Static and dynamic properties of Rochelle salt, as a system close to the double critical point

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Theoretical descriptions of Rochelle salt as a system with a double critical point are developed, and it is shown that the phenomenological theory is correct for this crystal over a wide interval of pressures, substitution concentrations, and temperatures up to the melting point. A unified quantitative description is obtained of the anomalous temperature behavior of the piezoconstants and piezomoduli, the elastic pliancy and elasticity, the permittivity and the spontaneous polarization, and the absorption of ultrasound and the soft-mode parameters.

1. INTRODUCTION

Rochelle salt (RS) is of interest not only as the forerunner of two broad new classes of substances—ferroelectrics and ferroelastics, but also as a unique solid-state physics example of a system, the ordered state of which exists in a relatively narrow temperature interval ($255\text{ K} < T < 297\text{ K}$) between two disordered (nonpolar) phases having the same symmetry $P2_12_12$. In spite of the large number of experimental and theoretical papers over the almost three-hundred year history of this ferroelectric, the nature of this unusual ordering has still not yet been clarified. Additionally, the opinion is widespread that the RS phase transitions are very poorly described by the classical Landau-Ginzburg phenomenological theory. A number of facts, it would seem, bear witness to this. Firstly, substantial departures from the Curie law for the dielectric permittivity ($\varepsilon \sim |T - T_C|^{-1}$) are observed in ranges on the order of several degrees K from the high ($T_{C1} = 297$ K) and low ($T_{C2} = 255$ K) Curie points, while for all other ferroelectrics it is satisfied in a significantly wider temperature interval.[1] Secondly, at both Curie points the heat capacity jumps are anomalously small (three orders of magnitude below "normal" values) and the behavior of its anomalous part ΔC_p in the ferroelectric phase, where it is found to be negative over a significant temperature interval,[2] is unusual. Thirdly, as recent measurements[3] have shown, there is no region in RS crystals where the usual linear law for the temperature dependence of the critical relaxation frequency ($1/2\pi\tau \sim |T - T_C|$) is applicable. Rather it follows, over a wide temperature interval in the lower paraphase, the cubic law

$$1/2\pi\tau \propto (T^* - T)^3, \qquad (1)$$

where T^* coincides not with T_{C2}, but with the center of the ferroelectric phase $T^* \approx (T_{C1} + T_{C2})/2$.

Among a number of unintelligible facts, which do not fit into any of the presently available phenomenological or microscopic theories, is the considerable influence on the RS phase transitions of the pressure p in combination with the isomorphous substitution of a fraction X of the potassium atoms by ammonia molecules. It is found[4] that for very small concentration of NH_4 ($X \geqslant 2.4\%$) the ferroelectric phase disappears, then reappears for $X > 18\%$, but at significantly lower temperatures (Fig. 1). In the interval $2.4\% < X < 5.4\%$ the application of pressure restores the crystal to the initial ferroelectric state (but now at high temperatures), while in the interval $6\% < X < 18\%$ the ferroelectric phase does not materialize for any pressures whatsoever. For $X > 18\%$, the ferroelectric transition reappears. However, in contrast to the case of small X, its temperature decreases with increasing p (see Ref. 5 and Fig. 2).

A number of theoretical approaches have been proposed to explain the anomalous critical properties of RS. The presence of two phase transitions in RS had already been connected, in an early phenomenological theory of Müller,[6] with the unusual parabolic temperature dependence of the inverse susceptibility of a "clamped" crystal

$$\chi_{cl}^{-1}(T) = 4\pi/[\varepsilon_{cl}(T) - 1],$$

which reaches a minimum at T_m. Moreover, in a clamped crystal (that is, without considering shear deformations) $\chi_{\text{cl}}^{-1}(T_m) > 0$ and phase transitions are absent, while in the free crystal (taking into account shear deformations) the total inverse susceptibility χ^{-1} at T_m is negative, as a result of which the paraelectric phase loses stability and in some temperature interval near T_m, the crystal passes into the ferroelectric phase. Ginzburg[7] significantly simplified Müller's quite complicated thermodynamic theory and pointed out its connection to Landau's general phenomenological theory of phase transitions.[8] Furthermore, the problem was posed in Ref. 7 of describing all the RS anomalous properties, relying only upon the experimentally known temperature dependence of the susceptibility χ of the free or clamped crystal. However, this problem has not yet been solved.

Instead, the theory developed through the formulation of various micro- and semimicroscopic models of RS, explaining the observed temperature path $\chi(T)$, but not giving a quantitative explanation of all the available experimental facts as a whole.[9,10] So, to interpret those or other data, the semimicroscopic model of Mitsui[9] is normally called upon. However, even this model, which contains a number of free phenomenological parameters, yields at best only some basic features of the ferroelectric ordering mechanism and can hardly be presumed to serve as a complete quantitative description of the experimental data in a crystal as complicated as RS, containing 112 atoms in an elementary cell.

Dissatisfaction with the state of the theory of the phase transitions in Rochelle salt was reflected in the attempt by Levanyuk and Sannikov[11] to attribute the three observable phases of RS to different distortions of the lattice of one and

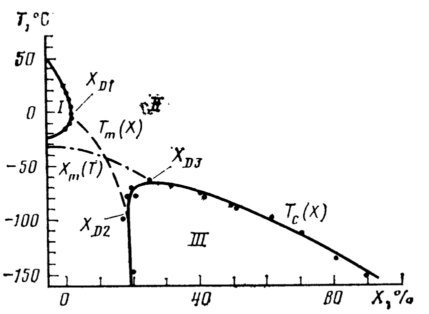

FIG. 1. Phase diagram of mixed RS–ARS crystals under an atmosphere of pressure. The points are the data (Ref. 4).

the same highly symmetric paraphase. Despite a number of attractive features (for example, the explanation of the complicated path $\chi(T)$ by the linear temperature dependence of just one phenomenological coefficient in the thermodynamic potential density), one must acknowledge that this attempt was unsuccessful, since it follows from Ref. 11 that a continuous transition from a high- to a low-temperature nonpolar phase, avoiding an intermediate phase of lower or higher symmetry, is impossible. Meanwhile, it is well known[1,4,5] that in clamped RS crystals or in free crystals containing more than 2.4% NH_4 ions, such a smooth transition occurs.

In this paper we will show that the entire complex of RS anomalous physical properties can be fully described using the original Landau-Müller-Ginzburg phenomenological theory, accounting suitably for the parabolic temperature path of the inverse susceptibility, or, what is the same, accounting for the proximity of the RS phase transitions to the double critical point.

2. DOUBLE CRITICAL POINT

The term double critical point (DCP) is encountered in the theory of binary fluid solutions,[12] where it means a point in a phase diagram (Fig. 3) at which lines of upper and lower critical points of a phase separation unite. The role of the variable x, on which the upper and lower critical temperatures of phase separation depend, can moreover be played by the pressure (as this occurs in the case of β-picoline-H_2O solutions[13]) or the concentration of modest amounts of a third component (for example, a glycerine-guaiacol system[14]). In Fig. 3a the region under the line of critical points $T_C(x)$ corresponds to the stratified state of solutions. The solution is homogeneous throughout this region. Moreover, the point (T_D, x_D), corresponding to the maximum on the line $T_C(x)$, is precisely the DCP.

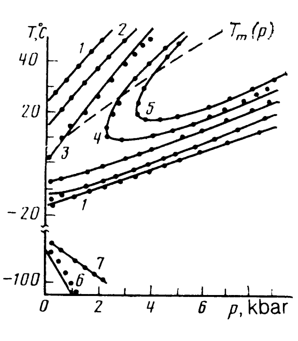

FIG. 2. Phase diagram of mixed RS–ARS crystals under pressure for various concentrations X: 1—0, 2—1,1, 3—2,2, 4—3,1, 5—3,9, 6—21, 7—32%. The points are the data (Ref. 5).

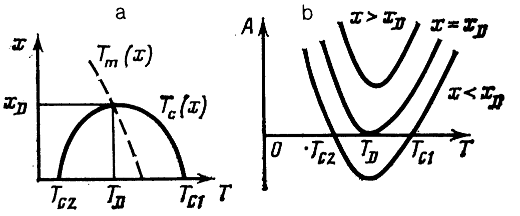

FIG. 3. Phase diagram (a) and temperature dependence of the coefficient A (b) in systems with DCP.

It is clear from Fig. 3a that the term DCP characterizes not a new type of critical behavior, but a method of approximating the line of critical points: along the tangent to the indicated line. In particular, if the approximation to the line $T_C(x)$ is not with respect to temperature, but along some other direction in the plane (T,x), then some other point of the line of critical points will play the role of DCP.[15-17] Below, however, we consider that the phase transitions are approached by means of temperature change, as usually occurs in an experiment.

In the case of Rochelle salt the analog of the critical points is evidently the Curie points. The role of x, on which the upper and lower Curie temperatures depend, can be played, for example, by the negative hydrostatic pressure, the maximum admissible magnitude of shear deformations, or the substitution concentration. The most thoroughly studied of these is the mixture of ammonia molecules, replacing potassium ions.[4,5] For pure RS at atmospheric pressure, a DCP materializes in a clamped crystal, that is, in the absence of a linear coupling between the component $P_z \equiv P$ of the polarization vector along the ferroelectric axis (the axis of spontaneous polarization) and the corresponding component $u_{xy} = u$ of the strain tensor.[6] In the same case of mixed crystals of ordinary (RS) and ammoniated (ARS) Rochelle salt, there are even two DCP's, one of which corresponds to an ammonia ion concentration $X = X_{D1} \approx 2.4\%$, and the second to $X = X_{D2} \approx 18\%$ (Fig. 1). Moreover, the coordinates of the double critical point change in an interesting manner with pressure (Fig. 2).

Besides the term DCP, the term "hypercritical point" is also applied to binary fluid solutions. However, DCP seems to us more apt,[15] since at a DCP two critical temperatures merge at one point and, simultaneously, a number of critical exponents double.[16,17]

Systems with a DCP are also sometimes referred to as systems with a recurrent phase or with a recurrent phase transition in the disordered state. The last term is used, for example, in the case of certain fluid-crystal materials experiencing during a temperature decrease second-order phase transitions from a nematic to a smectic A-phase, and conversely.[18] The unstandardized terminology reflects, in our view, the fact that although some systems with a DCP have long been known, the peculiarities of their critical behavior have only recently begun to be intensively analyzed.

3. THE LANDAU-GINZBURG THEORY FOR SYSTEMS WITH A DOUBLE CRITICAL POINT

In the neighborhood of a DCP, in contrast to an ordinary Curie point, the temperature dependence of the inverse dielectric susceptibility is described not by a linear, but by a quadratic law,

$$\chi^{-1}(x,\ T)\equiv A(x,\ T)=\tilde{A}_0(x)+\tilde{A}_2(x)[T-T_m(x)]^2+\ldots. \tag{2}$$

Moreover, at the DCP itself, the top of the parabola is tangent to the temperature axis. For $x<x_D$ it falls below the temperature axis (which is tied to the presence of two phase transitions), and for $x>x_D$, the parabola rises above the abscissa (Fig. 3b). As a result for $x>x_D$, the nonpolar phase does not lose stability at any temperature, but there is a pronounced maximum for the susceptibility dependence at $T=T_m(x)$. The lines of extrema of the susceptibility—the maxima in the paraphase and the minima in the ferroelectric phase—are shown in Figs. 1 and 2 by the dashed and dot-dash lines.

In the language of the Landau-Ginzburg theory, expression (2) determines the temperature dependence of the coefficient A in the expansion of the thermodynamic potential density in powers of the order parameter $P\equiv P_z$:

$$\Phi=\Phi_0(x,T)+\frac{A(x,T)}{4}P^2+\frac{B(x,T)}{4}P^4-EP, \tag{3}$$

where $E\equiv E_z$ is the component of the electric field along the axis of spontaneous polarization. Let us observe that relation (2) between χ^{-1} and A is valid only in the high-symmetry (nonpolar) phase, while in the low-symmetry (ferroelectric) phase

$$\chi^{-1}=-2A. \tag{4}$$

In all previous papers, expansion (3) was applied only in very narrow temperature intervals near the lower and upper Curie points, where by custom the coefficient A is regarded as linearly dependent on the differences $T-T_{C1}$ and $T-T_{C2}$. Actually though, in the case of Rochelle salt (and, in general, systems with a DCP, see Ref. 15), it is advisable to expand the coefficients of the thermodynamic potential in a series, not in powers of the differences $T-T_{C1}$ and $T-T_{C2}$, but in powers of the deviation of T from the temperature of the minimum of A, that is to use an expression of type (2) for the temperature dependence of $A(T)$.

In this way, as we see below (see also Ref. 19), one can successfully describe quantitatively practically all the thermodynamic and dynamic properties of RS crystals in a wide temperature region, including all the upper paraphase, the ferroelectric phase and a significant part of the lower paraphase.

4. THE THERMODYNAMIC PROPERTIES OF ROCHELLE SALT

a. Determining the temperature dependence of the coefficient *A*

For subsequent convenience let us introduce the dimensionless temperature

$$t=(T-T_m)/T_0, \tag{5}$$

measured from the temperature of the minimum of A and normed by the mean of the ferroelectric phase $T_0=(T_{C1}+T_{C2})/2=276\,\mathrm{K}$, and let us rewrite expression (2) for A in the following manner:

$$A=A_0+A_2t^2+A_3t^3+A_4t^4+\ldots. \tag{6}$$

Moreover, if there is not any distinguished energy parameter other than T_0 in the problem, one can naturally expect the coefficients $A_2, A_3,\ldots$ to have identical orders of magnitude, and A_0 to be small moderately close to the DCP, that is, it scales with the narrow half-width of the ferroelectric phase $(T_{C1}-T_{C2})/2$ in comparison with T_0. For RS under an atmosphere of pressure, the parameter $t^*=(T_{C1}-T_{C2})/2T_0=7.61\cdot10^{-2}$ and, thus, the DCP is actually very close. In analyzing experimental data near and between T_{C1} and T_{C2}, in this case we can calculate only the first two terms in (6). It is easy to find A_0 and A_2, knowing the half-width of the ferroelectric region and the difference of the inverse susceptibilities of the free and clamped crystals[3,20,21]:

$$A_0=A-A_{cl}=\chi^{-1}-\chi_{cl}^{-1},\quad A_2=-A_0/(t^*)^2. \tag{7}$$

After this it is possible to make T_m more precise, and to improve the coefficient values by means of higher terms of the expansion, requiring that they agree as well as possible with the temperature dependence of χ in the lower and upper paraphases. Proceeding in the manner indicated, we found that in a very wide temperature interval ($|T-T_m|<150°$), $A(T)$ can be described by the following expression (Fig. 4):

$$A=-0.0647+11.744t^2-14.814t^2-45.536t^4,$$

$$t=(T-T_m)/T_0,\ T_m=274.8\,\mathrm{K}. \tag{8}$$

In this expansion, which in general lacks a linear term, the basic contribution to $A(T)$ near T_m is given by a term quadratic in the temperature. For a significant departure from T_m, higher-degree terms come into play.

The measurements of the susceptibility χ in the ferroelectric phase are not considered in the choice of the coefficients in (8), since there terms of higher order in the free energy expansion in powers of P can have a substantial influence on χ. For example, if we add $CP^6/6$ to (3), then expression (4) for χ in the ferroelectric phase is modified as follows

$$\chi^{-1}=\frac{B^2-4AC-B(B^2-4AC)^{1/2}}{C}\approx-2A\left(1-\frac{AC}{B^2}+\ldots\right) \tag{9}$$

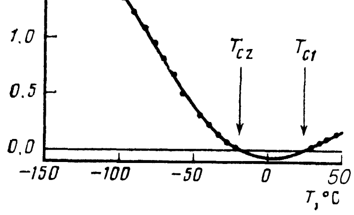

FIG. 4. Temperature dependence of the coefficient A at one atmosphere in Rochelle salt crystals.

with $AC/B^2 \ll 1$. A comparison with experimental data shows that even in the center of the ferroelectric phase, the values χ depart from those computed by (4) and (8) by less than 15%. This shows that A_0C/B^2 is small and that the simple expression (3) is applicable practically everywhere in the ferroelectric phase.

The values of the Curie constant $C^* = 4\pi(dA/dT)^{-1}$ at T_{C1} and T_{C2}, computed by (8), are $C_1^* = +2.2\cdot 10^3$ K and $C_2^* = -1.8\cdot 10^3$ K. These values differ somewhat from the values $C_1^* = +2.1\cdot 10^3$ K and $C_2^* = -1.5\cdot 10^3$ K usually presented in the literature (see, for example, Refs. 9 and 20). In our view, the cause of the discrepancies is that the reference data Curie constants are obtained by averaging the derivatives dA/dT over some finite temperature interval near T_{C1} and T_{C2}. In fact, complete agreement with the reference data can be achieved by letting

$$C_1^* = 4\pi\,(dA/dT)^{-1}_{T=T_{C1}+0.8^\circ} \text{and} C_2^* = 4\pi\,(dA/dT)^{-1}_{T=T_{C2}-3.6^\circ}.$$

Our analysis of the experimental data[3,20,21] showed that, in agreement with (7), the temperature dependences of the inverse susceptibilities of a free and clamped crystal in the upper and lower paraphases differ from each other almost precisely by the constant A_0. This means [see (6)] that in a clamped crystal, $A_{\text{cl}}(T)$ dose not intersect the abscissa at T_{C1} and T_{C2}, while in a free crystal, it touches it only at T_m. In other words, from the viewpoint of high-frequency (higher than piezoresonance frequencies) properties, the temperature T_m for Rochelle salt crystals is the DCP.

b. Spontaneous polarization

Using (3), we determine the temperature dependence of the spontaneous polarization P_s in the ferroelectric phase by

$$P_s^2 = -A/B, \tag{10}$$

and if $CP^6/6$ is added to (3), P_s can be found by solving

$$A + BP_s^2 + CP_s^4 = 0. \tag{11}$$

Adding to this equation the expression for the inverse susceptibility

$$\chi^{-1} = A + 3BP_s^2 + 5CP_s^4 \tag{12}$$

and solving (11) and (12) for B and C, we find that they are connected with the coefficient $A(T)$ we have computed from measurements in the paraphase [see (8)], and the variables $P_{s,\text{exp}}(T)$ and $\chi_{\text{exp}}(T)$ measured in the ferroelectric phase through the relations

$$B = \frac{-4A - \chi_{\text{exp}}^{-1}}{2P_{s,\text{exp}}^2}, \quad C = \frac{\chi_{\text{exp}}^{-1} + 2A}{2P_{s,\text{exp}}^4}. \tag{13}$$

Substituting the corresponding experimental values[20] in (13) leads to the conclusion that in the entire temperature interval between T_{C1} and T_{C2}, the coefficients B and C are practically constant and equal

$$B = B(T_m) = +1.37 \text{ cm}^{-4}\cdot\mu\text{C}^2,$$

$$C = C(T_m) = -5.31 \text{ cm}^{-8}\cdot\mu\text{C}^4. \tag{14}$$

The extent of agreement of (11), (8), and (14) with the experimental data is clear from Fig. 5.

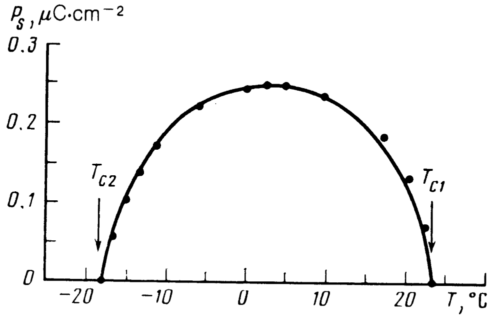

FIG. 5. Temperature dependence of the spontaneous polarization in RS at one atmosphere.

The value of B obtained is close to that found in Ref. 6 from measurements of RS nonlinear dielectric properties, and it has a normal atomic order of magnitude. This proves that the RS phase transitions are "good" second-order phase transitions far from the tricritical point. As is well known, this behavior is unusual among the ferroelectrics, not to mention the unique circumstance that the Landau-Müller Ginzburg theory is correct here over the entire ferroelectric phase, keeping only the first three terms in P^2 in the free energy expansion.

c. Heat capacity

Figure 6 presents values of the anomalous molar heat capacity ΔC_p of a one-domain RS crystal measured by high-resolution calorimetry.[2] It is apparent from the figure that the magnitudes of the jumps C_p at the Curie points are of the order of 1 J/K·mol, or converting to one degree of freedom $\Delta C_p/3n \approx 10^{-3} R$, where $R = 8.314$ J/K·mol is the universal gas constant, and $n = 28$ is the number of atoms in one molecule of RS. Let us recall that usually in structure second-order phase transitions, the change of the molar heat capacity in a calculation for one degree of freedom, is R. Thus, the jumps of the RS heat capacity at the phase transition points are three orders of magnitude weaker than in other ferroelectrics.

The second notable feature of the data shown in Fig. 6 is the unusually abrupt temperature dependence of C_p in the ferroelectric phase, where in a neighborhood of T_m the anomalous contribution to the heat capacity even becomes negative, while in all other ferroelectrics one finds $\Delta C_p > 0$.

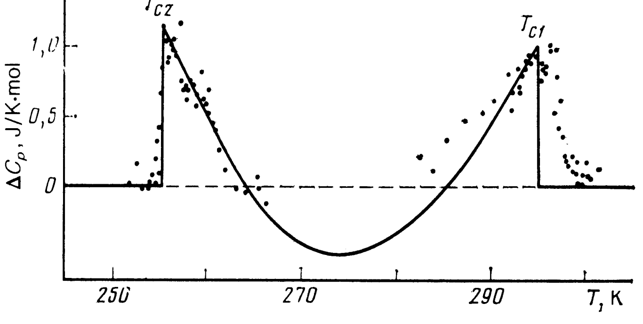

FIG. 6. Temperature dependence of the anomalous heat capacity for RS at one atmosphere.

Both these features of the experimental data[2] are easily explained by the nearness of the phase transitions in RS to the double critical point. Actually, differentiating the free energy (3) twice with respect to T gives

$$\Delta C_p=-TM\frac{d^2}{dT^2}\left(\frac{1}{2}AP_s^2+\frac{1}{4}BP_s^4\right)=+\frac{TM}{4B}\frac{d^2}{dT^2}[A^2(T)]$$

$$=\frac{TM}{2B}[(A_T')^2+AA_{TT}''], \tag{15}$$

where $M = 282.12$ a.e. is the molar mass. One usually considers that A is linear in a neighborhood of the second-order phase transitions. On this basis, the second term in the square bracket in (15) is disregarded. However, in the case of interest to us in the center of the ferroelectric phase $A_T' = 0$, and the anomalous contribution to the heat capacity is determined here precisely by the second term

$$\Delta C_p(T_m)=\frac{T_mM}{B}\frac{A_0A_2}{T_0^2}=-0.56(\text{ J/K}\cdot\text{mol })<0, \tag{16}$$

where we have used (8) and (14) for the numerical values.

The jumps of the heat capacity at the Curie points are determined, it is understood, by the first term in (15), which, however, is very small compared to the usual case, owing to the smallness of $(t^*)^2 = (7.6\cdot10^{-2})^2 = 5\cdot10^{-3}$, owing to the proximity of T_{C1} and T_{C2}.

Relation (15) is easily generalized, even to the case of arbitrary dependence of the free energy density on P (but by assumption, only the coefficient A in it depends on the temperature):

$$\Delta C_p(T)=TMP^2_{s,\exp}(T)\ [\chi^{-1}_{\exp}(T)\,(A_T')^2-A''(T)]. \tag{17}$$

The dependence of $\Delta C_p(T)$ computed from this expression using (8) and the experimental data[20] for $P_s(T)$ and $\chi(T)$ is shown in Fig. 6.

The good agreement of the computed curve with the experimental data[2] is still one more convincing demonstration of the correctness of the Landau-Ginzburg theory for RS.

Thus, calculation of the proximity of RS to the DCP allows one to explain both the magnitude of the heat capacity jumps at the transition points, and the unusual character of the anomaly $\Delta C_p(T)$ in the ferroelectric phase.

d. Elastic properties

To calculate the temperature dependence of the elastic modulus, $C^E_{44}(T)$ the elastic pliancy $S^E_{44}(T)$, the electromechanical coupling coefficient $k_{14}(T)$ and the peizomodulus $d_{14}(T)$, we used the well known thermodynamic relationships[6]

$$C_{44}^E=C_{44}^P/(1+\chi\theta)=1/S_{44}^E,\qquad k_{14}^2=\chi\theta/(1+\chi\theta),\qquad d_{14}=\chi\theta/f_{14}^P \tag{18}$$

and the analytic expressions (2), (8), and (9) for the susceptibility χ. In (18) the piezoconstant f^P_{14} and the elastic modulus C^P_{44} are regarded as temperature-dependent,[22] and we set $\theta = -A_0$. The observable elastic anomalies are completely describable by the approach used here and do not require for their explanation calculations of fluctuation effects near the phase transitions. This means that in the case of Rochelle salt crystals, the Landau theory can be used right up to T_{C1} and T_{C2} in complete agreement with the deductions of Ref. 23 concerning the dramatic suppression of critical fluctuation effects in proper ferroelastics.

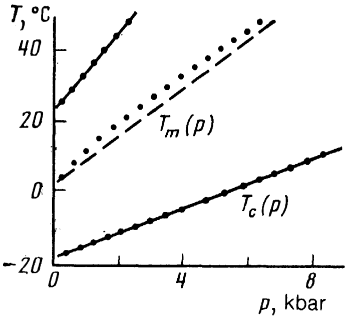

FIG. 7. Phase diagram in pure RS.

e. Effect of pressure

The experimental data[24] on the effect of pressure on the RS phase diagram are presented in Fig. 7. It is clear that with the growth of the hydrostatic pressure, both Curie points T_{C1} and T_{C2} merge on the high temperature side, where the ferroelectric region between them widens. To describe the effect of the pressure p on RS crystal properties, we use expression (8) and assume (Fig. 8) that in this expression T_m and A_0 change linearly with the pressure, while, to a first approximation, A_2 and A_3 can be considered as independent of p. According to Ref. 24, the displacement of the upper and lower Curie points is characterized by the following parameters: $dT_{C1}/dp = 3.84$ K/kbar and $dT_{C2}/dp = 10.93$ K/kbar. Differentiating the equation $A(p,T_{Ci}) = 0$, determining the position of the upper and lower branches of the line of Curie points for $i = 1,2$, with respect to p, and solving the resulting system of algebraic equations for dA_0/dp and dT_m/dp, we find that the merging of T_m and A_0 under the action of p is described by

$$A_0(p)=-2.13\cdot10^{-2}\,p-0.0647,$$

$$T_m(p)=+7.0\,p+275\text{ K}. \tag{19}$$

Let us note that according to (19) the upper and lower Curie points must merge at one double critical point for $p = -3$ kbar.

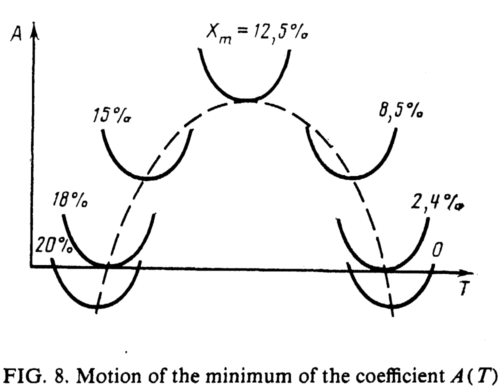

FIG. 8. Motion of the minimum of the coefficient $A(T)$ for various concentrations X.

f. The effect of isomorphous substitutions

The proximity of RS to a double critical point immediately becomes apparent in the phase diagram of the mixed compound $Na[K_x(NH_4)_{1-x}]\cdot C_4H_4O_6\cdot 4H_2O$ (Ref. 4), shown in Fig. 1. When part of the K atoms in RS are replaced by NH_4, the distance between the Curie temperature T_{C1} and T_{C2} decreases and, for a NH_4 concentration equal to just 2.4%, vanishes (region I). A further increase in the concentration (region II) causes the complete disappearance of ferroelectric properties. However, a wide indistinct maximum remains on the temperature dependence of the dielectric permittivity. The most interesting aspect of the mixed crystals under consideration is this second appearance of ferroelectric activity at concentrations greater than 18% (region III). According to the data of Makita and Takagi,[4] obtained in the interval 80–300 K, this new ferroelectric phase is characterized by only one Curie point, which, as established in Ref. 25, also is a second-order transition. In the concentration region IV, the direction of spontaneous polarization in the crystal changes by a 90° jump (a new order parameter emerges) and a transition to a new phase occurs, the physical properties of which are not discussed here (see, for example, Ref. 1).

Qualitatively, it is possible to explain the behavior of the crystals in regions I–III in the following manner (Fig. 8). With an increase of the concentration X from zero (region I), the minimum on the curve $A(T)$ monotonically arises and touches the temperature axis at the DCP for $X_{D1} = 2.4\%$ and $T_{D1} = -5.5$ °C. The disappearance of the ferroelectric phase for $X \gtrsim X_{D1}$ is convincingly evidenced by the common nature of the two second-order phase transitions and the identical symmetry of both nonpolar phases in pure RS crystals.

In region II the minimum on the curve $A(T)$ rises above the abscissa, reflecting the fact that there are no phase transitions for $X > X_{D1}$ in the system, although a more or less sharp maximum is preserved on $\varepsilon(X,T)$, reflecting the parabolic character of the dependence of $A(T)$. However, as X increases further, the minimum in $A(T)$ again begins to fall and for $X_{D2} \approx 18\%$ and $T_{D2} = -100$ °C, the system reaches a second DCP, with which we, in fact, connect the second appearance of ferroelectricity for $X \gtrsim X_{D2}$. Thus, in region II the motion of the minimum of $A(T)$ occurs along a dome-shaped curve (the dashed curve in Fig. 8) with the maximum at $X_m = 12.5\%$ and $T_m = -43$ °C. Further into regions III and IV, the minimum of $A(T)$ continues to fall lower and lower, as a result of which this curve again intersects the temperature axis at two points: $T_{C1}(X)$ and $T_{C2}(X)$, where the second Curie point $T_{C2}(X)$ quite quickly goes off to the negative temperature region. Let us note that in region IV not even the upper transition for $T_{C2}(X)$ materializes, since here there is time for a structural first-order phase transition to another crystallographic modification, accompanying the rotation of the spontaneous polarization axis by 90°.

If one is interested in the dependence of A on X for fixed T, then it is also possible to regard as a DCP an extremum of A on the line of phase transitions (that is a point, at which simultaneously $A(X) = 0$ and $A'_X = 0$), but now with respect to X. In Fig. 1 this point is denoted $X_{D3} = 27\%$ and $T_{D3} = -68$ °C.

A quantitative description of the phase diagram of the mixed crystal of ordinary and ammoniated Rochelle salt (shown in Figs. 1 and 2) is given in Ref. 33.

5. DYNAMICAL PROPERTIES OF ROCHELLE SALT

a. Ultrasound absorption

It was established in the experiments of Yakolev *et al.*[26] that in the T_{C1} and T_{C2} regions in Rochelle salt, anomalously strong absorption of a transverse elastic wave (Fig. 9) appears, spreading along the crystallographic axis **c** and polarized along the **b** axis. This wave creates a shear deformation u_{xy} in the crystal, under the action of which a change of the equilibrium order parameter (the polarization) occurs along the ferroelectric axis **a**. That, in fact, leads eventually to the decay and dispersion of the transverse elastic waves.

According to the theory of the relaxation mechanism of sound absorption near phase transition points,[27] developed and applied to RS by Landau,[26] the anomalous part of the absorption coefficient $\Delta\alpha$ and the velocity v of the transverse acoustic wave are determined by

$$\Delta\alpha = \frac{\gamma (f_{14}{}^{P})^2 (\omega\tau)^2}{2\rho v^3}\frac{1}{1+(\omega\tau)^2},$$
$$v^2 = \frac{C_{44}{}^{P}}{\rho}\left[1-\frac{\gamma\tau\theta}{1+(\omega\tau)^2}\right], \qquad (20)$$

where τ is the relaxation time of the polarization, γ is a constant rate coefficient, $\omega = 2\pi f$ is the angular frequency of the sound wave, and ρ is the density of the crystal. Taking into consideration (7) and the relationship[26,27] connecting τ with the clamped crystal susceptibility χ_{cl}:

$$\tau = \chi_{cl}\gamma^{-1}, \qquad (21)$$

it is possible to rewrite the expressions (20) for $\Delta\alpha$ and v in the paraelectric phase for $\omega\tau \ll 1$ as

$$\Delta\alpha = \omega^2 C_{44}{}^{P}\theta/(A+\theta)^2 2\rho v^3\gamma,$$
$$v^2 = \frac{C_{44}{}^{P}}{\rho}\left(1-\frac{\theta}{A+\theta}\right), \qquad (22)$$

where the dependence $A(T)$, as before, is determined by the expansion (8), and $\theta = -A_0$.

It is clear from the relationships presented that the acoustic subsystem of the crystal by itself does not possess properties which change with the temperature in a critical fashion (that is, vanish or turn infinite at Curie points). The

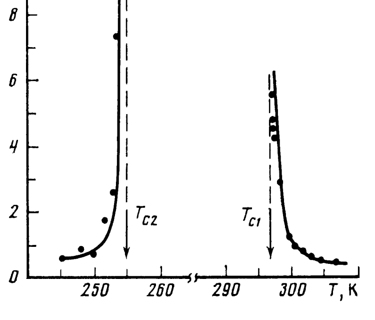

FIG. 9. Temperature dependence of the absorption coefficient of ultrasound in pure RS.

behavior of the ferroelectrically active subsystem also is not in itself critical. This follows, in particular, from the fact that the relaxation time τ, according to Ref. 21, remains finite at T_{C1} and T_{C2}. However, the parabolic temperature dependence of A and the bilinear coupling of deformations with the polarization $f_{14}^{P} u_{xy} P_z$ gives rise to some "compensation" at T_{C1} and T_{C2} of the elastic and ferroelectric interactions in the free crystal. As a result of this , the transverse sound velocity v vanished after A vanishes [see (7)], and the decay of this sound turns infinite. Thus, from the viewpoint of lattice dynamics, one must regard the initial cause of the appearance in RS of two phase transitions close in temperature as the sharp deceleration of the relaxation velocity of the order parameter (polarization), connected with the parabolic temperature dependence $A_{\rm cl}$. Their immediate cause is the softening of the long-wave acoustic phonon.

With the help of (8), (22), and relations similar to (22), we have succeeded in describing the experimental data[26] in terms of the absorption of transverse sound (Fig. 9), and also of the quasilongitudinal sound[28] and the Brillouin scattering by the sound,[29] in a substantially wider temperature region than previously done.

b. The soft mode in Rochelle salt

Direct observation of the RS ferroelectric soft mode were carried out in terms of the dielectric spectra $\varepsilon^*(\nu,T)$ in the microwave and submillimeter[30] bands. This investigation showed that there are two characteristic regions in the behavior of the soft mode.

1. In the interval 180–320 K, including the ferroelectric phase, the dispersion $\varepsilon^*(\nu) = \varepsilon' - i\varepsilon''$ resembles a typical Debye relaxation. The temperature dependence of its frequency $1/2\pi\tau$ (Fig. 10) is essentially nonlinear and has anomalies at T_{C1} and T_{C2}. In the region 180–230 K, the relaxation frequency sharply increases and changes with temperature following a cubic law, unusual for ferroelectrics [see (1)]. Moreover, the relaxation oscillator force $f' = \Delta\varepsilon/2\pi\tau$ corresponding to the soft mode remains practically constant.

2. The cubic law is broken as the temperature decreases ($T < 180$ K) and the relaxation soft mode, quickly increasing in frequency, turns into a high-quality ($Q \sim 300$) optical phonon, stabilizing in the spectrum at $\nu_0 = 22$ cm^{-1}. In the region of transition from the relaxed to the oscillating regime ($150\,\text{K} < T < 180\,\text{K}$), along with the decay of the G mode, its oscillator force $f = \Delta\varepsilon\nu_0^2$ changes noticeably. This means that the observed temperature evolution of the soft mode is the result of its interaction with another temperature-unstable lattice excitation. Therefore, the model of one quasiharmonic soft mode does not suffice to interpret the data of dynamical high-frequency experiments.

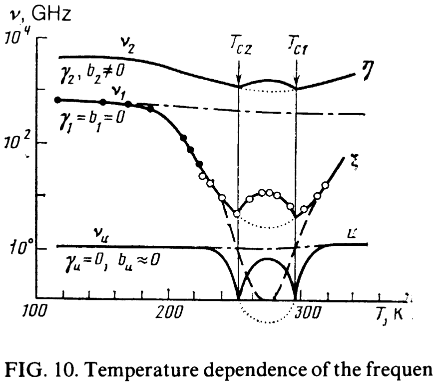

FIG. 10. Temperature dependence of the frequencies of phonon modes in RS at one atmosphere: η and ξ are optical phonons, and u an acoustic phonon. The points and circles are the data (Refs. 3, 21, and 30). The characteristic frequencies of the modes ξ and u lie on the dash-dot line.

In Ref. 31 we attempted to explain the highly unusual behavior of the Rochelle salt soft mode on the basis of a simple phenomenological model of two coupled optical modes. One of them (ξ-mode) is a low-intensity "hard" optical phonon, which is observed in the experiment at low temperatures (Fig. 10), and the second (η-mode) is an oscillating optical mode softening in frequency, located in the frequency region $\nu > 30$ cm^{-1} at all temperatures (Fig. 10). Considering that the η- and ξ-modes in the general case have an oscillatory (resonant) dynamic character, let us write the equations of motion for η and ξ as

$$m\ddot{\xi}+\gamma_1\dot{\xi}+a_{11}\xi+a_{12}\eta=b_1E,$$

$$\mu\ddot{\eta}+\gamma_2\dot{\eta}+a_{12}\xi+a_{22}\eta=b_2E, \tag{23}$$

where $m, \mu, \chi_1\gamma_2, \nu_1^2 = a_{11}/m$, $\nu_2^2 = a_{22}/\mu$, b_1 and b_2 are the effective masses, the decay coefficients, the oscillations characteristic frequencies and the oscillator forces of ξ and η (in the absence of interaction between them), and a_{12} is the coupling coefficient.

In principle it is also necessary to add an equation of motion for the component u_{xy} of the elastic strain tensor to (23), since this component is also linearly coupled with the polarization $P_s = b_1\xi + b_2\eta$. However, in the region of interest to us, that of the short (submillimeter) wavelengths, the characteristic acoustic frequencies are very small. To a good approximation it is possible to consider the oscillations of η and ξ as occurring for a fixed value u_{xy}, that is, in a clamped crystal.

Using the assumption that the frequency of the initial (still not experimentally detected) softening η-mode has a temperature dependence determined by (8), but with a significantly larger A_0, and its decay is the usual linear function of temperature, we obtain for the parameters of the ξ-mode

$$G=\nu_1{}^2\gamma_2A_0/a_{22}{}^2,\quad \nu_0{}^2=\nu_1{}^2(1-A_0/a_{22}),$$

$$f=4\pi b_2{}^2\nu_1{}^2A_0/a_{22}{}^2, \tag{24}$$

where $A_0 = a_{12}^2/a_{11} \approx 0.5$, $a_{22}(T) = b_2^2A(T)$. These relationships allow one to fully describe the behavior of the Rochelle salt soft mode in the low-temperature phase.

Thus, the complete picture of the dynamics of Rochelle salt is now the following. For low temperatures at a frequency of approximately 100 cm^{-1}, crystal spectra contain a polar optical η-phonon softening in frequency (Fig. 10). Precisely this phonon is responsible for the anomalous behavior of the coefficient $A(T)$ in RS. In the temperature region $T \sim 150$ K it interacts with the other temperature-independent ξ-mode ($\nu = 22$ cm^{-1} for $T = 80$ K) and by transferring to it its oscillator strength and decay, converts it near T_{C1} and T_{C2} into a relaxation excitation, simultaneously softening greatly in frequency. In the absence of a piezoeffect (a clamped crystal) the relaxation ξ-mode frequency must vanish at the DCP $T_D \approx T_0$ (the dashed curve in Fig. 10). However, in the free crystal, due to the piezoeffect, the intermediate ξ-mode proves to be coupled with the transverse acoustic u-mode, as a result of which the soft mode then becomes the u-mode, which in fact causes the phase transitions for T_{C1} and T_{C2}.

The linear coupling between the initial softening η-mode and the other modes (ξ and u) makes it necessary to consider the frequency dispersion of A. In particular, for frequencies exceeding the piezoresonance frequency, the interaction of the intermediate ξ-mode with the transverse acoustic u-mode ceases to play a role, and the coefficient A is renormalized so that the minimum on $A(T)$ rises to the abscissa. For still higher frequencies ($\nu \geqslant 22\ \mathrm{cm}^{-1}$) the interaction of the ξ-mode with the temperature-unstable optical η-phonon ceases to be observed. Experimentally, this is perceived as a "transformation" of the intermediate relaxed soft excitation into the corresponding hard phonon and the appearance of temperature dependence in some high-lying optical mode. The temperature path of the frequency of this mode is determined completely by $A(T)$, but with a still further increasing coefficient A, now reaching ≈ 0.5.

6. CONCLUSION

The results of this study confirm that Rochelle salt is a very striking and at present unique solid-state physics example of a system with a DCP. The materialization in RS at once of two DCPs in the $Na[K_x(NH_4)_{1-x}]C_4H_4O_6\cdot 4H_2O$ phase diagram is also an exceptional fact, since a similar situation is presently known only for a fluid solution of β-picaline in water (β-$Na_2SO_4\cdot H_2O$) under pressure,[13] but is has been studied significantly less experimentally.

The atypical nature of the RS phase transitions appears strikingly in their low-frequency dynamics. Here the spectrum of the soft mode consists not of one mode, as was previously believed, but at least three strongly interacting low-frequency modes. Moreover, in the low-temperature region, all three of these modes are well defined resonant modes. Their evolution is determined by the temperature dependence of the frequency of the highest-frequency mode, coupled in the final analysis, as in the classical conception of the soft mode,[7,32] with the temperature dependence of the inverse static dielectric susceptibility χ^{-1}.

In planning questions for further investigations, along with the substitution considered in this paper of K by NH_4, other types of substitutions could also be of interest, including hydrogen H by deuterium D (DRS) and atoms of K by Rb, Tl, thiourea ($SC(NH_2)_2$) etc. Besides, it would be advisable to conduct new careful measurements of all the physical (and, especially, thermodynamic) variables in a possibly wider range of temperatures, pressures, and concentrations. This would allow one to more reliably verify the deductions of the approach laid out here and, possibly, bring to it some numerical corrections. This is probable, since many of the experimental results for RS were obtained in the 1930–50 period and have since not actually been sharpened. In concusion, we would like to emphasize (see also Ref. 15) that the study of systems with a DCP, opens exceptionally bright opportunities for the most complete and multifaceted verification of the existing theories of critical phenomena, be they the classical theory of Landau (as in the case of phase transitions in RS and, apparently, in certain fluid crystals[18]) or the fluctuation theory of phase transitions (as, for example, near the double DCP in fluids[12–17]).

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