Off-center Ti model of barium titanate

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It has recently been shown 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 the Girshberg-Yacoby off-center cation model of perovskite ferroelectrics assuming that the symmetrized occupation operators or "pseudospins" for the Ti off-center sites are linearly coupled to the normal coordinates for TO lattice vibrations. In the adiabatic limit, the coupling is eliminated by transforming to displaced phonon coordinates, and after excluding the self-interaction terms an effective Ti-Ti interaction is obtained. Using the Langevin equations of motion and the soft-spin formalism for the Ti pseudospin degrees of freedom with T_{1u} symmetry, the dynamic response of the coupled system is derived. The results are shown to be in qualitative agreement with the experimental data of Vogt *et al.* [Phys. Rev. B, **26**, 5904 (1982)] obtained by hyper-Raman scattering. The nature of the phase transition, which is of a mixed displacive and order-disorder type, is discussed.

I. INTRODUCTION

Barium titanate is a typical representative of perovskite ferroelectrics, which undergoes a cubic-to-tetragonal structural phase transition at the Curie temperature $T_C \simeq 408$ 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 pertinent questions regarding the role played by the Ti ions have so far remained unanswered. Chaves *et al.*[3] 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] cubic 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 demonstrated by NMR experiments,[5] which reveal that the order-disorder dynamics of Ti ions coexists with the observable displacive features of the TO soft mode. This off-center Ti picture of $BaTiO_3$ is also supported by the extended x-ray-absorption fine-structure (EXAFS) and x-ray-absorption near-edge structure (XANES) data.[6] While the NMR data imply an effective Ti displacement along the cubic unit cell edges, e.g., along [100], [010], and [001] directions, the EXAFS data show a Ti displacement along the cubic body diagonals, i.e., along the [111] directions. This apparent disagreement is due to different observation times in the two techniques. The NMR time scale is $\sim 10^{-8}$–10^{-5} s, whereas the EXAFS time scale is $\sim 10^{-15}$ s. Therefore NMR sees the time-averaged structure, whereas EXAFS probes the instantaneous local structure. The important point is that both of these techniques show that the Ti ions have off-center equilibrium positions already in the cubic phase.

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 po-

sition of the Ti ion in the high-temperature cubic phase, leading to a phase transition of a purely displacive type. First-principles calculations of the electronic structure also predict the off-center equilibrium position of the Ti ion, however, they do not support the idea that the ferroelectric distortion is due to the Ti ion "rattling" in the oxygen cage.[7,8] Some general features of the two types of phase transition have been discussed by Aubry[9] on the basis of a linearly coupled double-well model. The crossover between the order-disorder and displacive transition was investigated by means of molecular-dynamics calculations by Stachiotti *et al.*[10] who used a two-dimensional shell model of oxide perovskites.

A microscopic model of perovskite ferroelectrics has been developed by Girshberg and Yacoby,[11] who describe the degrees of freedom associated with the off-center displacements in terms of Ising pseudospins and introduce a linear coupling between the pseudospins and the TO soft mode. They derive an effective coupling between the off-center ions, which then leads to a pseudospin ordering transition. The corresponding transition temperature is shifted from the instability temperature for the unperturbed TO soft mode towards higher temperatures. For the dynamics, Girshberg and Yacoby introduce a phenomenological phonon damping parameter due to lattice anharmonicites as well as a Landau-Khalatnikov-type relaxation of the pseudospin degrees of freedom. The Girshberg-Yacoby (GY) model has been successfully applied to a number of perovskite ferroelectrics,[11–14] but to our knowledge not yet to $BaTiO_3$.

In this paper, we discuss in detail the applicability of the GY model to $BaTiO_3$. To describe the Ti off-center degrees of freedom we introduce a set of symmetrized occupation number operators and focus on the T_{1u} component, which is linearly coupled to the normal coordinates for the TO soft-mode displacements. On the time scale of Ti intersite jumps the phonon modes are considered to be fast. Thus in the adiabatic limit, the linear coupling can be eliminated by transforming to displaced phonon coordinates. This results in an effective static Ti-Ti interaction, which can be either
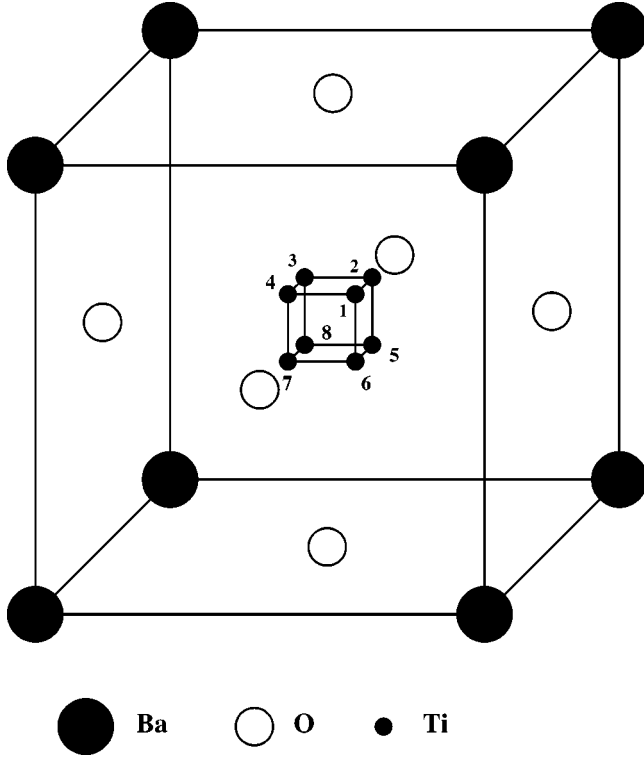
FIG. 1. Schematic diagram of the cubic unit cell of $BaTiO_3$, showing eight possible off-center displacements of the Ti ion along the [111] directions. [After Chaves *et al.* (Ref. 4).]

ferro- or antiferrodistortive. The last feature follows only after exclusion of the Ti self-interaction terms.[15]

To deal with the dynamics, we adopt the soft-spin formalism, which leads to the correct expression for the static Ti-Ti coupling in the zero-frequency limit. As shown by Girshberg and Yacoby for other perovskite systems, it is necessary to incorporate a phenomenological damping term into the dynamic response of the unperturbed soft mode. This damping is mainly responsible for the high-frequency part of the dynamic response, however, its shape is expected to be modified by the relaxational dynamics of the Ti subsystem. Thus the order-disorder and displacive components will merge into a single complex spectrum in the entire frequency range. Similarly, the phase transition will be characterized by a combined effect of displacive and order-disorder features such as the soft-mode behavior of the renormalized vibrational mode and the accompanying ordering of the Ti subsystem.

II. COUPLED TITANIUM-PHONON SYSTEM: STATICS

The unit cell of $BaTiO_3$ with eight possible off-center sites for the Ti ion along the [111] directions is displayed schematically in Fig. 1. Following Chaves *et al.*[3] we define the occupation probabilities $n_{il} = \{1, 0\}$ for the off-center Ti sites in the ith unit cell, where $l = 1, 2, \ldots, 8$. (see Fig. 1). Obviously, $\Sigma_l n_{il} = 1$. 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

$$Y_{A1g} = n_1 + n_2 + n_3 + n_4 + n_5 + n_6 + n_7 + n_8, \tag{1}$$

$$Y_{A1u} = n_1 + n_3 + n_5 + n_7 - n_2 - n_4 - n_6 - n_8, \tag{2}$$

$$Y_{T1u,1} = n_1 + n_2 + n_3 + n_4 - n_5 - n_6 - n_7 - n_8, \tag{3a}$$

$$Y_{T1u,2} = n_1 + n_2 + n_5 + n_6 - n_3 - n_4 - n_7 - n_8, \tag{3b}$$

$$Y_{T1u,3} = n_1 + n_4 + n_6 + n_7 - n_2 - n_3 - n_5 - n_8, \tag{3c}$$

$$Y_{T2g,1} = n_1 + n_2 + n_7 + n_8 - n_3 - n_4 - n_5 - n_6, \tag{4a}$$

$$Y_{T2g,2} = n_1 + n_4 + n_5 + n_6 - n_2 - n_3 - n_7 - n_8, \tag{4b}$$

$$Y_{T2g,3} = n_1 + n_3 + n_6 + n_8 - n_2 - n_4 - n_5 - n_7. \tag{4c}$$

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

$$Y_{i\Gamma}^2 = 1. \tag{5}$$

This implies, for example, that the T_{1u} polar modes (3) can be effectively represented by three independent Ising-type variables.[11]

We will assume that there exists a direct coupling between the symmetrized occupation probabilities or "pseudospins" $Y_{i\Gamma}$ due to long-range dipolar interactions, which has the form

$$\mathcal{H}_{dir} = -\frac{1}{2} \sum_{i \neq j} \sum_{\Gamma\Gamma'} I_{ij}^{\Gamma\Gamma'} Y_{i\Gamma} Y_{j\Gamma'}. \tag{6}$$

In addition, we consider the interaction between the pseudospins and the phonon normal coordinates $Q_{\vec{q}p}$[11,12]

$$\mathcal{H}_{int} = -\sum_{\vec{q}p\Gamma} f_{\vec{q}p}^{\Gamma} Q_{\vec{q}p} Y_{-\vec{q}\Gamma}, \tag{7}$$

where $\vec{q}$ is the wave vector and p the branch index of lattice normal modes, $f_{\vec{q}p}^{\Gamma}$ the coupling constant, and $Y_{\vec{q}\Gamma} = (1/\sqrt{N}) \Sigma_i Y_{i\Gamma} \exp(-i\vec{q} \cdot \vec{R}_i)$. Introducing the phonon momenta $P_{\vec{q}p}$ and frequencies $\omega_{\vec{q}p}$, we can write down the phonon Hamiltonian[16]

$$\mathcal{H}_{ph} = \frac{1}{2} \sum_{\vec{q}p} (\omega_{\vec{q}p}^2 Q_{\vec{q}p} Q_{-\vec{q}p} + P_{\vec{q}p} P_{-\vec{q}p}). \tag{8}$$

It is well known that in $BaTiO_3$ and other perovskite ferroelectrics[17] a soft TO phonon mode exists. In general, the soft mode may have a nonzero wave vector $\vec{q}_0$. Here we will limit ourselves to the case of a soft mode at the zone center, i.e., $\vec{q}_0 = 0$ as in $BaTiO_3$, having the symmetry $\Gamma = T_{1u,\lambda}$, where λ is the corresponding polarization index. In the simplest approximation, the frequency of this soft mode is assumed to go to zero at the stability limit T_s in accordance with the Cochran relation $\omega_{0\lambda}^2 \simeq a(T - T_s)$. In some cases a more general relation is required,[13,16] namely,

$$\omega_{0\lambda}^2 = a\left[\frac{T_1}{2}\coth\left(\frac{T_1}{2T}\right) - T_0\right]. \quad (9)$$

Here $T_1 \equiv \hbar\omega_1/k$ and T_0 are two adjustable parameters, which determine T_s, with ω_1 representing a local vibrational frequency.[18] As discussed in Sec. IV, in BaTiO$_3$ the frequency $\omega_{0\lambda}^2$ shows a moderate temperature nonlinearity, which can be described by Eq. (9). Of course, for $T \gtrsim T_1$ one recovers the linear Cochran relation with $T_s \simeq T_0$.

The pseudospin and phonon degrees of freedom can now be decoupled by introducing displaced phonon coordinates[11,12,15]

$$\tilde{Q}_{\vec{q}p} = Q_{\vec{q}p} - \sum_{\Gamma'} \frac{f_{-\vec{q}p}^{\Gamma'}}{\omega_{\vec{q}p}^2} Y_{\vec{q}\Gamma'}. \quad (10)$$

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 $Q_{\vec{q}p}$ adapt adiabatically to any change of the pseudospin coordinates $Y_{i\Gamma}$. Thus we obtain the adiabatic Hamiltonian

$$\mathcal{H}_{ad} = \mathcal{H}_{dir} + \frac{1}{2}\sum_{\vec{q}p}(\omega_{\vec{q}p}^2 \tilde{Q}_{\vec{q}p}\tilde{Q}_{-\vec{q}p} + P_{\vec{q}p}P_{-\vec{q}p})$$

$$- \frac{1}{2}\sum_{ij}\sum_{\Gamma\Gamma'} K_{ij}^{\Gamma\Gamma'} Y_{i\Gamma}Y_{j\Gamma'}. \quad (11)$$

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

$$K_{ij}^{\Gamma\Gamma'} = \frac{1}{N}\sum_{\vec{q}p}\frac{f_{\vec{q}p}^{\Gamma}f_{-\vec{q}p}^{\Gamma'}}{\omega_{\vec{q}p}^2}\exp[i\vec{q}\cdot(\vec{R}_i - \vec{R}_j)]. \quad (12)$$

On a mesoscopic scale, we are not interested in the microscopic mechanisms leading to the pseudospin-phonon coupling $f_{\vec{q}p}^{\Gamma}$ and we merely adopt its established functional form.[11,12] In general, $f_{\vec{q}p}^{\Gamma}$ 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.[8,19] Therefore the contribution of short-range forces to $f_{\vec{q}p}^{\Gamma}$, and hence to $K_{ij}^{\Gamma\Gamma'}$ is expected to be dominant, although long-range electrostatic dipole-dipole interactions contained in $I_{ij}^{\Gamma\Gamma'}$ are also needed to establish ferroelectric order.[8]

The $i \neq j$ part of the last term in Eq. (11) has the same structure as the direct interaction (6). 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 Γ and Γ', 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 $K_{ij}^{\Gamma\Gamma'}$ into a single coupling parameter $J_{ij}^{\Gamma\Gamma'} \equiv I_{ij}^{\Gamma\Gamma'} + K_{ij}^{\Gamma\Gamma'}$.

The $i = j$ terms in Eq. (12) represent a constant shift of the local energy and do not contribute to the ordering of Ti

ions.[15] 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

$$K_{\vec{q}\Gamma} = \sum_p \frac{|f_{\vec{q}p}^{\Gamma}|^2}{\omega_{\vec{q}p}^2} - \frac{1}{N}\sum_{\vec{q}'p}\frac{|f_{\vec{q}'p}^{\Gamma}|^2}{\omega_{\vec{q}'p}^2}. \quad (13)$$

The second term is often neglected, however, as shown in Ref. 15, its presence is crucial in order to ensure a zero value of the $\vec{q}$ average of $K_{\vec{q}\Gamma}$. In the $\vec{q} \to 0$ limit, we have $K_{0\Gamma} > 0$ if $\Sigma_p |f_{\vec{q}p}^{\Gamma}|^2/\omega_{\vec{q}p}^2$ has a maximum at the zone center. For the symmetry $\Gamma = T_{1u}$ this then favors a ferroelectric ordering of the Ti subsystem provided that $J_{0\Gamma} \equiv I_{0\Gamma} + K_{0\Gamma} > 0$, implying that $\langle Y_{0T1u,\lambda}\rangle \neq 0$, ($\lambda = 1, 2$, or 3). If, however, the maximum occurs at the zone boundary, we can have $K_{0\Gamma} < 0$. For $J_{0\Gamma} < 0$, the ordering is antiferroelectric. It should be stressed that in view of relation (9) the interaction $K_{\vec{q}\Gamma}$ is, in general, temperature dependent.

The off-diagonal coupling $J_{\vec{q}}^{\Gamma\Gamma'}$ 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. In Sec. V, 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 $K_{\vec{q}\Gamma}$ will come from the soft TO mode with phonon coordinate $\tilde{Q}_{0\lambda}$ and frequency $\omega_{0\lambda}$ as given by Eq. (9). The Ti subsystem will undergo a phase transition into an ordered state with nonzero value of the pseudospin thermal average $\langle Y_{0\lambda}\rangle \neq 0$. The transition temperature is determined by the mean-field relation $kT_c = J_{0\lambda}$, i.e.,

$$kT_c = I_{0\lambda} + \frac{f_{0\lambda}^2}{\omega_{0\lambda}^2(T_c)} - \frac{1}{N}\sum_{\vec{q}'}\frac{|f_{\vec{q}'\lambda}|^2}{\omega_{\vec{q}'\lambda}^2}, \quad (14)$$

where $\omega_{0\lambda}^2(T)$ is given by Eq. (9). To evaluate the sum over $\vec{q}'$, one should know the details of the phonon spectrum as well as the $\vec{q}$ dependence of the coupling. Using Eq. (9) for $\omega_{0\lambda}^2$ and adding a q^2 term, we can show that the leading contribution to the sum over $\vec{q}'$ is roughly independent of temperature, and thus the sum can be approximated by a constant.

For a system with a linear temperature dependence of $\omega_{0\lambda}^2$ we find the critical temperature

$$T_c \simeq \frac{1}{2}[T_0 + L_0/k + \sqrt{(T_0 - L_0/k)^2 + 4f_0^2/ka}], \quad (15)$$

where $L_{0\lambda} \equiv I_{0\lambda} - (1/N)\Sigma_{\vec{q}'} |f_{\vec{q}'\lambda}|^2/\omega_{\vec{q}'\lambda}^2$ and we have dropped the indices λ. This result differs from the corresponding expression of Girshberg and Yacoby (Ref. 11) by the presence of the L_0 term, which is generally different from zero. We will consider the case $0 < L_0 < T_0$, implying that $T_c > T_s$, i.e., the ordering will take place above the stability limit of the unperturbed soft mode. It is easily seen that in this case, the impact of L_0 is a shift of T_c towards higher temperatures.

III. SOFT-MODE DYNAMICS

We now consider the response of the soft TO phonon mode $Q_{\vec{q}\lambda}$ to a time-dependent electric field $E_{-\vec{q}\lambda}$ associated with an optic wave in a light-scattering experiment. Close to the transition, the time scales for the soft mode and for the relaxational motion of the Ti ions become comparable, and the dynamics based on the adiabatic Hamiltonian (11) is not applicable. The soft-mode dynamics is governed by the corresponding part of the original Hamiltonian, namely,

$$\mathcal{H}_{sm} = -\frac{1}{2}\sum_{\vec{q}'} I_{q'\lambda}^{\vec{}} Y_{q'\lambda}^{\vec{}} Y_{-\vec{q}'\lambda} + \frac{1}{2}\sum_{\vec{q}'} (\omega_{\vec{q}'\lambda}^2 Q_{q'\lambda}^{\vec{}} Q_{-\vec{q}'\lambda}$$
$$+ P_{q'\lambda}^{\vec{}} P_{-\vec{q}'\lambda}) - \sum_{\vec{q}'} f_{q'\lambda}^{\vec{}} Q_{q'\lambda}^{\vec{}} Y_{-\vec{q}'\lambda} - \mu E_{-\vec{q}\lambda} Q_{\vec{q}\lambda} \exp(i\omega t).$$

$$(16)$$

Here $\mu = e^*/\sqrt{m^*}$ is a field-coupling parameter for the TO mode involving the effective charge e^* and reduced mass m^*. For simplicity, we do not include the direct coupling between the light vector $E_{-\vec{q}\lambda}$ and the dipole moment associated with the Ti-O bonds. As found in Ref. 6, the off-center Ti displacements in BaTiO$_3$ are rather small and can be ignored here. Moreover, Girshberg and Yacoby (Ref. 14) have shown that in other perovskite ferroelectrics the contribution of Ti ions to the Curie constant is practically negligible.

The time evolution of the soft-mode operators $Q_{\vec{q}\lambda}$ and $P_{\vec{q}\lambda}$ is governed by the Heisenberg equations of motion. On the other hand, the time-dependent thermodynamic fluctuations of the variables $Y_{i\lambda}(t)$ will be assumed to exhibit a pure relaxational motion with a single characteristic relaxation time τ, 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,[20] which is based on the continuous or "soft" spin variables $-\infty < Y_{i\lambda}(t) < +\infty$ with effective Hamiltonian

$$\beta\mathcal{H}_{eff} = \beta H_{sm} + \sum_i \left(\frac{1}{2}rY_{i\lambda}^2 + \frac{1}{4}uY_{i\lambda}^4\right). \qquad (17)$$

For $u = -r \rightarrow \infty$ one recovers the discrete limit $Y_{i\lambda}^2 = 1$ [cf. Eq. (5)]. The Langevin equation of motion is

$$\tau\frac{\partial Y_{i\lambda}}{\partial t} = -\frac{\partial \beta(\mathcal{H}_{eff})}{\partial Y_{i\lambda}} + \xi_{\vec{q}\lambda}(t), \qquad (18)$$

where the Langevin noise $\xi_{i\lambda}(t)$ is a Gaussian random variable with zero mean and variance,

$$\langle \xi_{i\lambda}(t)\xi_{j\lambda}(t')\rangle = 2\tau\delta_{ij}\delta(t-t'). \qquad (19)$$

Introducing the Fourier components $Y_{\vec{q}\lambda}(\omega)$, etc., we obtain the linearized equations of motion

$$i\omega Q_{\vec{q}\lambda} = P_{\vec{q}\lambda}; \qquad (20a)$$

$$i\omega P_{\vec{q}\lambda} = -\omega_{\vec{q}\lambda}^2 Q_{\vec{q}\lambda} - 2i\omega\Gamma_{\vec{q}\lambda} Q_{\vec{q}\lambda} + f_{-\vec{q}\lambda} Y_{\vec{q}\lambda} + \mu E_{\vec{q}}; \qquad (20b)$$

$$i\omega\tau Y_{\vec{q}\lambda} = -(r - \beta I_{\vec{q}\lambda} - \Sigma_{\vec{q}\lambda})Y_{\vec{q}\lambda} + \beta f_{\vec{q}\lambda} Q_{\vec{q}\lambda} + \xi_{\vec{q}\lambda}(\omega). \qquad (20c)$$

Here we have included, following Girshberg and Yacoby, a phenomenological parameter $\Gamma_{\vec{q}\lambda}$ describing phonon damping due to the third- and fourth-order lattice anharmonicites. In the last equation, $\Sigma_{\vec{q}\lambda}$ is the soft-spin self-energy which can, in principle, be calculated by a diagrammatic expansion involving the parameter u and the pseudospin-phonon coupling $f_{\vec{q}\lambda}$. In the following we will ignore the frequency dependence of $\Gamma_{\vec{q}\lambda}$ and $\Sigma_{\vec{q}\lambda}$ in the soft-mode regime.

We can now introduce the static response of the Ti subsystem $\chi_{\vec{q}\lambda} = \langle \delta Y_{\vec{q}\lambda}/\delta\xi_{\vec{q}\lambda}\rangle$, i.e.,

$$\chi_{\vec{q}\lambda} = \frac{1}{kT(r - \Sigma_{\vec{q}\lambda}) - I_{\vec{q}\lambda}}, \qquad (21)$$

and redefine the relaxation time by writing $\tau_{\vec{q}\lambda} \equiv \tau\chi_{\vec{q}\lambda}/\beta$. The solutions of the above equations can then be expressed in the form

$$Q_{\vec{q}\lambda}(\omega) = \frac{\mu E_{\vec{q}}}{\omega_{\vec{q}\lambda}^2 - \omega^2 + 2i\omega\Gamma_{\vec{q}\lambda} - |f_{\vec{q}\lambda}|^2\chi_{\vec{q}\lambda}/(1 + i\omega\tau_{\vec{q}\lambda})}, \qquad (22)$$

and

$$Y_{\vec{q}\lambda}(\omega) = \frac{f_{\vec{q}\lambda}\chi_{\vec{q}\lambda}}{1 + i\omega\tau_{q\lambda}} Q_{q\lambda}(\omega), \qquad (23)$$

where the random force term has been averaged out. Equation (22) is equivalent to the expression given by Girshberg and Yacoby (Ref. 11), but it has been derived here in a more general context in view of the exclusion of the self-interaction term in Eq. (13), which cannot be accomplished within the usual random-phase approximation.

We now consider the $\vec{q} = 0$ case corresponding to a TO soft mode at the zone center. Dropping the subscripts λ and introducing the far-infrared dielectric response $\chi_Q(\omega) = Q_0(\omega)/(\mu E_0)$ we get

$$\chi_Q(\omega) = \frac{1 + i\omega\tau_0}{(\omega_0^2 - \omega^2 + 2i\omega\Gamma_0)(1 + i\omega\tau_0) - f_0^2\chi_0}. \qquad (24)$$

The contribution to the corresponding dielectric function can be written

$$\epsilon_Q(\omega) = \frac{\mu^2}{\epsilon_0 v_0}\chi_Q(\omega), \qquad (25)$$

where v_0 is the unit-cell volume. It should be noted that the static dielectric constant $\epsilon(0)$, and hence the Curie constant, cannot be derived from Eq. (25) by simply taking the limit $\omega \rightarrow 0$. The correct value of $\epsilon(0)$ is related to the static TO response via the generalized Lyddane-Sachs-Teller relation[16]

$$\epsilon(0) = \epsilon_\infty \prod_j \frac{\omega_{LO,j}^2}{\omega_{TO,j}^2}, \qquad (26)$$

where the product is over all optical branches j.

In the absence of the pseudospin-phonon coupling, $f_0 \rightarrow 0$, the static response $\chi_Q(0)$ diverges at a temperature T_s, which is the solution of $\omega_0^2(T)=0$ with $\omega_0^2(T)$ given by Eq. (9). For $f_0 \neq 0$, the critical temperature is determined from the denominator of Eq. (24) at $\omega=0$ as the temperature at which the renormalized soft-mode frequency,

$$\Omega_r^2(T) = \omega_0^2 - f_0^2 \chi_0, \qquad (27)$$

tends to zero. Using Eq. (21) we thus obtain the equation for T_c,

$$\omega_0^2(T) = \frac{f_0^2}{kT(r - \Sigma_0) - I_0}. \qquad (28)$$

Returning to the discrete limit $Y_{i\lambda}^2 = 1$, we require that the last result should be consistent with Eq. (14). This condition will be fulfilled if we choose

$$r - \Sigma_0 = 1 + \frac{\beta}{N} \sum_{\vec{q}'} \frac{|f_{\vec{q}'}|^2}{\omega_{\vec{q}'}^2}. \qquad (29)$$

Thus in the discrete limit the critical temperature T_c derived from the soft-mode dynamics will be precisely equal to the static value (15). This means that the renormalized soft mode becomes unstable at the static ordering temperature T_c of the coupled system. The response of the Ti subsystem (21) now becomes simply $\chi_0 = 1/(kT - L_0)$.

IV. COMPARISON WITH EXPERIMENTS

The dielectric response of BaTiO$_3$ in the optical regime was measured by Vogt et al.[2] using the hyper-Raman scattering technique. The frequency dependence of the dielectric constant was analyzed in terms of the response of a damped harmonic oscillator,

$$\epsilon''(\omega) = \frac{4\pi\rho \, \Omega_0^2 \gamma \omega}{(\Omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}. \qquad (30)$$

Here Ω_0, γ, and $4\pi\rho$ are the frequency, damping constant, and oscillator strength of the soft mode, where $\rho \propto \Omega_0^{-2}$. The results for Ω_0^2 and Ω_0^2/γ are displayed in Fig. 2. One of the conclusions of Ref. 2 is that the resonance frequency tends to zero close to the transition temperature and no saturation of the frequency at a finite value reported earlier occurs.[21]

The present result (24) for $\chi_Q(\omega)$ differs from Eq. (30) by the presence of the relaxation time τ_0. A detailed numerical analysis of Eq. (24) shows, however, that for $\Gamma_0 \gtrsim 60$ cm^{-1}, τ_0 does not affect the high-frequency (i.e., $\omega \gtrsim 2$ cm^{-1}) part of $\chi_Q''(\omega)$, but is mainly responsible for the low-frequency relaxation. Therefore in the high-frequency range we can approximate the renormalized frequency Ω_r by Ω_0 and Γ_0 by $\gamma/2$. Combining Eqs. (27) and (9) we can write

$$\Omega_r^2 = a \left[\frac{T_1}{2} \coth\left(\frac{T_1}{2T}\right) - T_0 \right] - \frac{f_0^2}{T - T_L}, \qquad (31)$$

where we have set $T_L = L_0/k$ ($k=1$). This expression contains too many parameters to permit a best-fit analysis of the data. A possible alternative is to fix some of the parameters, say,
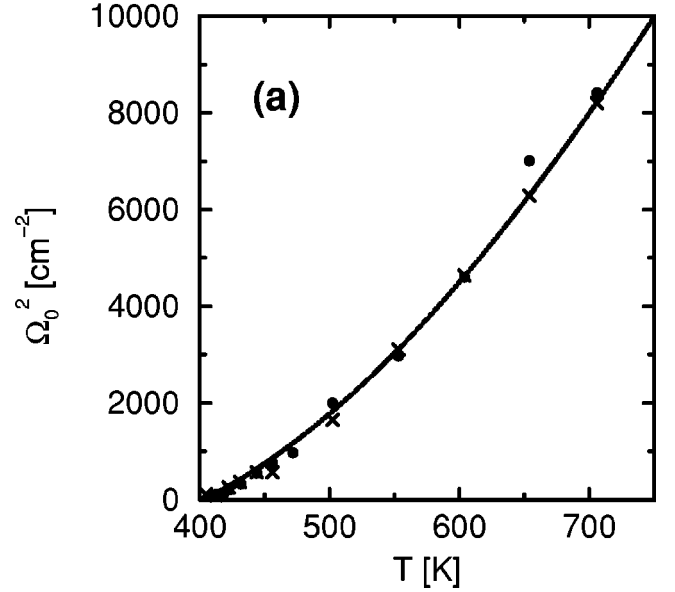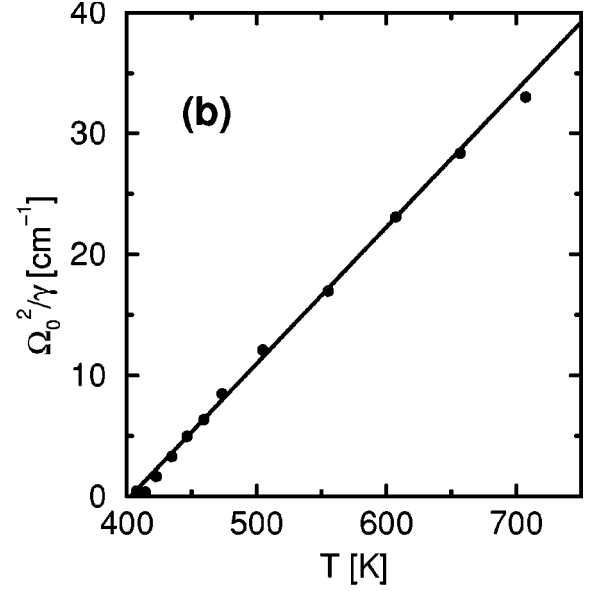

FIG. 2. (a) Renormalized frequency of the TO soft mode calculated from Eq. (31) with parameter values explained in the text. Dots and crosses: Experimental data of Vogt et al. (Ref. 2). (b) Ratio between renormalized frequency and soft-mode damping parameter, determined experimentally in Ref. 2 (dots). Solid line: linear fit (see the text).

$T_c = 403$ K[2], $T_0 = 400$ K, and $T_L = 300$ K, and adjust a and T_s—the temperature at which the unperturbed soft-mode frequency ω_0 vanishes—to fit the data. The parameter T_1 is then determined by solving the equation $\omega_0^2 = 0$, and the coupling strength is given by $f_0^2 = a(T_c - T_L)[(T_1/2)\coth(T_1/2T_c) - T_0]$. Thus we obtain the following values: $a = 70$ cm^{-2} K^{-1}, $T_s = 385$ K, and $T_1 = 1939.4$ K, implying $f_0 = 64$ cm^{-1} K$^{1/2}$. The resulting temperature dependence of Ω_r^2 is shown in Fig. 2(a). The fit turns out to be rather stable with respect to a variation of T_0, T_L, and even T_c.

The temperature dependence of the ratio Ω_0^2/γ is displayed in Fig. 2(b) and can be well described by a straight line $\Omega_0^2/\gamma = \alpha(T - T_c)$, where $\alpha = 0.113$ cm^{-1} K^{-1}.
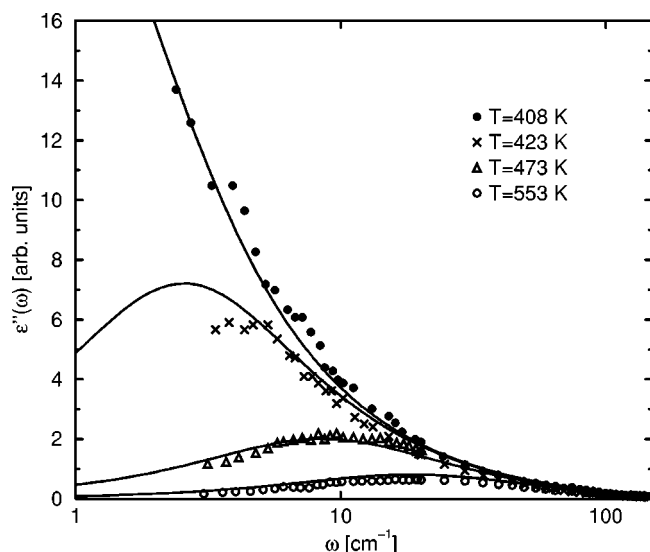
FIG. 3. Calculated frequency dependence of the imaginary part of the dielectric susceptibility at four different temperatures, as indicated. Symbols: experimental data from Ref. 2.

The temperature and frequency dependence of the imaginary part of the dynamic response $\chi_Q(\omega) = \chi'_Q(\omega) - i\chi''_Q(\omega)$ can now be evaluated from Eq. (24) and compared with the data for $\epsilon''(\omega)$ from Ref. 2. We can calculate the values of ω_0 and Ω_r from Eqs. (9) and (31), respectively, and determine $\Gamma_0 = \gamma/2$ from the above linear relation using the parameter values specified above. We adopt an Arrhenius-type relaxation time τ (Refs. 11 and 12) and write $\tau_0 = \tau_a \exp(u/T)T/(T-T_L)$, where $\tau_a = 0.05$ cm and $u = 3T_0$. As already stated, the high-frequency behavior is not sensitive to these values. A more precise determination of the relaxation time τ would require additional data at frequencies lower than ~ 2 cm^{-1}. An overall proportionality factor $A = 4.624 \times 10^3$ cm^{-2} has been included to match $\epsilon''(\omega)$ at $T = 408$ K with the corresponding data. The calculated spectrum is plotted in Fig. 3 at four different temperatures using a logarithmic horizontal scale, and is in qualitative agreement with the data. Some deviations occur in the high-frequency tail of the spectrum. A better agreement could be achieved by using a temperature-dependent prefactor and by readjusting the values of $\Gamma_0(T)$, but there is obviously no justification for doing that. A similar problem is encountered in fitting the data with the damped harmonic oscillator formula (30).

V. DISCUSSION

Traditionally, ferroelectric phase transitions have been divided into two classes, namely, (i) displacive and (ii) order-disorder transitions. It may, however, be argued that this classification is too rigid. A coexistence of displacive and order-disorder phenomena has been demonstrated by NMR experiments in hydrogen bonded materials such as squaric acid[22,23] and KDP,[24] where the expected order-disorder transition was found to contain a displacive component as well. This is analogous to the present case of BaTiO$_3$, where a ferroelectric phase transition, long believed to be of a displa-

cive type, has been shown to contain order-disorder components.

To specify the type of the phase trasition occurring in BaTiO$_3$, we introduce the order parameter as the thermal average $P = \langle Q_0 \rangle$, which is related to $\langle Y_0 \rangle$ through Eq. (23) at $\omega = 0$, i.e., $\langle Y_0 \rangle = f_0 \chi_0 P$. We can then write down a Landau-type free energy

$$\mathcal{F}(P) = \frac{1}{2}\chi_Q(0)^{-1}P^2 + \frac{1}{4}b\ P^4 + \frac{1}{6}c\ P^6 + \dots, \quad (32)$$

where the coefficient $\chi_Q(0)^{-1}$ is determined by the static soft-mode response (24),

$$\chi_Q(0)^{-1} = \omega_0^2 - f_0^2\chi_0 = \Omega_r^2, \quad (33)$$

and vanishes at T_c according to Eqs. (27) and (28). At high temperatures, $\chi_Q(0)^{-1} \sim (T - T_c)$, where T_c is given by Eq. (15). The coefficients b and c can be determined within a molecular field approximation, however, it turns out that this 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 strains.[25] The appearance of a nonzero value of the order parameter would thus be accompanied by a macroscopic deformation of the lattice of tetragonal symmetry. In practice, b and c are often considered as phenomenological parameters. Hatta and Ikushima[26] applied an expression of the above form to analyze the measured heat capacity of BaTiO$_3$ at constant electric field. They used the value $T_c = 383$ K (in our notation) and found that $b < 0$ and $c > 0$, implying a first-order phase transition which takes place at $T_C \simeq 398$ K (or at $\simeq 408$ K, depending on the sample preparation method). They also determined the jump in the heat capacity at T_C of the order $\Delta C \simeq 0.19k$, 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 1, but their actual number is only relevant for the proper definition of the Ti pseudospin variables. If we restrict the discussion to the adiabatic Hamiltonian (11), the phase transition appears to be of order-disorder type. However, the present approach involving the 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.

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.[27] who determined the symmetry by Raman scattering and found that the *microscopic* symmetry was $P4mm$ both above and below T_c. Since the orientation of the tetragonal axis varies across the crystal, the *macroscopic* symmetry is $Pm\bar{3}m$ above the transition and $P4mm$ below T_C. This can be accounted for in the present model if we return to the Ti-Ti coupling terms (6) and (12) and allow for off-diagonal interactions with $\Gamma' \neq \Gamma$. This then

gives rise to extra terms in the equations of motion (20c) for $Y_{\vec{q}\lambda}$, e.g.,

$$i\omega\tau Y_{\vec{q}\Gamma} = -(r - \beta I_{\vec{q}\Gamma} - \Sigma_{\vec{q}\Gamma})Y_{\vec{q}\Gamma} + \beta f_{\vec{q}\Gamma}Q_{\vec{q}\Gamma}$$
$$+ \beta \sum_{\Gamma' \neq \Gamma} J_{\vec{q}}^{\Gamma\Gamma'} Y_{\vec{q}\Gamma'} + \xi_{\vec{q}\Gamma}(\omega). \tag{34}$$

On the time scale of the TO soft mode and of the Ti relaxation mode $Y_{\vec{q}\Gamma} = Y_{\vec{q}T1u,\lambda}$, the variables $Y_{\vec{q}\Gamma'}$ are much slower and appear to be "frozen" in a given configuration. Thus the sum over Γ' will play the role of a random variable $h_{\vec{q}\Gamma} = \Sigma_{\Gamma' \neq \Gamma} J_{\vec{q}}^{\Gamma\Gamma'} Y_{\vec{q}\Gamma'}(t)$, 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 $Y_{\vec{q}\Gamma}(t)$. This field will give rise to a slowly varying deformation of T_{1u} symmetry, which is experimentally observable in both NMR and Raman experiments. Since the orientation of the deformation axis λ varies both in space and time, the average symmetry of the system remains cubic.

VI. CONCLUSIONS

Recent NMR (Ref. 5) and EXAFS (Ref. 6) experiments provide evidence that the Ti ion in the cubic phase of BaTiO$_3$ occupies one of the eight off-center positions in the unit cell along the [111] directions. An analogous situation occurs in other oxide ferroelectrics.[28,29] Following the model of Girshberg and Yacoby[11] for other perovskite ferroelectrics we have presented a derivation of the model suitable for BaTiO$_3$, based on the assumption 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 pseudospin configuration. In this adiabatic approximation, the pseudospin-phonon coupling gives rise to a static phonon-mediated effective Ti-Ti interaction after a proper exclusion of the self-interaction terms. 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_s. In general, $T_c \gtrsim T_s$, 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 he TO soft mode, the time scales for the Ti and lattice motion become comparable and a dynamic treatment becomes necessary. In the present approach, the oscillator frequency corresponds to the frequency of the renormalized soft mode, which depends on the Ti-phonon coupling. The oscillator damping parameter has been included in a phenomenological manner, as suggested by Girshberg and Yacoby.[11] Similarly, an Arrhenius-type expression[11] for the relaxation time τ describing the Ti reorientation has been assumed. The calculated frequency and temperature dependence of the dielectric function is in qualitative agreement with the hyper-Raman scattering data of Vogt *et al.*[2] New data at frequencies lower than ~ 2 cm^{-1} would be needed to determine more precisely the value of τ.

To calculate the complete free energy of the system one would have to include a coupling between the soft mode and lattice strains into the model. This may be possible in a phenomenological approach[25] describing 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 will generally be higher than the instability temperature T_c associated with the condensation of the renormalized soft mode.

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