G. V. Kozlov, A. A. Volkov, and S. P. Lebedev. *Dielectric spectroscopy of soft modes in ferroelectrics.* An important constituent part of the phase-transition problem—one of the central problems in contemporary physics[1]—is study of temperature-unstable oscillations of crystal lattices (soft modes). The soft-mode concept, which took form about twenty years ago,[2-4] has now been transformed from an object of verification and intensive study into a powerful tool for investigation of the mechanisms of structual phase transitions in crystals. The dynamic aspects of phase transitions are being studied on a very broad front, both with respect to the number of materials being investigated and with respect to the variety of experimental-research methods. It is still possible, however, to distinguish against this background trends that have been especially productive. One of them is unquestionably the spectroscopy of phase transitions in ferroelectric crystals. Since the soft modes in these crystals are in many cases polar oscillations with small wave vectors, far-infrared spectroscopy has become the most important of the methods used to study them. Here the objective is to acquire data on the dispersion of the dielectric constant and use them to determine the parameters of the soft modes causing this dispersion. Of particular interest from the standpoint of the dynamic theory of ferroelectricity are data pertaining to the lowest frequencies of the infrared band (the submillimeter band), since it is into this band that the frequency of a soft mode is shifted as the temperature of the crystal approaches the phase-transition point.

With the advent of the new techniques known as Fourier spectroscopy and backward-wave-tube (BWT) spectroscopy, experimental research in the submillimeter wavelength band (~3–30 cm^{-1}), which was long difficult of access for the experimenter, is now going through a period of intensive development. In this paper we report experience gained in our studies of a number of ferroelectrics and similar crystals in which we used BWT spectroscopy, which, in our opinion, has become a highly effective tool for experimental study of low-frequency crystal-lattice dynamics. It is sufficient to note that modern BWT spectrometers are capable of reliable measurement of the real and imaginary parts of the dielectric constant (ε' and ε'') in specimens with practically arbitrary dielectric properties.[5,6]

We studied a) classical ferroelectrics: the orthophosphates KH_2PO_4, KD_2PO_4, KH_2AsO_4, PbH_2PO_4,[7-11] $PbHPO_4$,[12] Rochelle salt RS and dRS,[11,13] triglycine sulfate TGS and dTGS,[11,14] $Pb_5Ge_3O_{11}$,[7]; b) ferroelectrics with noncommensurable phases: K_2SeO_4, $(NH_4)_2BeF_4$, $SC(NH_2)_2$, $Sr_2Nb_2O_7$, and Rb_2ZnCl_4,[15-17] and c) the ferroelectric-like crystals $NH_4H_2PO_4$, $ND_4D_2PO_4$, $KH_3(SeO_3)_2$, $KD_3(SeO_3)_2$, $CsCuCl_3$.[11,19-21]

By way of example, Fig. 1 shows certain typical submillimeter dielectric spectra/$\varepsilon'(\nu)$ and $\varepsilon''(\nu)$/, which correspond to various types of ferroelectric dispersion: relaxational (TGS), resonant ($CsCuCl_3$) and more complex two-mode dispersion ($BaMnF_4$ and K_2SeO_4). It will be seen that these plots are highly informative. Indeed, spectra of this kind usually enable us to determine all dispersion parameters of the ferroelectric polarization mechanism without use of supplementary data, and to follow their variations with temperature. The comparatively high accuracy of the data on $\varepsilon'(\nu, T)$ and $\varepsilon''(\nu, T)$ (~5%) permits confident selection of theoretical dispersion models that describe the experimental results not only when the complete absorption line is seen in the dielectric spectra ($CsCuCl_3$; see Fig. 1), but also when the experimental method used produces only part of the line (TGS; see Fig. 1).

To illustrate, Fig. 2 shows temperature curves ob-

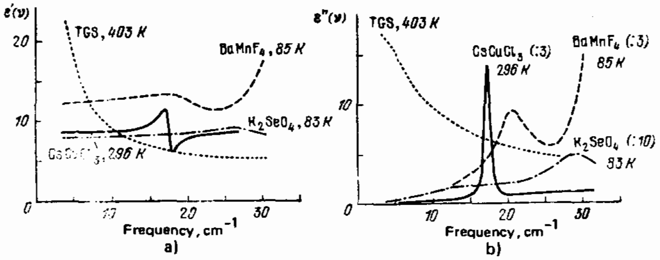

FIG.1. Dielectric submillimeter spectra $\varepsilon'(\nu)$ (a) and $\varepsilon''(\nu)$ (b) of TGS, $CsCuCl_3$, $BaMnF_4$ and K_2SeO_4 crystals. These experimental results are the point of departure in calculation of soft-mode parameters and microscopic polarization mechanisms.

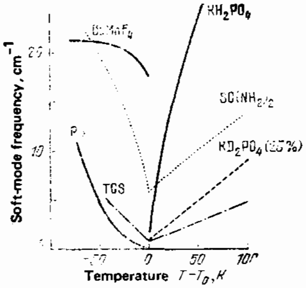

FIG. 2. Temperature curves of soft-mode frequencies of some of the crystals investigated. It is seen that the range of their principal variations falls in the submillimeter BWT-spectroscopic band (3-30 cm^{-1}).

tained for the frequencies of soft modes on the basis of submillimeter dielectric spectra. Information on the oscillator strengths of the excitations studied, on their dielectric contribution, and on the total contribution of all higher-frequency polarization mechanisms can also be extracted from the same spectra.

Submillimeter dielectric spectra are of fundamental importance for determination of the phase-transition mechanisms in most of the crystals listed above. In the case of crystals of the KH_2PO_4 family, for example, these data have delivered quantitative information on long-wave collective oscillations of protons on hydrogen bonds and have made it possible to establish the roles of specific atoms of the crystal in its ferroelectric dynamics. They have made it possible to compute the parameters of the microscopic interaction of the particles ordered in the phase transition on the basis of existing theoretical models. The submillimeter dielectric spectra of TGS and dTGS crystals have indicated the existence of previously unknown temperature-unstable modes and have thereby made it possible to resolve contradictions in traditional conceptions of the dynamics of the glycine groups in the lattices of these crystals. Analysis of similar data pertaining to RS and dRS crystals showed that the soft-mode frequency varies with temperature in a manner unusual for ferroelectrics, prompting critical reappraisal of the capability of the two-sublattice model for description of the properties of crystals with asymmetric potentials.

Dielectric spectroscopy has registered excitations associated with amplitude fluctuations of the incommensurable-polarization wave in crystals with incommensurable phases—K_2SeO_4, $SC(NH_2)_2$, $Sr_2Nb_2O_7$, Rb_2ZnCl_4, and $BaMnF_4$ and with phase fluctuations of this wave in K_2SeO_4—the latter result an especially interesting one in that it appears to be the first-ever observation of a phason in incommensurable-phase systems. A phason-type excitation has also been observed in $CsCuCl_3$ crystals with helicoidal commensurable structure modulation. This is still the only case in which an IR active soft mode has been observed in transitions in nonpolar point groups.

Thus, it can now already be stated that submillimeter dielectric spectroscopy has significantly advanced the experimental study of soft modes in ferroelectrics. The principal classical systems have been studied, general relationships have been traced in the longwave dynamics of crystal lattices, and the capabilities of dynamic phase-transition models have been analyzed on the basis of the data obtained. In most cases, the accumulated experimental material surpasses the level of the existing theoretical concepts.

At the same time, the problem range of soft-mode dielectric spectroscopy remains very broad, far exceeding the bounds of ferroelectricity. Apart from the familiar problems bearing on antiferromagnetism and superconductivity, we see good prospects for study of the dynamics of superionic conductors and crystals with metal-dielectric transitions. Here spectroscopic investigation may answer questions as to the nature of carrier motion, carrier effective mass, and the potential relief in the lattice. The capabilities of many experimental methods, including radio-frequency methods, are sharply limited in such systems with free carriers, and dielectric spectroscopy at submillimeter wavelengths acquires particular importance under these conditions.

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