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MODEL OF ISOSTRUCTURAL DYNAMICAL PHASE TRANSITION IN ANHARMONIC CRYSTAL WITH POSSIBLE RELEVANCE TO $SrTiO_3$

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We discuss a new type of phase transitions that correspond to a pairing of phonons of different lattice modes due to their anharmonic attraction in a crystal. We show that the main features of the isostructural phase transition observed in $SrTiO_3$ at $T \simeq 37\,K$ can be qualitatively explained with the phonon pairing phenomenon.

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Physical properties of the low-temperature phase of $SrTiO_3$ (STO) got recently much attention. Phase-transition-like anomalies in the temperature dependences of a number of structural and elastic characteristics of STO have been observed at the temperature $T = T_q \simeq 37$ K [1-6]. The anomalies are rather weak, have a form of more or less smeared breaks, while no change in the crystal symmetry is seen at $T = T_q$. There are a number of speculations about the nature of this phase transition and its low-temperature phase (being sometimes called "the Müller state", by the name of K.A. Müller who discovered this phase transition and attracted attention to it, see reviews [4-6]). The speculations include invoking a new kind of Bose condensation [5], some cooperative changes in the structure of dynamical polar clusters [4], etc, but any clear physical model for this phase transition seems to be lacking yet.

In the present work we suggest such a model. We adopt the qualitative considerations by Courtens [4] that the transition has a dynamical nature, and it is related to strong anharmonic interactions between the low-lying "soft" phonons that determine the dynamics of STO at low T under consideration. We suppose that this transition corresponds to a "pairing" of these phonons which in a number of formal aspects is analogous to the pairing of electrons in the standard BCS superconductivity theory. Physically, such phonon pairing corresponds to a spontaneous breaking of the lattice symmetry for some phonon modes which results in the relevant reconctruction of their energy spectrum and the character of their motion. We show that not only the isostructural phase transition, but also some peculiar features of the low-temperature dynamics of STO [2-4] seem to be naturally explained with this model.

To illustrate main features of the phonon pairing we consider at first a simplified model of only two interacting phonon branches, 1 and 2, with the following Hamiltonian

$$H = \frac{1}{2}\sum_{\mathbf{k}}\sum_{\alpha=1}^{2}(\dot{x}^{\alpha}_{\mathbf{k}}\dot{x}^{\alpha}_{-\mathbf{k}} + \omega^2_{\mathbf{k}\alpha h}x^{\alpha}_{\mathbf{k}}x^{\alpha}_{-\mathbf{k}}) + \frac{1}{4}\sum_{\mathbf{k}_i}\sum_{\alpha,\beta=1}^{2} V^{\alpha\alpha\beta\beta}_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3\mathbf{k}_4}x^{\alpha}_{\mathbf{k}_1}x^{\alpha}_{\mathbf{k}_2}x^{\beta}_{\mathbf{k}_3}x^{\beta}_{\mathbf{k}_4}. \qquad (1)$$

Here $\mathbf{k}$ or $\mathbf{k}_i$ is the phonon wave vector, and the sum of four $\mathbf{k}_i$ in the last term obeys the quasimomentum conservation condition; $x^{\alpha}_{\mathbf{k}}$ and $\dot{x}^{\alpha}_{\mathbf{k}}$ is the phonon normal coordinate

and momentum that obey the canonical commutation relations

$$[x^{\alpha}_{\mathbf{k}}, x^{\beta}_{\mathbf{q}}] = [\dot{x}^{\alpha}_{\mathbf{k}}, \dot{x}^{\beta}_{\mathbf{q}}] = 0, \qquad [\dot{x}^{\alpha}_{\mathbf{k}}, x^{\beta}_{\mathbf{q}}] = -i\hbar\delta_{\alpha\beta}\delta_{\mathbf{k}+\mathbf{q}}. \tag{2}$$

The quantity $\omega^2_{\mathbf{k}\alpha h}$ is the $\mathbf{k}\alpha$ phonon squared frequency found in the harmonic approximation. For the soft-mode crystals under consideration this quantity in some intervals of $\mathbf{k}$ can be negative [7]. Then the system is stabilized with anharmonic interactions that in our model are described by the last term of (1). The anharmonic potentials V^{1111} and V^{2222} are supposed to be mainly positive which ensures the lattice stability with respect to large values of x^{α}, while the inter-mode potential V^{1122} is supposed to be mainly negative which corresponds to an "attraction" of different modes.

To qualitatively investigate the phonon pairing we will treat the anharmonic interactions in (1) in the simplest mean-field (or Hartree – Fock, or "self-consistent phonon") approximation. This is a standard approach in treatments of anharmonic (in particular, of soft-mode) crystals, and in many problems it can be justified even quantitatively [7]. Within this approximation, each operator product $x^{\alpha}_{\mathbf{k}}x^{\beta}_{\mathbf{q}}$ in the last term of (1) is written as the sum of its average $\eta^{\alpha\beta} =< x^{\alpha}_{\mathbf{k}}x^{\beta}_{\mathbf{q}} >= \delta_{\mathbf{k}+\mathbf{q}}\eta^{\alpha\beta}_{\mathbf{k}}$ and the fluctuation $\xi^{\alpha\beta} = x^{\alpha}_{\mathbf{k}}x^{\beta}_{\mathbf{q}} - \eta^{\alpha\beta}$, and the interaction of fluctuations ξ is neglected [7]. Then the terms with the "diagonal" averages $\eta^{\alpha\alpha}$ can be included in the values of the renormalised (and thus temperature-dependent) squared frequencies in (1), which is a conventional procedure, for example, in the perturbative treatments of soft modes [7]. However, the non-diagonal, "anomalous" averages $\eta^{12}_{\mathbf{k}} =< x^{(1)}_{\mathbf{k}}x^{(2)}_{-\mathbf{k}} >$ are absent in any perturbative treatment, and their spontaneous rise at a certain temperature T_p corresponds to the phonon pairing phase transition.

Denoting for brevity $\eta^{\alpha\alpha}_{\mathbf{k}} = \eta^{\alpha}_{\mathbf{k}}$, $\eta^{12}_{\mathbf{k}} = \eta_{\mathbf{k}}$, $V^{\alpha\alpha\beta\beta}_{\mathbf{k},-\mathbf{k},\mathbf{q},-\mathbf{q}} = U^{\alpha\beta}_{\mathbf{kq}}$, and $V^{1122}_{\mathbf{k},\mathbf{q},-\mathbf{k},-\mathbf{q}} = -V_{\mathbf{kq}}$, we can write the resulting Hamiltonian as

$$H = \frac{1}{2}\sum_{\mathbf{k}}\left(\dot{x}^{\alpha}_{\mathbf{k}}\dot{x}^{\alpha}_{-\mathbf{k}} + \tilde{\omega}^2_{\mathbf{k}\alpha}x^{\alpha}_{\mathbf{k}}x^{\alpha}_{-\mathbf{k}} - 2\Delta_{\mathbf{k}}x^{(1)}_{\mathbf{k}}x^{(2)}_{-\mathbf{k}}\right) - \frac{1}{2}\sum_{\mathbf{kq}}U^{\alpha\beta}_{\mathbf{kq}}\eta^{\alpha}_{\mathbf{k}}\eta^{\beta}_{\mathbf{q}} + \frac{1}{2}\sum_{\mathbf{kq}}V_{\mathbf{kq}}\eta_{\mathbf{k}}\eta_{\mathbf{q}}. \tag{3}$$

The repeating indices α or β here and below imply summation over α or β from 1 to 2, while the quantities $\tilde{\omega}^2_{\mathbf{k}\alpha}$ and $\Delta_{\mathbf{k}}$ are related to the averages $\eta^{\alpha}_{\mathbf{k}}$ and $\eta_{\mathbf{k}}$ as

$$\tilde{\omega}^2_{\mathbf{k}\alpha} = \omega^2_{\mathbf{k}\alpha h} + \sum_{\mathbf{q}}U^{\alpha\beta}_{\mathbf{kq}}\eta^{\beta}_{\mathbf{q}}, \tag{4}$$

$$\Delta_{\mathbf{k}} = \sum_{\mathbf{q}}V_{\mathbf{kq}}\eta_{\mathbf{q}}. \tag{5}$$

The Hamiltonian (3) can be diagonalised with the unitary transformation

$$x^{(1)}_{\mathbf{k}} = u^{(1)}_{\mathbf{k}}\cos\theta_{\mathbf{k}} + u^{(2)}_{\mathbf{k}}\sin\theta_{\mathbf{k}}, \qquad x^{(2)}_{\mathbf{k}} = -u^{(1)}_{\mathbf{k}}\sin\theta_{\mathbf{k}} + u^{(2)}_{\mathbf{k}}\cos\theta_{\mathbf{k}}, \tag{6}$$

and similarly for $\dot{x}^{\alpha}_{\mathbf{k}}$ and $\dot{u}^{\alpha}_{\mathbf{k}}$, where $u^{\alpha}_{\mathbf{k}}$ and $\dot{u}^{\alpha}_{\mathbf{k}}$ are the new canonical variables obeying the commutation relations analogous to (2). The diagonalized Hamiltonian has the form

$$H = \frac{1}{2}\sum_{\mathbf{k}}\left(\dot{u}^{\alpha}_{\mathbf{k}}\dot{u}^{\alpha}_{-\mathbf{k}} + \Omega^2_{\mathbf{k}\alpha}u^{\alpha}_{\mathbf{k}}u^{\alpha}_{-\mathbf{k}}\right) - \frac{1}{2}\sum_{\mathbf{kq}}U^{\alpha\beta}_{\mathbf{kq}}\eta^{\alpha}_{\mathbf{k}}\eta^{\beta}_{\mathbf{q}} + \frac{1}{2}\sum_{\mathbf{kq}}V_{\mathbf{kq}}\eta_{\mathbf{k}}\eta_{\mathbf{q}}, \tag{7}$$

where the new frequencies $\Omega_{\mathbf{k}\alpha}$ are related to the original ones $\tilde{\omega}_{\mathbf{k}\alpha}$ as

$$\Omega^2_{\mathbf{k}1,2} = \frac{1}{2}\left\{\tilde{\omega}^2_{\mathbf{k}1} + \tilde{\omega}^2_{\mathbf{k}2} \pm \left[(\tilde{\omega}^2_{\mathbf{k}1} - \tilde{\omega}^2_{\mathbf{k}2})^2 + 4\Delta^2_{\mathbf{k}}\right]^{1/2}\right\} \tag{8}$$

and the parameter $\theta_{\mathbf{k}}$ in (6) is determined by the equation: $\tan 2\theta_{\mathbf{k}} = 2\Delta_{\mathbf{k}}/(\tilde{\omega}^2_{\mathbf{k}1} - \tilde{\omega}^2_{\mathbf{k}2})$.

The quantity $\Delta_{\mathbf{k}}$ can be considered as the order parameter of the phase transition, and the self-consistency condition (5) for it yields the following equation

$$\Delta_{\mathbf{k}} = \sum_{\mathbf{q}} V_{\mathbf{kq}} \varphi(\mathbf{q}, \Delta^2_{\mathbf{q}}) \Delta_{\mathbf{q}} \tag{9}$$

where the function $\varphi(\mathbf{q}, \Delta^2_{\mathbf{q}})$ is

$$\varphi(\mathbf{q}, \Delta^2_{\mathbf{q}}) = \frac{f_{\mathbf{q}2} - f_{\mathbf{q}1}}{\Omega^2_{\mathbf{q}1} - \Omega^2_{\mathbf{q}2}} \qquad \text{with} \qquad f_{\mathbf{q}\alpha} = \frac{\hbar}{2\Omega_{\mathbf{q}\alpha}} \coth \frac{\hbar\Omega_{\mathbf{q}\alpha}}{2T}. \tag{10}$$

One can also obtain Eq. (9) minimizing the phonon free energy corresponding to the Hamiltonian (7) with respect to quantities $\eta_{\mathbf{k}}$ treated as variational parameters. The explicit form of Eq. (4) for $\tilde{\omega}^2_{\mathbf{k}\alpha}$ is obtained with the expressions for $\eta^{\alpha}_{\mathbf{k}}$ resulting from Eqs. (6) – (8):

$$\eta^{1,2}_{\mathbf{k}} = (f_{\mathbf{q}1} + f_{\mathbf{q}2}) \pm \frac{\tilde{\omega}^2_{\mathbf{k}1} - \tilde{\omega}^2_{\mathbf{k}2}}{\Omega^2_{\mathbf{q}1} - \Omega^2_{\mathbf{q}2}} (f_{\mathbf{q}1} - f_{\mathbf{q}2}). \tag{11}$$

Near the phase transition point T_p the $\Delta_{\mathbf{q}}$ values are small. Writing in Eq. (9) the function $\varphi(\mathbf{q}, \Delta^2_{\mathbf{q}})$ at small $\Delta_{\mathbf{q}}$ as $\varphi_{\mathbf{q}} - \Delta^2_{\mathbf{q}}\psi_{\mathbf{q}}$ with $\varphi_{\mathbf{q}} = \varphi(\mathbf{q}, 0)$, we obtain for T close to T_p

$$\sum_{\mathbf{q}} V_{\mathbf{kq}} \varphi_{\mathbf{q}} \Delta_{\mathbf{q}} - \Delta_{\mathbf{k}} = \sum_{\mathbf{q}} V_{\mathbf{kq}} \psi_{\mathbf{q}} \Delta^3_{\mathbf{q}}. \tag{12}$$

According to the definition (10), the function $\varphi_{\mathbf{q}}$ is positive. Below we show that for the soft-mode crystals under consideration the function $\psi_{\mathbf{q}}$ is normally positive, too. The positive $\psi_{\mathbf{q}}$ correspond to the second-order phase transition, while the negative $\psi_{\mathbf{q}}$ would lead to the first-order transition, i.e. to an instability with respect to small values of $\Delta_{\mathbf{q}}$.

The solution of Eq. (12) can be conveniently written in terms of eigenfunctions $\chi_{n\mathbf{k}}$ and eigenvalues λ_n of the linear integral equation corresponding to the lhs of (12):

$$\sum_{\mathbf{q}} V_{\mathbf{kq}} \varphi_{\mathbf{q}} \chi_{n\mathbf{q}} = \lambda_n \chi_{n\mathbf{k}}. \tag{13}$$

As the potential $V_{\mathbf{kq}}$ is symmetric in variables $\mathbf{k}$ and $\mathbf{q}$, $V_{\mathbf{kq}} = V_{\mathbf{qk}}$, the functions $\chi_{n\mathbf{q}}$ can be orthonormalised with the weight $\varphi_{\mathbf{q}}$, see e.g. [8]. At the transition point T_p the highest eigenvalue λ_0 in (13) reaches unity, and the pairing region corresponds to the values $\lambda_0 > 1$. Using in Eq. (12) the usual perturbative expansion $\Delta_{\mathbf{k}} = \sum_n c_n \chi_{n\mathbf{k}}$ with $c_{n\neq 0} \ll c_0$ and neglecting higher powers of $(\lambda_0 - 1)$, we obtain

$$\Delta_{\mathbf{k}} = (\lambda_0 - 1)^{1/2} A \chi_{0\mathbf{k}} \tag{14}$$

where the constant A is $(\sum_{\mathbf{q}} \psi_{\mathbf{q}} \chi^4_{0\mathbf{q}})^{-1/2}$. Near T_p the factor $(\lambda_0 - 1)$ is proportional to the difference $T_p - T$ (keeping in mind STO, we suppose the pairing to occur at $T < T_p$). Therefore, the order parameter has the usual Landau-type temperature dependence

$\Delta_{\mathbf{k}} \sim (T_p - T)^{1/2}$, which is natural for the mean-field approximation used. However, the observable phonon characteristics such as their spectra (8) include only even powers of $\Delta_{\mathbf{k}}$. Therefore, the temperature anomalies δf near T_p should usually have a form of breaks or more weak singularities: $\delta f \sim (T_p - T)\theta(T_p - T)$, $(T_p - T)^2\theta(T_p - T)$, etc, while the specific heat at $T = T_p$ should have a jump characteristic of the mean-field theory.

To illustrate the form of functions $\varphi_{\mathbf{q}}$ and $\psi_{\mathbf{q}}$ in (12) we consider the case when the transition temperature T_p exceeds values $\hbar\tilde{\omega}_{\mathbf{k}\alpha}/2$ for significant phonons (which seems to be the case for STO, see below). Then $f_{\mathbf{q}\alpha}$ in (10) becomes $T/\Omega^2_{\mathbf{q}\alpha}$, and Eq. (4) is simplified:

$$\tilde{\omega}^2_{\mathbf{k}\alpha} = \omega^2_{\mathbf{k}\alpha h} + T\sum_{\mathbf{q}} U^{\alpha\beta}_{\mathbf{kq}} \frac{1}{\tilde{\omega}^2_{\mathbf{q}\beta}} \left(1 - \frac{\Delta^2_{\mathbf{q}}}{\tilde{\omega}^2_{\mathbf{q}1}\tilde{\omega}^2_{\mathbf{q}2}}\right)^{-1}. \tag{15}$$

Let us write the small-Δ expansion of $\tilde{\omega}^2_{\mathbf{k}\alpha}$ as $\omega^2_{\mathbf{k}\alpha} + \Delta^2_{\mathbf{k}}\zeta_{\mathbf{k}\alpha}$ where $\omega_{\mathbf{k}\alpha}$ corresponds to the absence of pairing. Then the functions $\varphi_{\mathbf{q}}$ and $\psi_{\mathbf{q}}$ in (12) are

$$\varphi_{\mathbf{q}} = \frac{T}{\omega^2_{\mathbf{q}1}\omega^2_{\mathbf{q}2}}, \qquad \psi_{\mathbf{q}} = \frac{T}{\omega^2_{\mathbf{q}1}\omega^2_{\mathbf{q}2}}\left(\frac{\zeta_{\mathbf{q}1}}{\omega^2_{\mathbf{q}1}} + \frac{\zeta_{\mathbf{q}2}}{\omega^2_{\mathbf{q}2}} - \frac{1}{\omega^2_{\mathbf{q}1}\omega^2_{\mathbf{q}2}}\right), \tag{16}$$

while quantities $\zeta_{\mathbf{k}\alpha}$ are determined by the linear equations

$$\zeta_{\mathbf{k}\alpha} + T\sum_{\mathbf{q}}\left(\frac{\Delta_{\mathbf{q}}}{\Delta_{\mathbf{k}}}\right)^2 U^{\alpha\beta}_{\mathbf{kq}}\frac{\zeta_{\mathbf{q}\beta}}{\omega^4_{\mathbf{q}\beta}} = T\sum_{\mathbf{q}}\left(\frac{\Delta_{\mathbf{q}}}{\Delta_{\mathbf{k}}}\right)^2 U^{\alpha\beta}_{\mathbf{kq}}\frac{1}{\omega^2_{\mathbf{q}\beta}\omega^2_{\mathbf{q}1}\omega^2_{\mathbf{q}2}}. \tag{17}$$

For soft-mode crystals the sums over $\mathbf{q}$ in Eqs. (12) and (17) converge in the region of small wavevectors where the harmonic values $\omega^2_{\mathbf{k}\alpha h}$ in (15) are negative. Therefore, for these k and $T \simeq T_p$ the sum over $\mathbf{q}$ in Eq. (15) exceeds $\omega^2_{\mathbf{k}\alpha}$, even though the main contribution to this sum is made by the thermally averaged phonons with "average" frequencies $\tilde{\omega}_{\alpha}(T)$ rather than by small-q phonons with smaller frequencies $\omega_{\mathbf{q}} \sim \omega_0$. As the similar sums in Eq. (17) converge at small-q and thus include additional large factors $\sim \tilde{\omega}_{\alpha}/\omega_{0\alpha}$, one can see that the sum of two first terms in the brackets of Eq. (16) should, generally, exceed the third one, and thus the function $\psi_{\mathbf{q}}$ in (12) should be positive.

Let us now discuss the physical factors that can promote the phonon pairing. Let us suppose for simplicity the $\mathbf{k}$- and $\mathbf{q}$-dependence of the potential $V_{\mathbf{kq}}$ in Eqs. (9), (13) to be insignificant, so this potential can be approximated with its averaged value $V_0 =< V_{\mathbf{kq}} >$. Then the integral equations (9), (13) become the algebraic ones, and Δ does not depend on $\mathbf{k}$. Supposing again the temperature T to exceed the values $\hbar\omega_{\mathbf{q}\alpha}/2$ for significant phonons, we obtain the following equation for the transition temperature $T = T_p$:

$$V_0 T\sum_{\mathbf{q}}\frac{1}{\omega^2_{\mathbf{q}1}\omega^2_{\mathbf{q}2}} = 1. \tag{18}$$

Eq. (18) illustrates two necessary conditions for an emergence of the phonon pairing: (i) the effective inter-mode interaction should correspond to a sufficiently strong attraction which in our model corresponds to positive and sufficiently large values of V_0, and (ii) the phonon pairing under lowering T can occur only in a soft-mode crystal in which phonon frequencies $\omega_{\mathbf{k}\alpha}$ are both sufficiently small and sufficiently rapidly decrease with lowering T within significant intervals of wave vectors $\mathbf{k}$.

In discussion of a possible phonon pairing in STO one should consider that two families of soft modes are present in this crystal at small-k. They correspond to two kinds of the order parameter, the ferroelectric one represented by the polarization $\mathbf{P}$, and the "structural" one represented by the angle $\mathbf{\Phi}$ describing the staggered rotation of oxigen octahedra in the perovskite structure [5, 9]. At $T_a = 105$ K the structural phase transition from the cubic to the tetragonal phase occurs with the rise of the order parameter $\Phi = \Phi_z$. The ferroelectric transition does not happen up to $T = 0$ (though it can be induced by a small applied stress or by doping with a small amount of impurities), but the dielectric constant $\epsilon(T)$ rises at low T up to very high values $\epsilon(0) \sim 10^5$ [5, 9]. In accordance with that there are several soft modes in the small-k region: the ferroelectric transverse optical branches, in particular, those polarised along z-axis (to be called for brevity P_z branches) and along x or y-axis (P_x or P_y branches), as well as the structural soft modes desribing the octahedra rotation, both around z-axis (Φ_z branches) and around x or y-axis (Φ_x or Φ_y branches). Frequencies of all these modes are rather small and have a notable temperature dependence up to quite low T. For example, at $k = 0$ the values of $\hbar\omega(P_z)$, $\hbar\omega(P_x)$, $\hbar\omega(\Phi_z)$, and $\hbar\omega(\Phi_x)$ and $T = 4.2$ K according to data [9] are 27, 13, 65 and 21 K, respectively, while between $T = 58$ K and 22 K the $\hbar\omega(P_z)$ value varies from 47 to 32 K [2]. Therefore, the above-mentioned condition (ii) in STO can be satisfied.

To make an idea about the anharmonic interactions between P_i and Φ_j modes we can use the estimates of non-linear terms in the free energy of STO made by Uwe and Sakudo (US) [9]. As it was discussed in [7], these terms correspond to the $k_i \to 0$ limit of the appropriate anharmonic interactions. US wrote these terms for the cubic phase as

$$F_{int} = -\sum_{ijkl} t^x_{ijkl} P_i P_j \Phi_k \Phi_l. \tag{19}$$

Due to the cubic symmetry there are only three different parameters t^x_{ijkl} in (19): $t^x_{xxxx} = t^x_{11}$, $t^x_{xxyy} = t^x_{12}$, and $t^x_{xyxy} = t^x_{44}$. As the degree of tetragonality of STO at $T < T_a$ is actually quite small, Eq. (19) can be used for estimates of anharmonic interactions at any T. US found: $t^x_{11} \simeq -7.4$, $t^x_{12} \simeq 9.6$, and $|t^x_{11}| \simeq 5 - 9$, in 10^{15} cgs. Therefore, the above-mentioned condition (i) can be satisfied for interactions of those P_i and Φ_j modes which are normal to each other, such as P_z and Φ_x or Φ_y modes for $\mathbf{k}$ in the xy plane, or P_x and Φ_y modes for $\mathbf{k}$ in the yz plane. Let us also note that due to the fluctuative effects (neglected in the above-described mean-field treatment and in the US estimates) the effective interactions t^x in (19) can actually notably rise with lowering T together with the dielectric constant $\epsilon(T)$, which is the case, for example, for $BaTiO_3$ being a structural analogue of STO, see [10] or [7], Ch. 8. Such "fluctuative" rise of effective interactions t^x can be one more factor promoting the phonon pairing transition in STO under lowering T.

The presence of several soft P_i and Φ_j branches can imply that to describe the phonon pairing in STO one should employ not the above-described 2-mode model, but more complex 3- or 4-mode pairing models. To this end we have considered the 3-mode pairing model. Then the unitary transformation analogous to (6) includes three parameters, which can be taken as the Euler angles decribing a 3-dimensional rotation, see e.g. [11]. The resulting relations analogous to (5) – (12) become more cumbersome, but all qualitative conclusions, including those about the character of the phase transition and the anomalies near T_p, remain the same as those for the 2-mode model.

The phonon pairing can explain some anomalies in the dynamics of STO at $T \lesssim T_q$ observed by Courtens et al. [2–4]. In particular, the apparent "mixing" of the P_z- and Φ_x-type modes at small $\mathbf{k} = (k_x, k_y, 0)$ stressed by these authors should be a direct consequence of the above-discussed (P_z, Φ_x) pairing at these $\mathbf{k}$. The other anomaly, presence at similar $\mathbf{k}$ of an additional, "anomalous" acoustic-like branch A, does not seem to be quite clear yet. However, such branch may be related to "critical" soft collective excitations under the phonon pairing, analogous to those discussed for a number of other phase transitions, see e.g. [12]. Strong interactions between the acoustic modes (U-modes) and the soft P_i and Φ_j modes can also be important for an existence of the A-branch. The relations between frequencies of U, P_i and Φ_j modes at these $\mathbf{k}$ can be approximately resonance-like, $\omega^U_{\mathbf{k}} \simeq |\omega^P_{\mathbf{k}+\mathbf{q}} - \omega^{\Phi}_{\mathbf{q}}|$, in significant intervals of $\mathbf{q}$ [2–4]. It can promote an emergence of extra resonance-like excitations due to the anharmonic interactions. Under the phonon pairing (6) these interactions should notably rise as additional 3-phonon couplings of the $UP\Phi$-type emerge, which at higher T are forbidden by the lattice symmetry. At $T \gtrsim T_p$ these effects can also persist, due to the fluctuative pre-transition phenomena (neglected in the above-described mean-field treatment).

To summarise, the phonon pairing can be a new type of phase transitions in an anharmonic crystal, and the main features of the low-temperature isostructural phase transition in STO can be qualitatively explained with the phonon pairing.

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