Low-temperature transformations of the relaxational soft modes in crystals of the Rochelle salt family

A. A. Volkov, G. V. Kozlov, E. B. Kryukova, J. Petzelt[1)]

Institute of General Physics, Academy of Sciences of the USSR

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The dielectric spectra $\varepsilon^*(\nu,T)$ of crystals of the Rochelle salt family were measured at frequencies of 5–25 cm^{-1} and temperatures of 5–280 K by the method of monochromatic submillimeter spectroscopy. A resonance absorption line due to the temperature evolution of the previously known relaxational soft mode was observed at a frequency $\nu \sim 20$ cm^{-1}. It has been established that at low temperatures ($150 < T < 180$ K), crystals of this family develop an antipolar ordering of the ferroelectrically active particles in an asymmetric double-well potential.

1. INTRODUCTION

A large amount of experimental material has accumulated on the subject of the low-frequency lattice dynamics of crystals at structural phase transitions. It has become clear that, depending on the mechanism of the phase transition, the soft modes in the crystal can be relaxational as well as resonance excitations. Resonance soft modes, which are characteristic of displacive ferroelectrics, are optical phonons whose frequencies suffer an anomalous decrease near the phase transition points T_c on account of a decrease in the corresponding elastic force of the lattice. Relaxational soft modes, which are characteristic of order-disorder systems, basically involve the correlated motion of dipoles in a double-well potential. This motion is highly anharmonic, and the relaxational soft modes are generally not numbered among the $3N$ normal vibrations of the lattice.

Despite the difference in mechanisms, resonance and relaxational soft modes are very similar in terms of how they appear in the spectra near the phase transition points. As the temperature departs from T_c, the frequency of a resonance mode gradually increase to $\nu \approx 10$–100 cm^{-1}, and the mode becomes an ordinary lattice phonon. And what is the fate of a relaxational soft mode? Judging from the fact that the IR spectra of the crystals usually do not exhibit high-frequency relaxational modes ($\nu \gtrsim 20$–50 cm^{-1}), one can assume that the relaxational soft modes either vanish from the spectra (the relaxation oscillator strength falls off) or stabilize in frequency in the region $\nu \lesssim 20$–50 cm^{-1}. The available experimental data on this score are very limited and do not permit a definite conclusion.

In this study we have investigated the behavior of relaxational soft modes when the temperature is allowed to depart widely from T_c ($T_c/T \gg 1$). As objects of study we used crystals of the Rochelle salt family. Because these crystals have a bounded ferrophase region, they afford the rare possibility of moving away from T_c in the low-temperature direction in a nonpolar phase, in which the dynamics is not distorted by spontaneous polarization as in other ferroelectrics.

2. PROPERTIES OF ROCHELLE SALT

The presence of two phase transitions at nearby temperatures, $T_1 = -18$ °C and $T_2 = 24$ °C, bounding the only region in which the ferrophase exists, is the main distinctive feature of Rochelle salt (RS), the first known ferroelectric.[1] In spite of over two centuries of studies on RS, the phase transition mechanism, which underlies the anomalous properties of the crystal, remains unknown. The reason for this is that the RS structure is extremely complex—the unit cell of the crystal contains four formula units of $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, or 112 atoms.

To elucidate the role of the different groups of atoms in the ferroelectric effect in RS, many investigators have turned to the study of isomorphically substituted analogs of this compound. The most interesting from the standpoint of the influence of the hydrogen bonds is deuterated Rochelle salt ($\text{NaKC}_4\text{H}_2\text{D}_2\text{O}_6 \cdot 4\text{D}_2\text{O}$, or DRS), which is obtained by replacing the hydrogen (H) by deuterium (D) in the OH groups and in the molecules of the water of crystallization. Measurements of the elastic, electrical, and piezoelectric constants[2] and studies of the effect of hydrostatic pressure[3] have shown that the isotope effect in DRS is insignificant: the replacement of H by D widens the stability region of the ferrophase to $T_1 = -22$ °C and $T_2 = 35$ °C and increases the spontaneous polarization P_s at the maximum to 0.35

The ferroelectric dynamics of RS crystals has long been the object of intense experimental scrutiny. The nature of the phase transitions in RS was finally settled in the late 1960s with the rf and microwave detection of a relaxational soft mode,[4] a characteristic indicator of an order-disorder system. This low-frequency (in comparison with ordinary lattice vibrations) mode was observed in the dielectric spectra $\varepsilon^*(\nu,T)$ of RS in the form of wide and rather intense absorption lines with temperature-dependent parameters exhibiting anomalies at the phase transition points T_1 and T_2. Since that time, the $\varepsilon^*(\nu,T)$ curves obtained[4] in RS have become a classic example of Debye relaxational dispersion in ferroelectrics.

However, our recent dielectric measurements[5,6] in the submillimeter wavelength region have unexpectedly shown that the situation with regard to the soft mode in RS is far from the simplest case. It was found that in the interval 250–180 K the characteristic frequency $1/2\pi\tau$ of the soft mode varies with temperature not according to a linear law, as is typical of many order–disorder ferroelectrics, but according to a cubic law. As a result, in a relatively narrow temperature

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interval the frequency of the mode increases by more than two orders of magnitude, and for $T \lesssim 180$ K it enters the spectral region $\nu \gtrsim 10\ \mathrm{cm}^{-1}$ typical of lattice phonons. The results of earlier studies of the IR and Raman spectra contain no information on what happens to the soft mode as the temperature is decreased further.[7-9] In Ref. 10, the most complete study of the vibrational spectra of RS, it was established that the ferroelectric ordering in the crystal has some effect on the system of optical phonons, but the spectra showed no indications of the presence of soft modes.

It has been found[6,11] that deuteration of the crystal has practically no effect on the ferroelectric soft mode. All of the dynamical features of RS mentioned above are also present in DRS. Consequently, even if proton tunneling does occur, it has little effect on the properties of the ferroelectrically active subsystem of these crystals.

The most successful model of RS, which is based on analysis of the structural data, was proposed by Mitsui[12] and subsequently developed by other investigators.[13-16] According to this model, the phase transitions in the crystal are due to the motion of particles in asymmetric double-minimum potential wells, forming two interpenetrating mirror-symmetric sublattices. It is assumed that the interaction of the ferroelectrically active dipoles within each of the sublattices and the dipoles belonging to different sublattices are inequivalent and require two independent parameters for their description in the molecular field approximation. Depending on the values of these parameters, the Mitsui local field theory (unlike the Mason theory) yields different versions of the phase transitions in clamped crystals (including those observed experimentally in RS) and qualitatively explains the unusual properties of mixed crystals obtained by the partial replacement of the K atoms by NH_4, Rb, or Tl. Using the pseudospin formalism for hydrogen-bonded ferroelectrics and a two-sublattice Ising model with an asymmetric potential, Blinc, Shukla, and Žekš[14,15] extended the Mitsui theory to include dynamics, with tunneling taken into account. This has permitted the theoretical study of isotope effects[17] and the dynamical behavior of Rochelle salt.[14-16]

3. EXPERIMENT

In the present study we measured the dielectric spectra of crystals of the Rochelle salt family at frequencies between 5 and 25 cm^{-1} in the submillimeter wavelength region with an Epsilon laboratory spectrometer,[18] which uses monochromatic oscillators with electronic frequency tuning (backward wave tubes) as radiation sources.

The samples were plane parallel slabs with thicknesses of 200–600 μm and transverse dimensions of approximately 10×10 mm. The measurements were made under normal incidence of linearly polarized plane waves with electric field vector **E** parallel to the ferroelectric axis **a**, which lay in the plane of the sample. The ultimate results of the measurements were the frequency and temperature curves of the complex dielectric constant $\varepsilon^*(\nu,T) = \varepsilon'' - i\varepsilon''$, calculated from the experimental measurements of the transmission coefficient $t(\nu,T)$ and the phase shift $\varphi(\nu,T)$ of the wave in the sample.[18] The uncertainty in the determination of ε' and ε'' in the present measurements was around 5%.

4. EXPERIMENTAL RESULTS

Our measured dielectric spectra $\varepsilon'(\nu,T)$ and $\varepsilon''(\nu,T)$ for Rochelle salt are shown in Fig. 1. We see from the curves that both the real part ε'' and imaginary part ε'' of the dielectric constant have appreciable dispersion at frequencies of 3 to 30 cm^{-1} over a wide range of temperatures (4–280 K). The data indicate that a wide absorption line

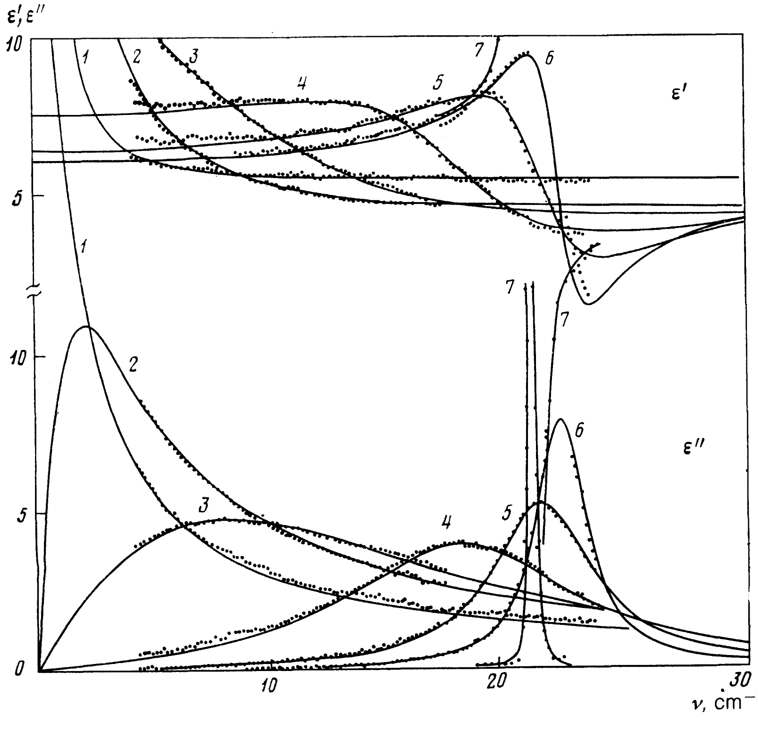

FIG. 1. Submillimeter dielectric spectra of Rochelle salt in the orientation **E**||**a** at temperatures: 1) 280 K, 2) 218 K, 3) 187 K, 4) 150 K, 5) 113 K, 6) 80 K. 7) 5 K. The points are experimental, the solid curves the result of processing the spectra in a single-oscillator model.

with temperature-dependent parameters (the soft mode) enters the working frequency region.

At relatively high temperatures, close to the phase transition T_1 (curves 1 and 2), ε' and ε'' decrease smoothly with increasing frequency. This situation is familiar and indicates that the characteristic frequency $1/2\pi\tau$ of the soft mode is small compared to the working frequencies. However, the picture changes qualitatively when the temperature is lowered. The $\varepsilon''(\nu)$ curves (3–7) exhibit a maximum, shifting to higher frequencies, which indicates that the soft mode frequency is passing through the submillimeter range. We see from Fig. 1 that cooling the crystal results in a sharp decrease (by almost two orders of magnitude) in the absorption linewidth. Beginning at 150 K, the frequency of the relaxational mode increases, and the mode converts into an excitation of a distinctly resonance nature (spectra 4 and 5). By liquid–nitrogen temperature (spectrum 6) this mode is simply an optical phonon at a frequency $\nu \approx 22$ cm^{-1} and with a half-width of 2 cm^{-1}. Its frequency remains practically unchanged right down to liquid-helium temperature (curve 7), while its Q-factor increases by a factor of 10, reaching a value of several hundred.

We made analogous dielectric measurements in the submillimeter range for deuterated Rochelle salt crystals (Fig. 2) and for the mixed compounds: 90%-NH$_4$ salt ($\mathrm{Na[(NH_4)_{0.9}K_{0.1}]C_4H_4O_6 \cdot 4H_2O}$) and 40%-TU salt ($\mathrm{Na[(SC(NH_2)_2)_{0.4}K_{0.6}]C_4H_4O_6 \cdot 4H_2o}$), which do not exhibit ferroelectric transitions.[1] It turned out that despite the qualitative difference in the static properties of these crystals, the curves obtained for $\varepsilon'(\nu,T)$ and $\varepsilon''(\nu,T)$ are practically identical to the RS spectra. They retain all the characteristic features, including the most important effect—the low-temperature transformation of the relaxational soft mode to a hard optical phonon.

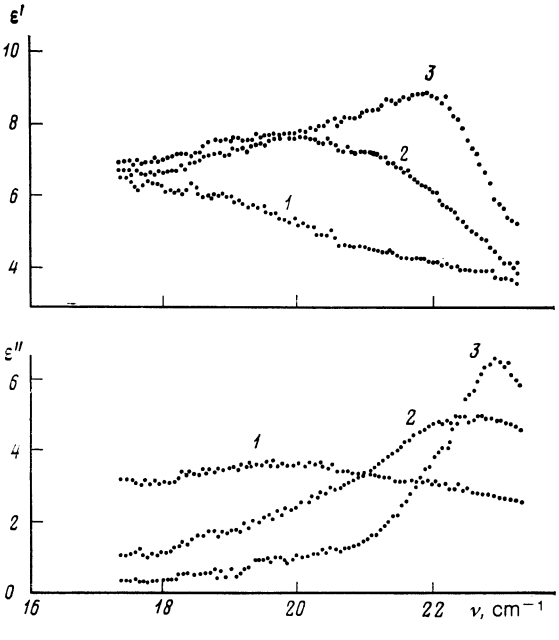

FIG. 2. Submillimeter dielectric spectra of deuterated Rochelle salt in the orientation E||a at temperatures: 1) 150 K, 2) 113 K, 3) 80 K.

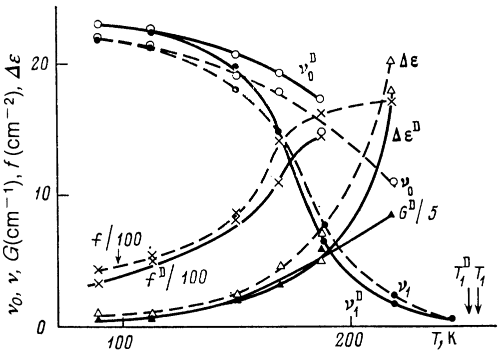

FIG. 3. Temperature dependence of the soft mode parameters in deuterated Rochelle salt (solid curves, superscript D) and ordinary Rochelle salt (dashed curves): $\Delta\varepsilon$ is the dielectric contribution, ν_0 is the frequency, G is the damping, $f = \Delta\varepsilon(\nu_0)^2$ is the oscillator strength, and ν_1 is the peak frequency of the absorption line [$G(T)$ is the same as $G^D(T)$]. The arrows indicate the phase transition points $T_1^D = 251$ K and $T_1 = 255$ K.

5. PROCESSING OF THE SPECTRA AND THE PARAMETERS OF THE PHENOMENOLOGICAL MODEL

We processed the spectra in the temperature region 4–180 K, where the soft mode exhibits distinct resonance properties, using a single-oscillator dispersion model. The four adjustable parameters of this model (the frequency ν_0, the dielectric contribution $\Delta\varepsilon$, the damping G, and the contribution ε_∞ from the high-frequency modes) were fitted by the least-squares method at individual temperature points by using the experimental values of $\varepsilon^* = \varepsilon' - i\varepsilon''$. The average deviation of the calculated values of ε' and ε'' from the experimental data is less than 5%.

Figure 3 shows the resonance parameters which describe the behavior of the soft mode in the ordinary and deuterated crystals at low temperature. At temperatures close to T_1 the damping of the mode becomes so large in comparison with its frequency that it is no longer possible to fit G and ν_0 unambiguously, and it is more appropriate to describe the dielectric spectra by a relaxation model. For tracking the migration of the soft mode through the spectrum over the temperature interval (4–255 K), in Fig. 3 we show the behavior of the peak frequency $\nu_1(T)$ of the absorption line $\varepsilon''(\nu)$, the most distinctive parameter in this regard. For a relaxation dispersion, ν_1 is identical with the reciprocal of the relaxation time $(1/2\pi\tau)$ and is essentially the same as the oscillator frequency ν_0 at small dampings G.

In the mixed crystals 90%–NH$_4$ salt and 40%-TU salt the parameters of the low-frequency lattice excitation under discussion are close to their values in RS and DRS. At $T = 87$ K the frequency and half-width of the latter are $\nu = 22.2$ cm^{-1} and $G = 2.6$ cm^{-1} in 90%-NH$_4$ salt and $\nu = 22.4$ cm^{-1} and $G = 4.6$ cm^{-1} in 40%-TU salt, i.e., practically the same as the values obtained for the RS and DRS crystals.

The behavior of the soft mode in RS is reminiscent of the familiar effect in ferroelectrics wherein the soft mode interacts with a central peak, with the result that the resonance excitation gradually transfers its oscillator strength to a low-frequency relaxational mode. This similarity, however, is purely superficial. The dielectric spectra of RS and

DRS showed no sign of such an interaction. At all temperatures the $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ curves were described to within the experimental accuracy by a single-frequency phenomenological model.

As we see from Fig. 3, the $\nu_1(T)$ curve has two characteristic regions.

1. In the interval 180–255 K the ferroelectric dynamics of the crystal is described through a Debye relaxation model of the dispersion. The $\nu_1(T)$ curve, in complete agreement with our previous results,[5,6] is substantially nonlinear and has a cubic temperature dependence:

$$1/2\pi\tau = A(T_0 - T)^3, \qquad (1)$$

where $A = 1.07 \cdot 10^{-5}$ cm^{-1} K^{-3} and $T_0 = 275$ K for RS and $A = 8 \cdot 10^{-6}$ cm^{-1} K^{-3} and $T_0 = 280$ K for DRS. The relaxation time for the ordering elements of the structure increases somewhat in consequence of deuteration, but the characteristic frequencies $1/2\pi\tau$ are nearly the same in RS and DRS over the entire temperature interval.

2. For $T < 180$ K the cubic dependence breaks down and the $\nu_1(T)$ curve gradually saturates. In this temperature region the relaxational soft mode goes over smoothly into a phonon, and the ferroelectric dynamics of the crystal takes on a resonance nature. This process is accompanied by a significant decrease in the damping G and dielectric contribution $\Delta\varepsilon$ of the soft mode. It is probably because $\Delta\varepsilon$ and expecially G are small that the phonon in question had not been detected earlier in the low-temperature Raman spectra of Rochelle salt.[10]

6. DISCUSSION OF RESULTS

Our experimental results indicate that the ferroelectric dynamics of RS and DRS is extremely unusual and exhibits features that go beyond the framework of the usual representations for order-disorder ferroelectrics.[19] These features include the cubic temperature dependence of the frequency $1/2\pi\tau$ and inverse dielectric contribution $1/\Delta\varepsilon$ of the soft mode, the transformation of the relaxational mode into an optical phonon, and the change in the oscillator strength $\Delta\varepsilon/2\pi\tau$ with temperature. In such a situation it is certainly of interest to consider these features of the ferroelectric dynamics of RS and DRS in the framework of the Mitsui model,[12] which is at present the most complete and consistent model for systems of this kind with asymmetric double-well potentials.

As we have mentioned, the dynamical properties of a generalized Mitsui model with allowance for quantum-mechanical effects were studied in Refs. 14 and 15. In this dynamical model the spectrum of polarization fluctuations is described approximately by a single relaxation time τ, which exhibits critical slowing down as the temperature approaches T_1 and T_2 regardless of the value of the tunneling integral Γ. This means that the tunneling motion of the protons in the hydrogen bonds does not directly influence the relaxational motion of the ferroelectrically active particles but acts on them only by changing the mean field acting on each spin. This assumption is completely consistent with the results of the present study: the dynamical properties of Rochelle salt (Fig. 3) remains practically unchanged on deuteration; the soft mode parameters in RS and DRS are very similar over the entire temperature range studied. Moreover, the cubic temperature dependence of $1/2\pi\tau$ and $1/\Delta\varepsilon$ in RS and DRS can also be described in the two-sublattice model.[20]

When the temperature decreases, however, the dynamical Mitsui model,[14,15] constructed in the Ising approximation with a local potential in the form of two infinitely deep wells, with only the motion of the particle between wells taken into account, no longer conveys the essence of the phenomena which occur in the crystal. As a result, by $T < 180$ K this theoretical model no longer describes the temperature dependence of the soft mode parameters or explains the transformation of the relaxational soft mode into an optical phonon, nor does it provide a reason for the appearance of the latter in the spectra of RS and DRS.

We think there are two possible interpretations for the transformation of the soft mode: 1) The asymmetry of the double-well local potential increases with decreasing temperature, and the potential becomes quasiharmonic; 2) at low temperatures the stochastic motion of the ferroelectrically active particles in the asymmetric local potential stops, and the particles become localized in deeper minima. In either version it is noteworthy that the phenomenon occurs in a system with two mirror-symmetric sublattices. As a result, the RS lattice exhibits an antipolar ordering at low temperatures. The ordering of the lattice in RS is not due to a change in the average symmetry of the crystal, i.e., it is an isostructural transformation. A decrease in temperature will bring on a redistribution of the particles in the asymmetric double-well potential: for $T > T_2$ there is total disorder; in the intermediate ferrophase there is a parallel arrangement of the dipoles, and at low temperatures ($T < T_1$) there is an antiparallel arrangement. We note, however, that the antipolar ordering for $T < T_1$ is not antiferroelectric, since it is impossible ro have a 180-degree flip of the ferroelectrically active dipoles without changing the free energy of the system. The temperature dependence of the frequency of collective motion of the ordering dipoles does not exhibit the critical slowing down that is characteristic for the soft mode of a structural phase transition.

The idea that the shape of the potential relief of the ordering particles changes with temperature has been used previously to explain the behavior of the relaxation time resulting from changes in temperature in ferroelectrics. For example, there is reason to believe that the height of the potential barrier separating the two equilibrium positions of the particles in CsH_2PO_4 and $NaNO_2$ changes substantially as the temperature is raised in the paraelectric phase.[21,22] This process affects both the relaxation time and the dielectric contribution of the soft mode.

Let us discuss the second hypothesis in more detail. A similar situation has been studied theoretically by Onodera,[23] who considered a unified model for order-disorder and displacive ferroelectrics in the form of a system of interacting classical oscillators moving in an anharmonic potential

$$V(x) = Ax^4 + Bx^2, \qquad (2)$$

($A > 0$ and $B \gtrless 0$ are the constants of the local potential) and calculated the dynamic susceptibility $\chi^*(\nu, T)$ of the system in the molecular field approximation. We find it very interesting that the Onodera model has deomonstrated that it is possible in principle for a relaxational mode to convert to an oscillatory mode in the case of the markedly anharmonic motion that can occur in a double-well potential when the thermal energy kT is of the order of the well depth $L = B^2/4A$. On the basis of the most general conclusions of this theory, which are valid for any order–disorder system (including Rochelle salt), we are justified in assuming that the resonance absorption peak observed in the spectra of RS and DRS at low temperatures ($T \lesssim 120$ K) corresponds to vibrations localized within deeper wells ($kT \ll L$) whose profile does not change as the temperature is lowered. This conclusion is supported by the temperature dependence of the frequency $\nu_0(T)$, damping $G(T)$, and oscillator strength $f(T)$ of the resonance mode, all of which vary little over the rather wide range of temperatures 4–120 K. Near the transition, when $kT \gtrsim L$, the motion of the particles is no longer localized within one of the wells but can occur between the wells, and the response of the system is described by a Debye relaxational mode. Here the transformation of the relaxational mode into an optical phonon will correspond to the gradual localization of the particle in the potential wells.

The dynamical unity of these crystals of the Rochelle salt family is due, we believe, to their having a low-temperature ordering process as a background against which one observes the features of the physical properties of each individual crystal. This ordering evidently involves the participation of the same groups of atoms $(OH)_5$ moving in asymmetric double-well potentials of the same form. At the same time, the presence of a pronounced isotope effect in RS in connection with various substitutions for the potassium atoms suggests, on the basis of the Onodera theory, that the reason for the difference in the thermodynamic properties between mixed compounds and ordinary RS is not so much a change in the parameters A and B of the local potential as a change in the interaction constants of the ferroelectrically active particles as a function of increasing concentration of the isomorphically substituted atoms. A similar conclusion can be reached using the Mitsui model,[12] which establishes how the nature of the phase transitions depends on the interaction constants of the particle in the same sublattices and in different sublattices as the concentration changes.

From the experimental data obtained in this study, we can conclude that the interaction energy of the ferroelectrically active particles in RS crystals decreases at low temperatures $T < 180$ K. This is manifested, in particular, in the fact that the ordering of the particles in the lattice occurs smoothly over a wide range of temperatures without the avalanche-like process that is observed at the higher-temperature ferroelectric phase transitions in these crystals. The decrease in the interaction energy is due to a decrease in the dipole moment of the vibrations of the particles undergoing localization in the quasiharmonic potential minimum.

7. CONCLUSION

In summary, our study of the submillimeter dielectric spectra of crystals of the Rochelle salt family has established that:

1) At low temperatures the nature of the motion of the particles in the soft mode of order-disorder type ferroelectrics having an asymmetric potential can change from relaxation to resonance. This phenomenon is due to the localization of the particles in the quasiharmonic potential minima and is accompanied by a substantial decrease in the relaxation oscillator strength of the soft mode.

2) The transformation of the relaxational soft mode into a hard optical phonon that is observed in crystals of the Rochelle salt family may be due to a low-temperature antipolar ordering of the ferroelectrically active particles without a change in the average symmetry of the lattice.

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[1)] Institute of Physics, Academy of Sciences of the Czechoslovak Socialist Republic.

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