Dielectric losses in displacive ferroelectrics

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A systematic theoretical analysis is made of the lattice loss in a displacive ferroelectric with a non-overdamped soft mode. Three main lattice-loss mechanisms are distinguished: quasi-Debye, three-quantum, and four-quantum. The physical nature of the mechanisms, their frequency and temperature dependence, and the order of magnitude of their contributions to the loss are all discussed. It is established that the pattern of lattice losses in a ferroelectric is qualitatively similar to that in an ordinary dielectric. In a number of cases the results obtained in this paper differ from those of previous theoretical studies both in terms of the temperature and frequency dependences and in the identification of the phonon processes responsible for the loss in each particular case. An analysis is made of the current experimental situation.

1. INTRODUCTION

The intrinsic dielectric losses in displacive ferroelectrics has been the subject of relatively few theoretical papers[1–4] (see also the book by Vaks[5]). As was shown by Balagurov, Vaks, and Shklovskiĭ,[3] outside the region of well-developed critical fluctuations the soft mode of a displacive ferroelectric should, generally speaking, be underdamped, i.e., the relative damping of the phonons of the soft mode should be much less than unity. Thus, in the region in which Landau theory applies to displacive ferroelectrics their phononic excitations are well defined, so that one can describe the intrinsic (lattice) losses with the aid of a perturbation theory in the lattice anharmonicity parameter. Such a "phononic" perturbation theory was used in Refs. 1–4. Although such a perturbation theory can give a systematic description of the dielectric loss, the authors of Refs. 1–4 used various auxiliary assumptions. The present paper gives a systematic theoretical analysis, free from *a priori* assumptions, of the intrinsic dielectric loss of a displacive ferroelectric outside the region of well-developed critical fluctuations. In a number of cases the results of this analysis differ from those of Refs. 1–4 both in the in temperature and frequency dependence of the dielectric loss tangent and in the identification of the phonon processes responsible for the loss in each particular case.

2. THE THREE MAIN LATTICE-LOSS MECHANISMS

From the standpoint of phonon kinetics there is no fundamental difference between displacive ferroelectrics with non-overdamped soft modes and ordinary dielectrics. For this reason our analysis need not rely solely on Refs. 1–4 but can also make use of the approach developed for ordinary dielectrics by Coombs and Cowley,[6] Gurevich,[7,8] and the present author[9,10] (see also the book[11] and review article[12] by Gurevich). The possibility of employing this approach for displacive ferroelectrics has been demonstrated by Gurevich and the present author.[10,13,14]

In discussing dielectric losses we shall always presume that the frequency ω of the electric field is much smaller than the limiting frequency ω_0 of the soft mode:

$$\omega \ll \omega_0. \tag{1}$$

It is this relation that is responsible for the most important features in the pattern of the dielectric losses. In fact, from a quantum-mechanical point of view the intrinsic losses reduce to interactions of the electric-field quanta with phonons. It seems quite natural that in a ferroelectric the most important interaction is with the long-wavelength phonons of the soft mode (it will be shown that this is in fact the case). Inequality (1) therefore shows that the characteristic energy of the phonons primarily responsible for the loss is much larger than the energy of the field quanta with which they are interacting. This energy spread makes it difficult to satisfy the conservation laws in processes involving the absorption of field quanta.[3] In such a complicated situation there are three most efficient means of absorption, which correspond to the three main lattice-loss mechanisms[120]: 1) three-quantum, 2) four-quantum, 3) quasi-Debye.

The three-quantum mechanism corresponds to field-quantum absorption processes involving two phonons having energy and quasimomentum conservation laws of the form

$$\Omega_j(\mathbf{q}) \pm \Omega_{j'}(\mathbf{q}') = \omega, \quad \mathbf{q} \pm \mathbf{q}' = 0, \tag{2}$$

where $\Omega_j(\mathbf{q})$ is the frequency of a phonon on branch j with wave vector $\mathbf{q}$.

The four-quantum mechanism corresponds to processes involving three phonons with conservation laws

$$\Omega_j(\mathbf{q}) \pm \Omega_{j'}(\mathbf{q}') \pm \Omega_{j''}(\mathbf{q}'') = \omega, \quad \mathbf{q} \pm \mathbf{q}' \pm \mathbf{q}'' = \mathbf{b}, \tag{3}$$

where $\mathbf{b}$ is a reciprocal lattice vector. The four-quantum processes correspond to the next (in comparison with the three-quantum processes) order of smallness in the lattice anharmonicity parameter, and so one can expect that the contribution to the dielectric loss from these processes will be parametrically small in comparison with the contribution from the three-quantum processes. However, the restrictions imposed on the participating phonons by conservation laws (3) are much less stringent than those imposed by (2). This circumstance diminishes the difference between the

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three- and four-quantum contributions and can even render them comparable.[1)]

These two mechanisms are the only intrinsic loss mechanisms in a centrosymmetric ferroelectric. Thus, because ferroelectrics of the displacive type are usually centrosymmetric in the paraphase, the intrinsic loss in the paraphase should be described by the three- and four-quantum contributions. In the ferrophase, however, where the center of inversion is lost, the extremely powerful quasi-Debye loss mechanism, which is present only in non-centrosymmetric crystals, also comes into play. This quasi-Debye loss derives from the relaxation of the phonon distribution function, which has been thrown out of equilibrium by the alternating electric field.[6,7]

3. THEORETICAL DESCRIPTION OF THE MAIN LOSS MECHANISMS

Following Gurevich,[7] we describe the interaction of the electric field **E** with the phonon gas of the crystal with the aid of the electrophonon potential $\Lambda^{jj'}(\mathbf{q})$, i.e., we write the linear field term H_E of the Hamiltonian in the form

$$H_E=\frac{\hbar}{2}\sum_{jj'\mathbf{q}}[\Omega_j(\mathbf{q})\Omega_{j'}(\mathbf{q})]^{1/2}\Lambda^{jj'}(\mathbf{q})E\hat{\xi}^{j}_{\mathbf{q}}\hat{\xi}^{j'}_{-\mathbf{q}}, \tag{4}$$

where $\hat{\xi}^{j}_{\mathbf{q}}=a^{+}_{\mathbf{q}j}+a_{-\mathbf{q}j}$ is the operator for the normal phonon coordinates, and a and a^{+} are the phonon creation and annihilation operators, respectively. Using (4), one can straightforwardly ascertain that the relative change in the phonon frequencies is expressed in terms of the diagonal components of Λ:

$$\Delta\Omega_j(\mathbf{q})/\Omega_j(\mathbf{q})=\Lambda^{jj}(\mathbf{q})\mathbf{E}. \tag{5}$$

The off-diagonal components are responsible for transitions between different branches of the phonon spectrum under the action of the alternating electric field.

a. Three-quantum losses

We shall assume that only the association contribution [the minus sign in formulas (2)] is actually important in ferroelectrics.[2)] The qualitative description of the three-quantum loss in the previous section of this paper literally corresponds to a calculation in first order of the usual quantum-mechanical perturbation theory in the lattice anharmonicity parameter.[3,7] Such a calculation does not take into account the finiteness of the phonon lifetime τ and is therefore valid only for sufficiently high field frequencies $\omega\gg\Gamma\equiv1/\tau$. To describe the loss for an arbitrary relationship between ω and Γ one must treat the problem in terms of the equation for the off-diagonal (in the spectral branches) components of the density matrix. The present author has shown[9] that the contribution to the imaginary part η of the dielectric constant in this case is given by the relation

$$\eta^{(3)}_{\alpha\beta}=\frac{4\pi\omega\hbar^2}{T}\sum_{j\neq j'}\int\frac{d^3q}{(2\pi)^3}\Omega_j(\mathbf{q})\Omega_{j'}(\mathbf{q})\Lambda^{jj'}_{\alpha}(\mathbf{q})\Lambda^{*jj'}_{\beta}(\mathbf{q})\frac{2\Gamma\bar{N}(\bar{N}+1)}{(\omega+\Delta_{jj'})^2+4\Gamma^2}, \tag{6}$$

$$\Delta_{jj'}=\Omega_j(\mathbf{q})-\Omega_{j'}(\mathbf{q}),\qquad \Gamma=\frac{1}{2}(\Gamma_{\mathbf{q}j}+\Gamma_{\mathbf{q}j'}),$$

$$\bar{N}=N\left(\frac{\Omega_j+\Omega_{j'}}{2}\right),\qquad N(x)=(e^{\hbar x/T}-1)^{-1},$$

where T is the temperature in energy units and $\Gamma_{\mathbf{q}j}$ is the damping of a phonon of frequency $\Omega_{\mathbf{q}j}$. The physical meaning of this formula is extremely simple: It takes into account that when phonons with a finite damping are involved in three-quantum processes, the energy conservation law (2) should be satisfied only to an accuracy of order $\hbar\Gamma$. That is, in order for the three-quantum process to be possible, the phonon branches must converge to the extent that $|\Delta_{jj'}|\sim\max[\omega,\Gamma]$. Formula (6) is valid under the condition that the main contribution to the integral comes from the region $|\Delta_{jj'}|\lesssim\max[\omega,\Gamma]$. In the opposite case, however, there is no point in considering the three-quantum losses, since they cannot compete with the other lattice-loss mechanisms.[9] Thus the three-quantum losses are described completely by formula (6) in its region of applicability.

b. Four-quantum losses

The qualitative description of the four-quantum losses in the previous section literally corresponds to a treatment in the second order of perturbation theory in the lattice anharmonicity parameter.[3] Because the conservation laws for four-quantum processes impose considerably weaker restrictions on the participating phonons than in the three-quantum case, allowance for the fact that interactions of damped phonons need to conserve energy only to within $\hbar\Gamma$ leads to only an insignificant change in the absorption. Therefore, for describing four-quantum losses it is sufficient to use ordinary second-order perturbation theory. The four-quantum losses have been analyzed in detail for the case of a centrosymmetric crystal by Balagurov, Vaks, and Shklovskiĭ.[3] The expression which they obtained is rather awkward and contains several terms which are, generally speaking, of the same order and have identical frequency and temperature dependences. Since we only intend to analyze the temperature and frequency dependence and make order-of-magnitude estimates of η, let us give just one of the terms in our notation[9]:

$$\eta^{(4)}_{\alpha\beta}=\frac{4\pi\hbar^2\omega}{T}\sum_{j\neq j'}\int\frac{d^3q}{(2\pi)^3}\Omega_j(\mathbf{q})\Omega_{j'}(\mathbf{q})\Lambda^{jj'}_{\alpha}(\mathbf{q})\times\Lambda^{*jj'}_{\beta}(\mathbf{q})\frac{N^j(N^j+1)\cdot4\Omega_j^2(\mathbf{q})\Gamma_{\mathbf{q}j}(\Omega_{j'})}{[\Omega_j^2-\Omega_{j'}^2]^2}, \tag{7}$$

where $N^j\equiv N(\Omega_j)$, and $\Gamma_{qj}(\Omega)$ is the imaginary part of the phonon mass operator to lowest order in the anharmonicity; the summation is over branches which do not have mutual points of degeneracy. The most important feature of the four-quantum contribution is that, unlike the three-quantum case, it is accumulated relatively uniformly over the space of wave vectors (**k** space). This fact is a consequence of the weakness of the restrictions imposed by conservation laws (3) in comparison with (2), even when the finiteness of the phonon lifetime is taken into account in the latter.

In the case of noncentrosymmetric crystals, a calcula-

tion to second order in the anharmonicity yields terms with a substantially different frequency dependence in addition to those considered in Ref. 3. As was shown in Ref. 11, the contribution of these terms is already included in that of the quasi-Debye mechanism.

c. Quasi-Debye loss

The simplest quantitative treatment of the quasi-Debye loss consists of solving the kinetic equation for the phonon distribution function for the case of a phonon spectrum which is a periodic function of time.[7,13] In the general case the problem cannot be solved in quadratures. Let us give the expression obtained for the quasi-Debye contribution to the imaginary part of the dielectric constant in the relaxation-time approximation, which is accurate enough for our subsequent analysis[7]:

$$\eta_{\alpha\beta}^{(q)}=\frac{4\pi\hbar^2\omega}{T}\sum_j\int\frac{d^3q}{(2\pi)^3}\Omega_j^2(\mathbf{q})\Lambda_\alpha^{jj}(\mathbf{q})\Lambda_\beta^{jj}(\mathbf{q})\frac{\Gamma_{\mathbf{q}j}N^j(N^j+1)}{\omega^2+\Gamma_{\mathbf{q}j}^2}. \quad (8)$$

We note that formally relations (7) and (8) can be regarded as particular cases of (6), but without the restriction on the summation over the branches. This corresponds to a qualitative interpretation of all three mechanisms from a unified point of view in the language of field-quantum absorption processes involving two phonons having a finite damping.

The three-quantum loss corresponds to transitions between states of different branches in a small region of **k** space where these branches either approach one another to the extent that the energy gap satisfies $|\Delta|_{jj'}\sim\omega$ or else substantially overlap on account of their natural widths Γ.

The four-quantum loss corresponds to transitions which go between states of different branches and are quite uniform over **k** space, since all the branches overlap to some degree at any point in **k** space.

The quasi-Debye loss corresponds to transitions which go between states of the same branch on account of its finite width Γ.

4. THE ELECTROPHONON POTENTIAL OF A FERROELECTRIC

To calculate the lattice loss of a ferroelectric one must know the electrophonon potential at least for the long-wavelength part of the soft mode and the acoustic branches; the significance of the interaction of the field with these parts of the branches was shown by Balagurov, Vaks, and Shklovskiĭ.[3] In what follows we shall discuss the temperature and frequency dependence and the order of magnitude of the observable effects. We shall therefore need only rough estimates of Λ. The formal derivation of these estimates on the basis of the relations between the electrophonon potential and the anharmonicity of the third-order force constants is given in Appendix 2. However, it is useful to obtain these estimates on a qualitative level in order to clearly demonstrate the reasons why the electrophonon potential in displacive ferroelectrics is large in comparison with its characteristic values in ordinary dielectrics.

According to Gurevich,[7] in an ordinary noncentrosymmetric dielectric all the components of Λ can be estimated as

$$|\Lambda^{jj'}(\mathbf{q})|\sim 1/\rho^{1/2}w, \quad (9)$$

where w is the average sound velocity and ρ is the density of the crystal. In centrosymmetric crystals the diagonal components of Λ are identically zero, and the off-diagonal components obey

$$|\Lambda^{jj'}(\mathbf{q})|\sim aq/\rho^{1/2}w, \quad (10)$$

where a is the average interatomic distance.

In a ferroelectrics as a polar crystal the effectivenesss of the interaction of an electric field with its lattice is characterized not by the value of the macroscopic field E, but by the polarization it induces, $P=\chi E$, where χ is the lattice susceptibility. Therefore, for all the phonon branches of a ferroelectric the electrophonon potential should be larger by roughly a factor of χ than in an ordinary dielectric. Thus, in a centrosymmetric paraphase the off-diagonal components of Λ for the noncritical branches are given not by (10) but by

$$|\Lambda^{jj'}(\mathbf{q})|\sim\chi aq/\rho^{1/2}w. \quad (11)$$

Below the transition one should take it into account that the spontaneous polarization P_s is small compared to the atomic polarization $P_a\sim e/a^2$, where e is the electron charge. The phenomenological theory of second-order phase transitions[16] implies that $P_a^2/P_s^2\sim\chi$ (for first-order phase transitions which are nearly second-order, we shall for simplicity use this same estimate). Considering that the "noncentrosymmetric" properties in the ferrophase arise in proportion to P_s, we have the following relations for the noncritical branches in the ferrophase:

$$|\Lambda^{jj'}(\mathbf{q})|\sim\frac{\chi}{\rho^{1/2}w}\frac{P_s}{P_a}=\frac{\chi^{1/2}}{\rho^{1/2}w}, \quad j=j',$$

$$|\Lambda^{jj'}(\mathbf{q})|\sim\frac{\chi}{\rho^{1/2}w}(qa+\chi^{-1/2}), \quad j\neq j'. \quad (12)$$

If the interaction with the electric field involves phonons of the soft mode, the electrophonon potential potential becomes still larger. For the off-diagonal components $\Lambda^{jj'}$, where j and j' are branches of the soft mode, the estimate

$$|\Lambda^{jj'}(\mathbf{q})|\sim\chi\frac{qa}{\rho^{1/2}w}\frac{\omega_D^2}{\Omega_j(\mathbf{q})\Omega_{j'}(\mathbf{q})} \quad (13)$$

where ω_D is the Debye frequency, is valid above the transition, while below the transition one has

$$|\Lambda^{jj'}(\mathbf{q})|\sim\frac{\chi}{\rho^{1/2}w}\frac{\omega_D^2}{\Omega_j(\mathbf{q})\Omega_{j'}(\mathbf{q})}(qa+\chi^{-1/2}). \quad (14)$$

For the diagonal components below the transition we have

$$|\Lambda^{jj}(\mathbf{q})|\sim\frac{\chi^{1/2}}{\rho^{1/2}w}\frac{\omega_D^2}{\Omega_j^2(\mathbf{q})}. \quad (15)$$

If one of the branches j and j' is the soft mode, while the second is an acoustic mode, then estimate (13) is valid both above and below the transition. The reason for the additional large factor in these last estimates is most simply explained for the example of the diagonal components of Λ. According

to (5), the magnitude of a diagonal component is characterized by the relative shift of the phonon frequency under the action of the field. It is easy to verify that the additional factor in (15) [as compared to (12)] makes for absolute values of the same order of magnitude for the shifts of the square frequencies of the soft mode and of an ordinary "stiff" optical branch with a frequency of the order of ω_D. This means that the changes of the corresponding "harmonic stiffnesses" are the same. This should obviously be the case, since for a soft mode only the harmonic stiffness is anomalously small, while the anharmonic properties for all the optical branches are quite similar.[5] In particular, upon a distortion of the lattice the harmonic stiffness should generally speaking be of the same order for all the optical branches.

In regard to the estimates obtained above it is important to note the following. As is the case for (9) and (10), these estimates are generally speaking valid only for accidental positions of the wave vector $\mathbf{q}$. Near the high-symmetry points of the Brillouin zone additional small factors can arise in estimates (9)–(15). These factors are not substantially different for a ferroelectric and for an ordinary dielectric, and a detailed analysis of them can be found in Refs. 3, 7, and 11.

5. SPECIFICS OF THE LATTICE LOSS IN DISPLACIVE FERROELECTRICS

The relations given above permit one to analyze the lattice loss in any displacive ferroelectric at temperatures not too close to the transition, where the soft mode is not yet overdamped. Let us consider only cubic and centrosymmetric (in the paraphase) crystals, since the majority of displacive ferroelectrics are of this type.

Let us illustrate the specific features of the loss in a ferroelectric by comparing the losses in an ordinary dielectric for temperatures above the Debye temperature ($T \geqslant \hbar\omega_D$) and in a ferroelectric of the same symmetry for temperatures at which the phonons of the soft mode are thermally excited ($T \gtrsim \hbar\omega_0$). Under such conditions in an ordinary dielectric the most important processes contributing to all the loss mechanisms are those involving thermal phonons,[7] i.e., phonons with frequencies of the order of ω_D. In a ferroelectric the processes involving long-wavelength phonons of the soft mode (with frequencies of order ω_0 and qa of order $\chi^{-1/2}$) turn out to be the most important, even if such phonons are deeply subthermal. This is immediately explained in the calculation and is a consequence of the growth of expressions (13)–(15) as $q \to 0$. Using (6)–(8) and (13)–(15) and bearing in mind the remark from the previous section, we obtain the contributions to the dielectric loss tangent $\operatorname{tg}\delta = \eta/\varepsilon$, where ε is the dielectric constant. For the contribution of the three-quantum loss we have

$$\operatorname{tg}\delta^{(3)} \sim \xi \frac{\omega\Gamma_0}{\omega_0^2}\left[\ln\frac{\omega_0^2}{\omega^2+4\Gamma_0^2}+\frac{\omega}{\Gamma_0}\operatorname{arctg}\frac{\omega}{2\Gamma_0}\right]n_0, \quad (16)$$

where $\xi = T\sqrt{\chi}/Mw^2$ is the correlation parameter, M is the average mass of the crystal atoms, and Γ_0 is the damping of the long-wavelength phonons of the soft mode. The three-quantum processes whose contribution is given by (16) occur either close to the symmetry-degeneracy lines of the soft-mode branches (as transverse vibrational branches they are degenerate in the directions of the symmetry axes C_3 and C_4 of the Brillouin zone[17]) or close to the accidental-degeneracy lines of the longitudinal acoustic branch and the soft mode. The governing contributions are that from the lines of symmetry degeneracy, which lie at appreciable angles to the direction of the measuring electric field, and that from the lines of accidental degeneracy.[13] In formula (16) n_0 is the total number of these lines. For the four-quantum loss we have

$$\operatorname{tg}\delta^{(4)} \sim \xi \frac{\omega\Gamma_0}{\omega_0^2}\left[\frac{m_0(m_0-1)}{2}+3m_0\right], \quad (17)$$

where m_0 is the number of soft-mode branches. The last factor is the number of possible binary combinations involving the soft mode for the low-lying branches of the long-wavelength part of the spectrum. The presence of this factor in the formula logically corresponds to the qualitative description of the four-quantum loss at the end of Sec. 3. For the quasi-Debye loss in the ferrophase we have

$$\operatorname{tg}\delta^{(q)} \sim \xi \frac{\omega\Gamma_0}{\omega^2+\Gamma_0^2} m_0. \quad (18)$$

Further analysis will require an estimate of the damping Γ_0 of long-wavelength phonons of the soft mode in displacive ferroelectrics. A systematic microscopic calculation[3] of the damping contributions from three-quantum ($\Gamma_0^{(3)}$) and four-quantum ($\Gamma_0^{(4)}$) collisions gives the order-of-magnitude estimates (in our notation)

$$\Gamma_0^{(3)} \sim \xi\omega_0, \qquad \Gamma_0^{(4)} \sim \xi^2\omega_0. \quad (19)$$

It is seen from (19) that the condition of a non-overdamped soft mode requires $\xi \ll 1$. Therefore, one can maintain consistency in the theory of a weakly anharmonic crystal without including the contribution to the soft-mode damping from four-quantum processes, i.e., one can take $\Gamma_0 \sim \Gamma_0^{(3)}$.

For comparison, let us give the analogous estimates[7,9] for an ordinary dielectric at $T \gtrsim \hbar\omega_D$:

$$\operatorname{tg}\delta^{(3)} \sim \mu \frac{\omega\Gamma}{\omega_D^2}\left[\ln\frac{\omega_D^2}{\omega^2+4\Gamma^2}+\frac{\omega}{\Gamma}\operatorname{arctg}\frac{\omega}{2\Gamma}\right]n, \quad (20)$$

$$\operatorname{tg}\delta^{(4)} \sim \mu \frac{\omega\Gamma}{\omega_D^2}\frac{m(m-1)}{2}, \quad (21)$$

$$\operatorname{tg}\delta^{(q)} \sim \mu \frac{\omega\Gamma}{\omega^2+\Gamma^2} m, \quad (22)$$

where $\mu = T/Mw^2$ is the lattice anharmonicity parameter, m is the number of branches in the phonon spectrum, n the number of degeneracy lines of the phonon spectrum that are important in the loss, and Γ is the damping of the thermal phonons (according to Ref. 7, $\Gamma \sim \mu\omega_D$). We note that the absolute magnitudes of the dampings Γ and Γ_0 are of the same order (if it is taken into account that $\omega_0 \sim \omega_D/\sqrt{\chi}$, the estimates for Γ and Γ_0 coincide).

Comparing the formulas for the contributions of the lattice-loss mechanisms [(20) with (16), (21) with (17), and (22) with (18)] and the formulas for the damping, we see that they are similar to within numerical factors in the sense of replacing the anharmonicity parameter μ by the correlation parameter $\xi = \mu\sqrt{\chi}$ and the Debye frequency ω_D by the limiting soft-mode frequency $\omega_0 \sim \omega_D/\sqrt{\chi}$. The conditions

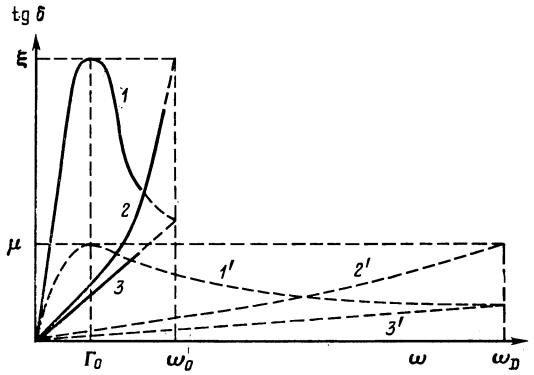

FIG. 1. Schematic comparison of the contributions to tan δ as functions of the frequency ω of the measuring field for a linear dielectric (dashed curves) and for a displacive ferroelectric with a non-overdamped soft mode (solid curves): 1,1') the quasi-Debye contribution; 2,2') the three-quantum contribution; 3,3') the four-quantum contribution. The temperature is assumed to be such that the lowest optical branch is thermally excited.

on the temperatures at which the formulas apply are also similar: $T \gtrsim \hbar\omega_D$ and $T \gtrsim \hbar\omega_0$.

The frequency dependences of the contributions from the lattice-loss mechanisms in a ferroelectric are similar in this same sense to those of the analogous mechanisms in a dielectric. The changes in the frequency dependences in going from an ordinary dielectric to a ferroelectric are shown in Fig. 1. It is seen that in going to the ferroelectric the contributions of all the mechanisms grow larger. The frequency dependences of the contributions of the main lattice-loss mechanisms have the following characteristic features:

1) The quasi-Debye loss reaches its maximum at $\omega \sim \Gamma_0$, with a value of $\max[\operatorname{tg} \delta^{(q)}] \sim \xi$ of the same order as that which would be reached by the three-quantum loss for [3] $\omega \to \omega_0$;

2) For $\omega < \Gamma_0$ all the mechanisms have a linear frequency dependence;

3) For $\omega \lesssim \Gamma_0$ the three-quantum contribution is larger than the four-quantum by an insignificant factor $(\ln \xi^{-2})$;

4) For $\omega \lesssim \Gamma_0$ the quasi-Debye contribution is larger than the other two contributions by a substantial factor (ξ^{-2});

5) For $\omega \gg \Gamma_0$ the three-quantum contribution grows quadratically with frequency while the quasi-Debye contribution falls off, becoming comparable to the linearly increasing four-quantum contribution in the limit $\omega \to \omega_0$.

Because the scale factor $\sqrt{\chi}$ does not contain the temperature explicitly, in going from an ordinary dielectric to a ferroelectric the form of the explicit functions of temperature should remain the same. For $\omega \gg \Gamma_0$ the quasi-Debye and four-quantum contributions are proportional to T^2, while the three-quantum contribution is proportional to T; for $\omega \ll \Gamma_0$ the three- and four-quantum contributions are proportional to T^2, while the quasi-Debye contribution has no explicit temperature dependence.[8,9] On the other hand, because of this scale factor the contributions exhibit critical (implicit) temperature dependences corresponding to the $\chi^{1/2}$ for the quasi-Debye mechanism and $\chi^{3/2}$ for the three- and four-quantum contributions. Therefore, above the transition, where the quasi-Debye mechanism does not operate, the temperature anomaly of tan δ corresponds to $\chi^{3/2}$. Below the transition the loss is governed by the Debye mechanism over practically the entire frequency range $(\omega \ll \omega_0 \xi^{1/3})$, and so the anomaly of tan δ corresponds to[4)] that of $\chi^{1/2}$.

Let us conclude this section by comparing our results with those of the earlier theoretical studies.[3,4]

Balagurov, Vaks, and Shklovskiĭ made the first detailed study[3] of the losses in the paraphase of a centrosymmetric cubic ferroelectric of the displacive type. We have used their results to describe the four-quantum loss. In considering the three-quantum loss they used single-particle perturbation theory, and so, strictly speaking, their results are valid only for $\omega \gg \Gamma_0$. Furthermore, the anisotropy of the phonon spectrum was neglected in that calculation,[3] so that the soft-mode branches were assumed degenerate over all of **k** space, while the lines of accidental degeneracy of the acoustic modes and the soft mode merge into a sphere. Because the three-quantum loss is extremely sensitive to the properties of the set of degeneracy points of the spectrum, it is natural that the estimate obtained in Ref. 3 for the three-quantum contribution does not agree with ours even for $\omega \gg \Gamma_0$. We note that the contribution due to the lines of degeneracy of the noncritical branches was discussed in Ref. 3 but was regarded as small and neglected. In our treatment this contribution is also small. The three-quantum contributions which we have taken into account correspond to degeneracy lines involving the soft mode.

Coombs and Cowley[44] considered the intrinsic dielectric loss is a ferroelectric both above and below the transition for arbitrary frequencies of the electric field. They were probably the first to point out the existence of the quasi-Debye loss mechanism in the ferrophase. However, their result for the quasi-Debye contribution to tan δ has the wrong temperature dependence (it was not taken into account that the contribution is governed by the interaction of the field with soft-mode phonons, for which $qa \approx \chi^{-1/2}$, and not with thermal phonons). Their result for the loss in the paraelectric phase corresponds to the simple oscillator model and gives $\tan \delta \propto \omega \chi T$ for $\omega \ll \omega_0$. According to our conclusions, such a combination of temperature and frequency dependences cannot occur in a cubic ferroelectric. Let us clarify the reason for the discrepancy in the results. In Ref. 4 the loss was expressed in terms of the Green function for the soft mode, with the imaginary part of the mass operator (the damping) assumed frequency independent and equal to its value on the mass surface. In the present problem the dispersion of the damping is generally large, and the neglect of this dispersion is the cause of the discrepancy in the results. In fact, everything we have done in this paper corresponds precisely to evaluating the frequency dispersion of the soft-mode damping at $\omega \ll \omega_0$.

6. COMPARISON WITH EXPERIMENT

The lattice loss should be most clearly manifested in the ferroelectric phase, where it is governed by the quasi-Debye mechanism. The loss reaches a maximum at frequencies in the range from tens to hundreds of gigahertz, with the con-

tribution to tan δ at the maximum being of the order of the correlation parameter ξ, i.e., the loss can easily reach values of the order of 0.1. Unfortunately, to the author's knowledge there have been no experiments done on the losses in the microwave and hundred-millimeter ranges in the ferrophase of a displacive ferroelectric with a non-overdamped soft mode, although lead titanate and lithium tantalate would be entirely suitable objects for such a study. Of the displacive ferroelectrics having a non-overdamped and non-frozen soft mode, there are reliable data apparently only for centrosymmetric strontium titanate in the microwave region.[18,19]

According to the data of Ref. 18, at $T = 78$–360 K and $\omega = 3$–72 GHz the frequency dependence of tan δ is linear, while the temperature dependence is a curve with a minimum at $T \approx 140$ K; at $T = 90$ K and $\omega = 22$ GHz one has $\tan\delta = 1.16 \cdot 10^{-3}$.

From the standpoint of the theory proposed above, in cubic noncentrosymmetric strontium titanate only the three-quantum (16) and four-quantum (17) losses are present. At frequencies smaller than the soft-mode damping Γ_0 (with $\Gamma_0 \lesssim 100$ GHz)[5] these two mechanisms have the same frequency and temperature dependence. The frequency dependence is linear, while the temperature dependence for $T > 80$ K is given by the formula $T^2/(T-T_0)^{3/2}$, where $T_0 = 37$ K. It has a minimum at $T_m = 4T_0 = 148$ K. As is seen from (16) and (17), the contributions for $\omega \ll \Gamma_0$ do not differ parametrically, but the large number of degeneracy lines ($n_0 \gtrsim 12$) and the logarithmic factor favor the three-quantum contribution:

$$\operatorname{tg}\delta = \operatorname{tg}\delta^{(3)} + \operatorname{tg}\delta^{(4)} \sim \xi^2 \frac{\omega}{\omega_0}\left[5n_0 + \frac{m_0(m_0-1)}{2} + 3m_0\right] = \xi^2 \frac{\omega}{\omega_0}\,[60+7]. \qquad (23)$$

Here it is taken into account that the soft mode has two branches ($m_0 = 2$). At $T = 90$ K and $\omega = 22$ GHz, with $\xi = 0.07$ and $\omega_0 = 1300$ GHz (Ref. 5), we obtain from (23) the rough order-of-magnitude estimate $\tan\delta \chi 5 \cdot 10^{-3}$.

The agreement between theory and experiment is thus rather fair: The frequency dependence and the shape of the temperature dependence (including the position of the minimum) are described correctly, and the theory gives the necessary order of magnitude of the loss (see Fig. 2). It must be stressed, however, that the available experimental data are insufficient for a serious experimental check of the theory. For example, it cannot be established whether or not the absorption is actually due to the neighborhoods of the degeneracy lines in the spectrum, since for $\omega \ll \Gamma_0$ it is impossible to distinguish the three- and four-quantum losses. The elucidation of this question will require higher-frequency measurements or measurements in the presence of a weak bias field.[13]

7. CONCLUSION

We have studied the lattice loss in a displacive ferroelectric outside the region of well-developed fluctuations. We have derived or adduced relations which describe the loss in any crystal of this type. We have analyzed in detail the case of ferroelectrics having a cubic paraphase. We have established that under conditions corresponding to thermal excitation of soft-mode phonons the pattern of lattice losses in a ferroelectric of this sort is qualitatively similar to that in an ordinary dielectric (of the same symmetry and above the Debye temperature) in the sense that the relations for estimating the contributions of the three main lattice-loss mechanisms in the former can be obtained from the corresponding relations for the latter by replacing the anharmonicity parameter μ by the correlation parameter $\xi = \mu\sqrt{\chi}$ and the Debye frequency ω_D by the soft-mode frequency $\omega_0 \sim \omega_D/\sqrt{\chi}$. The temperature and frequency dependences which we have obtained do not agree at any temperatures or frequencies with the result obtained in the simple oscillator model[16] or in a phenomenological treatment. We have obtained the critical exponents (in the region where Landau theory applies) for tan δ above and below the transition. These also disagree with a simple phenomenological treatment. Reasonable agreement is found with the available experimental data, but in the opinion of the author the existing experimental data are seriously inadequate for a rigorous check of the theory. Judging from the estimates, however, most of the predictions of the theory are completley amenable to verification by present-day experimental techniques.

Experimental research on the lattice loss is also urgent from the standpoint of checking the very concept of a displacive ferroelectric. It is well known that the displacive-ferroelectric model gives a fully satisfactory description of the thermodynamic properties.[5] We note, however, that a value of the Curie-Weiss constant of the order of 10^5 K can be reconciled with reasonable values of the transition temperature only at ordinary values of the anharmonicity coefficients. In this sense a displacive ferroelectric must be a weakly anharmonic cyrstal,[5] so that outside the region of well-developed fluctuations (i.e., for $\xi \ll 1$) the entire phonon spectrum should consist of weakly damped phonons. At this level a marked discrepancy appears: Although displacive ferroelectrics with overdamped soft modes are commonplace, there is still no reliable experimental evidence in support of their scaling behavior.[16] Outwardly it looks as if the

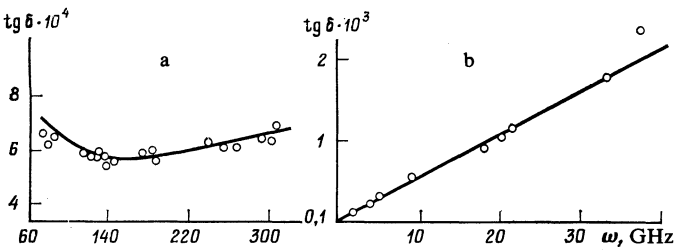

FIG. 2. (a) Temperature dependence of tan δ for strontium titanate at a field frequency of 9 GHz; b) frequency dependence of tan δ for the same material at a temperature of 140 K. The points are the experimental data of Ref. 18. The solid curves are theoretical (the three-quantum loss): $\tan\delta \propto \omega T^2(T-T_0)^{-3/2}$ ($\omega < 100$ GHz, $T > 80$ K, $T_0 = 37$ K). The theoretical position of the minimum is $T_m = 4T_0 = 148$ K.

model which describes the thermodynamic properties fails to describe the kinetic properties, and this would indicate an inherent contradiction in the concept of a displacive ferroelectric. In such a situation it is extremely important to do an experimental check on the results of a systematic theoretical analysis of the kinetic properties. The author believes that the theory presented here for the dielectric loss, with its many qualitative predictions, will provide such a possibility.

The experimental study of the three-quantum loss in a displacive ferroelectric is also of interest in regard to the basic concepts of phonon kinetics. The point is that the three-quantum loss mechanism in the "hydrodynamic" regime (for $\omega \lesssim \Gamma_0$) corresponds to a rather peculiar phonon kinetics. This is the only phonon system known to the author wherein the kinetic coefficient in the hydrodynamic regime governs the relaxation of the off-diagonal (in the branches of the spectrum) components of the single-particle density matrix. The experimental observation of this type of kinetics would certainly be of interest.

APPENDIX 1

Lattice loss in a ferroelectric with a "frozen" soft mode

For $T \ll \hbar\omega_0$ the number of thermally excited soft-mode phonons is exponentially small, and so the processes involving these phonons give an exponentially small contribution to the loss. At these low temperatures the contribution from the interaction with the acoustic modes is small in a power-law sense.[7] Therefore, in the presence of a frozen soft mode one should generally expect a substantial decrease in the lattice loss, so that one would hardly expect that at $T \ll \hbar\omega_0$ the lattice loss would be important in the overall balance. In such a situation a detailed theoretical analysis of the lattice loss is unwarranted, and we shall limit ourselves to an estimate of the lattice loss in the cubic virtual ferroelectrics $SrTiO_3$ and $KTaO_3$ at liquid-helium temperatures, in view of the considerable experimental interest in this question.[20–22]

As was mentioned earlier, the main loss mechanism in a cubic centrosymmetric crystal is the three-quantum mechanism. At liquid-helium temperatures there are two contributions that must be discussed: the exponentially small contribution from the neighborhoods of the lines of degeneracy of the soft-mode branches, and the contribution, small in a power-law sense, from the neighborhoods of the degeneracy of the transverse acoustic branches. Vaks[5] has estimated that in these materials at $T \sim \hbar\omega_0 \approx 30$–$40$ K the damping of the long-wavelength phonons of the soft mode is $\Gamma_0 \sim 10$ GHz. For $T < \hbar\omega_0$ the damping Γ_0 falls off very rapidly with cooling,[5] so that at liquid-helium temperatures the $\omega \gg \Gamma_0$ regime is realized in the microwave region. For the interaction with the acoustic modes, as the simplest of estimates shows, such a regime is realized with a large margin of safety. Using (6), (13), and (11) and recognizing that $\omega \gg \Gamma_0$, we have for the contributions from the interaction with the soft mode

$$\operatorname{tg}\delta^{M} \sim \xi\left(\frac{\omega}{\omega_0}\right)^2 n_0\left[10\left(\frac{T}{\hbar\omega_0}\right)^{1/2} e^{-\hbar\omega_0/T}\right] \sim \frac{\hbar\omega_D}{Mw^2}\cdot 10 n_0\left(\frac{\omega}{\omega_0}\right)^2\left(\frac{T}{\hbar\omega_0}\right)^{1/2} e^{-\hbar\omega_0/T} \tag{24}$$

(the factor in square brackets arises in going from $T \sim \hbar\omega_0$ to $T \ll \hbar\omega_0$) and from the interaction with the acoustic modes

$$\operatorname{tg}\delta^{a} \sim \chi\mu\left(\frac{T}{\hbar\omega_D}\right)^3\left(\frac{\omega}{\omega_D}\right)^2 n \sim \frac{\hbar\omega_D}{Mw^2}\frac{n}{\chi^2}\left(\frac{\omega}{\omega_0}\right)^2\left(\frac{T}{\hbar\omega_0}\right)^4. \tag{25}$$

Let us make a numerical estimate of the contributions for $T = 5$ K and $\omega = 20$ GHz. Let us take into account only the contributions of the symmetry degeneracy lines; then[9] $n_0 = n = 12$. We take the anharmonicity parameter at the Debye temperature, $\hbar\omega_D/Mw^2$, to be 10^{-2}. For $SrTiO_3$ we have $\hbar\omega_0 = 23$ K and $\chi = 800$, and for $KTaO_3$ we have $\hbar\omega_0 = 36$ K and $\chi = 200$ (Ref. 5). Then for $SrTiO_3$ we get $\tan\delta^{M} \approx 2\cdot 10^{-6}$, $\tan\delta^{a} \sim 10^{-12}$ and for $KTaO_3$ we get $\tan\delta^{M} \approx 2\cdot 10^{-8}$, $\tan\delta^{a} \sim 10^{-12}$. Thus we see that the intrinsic losses are very small and are governed by the interaction with the soft mode. The experimental values of $\tan\delta$ for $SrTiO_3$ and $KTaO_3$ under the same conditions are of the order of 10^{-3} and 10^{-5}, respectively.[20–22]

In summary, by comparing the experimental values of $\tan\delta$ with the estimated lattice-loss contributions, we can be certain that under the conditions considered here the actual value of $\tan\delta$ is substantially higher than the intrinsic-loss level of an ideal crystal.

APPENDIX 2

In this Appendix we show how estimates (12)–(15) can be obtained formally. Because a ferroelectric is a highly polar compound, the electrophonon potential can to good accuracy be expressed in terms of the third-order anharmonic force constants B relating the atomic displacements $R^{\mathbf{n}}_{\alpha p}$ ($\mathbf{n}$ is the lattice vector, p is the number of the atom in the cell, and α is a Cartesian coordinate) with the anharmonic contribution to the energy

$$H_{int} = \frac{1}{3!}\sum B^{\mathbf{n}\mathbf{n}'\mathbf{n}''}_{\alpha p\alpha' p'\alpha'' p''} R^{\mathbf{n}}_{\alpha p} R^{\mathbf{n}'}_{\alpha' p'} R^{\mathbf{n}''}_{\alpha'' p''}.$$

The corresponding expression is of the form[10]

$$\Lambda^{j'j''}_{\alpha}(\mathbf{q}) = \frac{1}{2\rho^2 V}\sum \frac{Q_p}{a^3}\frac{e_p^{\alpha}(0,j)\, e_{p'''}^{\alpha'''}(0,j)\, e_{p'}^{\alpha'}(\mathbf{q},j')\, e_{p''}^{\alpha''}(-\mathbf{q},j'')}{\Omega_j^2(0)\,\Omega_{j'}(\mathbf{q})\,\Omega_{j''}(\mathbf{q})} \times \exp[i\mathbf{q}(\mathbf{n}'-\mathbf{n}'')]\, B^{\mathbf{n}\mathbf{n}'\mathbf{n}''}_{\alpha''' p''' \alpha' p' \alpha'' p''}, \tag{26}$$

where Q_p is the effective charge of the ion, V is the volume of the crystal, $e_p^{\alpha}(\mathbf{q}, j)$ is the polarization vector of the displacements in vibrational branch j, and the summation in the last two formulas is over all the indices appearing in B [in (26) the summation over the optical branches j has already been done].

To obtain the necessary estimates it is sufficient to estimate the sum in (26). Estimates of this type of sum have been analyzed elsewhere,[11] so we shall discuss only the main points in the derivation.

According to Gurevich,[11] the tensor B falls off very rapidly as the differences $|\mathbf{n} - \mathbf{n}'|$ and $|\mathbf{n} - \mathbf{n}''|$ increase, and therefore the main contribution to the sum in (26) is from terms for which the values of these differences are of the order of unity. In an ordinary dielectric the components of B with small values of these differences are[11] of order ρw^2, and in a centrosymmetric crystal the only nonzero components

are those which are odd under the replacement $\mathbf{n}\to-\mathbf{n}$, $\mathbf{n}'\to-\mathbf{n}'$, and $\mathbf{n}''\to-\mathbf{n}''$. It is known that the anharmonic parameters of a displacive ferroelectric exhibit no anomalies.[5] Therefore, in a centrosymmetric paraphase, B is of the same order of magnitude as in an ordinary centrosymmetric crystal, i.e., the odd components are of order ρw^2 and the even components are zero. In the ferrophase the old estimate remains valid for the odd components, but in this phase even components arise as well; these, however, are obviously smaller than the odd components by a factor of the ratio of the spontaneous to the atomic polarization, i.e., a factor of order $\rho w^2\chi^{-1/2}$. With allowance for this circumstance one can obtain (12) by proceeding from (9) and (11).

To obtain (13)–(15) let us consider the sum in (26) in the long-wavelength limit. We shall regard q as nonzero only in the argument of the exponential function, which we shall expand in a series. We shall consider separately the contributions to the sum from the even and odd parts of B. For the even part, only terms with even powers of q can give a nonzero contribution, and for the odd part, only the odd powers contribute. For each part of B we shall consider in the sum only the first term that gives a nonzero contribution. Using the identity

$$\sum_{\mathbf{np}} B_{\alpha p\alpha' p'\alpha'' p''}^{\mathbf{nn}'\mathbf{n}''}=0,$$

which ensures the translational invariance of H_{int}, and recognizing that the polarization vector of the displacements for the acoustical branches at $q=0$ are independent of p, it is straightforward to show that the nonzero contribution to (26) comes from the terms of the expansion with powers of q larger than or equal to the number of acoustic branches between j' and j''. This observation permits one to find the first terms of the expansion which give nonzero contributions. Then, taking into account what was said above and recognizing that $\omega_0^2\sim\omega_D^2/\chi$, after straightforward transformations we arrive at estimates (13)–(15).

Note added in proof (26 April 1984): It has been pointed out by G. E. Pikus and E. L. Ivchenko that all of our statements concerning centrosymmetric crystals are, strictly speaking, valid only for crystals in which every atom is a center of inversion. However, in all the known cubic ferroelectrics of the displacive type every atom is in fact a center of inversion, so all of the conclusions of this paper remain in force.

[1)]We note that in going to the five-quantum processes the substantial benefit gained in the weakening of the restrictions imposed by the conservation laws does not occur. Therefore, the contributions of higher-order processes are smaller by a factor of the anharmonicity parameter, and one can neglect them or do more narrowly the sampling summation in all the orders (see, e.g., Refs. 9 and 15).

[2)]It was shown in Ref. 3 that the dissociation contribution [the plus sign in formulas (2)] is negligibly small in ferroelectrics.

[3)]Recall that all the results of this paper are valid only for $\omega\ll\omega_0$, and therefore the transition to the limit $\omega\to\omega_0$ should be understood in a formal sense.

[4)]More precisely, if the difference between a first-order phase transition that is close to second-order and a true second-order phase transition is taken into account, the anomaly of $\tan\delta$ in the ferrophase should correspond to the anomaly of $\chi^{3/2}P_s^2$.

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