified quantitative description of the temperature behavior of piezoelements and piezomodules, elastic pliancy and elastic modulus, spontaneous polarization and specific heat (Fig. 2), and also of other properties of Rochelle salt and the effects of hydrostatic pressure on them. Explanations were also given of the results of experiments on Mandel'shtam-

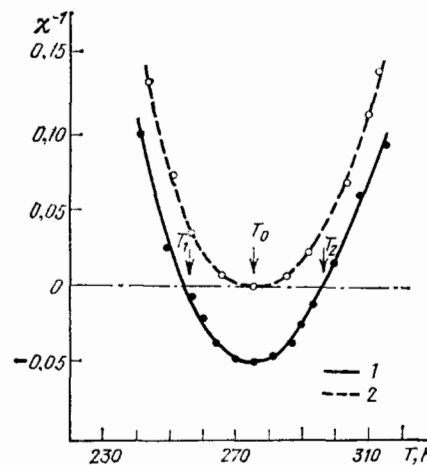


FIG. 1. Temperature dependences of the inverse dielectric susceptibility of the free (1) and clamped (2) RS crystals. The light and dark circles correspond, respectively, to the data from Refs. 1 and 9, the lines are a result of approximation.

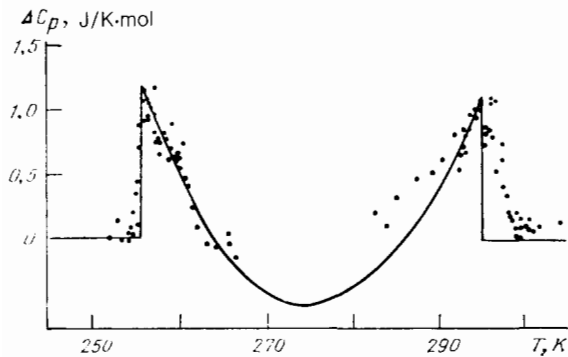


FIG. 2. Temperature dependence of anomalous heat capacity for RS. The points—the data from Ref. 2, the continuous line—calculated curve.

Brillouin scattering,<sup>7</sup> anomalous absorption of ultrasound<sup>8</sup> and microwave dispersion.<sup>9</sup> The only remaining difficulty was that it was not possible to give a quantitative description of the temperature dependence of the soft mode frequency ( $\nu$ ), i.e., the dependence that served as the starting point for the development of the approach being used. This question has been clarified by the low-temperature studies that we performed on the dielectric spectra of Rochelle salt. These studies have demonstrated that with a temperature decrease the relaxation soft mode transforms into an optical phonon with a high  $Q$ -factor ( $Q \sim 300$ ) which becomes stabilized in the spectrum at the frequency of  $22 \text{ cm}^{-1}$ . As can be seen from Fig. 3, as the crystal is cooled, together with the attenuation of the  $G$  mode its oscillator strength  $f$  also changes. This means<sup>11</sup> that the observed process of the soft mode temperature evolution is a result of the mode interaction with another thermally unstable process of lattice excitation. Assuming that the frequency of the given (but not yet experimentally observed) excitation has a temperature dependence that is also determined by the thermodynamic potential constructed by us, and that its decay is the usual linear function of temperature, we can obtain a complete description of the behavior of the soft mode of Rochelle salt in the low temperature phase.<sup>12</sup>

Thus, the complete picture of Rochelle salt dynamics can be visualized as follows. At low temperatures, at a frequency of approximately  $100 \text{ cm}^{-1}$ , crystal spectra contain a thermally unstable polar optical phonon. At a temperature near  $T \sim 150 \text{ K}$  this phonon interacts with another mode of lower frequency ( $\nu = 22 \text{ cm}^{-1}$  at  $T = 80 \text{ K}$ ) and, by transferring to it its oscillator strength and decay, changes it into relaxation excitation. In the absence of a piezoeffect (a clamped crystal) the frequency of the relaxation mode would have to become zero at the “double” critical point  $T_0$ . However, in a real crystal the soft mode becomes coupled,

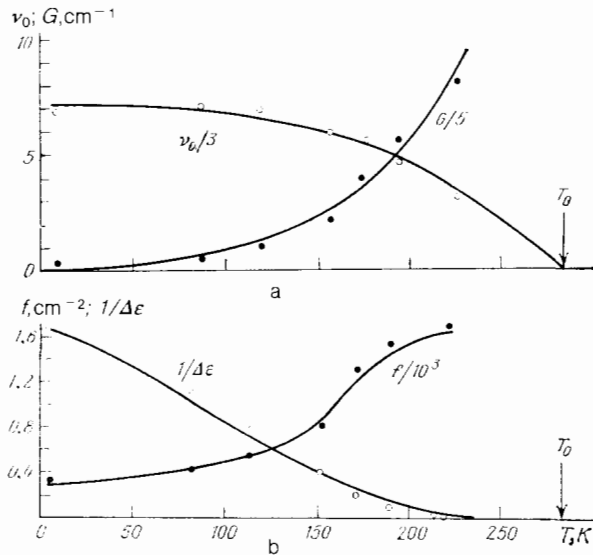


FIG. 3. Temperature dependences of the soft mode parameters for Rochelle salt: the frequency  $\nu_0$  and the attenuation  $G$  (a), and the inverse dielectric contribution  $1/\Delta\epsilon$  and the oscillator strength  $f = \Delta\epsilon \cdot \nu_0^2$  (b). The circles are the experimental data,<sup>12</sup> and the continuous lines are the calculations results based on a phenomenological model.

due to the piezoeffect, to the transverse acoustic mode, as a result of which the phase transitions take place at  $T_1$  and  $T_2$ .

Thus, Rochelle salt gives an interesting and very rare in solid state physics example of a system close to the “double” critical point, with a surprisingly diverse dynamics of phase transition.

<sup>1</sup>F. Jona and G. Shirane, *Ferroelectric Crystals*, Pergamon Press, Oxford (1962) (Russian translation, Mir, Moscow (1965)).

<sup>2</sup>M. Tatsumi, T. Matsuo, and H. Suga, *J. Chem. Phys. Sol.* **39**, 427 (1978).

<sup>3</sup>A. A. Volkov, G. V. Kozlov, and S. P. Lebedev, *Zh. Eksp. Teor. Fiz.* **79** 1430 (1980) [*Sov. Phys. JETP* **52**, 722 (1980)].

<sup>4</sup>A. A. Volkov, G. V. Kozlov, and S. P. Lebedev, *Fiz. Tverd. Tela* (Leningrad) **24**, 555 (1982) [*Sov. Phys. Solid State* **24**, 312 (1982)].

<sup>5</sup>A. A. Volkov, G. V. Kozlov, and E. B. Kryukova, *Izv. Akad. Nauk SSSR. Ser. Fiz.* **47**, 679 (1983) [*Bull. Acad. Sci. (USSR), Phys. Ser.* **47**, 52 (1983)].

<sup>6</sup>H. Mueller, *Phys. Rev.* **58**, 565 (1940).

<sup>7</sup>E. Sailer and H. G. Unruh, *Solid State Commun.* **16**, 615 (1975).

<sup>8</sup>I. A. Yakovlev and T. S. Velichkina, *Usp. Fiz. Nauk* **63**, 411 (1957).

<sup>9</sup>F. Sandy and R. V. Jones, *Phys. Rev.* **168**, 481 (1968).

<sup>10</sup>V. L. Ginzburg, *Usp. Fiz. Nauk* **38**, 490 (1949).

<sup>11</sup>V. L. Ginzburg, A. P. Levanyuk, and A. A. Sobyenin, *Usp. Fiz. Nauk* **130**, 615 (1980) [Expanded version in *Phys. Rep.* **57**(3), 152 (1980)].

<sup>12</sup>A. A. Volkov, G. V. Kozlov, E. B. Kryukova, and A. V. Sobyenin, *Fiz. Tverd. Tela* (Leningrad) **28**, 797 (1986) [*Sov. Phys. Solid State* **28**, 444 (1986)]; A. A. Volkov, G. V. Kozlov, E. B. Kryukova, and J. Petzelt, *Zh. Eksp. Teor. Fiz.* **90**, 192 (1986) [*Sov. Phys. JETP* **63**, 110 (1986)].