Observation of a soft optical phonon in Rochelle salt

A. A. Volkov, Yu. G. Goncharov, G. V. Kozlov, E. B. Kryukova, and J. Petzelt
Institute of General Physics, Academy of Sciences of the USSR

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A resonant absorption line ($\nu \sim 20$ cm^{-1}) has been found in the submillimeter dielectric spectra of Rochelle salt. This line forms at low temperatures ($T \lesssim 150$ K) as a result of the temperature dependence of a known soft relaxation mode.

Rochelle salt is a well-known ferroelectric, distinguished from other ferroelectrics by the fact that it exhibits, in addition to the ordinary phase transition from the paraelectric phase to the ferroelectric phase ($T_1 = 297$ K), yet another transition, which returns the crystal to a nonpolar state below $T_2 = 255$ K. The symmetry of the crystal in the low-temperature phase is the same[1] as at $T > T_1$, but we do not yet know to what extent the phases at $T < T_2$ and $T > T_1$ are equivalent in terms of microstructure.

A soft mode has been found in all three phases. First observed at radio frequencies as a dielectric relaxation with a critical dependence on the temperature,[2] it has since become a classic example of a soft mode in order-disorder ferroelectrics. Our recent dielectric measurements[3,4] at frequencies higher than those in Ref. 2 unexpectedly showed that the soft-mode situation in Rochelle salt is far from simple. In particular, it has been found that the frequency of the soft mode increases anomalously rapidly with distance from the phase-transition temperature T_2 (i.e., upon cooling),[1)] without any significant decrease in oscillator strength. Questions of fundamental importance arise here: How does the critical relaxation behave as a function of the temperature? Does it completely disappear far from the phase transition, as would be

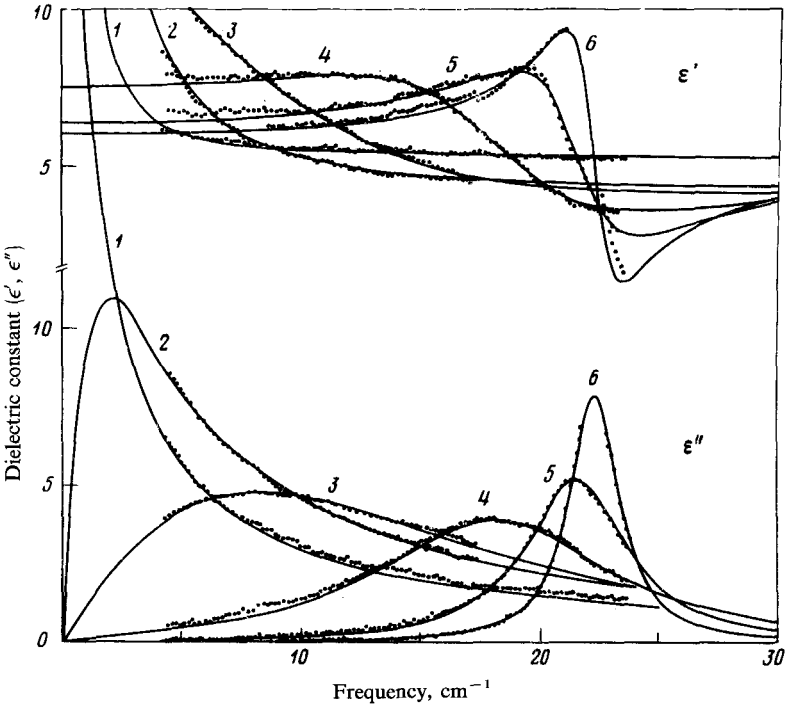

FIG. 1. Submillimeter dielectric spectra of Rochelle salt at several temperatures: 1—280 K; 2—218 K; 3—187 K; 4—150 K; 5—114 K; 6—80 K. Points—Experimental; lines—fit with a single-oscillator model (for the soft-mode parameters in Fig. 2).

expected if the crystal were an order-disorder ferroelectric? This problem is the subject of the present study.

We used the Épsilon submillimeter backward-wave-tube spectrometer[5] to measure the dielectric constants $\epsilon'(\nu)$ and $\epsilon''(\nu)$ of Rochelle salt in the frequency range 5–23 cm^{-1} at temperatures from room temperature down to liquid-nitrogen temperature. The experimental results pertaining to the ferroelectric axis of the crystal (the a axis) are shown in Fig. 1.

At comparatively high temperatures, near T_2, the $\epsilon'(\nu)$ and $\epsilon''(\nu)$ spectra exhibit a well-known[2-4] low-frequency relaxation dispersion (curves 1 and 2). As the temperature is lowered, the picture changes qualitatively: The relaxation mode, rising in frequency, becomes a pronounced resonant-type excitation (spectra 4 and 5). At liquid-nitrogen temperature, this excitation is simply an optical phonon, at the frequency $\nu \sim 20$ cm^{-1} with a half-width ~ 2 cm^{-1}.

Figure 2 shows the parameters of the resonator describing the behavior of the soft mode at low temperatures. Also shown here is the dependence $\nu_1(T)$ of the frequency of the peak of the $\epsilon''(\nu)$ line, which is the most nearly universal parameter in this case and which can be used to follow the movement of the soft mode along the spectrum over the entire temperature range. For the relaxation model of dispersion, we might note, ν_1 is identically equal to the reciprocal of the relaxation time, $1/2\pi\tau$. We see that as the crystal is cooled, the soft mode initially moves rapidly along the frequency scale

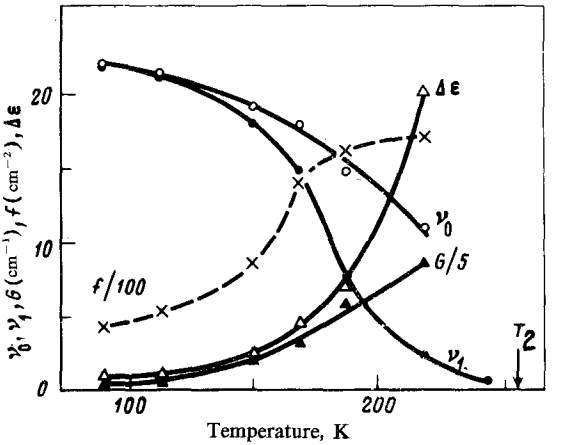

FIG. 2. Temperature dependence of the characteristics of the soft mode in Rochelle salt: the frequency ν_0, the dielectric contribution $\Delta\epsilon$, the damping G, the oscillator strength $f = \Delta\epsilon\nu_0^2$, and the frequency at the peak of the absorption line, ν_1.

(in the interval 255–180 K), and then stabilizes in the spectrum at ~ 22 cm^{-1} (at $T \lesssim 120$ K). This process is accompanied by a significant decrease in the damping G and in the oscillator strength $f = \Delta\epsilon\nu_0^2$ of the soft mode.

The observed temperature dependence of the parameters of the soft mode goes beyond the present understanding of Rochelle salt, which has the soft mode resulting from a stochastic motion of ferroelectrically active particles in a temperature-independent asymmetric two-minimum potential (the Mitsui model[6]). The conversion of the soft relaxation mode into an optical phonon means that the motion of the particles between the local minima of the potential is stopped. There are two possible ways in which such a situation could arise: 1) The particles localize in one potential minimum (the deeper one; a similar case was studied theoretically in Ref. 7); 2) as the temperature decreases, the asymmetry of the potential becomes more pronounced, and the shallower potential minimum disappears.

In either case, the effects would occur in a system with two mirror-symmetric sublattices. As a result, the disorder of the ferro-active subsystem would gradually give way to an antiferroelectric order as the temperature was reduced.

It may be that the shape of the potential may begin to change at temperatures above T_2 in certain crystals of the Rochelle-salt type. In this situation, the T_2 phase transition would differ in nature from the T_1 transition and would more likely be a displacive transition than an order-disorder transition. We believe that a study of the possibilities for the occurrence of various types of phase transitions in crystals of the Rochelle-salt family represents a new area of research on systems with an asymmetric two-minimum potential.

1)Unfortunately, it was not possible to follow the behavior of the soft mode far from T_1 (i.e., upon substantial heating), since the crystal decomposes at temperatures no higher than ~ 330 K.

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