Soft modes in betaine calcichloride: a new incommensurate ferroelectric

A. A. Volkov, Yu. G. Goncharov, G. V. Kozlov, J. Albers,[1)] and J. Petzelt[2)]
Institute of General Physics, Academy of Sciences of the USSR

(Submitted 2 October 1986)
Pis'ma Zh. Eksp. Teor. Fiz. **44**, No. 10, 469–471 (25 November 1986)

Soft modes of two high-temperature phase transitions have been observed in the submillimeter dielectric spectra of betaine calcichloride, which is a new ferroelectric with an incommensurate phase. Anomalies in the temperature dependence of these modes and a multiple production of additional faint lines in the ferroelectric phase have also been observed.

The betaines are a recently discovered family of organic crystals which includes crystals exhibiting ferroelectric[1] and antiferroelectric[2] properties. Betaine calcichloride dihydrate, $(CH_3)_3NCH_2COOCaCl_2 \cdot 2H_2O$, is the first crystal of this family known to exhibit an incommensurate phase.[3,4] In the temperature interval 43–164 K, this crystal undergoes a series of phase transitions, at $T_1 = 164$, $T_2 = 127$, $T_3 = 125$, $T_4 = 116$, $T_5 = 75$, $T_6 = 51$, $T_7 = 47$, and $T_8 = 43$ K. Peaks are observed in the static permittivity $\epsilon_b(T)$ at the points T_2, T_3, T_4, T_5, and T_8; in the interval between T_3 and T_6, dielectric hysteresis loops of unusual shape are observed. Below $T_3 = 51$ K these loops acquire the shape typical of a ferroelectric phase.[3]

 0021-3640/86/220603-04$01.00

The situation with regard to the incommensurate phase in betaine calcichloride is similar to that in the case of K_2SeO_4 (Ref. 5). Specifically, the high-temperature phases in these substances have the same symmetry, and the wave vector of the modulation wave, $\mathbf{K}_i$, has nearly the same value at the transition point $T_i = T_\mathrm{I}$ as in K_2SeO_4, $\mathbf{K}_i = 0.32\mathbf{C}^*$, differing only in direction. With decreasing temperature, $\mathbf{K}_i$ decreases to 2/7, 1/4, 1/5, and, ultimately ($T < T_7$), 1/6 of $\mathbf{C}^*$ (Ref. 4).

In a search for anomalously low-frequency lattice excitations responsible for the observed phase transitions, we undertook a study of the dielectric properties of betaine calcichloride in the submillimeter wavelength range. We use a quasioptical procedure with an Épsilon backward-wave-tube spectrometer[6] to measure the spectra of the real and imaginary parts of the permittivity, $\epsilon_b'(\nu)$ and $\epsilon_b''(\nu)$, over the frequency range 7–24 cm^{-1} and over the temperature range from room temperature down to liquid-helium temperature. The crystals are grown from an aqueous solution by an evaporation method at a constant temperature. The samples are synthesized as parallel-plane plates with transverse dimensions $\sim 10 \times 10$ mm and thicknesses of 0.1–0.5 mm. The ferroelectric axis lies in the plane of the plates.

Figure 1 shows some representative experimental results in the form of $\epsilon_b''(\nu)$ spectra. The lines are drawn through 200 experimental points for each spectrum. The scatter of the points with respect to the curves averages less than 5%. Curves 1–9 are labeled in accordance with a monotonic lowering of the temperature from room temperature to 40 K.

The primary feature of these spectra is the broad and intense absorption line at high temperatures (spectra 1 and 2). The maximum of this line, which occurs at the frequency $\nu \sim 15$ cm^{-1} at room temperature, shifts downward along the frequency scale as the crystal is cooled, while the intensity of the line increases. Below $T \sim T_2 = 125$ K the situation becomes the opposite: the line returns to the region $\nu \sim 15$ cm^{-1} and rapidly decreases in intensity (spectra 3–5).

At temperatures $T < T_\mathrm{I} = 164$ K, on the high-frequency slope of this absorption

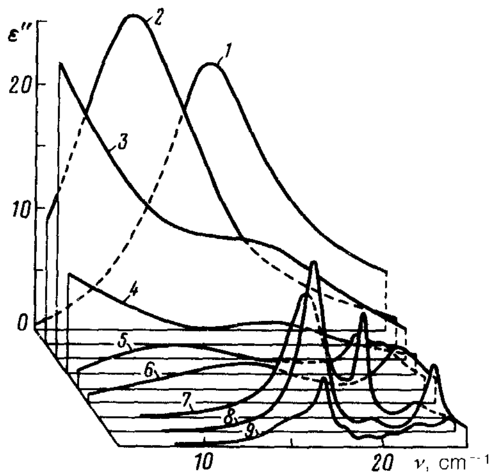

FIG. 1. Experimental spectra $\epsilon_b''(\nu)$ of betaine calcichloride. The different spectra correspond to different temperatures of the paraelectric, incommensurate, and ferroelectric phases. T, K: 1—273; 2—192; 3—145; 4—137; 5—102; 6—87; 7—54; 8—49; 9—43.

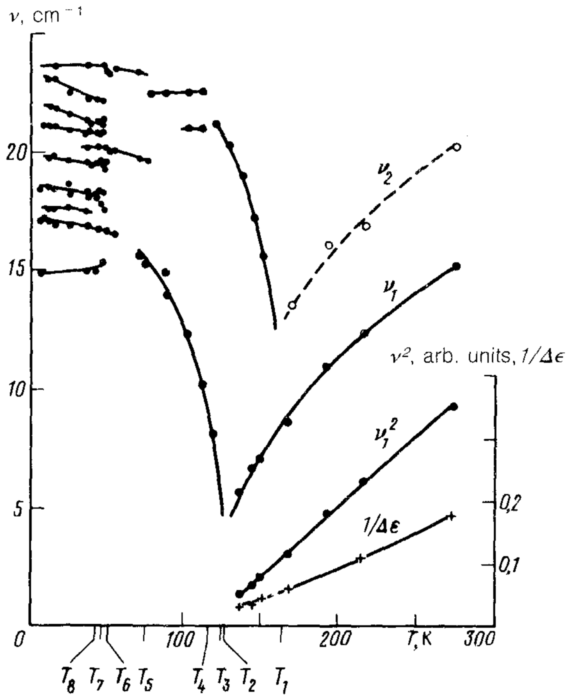

FIG. 2. Temperature dependence of the parameters of the lines found from an analysis of the dielectric spectra $\epsilon_b'(\nu)$ and $\epsilon_b''(\nu)$. The dashed line corresponds to the mode ν_2, which is observed in only some of the samples.

line (which we denote by ν_1), we can reliably identify another, fainter, mode, ν_2 (spectra 3 and 4). In experiments with samples of comparatively poor quality, the absorption line ν_2 is present in the spectra even at high temepratures, $T > T_1$. Like the ν_1 mode, the ν_2 mode is unstable in the face of temperature changes. Near the highest-temperature phase transition, $T_1 = 164$ K, its frequency decreases to the minimum value $\nu \sim 12$ cm^{-1}.

Below $T \sim T_4 = 116$ K the spectra split repeatedly; beginning at $T \sim T_5 = 75$ K, they acquire a rather complex shape (spectra 7–9). They can be described as a comb of lines which lie above $\nu \sim 15$ cm^{-1} on the frequency scale and apparently extend beyond the limiting frequency of our measurements, 24 cm^{-1}.

Figure 2 shows the results of an analysis of the $\epsilon_b'(\nu)$ and $\epsilon_b''(\nu)$ spectra on the basis of a model of noninteracting oscillators. These curves show the temperature dependence of the frequencies of the observed lines and also the temperature dependence of the dielectric contribution $\Delta\epsilon_1$ of the intense mode ν_1 (the lower curve).

The mode ν_1 is seen to belong to a branch of a soft mode: It has a linear dependence $\nu^2(T)$ and an approximately linear behavior of $1/\Delta\epsilon$, as prescribed by the Curie-Weiss law. Both curves extrapolate to zero values near the phase transitions T_2, T_3, and T_4, but the maximum values $\Delta\epsilon_1 \sim 30$, are totally incapable of explaining the anomalously large values of the static permittivity in this temperature interval ($\epsilon_b \sim 10^4$; Ref. 3). It follows that at low frequencies ($\nu \lesssim 3$ cm^{-1}) the dielectric spectrum has, in addition to mode ν_1, an intense temperature-unstable excitation, probably of a relaxation type, and that this excitation determines the peaks in ϵ_b at T_2 and T_3.

Mode ν_2 exhibits a pronounced instability, which is obviously related to the phase transition at $T_1 = 164$ K. Its manifestation in the spectra depends significantly on the quality of the samples, indicating that mode ν_2 is not a normal lattice mode from the center of the Brillouin zone and that its presence in the dielectric spectra at $T > 164$ K is due exclusively to a breaking of the translational symmetry of the lattice. In the region of the incommensurate phase, 51–125 K, mode ν_2 behaves as an amplitudon on K_2SeO_4 (Ref. 5). We do not detect a phason in the submillimeter spectra of betaine calcichloride; the phason is probably of lower frequency in this case. At the points T_4, T_5, and T_6 we observe anomalies in the behavior of the ν_2 mode: a splitting of this mode into separate branches, with sharp redistributions of the intensity.

At low temperatures, below 51 K, the spectra become rich in new lines; in the frequency interval 15–24 cm^{-1} there are at least nine of them. This effect can logically be linked with a multiplication (by a factor of six) of the unit cell of the crystal at the transition to the ferroelectric phase.

In summary, this study has shown that betaine calcichloride has an exceedingly rich ferroelectric dynamics. This circumstance combines with the possibility of obtaining large crystals of good quality from aqueous solutions to make betaine calcichloride a promising system for a study of the dynamics of a crystal lattice in a state with an incommensurate modulation and also a commensurate modulation of the structure.

[1)]Saarland University, Saarbrücken, FRG.
[2)]Institute of Physics, Czechoslovak Academy of Sciences, Prague.

[1]A. Klöpperpieper, H. J. Rother, J. Albers, and K. H. Ehses, Ferroelectrics Lett. **44**, 115 (1982).
[2]J. Albers, A. Klöpperpieper, H. J. Rother, and K. H. Ehses, Phys. Status Solidi **a74**, 553 (1982).
[3]H. J. Rother, J. Albers, and A. Klöpperpieper, Ferroelectrics **54**, 107 (1984).
[4]W. Brill and K. H. Ehses, Ferroelectrics 24 Suppl. 24-2, 826, 1985.
[5]J. Petzelt, G. V. Kozlov, A. A. Volkov, and Y. Isibashi, Z. Phys. **B33**, 369 (1979).
[6]A. A. Volkov, Yu. G. Goncharov, G. V. Kozlov, S. P. Lebedev, and V. I. Mal'tsev, Elektronnaya tekhnika, seriya elektronika SVCh **11**, 38 (1984).

Translated by Dave Parsons