N. N. Kristofel and P. I. Konsin. *The Vibronic Theory of Ferroelectricity.* The electron-phonon (vibron) interaction plays a significant role for many physical processes in solids and causes a number of striking effects. It now appears to be definite that the electron-phonon interaction is also the microscopic cause of the appearance of ferroelectric properties in dielectric and semiconductor crystals with phase transitions of the displacement type. This conclusion follows from a relatively new theory, the so-called vibron theory of ferroelectricity, which was developed in the USSR by the authors of the present communication (see, for example[1-3]) and by Bersuker *et al.* (see, for example, [4,5]).

In spite of the many theoretical studies, the microscopic causes of ferroelectricity remained unclear for a long time. The Ginzburg–Anderson–Cochrane theory indicated the existence in ferroelectrics of a soft phonon mode in which the crystal loses dynamic stability at the phase-transition point. The microscopic cause of the appearance of the soft mode was seen in cancellation of certain contributions of ion-ion interaction forces to the frequency of an active mode. Further improvements of the dynamic theory in the direction of more consistent allowance for phonon anharmonicity[6] merely assumed the presence of an imaginary bare (unrenormalized) active-mode frequency.

The question as to the decisive role of the vibronic interaction for the symmetry of the multinuclear skeleton of the physical system first arose in connection with the Jahn–Teller theorem.[7] This idea had originally been used in crystal physics to explain the anisotropic properties of impurity centers (see, for example, [8,9]). In the presence of electronic orbital degeneracy (or quasidegeneracy), the vibronic interaction leads here, as it were, to local phase transitions. Several authors[10-14] later posed the question of analysis of Jahn–Teller situations on the band states of the crystals. Spontaneous electrical polarization should arise in odd limiting optical vibrations of the crystal.

It was therefore natural to seek the cause of the ferroelectric transition in mixing of electron bands of opposite parity by odd active vibrations. This idea led to the creation of the vibron theory of ferroelectricity.

In this theory, a ferroelectric is described by the Hamiltonian

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_{ph} + \mathcal{H}_{e\text{-}ph} + \mathcal{H}_a, \tag{1}$$

which contains the electron-energy operator $\mathcal{H}_e$ of the valence band and conduction band, the harmonic phonon Hamiltonian $\mathcal{H}_{ph}$, the electron-phonon interaction $\mathcal{H}_{e\text{-}ph}$, and a term $\mathcal{H}_a$ describing the intrinsic phonon anharmonicity.

Disregarding the role of $\mathcal{H}_a$ for the time being (as is justified for narrow-gap systems) and allowing for the substantial renormalization of the electron energy spectrum by the vibron interaction $\mathcal{H}_{e\text{-}ph}$, the part of the system free energy that is active in the phase transition can be written

$$F(T, y_0) = -k_B T \sum_{\mathbf{k}} \ln \left\{ 2 \left[1 + \mathrm{ch} \left(\frac{1}{2k_B T} \sqrt{\Delta_{\mathbf{k}}^2 + \frac{4V^2}{N} y_0^2} \right) \right] \right\} + \frac{M\omega_0^2}{2} y_0^2; \tag{2}$$

where V is the constant of the interband vibronic interaction, $y_\mathbf{q}$ are the normal coordinates of the active branch of the vibrations, $\Delta_{\mathbf{k}} = \varepsilon_2(\mathbf{k}) - \varepsilon_1(\mathbf{k})$, and N is the number of unit cells.

It is clear from (2) that the vibronic interaction introduces an additional (vibronic) anharmonicity into the system. Concrete evaluation of (2) requires knowledge of the density of the bare electronic states of the crystal. An effective gap $\overline{\Delta} = \overline{\Delta}_{\mathbf{k}}$ can be introduced for narrow bands. Low-symmetry lattice distortion appears if the equation $\partial F(T, y_0)/\partial y_0 |_{y_{00}} = 0$ has a solution $y_{00}^2 > 0$ at $T > 0$. This solution, with the usual behavior of the order parameter $y_{00}(T)$ for a second-order phase transition, holds below the temperature

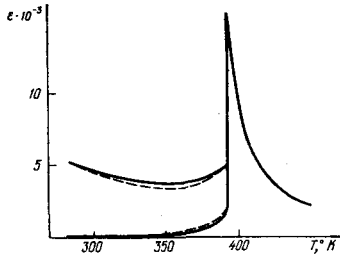$$k_B T_c = \frac{\overline{\Delta}}{4} (\mathrm{Arcth}\,\tau)^{-1}, \tag{3}$$

FIG. 1. Dielectric constant of $BaTiO_3$ as a function of temperature. The lower curve corresponds to the direction of spontaneous polarization in the tetragonal phase. The solid curves represent theory and the dashed curves experiment.

if the criterion

$$\tau = \frac{2V^2}{M\omega_0^2\overline{\Delta}} > 1 \tag{4}$$

is satisfied. The high-temperature phase, where $y_{00} = 0$, is stable above T_c. According to (4), the appearance of the phase transition promotes a strong interband vibronic interaction and significant bare deformability of the crystal in the active mode at a small energy $\overline{\Delta}$ of the bare electronic excitations. Similar conclusions are also obtained when the dispersion of the electron bands is taken consistently into account. [15–17]

What happens physically in the system is as follows. The vibronic interaction lowers the energy of the lower-band electrons and raises the energy of the upper-band electrons. If the resultant decrease in the energy of the electronic subsystem is larger than the priming value of the lattice potential energy for the active vibrations, the latter become soft. Spontaneous distortion of the lattice is caused by "freezing" of the ion shifts into the lattice, corresponding to the soft mode. As the temperature rises, the transfer of electrons into the upper band cancels these contributions at $T = T_c$, and the crystal completes the transition to the high-symmetry phase. Calculation of the composite branches of the system's electron-phonon excitations[1] indicates a significant temperature-dependent vibronic renormalization of the active-mode frequency. For example, the squared frequency of the soft mode in the high-symmetry phase is given by the following formula for narrow bands:

$$\Omega_c^2 = \omega_0^2 + \frac{2V^2}{M\overline{\Delta}}(f_2 - f_1). \tag{5}$$

where $f_{2,1}$ are the Fermi population numbers of the states with energies $\pm\overline{\Delta}/2$. Since $f_2 \leqslant f_1$, Ω_c decreases with temperature and vanishes at T_c. If the degeneracy of the active electron bands and vibrations is considered, the system may pass successively through low-symmetry phases with different symmetries, in which the frequency of the soft mode is split.

Active vibronic interaction leads also to an additional temperature dependence of the forbidden band in the electron spectrum. [18] External factors that change the latter (for example, a magnetic field) should also influence the ferroelectric characteristics of the sys-

tem. [15] In the limit as $\Delta \to 0$, the system is a semimetal. It can be shown that a semimetal-dielectric ferroelectric phase transition is possible in this case, since the interband vibronic interaction induces a non-zero energy gap in the system at the point T_c. [16,17] The semiconductor version of the vibronic theory explains the properties of the soft mode and of the permittivity of systems of the n-$Pb_{1-x}Sn_xTe$ type. [19,21]

However, the best-known class of ferroelectrics with a transition of the displacement type is composed of dielectric crystals of the $BaTiO_3$ type. Thermal transfers of electrons from the valence band to the conduction band do not occur here. Now it is necessary to take full account of the intrinsic phonon anharmonic interactions in the lattice. But the vibronic interaction continues to play a primary role even here, ensuring an imaginary value of the initial frequency of the active vibrational mode. [22]

The anharmonic interactions tend to stabilize the high-symmetry phase (like intraband scattering processes), and are the reason why the phase transition becomes a first-order transition.

The parameters of the corresponding variant of the vibronic theory were determined semiempirically for $BaTiO_3$ in[22]. Figures 1 and 2 show the theoretical and experimental temperature curves of the permittivity and electronic energy gap. The agreement between theory and experiment is good. The constant of the interband vibronic interaction was found to have a value normal for a dielectric, but the nonrenormalized frequency of the active vibration was anomalously low. This is essential if satisfaction of the necessary vibron phase transition criterion $\tau > 1$ is to be possible. Thus, the microscopic causes of ferroelectric properties in the $BaTiO_3$ class of crystals consists, roughly speaking, in the dynamic instability of the crystal induced by electron-phonon interaction when the crystal is highly deformable in a certain vibrational mode.

The vibronic theory gives a natural explanation of the effect of secondary-carrier concentration on the ferroelectric properties of the system. Application of the theoretically determined parameters to the case of $BaTiO_3$ yielded a quantitative explanation for the depression of the Curie point when the crystal is illuminated. [23] The influence of carriers of impurity origin on the ferroelectric properties of the system was also
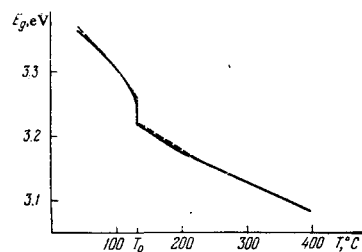

FIG. 2. Temperature dependence of forbidden band of $BaTiO_3$ with an absorption coefficient of 3000 cm^{-1}. The solid curve represents theory, the dashed curve experiment.
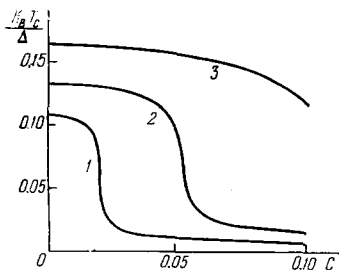
FIG. 3. Ferroelectric-semiconductor Curie point vs. concentration c of acceptors (0.005 eV from the band boundary, $\bar{\Delta} = 0.1$ eV) at $\tau = 1.02$ (1), 1.05 (2), and 1.1 (3).

studied.[24] This effect may be particularly distinct in semiconductors.[25]

Figure 3 shows curves of T_c plotted against acceptor concentration at various τ. Impurities also influence the shape of the temperature curves of the lattice distortion and the soft-mode frequency. If the impurity concentration is high enough to form an impurity band, its vibronic mixing with the base band may also result in ferroelectric ordering. A theory of ferroelectric $Ba_{1-x}Sr_xTiO_3$ solid solutions was developed in[26] on the basis of the vibronic theory.

In sum, we may state that the vibronic theory explains the basic laws known for ferroelectrics with displacement-type transitions from consistent premises.

A dynamic theory that is ideologically quite similar to the vibronic theory has also been developed for ferroelectrics with hydrogen bands; it is based on proton-phonon, proton-proton, and phonon-phonon interactions.[27,28]

There is now an urgent need to study the relation of ferroelectricity (and of structural transitions in general) to various kinds of electronic ordering, e.g., superconductivity. The vibronic theory evidently opens new prospects in this area.

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