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Theory of Perovskite Ferroelectrics

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A model Hamiltonian has been constructed for the ferroelectric transition in the perovskite structure in terms of localized-strain and soft-normal-mode coordinates and temperature-independent model parameters. No anharmonic interactions higher than fourth order are considered. The free energy for tetragonal, orthorhombic, and trigonal distortions is calculated in a molecular-field approximation with the cubic structure as a reference configuration. From the free energy, the polarization and the strain distortions are determined. The soft-mode frequencies and the shifts in the acoustic-phonon frequencies are calculated from linearized equations of motion describing the fluctuations about these average values. The soft-mode frequencies in cubic structure vanish at the supercooling temperature, as usually assumed. However, in the distorted structure they remain finite at the stability limit determining the superheating temperature. The model Hamiltonian describes first- or second-order transitions depending on the strength of the coupling with the strain. For suitable choice of model parameters, the model allows for transition from the cubic to the tetragonal phase as in $PbTiO_3$, to the trigonal phase as in $CsGeCl_3$ and various solid solutions, as well as a series of transitions from high- to low-symmetry structures, as in $BaTiO_3$.

I. INTRODUCTION

Traditionally two approaches have been used to describe displacive ferroelectric transitions. One is the phenomenological Devonshire theory[1] in which the free energy is expanded as a power series in the polarization and the strain. The coefficients are, in general, arbitrary functions of temperature which are determined experimentally. Although no explicit temperature dependences are calculated, this theory has been extremely useful in correlating experimental data. The other is a lattice-dynamical approach starting from very general anharmonic-lattice models. One or more of the harmonic normal-mode frequencies are assumed to be unstable. These modes are stabilized by anharmonic interactions. However, partly because of the formal nature of these theories and partly because of the large number of anharmonic-lattice coefficients, no attempt has been made to provide explicit descriptions of measured quantities such as the polarization soft-mode frequencies and strain distortions. With a few exceptions,[2,3] these calculations have been restricted to the quasiharmonic approximation in which the unstable harmonic soft-mode frequency is stabilized through interaction with the stable harmonic modes.[4-8] The interactions among the soft modes themselves are neglected.

Recently a calculation based on a model Hamiltonian containing a small number of temperature-independent parameters was able to give a quantitative description of the structural transition in the perovskites.[9] These papers will hereafter be referred to as I. This transition involves rotations of octahedral units. The analogous calculation for the ferroelectric transition is presented in this paper.

The model described in I was expressed in terms of localized normal-mode coordinates describing the rotations of the octahedra. A free-energy expression was constructed using a molecular-field approximation, including the contributions of the soft optical phonons. The order parameter, in this case the rotation angle, and the strain distortions were determined from the free energy. The soft optical-phonon frequencies and their interaction with the acoustic phonons were obtained from linearized equations of motion derived from the Hamiltonian.

The free-energy expression has a complicated functional dependence on the order parameter. If expanded in powers of the order parameter an infinite series results with generally temperature-dependent coefficients. These coefficients depend, however, only on combinations of the original model parameters, and the temperature dependence is determined by the theory. This should be compared with the Devonshire theory where each term in the power series introduces a new set of coefficients which are arbitrary functions of temperature. Usually only a few terms are kept and frequently the temperature dependence of all but the quadratic term is neglected. The Devonshire theory then predicts a strain distortion proportional to the square of the polarization,[10] and by an extension of the free-energy approach to give an approximate description of dynamic phenomena, predicts soft-mode frequencies in the distorted phase proportional to the order parameter.[10] From the calculations based on the model Hamiltonian, one of the soft-mode frequencies squared is found to be proportional to the order parameter squared, whereas the other frequency and the strain distortion are found to have a more complicated temperature dependence.[9]

It is also interesting to compare the approach used in I with the quasiharmonic approximation. If for simplicity we consider the undistorted cubic phase and only fourth-order anharmonic interactions, the soft-mode frequencies squared $\omega_\lambda^2(q)$ are given by[5-8]

$$\omega_\lambda^2(k)=\omega_{\lambda 0}^2(k)+\sum_{q\lambda'\neq\lambda_s} g^{(4)}_{\lambda\lambda'}(k,q)\,\frac{\coth\beta\omega_{\lambda' 0}(q)}{2\omega_{\lambda' 0}(q)}\ , \tag{1}$$

where $\omega_{\lambda 0}(k)$ are the harmonic normal-mode frequencies and $g^{(4)}_{\lambda\lambda'}(kq)$ are fourth-order anharmonic coupling constants. In the last term the actual phonon frequencies, renormalized by the anharmonic interactions, have been replaced by the harmonic phonon frequencies. This constitutes the quasiharmonic approximation. The summation runs over all the modes *except* the soft modes λ_s. These are neglected as the corresponding harmonic frequencies are purely imaginary.[11] For $\beta\omega_{\lambda' 0}(q)\ll 1$ and $k=0$, one obtains the usual Curie-Weiss behavior,

$$\omega_\lambda^2(0)=a_\lambda(T-T_0)\ ,$$

where

$$a_\lambda=k_B\sum_{q\lambda'\neq\lambda_s}\frac{g_{\lambda\lambda'}(0,q)}{2\omega_{\lambda'}^2(0,q)}$$

and

$$T_0=-\,\omega_{\lambda 0}^2(0)/a_\lambda\ .$$

By contrast, the soft-mode frequencies in I were determined by the self-consistency conditions[12]

$$\omega_\lambda^2(k)=\omega_{\lambda 0}^2(k)+\sum_{q\lambda'} g^{(4)}_{\lambda\lambda'}(kq)\,\frac{\coth\beta\omega_{\lambda'}(q)}{2\omega_{\lambda'}(q)}\ , \tag{2}$$

where the same soft-mode frequencies appear on the left-hand side and in the summation on the right-hand side. For the molecular-field approximation discussed in I, one obtains

$$\omega_\lambda^2(0)=a_\lambda(T-T_0)\qquad \text{for } T\gtrsim T_0$$

as before, whereas

$$\omega_\lambda^2(0)=b_\lambda T^{1/2}\qquad \text{for } T\to\infty\ .$$

From the form of Eq. (1) it follows that for equal coupling coefficients the contribution to the sum on the right-hand side is larger the lower the frequency. The terms involving the acoustic phonons and the soft-mode frequencies themselves may therefore be expected to be most important. In fact, in I only the soft-mode frequencies were considered. In the ferroelectric transition the interaction with the strain is much stronger as evidenced by the large change in the c/a ratios,[13] and in this paper the fourth-order coupling will be included. However, no anharmonic interactions higher than fourth order will be considered.

The harmonic Hamiltonian is usually assumed to consist of a positive contribution due to short-range forces and a negative contribution due to long-range dipolar forces.[14,15] The latter must then be larger than the positive contribution in order to have an instability. However, the short-range interaction need not always be positive. A displacive transition can then take place even in the absence of long-range dipolar forces. This appears to be the case for the structural transitions studied in I.

The anharmonic interactions will be assumed to be due to short-range forces only.

The ferroelectric transitions in the perovskites are usually first order.[13] In the Devonshire theory a description of a first-order transition requires sixth-order terms in the polarization with a negative fourth-order term. A negative contribution to the fourth-order coefficient is obtained from the third-order coupling to the strain when the strain is eliminated in terms of the polarization.[1,10] Similarly, in the molecular-field approximation, the model Hamiltonian gives a first-order transition for a sufficiently strong coupling to the strain, but without the need to introduce additional sixth-order terms. This suggests that a Hamiltonian with only a few model parameters may be sufficient to describe the ferroelectric transition also.

This differs from a model expressed in terms of optical-phonon soft-mode coordinates recently proposed by Lines.[16] The coupling to the strain is neglected and in order to describe a first-order transition an intrinsically negative fourth-order coefficient is introduced. To stabilize the system a positive sixth-order term is required as in the Devonshire theory. Evidence in favor of a correlation of strong coupling to strain with the order of the transition is provided by recent experiments on the $KTa_xNb_{1-x}O_3$ alloy system.[17] The soft modes were found to be underdamped in the cubic structure for values of x corresponding to a second-order transition and overdamped in case of a first-order transition. The damping is expected to be largely due to the coupling to the strain because of the relatively large density-of-states factors for acoustic phonons.

Ferroelectric transitions in the perovskites are known to occur from the cubic to the tetragonal phase as in $BaTiO_3$, $PbTiO_3$, and $KNbO_3$ with the polarization along the c axis.[13] Whereas $PbTiO_3$ remains tetragonal for all lower temperatures, as is well known, $BaTiO_3$ and $KNbO_3$ have subsequent transitions to orthorhombic and rhombohedral structures[13] with the polarization in the (1, 1, 0) and (1, 1, 1) directions, respectively. Direct transitions from cubic to rhombohedral structure have been observed in[18] $CsGeCl_3$ as well as in solid solutions, for example, in $PbZr_xTi_{1-x}O_3$.[19]

The free-energy and soft-mode frequencies appropriate for each of these distortions are calculated below. In constructing the model the high-temperature cubic structure is used as reference configuration.

II. MODEL HAMILTONIAN

In the absence of dipolar forces the soft mode in the undistorted structure is triply degenerate due to equivalent cube axes. We choose as a basic set normal-mode coordinates which describe displacements along each of the three cube axes. The soft mode can be built up from localized displacement fields $\vec{Q}(l)$, where l is a unit-cell index. $\vec{Q}(l)$ plays the same role for the ferroelectric transition as the vector operator $\vec{R}(l)$ describing rotations of the octahedral units for the structural transition. It is a linear combination of the displacements of the individual ions taking part in the soft mode, the condensation of which leads to the distorted structure. Independent translations along each of the cube axes permit the construction of three branches as required. We shall consider only these three degrees of freedom and their interactions with strain and acoustic phonons.

The dipolar forces split the triply degenerate mode of the cubic structure into a doubly degenerate transverse mode and a singlet longitudinal mode.

For the cubic perovskite structure the Hamiltonian describing the kinetic energy and the effect of short-range forces may be written

$$H_1 = \tfrac{1}{2} \sum_{\lambda l} P_\lambda^2(l) + \tfrac{1}{2} \Omega_0^2 \sum_{\lambda l} Q_\lambda^2(l) + \frac{\Gamma_1}{2} \sum_{\lambda} Q_\lambda^4(l) + \frac{\Gamma_2}{4} \sum_{\lambda \neq \lambda'} Q_\lambda^2(l) Q_{\lambda'}^2(l) , \qquad (3)$$

where $\vec{Q}$ and $\vec{P}$ are canonical conjugate variables

$$[Q_\lambda(l), P_{\lambda'}(l')] = i\delta_{\lambda\lambda'}\delta_{ll'} , \qquad (4)$$

and where anharmonic terms higher than fourth order have been neglected. Interactions between the cells, dominated by long-range dipolar forces, will be written

$$H_2 = \tfrac{1}{2} \sum_{\substack{\lambda\lambda' \\ ll'}} v_{\lambda\lambda'}(ll') Q_\lambda(l) Q_{\lambda'}(l') , \qquad (5)$$

where $v_{\lambda\lambda'}(ll')$ describes the total interaction of the displacements in cells l and l'. It includes the effect of the rearrangement of the electrons described by the electronic polarizability as well as the direct dipole-dipole interaction.

As is well known, $v_{\lambda\lambda'}(q)$ is nonanalytic at $q = 0$. Its value depends on the direction in which q goes to zero.[20-22] For $q \approx 0$, the interaction has the form[22-24]

$$v_{\lambda\lambda'}(q) = L\delta_{\lambda\lambda'} - C(q_\lambda q_{\lambda'}/q^2) \ . \tag{6}$$

We shall use the notation

$$\begin{aligned} v_{\lambda\lambda}(0) &= v_T(0) \ , \quad \vec{q} \perp \lambda \\ v_{\lambda\lambda}(0) &= v_L(0) \ , \quad \vec{q} \parallel \lambda \ . \end{aligned} \tag{7}$$

We also note that

$$(1/N) \textstyle\sum_q v_{\lambda\lambda'}(q) = 0 \ . \tag{8}$$

The interaction of the soft-mode coordinates $Q_\lambda(l)$ with the elastic strain and long-wavelength acoustic phonons may be expressed in terms of localized-strain tensor components $\epsilon_{ij}(l)$. We adopt the abbreviated notation

$$\begin{aligned} &\epsilon_i = \epsilon_{ii} \ , \quad i = 1, 2, 3 \\ &\epsilon_4 = \epsilon_{23}, \quad \epsilon_5 = \epsilon_{13}, \quad \epsilon_6 = \epsilon_{12} \ . \end{aligned} \tag{9}$$

The third- and fourth-order anharmonic interaction may then be written

$$H_3 = \sum_{i\lambda\lambda' l} G_{i\lambda\lambda'} \epsilon_i(l) Q_\lambda(l) Q_{\lambda'}(l) + \tfrac{1}{2} \sum_{ij\lambda l} g_{ij\lambda} \epsilon_i(l) \epsilon_j(l) Q_\lambda^2(l) \ . \tag{10}$$

The form of the coupling constants appropriate to cubic symmetry is listed in Appendix A. Three independent coupling constants $G_{i\lambda}$ and six independent constants $g_{ij\lambda}$ enter.

The Hamiltonian describing long-wavelength acoustic phonons may be expressed in terms of the localized-strain tensor components,

$$H_e = \tfrac{1}{2} M \sum_l \dot{\vec{u}}(l)^2 + \tfrac{1}{2} \sum_{ij\lambda} C_{ij}^0 \epsilon_i(l) \epsilon_j(l) \ , \tag{11}$$

where $u(l)$ is the displacement of the center of mass of the lth unit cell from its equilibrium position $X(l)$ due to the acoustic-phonon modes and M is the total mass of the unit cell. The constants C_{ij}^0 have units of energy and are related to the usual elastic constants c_{ij}^0 by

$$C_{ij}^0 = a^3 c_{ij}^0 \ .$$

The Hamiltonian given by Eqs. (3), (5), (10), and (11) has the symmetry appropriate for the cubic perovskite structure. The distortion from cubic symmetry below the transition temperature is described by nonvanishing expectation values of the operators $Q_\lambda(l)$ and the strains $e_{ij}(l)$. The strain tensor $e_{ij}(l)$ will, however, have nonvanishing expectation values also in the cubic phase above the transition temperature which then describes usual thermal expansion. We set

$$Q_\lambda(l) = A_\lambda + r_\lambda(l) \ , \tag{12}$$

$$\epsilon_i(l) = e_i + u_i(l) \ , \tag{13}$$

where A_λ and e_i are the thermal average of the soft-mode coordinate and the strain, respectively. The fluctuations about the average values of the strain may be expressed in terms of the normal-mode coordinates of the acoustic phonons in the usual way:

$$u_{ij}(l) = \frac{i}{2\sqrt{N}} \sum_{\mu q} e^{i\vec{q}\cdot\vec{x}(l)} \alpha_{ij}(\mu q) Q(\mu q) \ , \tag{14}$$

where

$$\alpha_{ij}(\mu q) = q_i e_j(\mu q) + q_j e_i(\mu q) \ , \tag{15}$$

and where $Q(\mu q)$ is the normal-mode coordinate for the μth acoustic branch of frequency $\omega(\mu q)$, wave vector q, and polarization vector $\vec{e}(\mu q)$. The tensors μ_{ij} and α_{ij} will usually be described using the abbreviated notation defined by Eq. (9).

When Eq. (13) is substituted in the elastic Hamiltonian, Eq. (11), it separates into static terms—terms which are linear in the fluctuation $u_i(l)$ and terms which are quadratic in the fluctuations. The latter are most conveniently expressed in terms of the acoustic normal-mode coordinates

$$H_e^{(2)} = \frac{1}{2M} \sum P(\mu q) P(\mu, -q) + \tfrac{1}{2} M \sum \omega_0^2(\mu q) Q(\mu q) Q(\mu, -q) \ , \tag{16}$$

where $P(\mu q)$ is the canonical-conjugate momentum to $Q(\mu q)$,

$$[Q(\mu\vec{q}), P(\mu'\vec{q}\,')] = i\delta_{\mu\mu'} \delta_{\vec{q}\vec{q}'} \ . \tag{17}$$

Similarly the strain variables in H_3 may be expressed in terms of the static strain and the acoustic normal-mode coordinates $Q(\mu q)$ by means of Eqs. (13) and (14).

III. EQUATIONS OF MOTION

The equation of motion for the displacement field $Q_\lambda(l)$ is obtained from the model Hamiltonian by means of the commutation relation, Eq. (4),

$$\begin{aligned} \frac{-\partial^2}{\partial t^2} Q_\lambda(l) = {} & \Omega_0^2 Q_\lambda(l) - \sum_{\lambda'} v_{\lambda\lambda'}(ll') Q_{\lambda'}(l') \\ & + \Gamma_1 Q_\lambda^2(l) + \Gamma_2 \sum_{\lambda' \neq \lambda} Q_\lambda(l) Q_{\lambda'}^2(l') + 2 \sum_{i\lambda'} G_{i\lambda\lambda'} \epsilon_i(l) Q_{\lambda'}(l) \\ & + \sum_{ij} g_{ij\lambda} \epsilon_i(l) \epsilon_j(l) Q_\lambda(l) \ . \end{aligned} \tag{18}$$

We substitute Eqs. (13) and (14) for $Q_\lambda(l)$ and $\epsilon_i(l)$ and linearize the equations of motion by replacing pairs of operators r_λ and u_i by their expectation values

$$\begin{aligned} \Delta_{\lambda\lambda'} &= \langle r_\lambda(l) r_{\lambda'}(l) \rangle \ , \\ D_{ij} &= \langle u_i(l) u_j(l) \rangle \ . \end{aligned} \tag{19}$$

We further neglect the resonant coupling to the acoustic phonons which will be discussed below. The equations of motion for the Fourier coefficients $r_\lambda(q)$ then take the form

$$\frac{-\partial^2}{\partial t^2} r_\lambda(q)$$

$$= \Omega_0^2 r_\lambda(q) - \sum_{\lambda'} v_{\lambda\lambda'}(q) r_{\lambda'}(q) + 3\Gamma_1 (A_\lambda^2 + \Delta_{\lambda\lambda}) r_\lambda(q)$$
$$+ \Gamma_2 \sum_{\lambda' \neq \lambda} [2(A_\lambda A_{\lambda'} + \Delta_{\lambda\lambda'}) r_{\lambda'}(q) + (A_{\lambda'}^2 + \Delta_{\lambda'\lambda'}) r_\lambda(q)]$$
$$+ 2 \sum_{i\lambda'} G_{i\lambda\lambda'} e_i r_{\lambda'}(q) + \sum_{ij} g_{ij\lambda} (e_i e_j + D_{ij}) r_\lambda(q) \ . \tag{20}$$

This set of equations may be diagonalized by introducing a canonical transformation

$$r_\lambda(q) = \sum_{\lambda'} b_{\lambda\lambda'}(q) s_{\lambda'}(q) \ ,$$
$$P_\lambda(q) = \sum_{\lambda'} p_{\lambda'}(q) b_{\lambda'\lambda}^{-1}(q) \ , \tag{21}$$

such that

$$\frac{\partial}{\partial t} s_\lambda(q) = p_\lambda(-q) \ ,$$
$$\frac{-\partial^2}{\partial t^2} s_\lambda(q) = \epsilon_\lambda^2(q) s_\lambda(q) \ , \tag{22}$$

where the coefficients $b_{\lambda\lambda'}(q)$ may be determined from Eq. (20). The eigenfrequencies $\epsilon_\lambda^2(q)$ depend on the correlation functions $\Delta_{\lambda\lambda'}$ and D_{ij}. From Eqs. (22) the former may be written

$$\Delta_{\lambda\lambda'} = \frac{1}{N} \sum_{q\bar\lambda\bar\lambda'} b_{\lambda\bar\lambda}(q) b_{\lambda'\bar\lambda'}(-q) \langle s_{\bar\lambda}(q) s_{\bar\lambda'}(-q) \rangle \ . \tag{23}$$

Then making use of the fluctuation-dissipation theorem we obtain the following self-consistency conditions:

$$\Delta_{\lambda\lambda'} = \frac{1}{N} \sum_{q\bar\lambda} b_{\lambda\bar\lambda}(q) b_{\lambda'\bar\lambda}(-q) \, [2\epsilon_{\bar\lambda}(q)]^{-1} \coth \tfrac{1}{2}\beta\epsilon_{\bar\lambda}(q) \ . \tag{24}$$

The determination of $b_{\lambda\lambda'}(q)$ and thus $\epsilon_\lambda^2(q)$ for arbitrary q requires an explicit model form for $v_{\lambda\lambda'}(q)$ throughout the Brillouin zone as well as the solution of a general cubic equation. The acoustic-phonon correlation function may be written correspondingly

$$D_{ij} = \sum_{q\mu} \alpha_i(\mu q) \alpha_j(\mu q) [2\omega(\mu q)]^{-1} \coth \tfrac{1}{2}\beta\omega(\mu q) \ , \tag{25}$$

where $\omega(\mu q)$ are the renormalized acoustic-phonon frequencies calculated below. The linearized acoustic-phonon equations of motion take the form

$$\frac{-\partial^2}{\partial t^2} Q(\mu q) = \tilde\omega(\mu q) Q(\mu q)$$
$$+ 2 \sum_{\lambda\lambda'\bar\lambda} \tilde G_{i\lambda\lambda'} A_{\lambda'} \alpha_i(\mu, -q) b_{\lambda\bar\lambda}(q) s_{\bar\lambda}(q) \ , \tag{26}$$

where $\tilde\omega(\mu q)$ are acoustic-phonon frequencies corresponding to elastic constants

$$\tilde C_{ij} = C_{ij}^0 + \sum_\lambda g_{ij\lambda}(A_\lambda^2 + \Delta_{\lambda\lambda}) \ , \tag{27}$$

and where

$$\tilde G_{i\lambda\lambda'} = G_{i\lambda\lambda} + \sum_j g_{ij\lambda} e_j \ , \quad \lambda = \lambda'$$
$$= G_{i\lambda\lambda'} \ , \quad \lambda \neq \lambda' \ . \tag{28}$$

The last term in Eq. (26) describes the resonant coupling with the soft-mode coordinates. The equation for the latter is written correspondingly

$$\frac{-\partial^2}{\partial t^2} s_\lambda(q) = \epsilon_\lambda^2(q) s_\lambda(q)$$
$$+ 2 \sum_{\lambda'\bar\lambda\mu i} \tilde G_{i\bar\lambda\lambda'} A_{\lambda'} \alpha_i(\mu q) b_{\bar\lambda\lambda}(-q) Q(\mu q) \ . \tag{29}$$

Introducing time Fourier transforms, we obtain the coupled-mode dispersion relation

$$[\omega^2 - \tilde\omega^2(\mu q)] Q(\mu q)$$
$$= 4 \sum \frac{f_{i\nu\lambda\bar\lambda}(\mu q) f_{i'\nu'\lambda'\bar\lambda}(\mu', -q) A_\lambda A_{\lambda'}}{\omega^2 - \epsilon_{\bar\lambda}^2(q)} Q(\mu' q) \ , \tag{30}$$

where

$$f_{i\nu\lambda\bar\lambda}(\mu q) = \tilde G_{i\nu\lambda} b_{\nu\bar\lambda}(q) \alpha_i(\mu, -q) \ . \tag{31}$$

The resonant interaction does not affect the soft-mode frequencies at $q = 0$ but only their dispersion. For the acoustic-phonon frequencies it leads to step discontinuities in the elastic constants at the transition point. In the small-q limit for sound propagation along particular symmetry directions a given acoustic mode couples only to a single optical-phonon mode λ. In the limit

$$\epsilon_\lambda^2(q) \gg \omega^2(\mu q)$$

the changes in the elastic constants are then obtained trivially. Explicit expressions in case of tetragonal distortion are given in Sec. V. The quadratic terms in the equations of motion have been neglected. An approximate discussion of the effect of these terms is given in I for $g_{ij\lambda} = 0$. Higher-order interactions which affect the q^2 dependence of the acoustic-phonon frequencies[25] are also neglected.

The soft-mode frequencies and the changes in the elastic constants depend on the static distortions A_λ and e_i. As in I these will be determined from an approximate self-consistent free-energy expression. The effect of the resonance interaction on the free energy may be neglected. For the optical phonons this interaction gives small changes in the q^2 coefficient of $\epsilon_\lambda^2(q)$. The acoustic phonons are only affected in the low-frequency region $\omega_\mu(q) \ll \epsilon_\lambda$, whereas the free energy involves summations over the whole Brillouin zone.

IV. FREE ENERGY

In order to derive an approximate expression for the free energy including the contribution of the phonon modes, we introduce a trial density matrix of the form

$$\rho_{\text{eff}} = e^{-\beta H_{\text{eff}}} / \mathrm{Tr}\, e^{-\beta H_{\text{eff}}} \ , \tag{32}$$

where H_{eff} is a diagonal Hamiltonian

$$H_{\mathrm{eff}}=E_0+\sum_{q\lambda}\epsilon_\lambda(q)a_\lambda^\dagger(q)a_\lambda(q)+\sum_{q\mu}\omega(q\mu)b_\mu^\dagger(q)b_\mu(q) \quad (33)$$

expressed in terms of temperature-dependent energies E_0, $\epsilon_\lambda(q)$, and $\omega(\mu q)$. By definition a_λ and $a_\lambda^\dagger$ are linear combinations of the set of operators $\{r_\lambda,\ P_\lambda\}$ satisfying Bose commutation relations,

$$[a_\lambda(q),\ a_{\lambda'}^\dagger(q')]=\delta_{\lambda\lambda'}\delta_{qq'}\ . \quad (34)$$

The operators $b_\mu(q)$ and $b_\mu^\dagger(q)$ are the corresponding annihilation and creation operators for the acoustic phonons.

In terms of the density matrix the free energy may be written

$$F=\mathrm{Tr}(\rho_{\mathrm{eff}}H+\beta^{-1}\rho_{\mathrm{eff}}\ln\rho_{\mathrm{eff}})\ , \quad (35)$$

where H is the original Hamiltonian. The effective Hamiltonian is used only to define a density-matrix diagonal in the number representations of the excitations $\epsilon_\lambda(q)$ and $\omega(\mu q)$.

For noninteracting Bose excitations the entropy contribution to the free energy

$$S=-k_B\ \mathrm{Tr}\rho_{\mathrm{eff}}\ \ln\rho_{\mathrm{eff}} \quad (36)$$

may be written in the form

$$S=k_B\sum_{q\lambda}\{[1+n_\lambda(q)]\ \ln[1+n_\lambda(q)]-n_\lambda(q)\ \ln n_\lambda(q)\}\ , \quad (37)$$

where $n_\lambda(q)$ is the Bose occupation number factor,

$$n_\lambda(q)=1/(e^{\beta\epsilon_\lambda(q)}+1)\ , \quad (38)$$

together with the corresponding term for the acoustic phonons.

In order to evaluate $\langle H\rangle$ we express $\{r_\lambda,\ P_\lambda\}$ in terms of the new normal-mode coordinates a_λ and $a_\lambda^\dagger$. It will be convenient to make use of the operators $s_\lambda(q)$ introduced in Eq. (22). We assume that s_λ may be expressed in terms of a_λ and $a_\lambda^\dagger$ with equal amplitudes for forward and backward propagating waves,

$$s_\lambda(q)=\ [2\epsilon_\lambda(q)]^{-1/2}[a_\lambda(q)+a_\lambda^\dagger(-q)]\ . \quad (39)$$

The form of $P_\lambda(q)$ follows from the requirement that the transformation be canonical. For this choice of $s_\lambda(q)$, $\langle H\rangle$ takes the form

$$\begin{aligned}\langle H\rangle=&\tfrac{1}{2}\sum_{\lambda q}\epsilon_\lambda(q)\,[n_\lambda(q)+\tfrac{1}{2}]+\tfrac{1}{2}\sum_{\mu q}\ \omega(\mu q)\,[n(\mu q)+\tfrac{1}{2}]-\tfrac{1}{2}\sum_{\lambda}v_{\lambda\lambda}(0)A_\lambda^2+\tfrac{1}{2}\Omega_0^2\sum_{\lambda}\ (A_\lambda^2+\Delta_{\lambda\lambda})+\tfrac{1}{2}\sum_{ij}C_{ij}^0(e_ie_j+D_{ij})\\&+\tfrac{1}{2}\Gamma_1\sum_{\lambda}(A_\lambda^4+6A_\lambda^2\Delta_{\lambda\lambda}+3\Delta_{\lambda\lambda}^2)+\tfrac{1}{4}\Gamma_2\sum_{\lambda\lambda'}(A_\lambda^2A_{\lambda'}^2+A_{\lambda'}^2\ \Delta_{\lambda\lambda}+A_\lambda^2\ \ \Delta_{\lambda'\lambda'}+4A_\lambda A_{\lambda'}\Delta_{\lambda\lambda'}+\Delta_{\lambda\lambda}\Delta_{\lambda'\lambda'}+2\,\Delta_{\lambda\lambda'}\Delta_{\lambda\lambda'})\\&+\sum_{i\lambda\lambda'}G_{i\lambda\lambda'}e_i\,(A_\lambda A_{\lambda'}+\Delta_{\lambda\lambda'})+\tfrac{1}{2}\sum_{ij\lambda}g_{ij\lambda}\,(e_ie_j+D_{ij})\,(A_\lambda^2+\Delta_{\lambda\lambda})\ ,\end{aligned} \quad (40)$$

where $\Delta_{\lambda\lambda'}$ and D_{ij} are given by Eqs. (24) and (25), respectively.

We choose the arbitrary function $E_0(T)$ in Eq. (33) such that the self-consistency condition

$$\langle H\rangle=\langle H_{\mathrm{eff}}\rangle \quad (41)$$

is satisfied.

As already discussed, $v_{\lambda\lambda'}(0)$ depends on the direction in which $q\rightarrow 0$. For each type of distortion we choose the direction for which F is a minimum.

The extremum conditions $\partial F/\partial A=0$ yield static part relationships which together with Eqs. (24) and (25) determine the thermally averaged quantities A, e_i, $\Delta_{\lambda\lambda}$, and D_{ij}.

The self-consistency condition, Eq. (24), involves summations over the Brillouin zone. In order to avoid complicated summations and the need to determine the k dependence of the modes explicitly, a molecular-field approximation will be used to determine the thermally averaged quantities in which the wave-vector-dependent interaction potential $v_{\lambda\lambda'}(q)$ is replaced by its average over the Brillouin zone. The corresponding molecular-field energy ω_λ is obtained from ϵ_λ by replacing the true harmonic normal-mode frequency by Ω_0. In the molecular-field approximation the correlation functions $\Delta_{\lambda\lambda'}$ take the form

$$\Delta_{\lambda\lambda'}=\sum_{\bar\lambda}b_{\lambda\bar\lambda}b_{\lambda'\bar\lambda}\,\frac{1}{2\omega_{\bar\lambda}}\,\coth\frac{\beta}{2}\,\omega_{\bar\lambda}\ , \quad (42)$$

expressed in terms of wave-vector-independent quantities.

The molecular-field free energy is obtained by replacing $\epsilon_\lambda(q)$ by the flat spectrum ω_λ in the trial density matrix.[26] Because of Eq. (8), the molecular-field equations are independent of the particular form of $v_{\lambda\lambda'}(q)$.

For an arbitrary distortion from cubic symmetry setting $\partial F/\partial e_i=0$ gives the six equations,

$$\sum_j\tilde C_{ij}e_j+\sum_{\lambda\lambda'}G_{i\lambda\lambda'}(A_\lambda A_{\lambda'}+\Delta_{\lambda\lambda'})=0\ . \quad (43)$$

For each type of distortion the extremum condition $\partial F/\partial A=0$ yields a relationship of the form

$$Ag(A^2,e_i\,,\Delta_{\lambda\lambda'}\,,D_{ij})=0\ . \quad (44)$$

We note that F always has an extremum at $A=0$. For a sufficiently strong coupling to the strain, the solution $A^2(T)$ determined from $g=0$ will have the

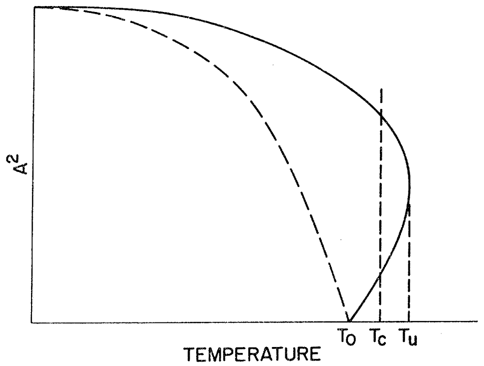

FIG. 1. Temperature dependence of the order parameter squared. T_0 and T_u are, respectively, the supercooling and the superheating temperatures. T_c is the transition temperature.

form shown by the solid curve in Fig. 1. For $T < T_0$ there is only one additional extremum of F as a function of A^2. The corresponding free energy is shown in Fig. 2(a). For $T_0 < T < T_u$ an additional extremum appears, characteristic of a first-order phase transition. The supercooling and superheating temperatures T_0 and T_u are defined by

$$g(A \to 0,\ T \to T_0) = 0 \tag{45}$$

and

$$\frac{dA}{dT_u}(T_u) = \infty\ , \tag{46}$$

respectively. The transition temperature T_c is defined as the temperature for which the local minima are equal as shown in Fig. 2(c). For $T > T_u$ there are no additional extrema and the undistorted cubic phase is stable.

The broken curve in Fig. 1 shows the corresponding result for a second-order transition. As already discussed, a second-order transition is obtained for relatively weak coupling to the strain, as, for example, in the structural transition of $SrTiO_3$ with a change in the c/a ratio which is roughly two orders of magnitude smaller than for the ferroelectric transition in Pb_3TiO_3 or $BaTiO_3$.

The condition for a first-order transition may be written

$$\left.\frac{d^2A^2}{dT^2}(T)\right|_{T=T_0} > 0\ , \tag{47}$$

with T_0 as defined by Eq. (45). This condition is a very complicated function of the model parameters and temperature. It is written down explicitly for the case of tetragonal distortion in Appendix B.

V. TETRAGONAL DISTORTION

For a tetragonal distortion corresponding to a static displacement of ions along a cube axis, only one of the components of $\vec{Q}(l)$ will be different from zero. We set

$$A_\lambda = A\delta_{\lambda 3}\ , \tag{48}$$

where the 3 axis has been chosen as c axis. For the correlation functions we obtain

$$\Delta_{\lambda\lambda'} = 0\ , \qquad \lambda = \lambda' \tag{49}$$

$$\Delta_{11} = \Delta_{22} = \Delta_1\ , \quad \Delta_{33} = \Delta_3\ , \tag{50}$$

where we have introduced the reduced notation for $\Delta_{\lambda\lambda'}$. Similarly for the static strains,

$$\begin{aligned} &e_i = 0\ , \qquad i > 3 \\ &e_1 = e_2 \neq e_3\ . \end{aligned} \tag{51}$$

The free energy is minimum for $\vec{q} \perp \vec{c}$ axis. In the molecular-field approximation it has the form

$$\begin{aligned} F = {}& \tfrac{1}{2}\sum_\lambda \omega_\lambda(n_\lambda + \tfrac{1}{2}) - kT\sum_\lambda\left[(1+n_\lambda)\ln(1+n_\lambda) - n_\lambda \ln n_\lambda\right] + \tfrac{1}{2}\omega_T^2(0)A^2 + \tfrac{1}{2}\Omega_0^2(2\Delta_1 + \Delta_3) \\ & + \tfrac{1}{4}\Gamma_1(A^4 + 6A^2\Delta_3 + 3\Delta_3^2 + 6\Delta_1^2) + \tfrac{1}{2}\Gamma_2(2A^2\Delta_1 + 2\Delta_1\Delta_3 + \Delta_1^2) + G_{11}[e_3(A^2+\Delta_3) + 2e_1\Delta_1] \\ & + 2G_{12}[e_3\Delta_1 + e_1(A^2 + \Delta_3 + \Delta_1)] + \tfrac{1}{2}\sum_{ij} C_{ij}^0(e_ie_j + D_{ij}) + \tfrac{1}{2}\sum_{ij}[g_{ij3}(A^2+\Delta_3) + 2g_{ij1}\Delta_1](e_ie_j + D_{ij})\ , \end{aligned} \tag{52}$$

where $\omega_T(0)$ is the transverse harmonic normal-mode frequency defined by

$$\omega_T^2(0) = \Omega_0^2 - v_T(0)\ . \tag{53}$$

For tetragonal distortion, $b_{\lambda\lambda'} = \delta_{\lambda\lambda'}$ and the correlation functions take the form

$$\Delta_1 = (1/2\omega_1)\coth\tfrac{1}{2}\beta\,\omega_1\ , \quad \Delta_3 = (1/2\omega_3)\coth\tfrac{1}{2}\beta\omega_3\ . \tag{54}$$

The molecular-field energies ω_λ are defined by

$$\omega_\lambda^2 = \epsilon_{\lambda T}^2(0) + v_T(0)\ , \tag{55}$$

where the transverse soft-mode frequencies $\epsilon_{\lambda T}^2(0)$ are defined below.

Because the contribution of the acoustic phonons to the free energy is to a very good approximation independent of the distortions, terms involving only the acoustic phonons have been neglected.

The extremum conditions $\partial F/\partial A = 0$ and $\partial F/\partial e_i = 0$ yield the static part relationships

$$\begin{aligned} A\,[&\omega_T^2(0) + \Gamma_1(A^2 + 3\Delta_3) + 2\Gamma_2\Delta_1 \\ &+ 2G_{11}e_3 + 4G_{12}e_1 + \sum_{ij} g_{ij3}(e_ie_j + D_{ij})] = 0 \end{aligned} \tag{56}$$

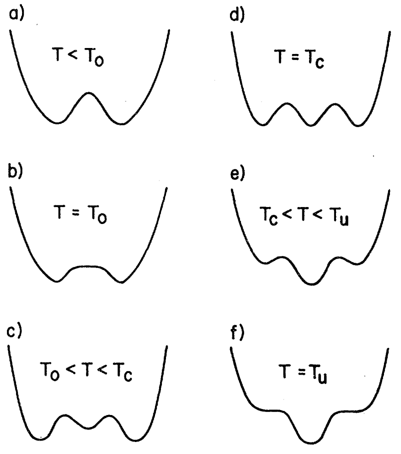

FIG. 2. Free energy as function of the order parameter for different temperatures.

and

$$(\tilde{C}_{11}+\tilde{C}_{13})e_3+\tilde{C}_{12}e_1+G_{11}\,\Delta_1+G_{12}(A^2+\Delta_1+\Delta_3)=0\ ,$$
$$\tilde{C}_{33}e_3+2\tilde{C}_{13}e_1+G_{11}(A^2+\Delta_3)+2G_{12}\,\Delta_1=0\ , \qquad (57)$$

where $\tilde{C}_{ij}$ are defined by the form of Eqs. (27) appropriate for tetragonal distortion. The change in the c/a ratio is given by

$$c/a-1=e_3-e_1\ .$$

From the equations of motion, Eq. (20), and the form of the interaction potential $v_{\lambda\lambda'}(q)$ it follows that pure longitudinal and transverse modes are obtained only for the propagation vectors in the 1, 2 plane and along the 3 axis. For $\vec{q}\perp\vec{c}$ there are two different transverse modes $\epsilon_{1T}(0)$ [E(TO)] and $\epsilon_{3T}(0)$ [A_1(TO)] and one longitudinal mode $\epsilon_{1L}(0)$ [E(LO)]. (The conventional group-theoretic notation for these modes is given in the square brackets.) For $\vec{q}\parallel\vec{c}$ there is a doubly degenerate mode $\epsilon_{1T}(0)$ [E(TO)] and one longitudinal mode $\epsilon_{3L}(0)$ [A_1(LO)]. The form of the soft-mode frequencies is determined from Eq. (20),

$$\epsilon^2_{1T}(0)=\omega^2_T(0)+3\Gamma_1\,\Delta_1+\Gamma_2\,(A^2+\Delta_1+\Delta_3)$$
$$+2(G_{11}+G_{12})e_1+2\,G_{12}\,e_3+\sum_{ij}g_{ij1}(e_ie_j+D_{ij})\ ,$$
$$\epsilon^2_{3T}(0)=\omega^2_T(0)+3\Gamma_1(A^2+\Delta_3)+2\Gamma_2\,\Delta_1 \qquad (58)$$
$$+4G_{12}e_1+2G_{11}e_3+\sum_{ij}g_{ij3}\,(e_ie_j+D_{ij})\ .$$

The corresponding longitudinal modes are given by

$$\epsilon^2_{\lambda L}(0)=\epsilon^2_{\lambda T}(0)+[v_T(0)-v_L(0)]\ , \qquad (59)$$

or making use of Eq. (6),

$$\epsilon^2_{\lambda L}(0)=\epsilon^2_{\lambda T}(0)+C\ . \qquad (60)$$

However, as is well known, these longitudinal modes are not directly comparable with the experimental values. They are further renormalized by a coupling of *all* the longitudinal modes through the polarization field.[27]

We may use the static part relationship, Eq. (56), to eliminate $\omega^2_T(0)$. We obtain

$$\epsilon^2_{1T}(0)=(\Gamma_2-\Gamma_1)A^2+(\Gamma_2\;-3\Gamma_1)\,(\Delta_3-\Delta_1)$$
$$+2(G_{12}-G_{11})\,(e_3-e_1)$$
$$+\sum_{ij}\,(g_{ij1}-g_{ij3})\,(e_ie_j+D_{ij})\ , \qquad (61)$$

$$\epsilon^2_{3T}(0)=2\Gamma_1A^2\ . \qquad (62)$$

We note that whereas $\epsilon_{3T}(0)$ is proportional to A and thus to the polarization, $\epsilon_{1T}(0)$ has a more complicated temperature dependence.

It is also interesting to note that for a first-order transition the frequencies of these modes do not vanish at $T=T_u$. At T_u the isothermal susceptibility is infinite. However, the adiabatic susceptibility, which is inversely proportional to the square of the optical-phonon frequency, remains finite.[28]

The form of the mixed modes for arbitrary direction of q may be obtained from Eq. (20).

The changes in the sound velocities due to the resonant interaction are similar to those at the structural transition except the longitudinal and transverse modes are no longer degenerate. For the cubic to tetragonal transition we obtain from Eq. (30)

$$c_{11}=\tilde{c}_{11}-\tilde{G}^2_{13}D^T_3\ ,\quad c_{33}=\tilde{c}_{33}-\tilde{G}^2_{11}\tilde{D}^L_3\ ,$$
$$c_{12}=\tilde{c}_{12}-\tilde{G}^2_{13}D^T_3\ ,\quad c_{44}=\tilde{c}_{44}-G^2_{44}D^{L,T}_1\ , \qquad (63)$$
$$c_{66}=\tilde{c}_{66}\ ,$$

where

$$D^{T,L}_{\lambda}=\frac{4\rho}{M}\,\frac{A^2}{\epsilon^2_{\lambda T,L}(0)}\ , \qquad (64)$$

where ρ is the density of the crystal. As in I this expression may be generalized to take into account the soft-mode damping.

These expressions have been derived under the assumption that $\omega_\mu \ll \epsilon_\lambda$. For $\omega_\mu \sim \epsilon_\lambda$ the effect of the resonant interaction cannot be expressed simply as a shift in the sound velocity. Instead the coupled-mode dispersion relation, Eq. (30), quadratic in ω^2, must be solved explicitly for the two eigenfrequencies.

The change in the elastic constant c_{13} cannot be expressed in terms of a pure longitudinal or transverse mode. The constant c_{66} is not affected by the resonant coupling, whereas c_{44} can have two different values depending on the particular propagation and polarization vectors considered.[29] A sound wave propagating along an a axis polarized along the c axis couples to a longitudinal mode, whereas a sound wave propagating along a c axis polarized along the a axis couples to the corresponding transverse mode.

The changes in the sound frequencies for arbitrary propagation direction and polarization and for arbitrary distortion may be determined from Eq. (30). Equations (63) predict step discontinuities in the low-frequency elastic constants as for the structural transition. We also note that the discontinuity is much larger when the acoustic wave couples to a transverse mode as compared to a longitudinal mode.[29]

VI. ORTHORHOMBIC DISTORTION

For orthorhombic distortion,

$$\begin{aligned} A_\lambda &= A/\sqrt{2}\,, \quad \lambda = 1, 2 \\ &= 0\,, \quad \lambda = 3 \end{aligned} \tag{65}$$

$$\begin{aligned} &e_1 = e_2 \neq e_3 \neq e_6 \neq 0\,, \\ &\Delta_1 = \Delta_2 \neq \Delta_3 \neq \Delta_6 \neq 0\,. \end{aligned} \tag{66}$$

The matrix $b_{\lambda\lambda'}$ takes the form

$$\vec{b} = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}\,. \tag{67}$$

The free energy is minimum for $q \to 0$ along the 3 axis and is given by

$$\begin{aligned} F = {} & \tfrac{1}{2}\sum_\lambda \omega_\lambda(n_\lambda + \tfrac{1}{2}) - kT\sum_\lambda [(1+n_\lambda)\ln(1+n_\lambda) - n_\lambda \ln n_\lambda] + \tfrac{1}{2}\omega_T^2(0)A^2 + \tfrac{1}{2}\Omega_0^2(2\Delta_1 + \Delta_3) \\ & + \tfrac{1}{4}\Gamma_1(\tfrac{1}{2}A^4 + 6A^2\Delta_1 + 6\Delta_1^2 + 3\Delta_3^2) + \tfrac{1}{2}\Gamma_2[\tfrac{1}{2}A^4 + (A^2 + \Delta_1)\Delta_1 + (A^2 + 2\Delta_1)\Delta_3 + 2A^2\Delta_6 + 2\Delta_6^2] \\ & + G_{11}[e_1(A^2 + 2\Delta_1) + e_3\Delta_3] + G_{12}[e_1(A^2 + 2\Delta_1 + 2\Delta_3) + e_3(A^2 + 2\Delta_1)] + 2G_{44}e_4(A_2 + 2\Delta_6) \\ & + \tfrac{1}{2}\sum_{ij} C_{ij}^0(e_ie_j + D_{ij}) + \tfrac{1}{2}\sum_{ij}[g_{ij1}(A^2 + 2\Delta_1) + g_{ij3}\Delta_3](e_ie_j + D_{ij})\,, \end{aligned} \tag{68}$$

where

$$\begin{aligned} \Delta_1 &= \frac{1}{4\omega_1}\coth\tfrac{1}{2}\beta\omega_1 + \frac{1}{4\omega_2}\coth\tfrac{1}{2}\beta\omega_2\,, \\ \Delta_3 &= \frac{1}{2\omega_3}\coth\tfrac{1}{2}\beta\,\omega_3\,, \\ \Delta_6 &= \frac{1}{4\omega_1}\coth\tfrac{1}{2}\beta\omega_1 - \frac{1}{4\omega_2}\coth\tfrac{1}{2}\beta\omega_2\,, \end{aligned} \tag{69}$$

with

$$\omega_\lambda^2 = \epsilon_{\lambda T}^2(0) + v_T(0)\,. \tag{70}$$

The static part relationships take the form

$$\begin{aligned} &\omega_T^2(0) + \Gamma_1(\tfrac{1}{2}A^2 + 3\Delta_1) + \Gamma_2(\tfrac{1}{2}A^2 + \Delta_1 + \Delta_3 + 2\Delta_6) \\ &\quad + 2G_{11}e_1 + 2G_{12}(e_1 + e_3) + 4G_{44}e_6 \\ &\quad\quad + \sum g_{ij1}(e_ie_j + D_{ij}) = 0\,, \end{aligned} \tag{71}$$

$$\begin{aligned} &\tilde{C}_{11}e_1 + \tilde{C}_{12}(e_1 + e_2) + G_{11}(\tfrac{1}{2}A^2 + \Delta_1) \\ &\quad + G_{12}(\tfrac{1}{2}A^2 + \Delta_1 + \Delta_3) = 0\,, \\ &\tilde{C}_{11}e_3 + 2\tilde{C}_{12}e_1 + G_{11}\Delta_3 + G_{12}(A^2 + 2\Delta_1) = 0\,, \\ &\tilde{C}_{44}e_6 + G_{44}(\tfrac{1}{2}A^2 + \Delta_6) = 0\,. \end{aligned} \tag{72}$$

For orthorhombic distortion the modes are all nondegenerate. Pure longitudinal and transverse modes are obtained only along the orthorhombic axes. For $\vec{q} = q(0, 0, 1)$, we obtain the frequencies ϵ_{1T}, ϵ_{2T}, ϵ_{3L}; for $\vec{q} = (q/\sqrt{2})(1, 1, 0)$, we obtain ϵ_{1T}, ϵ_{2L}, ϵ_{3T}; and for $\vec{q} = (q/\sqrt{2})(1, -1, 0)$, we obtain ϵ_{1L}, ϵ_{2T}, ϵ_{3T}, where

$$\begin{aligned} \epsilon_{1T}^2 &= (\Gamma_1 + \Gamma_2)A^2\,, \\ \epsilon_{2T}^2 &= (\Gamma_1 - \Gamma_2)A^2 - 4\Gamma_2\Delta_6 - 8G_{44}e_6\,, \\ \epsilon_{3T}^2 &= \tfrac{1}{2}(\Gamma_2 - \Gamma_1)A^2 + (3\Gamma_1 - \Gamma_2)(\Delta_3 - \Delta_1) \\ &\quad - 2\Gamma_2\Delta_6 + 2(G_{11} - G_{12})(e_3 - e_1) - 4G_{44}e_4 \\ &\quad\quad \times \sum_{ij}(g_{ij3} - g_{ij1})(e_ie_f + D_{ij})\,, \end{aligned} \tag{73}$$

where we have made use of Eq. (71) to eliminate $\omega_T^2(0)$. The longitudinal-mode frequencies are as before given by Eq. (60).

VII. TRIGONAL DISTORTION

For trigonal distortion,

$$\begin{aligned} A_\lambda^2 &= \tfrac{1}{3}A^2 && \text{for all } \lambda \\ e_i &= e_1\,, && i \leq 3 \\ &= e_4\,, && i > 3 \\ \Delta_{\lambda\lambda'} &= \Delta_1\,, && \lambda = \lambda' \\ &= \Delta_4\,, && \lambda \neq \lambda'\,. \end{aligned} \tag{74}$$

The matrix $b_{\lambda\lambda'}$ takes the form

$$\vec{b} = \begin{pmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 1/\sqrt{6} & 1/\sqrt{6} & -2/\sqrt{6} \end{pmatrix} \tag{75}$$

and the free energy may be written

$$F=\tfrac{1}{2}\sum_{\lambda}\omega_\lambda(n_\lambda+\tfrac{1}{2})-kT\sum_{\lambda}[(1+n_\lambda)\ln(1+n_\lambda)-n_\lambda\ln n_\lambda]+\tfrac{1}{2}\omega_T^2(0)A^2+\tfrac{3}{2}\Omega_0^2\Delta_1$$
$$+\tfrac{1}{4}\Gamma_1(\tfrac{1}{3}A^2+6A^2\Delta_1+3\Delta_1^2)+\tfrac{1}{2}\Gamma_2[\tfrac{1}{3}A^4+2A^2(\Delta_1+2\Delta_4)+\Delta_1^2+2\Delta_4^2]+(G_{11}+2G_{12})e_1(A^2+3\Delta_1)$$
$$+4G_{44}e_4(A^2+3\Delta_4)+\tfrac{1}{2}\sum_{ij}C_{ij}^0(e_ie_j+D_{ij})+\tfrac{1}{2}\sum_{ij}g_{ij\lambda}(e_ie_j+D_{ij})(A^2+3\Delta_1)\,, \quad (76)$$

where

$$\Delta_1=\frac{1}{3}\left(\frac{1}{2\omega_3}\coth\tfrac{1}{2}\beta\omega_3+\frac{1}{\omega_1}\coth\tfrac{1}{2}\beta\omega_1\right),$$
$$\Delta_4=\frac{1}{3}\left(\frac{1}{2\omega_3}\coth\tfrac{1}{2}\beta\omega_3-\frac{1}{2\omega_1}\coth\tfrac{1}{2}\beta\omega_1\right). \quad (77)$$

The static part relationships take the form

$$\omega_T^2(0)+\Gamma_1(\tfrac{1}{2}A^2+3\Delta_1)+2\Gamma_2(\tfrac{1}{3}A^2+\Delta_1+2\Delta_4)$$
$$+2(G_{11}+2G_{12})e_1+8G_{44}e_4+\sum_{ij}g_{ij\lambda}(e_ie_j+D_{ij})=0\,, \quad (78)$$

$$(\tilde{C}_{11}+2\tilde{C}_{12})e_1+(G_{11}+2G_{12})(\tfrac{1}{3}A^2+\Delta_1)=0\,,$$
$$\tilde{C}_{44}e_4+G_{44}(\tfrac{1}{3}A^2+\Delta_4)=0\,. \quad (79)$$

Pure longitudinal or transverse modes are obtained for $\vec{q}$ along the (1, 1, 1) direction in the plane perpendicular to this direction. For $\vec{q}\parallel(1,1,1)$ there is a doubly degenerate transverse mode of frequency ϵ_{1T} and a longitudinal mode ϵ_{3L}. For $\vec{q}\perp(1,1,1)$, we obtain the modes ϵ_{1L}, ϵ_{1T}, and ϵ_{3T}. The frequencies are given by

$$\epsilon_{1T}^2=2(\Gamma_1-\Gamma_2)\tfrac{1}{3}A^2-6\Gamma_2\Delta_4-12G_{44}e_4\,,$$
$$\epsilon_{3T}^2=2(\Gamma_1+2\Gamma_2)\tfrac{1}{3}A^2\,, \quad (80)$$

with $\epsilon_{\lambda L}^2$ given by Eq. (60).

VIII. CUBIC PHASE

The corresponding equations for the cubic structure are obtained as a limiting form from any of the distorted structures:

$$A_\lambda=0,$$
$$\Delta_\lambda=0\,,\quad \lambda\le 3$$
$$=0\,,\quad \lambda>3$$
$$e_1=e\,,\quad i\le 3$$
$$=0\,,\quad i\ge 3$$
$$b_{\lambda\lambda'}=\delta_{\lambda\lambda'}\,. \quad (81)$$

The free energy is given by

$$F=\tfrac{3}{2}\omega(n+\tfrac{1}{2})-kT3\,[(1+n)\ln(1+n)-n\ln n]$$
$$+\tfrac{3}{2}\Omega_0^2\Delta+\tfrac{3}{4}(3\Gamma_1+2\Gamma_2)\Delta^2+3(G_{11}+2G_{12})e\Delta$$
$$+\tfrac{1}{2}\sum_{ij}C_{ij}^0(e_ie_j+D_{ij})+\tfrac{3}{2}\Delta\sum_{ij}g_{ij\lambda}(e_ie_j+D_{ij}), \quad (82)$$

where the strain terms have the usual form appropriate to cubic symmetry. The molecular-field energy is defined by

$$\omega^2=\epsilon_T^2(0)+v_T(0)\,. \quad (83)$$

From $\partial F/\partial e=0$, we obtain

$$(\tilde{C}_{11}+2\tilde{C}_{12})e+(G_{11}+2G_{12})\Delta=0\,, \quad (84)$$

which determines the contribution to the thermal expansion of the coupling to the soft-mode coordinates.

For arbitrary direction of q there is a doubly degenerate transverse mode $\epsilon_T(0)$ and a singlet longitudinal mode $\epsilon_L(0)$, where

$$\epsilon_T^2(0)=\omega_T^2(0)+(3\Gamma_1+2\Gamma_2)\Delta$$
$$+2(G_{11}+2G_{12})e+\sum_{ij}g_{ij\lambda}(e_ie_j+D_{ij}), \quad (85)$$
$$\epsilon_L^2(0)=\epsilon_T^2(0)+C.$$

From Eqs. (45) and (56) the supercooling temperature is defined by

$$\omega_T^2(0)+(3\Gamma_1+2\Gamma_1)\Delta(T_0)+2(G_{11}+2G_{12})e(T_0)$$
$$+\sum_{ij}g_{ij\lambda}[e_i(T_0)e_j(T_0)+D_{ij}(T_0)]=0\,. \quad (86)$$

Eliminating the harmonic soft-mode frequency using the definition of T_0, the soft-mode frequencies may be written

$$\epsilon_T^2=(3\Gamma_1+2\Gamma_2)[\Delta(T)-\Delta(T_0)]+2(G_{11}+2G_{12})[e(T)-e(T_0)]+\sum_{ij}g_{ij\lambda}[e_i(T)e_j(T)-e_i(T_0)e_j(T_0)+D_{ij}(T)-D_{ij}(T_0)]\,, \quad (87)$$

which explicitly exhibits the fact that the soft-mode frequency vanishes at the stability limit $T=T_0$.

IX. CONCLUDING REMARKS

A simple model Hamiltonian has been constructed to describe the ferroelectric transitions in the perovskites. The temperature dependence of the polarization, strain distortions, and the transverse $q=0$ soft-mode frequencies have been calculated using the molecular-field approximation. The soft-mode frequency in the cubic phase vanishes at the supercooling temperature T_0, whereas the modes in the distorted structure remain finite at the superheating temperature T_u.

In order to calculate the q dependence of the modes, more detailed assumptions need be made as to which ions take part in the internal displacements and to the interactions among these ions. Hüller has considered a model for $BaTiO_3$, assuming that all the ions except the Ti ion are highly bound to their equilibrium positions but including the ionic polarizability of the oxygen ions.[24] The predicted anisotropy in the k dependence of the soft modes resulting from the anisotropic nature of the dipolar forces has been observed experimentally.[29] However, no attempt was made to give a realistic description of the temperature dependence of the modes.

In order to compare the expressions derived in this paper with the experimental results for particular materials such as $PbTiO_3$ and $BaTiO_3$, the nonlinear set of equations determining the soft-mode frequencies, the order parameter A, the correlation functions Δ_i, and the strain distortions e_i must be solved numerically for a given set of model parameters. The model parameters must be determined to give the best over-all fit with the experimental data. This program was carried out in I for the structural transitions in $SrTiO_3$ and $LaAlO_3$ for which the model parameters were well overdetermined. It will be of particular interest to see whether the series of transitions observed in $BaTiO_3$ may be correctly described by this simple model.

Very recently, calculations based on the self-consistent phonon approximation (SPA) have been carried out for a model ferroelectric containing only fourth-order anharmonic interactions.[30] The q dependence of the modes was calculated explicitly and the mode frequencies determined self-consistently using Eq. (2). A first-order transition was obtained. However, the molecular-field approximation used in this paper gives a second-order transition. In both these approximations, correlation functions containing more than two normal-mode coordinates are factorized into products of pair correlation functions. Such factorization approximations are only valid as long as the fluctuations are not too large. The molecular-field approximation effectively cuts off the long-wavelength fluctuations, whereas in SPA these become so large as to invalidate the factorization approximation. This is discussed in more detail elsewhere.[31]

APPENDIX A

For cubic symmetry there are three distinct coupling constants $G_{i\lambda\lambda'}$. Introducing the reduced notation for the last two indices, we may write

$$G_{11}=G_{111}=G_{222}=G_{333}\ ,$$

$$G_{12}=G_{122}=G_{133}=G_{211}=G_{233}=G_{311}=G_{322}\ ,$$

$$2G_{44}=G_{423}=G_{513}=G_{612}\ , \tag{A1}$$

all other coupling constants $G_{i\lambda\lambda'}$ being equal to zero.

The coupling constants $g_{ij\lambda}=g_{ji\lambda}$ for all i,j. There are six independent coupling constants $g_{ij\lambda}$. These are

$$\begin{aligned} &g_{111}=g_{222}=g_{333}\ ,\\ &g_{121}=g_{122}=g_{131}=g_{133}=g_{232}=g_{233}\ ,\\ &g_{112}=g_{113}=g_{221}=g_{223}=g_{331}=g_{332}\ ,\\ &g_{123}=g_{132}=g_{231}\ ,\\ &g_{442}=g_{443}=g_{551}=g_{553}=g_{661}=g_{662}\ ,\\ &g_{441}=g_{552}=g_{663}\ . \end{aligned} \tag{A2}$$

APPENDIX B

If we neglect the fourth-order coupling to the strain, setting all $g_{i\lambda\lambda'}=0$, and eliminate e_i in favor of A^2 and Δ_λ using Eqs. (57), then for tetragonal distortion, $g(A^2,\ \Delta_\lambda)$ defined by Eq. (44) may be written

$$\begin{aligned} g(A^2,\ \Delta_\lambda)=\omega_T^2(0)&+(\Gamma_1-\tfrac{4}{3}C_1-\tfrac{2}{3}C_2)A^2\\ &+(3\Gamma_1-\tfrac{4}{3}C_1-\tfrac{2}{3}C_2)\,\Delta_3+(2\Gamma_2+\tfrac{4}{3}C_1-\tfrac{4}{3}C_2)\,\Delta_1\ , \end{aligned} \tag{B1}$$

where

$$C_1=\frac{(G_{11}-G_{12})^2}{C_{11}-C_{12}}\ ,\quad C_2=\frac{(G_{11}+2G_{12})^2}{C_{11}+C_{12}}\ . \tag{B2}$$

If we ignore the contribution of the correlation functions Δ_1 and Δ_2 to the slope at $T=T_0$ of A^2 as determined from $g(A^2,\ \Delta_\lambda)=0$, the condition for a second-order transition takes the simple form

$$(\Gamma_1-\tfrac{4}{3}C_1-\tfrac{2}{3}C_2)>0\ . \tag{B3}$$

We note that for a sufficiently strong coupling to the strain this condition is no longer satisfied and the transition is first order.

Taking into account the A^2 dependence of the correlation functions the condition for a second-order transition is rather complicated,

$$a+b\gamma_1+c\gamma_2>0\ , \tag{B4}$$

where

$$\gamma_1=\frac{-\Gamma_1}{2\Omega_0^2}\left[\coth\tfrac{1}{2}\beta_0 v_T(0)+\tfrac{1}{4}\beta_0 v_T(0)\ \operatorname{csch}^2\tfrac{1}{2}\beta_0 v_T(0)\right]\ ,$$

$$\gamma_2=\frac{(d+\alpha e)\gamma_1}{2\Gamma_1}\ ,\qquad \alpha=\frac{-e\gamma_1}{e\gamma_1+2\Gamma_2}\ ,$$

$$\begin{aligned} &a=\Gamma_1-\tfrac{4}{3}C_1-\tfrac{2}{3}C_2\ ,\quad b=3\Gamma_1-\tfrac{4}{3}C_1-\tfrac{2}{3}C_2\ ,\\ &c=2\Gamma_2+\tfrac{4}{3}C_1-\tfrac{4}{3}C_2\ ,\quad d=\Gamma_2-\Gamma_1+2C_2\ ,\\ &e=\Gamma_2-3\Gamma_1+2C_2\ . \end{aligned} \tag{B5}$$

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