Hybrid soft-mode and off-center Ti model of barium titanate

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It has been recently established by NMR techniques that in the high temperature cubic phase of BaTiO$_3$ the Ti ions are not confined to the high symmetry cubic sites, but rather occupy one of the eight off-center positions along the [111] directions. The off-center Ti picture is in apparent contrast with most soft-mode type theoretical descriptions of this classical perovskite ferroelectric. Here we apply a mesoscopic model of BaTiO$_3$, assuming that the symmetrized occupation operators for the Ti off-center sites are linearly coupled to the normal coordinates for lattice vibrations. On the time scale of Ti intersite jumps, most phonon modes are fast and thus merely contribute to an effective static Ti-Ti interaction. Close to the stability limit for the soft TO optic modes, however, the phonon time scale becomes comparable to the relaxation time for the Ti occupational states of $T_{1u}$ symmetry, and a hybrid vibrational-orientational soft mode appears. The frequency of the hybrid soft mode is calculated as a function of temperature and coupling strength, and its role in the ferroelectric phase transition is discussed.

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I. INTRODUCTION

Barium titanate is a typical representative of perovskite ferroelectrics, which undergoes a cubic-to-tetragonal structural phase transition at the Curie temperature $T_C \approx 403$ K. The soft-mode nature of this transition has been determined by neutron scattering [1] as well as by hyper-Raman scattering [2], however, some open questions concerning the role played by the Ti ions have so far remained unanswered. Chaves et al. [2] proposed a thermodynamic model following the assumption of Comes et al. [4] that the Ti ion occupies one of the eight equivalent off-center sites along the [111] directions, which predicts a nonzero microscopic dipole moment of each unit cell and hence a transition of an order-disorder type.

The off-center displacements of Ti ions in the high-temperature cubic phase of BaTiO$_3$ have recently been confirmed by NMR experiments [5], which revealed the order-disorder dynamics of Ti ions to be coexisting with the observable displacive features of the TO soft mode. This immediately raises the question about the appropriate theoretical model for BaTiO$_3$ and related systems, as the widely accepted soft-mode description implies a central position of the Ti ion in the high temperature cubic phase, leading to a phase transition of a purely displacive type. Also, first-principles calculations of the electronic structure [6] do not support the idea that the ferroelectric distortion is due to the Ti ion ‘rattling’ in the oxygen cage. Some general features of the two types of phase transition have been discussed by Aubry [7] on the basis of a linear coupled double-well model. The crossover between the order-disorder and displacive transition was investigated by molecular dynamics calculations by Stachiotti et al. [8] who used a two-dimensional shell model of oxide perovskites. A microscopic treatment of perovskite ferroelectrics has been carried out by Girshberg and Yacoby (GY) [9, 10], who describe the degrees of freedom associated with the off-center displacements in terms of Ising pseudospin operators and introduce a linear pseudospin-phonon coupling. They derive an effective coupling between the off-center ions, which leads to a pseudospin ordering transition. The corresponding transition temperature is shifted from the instability temperature of the TO soft mode.

In this paper, we make an attempt to develop a mesoscopic treatment which combines the order-disorder and displacive features of the phase transition. We introduce a simple mechanism at the mesoscopic level, which is closely related to the above GY model, i.e., we adopt the linear coupling between the symmetrized occupation operators for the off-center Ti sites and the normal coordinates for lattice displacements. Assuming that on the time scale of Ti intersite jumps most phonon modes are fast, we show that these modes essentially contribute to a renormalization of the static Ti-Ti interactions, which can be either ferro- or antiferro-distortive. Meanwhile, close to the Ti ordering transition the time scale of the soft TO mode becomes asymptotically comparable to the characteristic time for the relaxation of the Ti dipole moment. Thus a new vibrational-orientational hybrid mode appears, which retains some of its original soft-mode character, however, its frequency and width is determined by the the relaxational dynamics of the Ti subsystem. In addition to the hybrid mode, a purely relaxational mode describing the intersite jumps of the Ti ions exists. It should be noted that the unperturbed TO soft mode describes the anharmonic vibrations of all the ions, and thus also include the oscillations of Ti ions around their average equilibrium positions. Apart from the time scales involved, the conditions for the formation of a hybrid soft mode may also depend on the strength of the Ti-phonon coupling, which thus plays the role of a control parameter in the present model.
II. COUPLED TITANIUM-PHONON SYSTEM: STATICS

Following Chaves et al., we define the occupation probabilities \( n_{il} = \{1, 0\} \) for the off-center Ti sites in the \( i\)-th unit cell, where \( l = 1, 2, \ldots, 8 \) according to the convention specified in Ref. \cite{2}. Obviously, \( \sum_l n_{il} = 1 \). Next, we introduce a set of symmetry adapted linear combinations of the \( n_{il} \) variables, which transform according to the irreducible representations \( A_{1g}, A_{1u}, T_{1u}, \) and \( T_{2g} \) of the cubic group,

\[
Y_{A_{1g}} = n_1 + n_2 + n_3 + n_4 + n_5 + n_6 + n_7 + n_8, \quad (1)
\]

\[
Y_{A_{1u}} = n_3 + n_4 + n_5 + n_7 - n_1 - n_2 - n_6 - n_8, \quad (2)
\]

\[
Y_{T_{1u,1}} = n_1 + n_2 + n_3 + n_4 - n_5 - n_6 - n_7 - n_8, \quad (3a)
\]

\[
Y_{T_{1u,2}} = n_1 + n_2 + n_5 + n_6 - n_3 - n_4 - n_7 - n_8, \quad (3b)
\]

\[
Y_{T_{1u,3}} = n_1 + n_4 + n_7 + n_8 - n_2 - n_3 - n_5 - n_6, \quad (3c)
\]

\[
Y_{T_{2g,1}} = n_1 + n_2 + n_7 + n_8 - n_3 - n_4 - n_5 - n_6, \quad (4a)
\]

\[
Y_{T_{2g,2}} = n_1 + n_4 + n_5 + n_8 - n_2 - n_3 - n_6 - n_7, \quad (4b)
\]

\[
Y_{T_{2g,3}} = n_1 + n_3 + n_6 + n_8 - n_2 - n_4 - n_5 - n_7, \quad (4c)
\]

Here we have omitted the cell index \( i \). The variables \( Y_{il} \), where \( \Gamma = 1, 2, \ldots, 8 \) labels the symmetries in the above order, satisfy the relation

\[
Y_{il}^2 = 1. \quad (5)
\]

This implies, for example, that the \( T_{1u} \) polar modes (3) can be effectively represented by three independent Ising-type variables \cite{10}.

We will assume that there exists a direct coupling between the symmetrized occupation probabilities or ‘pseudospins’ \( Y_{il} \) due to long range dipolar interactions, which has the form

\[
\mathcal{H}_{\text{dir}} = -\frac{1}{2} \sum_{\substack{i \neq j \Gamma}} \sum_l I_{ij}^{\Gamma\Gamma'} Y_{il} Y_{j\Gamma'}, \quad (6)
\]

In addition, we consider the interaction between the pseudospins and the phonon normal coordinates \( Q_{\bar{q}p} \),

\[
\mathcal{H}_{\text{int}} = -\frac{1}{\sqrt{N}} \sum_i \sum_{\bar{q}p} f_{\bar{q}p} Q_{\bar{q}p} Y_{il} \exp(i\bar{q} \cdot \vec{R}_i), \quad (7)
\]

where \( \bar{q} \) is the wave vector and \( p \) the branch index of lattice normal modes, \( f_{\bar{q}p} \) the coupling constant, and \( \vec{R}_i \) the lattice vector. Introducing the phonon momenta \( P_{\bar{q}p} \) and frequencies \( \omega_{\bar{q}p} \), we can write down the phonon Hamiltonian \cite{13}

\[
\mathcal{H}_{\text{ph}} = \frac{1}{2} \sum_{\bar{q}p} \left( \omega_{\bar{q}p}^2 Q_{\bar{q}p} Q_{\bar{q}p} - P_{\bar{q}p} P_{\bar{q}p} \right). \quad (8)
\]

It has long been established that in BaTiO\(_3\) and other perovskite ferroelectrics \cite{12} a soft TO phonon mode exists. Here we assume that the soft TO mode has a wave vector \( \bar{q}_0 \) and symmetry \( \Gamma = T_{1u}, \) where \( s \) is the corresponding branch index. The frequency of this soft mode vanishes at the stability limit \( T_0 \) in accordance with the Cochran relation

\[
\omega_{\bar{q}_0}^2 = a(T - T_0). \quad (9)
\]

In the following we will limit ourselves to the case where the soft mode condenses at the zone center, i.e., \( \bar{q}_0 = 0 \), as in BaTiO\(_3\).

It is well known that the pseudospin and phonon degrees of freedom can be decoupled by introducing displaced phonon coordinates \cite{4} \cite{10} \cite{12}

\[
\tilde{Q}_{\bar{q}p} = Q_{\bar{q}p} - \frac{1}{\sqrt{N}} \sum_{\bar{j}\Gamma'} \sum_{\bar{q}p'} f_{\bar{q}p}^{\Gamma\Gamma'} \omega_{\bar{q}p}^2 Y_{\bar{j}\Gamma'} \exp(-i\bar{q} \cdot \vec{R}_i). \quad (10)
\]

In this so-called adiabatic approach it is implied that the time scale for the Ti ion motion is much longer than the period of oscillation for phonon modes, so that phonon coordinates \( Q_{\bar{q}p} \) adapt adiabatically to any change of the pseudospin coordinates \( Y_{\bar{j}\Gamma'} \). Thus we obtain the adiabatic Hamiltonian

\[
\mathcal{H}_{ad} = \mathcal{H}_{\text{dir}} + \frac{1}{2} \sum_{\bar{q}p} \left( \omega_{\bar{q}p}^2 \tilde{Q}_{\bar{q}p} \tilde{Q}_{-\bar{q}p} + P_{\bar{q}p} P_{-\bar{q}p} \right) - \frac{1}{2} \sum_{ij} \sum_{\Gamma \Gamma'} K_{ij}^{\Gamma\Gamma'} Y_{i\Gamma} Y_{j\Gamma'}. \quad (12)
\]

In the last term, the Ti-Ti coupling constant is given by

\[
K_{ij}^{\Gamma\Gamma'} = \frac{1}{N} \sum_{\bar{q}p} f_{\bar{q}p}^{\Gamma\Gamma'} f_{\bar{q}p}^{\Gamma'\Gamma} \exp[i\bar{q} \cdot (\vec{R}_i - \vec{R}_j)]. \quad (13)
\]

On a mesoscopic scale, we are not interested in the microscopic mechanisms leading to the pseudospin-phonon coupling \( f_{\bar{q}p}^{\Gamma\Gamma'} \) and merely adopt the established functional form \cite{10}. In general, \( f_{\bar{q}p}^{\Gamma\Gamma'} \) contains the contributions of both short- and long-range interactions between the Ti and all the other ions. Short-range interactions are expected to be primarily responsible for the local potential of the Ti ion. Indeed, first-principles calculations indicate that ferroelectricity in BaTiO\(_3\) appears as the result of hybridization of the Ti-O bond \cite{12} \cite{14}. Therefore, the contribution of short-range forces to \( f_{\bar{q}p}^{\Gamma\Gamma'} \) and hence to \( K_{ij}^{\Gamma\Gamma'} \) is expected to be dominant, although long-range electrostatic dipole-dipole interactions contained in \( f_{\bar{q}p}^{\Gamma\Gamma'} \) are also needed to establish ferroelectric order \cite{4}.

The \( i \neq j \) part of the last term in Eq. (12) has the same structure as the direct interaction \cite{4}. Therefore, \( K_{ij}^{\Gamma\Gamma'} \).
for \( i \neq j \) represents an additional interaction between the Ti ions at two different sites, which together with the direct coupling \( I_{ij}^{\Gamma \Gamma} \) can lead to an order-disorder transition into a \( T_{1u} \) polarized state of the Ti subsystem. In general, this interaction involves two different symmetries \( \Gamma \) and \( \Gamma' \), and is real after being symmetrized with respect to the exchange \( \Gamma \leftrightarrow \Gamma' \). Thus we can combine the two coupling constants \( I_{ij}^{\Gamma \Gamma} \) and \( I_{ij}^{\Gamma \Gamma'} \) into a single coupling parameter \( J_{ij}^{\Gamma \Gamma'} = I_{ij}^{\Gamma \Gamma} + I_{ij}^{\Gamma \Gamma'} \).

The \( i = j \) terms in Eq. (13), however, represent a constant shift of the local energy and do not contribute to the ordering of Ti ions \[13\]. It can be shown by symmetry arguments that \( K_{ii}^{\Gamma \Gamma'} \) is zero unless \( \Gamma' = \Gamma \).

In the following we will focus on the symmetric part of the interaction \( K_{ij,\Gamma} \equiv K_{ij}^{\Gamma \Gamma} \). Its Fourier transform is given by

\[
K_{q\Gamma} = \sum_p \frac{|f_{qp}^\Gamma|^2}{\omega_{qp}^\Gamma} - \frac{1}{N} \sum_{q',p} \frac{|f_{q'p}^\Gamma|^2}{\omega_{q'p}^\Gamma}, \tag{14}
\]

The second term is often neglected, however, as shown in Ref. \[13\] its presence is crucial in order to ensure a zero average value of \( K_{q\Gamma} \). In the \( q \to 0 \) limit, we have \( K_{q\Gamma} > 0 \) if \( \sum_p |f_{qp}^\Gamma|^2/\omega_{qp}^\Gamma \) has a maximum at the zone center. For symmetry \( \Gamma = T_{1u} \) this favors a ferroelectric ordering of the Ti subsystem provided that \( J_{0\Gamma} \equiv I_{0\Gamma} + K_{q\Gamma} > 0 \), implying that \( \langle Y_{0\Gamma T_{1u}} \rangle \neq 0 \), \( (s = 1, 2, \text{or 3}). \) If, however, the maximum occurs at the zone boundary, we can have \( K_{q\Gamma} < 0 \). For \( J_{0\Gamma} < 0 \), the ordering is antiferroelectric. It should be stressed that in view of relation \[13\] the interaction \( K_{q\Gamma} \) is, in general, temperature dependent.

The off-diagonal coupling \( J_{q}^{\Gamma \Gamma'} \) with \( \Gamma' \neq \Gamma \) leads to anisotropic interactions, which are assumed to be weaker than the isotropic part and can thus be treated by perturbation theory. Below, we will discuss the possibility that anisotropic interactions give rise to time-dependent random fields acting on the pseudospin variables.

In a ferroelectric system like BaTiO\(_3\), the main contribution to the coupling \( K_{q\Gamma} \) will come from the soft TO mode with phonon coordinate \( \tilde{Q}_{0s} \) and frequency \( \omega_{0s} \) as given by Eq. (12). The Ti subsystem will undergo a phase transition into an ordered state with nonzero value of the pseudospin thermal average \( \langle Y_{0s} \rangle \neq 0 \). The transition temperature is determined by the relation

\[
kT_c = L_{s0} + \frac{f_{0s}^2}{a(T_c - T_0)} - L_{s0}, \tag{15}\]

where we have substituted expression \[9\] for \( \omega_{0s}^2 \) and written \( L_{s0} \equiv (1/N) \sum_q |f_{q0}^{\Gamma'}|^2/\omega_{q0}^{\Gamma'} \). To evaluate \( L_{s0} \), we should know the details of the phonon spectrum as well as the \( q \)-dependence of the coupling. By adding a \( q^2 \)-term to \( \omega_{0s} \) in Eq. (13), it can be shown that the leading contribution to \( L_{s0} \) is a constant independent of temperature. Thus we find

\[
T_c = \frac{1}{2} \left[ T_0 + M_0/k + \sqrt{(T_0 - M_0/k)^2 + 4f_{00}^2/k\alpha} \right], \tag{16}\]

where \( M_0 \equiv I_0 - L_0 \) and we have dropped the indices \( s \). Expression (16) differs from the result of GY by the presence of the \( M_0 \)-term, which is, in general, different from zero. We will assume that \( I_0 > L_0 \) and \( 0 < M_0 < T_0 \), implying that \( T_c > T_0 \), i.e., the ordering takes place above the stability limit of the unperturbed soft mode. It can easily be seen that in the above case, the effect of \( M_0 \) is to shift \( T_c \) towards higher temperatures.

### III. SOFT MODE DYNAMICS

We now consider the response of the soft TO phonon mode \( Q_{q\tilde{q}} \) to a time-dependent electric field \( E_{-q\tilde{q}} \) associated with an optic wave in a light scattering experiment. Close to the transition, the time scales for the soft mode and for the relaxation of the Ti ions become comparable, and the dynamics based on the adiabatic Hamiltonian (12) is not applicable. The soft mode dynamics is governed by the corresponding part of the original Hamiltonian, namely,

\[
\mathcal{H}_{sm} = -\frac{1}{2} \sum_q \sum_{s=1,2,3} \sum_{\tilde{q}} f_{q\tilde{q}s} Y_{q\tilde{q}s} Y_{-q\tilde{q}s} + \frac{1}{2} \sum_q \sum_{s=1,2,3} \sum_{\tilde{q}} \left( \omega_{q\tilde{q}s} Q_{q\tilde{q}s} Y_{q\tilde{q}s} - P_{q\tilde{q}s} P_{-q\tilde{q}s} \right) - \left( \frac{1}{N} \sum_s \sum_{\tilde{q}} f_{q\tilde{q}s} Q_{q\tilde{q}s} Y_{q\tilde{q}s} - \mu E_{-q\tilde{q}} Q_{q\tilde{q}s} \exp(i\omega t) \right). \tag{17}\]

Here \( \mu = e^{-\sqrt{m^*}} \) is a coupling parameter involving the effective charge \( e^{-} \) and reduced mass \( m^* \). For simplicity, we do not include the direct coupling between the light vector \( E_{-q\tilde{q}} \) and the dipole moment associated with the Ti-O bond. We could, in principle, assume a nonzero value of the off-center Ti dipole moment, however, as shown by GY its contribution to the Curie constant is negligible in other perovskite ferroelectrics and can thus be ignored.

The time evolution of the soft-mode operators \( Q_{q\tilde{q}} \) and \( P_{q\tilde{q}} \) is governed by the Heisenberg equations of motion \( dQ_{q\tilde{q}}/dt = -(\hbar/\mu)[Q_{q\tilde{q}}, \mathcal{H}_{sm}] \). In contrast, the time dependent thermodynamic fluctuations of the variables \( Y_{is}(t) \) will be assumed to exhibit a pure relaxation motion with a single characteristic relaxation time \( \tau \), i.e., we will ignore the possibility of coherent dipole moment flips. The corresponding equation of motion can be obtained from the classical Langevin model (17), which is based on the continuous or ‘soft’ spin variables \(-\infty < Y_{is}(t) < +\infty \) with effective Hamiltonian

\[
\beta\mathcal{H}_{c.f} = \beta\mathcal{H}_{sm} + \sum_i \left( \frac{1}{2} r^2 Y_{is}^2 + \frac{1}{4} uY_{is}^4 \right). \tag{18}\]

For \( u = -r \to -\infty \) one recovers the discrete limit \( Y_{is}^2 = 1 \).
(cf. Eq. 20). The Langevin equation of motion is
\[ \frac{\partial Y_{qs}}{\partial t} = -\frac{\partial \beta (H_{eff})}{\partial Y_{qs}} + \xi_{qs}(t), \]  
where the Langevin noise \( \xi_{qs}(t) \) is a Gaussian random variable with zero mean and variance
\[ \langle \xi_{qs}(t) \xi_{qs}(t') \rangle = 2 \tau \delta_{ij} \delta(t-t'). \]  
Introducing the Fourier components \( Y_{qs}(\omega) \) etc., we obtain the linearized equations of motion
\[ i\omega Q_{qs} = P_{qs}; \]  
\[ i\omega P_{qs} = -\omega^2 Q_{qs} + \frac{1}{\sqrt{N}} \mathcal{F}_{qs} Y_{qs} + \mu E_{qs}; \]  
\[ i\omega \tau Y_{qs} = -(r - \beta I_{qs} - \Sigma_{qs}) Y_{qs} + \beta \sqrt{N} f_{qs} Q_{qs} + \xi_{qs}(\omega). \]  
Here \( \Sigma_{qs} \) is the self energy which can, in principle, be calculated by a diagrammatic expansion involving the parameter \( u \) and the pseudospin-phonon coupling \( f_{qs} \). In the following we will ignore the frequency dependence of \( \Sigma_{qs} \) in the soft-mode regime.

We can now introduce the static pseudospin response \( \chi_{qs} = \langle \delta Y_{qs}/\delta \xi_{qs} \rangle \), i.e.,
\[ \chi_{qs} = \frac{\beta}{r - \beta I_{qs} - \Sigma_{qs}}, \]  
and redefine the relaxation time by writing \( \tau_{qs} = \tau \chi_{qs}/\beta \). The solution of the above equations can then be expressed in the form
\[ Q_{qs}(\omega) = \frac{1}{\omega_{qs}^2 - \omega^2 - |f_{qs}|^2 \chi_{qs}/(1 + i\omega \tau_{qs})} \mu E_{qs}, \]  
and
\[ Y_{qs}(\omega) = \frac{\beta \sqrt{N} f_{qs} \chi_{qs}}{1 + i\omega \tau_{qs}} Q_{qs}(\omega), \]
where the random force term has been averaged out. Eq. 23 is similar, but not identical to the expression given by GY, which contains an extra term \( i\omega \Gamma_{qs} \) in the denominator, describing the damping of the TO soft mode due to lattice anharmonicity. Here we absorb this damping into the \( i\omega \tau_{qs} \) term by a proper redefinition the relaxation time \( \tau_{qs} \).

We now consider the \( \vec{q} = 0 \) case corresponding to a TO soft mode at the zone center. Dropping the subscripts \( s \) and introducing the far-infrared dielectric response \( \chi_Q(\omega) = Q_0(\omega)/\mu E_0 \) we get
\[ \chi_Q(\omega) = \frac{1 + i\omega \tau_0}{(\omega_0^2 - \omega^2)(1 + i\omega \tau_0) - f_0^2 \chi_0}. \]  
The contribution to the corresponding dielectric function is given by
\[ \epsilon_Q(\omega) \simeq \epsilon_\infty + \frac{\mu^2}{\epsilon_0 v_0} \chi_Q(\omega), \]
where \( v_0 \) is the unit cell volume.

In the absence of pseudospin-phonon coupling, \( f_0 \rightarrow 0 \), the static response \( \chi_Q(0) \) diverges at \( T_c = T_0 \) in view of Eq. 20. For \( f_0 \neq 0 \), the critical temperature is obtained from the equation \( \omega_0^2 - f_0^2 \chi_0 = 0 \), or after applying Eq. 22 from the relation
\[ a(T - T_0) = \frac{\beta f_0^2}{(r - \beta f_0 - \Sigma_0)}. \]  
Returning to the discrete limit \( Y_{qs}^2 = 1 \) we notice that the last result will be equivalent to Eq. 14 provided that \( r - \Sigma_0 \simeq 1 + \beta L_0 \). Thus, in the above limit the critical temperature \( T_c \) derived from the soft-mode dynamics will be precisely equal to the static value 10. This means that the hybrid soft mode becomes unstable at the static ordering temperature \( T_c \) of the Ti subsystem. It should be added that the technical reason for using the soft spin variables and Langevin dynamics is the fact that only in this formalism we were able to properly take into account the presence of the second term in Eq. 14.

To illustrate the frequency dependence of \( \chi_Q(\omega) \) we introduce dimensionless parameters \( f_0 \rightarrow f_0 \tau_0/\sqrt{N} \) and \( a \rightarrow a T_0 \tau_0^2 \), and choose their representative values as \( f_0 = 0.4 \) and \( a = 0.145 \), respectively. Also, we fix the value of the parameter \( M_0 \) at \( M_0/kT_0 = 0.5 \) and rescale the frequencies as \( \omega \rightarrow \omega \tau_0 \). In all numerical calculations we furthermore set \( \tau_0 = \text{const.} \), i.e., we ignore the noncritical temperature dependence of the relaxation time. We can then evaluate the spectral function
\[ I_Q(\omega) = \frac{\chi_Q''(\omega)}{\omega}, \]
which is related to the Raman scattering intensity. Here the imaginary part of the response is defined by \( \chi_Q(\omega) = \chi_Q(\omega) - i\chi_Q'(\omega) \). In Fig. 1, we plot \( I_Q(\omega) \) at five different temperatures \( T/T_c \). Far from \( T_c \), the spectrum is characterized by a single peak, the position of which moves towards zero frequency as \( T \rightarrow T_c \) in accordance with the expected soft-mode behavior.

The hybrid soft-mode frequency approximately corresponds to the position of the peak in \( I_Q(\omega) \). To obtain an unambiguous definition it is necessary to consider the complex poles of the response function 22. After introducing a new variable \( z = i\omega \tau_0 \), the denominator takes the standard form of a cubic polynomial with real coefficients
\[ z^3 + z^2 + \omega_0^2 \tau_0^2 z + (\omega_0^2 - f_0^2 \chi_0) \tau_0^2 = (z - z_1)(z - z_2)(z - z_3) = 0. \]  
The complex zeros \( z_n, n = 1, 2, 3, \) are given by the Cardano formula. The corresponding analytic expressions for \( z_n \) are cumbersome, but can easily be evaluated numerically. They then lead to three complex frequencies \( \omega_n = x_n + iy_n \) having the following properties: (i) One of the frequencies is always imaginary, say, \( \omega_1 = iy_1 \); (ii) The remaining two solutions are, in general, complex and
such that always \( x_3 = x_2 \); (iii) If \( x_2 = 0 \), then \( y_3 \neq y_2 \), however, for \( x_2 \neq 0 \) we have \( y_3 = y_2 \); (iv) In general, \( \sum_{n} y_n = 1/\tau_0 \), and (v) \( \omega_1 \omega_2 + \omega_2 \omega_3 + \omega_3 \omega_1 = -\omega_0^2 \).

The response \( \chi_{Q}(\omega) \) thus becomes

\[
\chi_{Q}(\omega) = -\frac{\omega - i\nu_0'}{\omega - iy_1}(\omega - \Omega_0^2 - i\omega') ,
\]

where \( \nu_0' = 1/\tau_0 \) and the resonance frequency \( \Omega_0 \) is given by

\[
\Omega_0^2 = -\omega_2 \omega_3 = x_2^2 + y_2 y_3 ,
\]

while the damping parameter is

\[
\gamma = y_2 + y_3 .
\]

The term \( i(x_2 y_3 + x_3 y_2) \) formally appearing in the product \( \omega_2 \omega_3 \) is zero in view of the properties (ii) and (iii) above. It further follows from (iv) that \( y_1 = \nu_0 - \gamma \), whereas from (v) we obtain a relation between \( \Omega_0 \) and \( \gamma \), namely,

\[
\Omega_0^2 + \gamma(\nu_0 - \gamma) = \omega_0^2 .
\]

We can now rewrite the spectral function \( \chi_{Q}(\omega) \) in the form

\[
I_{Q}(\omega) = \frac{A}{\omega^2 + y_1^2} + \frac{B - A\omega^2}{(\omega^2 - \Omega_0^2)^2 + \omega^2\gamma^2} ,
\]

where \( A = \gamma/(\Omega_0^2 + y_1^2 - y_1\gamma) \) and \( B = (2\Omega_0^2 + y_1^2 - \gamma^2)A \).

The first term represents a central peak associated with the relaxational motion of the Ti ions, whereas the second term describes a resonance occurring at \( \Omega_0 \). It should be noted, however, that because of the \( -A\omega^2 \) term in the numerator the last expression deviates from the standard spectral function for the damped harmonic oscillator. Furthermore, the \( -A\omega^2 \) term partially compensates the contribution of the relaxational term in Eq. \( \chi_{Q}(\omega) \), so that a separate central peak cannot be discerned at temperatures of interest, as it is evident from Fig. 1.

In Fig. 2, we plot \( \Omega_0^2 \) as a function of temperature with the same parameter values as in Fig. 1. For \( f_0 \) smaller than a limiting value \( f_0^m \), where \( f_0^m = 0.6721 \) for the present choice of representative parameter values, the temperature dependence of \( \Omega_0^2 \) near \( T_c \) is quasi linear,

\[
\Omega_0^2 \approx a'(T - T_c) ,
\]

where \( a' = a'(f_0) \) with \( a' \geq a \) and \( T_c \geq T_0 \). Thus we are dealing with a hybrid soft mode, which condenses at the instability temperature \( T_c \) given by the static critical temperature \( T_0 \).

The temperature dependence of the damping constant \( \gamma \) is shown in Fig. 3. For \( f_0 < f_0^m \) we have \( 0 < \gamma < \nu_0 \), whereas for \( f_0 > f_0^m \) we can see that \( \gamma \rightarrow \nu_0 \) as \( T \rightarrow T_c \).

It can be shown that in the hybrid soft mode regime \( f_0 < f_0^m \) the reduced damping constant \( \gamma_0 = \gamma/\Omega_0 \) diverges on approaching \( T_c \) from above as \( \gamma_0 \sim (T - T_c)^{-1/2} \). The temperature dependence of \( \gamma_0 \) is shown in the inset of Fig. 3.

The static susceptibility as obtained from Eq. \( \chi_{Q}(\omega) \) is given by

\[
\chi_{Q}(0) = \frac{1}{\tau_0 \Omega_0^2 (\nu_0' - \gamma') ,
\]

and is found to diverge at \( T_c \) as \( \chi_{Q}(0) \sim (T - T_c)^{-1} \) for all values of \( f_0 \). As already stated, for \( f_0 > f_0^m \) the damping parameter \( \gamma \) approaches the value \( \gamma \rightarrow \nu_0 \) as \( T \rightarrow T_c \), and thus \( \chi_{Q}(0) \) diverges even for \( \Omega_0(T_c) \neq 0 \). The temperature dependence of the inverse static response \( \chi_{Q}^{-1} \) is displayed in Fig. 2. For \( T < T_c \), we formally have \( \Omega_0^2 < 0 \) and the system becomes unstable. In principle, it should be stabilized by including anharmonic terms into the phonon Hamiltonian as well as a coupling to elastic strains.

For \( f_0 > f_0^m \), \( \Omega_0 \) is always nonzero and strictly speaking the hybrid soft-mode concept is not applicable in that case. The corresponding limiting value of the instability temperature corresponding to the representative parameter values used in numerical calculations here is \( T_0^c/f_0^m = 2.533 \). This is a fairly large value, suggesting that any real system is likely to be in the soft-mode regime \( 0 < f_0 < f_0^m \).
FIG. 2: Resonance frequency \( \Omega_0 \) as a function of temperature for several values of coupling strength \( f_0 \) (solid lines). For \( f_0 < f_0^c = 0.6721 \) a soft-mode behavior is observed. Also shown is the temperature dependence of the inverse static response (dashed lines).

FIG. 3: Damping parameter \( \gamma \) as a function of temperature for several values of coupling strength \( f_0 \). Inset: Reduced damping parameter \( \gamma_0 = \gamma / \Omega_0 \) for the same values of \( f_0 \).

IV. DISCUSSION

To determine the type of the phase transition occurring at \( T = T_c \), we introduce the order parameter as the thermal average of the Ti pseudospin variable \( P = \langle Y_0 \rangle \), which is related to \( \langle Q_0 \rangle \) through Eq. (24) at \( \omega = 0 \). We can then write down a Landau-type free energy

\[
\mathcal{F}(P) = \frac{1}{2} \chi_{Y}(0)^{-1} P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 + \cdots ,
\]

(37)

where the static pseudospin response \( \chi_{Y}(0) \) is related to the hybrid soft-mode response \( \chi_0(Q) \) and the rigid static pseudospin response \( \chi_0 \), namely,

\[
\chi_{Y}(0) = \chi_0(Q) \frac{\omega_0^2}{\omega_0^2 - f_0^2 \chi_0} \left( \frac{\omega_0^2}{f_0^2 \chi_0} \right) .
\]

(38)

As noted in deriving Eq. (27), the first denominator vanishes as \( T \to T_c \), while in the same limit the last factor approaches the value \( \omega_0^2 / f_0^2 \chi_0 \to 1 \). Eq. (38) is reminiscent of the Lyddane-Sachs-Teller relation for the static dielectric response. It follows that the coefficient of the quadratic term in \( \mathcal{F}(P) \) vanishes at \( T_c \) as \( \sim (T - T_c) \). The coefficients \( b \) and \( c \) can easily be determined within a molecular field approximation, however, it turns out that this approximation would predict a second order phase transition, in disagreement with observations in BaTiO\(_3\).

To derive the correct value of the coefficient \( b \) in the free energy we would have to include, for example, a coupling between the soft mode and elastic strain \( \chi_{str} \), or equivalently, between the strain and the Ti pseudospin variable. The appearance of a nonzero value of the order parameter will thus be accompanied by a macroscopic deformation of the lattice with tetragonal symmetry. In practice, \( b \) and \( c \) are often considered as phenomenological parameters. Hatta and Ikushima \( [17] \) applied an expression of the above form to analyze the measured heat capacity of BaTiO\(_3\) at constant electric field. They used the value \( T_c = 383 \text{ K} \) (in our notation) and found that \( b < 0 \) and \( c > 0 \), implying a first order phase transition which takes place at \( T_C \simeq 398 \text{ K} \) (or at \( \simeq 408 \text{ K} \), depending on the sample preparation method). They also determined the jump in the heat capacity at \( T_c \) of the order \( \Delta C \simeq 0.19 \text{ k} \), from which it was concluded that the Ti ion lies in a single minimum potential, in apparent disagreement with the off-center Ti picture. According to the present model the number of equilibrium positions of Ti is greater than one, but their actual number is only relevant for the definition of the Ti pseudospin variables. If we restrict the discussion to the adiabatic Hamiltonian \( [12] \), the phase transition appears to be of order-disorder type. However, the above approach involving hybrid soft-mode dynamics—which leads to the same critical temperature as the static approach—clearly has the characteristics of a displacive transition, but with a simultaneous ordering of the Ti subsystem as an additional order-disorder feature.

Evidence of a TO soft mode with \( T_{1u} \) symmetry in BaTiO\(_3\) has been found by Vogt et al. \( [2] \) using the hyper-
Raman scattering technique. The dielectric function has been fitted by a classical single oscillator dispersion formula, which is equivalent to the second term of Eq. (31) without the $\omega^2$-term in the numerator. One of the important results of Ref. 2 is that the frequency of the soft mode tends to zero close to the transition temperature and no saturation of the frequency at a finite value reported earlier occurs [15], in agreement with the predictions of the present model. Close to $T_c$, the temperature dependence of the soft-mode frequency can be described by the relation \( \omega \sim a T^{1/2} \) with \( a \approx 1.4 \times 10^{12} \text{s}^{-1} \). The relative damping constant $\gamma/\omega_0$ was found to exceed the value of 2 at all temperatures, whereas in the present model this is true only close to $T_c$.

It has been shown by NMR methods [5] that in the high temperature phase of BaTiO$_3$ the unit cells are tetragonally distorted, although the overall macroscopic symmetry is cubic. This agrees with Wada et al. [19] who determined the symmetry by Raman scattering and found that the macroscopic symmetry was P4mm both above and below $T_c$. Since the orientation of the tetragonal axis varies across the crystal, the macroscopic symmetry is Pm3m above the transition and P4mm below $T_c$. This can be accounted for by the present model if we return to the Ti-Ti coupling terms (6) and (13), and allow for off-diagonal interactions with $\Gamma' \neq \Gamma$. This then gives rise to extra terms the equations of motion (21c) for $Y_{qs}$, e.g.,

$$i\omega Y_{\bar{q}q} = - (r - \beta I_{\bar{q}q} - \Sigma_{\bar{q}q}) Y_{\bar{q}q} + \beta \sqrt{N} f_{\bar{q}q} Q_{\bar{q}q} + \beta \sum_{\bar{q}' \neq \bar{q}} J_{\bar{q}' \bar{q}} Y_{\bar{q}'q} + \xi_{\bar{q}q}(\omega).$$

On the time scale of the TO soft mode and of the Ti relaxation mode $Y_{\bar{q}q} = Y_{\bar{q}s}$, the variables $Y_{\bar{q}'q}$ are much slower and appear to be “frozen” in a given configuration. Thus the sum over $\Gamma'$ will play the role of a random variable $h_{\bar{q}q} = \sum_{\Gamma' \neq \Gamma} J_{\bar{q}' \bar{q}} Y_{\bar{q}'q}(t)$ analogous to the random electric field in dipolar glasses. Instead of spatial randomness, however, we are dealing here with a temporal disorder, which appears to be “quenched” on the time scale of $Y_{\bar{q}q}(t)$. This field will give rise to a slowly varying deformation of $T_{1u,s}$ symmetry, which is experimentally observable in both NMR and Raman experiments. Since the orientation of the deformation axis $s$ varies both in space and time, the average symmetry of the system remains cubic.

V. CONCLUSIONS

Recent experiments provided new evidence that the Ti ion in the cubic phase of BaTiO$_3$ [20, 21] and other oxide ferroelectrics occupies one of the eight off-center positions in the unit cell along the [111] directions. We have presented a simple mesoscopic model of BaTiO$_3$, assuming that the symmetrized occupational probabilities for the Ti sites or pseudospins are linearly coupled with the normal coordinates of lattice vibrations. On the time scale of Ti intersite jumps, lattice modes act as fast variables, which can adapt instantaneously to any change of the pseudospin configuration. In this adiabatic approximation, the pseudospin-phonon coupling gives rise to a static phonon mediated effective Ti-Ti interaction. The Ti subsystem thus undergoes an order-disorder transition into a polarized state of $T_{1u}$, symmetry, and the critical temperature $T_c$ is determined by a sum of the contributions from the direct Ti-Ti coupling and the pseudospin-lattice part. The leading contribution is due to the TO soft mode, the frequency of which tends to zero at the instability temperature $T_0$. In general, $T_c \geq T_0$, where the shift of $T_c$ depends both on the direct interaction as well as the pseudospin-phonon coupling.

Close to the stability limit for the TO soft mode, the time scales for the Ti and lattice motion become comparable and a dynamic treatment becomes necessary. By combining the classical Langevin equations of motion for the relaxation of the Ti pseudospins and the quantum Heisenberg equations for the TO soft mode coordinate, we have obtained the response of the system to an oscillating electric field, typically in an optical scattering experiment. The spectral function of this response consists of a central peak and a resonance, belonging to a new hybrid soft mode with $T_{1u}$ symmetry, which describes the in-phase motion of the TO soft optic mode and the relaxational decay of the symmetrized Ti pseudospin variable. The frequency of the hybrid soft mode tends to zero at the static critical temperature $T_c$. The central peak component is determined by the relaxational motion of the Ti subsystem and can be regarded as a typical order-disorder feature of the total response, in contrast to the resonance which shows a mixed displacive and order-disorder character.

The TO soft mode in BaTiO$_3$ has been observed experimentally by hyper-Raman scattering [21], and has been described by a damped harmonic oscillator, similar to our resonance term in the dynamic response. The soft mode frequency was found to extrapolate to zero close to the thermodynamic transition temperature $T_C$.

The frequency of the hybrid soft mode depends on the Ti-phonon coupling strength and exists only in a finite interval $0 < f_0 < f_m$, where the value of $f_m$ depends on the model parameters. Outside this interval, the soft mode concept is not applicable, however, the static response always diverges at $T_c$.

To calculate the free energy of the system we would have to include a coupling between the soft mode and lattice strains into the model. This can be done in a phenomenological approach [19], which describes the first order phase transition from the high temperature phase with macroscopic cubic symmetry to a tetragonal low temperature phase. The corresponding Curie temperature $T_C$ is generally higher than the instability temperature $T_0$, associated with the condensation of the hybrid soft mode.
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