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The long-time correlations induced by defects in the quantum paraelectrics SrTiO₃ and KTaO₃

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Abstract. The long-time correlations of fluctuations of lattice displacements in the quantum paraelectrics SrTiO₃ and KTaO₃ are studied within the framework of the mode-coupling theory of the dynamic transition from an ergodic to a non-ergodic state caused by defects. It is shown that the very hard local non-symmetry-breaking defects formed by the oxygen vacancies can induce the dynamic transition at T_d . The low-temperature non-ergodic state is characterized by long-time correlations of local fluctuations of the polar displacements, which continuously arise for $T \leq T_d$. Simultaneously, the local non-symmetry-breaking defects lead to the appearance of long-time correlations of long-wavelength fluctuations of acoustic displacements via the local random piezoelectric coupling for $T \leq T_d$. The random local piezoelectric coupling is caused by the electrostrictive interaction, which is modified by the random electric fields of the frozen symmetry-breaking defects. The conditions that must be met for the dynamic transition to be induced by the oxygen vacancies are analysed. It is also shown that the unavoidable oxygen vacancies in the nominally pure SrTiO₃ and KTaO₃ are quite sufficient in number to cause the non-ergodic state. The role of the dynamic transition in the formation of the glass state for lightly doped KTaO₃ and SrTiO₃ is discussed.

1. Introduction

It is well known that quantum paraelectrics (QPE) with the perovskite structure ABO₃, such as strontium titanate (SrTiO₃) and potassium tantalate (KTaO₃), show a strong increase in dielectric susceptibility at low temperatures, which is caused by softening of the polar transverse optical modes. Over the temperature range $T > 50$ K, the dielectric susceptibility follows the usual Curie–Weiss law with the extrapolated ferroelectric transition temperature T_c . However, the divergence does not occur at T_c . It is suggested that quantum fluctuations suppress the ferroelectric long-range order at low temperatures. As a result, the QPE do not undergo a phase transition, and the paraelectric state persists down to the lowest temperatures, $T \rightarrow 0$ [1]. Nevertheless, the ferroelectric phase transition can be induced by the introduction of even small concentrations of impurities (of dipole [2, 3] or quadrupole [4] type) or application of uniaxial stress [5]. Usually, it is suggested that the ferroelectric phase transition in the QPE can be induced by local symmetry-breaking (SB) defects [2, 3], or the soft non-symmetry-breaking (NSB) defects that lead to an increase of the local ferroelectric transition temperature [6].

Raman spectroscopy and inelastic neutron scattering studies have revealed the tremendous effect of the oxygen vacancies on the ferroelectric soft mode in reduced SrTiO₃

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[7]. Similar results have been obtained for KTaO_3 [8]. In these cases, the oxygen vacancies act as very hard local NSB defects [7], which give rise to a decrease of the local ferroelectric transition temperature. Unfortunately, the microscopic nature of the very strong NSB defects formed by the oxygen vacancies is unknown, and cannot be explained by the weak effect of dilatational centres via the electrostriction [7]. For the QPE, it is suggested that the hard NSB defects lead only to stiffening of the ferroelectric mode.

However, the studies of the three-dimensional lattice φ^4 -model with NSB defects [9–11] have shown that NSB defects (and hard NSB defects also) and/or anharmonicity of the pure lattice can give rise to a dynamic transition from an ergodic to a non-ergodic state. The non-ergodic state is characterized by the formation of a long-time correlation (LTC) of the fluctuations of the lattice distortions for $T_d > T_c$, which correspond to the appearance of quasi-static displacements (precursor order clusters). Generally, the appearance of a non-zero value of the LTC of the fluctuations in the limit $t \rightarrow \infty$ gives rise to ergodic breaking [12, 13]. Similar dynamic transitions from an ergodic to a non-ergodic state within the framework of the self-consistent mode-coupling approximation were found for the liquid–glass transition [14], orientational glasses [15], and particle localization in random potentials [16].

The peculiarities of the dynamic transition are determined by the form of the non-linear interaction or anharmonicity of the lattice. The anharmonicity of the φ^4 -model without defects leads to a discontinuous appearance of the LTC of the lattice distortions [10, 11], while the NSB defects give rise to a continuous formation of LTC of the lattice distortions for $T \leq T_d$ [9, 10]. In the case of NSB defects, the temperature T_g lies far from T_c [9, 10], while T_d , the temperature of the discontinuous dynamic transition, lies in the vicinity of T_c but outside the critical region [11].

As noted above, the ferroelectric soft modes in the QPE take small but finite values as $T \rightarrow 0$ and the NSB defects induced by oxygen vacancies are very strong. In this case, the conditions are more suited to a continuous dynamic transition than to the discontinuous dynamic transition that can take place in the vicinity of T_c . It should be pointed out that studies of the dynamic transition induced by the hard NSB defects give us the opportunity to clarify the role of reduction treatment in the formation of the non-ergodic state in ferroelectric crystals. In the case of very strong NSB defects formed by the oxygen vacancies, only a very small concentration of defects is required in order to induce the dynamic transition. As a rule, there are unavoidably oxygen vacancies in the nominally pure QPE. Therefore, studies of the dynamic transition induced by the unavoidable oxygen vacancies in the nominally pure KTaO_3 and SrTiO_3 are very important. The latest investigations of the effect of the cooling rate on the long-time dependence of the dielectric constant [17] reveal the existence of a non-ergodic state not only in the dipole glass state of $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ ($x \leq 0.025$) but also in nominally pure KTaO_3 . The results have been discussed in terms of a non-ergodic ageing phenomenon observed in the spin-glass state [18]. Unfortunately, this treatment cannot explain the appearance of this same non-ergodic state in the nominally pure KTaO_3 , where the only unavoidable SB defects are non-interacting ones. In addition, ^{181}Ta NMR measurements on nominally pure and lightly Nb-, Li-, and Na-doped KTaO_3 crystals [19] have shown that Ta ions suddenly site in a local non-cubic environment on a timescale of $t \geq 10^{-7}$ s for $T \leq 40$ K. The sudden formation and continuous increase in magnitude of quasi-static displacements of Ta ions are not accompanied by a static structural modification of the lattice for $T \leq 40$ K. This phenomenon is like the continuous dynamic transition. The measurements also demonstrate that the sharp appearance of the quasi-static distortions of the lattice for $T \leq 40$ K does not depend on there being a weak concentration of SB defects, and, in fact, is not connected with the SB defects [19]. For the low-temperature

region of the QPE, the SB defects are frozen and act as random fields. However, studies of a model system for dipole glasses (the mixed crystals of Rb_{1-x}(NH₄)_xH₂PO₄) [20] show that the random electric fields can modify the electrostrictive interaction of the polarization and elastic deformation, which leads to the formation of the acoustic anomalies of the dipole glass state. The electrostriction is the main cause of the coupling of the polarization and elastic deformation in the QPE. In this case, the modified interaction can play an important role in the formation of the LTC of the elastic deformation in the systems with random fields. Hence, consideration of the conditions that must be met for a dynamic transition to be induced by the hard NSB defects in the QPE with SB defects requires the presence of the random electric fields to be taken into account.

It should be noted that the results of the work described in [19] are discussed there as representing a possible case of transition-like phenomena, which were detected for $T \simeq 37$ K in SrTiO₃ [21]. These phenomena are treated in terms of an anharmonicity of a defect-free lattice [22, 23, 27]. Nevertheless, the anomalies [24]—in particular for $T \simeq 32$ K [25, 26]—which are considered as results of transition-like phenomena may in fact be connected with the unavoidable oxygen vacancies [23, 26].

The main purpose of this paper is to study the sharp appearance of the LTC of the polar displacements caused by oxygen vacancies in the QPE. The consideration is carried out on the basis of the mode-coupling theory of a dynamic transition from an ergodic to a non-ergodic state induced by the hard NSB defects. The effect of the random electric fields on the formation of the LTC of the elastic deformations is investigated also. It will be shown that even the unavoidable NSB defects formed by the oxygen vacancies can give rise to a dynamic transition in the nominally pure QPE.

The article is organized as follows. In section 2 we present the model Hamiltonian that takes into account the effects of the strong local NSB and the weak SB defects on the polar optical soft modes and the electrostrictive interaction of the polarization with the elastic deformation. In section 3 we consider the closed dynamic equations for the polar and the elastic displacement–displacement relaxation functions within the framework of the mode-coupling theory. In section 4 we show, on the basis of the self-consistent equations for the non-ergodic parts of the relaxation functions, that defects like the oxygen vacancies can induce a dynamic transition from an ergodic to a non-ergodic state in QPE. We also analyse the conditions that must be met for the dynamic transition to be induced by the unavoidable oxygen vacancies in the nominally pure SrTiO₃ and KTaO₃. Finally, in section 5, we list our conclusions.

2. The model Hamiltonian

The lattice of QPE exhibits a ferroelectric instability, which is described by the Hamiltonian [28]

$$H_o^{ph} = \sum_{r,\alpha} \frac{1}{2} \left[\mu \xi_\alpha^2(\mathbf{r}) + A \xi_\alpha^2(\mathbf{r}) + C \sum_{r'} (\xi_\alpha(\mathbf{r}') - \xi_\alpha(\mathbf{r}))^2 \right] + \sum_{\mathbf{r}} U^{ah}(\mathbf{r}) \quad (1)$$

$$U^{ah}(\mathbf{r}) = \frac{B_{11}}{4} [\xi_1^4(\mathbf{r}) + \xi_2^4(\mathbf{r}) + \xi_3^4(\mathbf{r})] + \frac{B_{12}}{2} [\xi_1^2(\mathbf{r})\xi_2^2(\mathbf{r}) + \xi_1^2(\mathbf{r})\xi_3^2(\mathbf{r}) + \xi_3^2(\mathbf{r})\xi_2^2(\mathbf{r})] \quad (2)$$

where $A < 0$ is the condition for ferroelectric instability, which is stabilized by the anharmonic terms $U^{ah}(\mathbf{r})$, the local polarization is defined by the $P_\alpha(\mathbf{r}) = z\xi_\alpha(\mathbf{r})/v_c$ (z is the electric charge, $v_c = a^3$ is the volume of a cell, a is the lattice constant), μ is the

reduced mass. Using the Fourier transforms

$$\xi_\alpha(\mathbf{r}) = \frac{1}{\sqrt{\mu N}} \sum_{\mathbf{k}\nu} e_\alpha^\nu(\mathbf{k}) y_\nu(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

the Hamiltonian (1) can be expressed in terms of ferroelectric soft modes for the paraelectric state in the long-wavelength limit as [28]

$$H_o^{ph} = \sum_{\mathbf{k},\nu} \frac{1}{2} [\dot{y}_\nu(-\mathbf{k})\dot{y}_\nu(\mathbf{k}) + w_\nu^2(\mathbf{k}, T) y_\nu(-\mathbf{k}) y_\nu(\mathbf{k})]. \quad (3)$$

Here the ferroelectric soft modes have the usual form

$$\begin{aligned} w_\nu^2(\mathbf{k}, T) &= w_\nu^2(\mathbf{0}, T) + s^2 k^2 \\ w_\nu^2(\mathbf{0}, T) &= \delta_{\nu\nu} \Omega_o^2 + \Delta_\nu(T) \end{aligned} \quad (4)$$

with $\Omega_o^2 = A/\mu$ and $s^2 \approx Ca^2/\mu$. The ferroelectric instability ($\Omega_o^2 < 0$) is stabilized by the anharmonicity of the lattice $\Delta_\nu(T)$, which is mainly caused by the term (2) in the form

$$\Delta_\nu(T) = \sum_{\gamma q} B \begin{pmatrix} \nu & \nu & \gamma & \gamma \\ \mathbf{0} & \mathbf{0} & -\mathbf{q} & \mathbf{q} \end{pmatrix} \langle y_\gamma(-\mathbf{k}) y_\gamma(\mathbf{k}) \rangle$$

where the first coefficient can be expressed as B_{11} and B_{12} , and $\langle y_\gamma(-\mathbf{k}) y_\gamma(\mathbf{k}) \rangle$ is the thermodynamic mean square displacement fluctuation. For the QPE, the condition $\Delta_\nu(T) = \delta_{\nu\nu} \Delta(T)$ is realized. This leads to $w_\nu^2(\mathbf{0}, T) = \delta_{\nu\nu} w_o^2(\mathbf{0}, T)$. The temperature dependence of $\Delta(T)$ is determined by

$$\langle y_\gamma(-\mathbf{k}) y_\gamma(\mathbf{k}) \rangle = \frac{\hbar}{2w_\gamma(\mathbf{k}, T)} \left[\coth\left(\frac{\hbar\beta w_\gamma(\mathbf{k}, T)}{2}\right) \right] \quad (5)$$

where $\beta = 1/k_B T$. For a lattice which undergoes a ferroelectric phase transition, the condition $w_o^2(\mathbf{0}, T_c) = \Omega_o^2 + \Delta(T_c) = 0$ is realized. The identifying feature of the quantum paraelectrics SrTiO₃ and KTaO₃ is that

$$w_o^2(\mathbf{0}, T = 0) = \Omega_o^2 + \Delta(T = 0) > 0$$

(see [29] and [30]). In this case, due to quantum mechanical zero-point oscillations, the ferroelectric instability is suppressed by the quantum mechanical zero-point fluctuations that give rise to the non-zero value of the mean square displacement fluctuations (5) near $T = 0$, and the paraelectric state remains stable down to the lowest temperatures. This gives rise to the peculiarities of the temperature dependence of the soft modes $w_o^2(\mathbf{0}, T)$. As follows from (5), the temperature dependence of $w_o^2(\mathbf{0}, T)$ in the QPE is linear in T for large $k_B T > \hbar w_o(\mathbf{k}, T)$ (the classical region) and temperature independent for small $k_B T \ll \hbar w_o(\mathbf{0}, 0)$ (the quantum region). As a result, the ferroelectric mode $w_o^2(\mathbf{0}, T)$ in the QPE softens as $T \rightarrow 0$ and takes the small value $w_o^2(\mathbf{0}, T = 0) > 0$ near $T = 0$. For further details on this topic, we refer the reader to [29] and [30].

The interaction of the polarization $P_\alpha(\mathbf{r})$ with the elastic deformation $u_{\alpha\beta}(\mathbf{r})$ in the QPE takes place via the electrostriction. The electrostriction is the third-order anharmonic term

$$\begin{aligned} H_{o-a}^{str} &= -v_c D_{\alpha\beta\gamma\delta} \sum_{\mathbf{r}} P_\alpha(\mathbf{r}) P_\beta(\mathbf{r}) u_{\gamma\delta}(\mathbf{r}) \\ u_{\alpha\beta}(\mathbf{r}) &= \frac{1}{2} \left[\frac{\partial u_\alpha(\mathbf{r})}{\partial r_\beta} + \frac{\partial u_\beta(\mathbf{r})}{\partial r_\alpha} \right] \end{aligned} \quad (6)$$

where $u_\alpha(\mathbf{r})$ is the displacement centre of mass of a unit cell. It also contributes to the formation of $\Delta(T)$ in (4) [28]; however, this contribution is small (the second order of the

perturbation theory) in comparison with the main contribution from the term (2) (the first order of the perturbation theory).

Let us consider the effects of defects on the lattice. In this paper, we consider the case of a small concentration of independent defects. The interactions of the defects with the lattice have the form

$$H^d = \sum_{r,\alpha} \frac{1}{2} c(\mathbf{r}) (A_d - A) \xi_\alpha^2(\mathbf{r}) + \sum_{r,\alpha} E_\alpha^{rf}(\mathbf{r}) \xi_\alpha(\mathbf{r})$$

$$c(\mathbf{r}) = \sum_{r_i} \delta_{rr_i} = \overline{c(\mathbf{r})} + \Delta c(\mathbf{r}).$$
(7)

Here $A_d < 0$ and $A_d > 0$ correspond to the soft and the hard local NSB defects at sites r_i with the concentration $c(\mathbf{r})$. $\overline{c(\mathbf{r})} = c$ is the mean concentration, and $\Delta c(\mathbf{r}) = c(\mathbf{r}) - c$ is the fluctuation of the concentration with

$$\overline{\Delta c(\mathbf{r})} = 0 \quad \overline{\Delta c(\mathbf{r}) \Delta c(\mathbf{r}')} = \delta_{\mathbf{r}\mathbf{r}'} c(1 - c). \quad (8)$$

$E_\alpha^{rf}(\mathbf{r})$ represents the random field induced by the local SB defects ($\overline{E_\alpha^{rf}(\mathbf{r})} = 0$); the overbar indicates configurational averaging. The defects (7) can modify the parameters of the lattice. So, the local NSB defects modify the parameter A as follows:

$$A(\mathbf{r}) = A + c(A_d - A) + \Delta c(\mathbf{r})(A_d - A) \quad (9)$$

whereas the random local fields $E_\alpha^{rf}(\mathbf{r})$ of the SB defects give rise to displaced oscillators with the thermal fluctuations $\xi'_\alpha(\mathbf{r})$ near the new equilibrium positions $\xi_\alpha^{st}(\mathbf{r})$:

$$\xi'_\alpha(\mathbf{r}) = \xi_\alpha(\mathbf{r}) - \xi_\alpha^{st}(\mathbf{r}). \quad (10)$$

In terms of the $\xi'_\alpha(\mathbf{r})$ and $\xi_\alpha^{st}(\mathbf{r})$, the anharmonic interactions H_{o-a}^{str} are modified. Using the Fourier transforms

$$\xi'_\alpha(\mathbf{r}) = \frac{1}{\sqrt{\mu N}} \sum_{\mathbf{k}} \xi'_\alpha(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{1}{\sqrt{\mu N}} \sum_{\mathbf{k}\nu} e_\alpha^\nu(\mathbf{k}) x_\nu(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$u_\alpha(\mathbf{r}) = \frac{1}{\sqrt{MN}} \sum_{\mathbf{k}} u_\alpha(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

one can represent the random local piezoelectric coupling, which is the main contribution of the third-order anharmonic interaction (6), in the form

$$H_{o-a}^{str} = - \sum_{p\mathbf{k}\mathbf{q}} Q \begin{pmatrix} \nu & \mu & \gamma \\ \mathbf{k} & \mathbf{p} & \mathbf{q} \end{pmatrix} \xi_\nu^{st}(\mathbf{k}) x_\mu(\mathbf{p}) u_\gamma(\mathbf{q}) \quad (11)$$

$$Q \begin{pmatrix} \nu & \mu & \gamma \\ \mathbf{k} & \mathbf{p} & \mathbf{q} \end{pmatrix} = i \frac{\lambda^2 v_c}{2\sqrt{NM}} (D_{\alpha\beta\gamma\delta} + D_{\beta\alpha\gamma\delta}) e_\alpha^\nu(\mathbf{k}) e_\beta^\mu(\mathbf{p}) q_\delta \Delta(\mathbf{k} + \mathbf{p} + \mathbf{q})$$

where the usual electrostrictive term, which is expressed in terms of the $x_\nu(\mathbf{k})$ and the $u_\alpha(\mathbf{k})$ only, can be omitted, because it does not give rise to any dynamic anomaly [20], N is the total number of cells in the lattice, M is the mass of a cell, $\Delta(\mathbf{k}_1 + \dots + \mathbf{k}_n)$ is equal to one or zero depending on whether $\mathbf{k}_1 + \dots + \mathbf{k}_n$ is equal to a vector of the reciprocal lattice or not, and $\lambda^2 = z^2/v_c^2\mu$. It is such an effect of the $E_\alpha^{rf}(\mathbf{r})$ on the lattice with electrostrictive interaction that is observed in the mixed crystals $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ [20]. Using the lattice parameters modified by the defects, H_o^{ph} can be represented in the long-wavelength limit as

$$H_o^{ph} = \sum_{\mathbf{k},\nu} \frac{1}{2} [\dot{x}_\nu(-\mathbf{k})\dot{x}_\nu(\mathbf{k}) + w_\nu^2(\mathbf{k}, T, c)x_\nu(-\mathbf{k})x_\nu(\mathbf{k})]$$

$$+ \sum_{p\mathbf{k}\mathbf{q}} \frac{1}{2} Q \begin{pmatrix} \nu & \mu \\ \mathbf{k} & \mathbf{p} & \mathbf{q} \end{pmatrix} \Delta c(\mathbf{k}) x_\nu(\mathbf{p}) x_\mu(\mathbf{q}) \quad (12)$$

where the modified ferroelectric soft modes have the form

$$\begin{aligned} w_v^2(\mathbf{k}, T, c) &= w_o^2(\mathbf{0}, T, c) + s^2 k^2 \\ w_o^2(\mathbf{0}, T, c) &= \Omega_o^2 + \Delta(T) + cG \end{aligned} \quad (13)$$

with $G = (A_d - A)/\mu$. The second term in (12) represents the random transition temperature with

$$\mathcal{Q} \left(\begin{array}{c} v \quad \mu \\ \mathbf{k} \quad \mathbf{p} \quad \mathbf{q} \end{array} \right) = \frac{1}{\sqrt{N}} \sum_{\alpha} G e_{\alpha}^v(\mathbf{p}) e_{\alpha}^{\mu}(\mathbf{q}) \Delta(\mathbf{k} + \mathbf{p} + \mathbf{q}).$$

In terms of the displacements $u_{\alpha}(\mathbf{k})$, the Hamiltonian of the acoustic modes can be written in the long-wavelength limit as

$$\begin{aligned} H_a^{ph} &= \sum_{\mathbf{k}} \frac{1}{2} [\dot{\mathbf{u}}(-\mathbf{k}) \cdot \dot{\mathbf{u}}(\mathbf{k}) + A_{\alpha\beta}(\mathbf{k}) u_{\alpha}(-\mathbf{k}) u_{\beta}(\mathbf{k})] \\ A_{\alpha\beta}(\mathbf{k}) &= v_t^2 k^2 g_{\alpha\beta}^t + v_l^2 k^2 g_{\alpha\beta}^l \end{aligned} \quad (14)$$

where $g_{\alpha\beta}^t = \delta_{\alpha\beta} - n_{\alpha} n_{\beta}$ is the projection operator of the transverse acoustic mode, $g_{\alpha\beta}^l = n_{\alpha} n_{\beta}$ is the projection operator of the longitudinal acoustic mode, and $n_{\alpha} = k_{\alpha}/k$.

Using (11)–(14), the model Hamiltonian, which takes into account the effect of the defects on the lattice parameters, has the form

$$H = H_o^{ph} + H_a^{ph} + H_{o-a}^{str}. \quad (15)$$

As indicated above, the quantum fluctuations are very important in the study of the low-temperature phase in the QPE and, therefore, the quantum commutation relations have to be taken into account. The commutation relations for the ferroelectric modes have the usual form

$$\begin{aligned} [x_v(-\mathbf{q}), \dot{x}_{\mu}(\mathbf{k})] &= i\delta_{v\mu} \Delta(\mathbf{k} - \mathbf{q}) \\ [x, x] &= [\dot{x}, \dot{x}] = 0. \end{aligned}$$

The commutation relations for acoustic modes are written in the form

$$\begin{aligned} [u_{\alpha}(-\mathbf{q}), \dot{u}_{\beta}(\mathbf{k})] &= i\delta_{\alpha\beta} \Delta(\mathbf{k} - \mathbf{q}) \\ [u, u] &= [\dot{u}, \dot{u}] = 0. \end{aligned}$$

3. Dynamic equations

To study the dynamic behaviour, we derive the dynamic equations for the relaxation function $\Phi_{ij}(t)$. The function $\Phi_{ij}(t)$ is defined by [31]

$$\Phi_{ij}(t) = (A_i | e^{-i\mathcal{L}t} | A_j) = \frac{1}{\beta} \int_0^{\beta} d\tau \langle A_i(t - i\tau), A_j \rangle \quad (16)$$

where $\langle \dots \rangle$ is the thermodynamic average of a set secular dynamic variables $\{A_i\}$, $A_i = A_i' - \langle A_i' \rangle$ is the dynamic fluctuation of A_i' , and $\mathcal{L}A_i = [H, A_i]$ is the Liouville operator. The relaxation function $\Phi_{ij}(t = 0)$ determines the static thermodynamic susceptibility

$$\chi_{ij} = \beta(A_i | A_j) = \beta\Phi_{ij}(t = 0). \quad (17)$$

The long-time anomalies of $\Phi_{ij}(t)$ can be characterized by singularities of the Laplace transform:

$$\Phi_{ij}(z) = -(A_i | (z - \mathcal{L})^{-1} | A_j) = i \int_0^{\infty} dt e^{izt} \Phi_{ij}(t) \quad (18)$$

for $z \rightarrow 0$ for $\text{Im } z > 0$. $\Phi_{ij}(z)$ defines the Kubo susceptibility $\chi_{ij}(z)$ as follows:

$$\chi_{ij}(z) - \chi_{ij} = \beta z \Phi_{ij}(z). \quad (19)$$

Within the framework of the Mori projection method, the relaxation function $\hat{\Phi}(z)$ obeys the matrix equation [31]

$$[z \mathbf{I} - \mathbf{\Omega} - \mathbf{\Sigma}(z)] \mathbf{\Phi}(z) = -\beta^{-1} \mathbf{\chi}(z) \quad (20)$$

where the matrix $\mathbf{\Omega}$ is given by

$$\Omega_{ij} = \beta (A_i | \mathcal{L} | A_k) \chi_{kj}^{-1} \quad (21)$$

and the relaxation kernel $\mathbf{\Sigma}(z)$ is given by

$$\Sigma_{ij}(z) = \beta (Q \mathcal{L} A_i | (z - Q \mathcal{L} Q)^{-1} | Q \mathcal{L} A_k) \chi_{kj}^{-1} \quad (22)$$

where $Q = 1 - P$ is the projector onto the space of non-secular variables; the projector onto the space of secular variables P is defined by

$$P A = \sum_{ij} A_i (A_i | A_j)^{-1} (A_j | A). \quad (23)$$

Here we study the anomalies of the dynamic behaviour of the QPE on the basis of the set of secular variables $\{A_i\} = \{u_\alpha(\mathbf{k}), \dot{u}_\alpha(\mathbf{k}), x_\nu(\mathbf{k}), \dot{x}_\nu(\mathbf{k})\}$ for the averaged relaxation function

$$\Phi_{ij}(t) = \frac{1}{\beta} \int_0^\beta d\tau \overline{A_i(t - i\tau), A_j} \quad (24)$$

within the framework of the virtual-crystal approximation.

The matrix static thermodynamic susceptibility (17) has the form

$$\mathbf{\chi}(\mathbf{k}) = \begin{pmatrix} \chi^a(\mathbf{k}) & 0 & 0 & 0 \\ 0 & \mathbf{I} & 0 & 0 \\ 0 & 0 & \chi^o(\mathbf{k}) & 0 \\ 0 & 0 & 0 & \mathbf{I} \end{pmatrix} \quad (25)$$

where the displacement–displacement susceptibility of the $u_\alpha(\mathbf{r})$ is given by

$$\chi_{\alpha\beta}^a(\mathbf{k}) = \beta \overline{u_\alpha(-\mathbf{k}) | u_\beta(\mathbf{k})} = A_{\alpha\beta}(\mathbf{k})^{-1} \quad (26)$$

and the conjugate momentum susceptibilities are given by

$$\beta \overline{\dot{u}_\alpha(-\mathbf{k}) | \dot{u}_\beta(\mathbf{k})} = \delta_{\alpha\beta} \quad (27)$$

$$\beta \overline{\dot{x}_\nu(-\mathbf{k}) | \dot{x}_\mu(\mathbf{k})} = \delta_{\nu\mu} \quad (28)$$

while the displacement–displacement susceptibility of the $x_\nu(\mathbf{k})$ is given by

$$\chi_{\nu\mu}^o(\mathbf{k}) = \beta \overline{x_\nu(-\mathbf{k}) | x_\mu(\mathbf{k})} = \frac{\delta_{\nu\mu}}{w_o^2(T, c, \mathbf{k})}. \quad (29)$$

Here the ferroelectric modes have the form (13).

For the matrix $\mathbf{\Omega}$, equation (21), the matrix elements $\overline{(A_i | \mathcal{L} | A_k)}$ are given by

$$\overline{(A_i | \mathcal{L} | A_k)} = \beta^{-1} \begin{pmatrix} 0 & i\delta_{\alpha\beta} & 0 & 0 \\ -i\delta_{\beta\alpha} & 0 & 0 & 0 \\ 0 & 0 & 0 & i\delta_{\nu\mu} \\ 0 & 0 & -i\delta_{\mu\nu} & 0 \end{pmatrix}. \quad (30)$$

Using the (25) and (30), the matrix Ω is written as

$$\Omega = \begin{pmatrix} 0 & \mathbf{i} & 0 & 0 \\ -i\chi^a(\mathbf{k})^{-1} & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{i} \\ 0 & 0 & -i\chi^o(\mathbf{k})^{-1} & 0 \end{pmatrix}. \quad (31)$$

The matrix of the relaxation kernel $\Sigma(z, \mathbf{k})$, equation (22), has the form

$$\Sigma(z, \mathbf{k}) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \Sigma^a(z, \mathbf{k}) & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \Sigma^o(z, \mathbf{k}) \end{pmatrix} \quad (32)$$

with non-vanishing elements

$$\Sigma_{ij}^\sigma(z, \mathbf{k}) = \overline{\beta(Q\mathcal{L}\dot{A}_i|(z - Q\mathcal{L}Q)^{-1}|Q\mathcal{L}\dot{A}_j)_k}$$

where $\sigma = a$ and $\sigma = o$ correspond to secular variables $\dot{u}_\alpha(\mathbf{k})$ and $\dot{x}_v(\mathbf{k})$. Unfortunately, the relaxation kernels have an intricate form. The form of $\Sigma_{ij}^\sigma(z, \mathbf{k})$ can be simplified by making a mode-coupling approximation, i.e. the relaxation kernel becomes a power of the relaxation function, taking into account $Q\mathcal{L}Q \rightarrow \mathcal{L}$ [9, 15, 32]. In addition, configurational averaging has to be carried out. In this work, it proceeds by means of the VCA. Within the framework of the VCA, the relaxation kernel can be represented as a power of the averaged relaxation functions $\Phi^\sigma(z, \mathbf{k})$ (see [9] and [15]). As a result, the relaxation kernels $\Sigma^\sigma(z, \mathbf{k})$ are given by

$$\Sigma_{\gamma\rho}^a(z, \mathbf{k}) = -\beta \sum_{\mathbf{p}} Q \begin{pmatrix} v & \mu & \gamma \\ -\mathbf{k} - \mathbf{p} & \mathbf{p} & \mathbf{k} \end{pmatrix} Q \begin{pmatrix} v & \mu & \rho \\ \mathbf{k} + \mathbf{p} & -\mathbf{p} & -\mathbf{k} \end{pmatrix} \times \overline{\xi_\mu^{st}(-\mathbf{p})\xi_\mu^{st}(\mathbf{p})\Phi_{v\nu}^o(z, -\mathbf{p} - \mathbf{k})} \quad (33)$$

$$\Sigma_{\nu\nu}^o(z, \mathbf{k}) = -\beta \sum_{\mathbf{p}} Q \begin{pmatrix} \mu & v \\ \mathbf{p} & -\mathbf{p} - \mathbf{k} & \mathbf{k} \end{pmatrix} Q \begin{pmatrix} \mu & v \\ -\mathbf{p} & \mathbf{p} + \mathbf{k} & -\mathbf{k} \end{pmatrix} \times \overline{\Delta c(-\mathbf{p})\Delta c(\mathbf{p})\Phi_{\mu\mu}^o(z, -\mathbf{p} - \mathbf{k})} - \beta \sum_{\mathbf{p}} Q \begin{pmatrix} v & \mu & \gamma \\ \mathbf{k} & \mathbf{p} & -\mathbf{p} - \mathbf{k} \end{pmatrix} Q \begin{pmatrix} v & \mu & \rho \\ -\mathbf{k} & -\mathbf{p} & \mathbf{p} + \mathbf{k} \end{pmatrix} \times \overline{\xi_\mu^{st}(-\mathbf{p})\xi_\mu^{st}(\mathbf{p})\Phi_{\gamma\rho}^a(z, -\mathbf{p} - \mathbf{k})} \quad (34)$$

where $\Phi_{\alpha\beta}^a(z, \mathbf{k})$ is the acoustic displacement–displacement relaxation function

$$\Phi_{\alpha\beta}^a(z, \mathbf{k}) = \Phi_{\alpha\beta}^{uu}(z, \mathbf{k}) = \overline{-(u_\alpha(\mathbf{k})|(z - \mathcal{L})^{-1}|u_\beta(\mathbf{k}))} \quad (35)$$

and $\Phi_{\nu\nu}^o(z, \mathbf{k})$ is the optical displacement–displacement relaxation function

$$\Phi_{\nu\nu}^o(z, \mathbf{k}) = \Phi_{\nu\nu}^{xx}(z, \mathbf{k}) = \overline{-(x_\nu(\mathbf{k})|(z - \mathcal{L})^{-1}|x_\nu(\mathbf{k}))}. \quad (36)$$

It should be pointed out that the VCA can be used in the case of independent defects. However, this condition cannot be satisfied for the concentrations for which the correlations between the defects arise. In the soft lattice of the QPE, this effect can be important for concentrations of the SB defects of $c_d \geq 10^{-3}$ (see [2] and [3]) and of the NSB defects formed by oxygen vacancies with $c \geq 10^{-2}$ [7].

Using (20), (25), (31), and (32), we can obtain the dynamic matrix equations:

$$\begin{pmatrix} z\mathbf{1} & -i\mathbf{l} & 0 & 0 \\ i(\chi^a)^{-1} & z\mathbf{1} - \Sigma^a & 0 & 0 \\ 0 & 0 & z\mathbf{1} & -i\mathbf{l} \\ 0 & 0 & i(\chi^o)^{-1} & z\mathbf{1} - \Sigma^o \end{pmatrix} \begin{pmatrix} \Phi^{uu} & \Phi^{u\dot{u}} & \Phi^{ux} & \Phi^{u\dot{x}} \\ \Phi^{\dot{u}u} & \Phi^{\dot{u}\dot{u}} & \Phi^{\dot{u}x} & \Phi^{\dot{u}\dot{x}} \\ \Phi^{xu} & \Phi^{x\dot{u}} & \Phi^{xx} & \Phi^{x\dot{x}} \\ \Phi^{\dot{x}u} & \Phi^{\dot{x}\dot{u}} & \Phi^{\dot{x}x} & \Phi^{\dot{x}\dot{x}} \end{pmatrix} \\ = -\beta^{-1} \begin{pmatrix} \chi^a & 0 & 0 & 0 \\ 0 & \mathbf{1} & 0 & 0 \\ 0 & 0 & \chi^o & 0 \\ 0 & 0 & 0 & \mathbf{1} \end{pmatrix}. \quad (37)$$

For the first column of the matrix Φ in (37), we obtain

$$z\Phi^{uu} - i\Phi^{\dot{u}u} = -\beta^{-1}\chi^a \quad (38)$$

and

$$i(\chi^a)^{-1}\Phi^{uu} + (z\mathbf{1} - \Sigma^a)\Phi^{\dot{u}u} = 0. \quad (39)$$

After elimination of $\Phi^{\dot{u}u}$, we find the equation for the displacement–displacement relaxation matrix $\Phi^{uu} = \Phi^a(z, \mathbf{k})$:

$$[z^2\mathbf{1} - z\Sigma^a(z, \mathbf{k}) - \chi^a(\mathbf{k})^{-1}]\Phi^a(z, \mathbf{k}) = -\beta^{-1}[z\mathbf{1} - \Sigma^a(z, \mathbf{k})]\chi^a(\mathbf{k}). \quad (40)$$

Using the third column of the matrix Φ , a similar equation is obtained for the displacement–displacement relaxation matrix $\Phi^{xx} = \Phi^o(z, \mathbf{k})$:

$$[z^2\mathbf{1} - z\Sigma^o(z, \mathbf{k}) - \chi^o(\mathbf{k})^{-1}]\Phi^o(z, \mathbf{k}) = -\beta^{-1}[z\mathbf{1} - \Sigma^o(z, \mathbf{k})]\chi^o(\mathbf{k}). \quad (41)$$

From the closed set of dynamic equations (33), (34), (40), and (41), one can determine the displacement–displacement relaxation function $\Phi_{ij}^\sigma(z, \mathbf{k})$. Using the $\Phi_{ij}^\sigma(z, \mathbf{k})$, the corresponding correlation function $\overline{\langle A_i(t), A_j \rangle}$ can be obtained by means of the fluctuation–dissipation theorem [31]:

$$\frac{1}{2}\overline{\langle A_i(t), A_j \rangle} = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} e^{-i\omega t} \frac{\beta\omega}{1 - e^{-\beta\omega}} \text{Im} \Phi_{ij}^\sigma(z = \omega + i\epsilon). \quad (42)$$

As a result, the time dependence of the correlation functions $\overline{\langle A_i(t), A_j \rangle}$ enables us to study the changes of the dynamic behaviour of the QPE.

4. The non-ergodic state induced by defects

The type of the dynamic state (ergodic or non-ergodic) is determined by the behaviour of the long-time correlation function of the fluctuations $\overline{\langle A_i(t \rightarrow \infty), A_j \rangle}$. In the ergodic state, there is a decay of the correlation function of the fluctuations over time to zero: $\langle A_i(t \rightarrow \infty), A_j \rangle = 0$. In the non-ergodic state, there is a decay of the correlation function of the fluctuations over time to a non-zero value: $\langle A_i(t \rightarrow \infty), A_j \rangle / 2 = L_{ij}^\sigma > 0$. As seen from (42), the non-zero value of the non-ergodic parameter $L_{ij}^\sigma > 0$ corresponds the spectral function

$$\text{Im} \Phi_{ij}^\sigma(z = \omega + i\epsilon) = \pi L_{ij}^\sigma \delta(\omega) + \text{regular terms}$$

which demonstrates the central-peak phenomenon, or the relaxation function in the form [32]

$$\Phi_{ij}^\sigma(z) = -\frac{L_{ij}^\sigma}{z}. \quad (43)$$

Let us transform (40) and (41) into the form (19). We have

$$\beta \mathbf{L}^\sigma(\mathbf{k}) = \beta \lim_{z \rightarrow i\epsilon} (-z \Phi^\sigma(z, \mathbf{k})) = \chi^\sigma(\mathbf{k}) - \chi^\sigma(z, \mathbf{k}) \quad (44)$$

$$\chi^\sigma(z, \mathbf{k}) = \frac{1}{z \Sigma^\sigma(z, \mathbf{k}) + (\chi^\sigma(\mathbf{k}))^{-1}}$$

where $\chi^\sigma(z, \mathbf{k})$ is the matrix of the Kubo susceptibility [31], and $\chi^\sigma(\mathbf{k})$ is the matrix of the thermodynamic susceptibility (equations (26) and (29)). As seen from (44), the non-ergodic state takes place ($\mathbf{L}^\sigma(\mathbf{k}) > 0$) if the conditions

$$\lim_{z \rightarrow i\epsilon} z \Sigma_{ij}^\sigma(z, \mathbf{k}) > 0$$

are fulfilled.

Let us study the condition that must be met for the dynamic transition from an ergodic to a non-ergodic state to occur in detail. To simplify further consideration, we use the approximations for $\Sigma_{\nu\nu}^o(z, \mathbf{k})$ of (34). (i) We neglect the second term in $\Sigma_{\nu\nu}^o(z, \mathbf{k})$ (the case of strong NSB and weak SB defects). (ii) As noted above, the lattice of the QPE does not undergo a ferroelectric phase transition and does not have a critical region. In this case, the consideration can be carried out in terms of a mean-field-type approximation that gives a \mathbf{k} -independent $L_{\nu\nu}^o(\mathbf{k}) \approx L_{\nu\nu}^o$ non-ergodic parameter. This approximation was also used for the study of the appearance of the dynamic transition from an ergodic to a non-ergodic state outside the critical region of the ferroelastic phase transition for the mixed cyanide crystals $\text{K}(\text{CN})_x\text{Br}_{1-x}$ and $(\text{KCN})_x(\text{NaCN})_{1-x}$ [15]. As follows from (8), the correlation function of the density of the NSB defects is also \mathbf{p} -independent: $\overline{\Delta c(-\mathbf{p}) \Delta c(\mathbf{p})} = c(1-c)$. As a consequence of the proposed approximations, the optical relaxation kernel is \mathbf{k} -independent: $\Sigma_{\nu\nu}^o(z, \mathbf{k}) \approx \Sigma_{\nu\nu}^o(z)$. Using the polarization $P_\alpha(\mathbf{k})$ instead of the variables $x_\nu(\mathbf{k})$, the self-consistent equations (34) and (41) can be written in the more convenient form for one of the $\langle 100 \rangle$ directions:

$$\frac{\beta L_{\alpha\alpha}^p / \chi_{\alpha\alpha}^p(\mathbf{k})}{1 - \beta L_{\alpha\alpha}^p / \chi_{\alpha\alpha}^p(\mathbf{k})} = -z \Sigma_{\alpha\alpha}^p(z) \chi_{\alpha\alpha}^p(\mathbf{k}) = \frac{c(1-c)G^2}{\lambda^4} \beta L_{\alpha\alpha}^p \chi_{\alpha\alpha}^p(\mathbf{k}). \quad (45)$$

Here the relations $L_{xx}^p = L_{yy}^p = L_{zz}^p$ are assumed, and $L_{\alpha\alpha}^p$ is written in terms of the local polarizations $P_\alpha(\mathbf{r})$ as

$$L_{\alpha\alpha}^p = \frac{1}{2} \left[\overline{\langle P_\alpha(\mathbf{r}, t \rightarrow \infty), P_\alpha(\mathbf{r}) \rangle} - q^p \right] \quad (46)$$

$$q_\alpha^p = \overline{(P_\alpha^{st}(\mathbf{r}))^2} = \overline{\langle P_\alpha(\mathbf{r}) \rangle^2} \sim c_d(1-c_d) \quad (47)$$

where q^p is the static glasslike parameter that is induced by the frozen SB defects with concentration c_d , and $\chi_{\alpha\alpha}^p(\mathbf{k}) = \lambda^2 / w_o^2(T, c, \mathbf{k})$. For the parameter $\varphi^p = \beta L_{\alpha\alpha}^p / \chi_{\alpha\alpha}^p(\mathbf{0})$, equation (45) at $\mathbf{k} = 0$ takes the simple form

$$\frac{\varphi^p}{1 - \varphi^p} = F^p(T, c) \varphi^p \quad (48)$$

$$F^p(T, c) = c(1-c) \left(\frac{G}{w_o^2(T, c, 0)} \right)^2. \quad (49)$$

According to the article [32], the continuous dynamic transition from an ergodic to a non-ergodic state takes place under the condition $F^p(T, c) \geq 1$. As a result, the parameter

$$\varphi^p = 1 - \frac{1}{F^p(T, c)} \quad (50)$$

which characterizes the non-ergodic state rises continuously for $T \leq T_d$. The temperature of the dynamic transition T_d is found from the condition

$$F^p(T_d, c) = 1. \quad (51)$$

The conditions for the existence of a dynamic transition from an ergodic to a non-ergodic state (equations (49) and (51)) require a weak stiffening of the soft mode $\omega_v^2(T, c, \mathbf{0}) = \omega_v^2(T) + Gc$ and a strong dispersion of the random transition temperatures described by $\Sigma_{vv}^o(z, \mathbf{k} = 0) (\sim c(1-c)G^2)$. This case corresponds to very hard defects (i.e. a very large value of the parameter G).

Let us estimate the lowest concentration of NSB defects that can induce the dynamic transition in the nominally pure QPE. In this work, we suggest considering the oxygen vacancies as very strong NSB defects that can actually induce a dynamic transition. This suggestion is based on the experimentally observed tremendous shift in the ferroelectric mode frequency with change in the oxygen vacancy concentration in SrTiO₃ [7]. The effect of oxygen vacancies corresponds to the action of very hard NSB defects ($A_d \gg |A|$) with a very large value, $G \approx 6800 \text{ cm}^{-2}$ per at.% of oxygen vacancies (or $\Delta T_c/\text{at.}\%$ of oxygen vacancies $\approx 250 \text{ K}$) [7]. A similar effect of oxygen vacancies occurs for the soft structural modes in SrTiO₃ [33, 34]. Nevertheless, the value of G for the ferroelectric mode is one order of magnitude larger than that for the structural mode [34]. Substituting the value of G and the experimental value $w_o^2(T \approx 30 \text{ K}, c, 0) \approx 500 \text{ cm}^{-2}$ [2] into the condition (51), we obtain $c \sim 0.6 \times 10^{-6}$ for $T_d = 30 \text{ K}$ in the nominally pure SrTiO₃. In KTaO₃, the effect of oxygen vacancies is also very strong [8], but the value of G , unfortunately, is unknown. If we take the value of G for SrTiO₃ and $w_o^2(T \approx 40 \text{ K}, c, 0) \approx 900 \text{ cm}^{-2}$ [2], we can estimate the lowest concentration of oxygen vacancies which can induce a dynamic transition in KTaO₃. As a result, we have $c \sim 1.7 \times 10^{-6}$ for $T_d = 40 \text{ K}$ in nominally pure KTaO₃. On the basis of the experimental study of the effect of oxygen vacancies on the soft structural modes in SrTiO₃, the estimate of the concentration of oxygen vacancies in nominally pure SrTiO₃ is $c \sim 2.5 \times 10^{-5}$ [33]. This concentration is considerably higher than the concentration of oxygen vacancies needed to give rise to the formation of a non-ergodic state at low temperatures. Hence, a dynamic transition from an ergodic to a non-ergodic state can actually be induced by the unavoidable oxygen vacancies acting as very hard NSB defects in SrTiO₃ and KTaO₃.

A non-zero value of the polar non-ergodic parameter φ^p for $T \leq T_q$ can also give rise to non-ergodic behaviour of the acoustic displacement–displacement relaxation function $\Phi^a(z, \mathbf{k})$ because

$$\lim_{z \rightarrow i\epsilon} (-z \Sigma^a(z, \mathbf{k})) > 0.$$

To simplify further investigation, the approximations for the acoustic relaxation kernel $\Sigma^a(z, \mathbf{k})$ are used. As in equation (45), we neglect the p -dependence of both the polar relaxation function $\Phi^p(z, \mathbf{p})$ and the correlation function of the static polar displacements $\overline{\xi_{\mu}^{st}(-\mathbf{p}) \xi_{\mu}^{st}(\mathbf{p})}$ induced by the random fields of the SB defects. As a result, we obtain for \mathbf{k} along one of the $\langle 100 \rangle$ directions

$$\lim_{z \rightarrow i\epsilon} (-z \Sigma^a(z, k_{\alpha}) = \frac{k_{\alpha}^2}{\rho} v_c D_{11}^2 q^p \beta L_{\alpha\alpha}^p \quad (52)$$

where $L_{\alpha\alpha}^p$ and q^p are given by (46) and (47) respectively, the conditions for the electrostrictive constants $D_{11} \gg D_{12}, D_{44}$ [5] are used, and $\rho = M/v_c$. To study the behaviour of the acoustic non-ergodic parameter

$$\mathbf{L}^a(\mathbf{k}) = \lim_{z \rightarrow i\epsilon} (-z \Phi^a(z, \mathbf{k}))$$

in detail, we transform (40) into a more convenient form, for \mathbf{k} along one of the (100) directions:

$$\frac{\beta L_{\alpha\alpha}^a(k_\alpha) A_{\alpha\alpha}(k_\alpha)}{1 - \beta L_{\alpha\alpha}^a(k_\alpha) A_{\alpha\alpha}(k_\alpha)} = -z \Sigma_{\alpha\alpha}^a(z, k_\alpha) \chi_{\alpha\alpha}^a(k_\alpha) = \frac{k_\alpha^2}{\rho} v_c D_{11}^2 q^p \beta L_{\alpha\alpha}^p A_{\alpha\alpha}^{-1}(k_\alpha) \quad (53)$$

where $A_{\alpha\alpha}(k_\alpha)$ is defined by (14). In addition, it should be noted that the right-hand part of equation (53) is k -independent. As a result, the parameter $\varphi^a = \beta L_{\alpha\alpha}^a(k_\alpha) A_{\alpha\alpha}(k_\alpha)$ is k -independent also. For the parameter φ^a , equation (53) has the form

$$\frac{\varphi^a}{1 - \varphi^a} = F^a(T, c_d) \varphi^p \quad (54)$$

$$F^a(T, c_d) = \frac{\varepsilon(T)}{4\pi C_{11}} D_{11}^2 q^p \sim c_d(1 - c_d). \quad (55)$$

Here $\varepsilon(T) = 4\pi\lambda^2 v_c / w_o^2(T, c)$ is the dielectric susceptibility, and $C_{11} = \rho v_l^2$ is the elastic constant. As seen from (54), the conditions for a non-zero value of the φ^a -parameter, which characterizes the non-ergodic behaviour of the fluctuations of the acoustic displacements, are $F^a(T, c_d) > 0$ and $\varphi^p > 0$, which are the same as the conditions for a non-zero value of φ^p , equation (51) (i.e. $T \leq T_d$). Hence, the SB defects do not change the condition (51), but have the effect on the formation of LTC of fluctuations of acoustic displacements. As noted above, a similarly unusual sudden formation of polar quasi-static lattice distortions of nominally pure KTaO_3 lightly doped with SB defects at $T \sim 40$ K was detected by the NMR method [19]. From (54), one obtains

$$\varphi^a = \frac{F^a(T, c_d) \varphi^p}{1 + F^a(T, c_d) \varphi^p} \quad (56)$$

where the parameter φ^a is k -independent, while the acoustic non-ergodic parameter $L_{\alpha\alpha}^a(k_\alpha)$ is k -dependent and has the form

$$L_{\alpha\alpha}^a(k_\alpha) = \frac{\varphi^a}{k_\alpha^2 \beta v_l^2}. \quad (57)$$

As seen from (57), the k -dependence of the acoustic non-ergodic parameter corresponds to the formation of a long-time correlation of long-wavelength fluctuations of the acoustic displacements (or a strain-domain-like state). In this case, the large correlated regions of the acoustic displacements (or strains) are formed more easily than the small correlated regions of the acoustic displacements. A similar phenomenon takes place in the non-ergodic state of the mixed cyanide crystals $\text{K(CN)}_x\text{Br}_{1-x}$ and $(\text{KCN})_x(\text{NaCN})_{1-x}$ [15].

The LTC of long-wavelength fluctuations of the acoustic displacements is very important for clarifying the origin of the domain-like state. It should be noted that the magnitude of the acoustic parameter φ^a is much less than that of the polar parameter φ^p (for the case of very hard NSB defects). In this case, the weak long-time correlation of the long-wavelength fluctuations of the acoustic displacements is difficult to observe in comparison with the long-time correlation of the local fluctuations of the polar displacements. To make the strain-domain-like state easy to observe, the crystals of QPE need to be doped with SB defects that induce random electric fields. The latest investigations of KTaO_3 lightly doped with off-centre Li ions [35] show that the slowly hopping dynamics of dipole (electric and elastic) moments of Li is frozen in the non-equilibrium state at $T > 50$ K, and they cannot take on long-range order, while linear birefringence develops for $T \leq T_d$, which corresponds to the formation of a strain-domain-like state [36]. In this case, the frozen dipole moments can act as random fields, and can give rise to a readily observed strain-domain-like state. Furthermore, the threshold temperature of the dipole glass state, $T_g \simeq 40$ K for $x \approx 0.22$

for K_{1-x}Li_xTaO₃ [37], corresponds to the temperature of the anomaly in the vicinity of 40 K for nominally pure KTaO₃ [19]. In this case, the condition for a non-ergodic state in nominally pure KTaO₃ can dictate the condition for glass state formation in K_{1-x}Li_xTaO₃. The latest study of the effect of the cooling rate on the time dependence of the dielectric constant [17] confirms the existence of non-ergodic states in both nominally pure KTaO₃ and K_{1-x}Li_xTaO₃ ($x \leq 0.025$). A similar phenomenon, in the form of non-analytic behaviour of the polarization response, which depends significantly on the small electric field amplitude and is independent of the frequency, has been observed for KTa_{1-x}Nb_xO₃ ($x \leq 0.009$) [38], for which the dipole glass state appears at T_g . Furthermore, this behaviour—in contrast to the case for the usual dipole glass—persists for temperatures (~ 45 K) that are appreciably higher than the temperature at which the peak of the response is observed. In view of this, the non-analytic behaviour of the response can be associated with the existence of a non-ergodic state caused by oxygen vacancies for $T_d > T_g$.

The results presented above demonstrate that a dynamic transition can be induced by oxygen vacancies in SrTiO₃ and KTaO₃. In this case, the concentration of the oxygen vacancies is the crucial parameter of the theory. The theory can be easily verified by means of reduction (i.e. the increase of the concentration of the oxygen vacancies) or oxidation (i.e. the decrease of the concentration of the oxygen vacancies) treatment of SrTiO₃ and KTaO₃. For lightly reduced samples of QPE with $c \leq 10^{-4}$, one has $w_o^2(T, c, \mathbf{0}) \approx w_o^2(T, 0, \mathbf{0})$, where the ferroelectric mode of the pure lattice $w_o(T, 0, \mathbf{0})$ softens as $T \rightarrow 0$. In this case, as seen from (49) and (51), the temperature of the dynamic transition T_d increases with increasing concentration of oxygen vacancies. In connection with this, it would be of considerable interest and is of importance to test the effects of reduction and oxidation treatment on the non-ergodic states in SB-doped and nominally pure SrTiO₃ and KTaO₃.

5. Conclusions

On the basis of a closed set of dynamic equations under the mode-coupling approximation, this investigation demonstrates that hard NSB defects formed by the oxygen vacancies can cause a dynamic transition from an ergodic to a non-ergodic state in the QPE. As a consequence of this, LTC of the local fluctuations of the polar displacements (the polar non-ergodic parameter) continuously arises for $T \leq T_d$.

At the same time, LTC of long-wavelength fluctuations of the acoustic displacements (the acoustic non-ergodic parameter) is also induced by NSB defects via the random local piezoelectric coupling for $T \leq T_d$. The random local piezoelectric coupling is caused by the electrostrictive interaction modified by the random electric fields of the SB defects. The acoustic non-ergodic parameter manifests itself as a strain-domain-like state without modification of the lattice symmetry.

The estimations which are based on the conditions that must be met for the dynamic transition to occur obtained here show that the unavoidable oxygen vacancies in the nominally pure SrTiO₃ and KTaO₃ can lead to a non-ergodic state. If the unavoidable oxygen vacancies are not sufficient in number to induce a dynamic transition, the required concentration can be obtained by a reduction treatment.

The conditions that must be met for a non-ergodic state to be induced by oxygen vacancies in the vicinity of $T \sim 40$ K in nominally pure KTaO₃ can determine the threshold condition for the appearance of the glass state in K_{1-x}Li_xTaO₃, where the dipole moments of Li off-centre impurities are frozen in the non-equilibrium state for $T > T_d$ and cannot take on a long-range order.

The results obtained above show that the elucidation of the role of oxygen vacancies in the formation of a non-ergodic state in SrTiO₃ and KTaO₃ is a very important and interesting problem, and requires further experimental and theoretical investigation.

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