PHYSICAL REVIEW VOLUME 151, NUMBER 2 11 NOVEMBER 1966

Free Energy of Displacive Ferroelectrics*

P. C. KWOK AND P. B. MILLER
IBM Watson Research Center, Yorktown Heights, New York

(Received 11 May 1966)

A power series for the free energy is derived in the linear anharmonic approximation. This free energy is expressed in terms of a complete set of microscopic order parameters which determine the ionic displacements in the ferroelectric transition. In general this complete set of microscopic order parameters is larger than the set of order parameters used in the phenomenological free energy of Devonshire. However, for those ferroelectric crystals which are characterized by only one soft optical branch, this larger set may be reduced to the same number as used by Devonshire. Such a reduction is explicitly carried out for the perovskite structure and the resulting expression is the same as that derived phenomenologically by Devonshire with the coefficients expressed in terms of microscopic lattice parameters.

I. INTRODUCTION

FERROELECTRIC crystals may be conveniently separated into two classes according to the nature of the phase change occurring at the Curie point.[1] The first group is characterized by an order-disorder-type transition, e.g., triglycine sulfate. The second group is characterized by a displacive-type transition as exemplified by $BaTiO_3$. In this paper we shall confine ourselves to a study of the displacive ferroelectrics since its nature is better understood.

The main properties of ferroelectrics may be understood with the aid of a single phenomenological free-energy function describing both the paraelectric and the ferroelectric phase. Such a free energy was first introduced by Devonshire.[2] This free energy is a power-series expansion in the macroscopic order parameters: the polarization per unit volume **P** and the strain tensor S. The coefficients of the power series are phenomenological constants which may be determined from the properties of the paraelectric phase. The essential validity of this free energy has been confirmed by numerous experiments.[3]

The understanding of ferroelectrics from a microscopic approach was developed in the work of several authors. Slater pointed out that the dielectric catastrophe at the Curie point of perovskite-type ferroelectrics may be understood to be a consequence of an unusually large Lorentz factor between a pair of atoms in this structure.[4] A further advance was made by Cochran,[5] Anderson,[6] and Landauer *et al.*,[7] who put forward the idea of an anomalously soft and temperature-dependent transverse optic branch to explain the origin of displacive ferroelectrics. The temperature-dependent soft transverse optic branch was subsequently observed by infrared-reflectivity measurements[8] and inelastic-neutron-scattering experiments.[9] These fundamental ideas provided a firm basis for further quantitative and more detailed studies of ferroelectricity.

One line of development of a quantitative microscopic theory of ferroelectrics has been devoted to the study of the properties of the paraelectric phase. For example, Silverman and Joseph[10] and also Cowley[11] have investigated the temperature dependence of the lattice-vibration frequencies arising from anharmonic interactions between the normal modes in the paraelectric phase. Another line of development is the derivation of a single free-energy function which may be used to describe both the paraelectric and ferroelectric phases. Cowley[11] has indicated how this may be carried out using a diagrammatic technique, and Doniach has outlined a derivation of the free energy based on a variational principle.[12]

The purpose of this paper is to approach the problem of displacive ferroelectrics along the latter line of development mentioned above and to present a detailed and explicit derivation of the free-energy function from a microscopic Hamiltonian describing the lattice dynamics of the anharmonic crystal. One obtains in the linear anharmonic approximation a free energy which is a power series in a set of microscopic order parameters. The set of microscopic order parameters consist of (a) the thermal-expectation values of the normal coordinates of all the optical branches in the long-wavelength limit which determine the change of the equlibrium ionic positions in the ferroelectric transition, and (b) the thermal-expectation values of the

---

* Supported in part by Contract DA36-039 AMC-02280(E) (U. S. Army Electronics Command, Fort Monmouth, New Jersey).

[1] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962).

[2] A. F. Devonshire, Advan. Phys. **3**, 85 (1954).

[3] See, for example, W. J. Merz, Phys. Rev. **91**, 513 (1953); M. E. Drougard, R. W. Landauer, and D. R. Young, *ibid.* **98**, 1010 (1955); and S. Triebwasser, *ibid.* **101**, 993 (1956).

[4] J. C. Slater, Phys. Rev. **78**, 748 (1950).

[5] W. Cochran, Advan. Phys. **9**, 387 (1960).

[6] P. W. Anderson, in *Fizika Dielektrikov*, edited by G. I. Skanavi (Akademica Nauk SSSR Fisicheskii Institutim, P. N. Lebedeva, Moscow, 1960), in Russian.

[7] R. W. Landauer, H. Juretschke, and P. P. Sorokin (unpublished).

[8] A. S. Barker, Jr., and M. Tinkham, Phys. Rev. **125**, 1527 (1962).

[9] R. A. Cowley, Phys. Rev. Letters **9**, 159 (1962); and R. A. Cowley, Phys. Rev. **134**, A981 (1964).

[10] B. D. Silverman and R. I. Joseph, Phys. Rev. **129**, 2062 (1963); R. I. Joseph and B. D. Silverman, *ibid*, **133**, A207 (1964); and B. D. Silverman, *ibid.* **135**, A1596 (1964).

[11] R. A. Cowley, Phil. Mag. **11**, 673 (1965).

[12] S. Doniach, in *Proceedings of the International Conference on Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Ltd., London, 1965).

normal coordinates of the acoustic branch in the long-wavelength limit which determines the spatially uniform strain tensor. This is a more general free-energy power series than the phenomomenological free energy introduced by Devonshire because the latter is expressed in terms of a smaller set of order parameters, i.e., the entire set of optical branch order parameters is replaced by the polarization per unit volume. However, it is shown that when the frequency of the soft optical branch (in the long-wavelength limit) is much smaller than the frequencies of the other optical branches the general free-energy function reduces to the Devonshire form. The coefficients of the free-energy function are then explicitly evaluated in terms of anharmonic couplings parameters.

In Sec. II we discuss the Hamiltonian describing the ionic motion of the ferroelectric crystal. In Sec. III we derive the equations for the thermal expectation values of the normal coordinates and their correlation function (i.e., the phonon Green's function). In Sec. IV a general power series for the free energy in terms of all the microscopic order parameters is derived in the linear anharmonic approximation. In Sec. V the general free energy is evaluated for the perovskite ferroelectrics and is shown to reduce to the Devonshire form. Finally in Sec. VI the results are summarized and discussed.

II. HAMILTONIAN FOR FERROELECTRIC CRYSTAL

We wish to construct a Hamiltonian for the nuclear motion which is able to give rise to a ferroelectric transition and which also incorporates most of the important properties of ferroelectric crystals. These properties include a large dielectric constant, spontaneous polarization, electrostriction, as well as many other properties, all of which are conveniently contained in the phenomenological power series for the free energy devloped by Devonshire.[2]

In the adiabatic approximation an effective potential function Φ exists for the nuclear motion. The nuclear Hamiltonian may then be expressed as a power series in the nuclear displacements of the kth atom in the lth unit cell $[u(lk)]$ from its equilibrium position $\mathbf{x}^0(lk)$. The equilibrium position is defined as the position where the potential energy has an extremum so that H has no linear terms in the displacement,

$$H=\sum \tfrac{1}{2}m_k\dot{u}(lk)\dot{u}(lk)+\sum \frac{1}{2!}\Phi_{\alpha_1\alpha_2}(l_1k_1;l_2k_2)u_{\alpha_1}(l_1k_1)\times u_{\alpha_2}(l_2k_2)+\frac{1}{3!}\sum \Phi_{\alpha_1\alpha_2\alpha_3}(l_1k_1;l_2k_2;l_3k_3)\times u_{\alpha_1}(l_1k_1)u_{\alpha_2}(l_2k_2)u_{\alpha_3}(l_3k_3)\cdots. \quad (1)$$

We use a notation which is the same as that of Born and Huang,[13] except where other symbols are explicitly noted. Thus $\Phi_{\alpha_1\ldots\alpha_n}(l_1k_1\cdots l_nk_n)$ is the nth derivative of the potential with respect to the displacements indicated in the arguments of the function. The Einstein summation convention is also used where convenient. It is important to recognize that the equilibrium position which has been used for the expansion of H is only an extremum of the potential energy [i.e., $\Phi_\alpha(lk)=0$] and not necessarily an absolute minimum. To describe a solid which undergoes a ferroelectric transition from a paraelectric to a polar phase it is convenient to choose the equilibrium positions as being the atomic positions in the paraelectric phase. The success of the *single* free-energy function of Devonshire in describing the properties of both the paraelectric and the ferroelectric (polar) phase suggests that the expansion of H about the equilibrium positions in the paraelectric phase will enable us to describe both the paraelectric and the ferroelectric phase.

We define normal coordinates $Q(jp)$ by

$$u_\alpha(lk)=(m_kN)^{-1/2}\sum_{\mathbf{p}j} e_k{}^\alpha(j\mathbf{p})\dot{Q}(j\mathbf{p})\times\exp[i\mathbf{p}\cdot\mathbf{x}_l{}^0+i\mathbf{p}\cdot\mathbf{x}_k{}^0], \quad (2)$$

where m_k is the mass of the kth atom, N is the number of unit cells in the volume, $\mathbf{x}_l{}^0$ denotes the equilibrium position of the lth unit cell, and $\mathbf{x}_k{}^0$ the relative position of the kth atom in the cell and $\mathbf{x}^0(lk)=\mathbf{x}_l{}^0+\mathbf{x}_k{}^0$. Also the polarization vectors $e_k(jp)$ are the eigenvectors of the *harmonic* dynamical matrix corresponding to branch j and momentum $\mathbf{p}$. The eigenvectors satisfy the orthogonality and completeness relations

$$\sum_{k\alpha} e_k{}^\alpha(j\mathbf{p})e_k{}^{\alpha*}(j'\mathbf{p})=\delta_{jj'};\qquad \sum_{j} e_k{}^\alpha(j\mathbf{p})e_{k'}{}^{\beta*}(j,\mathbf{p})=\delta_{\alpha\beta}\delta_{kk'}. \quad (3)$$

The Hamiltonian may be expressed in terms of normal modes as

$$H=\tfrac{1}{2}\sum_{j\mathbf{p}} [\dot{Q}(j\mathbf{p})\dot{Q}(j-\mathbf{p})+\omega^0(j\mathbf{p})^2Q(j\mathbf{p})Q(j-\mathbf{p})]+\frac{1}{n!}\sum_{n=3}^{\infty} U_{\mathbf{p}_1j_1;\mathbf{p}_2j_2;\ldots\mathbf{p}_nj_n}{}^{(n)}Q(j_1\mathbf{p}_2)\times Q(j_2\mathbf{p}_2)\cdots Q(j_n\mathbf{p}_n), \quad (4)$$

where the squares of the harmonic frequencies $[\omega^0(j\mathbf{p})]^2$ are the eigenvalues of the harmonic dynamical matrix and the anharmonic coefficients are defined by

$$U_{\mathbf{p}_1j_1;\mathbf{p}_2j_2;\ldots\mathbf{p}_nj_n}{}^{(n)}=N^{-n/2}\sum \frac{\Phi_{\alpha_1\alpha_2\ldots\alpha_n}(l_1k_1;l_2k_2\cdots l_nk_n)}{(m_{k_1}m_{k_2}\cdots m_{k_n})^{1/2}}\times e_{k_1}{}^{\alpha_1}(j_1\mathbf{p}_1)e_{2k_2}{}^{\alpha_2}(j_2\mathbf{p}_2)\cdots e_{k_n}{}^{\alpha_n}(j_n\mathbf{p}_n)\times\exp[i\mathbf{p}_1\cdot\mathbf{x}^0(l_1k_1)+i\mathbf{p}_2\cdot\mathbf{x}^0(l_2k_2)+\cdots i\mathbf{p}_n\cdot\mathbf{x}^0(l_nk_n)]. \quad (5)$$

---

[13] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (The Clarendon Press, Ltd., Oxford, England, 1954).

The anharmonic coefficients are nonvanishing only when the wave vector sum

$$\sum_{i=1}^{n} \mathbf{p}_i$$

is a reciprocal lattice vector or zero.

It has been pointed out by several authors[5–7] that the behavior of ferroelectrics may be understood in terms of an optical branch with an anomalously low frequency near $\mathbf{p}=0$. The soft optical modes near $\mathbf{p}=0$ arise from a close cancellation of short-range repulsive forces and of attractive Coulomb forces.[5,6] It has also been shown that the renormalized frequencies of the soft optical modes near $\mathbf{p}=0$ are strongly temperature-dependent owing to anharmonic effects.[5–7,10] The temperature dependence of the renormalized frequencies has been directly observed in $\mathrm{SrTiO_3}$ by Barker and Tinkham[8] from infrared reflectivity measurements and by Cowley from inelastic scattering of neutrons.[9] Thus, to describe a crystal which makes a transition from a paraelectric to a polar phase we characterize it by imaginary *harmonic* frequencies for some soft optical branch near $\mathbf{p}=0$.[5–7,10] On the other hand a crystal which is paraelectric at all temperatures is characterized by positive harmonic frequencies for all branches.[14] Since our main interest here will be to describe both the paraelectric and the ferroelectric phase we will usually think of the soft mode optical branch with imaginary harmonic frequencies near $\mathbf{p}=0$, i.e., for the soft mode near $\mathbf{p}=0$, $\omega^0(j\mathbf{p})^2<0$.

In choosing the anharmonic terms for our model Hamiltonian we may be guided by the phenomenological Devonshire free energy. The total Hamiltonian given by Eq. (4) includes anharmonic terms of all orders and we include in our model only the orders which are needed to derive the phenomenological Devonshire free energy. Thus, the cubic anharmonicity ($n=3$) is retained because it leads to an electrostrictive coupling between the strain and the polarization in addition to the usual thermal strain. The quartic anharmonicity ($n=4$) is retained because it leads to a P^4 contribution to the free energy which appears in the Devonshire free energy. The fifth-order anharmonicity ($n=5$) will be dropped because it leads to a contribution to the free-energy linear in strain and quartic in polarization. Such a term does not appear in the Devonshire free energy and represents a correction to the electrostrictive coupling between the strain and the polarization. We retain the sixth-order anharmonicity ($n=6$) because it leads to a P^6 contribution to the free energy which is essential in describing a first-order transition. According to Devonshire no terms beyond P^6 need be retained in the free energy so that we drop all anharmonicities of order $n>6$.

The Hamiltonian we have discussed so far has neglected the interaction of the lattice vibrations with hte *macroscopic* electromagnetic field produced by the lattice vibrations themselves. The local field has of course been included in the definition of the harmonic frequencies. We may separate the macroscopic field $\mathbf{E}$ into a solenoidal part ($\mathbf{E}_\perp$) and a irrotational part ($\mathbf{E}_{\parallel}$). The transverse part $\mathbf{E}_\perp$ is readily shown to be strictly a retardation field[13] which vanishes in the static limit. Therefore, it does not play a direct role in determining the ferroelectric transition in which only the appearance of static-order parameters like the static polarization per unit volume are considered. Nevertheless, $\mathbf{E}_\perp$ has an indirect effect on the transition because of its coupling to the transverse optic lattice vibrations which give rise to the well-known change, in the phonon and photon dispersion curves in the long-wavelength region of momentum space[13] ($\mathbf{p}\lesssim 10^3$ cm^{-1}). In our formalism this corresponds to a change in the phonon Green's functions for the transverse optical phonons in the small region near $\mathbf{p}=0$. As the coefficients of the free energy contain these Green's functions, $\mathbf{E}_\perp$ has a finite effect. However, this effect is negligibly small because as we shall see only the averages of the Green's functions over all momentum space appear in the coefficients. Thus, we are justified in neglecting the transverse macroscopic field entirely. For the longitudinal macroscopic field $\mathbf{E}_{\parallel}$, one can shown that it is essentially electrostatic in nature.[31] Although the decomposition of $\mathbf{E}$ into solenoidal and irrotational parts is not unique it is convenient to make the choice that $\mathbf{E}_{\parallel}$ be the instantaneous Coulomb field of the charge distribution.[13] For wavelengths short compared to the size of the crystal (but still large compared to the interatomic distance), $\mathbf{E}$ is given by $-4\pi\mathbf{P}_{\parallel}$, where $\mathbf{P}$ is the polarization per unit volume. This leads to the familiar separation of the frequencies for longitudinal and transverse optical vibrations. On the other hand, when the wavelength is comparable or larger than the size of the crystal, $\mathbf{E}_{\parallel}$ is no longer equal to $-4\pi\mathbf{P}_{\parallel}$ since surface effects must also be taken into account. The effects of $\mathbf{E}_{\parallel}$ on the optical vibrational spectra cannot be determined explicitly as easily as before. But for our purpose we shall simply assume that the contribution of the longitudinal macroscopic field is included in the harmonic frequencies and rely on macroscopic symmetry principles to determine the nature of these frequencies in the long-wavelength limit.

III. DERIVATION OF EQUATIONS FOR THE PHONON GREEN'S FUNCTIONS AND THE THERMAL EXPECTATION VALUES OF THE NORMAL COORDINATES

In this section we will derive the necessary equations to determine the lattice free energy. We begin by finding the equations of motion for the normal coordinates $Q_{j\mathbf{p}}$. For the purpose of formal manipulation we in-

---

[14] A small correction to this classification arises because the zero-point motion of the atoms renormalizes the frequencies even at zero temperature as shown in more detail in Sec. III.

troduce an additional fictitious "source" term in the Hamiltonian (4) that has the following form:

$$H_S=\sum_{j\mathbf{p}} J(j,\mathbf{p};t)Q_{j\mathbf{p}}(t). \tag{6}$$

J is to be set equal to zero after the desired equations are generated. Then from (4) and (6) and the canonical commutation relations

$$i[\dot{Q}_{j\mathbf{p}}(t),Q_{j'\mathbf{p}'}(t)]=\delta_{jj'}\delta_{\mathbf{p}\mathbf{p}'}, \tag{7}$$

we obtain

$$\begin{aligned}(\partial^2/\partial t^2)Q_\mu(t)+\omega_\mu{}^{02}Q_\mu(t)&+\frac{1}{2!}\sum_{\mu_1\mu_2}U_{-\mu,\mu_1,\mu_2}{}^{(3)}Q_{\mu_1}(t)Q_{\mu_2}(t)\\&+\frac{1}{3!}\sum_{\mu_1\mu_2\mu_3}U_{-\mu,\mu_1,\mu_2,\mu_3}{}^{(4)}Q_{\mu_1}(t)Q_{\mu_2}(t)Q_{\mu_3}(t)\\&+\frac{1}{5!}\sum_{\mu_1\cdots\mu_5}U_{-\mu,\mu_1,\ldots,\mu_5}{}^{(6)}Q_{\mu_1}(t)\cdots Q_{\mu_5}(t)=-J_{-\mu}(t),\end{aligned} \tag{8}$$

where the subscript μ is used to denote the pair $(j,\mathbf{p})$ and $-\mu$ denotes $(j,-\mathbf{p})$.

We will now define in the usual manner[15] the thermal-expectation value of any operator $A(t)$ in the presence of the source J as

$$\langle A\rangle_J=\frac{\mathrm{Tr}e^{-\beta H}(SA)_+}{\mathrm{Tr}e^{-\beta H}S}, \tag{9}$$

where $\beta=1/k_BT$, T being the temperature; H is the Hamiltonian (4); and S is given by

$$S=\left[\exp\left(-i\int_0^{-i\beta}dt'\sum_\mu J_\mu(t')Q_\mu(t')\right)\right]_+. \tag{10}$$

All times are purely imaginary and restricted to the interval $\{0,-i\beta\}$, and $+$ denotes a positive time ordering in this interval. Note that the definition (9) reduces to the definition of thermal-equilibrium expectation value when J is zero. For convenience we will make the substitution

$$t=-i\tau. \tag{11}$$

Thus, τ is real and runs from 0 to β. Equation (10) for S then becomes

$$S=\left(\exp\left[-\int_0^\beta d\tau'\sum_\mu J_\mu(\tau')Q_\mu(\tau')\right]\right)_+. \tag{12}$$

The equation satisfied by the thermal expectation values $\langle Q_\mu(t)\rangle_J$ or $\langle Q_\mu(\tau)\rangle_J$ can be directly obtained from (8)

$$\begin{aligned}-(\partial^2/\partial\tau^2)\langle Q_\mu(\tau)\rangle_J+\omega_\mu{}^{02}\langle Q_\mu(\tau)\rangle_J&+\frac{1}{2!}\sum_{\mu_1\mu_2}U_{-\mu,\mu_1,\mu_2}{}^{(3)}\\&\times\langle Q_{\mu_1}(\tau)Q_{\mu_2}(\tau)\rangle_J+\frac{1}{3!}\sum_{\mu_1\mu_2\mu_3}U_{-\mu,\mu_1,\mu_2,\mu_3}{}^{(4)}\\&\times\langle Q_{\mu_1}(\tau)Q_{\mu_2}(\tau)Q_{\mu_3}(\tau)\rangle_J+\frac{1}{5!}\sum_{\mu_1\cdots\mu_5}U_{-\mu,\mu_1,\ldots,\mu_5}{}^{(6)}\\&\times\langle Q_{\mu_1}(\tau)\cdots Q_{\mu_5}(\tau)\rangle_J=-J_{-\mu}(\tau).\end{aligned} \tag{13}$$

The phonon Green's functions which describe the vibrational excitation spectra are defined in the presence of J as

$$\begin{aligned}D_{\mu,\mu'}(\tau,\tau';J)&=-\langle([Q_\mu(\tau)-\langle Q_\mu(\tau)\rangle_J]\\&\qquad\times[Q_{\mu'}(\tau')-\langle Q_{\mu'}(\tau')\rangle_J])_+\rangle_J\\&=-\langle(Q_\mu(\tau)Q_{\mu'}(\tau'))_+\rangle_J\\&\qquad+\langle Q_\mu(\tau)\rangle_J\langle Q_{\mu'}(\tau')\rangle_J.\end{aligned} \tag{14}$$

Equation (14) can be written equivalently in the following formal way upon using the definition (9) and the fact that boson operators commute inside the time-ordering sign

$$\begin{aligned}D_{\mu,\mu'}(\tau,\tau';J)&=(\delta/\delta J_{-\mu'}(\tau'))\langle Q_\mu(\tau)\rangle_J\\&=(\delta/\delta J_\mu(\tau))\langle Q_{-\mu'}(\tau')\rangle_J.\end{aligned} \tag{15}$$

This allows us to write down immediately the equations for the Green's functions by taking the functional derivative of Eq. (13) We get

$$\begin{aligned}&\frac{\partial^2}{\partial\tau^2}D_{\mu,\mu'}(\tau,\tau';J)+\omega_\mu{}^{02}D_{\mu,\mu'}(\tau,\tau';J)\\&+\frac{1}{2!}\sum_{\mu_1\mu_2}U_{-\mu,\mu_1,\mu_2}{}^{(3)}\frac{\delta}{\delta J_{-\mu'}(\tau')}\langle Q_{\mu_1}(\tau)Q_{\mu_2}(\tau)\rangle_J\\&+\frac{1}{3!}\sum_{\mu_1\mu_2\mu_3}U_{-\mu,\mu_1,\mu_2,\mu_3}{}^{(4)}\frac{\delta}{\delta J_{-\mu'}(\tau')}\langle Q_{\mu_1}(\tau)Q_{\mu_2}(\tau)Q_{\mu_3}(\tau)\rangle_J\\&+\frac{1}{5!}\sum_{\mu_1\cdots\mu_5}U_{-\mu,\mu_1,\ldots,\mu_5}{}^{(6)}\frac{\delta}{\delta J_{-\mu'}(\tau')}\langle Q_{\mu_1}(\tau)\cdots Q_{\mu_5}(\tau)\rangle_J\\&\qquad=-\delta_{\mu\mu'}\delta(\tau-\tau').\end{aligned} \tag{16}$$

Our next step is to express all expectation values of more than one normal coordinates and their functional derivatives in (13) and (16) in terms of the phonon Green's functions and their functional derivatives. This can be readily done by using (9), (14), and (15) systematically. For example, we have

$$\begin{aligned}\langle Q_{\mu_1}(\tau)Q_{\mu_2}(\tau)\rangle_J&=-D_{\mu_1,-\mu_2}(\tau,\tau;J)\\&\qquad+\langle Q_{\mu_1}(\tau)\rangle_J\langle Q_{\mu_2}(\tau)\rangle_J,\end{aligned} \tag{17}$$

---

[15] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

$$\frac{\delta}{\delta J_{-\mu'}(\tau')}\langle Q_{\mu1}(\tau)Q_{\mu2}(\tau)\rangle_J=-\frac{\delta}{\delta J_{-\mu'}(\tau')}D_{\mu1,-\mu2}(\tau,\tau;J)$$
$$+\langle Q_{\mu1}(\tau)\rangle_J D_{\mu2,\mu'}(\tau,\tau';J)$$
$$+\langle Q_{\mu1}(\tau)\rangle_J D_{\mu2,\mu'}(\tau,\tau;J)\,. \quad (18)$$

The result is a set of very complicated coupled equations for the phonon Green's functions and the thermal-expectation values $\langle Q_\mu\rangle_J$. These equations in principle give a complete description of the system. The free energy may be obtained by integrating Eq. (13) in the limit of $J\to 0$ with respect to the $\langle Q_\mu\rangle$. A power-series solution to the free energy will result if we expand the exact Green's functions in (13) in terms of the harmonic Green's functions and the anharmonic coupling parameters. However, such an expansion cannot be made for the soft-branch Green's function because the harmonic frequencies are imaginary. Thus for our purpose of deriving a free-energy power series of Devonshire form we must drop the Green's function for the soft branch. Furthermore, to simplify our derivation it is convenient to consider that all the anharmonic coupling parameters are small and hence that we need to retain only terms linear in these parameters. This linear anharmonic approximation is not necessary for obtaining a power series for the free energy but greatly simplifies the derivation. In some crystals such an approximation may not be valid because the anharmonic coefficients are not small so that for example[10] the anharmonic correction proportional to $[U^{(3)}]^2$ is comparable to that proportional to $U^{(4)}$. Our formalism can be readily extended to treat this more complicated situation. The linear anharmonic approximation is obtained first of all by neglecting all the anharmonic terms in (13) and (16) that contain the functional derivatives of the phonon Green's functions since these lead to terms which are nonlinear in the $U^{(n)}$.

When we drop all the terms that contain $\delta D/\delta J$, Eqs. (15) and (16) become

$$\omega_\mu{}^{02}\langle Q_\mu\rangle+\frac{1}{2!}\sum_{\mu1\mu2}U_{-\mu,\mu1,\mu2}{}^{(3)}(\langle Q_{\mu1}\rangle\langle Q_{\mu2}\rangle-D_{\mu1,-\mu2}(0))+\frac{1}{3!}\sum_{\mu1\mu2\mu3}U_{-\mu,\mu1,\mu2,\mu3}{}^{(4)}(\langle Q_{\mu1}\rangle\langle Q_{\mu2}\rangle\langle Q_{\mu3}\rangle-3\langle Q_{\mu1}\rangle D_{\mu2,-\mu3}(0))$$
$$+\frac{1}{5!}\sum_{\mu1\cdots\mu5}U_{-\mu,\mu1,\ldots,\mu5}{}^{(6)}(\langle Q_{\mu1}\rangle\cdots\langle Q_{\mu5}\rangle-10\langle Q_{\mu1}\rangle\cdots\langle Q_{\mu3}\rangle D_{\mu4,-\mu5}(0)+15\langle Q_{\mu1}\rangle D_{\mu2,-\mu3}(0)D_{\mu4,-\mu5}(0))=0 \quad (19)$$

and

$$-\frac{\partial^2}{\partial\tau^2}D_{\mu,\mu'}(\tau-\tau')+\omega_\mu{}^{02}D_{\mu,\mu'}(\tau-\tau')+\sum_{\mu1\mu2}U_{-\mu,\mu1,\mu2}{}^{(3)}\langle Q_{\mu1}\rangle D_{\mu2,\mu'}(\tau-\tau')+\frac{1}{2!}\sum_{\mu1\mu2\mu3}U_{-\mu,\mu1,\mu2,\mu3}{}^{(4)}$$
$$\times(\langle Q_{\mu1}\rangle\langle Q_{\mu2}\rangle-D_{\mu1,-\mu2}(0))D_{\mu3,\mu'}(\tau-\tau')+\frac{1}{4!}\sum_{\mu1\cdots\mu5}U_{-\mu,\mu1,\ldots,\mu5}{}^{(6)}(\langle Q_{\mu1}\rangle\cdots\langle Q_{\mu4}\rangle-6\langle Q_{\mu1}\rangle\langle Q_{\mu2}\rangle D_{\mu4,-\mu5}(0)$$
$$+3D_{\mu1,-\mu2}(0)D_{\mu3,-\mu4}(0))D_{\mu5,\mu'}(\tau-\tau')=-\delta_{\mu\mu'}\delta(\tau-\tau')\,, \quad (20)$$

where we have let the external source J go to zero and used the fact that as a result the thermal-equilibrium expectation values of the normal coordination become time-independent, i.e., $\langle Q_\mu(\tau)\rangle_{J=0}=\langle Q_\mu\rangle$ and the phonon Green's Functions become functions only of the relative times. $D_{\mu_1,\mu_2}(0)$ is used to denote $D_{\mu_1,\mu_2}(\tau,\tau)$. It is now more convenient to describe (19) and (20) in terms of the Fourier transforms of Green's functions $D_{\mu,\mu'}(\omega_n)$ defined according to

$$D_{\mu,\mu'}(\tau-\tau')=\frac{1}{\beta}\sum_n e^{-i\omega_n(\tau-\tau')}D_{\mu,\mu'}(\omega_n)\,, \quad (21)$$

where

$$\omega_n=(2\pi/\beta)n;\quad n=\text{integer}. \quad (22)$$

From (20) we see that in the harmonic approximation $D_{\mu,\mu'}(\omega_n)$ is given by

$$D_{\mu,\mu'}{}^0(\omega_n)=\delta_{\mu\mu'}\left(\frac{-1}{\omega_n{}^2+\omega_\mu{}^{02}}\right)\,, \quad (23)$$

which is diagonal in μ where we recall that μ denotes the pair of quantum numbers $j\mathbf{p}$. In the presence of anharmonicity the Green's functions are no longer diagonal. However, one can easily verify from (20) that the off-diagonal Green's functions are small compared to the diagonal ones and may be neglected. We then find that

$D_{j\mathbf{p},j'\mathbf{p}'}(\omega_n)$ reduces to an identical form as that of (23), namely

$$D_{j\mathbf{p},j'\mathbf{p}'}(\omega_n)=\delta_{jj'}\delta_{\mathbf{p}\mathbf{p}'}\left(\frac{-1}{\omega_n{}^2+\omega_{j\mathbf{p}}{}^2}\right). \tag{24}$$

The $\omega_{j\mathbf{p}}{}^2$ are the squares of the renormalized phonon frequencies and are given by

$$\begin{aligned}\omega_{j\mathbf{p}}{}^2=\omega_{j\mathbf{p}}{}^{02}&+\sum_{j_1\mathbf{p}_1}U_{j-\mathbf{p},j\mathbf{p},j_1\mathbf{p}_1}{}^{(3)}\langle Q_{j_1\mathbf{p}_1}\rangle+\tfrac{1}{2}\sum_{1\mathbf{p}_1}U_{j-\mathbf{p},j\mathbf{p},j_1\mathbf{p}_1,j_1-\mathbf{p}_1}{}^{(4)}\left(\frac{1}{2\omega_{j_1\mathbf{p}_1}}+\frac{N(\omega_{j_1\mathbf{p}_1})}{\omega_{j_1\mathbf{p}_1}}\right)+\tfrac{1}{2}\sum_{1j_2\mathbf{p}_2}U_{j-\mathbf{p},j\mathbf{p},j_1\mathbf{p}_1,j_2\mathbf{p}_2}{}^{(4)}\langle Q_{j_1\mathbf{p}_1}\rangle\\&\times\langle Q_{j_2\mathbf{p}_2}\rangle+\tfrac{1}{8}\sum_{j_1\mathbf{p}_1j_2\mathbf{p}_2}U_{j-\mathbf{p},j\mathbf{p},j_1\mathbf{p}_1,j_1-\mathbf{p}_1,j_2\mathbf{p}_2,j_2-\mathbf{p}_2}{}^{(6)}\left(\frac{1}{2\omega_{j_1\mathbf{p}_1}}+\frac{N(\omega_{j_1\mathbf{p}_1})}{\omega_{j_1\mathbf{p}_1}}\right)\left(\frac{1}{2\omega_{j_2\mathbf{p}_2}}+\frac{N(\omega_{j_2\mathbf{p}_2})}{\omega_{j_2\mathbf{p}_2}}\right)+\tfrac{1}{4}\sum_{j_1\mathbf{p}_2\cdots j_3\mathbf{p}_3}\\&\times U_{j-\mathbf{p},j\mathbf{p},j_1\mathbf{p}_1,j_2\mathbf{p}_2,j_3\mathbf{p}_3,j_3-\mathbf{p}_3}{}^{(6)}\langle Q_{j_1\mathbf{p}_1}\rangle\langle Q_{j_2\mathbf{p}_2}\rangle\left(\frac{1}{2\omega_{j_3\mathbf{p}_3}}+\frac{N(\omega_{j_3\mathbf{p}_3})}{\omega_{j_3\mathbf{p}_3}}\right)+\frac{1}{24}\sum_{j_1\mathbf{p}_1\cdots j_4\mathbf{p}_4}U_{j-\mathbf{p},j\mathbf{p},j_1\mathbf{p}_1\ldots j_4\mathbf{p}_4}{}^{(6)}\langle Q_{j_1\mathbf{p}_1}\rangle\cdots\langle Q_{j_4\mathbf{p}_4}\rangle.\end{aligned} \tag{25}$$

We have made use of the identity

$$\begin{aligned}D_{j\mathbf{p},j\mathbf{p}}(0)=D_{j\mathbf{p},j\mathbf{p}}(\tau-\tau)&=\frac{1}{\beta}\sum_n D_{j\mathbf{p},j\mathbf{p}}(\omega_n)\\&=-\left(\frac{1}{2\omega_{j\mathbf{p}}}+\frac{N(\omega_{j\mathbf{p}})}{\omega_{j\mathbf{p}}}\right)\end{aligned} \tag{26}$$

and

$$N(\omega_{j\mathbf{p}})=(e^{\beta\omega_{j\mathbf{p}}}-1)^{-1} \tag{27}$$

is the equilibrium phonon-distribution function. The equations satisfied by the thermal-expectation values of the normal coordinates are readily obtained from (19) to be

$$\begin{aligned}-\omega_{j\mathbf{p}}{}^{02}\langle Q_{j\mathbf{p}}\rangle=&\tfrac{1}{2}\sum_{j_1\mathbf{p}_1}U_{j-\mathbf{p},j_1\mathbf{p}_1,j_1-\mathbf{p}_1}{}^{(3)}\left(\frac{1}{2\omega_{j_1\mathbf{p}_1}}+\frac{N(\omega_{j_1\mathbf{p}_1})}{\omega_{j_1\mathbf{p}_1}}\right)+\tfrac{1}{2}\sum_{j_1\mathbf{p}_1j_2\mathbf{p}_2}U_{j-\mathbf{p},j_1\mathbf{p}_1,j_2\mathbf{p}_2}{}^{(3)}\langle Q_{j_1\mathbf{p}_1}\rangle\langle Q_{j_2\mathbf{p}_2}\rangle\\&+\tfrac{1}{2}\sum_{j_1\mathbf{p}_1j_2\mathbf{p}_2}U_{j-\mathbf{p},j_1\mathbf{p}_1,j_2\mathbf{p}_2,j_2-\mathbf{p}_2}{}^{(4)}\langle Q_{j_1\mathbf{p}_1}\rangle\left(\frac{1}{2\omega_{j_2\mathbf{p}_2}}+\frac{N(\omega_{j_2\mathbf{p}_2})}{\omega_{j_2\mathbf{p}_2}}\right)+\tfrac{1}{6}\sum_{j_1\mathbf{p}_1\cdots j_3\mathbf{p}_3}U_{j-\mathbf{p},j_1\mathbf{p}_1,j_2\mathbf{p}_2,j_3\mathbf{p}_3}{}^{(4)}\langle Q_{j_1\mathbf{p}_1}\rangle\langle Q_{j_2\mathbf{p}_2}\rangle\langle Q_{j_3\mathbf{p}_3}\rangle\\&+\tfrac{1}{8}\sum_{j_1\mathbf{p}_1\cdots j_3\mathbf{p}_3}U_{j-\mathbf{p},j_1\mathbf{p}_1,j_2\mathbf{p}_2,j_2-\mathbf{p}_2,j_3\mathbf{p}_3,j_3-\mathbf{p}_3}{}^{(6)}\langle Q_{j_1\mathbf{p}_1}\rangle\left(\frac{1}{2\omega_{j_2\mathbf{p}_2}}+\frac{N(\omega_{j_3\mathbf{p}_3})}{\omega_{j_2\mathbf{p}_2}}\right)\left(\frac{1}{2\omega_{j_3\mathbf{p}_3}}+\frac{N(\omega_{j_3\mathbf{p}_3})}{\omega_{j_3\mathbf{p}_3}}\right)+\frac{1}{12}\sum_{j_1\mathbf{p}_1\cdots j_4\mathbf{p}_4}\\&\times U_{j-\mathbf{p},j_1\mathbf{p}_1\ldots j_3\mathbf{p}_3,j_4\mathbf{p}_4,j_4-\mathbf{p}_4}{}^{(6)}\langle Q_{j_1\mathbf{p}_1}\rangle\langle Q_{j_2\mathbf{p}_2}\rangle\langle Q_{j_3\mathbf{p}_3}\rangle\left(\frac{1}{2\omega_{j_4\mathbf{p}_4}}+\frac{N(\omega_{j_4\mathbf{p}_4})}{\omega_{j_4\mathbf{p}_4}}\right)\\&+\frac{1}{120}\sum_{j_1\mathbf{p}_1\cdots j_5\mathbf{p}_5}U_{j-\mathbf{p},j_1\mathbf{p}_1\ldots j_5\mathbf{p}_5}{}^{(6)}\langle Q_{j_1\mathbf{p}_1}\rangle\cdots\langle Q_{j_5\mathbf{p}_5}\rangle.\end{aligned} \tag{28}$$

To complete the linear anharmonic approximation we replace the renormalized phonon frequencies $\omega_{j\mathbf{p}}$ appearing in (25) and (26) by the harmonic phonon frequencies $\omega_{j\mathbf{p}}{}^0$. This cannot be done for the soft phonon modes, i.e., those with an imaginary $\omega_{j\mathbf{p}}{}^0$. These soft modes, as discussed in the Introduction, belong to certain optical branch and occur near $\mathbf{p}=0$. We therefore omit all the terms in (25) and (26) that contain the factor $(1/2\omega_{j\mathbf{p}}+N(\omega_{j\mathbf{p}})/\omega_{j\mathbf{p}})$, where j corresponds to this soft branch. As discussed earlier such a step is necessary to obtain a power series for the free energy. The essential validity of the Devonshire power-series expansion has been verified by a considerable amount of experimental data. For example in a first-order transition the power series for F implies a relation between the dielectric constant of the two phases at T_c, $\epsilon_{\text{para}}=4\epsilon_{\text{ferro}}$. This relation has been experimentally verified.[3] On the other hand, it is of considerable theoretical interest to retain and examine the soft-mode terms which give rise to extra terms in the free energy that have no power-series expansion in the $\langle Q\rangle$ which may play a significant role at temperature close enough to the transition temperature. In the present analysis we shall not investigate the implication of these terms.

IV. ORDER PARAMETERS AND FREE ENERGY

In this section we examine the equations derived in Sec. III for the thermal-expectation values of the normal coordinate displacements $\langle Q_{j\mathbf{p}}\rangle$ in the linear anharmonic coupling approximation. From these equations for the normal coordinates $\langle Q_{j\mathbf{p}}\rangle$ we shall also derive the free energy by integration. We shall refer to the thermal expectation values of the normal coordinate displacements as simply microscopic order parameters for reasons which will become evident from the subsequent discussion. The relation between the microscopic order parameters $\langle Q_{j\mathbf{p}}\rangle$ and the macroscopic order parameters appearing in the Devonshire free energy (F_D) will also be derived.

The macroscopic order parameters appearing in F_D are a spatially uniform polarization vector per unit volume $\mathbf{P}$ and a spatially uniform strain tensor whose components are denoted as $S_{\alpha\beta}$. We may relate the macroscopic and spatially uniform strain to the microscopic order parameters of the acoustic branch by

$$S_{\alpha\beta}=(NM)^{-1/2}\sum_j \tfrac{1}{2}$$
$$\times\{[e^\alpha(\mathbf{p}j)\hat{p}_\beta+e^\beta(\mathbf{p}j)\hat{p}_\alpha]ip\langle\dot{Q}_{j\mathbf{p}}\rangle\}_{\lim\,\mathbf{p}\to 0}, \quad (29)$$

where M is the total ionic mass in a unit cell and ϵ is the polarization vector normalized to unity. The uniform strain is thus related to the limit of the order parameters as $\mathbf{p}\to 0$ and depends on the direction of $\mathbf{p}$ in which this limit is taken. We shall subsequently find that the equations for the order parameters imply that $p\langle Q_{j\mathbf{p}}\rangle_{\lim\,p\to 0}$ remains finite for the acoustic branch only so that only the acoustic order parameters contribute to the macroscopic strain tensor. We may also relate the macroscopic order parameter $\mathbf{P}$ to the microscopic order parameters by

$$P_\alpha=(v_0N)^{-1}\sum_{kl} Z_k^*\langle u_\alpha(lk)\rangle, \quad (30)$$

where Z_k^* is the effective charge of the kth atom in a unit cell and v_0 is the volume of the unit cell. By using the expansion in normal coordinates [Eq. (2)] this may also be written as

$$P_\alpha=(v_0N^{1/2})^{-1}\sum_{kj} Z_k^*\left\{\frac{e_k{}^\alpha(j\mathbf{p})}{m_k{}^{1/2}}\langle Q_{j\mathbf{p}}\rangle\right\}_{\lim\,\mathbf{p}\to 0}. \quad (31)$$

In the long-wavelength limit we may use the method of Born to expand the eigenvectors as a power series in p along some fixed direction of the vector $\mathbf{p}$ denoted as $\hat{p}$,[16]

$$e_k{}^\alpha(j\mathbf{p})=W_{\alpha,k}{}^{(0)}(j\hat{p})+ipW_{\alpha,k}{}^{(1)}(j\hat{p})+\cdots. \quad (32)$$

For the acoustic branch $W_{\alpha,k}{}^{(0)}(j\hat{p})$ is proportional to $m_k{}^{1/2}$ so that this term does not contribute to P_α because of charge neutrality, i.e., $\sum_k Z_k^*=0$. The polarization may then be separated into a sum from optical and acoustic branches as

$$P_\alpha=(v_0N^{1/2})^{-1}\sum_{kj=\text{opt.}}\frac{Z_k^*}{m_k{}^{1/2}}W_{\alpha,k}{}^{(0)}(j)\langle Q_j\rangle$$
$$+(v_0N^{1/2})^{-1}\sum_{kj=\text{ac}}\frac{Z_k^*}{m_k{}^{1/2}}\{ip\langle Q_{j\mathbf{p}}\rangle\}_{\lim\,p\to 0}$$
$$\times W_{\alpha,k}{}^{(1)}(j\hat{p}), \quad (33)$$

where we have made use of $\{p\langle Q_{j\mathbf{p}}\rangle\}_{\lim p\to 0}=0$ for the optical branches. The symbol $\langle Q_j\rangle$ is an abbreviation for $\langle Q_{j\mathbf{p}=0}\rangle$. For any crystal with inversion symmetry about every atomic position (e.g., perovskite structure) $W_{\alpha,k}{}^{(1)}(j\hat{p})$ vanishes so that the acoustic branch does not contribute to the polarization.

From the discussion of the microscopic and macroscopic order parameters it becomes clear that a spatially uniform ferroelectric transition may be described by the set of order parameters $\langle Q_{j\mathbf{p}}\rangle$ in the limit $p\to 0$. We also note that the microscopic set of order parameters is more complete than the macroscopic set because the macroscopic polarization $\mathbf{P}$ lumps all the optical-mode order parameters $\langle Q_j\rangle$ together rather than specifying the value of each optical-mode order parameter separately.

Consider the equations for the microscopic order parameters in the linear anharmonic approximation. As discussed in Sec. II this amounts to replacing all renormalized phonon frequencies $\omega_{j\mathbf{p}}$ appearing in the anharmonic terms of Eq. (28) by the harmonic frequencies $\omega_{j\mathbf{p}}{}^0$ and omitting all anharmonic terms on the right-hand side of (28) which contain the factor $(1/2\omega_{j\mathbf{p}}+N(\omega_{j\mathbf{p}})/\omega_{j\mathbf{p}})$ when j corresponds to the soft optical branch. The first term on the right-hand side of Eq. (28) is proportional to $U^{(3)}$ and describes the ordinary thermal expansion of the crystal. For many crystal structures, including, for example, the perovskites, the thermal expansion only contributes to the acoustic branch displacements, i.e., the contribution of thermal expansion vanishes when j is an optical branch. This is shown explicitly for the perovksite structure in Sec. V and Appendix A. For simplicity we shall limit our discussion to those crystal structures where this holds, although the discussion may be extended to other crystals by subtracting out the contribution of thermal expansion to the optical-mode displacement. The solution of Eq. (28) for all the optical modes that corresponds to the paraelectric phase is then $\langle Q_j\rangle=0$. However in general there are other solutions of Eqs.

---

[16] See Ref. 13, p. 229.

(28) which correspond to the ferroelectric phase, i.e., $\langle Q_j\rangle \neq 0$ for some optical branches. The conditions necessary for a ferroelectric phase solution to exist as well as its relative stability with respect to the paraelectric phase are most easily discussed from the free-energy function to be derived later in this section. We first wish to note two important properties of the solution corresponding to the ferroelectric phase obtained from the Eqs. (28) for all branches j.

(a) Let us consider Eq. (28) for the acoustic-branch order parameter, i.e., $\langle Q_{j_{\mathrm{ac}};p}\rangle$ in the long-wavelength limit. A general property of the anharmonic coefficient involving the acoustic branch is that $U_{j_{\mathrm{ac}},\mathbf{p};j_2\mathbf{p}_2\ldots j_n\mathbf{p}_n}{}^{(n)}$ vanishes at least linearly in p. This property follows directly from translation invariance and the properties of the eigenvectors of the acoustic modes in the long-wavelength limit. Thus, the right-hand side of Eq. (28) vanishes linearly with p. Since the square of the harmonic frequency for the acoustic branch vanishes as p^2 we conclude that $\{p\langle Q_{j_{\mathrm{ac}},p}\rangle\}_{\lim p\to 0}$ is finite. The corresponding strain is given by Eq. (29) and is also finite in the limit $p\to 0$ as one would expect. In order to describe the most general strain the limit $\mathbf{p}\to 0$ must be considered along three different axes. The character of the solution of Eq. (28) for an optical-branch order parameter is quite different since neither the square of the harmonic frequency nor the anharmonic coefficients vanish in the long-wavelength limit. This implies that $\langle Q_{j_{\mathrm{op}},p=0}\rangle$ is finite so that

$$\{p\langle Q_{j_{\mathrm{op}},p}\rangle\}_{\lim p\to 0}=0\,.$$

(b) The particular optical branch index j enters in the right-hand side of Eqs. (28) only through the anharmonic coefficients. Therefore, it we make the reasonable assumption that the average anharmonic coefficients for the different optical branches are of the same order of magnitude we see that the left-hand side of Eq. (28) is of the same order of magnitude for all optical modes j. This implies that in the ferroelectric phase the ratios of the optical-order parameters are roughly inversely proportional to the squares of their harmonic frequencies

$$\langle Q_{j_1}\rangle/\langle Q_{j_2}\rangle \approx (\omega_{j_2}{}^0)^2/(\omega_{j_1}{}^0)^2\,. \tag{34}$$

Since for most ferroelectric crystals the square of harmonic frequency of the soft optical branch is much smaller than the remaining optical branches we conclude that the largest order parameter (i.e., displacement coordinate) in the ferroelectric phase is the soft mode $\langle Q_s\rangle$ (which may be degenerate) and the displacements of all other optical modes j are smaller by the ratio $\approx \omega_s{}^{02}/\omega_j{}^{02}$. This important conclusion will be further discussed and compared with experiment in the application of the general theory to the perovskite structure (Sec. V). This conclusion will also enable us to eliminate the nonsoft optical modes and thus derive a greatly simplified form of the free energy which will reduce to the phenomenological Devonshire free-energy (F_D).

We may derive the Helmholtz free-energy F by integrating Eq. (28) for the order parameters. The integration is particularly simple in the linear anharmonic approximation because all the frequencies appearing in Eq. (28) are harmonic frequencies and hence independent of the order parameters. The integration yields a free energy given by

$$\begin{aligned}F=&\frac{1}{2!}\sum(\omega_{j_1\mathbf{p}_1}{}^0)^2\langle Q_{j_1\mathbf{p}_1}\rangle\langle Q_{j_1-\mathbf{p}_1}\rangle+\frac{1}{2!}\sum V_{j_1+\mathbf{p}_1;j_2\mathbf{p}_2}{}^{(2)}\langle Q_{j_1\mathbf{p}_1}\rangle\langle Q_{j_2\mathbf{p}_2}\rangle+\frac{1}{2!}\sum U_{j_1+\mathbf{p}_1;j_2\mathbf{p}_2;j_2-\mathbf{p}_2}{}^{(3)}\left(\frac{1}{2\omega_{j_2\mathbf{p}_2}{}^0}+\frac{N(\omega_{j_2\mathbf{p}_2}{}^0)}{\omega_{j_2\mathbf{p}_2}{}^0}\right)\\&\times\langle Q_{j_1\mathbf{p}_1}\rangle+\frac{1}{3!}\sum U_{j_1+\mathbf{p}_1;j_2\mathbf{p}_2;j_3\mathbf{p}_3}{}^{(3)}\langle Q_{j_1\mathbf{p}_1}\rangle\langle Q_{j_2\mathbf{p}_2}\rangle\langle Q_{j_3\mathbf{p}_3}\rangle+\frac{1}{4!}\sum V_{j_1+\mathbf{p}_1;j_2\mathbf{p}_2;j_3\mathbf{p}_3;j_4\mathbf{p}_4}{}^{(4)}\langle Q_{j_1\mathbf{p}_1}\rangle\langle Q_{j_2\mathbf{p}_2}\rangle\langle Q_{j_3\mathbf{p}_3}\rangle\langle Q_{j_4\mathbf{p}_4}\rangle\\&+\frac{1}{6!}\sum U_{j_1+\mathbf{p}_1;j_2\mathbf{p}_2;j_3\mathbf{p}_3;j_4\mathbf{p}_4;j_5\mathbf{p}_5;j_6\mathbf{p}_6}{}^{(6)}\langle Q_{j_1\mathbf{p}_1}\rangle\langle Q_{j_2\mathbf{p}_2}\rangle\langle Q_{j_3\mathbf{p}_3}\rangle\langle Q_{j_4\mathbf{p}_4}\rangle\langle Q_{j_5\mathbf{p}_5}\rangle\langle Q_{j_6\mathbf{p}_6}\rangle+R(T)\,.\end{aligned}\tag{35}$$

The coefficients $V^{(2)}$ and $V^{(4)}$ are linear combinations of the anharmonic coefficients $U^{(2)}$, $U^{(4)}$, and $U^{(6)}$ given by

$$\begin{aligned}V_{j_1+\mathbf{p}_1;j_2\mathbf{p}_2}{}^{(2)}=&\tfrac{1}{2}\sum U_{j_1+\mathbf{p}_1;j_2\mathbf{p}_2;j\mathbf{p};j-\mathbf{p}}{}^{(4)}\left(\frac{1}{2\omega_{j\mathbf{p}}{}^0}+\frac{N(\omega_{j\mathbf{p}}{}^0)}{\omega_{j\mathbf{p}}{}^0}\right)\\&+\tfrac{1}{8}\sum U_{j_1+\mathbf{p}_1;j_2\mathbf{p}_2;j\mathbf{p};j-\mathbf{p};j'\mathbf{p}';j'-\mathbf{p}'}{}^{(6)}\left(\frac{1}{2\omega_{j\mathbf{p}}{}^0}+\frac{N(\omega_{j\mathbf{p}}{}^0)}{\omega_{j\mathbf{p}}{}^0}\right)\left(\frac{1}{2\omega_{j'\mathbf{p}'}{}^0}+\frac{N(\omega_{j'\mathbf{p}'}{}^0)}{\omega_{j'\mathbf{p}'}{}^0}\right).\end{aligned}\tag{36}$$

$$V_{j_1+\mathbf{p}_1;j_2\mathbf{p}_2;j_3\mathbf{p}_3;j_4\mathbf{p}_4}{}^{(4)}=U_{j_1+\mathbf{p}_1;j_2\mathbf{p}_2;j_3\mathbf{p}_3;j_4\mathbf{p}_4}{}^{(4)}+\tfrac{1}{2}\sum U_{j_1+\mathbf{p}_1;j_2\mathbf{p}_2;j_3\mathbf{p}_3;j_4\mathbf{p}_4;j\mathbf{p};j-\mathbf{p}}{}^{(6)}\left(\frac{1}{2\omega_{j\mathbf{p}}{}^0}+\frac{N(\omega_{j\mathbf{p}}{}^0)}{\omega_{j\mathbf{p}}{}^0}\right).\tag{37}$$

In the linear anharmonic approximation we recall that the sum over branches will exclude all terms which contain the factor

$$\left(\frac{1}{2\omega_{j\mathbf{p}}{}^0}+\frac{N(\omega_{j\mathbf{p}}{}^0)}{\omega_{j\mathbf{p}}{}^0}\right)$$

when j is a soft mode. Also since $R(T)$ denotes an arbitrary function of temperature which is independent of the order parameters it plays no role in determining differences between the ferroelectric and paraelectric phases. In our approximation the free energy given by Eq. (35) is linear in the anharmonic coupling coefficients.

In order to transform the free energy into a more meaningful physical form we proceed in the general case as follows.

(a) Since the ferroelectric phase is spatially uniform then for the optical modes only the $\mathbf{p}=0$ order parameter is nonzero, i.e., $\langle Q_{j_{\mathrm{op}},p}\rangle=\delta_{\mathbf{p},0}\langle Q_{j_{\mathrm{op}}}\rangle$.

(b) To describe a spatially uniform strain in the ferroelectric (and paraelectric) phase we assume as discussed earlier that only the limit $\{p\langle Q_{j_{\mathrm{ac}},\mathbf{p}}\rangle\}_{\lim p\to 0}$ is nonzero. Also the most general strain tensor may be described by taking the limit of $\{p\langle Q_{j_{\mathrm{ac}},\mathbf{p}}\rangle\}_{p\to 0}$ along three orthogonal directions for each of the three polarizations specified by the index j_{ac}.

This procedure will thus enable us to express F in terms of $(3n_0-3)$ microscopic optical order parameters and nine microscopic acoustic-mode order parameters (which combine to make up six independent elements of the symmetric strain tensor) where n_0 is the number of atoms per unit cell. In general, this will be a larger number of order parameters than used in the phenomenological free energy of Devonshire (P_α, $S_{\alpha\beta}$). However, we may use the result obtained earlier that $\langle Q_j\rangle$ is small for all optical branches which differ from the soft branches to reduce the number of microscopic order parameters to the same number as the macroscopic order parameters. We may then also eliminate the microscopic order parameters in favor of the macroscopic ones by using the relations between them [Eqs. (29) and (33)]. This procedure will produce a free energy with the same order parameters as the phenomenological free energy of Devonshire (F_D) but with the coefficients expressed in terms of microscopic temperature dependent parameters.

The general procedure outlined above for reducing the free energy is further clarified by considering a specific example. Since the best known class of displacive ferroelectrics have the perovskite structure we shall consider this structure explicitly in the next section. We shall explicitly carry out the general steps outlined above for the perovskite structure and show that it leads to the free energy of Devonshire with the coefficients expressed in terms of microscopic parameters.

V. APPLICATION TO THE PEROVSKITE STRUCTURE

In this section we apply the general procedure described in Sec. IV to derive the free energy and other ferroelectric properties of crystals with a perovskite structure. This structure includes such well-known displacive ferroelectrics as $\mathrm{BaTiO_3}$ and $\mathrm{KNbO_3}$.

The perovskite structure belongs to the cubic space group *Pm*3*m* when the crystal is in the paraelectric phase. We recall that our Hamiltonian has been expanded about the equilibrium atomic positions in the paraelectric phase so that all the coefficients of the free energy will have the symmetry of the paraelectric phase. The ions are located on five interpenetarting simple cubic lattices so that there are five atoms per unit cell. For our purpose the most important symmetry property of this space group is the nature of the lattice vibrations at zero wave vector $\mathbf{p}=0$. The group of the wave vector at $\mathbf{p}=0$ (i.e., the little group) is *m*3*m* and the lattice vibrations may be classified in terms of the irreducible representations of the little group which are $4\Gamma_{15}+\Gamma_{25}$. Each of these representations is threefold degenerate.[17] The five different lattice vibration branches will be specified by a branch index (b) and each threefold degenerate branch will be further specified by a polarization index σ. [Thus, in the notation of Sec. IV the index j represents the pair of indices (b,σ).] The eigenvectors which form the basis for the irreducible representations $4\Gamma_{15}$ and Γ_{25} are polarized along a cubic axis and therefore may be written as

$$\mathbf{e}_k(b,\sigma;\mathbf{p}=0)=m_k{}^{1/2}v_k(b)\hat{e}(\sigma)\,, \tag{38}$$

where $\hat{e}(\sigma)$ is a unit vector lying in turn along each of the three cubic axes as the index σ runs over the values 1, 2, 3. $v_k(b)$ for the acoustic modes is simply $\mathrm{M}^{-1/2}$, where M is the total mass in a unit cell. So far we have not considered the effect of the macroscopic electric field accompanying the lattice vibrations at $\mathbf{p}=0$ on their symmetry. However, we recall from Sec. I that only the longitudinal and static part of the macroscopic electric field enters into the equations for the $\langle Q\rangle$'s and the expression for the free energy. Therefore, to retain the full symmetry of the cubic group we shall assume that the shape of the crystal is such (e.g., a cube or a sphere) that at $\mathbf{p}=0$ the electric field does not destroy the cubic symmetry.

Our method for simplifying the free energy and the anharmonic coupling coefficients by symmetry arguments will make explicit use of the symmetry property of the eigenvectors given in Eq. (38). One may also reduce the free energy for the perovskite structure to the form given by Devonshire by the use of very general

---

[17] The irreducible representations of this group are discussed in most books on group theory, e.g., H. Jones, *The Theory of Brillouin Zones and Electronic States in Crystals* (North-Holland Publishing Company, Amsterdam, 1960).

group-theoretical arguments.[18] However, these general arguments do not of course express the coefficients of F in terms of the microscopic anharmonic coefficients. Since we wish to exhibit the explicit relations between the coefficients in F and the anharmonic coefficients we shall find it more convenient to use symmetry properties such as Eq. (38) explicitly in our considerations.

The microscopic order parameters that are necessary to describe the ferroelectric transition from the nonpolar cubic to the ferroelectric phase are the same as those discussed in the previous section. They are the thermal average values of the optical normal coordinates at $\mathbf{p}=0\langle Q_{b_0\sigma}\rangle$, where b_0 denotes the optical branches, and the uniform strain tensor $S_{\alpha\beta}$. For the perovskites the strain tensor as given by (29) can be written in the following manner with the help of (38):

$$S_{\alpha\beta}=\frac{1}{(NM)^{1/2}}\lim_{p\to 0}\sum_{\hat{p},\sigma}\tfrac{1}{2}(\hat{e}^{\alpha}(\sigma)\hat{p}^{\beta}+\hat{e}^{\beta}(\sigma)\hat{p}^{\alpha})ip\langle Q_{b_a\mathbf{p}}\rangle\,, \quad (39)$$

where b_a refers to the acoustic branch and the summation for the unit vector $\hat{p}$ is over the three cubic axes. One can now obtain from Eq. (25) the free energy involving all these order parameters. However, this more complete form of the free energy is usually not necessary for the description of the general properties of the ferroelectric transition. The reason is that all optical-mode order parameters except the $\langle Q_{s,\sigma}\rangle$ for the three degenerate soft optical modes are unimportant and may be neglected. From the discussion in Sec. IV we see that the ratio of the order parameters $\langle Q_{b_0\neq s,\sigma}\rangle/\langle Q_{s,\sigma'}\rangle$ in the ferroelectric phase is given approximately by

$$\langle Q_{b_0\neq s,\sigma}\rangle/\langle Q_{s,\sigma'}\rangle\simeq|(\omega_s^0)^2/(\omega_{b_0\neq s}^0)^2|\ll 1\,. \quad (40)$$

As the magnitude of the harmonic frequency for the soft mode is usually much smaller than that for the other modes this ratio is very small. When we neglect the effects of all the nonsoft optical modes the relative atomic displacements in a unit cell in the ferroelectric phase is then simply

$$u_\alpha(k)=\frac{1}{N^{1/2}}\frac{e_k{}^{\alpha}(s,\sigma)}{m_k{}^{1/2}}\langle Q_{s,\sigma}\rangle$$

or (41)

$$=\frac{1}{N^{1/2}}\hat{e}^{\alpha}(\sigma)v_k(s)\langle Q_{s,\sigma}\rangle$$

according to Eq. (38). We are using the fact that the polar tetragonal phase is described by the nonvanishing of one of the three equivalent $\langle Q_{s,\sigma}\rangle$, $\sigma=1, 2, 3$. This will become clear later when we relate the $\langle Q_{s,\sigma}\rangle$ directly to the polarization per unit volume P_σ. In order to correlate the above conclusion on the ionic displacements in the ferroelectric phase with experimental observations one must first recall that all the eigenvectors $e_k{}^{\alpha}(b,\sigma)$ including the soft-mode eigenvector $e_k{}^{\alpha}(s,\sigma)$ have been defined in Sec. II as the eigenvectors of the harmonic dynamical matrix. However, from straightforward perturbation theory it can be readily seen that the mixing of the eigenvectors of the other optical modes in the renormalized soft-mode eigenvector due to anharmonicity is small as long as the anharmonic dynamical matrix elements are small compared to the differences of their frequencies squared $(\omega_{b_0\neq s}{}^0)^2-(\omega_s{}^0)^2$ or simply $(\omega_{b_0\neq s}{}^0)^2$. Consistent with our linear anharmonic approximation we shall assume that the above condition is satisfied. This is borne out by the experimental observation of the relative temperature independence of the renormalized nonsoft optical-mode frequencies. Thus, the anharmonic corrections to the dynamical matrix renormalize the soft-mode frequency but do not appreciably change the eigenvector; i.e., in Eq. (41) we may identify $e_k{}^{\alpha}(s,\sigma)$ with the experimentally observed soft-mode eigenvector in the paraelectric phase.

The conclusion we can draw from Eq. (41) and the subsequent discussion is that the ionic displacements in the (tetragonal) ferroelectric phase are proportional to the ionic displacements of the soft optical mode. This conclusion has previously been suggested by several authors.[5,11] The ionic displacements in the tetragonal phase of $BaTiO_3$ have been observed by x-ray diffraction.[19] However, a direct comparison between this observation and the theoretical conclusion is not possible because the eigenvector of the soft mode in the paraelectric phase of $BaTiO_3$ has not been measured. Nevertheless as pointed out by Cowley[9] a qualitative agreement is obtained when one uses the soft-mode eigenvector of $SrTiO_3$ that has been deduced from neutron scattering experiments by Cowley[9] and infrared reflectivity experiments by Axe.[20]

We shall now neglect all the nonsoft-mode order parameters $\langle Q_{b_0\neq s,\sigma}\rangle$ in the following derivation of the free energy since they have been shown to be small. Furthermore, we shall express the soft-mode parameters $\langle Q_{s,\sigma}\rangle$ in terms of the components of the polarization per unit volume. From the definition of the polarization Eq. (31) and the property of the soft-mode eigenvector Eq. (28) it is readily found that

$$\langle Q_{s,\sigma}\rangle=(1/q(s))P_\sigma\,, \quad (42)$$

where

$$q(s)=\frac{\mathrm{P}}{v_0N^{1/2}}\sum_k z_k{}^*v_k(s)$$

and P_σ is the component of the polarization vector along the cubic axis σ. The general expression Eq. (35) for the free energy can now be used to derive an F that only involves the uniform polarization P_σ and the uniform strain tensor $S_{\alpha\beta}$. We shall also make use of various properties of the coefficients of the free energy

---

[18] C. Haas, Phys. Rev. **140**, A863 (1965).

[19] B. C. Frazer, H. R. Danner, and R. Pepinsky, Phys. Rev. **100**, 745 (1955).

[20] J. D. Axe (to be published).

which are listed below. These properties of the free-energy coefficients for the perovskite structure are proven in Appendices A–D. In the following all limits of $\mathbf{p}$ going to zero are taken along one of the cubic axes. Consider the following anharmonic coefficients of the free energy.

$$\text{(i)}\ \lim_{\mathbf{p}\to 0} V_{j_1\mathbf{p},j_2-\mathbf{p}}$$

$V^{(2)}$ is defined in terms of $U^{(4)}$ and $U^{(6)}$ according to Eq. (36). It is shown in Appendix B that (a) when one of j_1 and j_2 is an acoustic mode $(b_a\sigma_1)$ while the other is a soft optical mode $(s\sigma_2)$

$$\lim_{\mathbf{p}\to 0} U_{j_1\mathbf{p},j_2-\mathbf{p}}{}^{(2)}=\lim_{\mathbf{p}\to 0}\sum \lambda_{\alpha\beta\gamma}\hat{e}^{\alpha}(\sigma_1)\hat{e}^{\beta}(\sigma_2)p^{\gamma}, \tag{43}$$

where λ is a third-rank tensor independent of p which vanishes identically for the perovskites. (b) When both j_1 and j_2 are the soft modes $(s\sigma_1)$ and $(s\sigma_2)$ it is shown that $V^{(2)}$ is nonzero only when the polarization σ is the same,

$$\lim_{\mathbf{p}\to 0} V_{j_1\mathbf{p},j_2-\mathbf{p}}{}^{(2)}=V_{s\sigma_1,s\sigma_2}{}^{(2)}=\delta_{\sigma_1\sigma_2}V_{s,s}{}^{(2)}. \tag{44}$$

We will neglect the term in the free energy that is quadratic in the strain that arises from $V^{(2)}$ where both j_1 and j_2 are acoustic modes because the term only represents a small anharmonic correction to the elastic strain energy which comes from the first term in Eq. (35).

$$\text{(ii)}\ \lim_{\mathbf{p}\to 0}\sum_{\mu\neq s} U_{j\mathbf{p},\mu,-\mu}{}^{(3)}\left(\frac{1}{2\omega_{\mu}{}^{0}}+\frac{N(\omega_{\mu}{}^{0})}{\omega_{\mu}{}^{0}}\right)$$

In Appendix A we will show that the quantity is zero when j is one of the soft optical modes. When j is an acoustic mode $(b_a\sigma)$ we find that

$$\lim_{\mathbf{p}\to 0}\sum_{\mu\neq s} U_{j\mathbf{p},\mu,-\mu}{}^{(3)}\left(\frac{1}{2\omega_{\mu}{}^{0}}+\frac{N(\omega_{\mu}{}^{0})}{\omega_{\mu}{}^{0}}\right)=\lim_{\mathbf{p}\to 0} i\sum \lambda_{\beta\gamma}\hat{e}^{\beta}(\sigma)p^{\gamma};$$

$$\lambda_{\beta\gamma}=\delta_{\beta\gamma}\lambda, \tag{45}$$

where $\lambda_{\beta\gamma}$ is a diagonal second-rank tensor. When Eq. (45) is substituted into the third term in the free-energy Eq. (35) we obtain a thermal-expansion term that is the diagonal strain components $S_{\sigma\sigma}$.

$$\text{(iii)}\ \lim_{\mathbf{p}_1,\mathbf{p}_2\to 0} U_{j_1\mathbf{p}_1,j_2\mathbf{p}_2,j_3-\mathbf{p}_2}{}^{(3)}$$

In Appendix A it is shown that the most important contribution comes from the $U^{(3)}$ in which only one of the j_1, j_2 and j_3 is an acoustic mode $(b_a\sigma_1)$ and the remaining ones are soft modes $(s\sigma_2)(s\sigma_2)$. We then have

$$\lim_{\mathbf{p}_1,\mathbf{p}_2\to 0} U_{j_1\mathbf{p}_1,j_2\mathbf{p}_2,j_3-\mathbf{p}_2}{}^{(3)} =\lim_{\mathbf{p}_1,\mathbf{p}_2\to 0}\sum \lambda_{\gamma\gamma'}{}^{\beta\beta'}\hat{e}^{\beta}(\sigma_1)p_1{}^{\beta'}\hat{e}^{\gamma}(\sigma_2)p_2{}^{\gamma'}. \tag{46}$$

The nonzero tensor $\lambda_{\gamma\gamma'}{}^{\beta\beta'}$ is diagonal in $\beta\beta'$ and $\gamma\gamma'$

$$\lambda_{\gamma\gamma'}{}^{\beta\beta'}=\delta_{\beta\beta'}\delta_{\gamma\gamma'}\lambda(\beta,\gamma). \tag{47}$$

Therefore, we must have $\sigma_2=\sigma_3$ and $\hat{e}(\sigma_1)$ along $\hat{p}_1$. These give rise to the electrostrictive terms in the free energy that are proportional to $S_{\sigma\sigma}P_{\sigma'}{}^2$. When all three j's are the optical soft mode

$$\lim\nolimits_{\mathbf{p}_1,\mathbf{p}_2\to 0} U_{j_1\mathbf{p}_1,j_2\mathbf{p}_2,j_3-\mathbf{p}_2}{}^{(3)}$$

vanishes identically. When only two of them are acoustic modes we have

$$\lim_{\mathbf{p}_1,\mathbf{p}_2\to 0} U_{j_1\mathbf{p}_1,j_2\mathbf{p}_2,j_3-\mathbf{p}_2}{}^{(3)} =i^2\sum \lambda_{\alpha_1\alpha_2\alpha_3\beta\gamma}\hat{e}^{\alpha_1}(\sigma_1)\hat{e}^{\alpha_2}(\sigma_2)\hat{e}^{\alpha_3}(\sigma_4)p_1{}^{\beta}p_2{}^{\gamma} \tag{48}$$

in which $\lambda_{\alpha_1\alpha_2\alpha_3\beta\gamma}$ is zero. We will neglect the case when all the j's are acoustic modes because such terms in the free energy are cubic in the strain.

$$\text{(iv)}\ \lim_{\{\mathbf{p}\}\to 0} V_{j_1\mathbf{p}_1,j_2\mathbf{p}_2,j_3\mathbf{p}_3,j_4\mathbf{p}_4}{}^{(4)}$$

$V^{(4)}$ is defined in terms of $U^{(4)}$ and $U^{(6)}$ in Eq. (37). The only case we consider is when all j's are the soft modes (s,σ_1), (s,σ_2), (s,σ_3), and (s,σ_4). In Appendix C it is shown that $V^{(4)}$ is nonzero only when the polarizations $(\sigma_1,\cdots\sigma_4)$ appear in even powers. The corresponding terms in the free energy have the form $P_\sigma{}^2P_{\sigma'}{}^2$. We neglect the contributions in the free energy from $V^{(4)}$ that involves the acoustic modes which are proportional to S^2P^2 and S^4.

$$\text{(v)}\ \lim_{\{\mathbf{p}\}\to 0} U_{j_1\mathbf{p}_1,\ldots,j_6\mathbf{p}_6}{}^{(6)}$$

Similar to our consideration for $V^{(4)}$ only those $U^{(6)}$ in which all the j's are the soft modes are retained. It is shown in Appendix D that the polarizations $(\sigma_1,\cdots\sigma_6)$ must appear in even powers. The other contributions from $U^{(6)}$ to the free energy that are neglected are proportional to S^2P^4, S^4P^2, and S^6.

Using these properties we find that the free energy reduces to the following Devonshire form

$$\begin{aligned}F={}&\tfrac{1}{2}a\sum_{\sigma}P_\sigma{}^2+\tfrac{1}{4}b_1\sum_{\sigma}P_\sigma{}^4+\tfrac{1}{4}b_2\sum_{\substack{\sigma,\sigma'\\(\sigma\neq\sigma')}}P_\sigma{}^2P_{\sigma'}{}^2\\&+\tfrac{1}{6}d_1\sum_{\sigma}P_\sigma{}^6+\tfrac{1}{6}d_2\sum_{\substack{\sigma,\sigma'\\(\sigma\neq\sigma')}}P_\sigma{}^4P_{\sigma'}{}^2+\tfrac{1}{6}d_3P_\sigma{}^2P_{\sigma'}{}^2P_{\sigma''}{}^2\\&+\tfrac{1}{2}e_1\sum_{\sigma}S_{\sigma\sigma}{}^2+\tfrac{1}{2}e_2\sum_{\substack{\sigma,\sigma'\\(\sigma\neq\sigma')}}S_{\sigma\sigma'}{}^2-e\gamma_T\sum_{\sigma}S_{\sigma\sigma}\\&+g_1\sum_{\sigma}S_{\sigma\sigma}P_\sigma{}^2+g_2\sum_{\substack{\sigma,\sigma'\\(\sigma\neq\sigma')}}S_{,\sigma}P_{\sigma'}{}^2.\end{aligned} \tag{49}$$

The coefficients a, b, $\cdots$, h are given by

$$a=\frac{1}{q(s)^2}(\omega_s{}^{02}+\lim_{\mathbf{p}\to 0}V_{s\sigma\mathbf{p},s\sigma-\mathbf{p}}{}^{(2)}),\quad \text{for any } \sigma \tag{50}$$

$$b=\frac{1}{3!q(s)^4}\Big(\lim_{\{\mathbf{p}\}\to 0} V_{s\sigma\mathbf{p}1,s\sigma\mathbf{p}2,s\sigma\mathbf{p}3,s\sigma\mathbf{p}4}{}^{(4)}\Big),\quad \text{for any } \sigma \tag{51}$$

$$c=\frac{1}{q(s)^4}\Big(\lim_{\{\mathbf{p}\}\to 0} V_{s\sigma\mathbf{p}1,s\sigma\mathbf{p}2,s\sigma'\mathbf{p}3,s\sigma'\mathbf{p}4}{}^{(4)}\Big),\quad \sigma\neq\sigma' \tag{52}$$

$$d_1=\frac{1}{5!q(s)^6}\Big(\lim_{\{\mathbf{p}\}\to 0} U_{s\sigma\mathbf{p}1,\ldots,s\sigma\mathbf{p}6}{}^{(6)}\Big),\quad \text{for any } \sigma \tag{53}$$

$$d_2=\frac{1}{4q(s)^6}\Big(\lim_{\{\mathbf{p}\}\to 0} U_{s\sigma\mathbf{p}1,\ldots,s\sigma\mathbf{p}4,s\sigma'\mathbf{p}5,s\sigma'\mathbf{p}6}{}^{(6)}\Big),\quad \sigma\neq\sigma' \tag{54}$$

$$d_3=\frac{3}{q(s)^6}\Big(\lim_{\{\mathbf{p}\}\to 0} U_{s\sigma\mathbf{p},1s\sigma\mathbf{p}2,s\sigma'\mathbf{p}3,s\sigma'\mathbf{p}4,s\sigma''\mathbf{p}5,s\sigma''\mathbf{p}6}{}^{(6)}\Big) \tag{55}$$

$$e_1=NMv_l^2,\quad v_l=\text{longitudinal sound velocity} \tag{56}$$

$$e_2=NMv_t^2,\quad v_t=\text{transverse sound velocity} \tag{57}$$

$$\gamma_T=\frac{-1}{(NM)^{1/2}v_l^2}\lim_{\mathbf{p}\to 0}\frac{1}{ip}\sum_{\mu\neq s} U_{ba\sigma\mathbf{p},\mu,-\mu}{}^{(3)} \times\left(\frac{1}{2\omega_\mu{}^0}+\frac{N(\omega_\mu{}^0)}{\omega_\mu{}^0}\right), \tag{58}$$

$\hat{p}$, $\hat{e}(\sigma)$ along same direction,

$$g_1=\frac{1}{2q(s)^2}(NM)^{1/2}\lim_{\substack{\mathbf{p}\to 0\\ \mathbf{p}'\to 0}}\frac{1}{ip}U_{ba\mathbf{p},s\sigma\mathbf{p}',s\sigma-\mathbf{p}'}{}^{(3)}$$

$\hat{p}$, $\hat{e}(\sigma)$ along same direction, (59)

$$g_2=\frac{1}{2q(s)^2}(NM)^{1/2}\lim_{\substack{\mathbf{p}\to 0\\ \mathbf{p}'\to 0}}\frac{1}{ip}U_{ba\sigma\mathbf{p},s\sigma'\mathbf{p}',s\sigma'-\mathbf{p}'}{}^{(3)}$$

$\hat{p}$, $\hat{e}(\sigma)$ along same direction; $\sigma\neq\sigma'$. (60)

This Helmholtz free energy describes the ferroelectric transitions of the perovskites in the absence of external electric field and external stress. The coefficient a is proportional to the renormalized frequency of the soft optical branch [see Eq. (25)] and is strongly temperature dependent since $\omega_s{}^{02}$ is small. The temperature dependence of the renormalized frequency has been discussed by Silverman and Joseph[10] and by Cowley.[11] The coefficients b, c, d, and g are proportional to anharmonic coefficients with a leading temperature-independent part and a temperature-dependent correction. Since this free energy and the thermodynamic properties that follow from it have been thoroughly investigated by Devonshire[2] in connection with the ferroelectric transitions in BaTiO$_3$ we shall not repeat the discussion here.

VI. CONCLUSIONS

It was shown in Secs. III and IV that in order to derive a power-series expansion for the free energy it is sufficient (but not necessary) to make the linear anharmonic approximation. This approximation is meaningful because most of the phonon modes are largely unaffected by the transition as was first emphasized by Anderson.[6] The free energy derived in this approximation is expressed in terms of the complete set of microscopic order parameters which is in general larger than the set of order parameters used in the phenomenological free energy of Devonshire. Many ferroelectric crystals have the property that one optical branch is much softer than all the other optical branches. For such crystals it was shown in Sec. IV that the ratio of the order parameters in the ferroelectric phase $\langle Q_j\rangle/\langle Q_s\rangle$ is much less than unity where s denotes the soft mode and j any other optical mode. This implies that the ionic displacement in the ferroelectric transition is determined mainly by the soft-mode eigenvector. This conclusion has previously been suggested by several authors.[5,11] There also appears to be some qualitative experimental evidence for the perovskites to support this conclusion as discussed in Sec. V. Furthermore, this conclusion allows us to reduce the number of microscopic order parameters to the same number as used in the phenomenological theory of Devonshire. Such a reduction was explicitly carried out in Sec. V for the perovskites and the resulting expression is identical with that derived phenomenologically by Devonshire with the coefficients determined in terms of microscopic lattice parameters.

ACKNOWLEDGMENTS

We would like to thank Dr. J. D. Axe and Dr. G. Burns for helpful discussions concerning these topics.

APPENDIX A

We wish to prove here several properties of the coefficients of the free energy for the perovskite structure which have been used in Sec. V. The proofs will be based on several simple properties of the lattice vibration eigenvectors in the long-wavelength limit. For the optical modes at $\mathbf{p}=0$, the group theory discussion of Sec. V shows the eigenvectors are of the form given by Eq. (38)

$$\mathbf{e}_k(b\sigma;\,\mathbf{p}=0)=m_k{}^{1/2}v_k(b)\hat{e}(\sigma)\,, \tag{A1}$$

where $\hat{e}(\sigma)$ is a unit vector lying in turn along each of the three cubic axes as the index σ runs over the values 1, 2, 3. For the acoustic branch we use the method of Born to expand the eigenvectors as a power series in p along some fixed direction ($\hat{p}$) of the vector $\mathbf{p}$,[16]

$$e_k{}^\alpha(b\sigma;\mathbf{p})=W_{\alpha,k}{}^{(0)}(b\sigma;\hat{p}) +ipW_{\alpha,k}{}^{(1)}(b\sigma;\hat{p})+\cdots. \tag{A2}$$

We need only consider the direction $\hat{p}$ as being along one of the cubic axes. For crystals such as the perovskites which have inversion symmetry about every atom $W^{(1)}$ vanishes because the dynamical matrix is real so that a power series expansion in p contains no linear term. Also we may use the same group theory argument as for the optical mode to write $W^{(0)}$ in the form of Eq. (A1). Thus in summary Eq. (A1) is valid for all branches and no linear term in p appears in the expansion of the acoustic eigenvector.

Let us first examine the contributions of cubic anharmonicity to F. The thermal-expansion contribution to F is proportional to

$$a_3(b\sigma;\mathbf{p})=\lim_{p\to 0}\sum_{\substack{j'\mathbf{p}'\\(j'\neq s)}} U_{b\sigma\mathbf{p};j'\mathbf{p}';j'-\mathbf{p}'}{}^{(3)}g(\omega_{j'\mathbf{p}'}{}^{0}). \quad \text{(A3)}$$

The index j' denotes both the branch (b') and polarization (σ'). Also the function $g(x)$ is defined as $g(x)=x^{-1}(\frac{1}{2}+N(x))$.

From Sec. II we recall that the anharmonic coefficients are related to the derivatives of the interatomic potential by Eq. (5) of the text. Thus, the thermal expansion is proportional to

$$a_3(b\sigma;\mathbf{p})=\lim_{p\to 0}\sum_{lk}\theta_\alpha(lk)\frac{e_k{}^\alpha}{m_k{}^{1/2}}(b\sigma;\mathbf{p})\exp i\mathbf{p}\cdot\mathbf{x}(lk), \quad \text{(A4)}$$

where

$$\theta_\alpha(lk)=N^{-3/2}\sum\Phi_{\alpha\alpha_1\alpha_2}(lk;l_1k_1;l_2k_2)\frac{e_{k_1}{}^{\alpha_1}(j'\mathbf{p}')}{m_{k_1}{}^{1/2}}$$
$$\times\frac{e_{k_1}{}^{\alpha_2}(j'-\mathbf{p}')}{m_{k_2}{}^{1/2}}\exp i\mathbf{p}'[\mathbf{x}^0(l_1k_1)-\mathbf{x}^0(l_2k_2)]g(\omega_{j'\mathbf{p}'}{}^{0}). \quad \text{(A5)}$$

Note the index α denotes the component along a Cartesian coordinate axis. Using the result for the eigenvector given in Eq. (A1) we find

$$a_3(b\sigma;\mathbf{p})-\lim_{p\to 0}\sum_{lk}\theta_\alpha(lk)v_k(b)\hat{e}_\alpha(\sigma)\exp i\mathbf{p}\cdot\mathbf{x}^0(lk), \quad \text{(A6)}$$

In a power-series expansion in p the term independent of p vanishes because

$$\sum_{lk}\theta_\alpha(lk)v_k(b)$$

is a vector which must vanish in any crystal possessing a center of inversion.

For the acoustic branch we also require the linear term in p which may be written as

$$a_3(b_a\sigma;\mathbf{p})=i\sum_{\alpha\beta}p_\beta\hat{e}_\alpha(\sigma)T_{\alpha\beta}, \quad \text{(A7)}$$

where the tensor $T_{\alpha\beta}$ is

$$T_{\alpha\beta}=\sum_{lk}\theta_\alpha(lk)x_\beta{}^0(lk)v_k(b). \quad \text{(A8)}$$

Since the perovskite structure is cubic the tensor T must be diagonal, so that Eq. (45) of the text follows.

Let us examine the cubic anharmonic coefficient $U_{j_1\mathbf{p}_1;j_2\mathbf{p}_2;j_3-\mathbf{p}_3}{}^{(3)}$ in the limit p_1, $p_2\to 0$. When all three j's are optical we have using Eq. (A1) together with the definition of the anharmonic coefficients (Sec. II)

$$U_{b_1\sigma_1\mathbf{p}_1;b_2\sigma_2\mathbf{p}_2;b_3\sigma_3-\mathbf{p}_3}{}^{(3)}$$
$$=\sum_{\alpha_1\alpha_2\alpha_3}\{N^{-3/2}\sum\Phi_{\alpha_1\alpha_2\alpha_3}(l_1k_1;l_2k_2;l_3k_3)$$
$$\times v_{k_1}(b_1)v_{k_2}(b_2)v_{k_3}(b_3)\}\hat{e}_{\alpha_1}(\sigma_1)\hat{e}_{\alpha_2}(\sigma_2)\hat{e}_{\alpha_3}(\sigma_3). \quad \text{(A9)}$$

Since the quantity in the bracket is a third-rank tensor it vanishes due to the inversion symmetry of the perovskite lattice. The term involving one acoustic branch (b_a) and two optic branches $(b_{02}$ and $b_{03})$ gives rise to an electrostrictive coupling linear in p given by

$$\lim_{\mathbf{p}_1,\mathbf{p}_2\to 0}U_{b_a\sigma_1\mathbf{p}_1;b_{02}\sigma_2\mathbf{p}_2;b_{03}\sigma_3-\mathbf{p}_3}{}^{(3)}$$
$$=ip_{1\beta}\lambda_{\alpha_2\alpha_3}{}^{\alpha_1\beta}(b_a,b_{02},b_{03})\hat{e}_{\alpha_1}(\sigma_1)\hat{e}_{\alpha_2}(\sigma_2)\hat{e}_{\alpha_3}(\sigma_3), \quad \text{(A10)}$$

where the Einstein summation convention is used and $\lambda_{\alpha_2\alpha_3}{}^{\alpha_1\beta}$ is given by

$$\lambda_{\alpha_2\alpha_3}{}^{\alpha_1\beta}=N^{-3/2}\Phi_{\alpha_1\alpha_2\alpha_3}(l_1k_1;l_2k_2;l_3k_3)$$
$$\times x_\beta{}^0(l_1k_1)v_{k_1}(b_a)v_{k_2}(b_{02})v_{k_3}(b_{03}). \quad \text{(A11)}$$

To show that $\lambda_{\alpha_2\alpha_3}{}^{\alpha_1\beta}$ is diagonal in the superscripts we form the second-rank tensor

$$\Lambda_{\alpha_1\beta}(\sigma_2\sigma_3)=\lambda_{\alpha_2\alpha_3}{}^{\alpha_1\beta}\hat{e}_{\alpha_2}(\sigma_2)\hat{e}_{\alpha_3}(\sigma_3). \quad \text{(A12)}$$

In the cubic perovskite lattice any second-rank tensor is diagonal so that Λ is diagonal for all polarization indices (σ_2,σ_3). This implies that λ is diagonal in its superscripts. In a similar manner one may show λ is diagonal in its subscripts so that Eqs. (46) and (47) of the text follow.

Finally let us consider the case of two acoustic and one optic branch which would lead to a term in F of the form S^2P.

$$\lim_{\mathbf{p}_1,\mathbf{p}_2\to 0}U_{b_{a1}\sigma_1\mathbf{p}_1;b_{a2}\sigma_2\mathbf{p}_2;b_{03}\sigma_3-\mathbf{p}_3}{}^{(3)}$$
$$=i^2\lambda_{\alpha_1\alpha_2\alpha_3\beta\gamma}\hat{e}_{\alpha_1}(\sigma_1)\hat{e}_{\alpha_2}(\sigma_2)\hat{e}_{\alpha_3}(\sigma_3)p_{1\beta}p_{2\gamma}, \quad \text{(A13)}$$

where the fifth-rank tensor λ given by

$$\lambda_{\alpha_1\alpha_2\alpha_3\beta\gamma}=N^{-3/2}\Phi_{\alpha_1\alpha_2\alpha_3}(l_1k_1;l_2k_2;l_3k_3)$$
$$\times x_\beta{}^0(l_1k_1)x_\gamma{}^0(l_2k_2)v_{k_1}(b_{a_1})v_{k_2}(b_{a_2})v_{k_3}(b_{0_3}). \quad \text{(A14)}$$

Due to inversion symmetry the fifth-rank tensor λ vanishes so that no coupling of the form S^2P appears in F.

APPENDIX B

Consider the symmetry of $V^{(2)}$ which is the coefficient of quadratic terms in F. $V^{(2)}$ is defined in terms of

$U^{(4)}$ and $U^{(6)}$ according to Eq. (36) of the text so that

$$\begin{aligned}
V_{\substack{b_1\sigma_1\mathbf{p}_1;\,b_2\sigma_2-\mathbf{p}_1\\ \lim p_1\to 0}}{}^{(2)} ={}& \hat{e}_{\alpha_1}(\sigma_1)\hat{e}_{\alpha_2}(\sigma_2)\{N^{-2}\Phi_{\alpha_1\alpha_2\alpha_3\alpha_4}(l_1k_1;l_2k_2;l_3k_3;l_4k_4)v_{k_1}(b_1)v_{k_2}(b_2)e_{k_3}{}^{\alpha_3}(b\sigma;\mathbf{p})e_{k_4}{}^{\alpha_4}(b\sigma;-\mathbf{p})\exp i\mathbf{p}_1\\
&\times[\mathbf{x}^0(l_1k_1)-\mathbf{x}^0(l_2k_2)]\exp i\mathbf{p}\cdot[\mathbf{x}^0(l_3k_3)-\mathbf{x}^0(l_4k_4)]g(\omega_{b\sigma;\mathbf{p}}{}^0)+N^{-3}\Phi_{\alpha_1\alpha_2\ldots\alpha_6}(l_1k_1;l_2k_2\cdots l_6k_6)v_{k_1}(b_1)v_{k_2}(b_2)e_{k_3}{}^{\alpha_3}(b\sigma;\mathbf{p})\\
&\times e_{k_4}{}^{\alpha_4}(b\sigma;-\mathbf{p})e_{k_5}{}^{\alpha_5}(b'\sigma';\mathbf{p}')e_{k_6}{}^{\alpha_6}(b'\sigma';-\mathbf{p}')\exp i\mathbf{p}_1\cdot[\mathbf{x}^0(l_1k_1)-\mathbf{x}^0(l_2k_2)]\exp i\mathbf{p}\cdot[\mathbf{x}^0(l_3k_3)-\mathbf{x}^0(l_4k_4)]\\
&\times\exp i\mathbf{p}'\cdot[\mathbf{x}^0(l_5k_5)-\mathbf{x}^0(l_6k_6)]g(\omega_{b\sigma;\mathbf{p}})g(\omega_{b'\sigma';\mathbf{p}'})\}\,. \qquad \text{(A15)}
\end{aligned}$$

For the case when b_1 and b_2 are optical branches we require only the term with $p_1=0$ so that the quantity in the curly bracket becomes a second rank tensor component $T_{\alpha_1\alpha_2}$. Since the perovskites are cubic this tensor must be diagonal so that $V^{(2)}$ is diagonal in the polarization index, i.e.,

$$\lim_{p_1\to 0} V_{b_{01}\sigma_1\mathbf{p}_1;b_{02}\sigma_2-\mathbf{p}_1}{}^{(2)}=\delta_{\sigma_1,\sigma_2}V_{b_{01},b_{02}}{}^{(2)}\,.$$

When b_1 is an acoustic branch and b_2 an optical one we first note that the term with $p_1=0$ vanishes because the sum over (l_1k_1) in the curly bracket vanishes since for an acoustic mode $u_{k_1}(b_1)$ is independent of k_1 and by translational invariance $\sum_{l_1k_1}\Phi_{\alpha_1\ldots\alpha_n}(l_1k_1;\cdots l_nk_n)=0$. For the term linear in p_1 the curly bracket is equal to $i\lambda_{\alpha_1\alpha_2\gamma}p_{1\gamma}$, where λ is a third-rank tensor independent of p_1 which vanishes due to inversion symmetry.

APPENDIX C

Consider the symmetry of $V^{(4)}$ which is the coefficient of quartic terms in F. $V^{(4)}$ is defined in terms of $U^{(4)}$ and $U^{(6)}$ according to Eq. (37) of the text. We consider all four indices to be optical so that

$$\begin{aligned}
V_{\substack{b_{01}\sigma_1\mathbf{p}_1;\,b_{02}\sigma_2\mathbf{p}_2;\,b_{03}\sigma_3\mathbf{p}_3;\,b_{04}\sigma_4\mathbf{p}_4\\ \lim p_{1,2,}p_{3,}\to 0}}{}^{(4)} ={}& \hat{e}_{\alpha_1}(\sigma_1)\hat{e}_{\alpha_2}(\sigma_2)\hat{e}_{\alpha_3}(\sigma_3)\hat{e}_{\alpha_4}(\sigma_4)\{N^{-2}\Phi_{\alpha_1\alpha_2\alpha_3\alpha_4}(l_1k_1;l_2k_2;l_3k_3;l_4k_4)v_{k_1}(b_{01})v_{k_2}(b_{02})v_{k_3}(b_{03})\\
&\times v_{k_4}(b_{04})+N^{-3}\Phi_{\alpha_1\ldots\alpha_6}(l_1k_1;\cdots l_6k_6)v_{k_1}(b_{01})v_{k_2}(b_{02})v_{k_3}(b_{03})v_{k_4}(b_{04})e_{k_5}{}^{\alpha_5}(b\sigma;\mathbf{p})e_{k_6}{}^{\alpha_6}(b\sigma;-\mathbf{p})g(\omega_{b\sigma;\mathbf{p}})\}\,. \qquad \text{(A16)}
\end{aligned}$$

The quantity in the curly bracket is a fourth-rank tensor. In a cubic crystal the only nonvanishing components of a fourth rank tensor are those whose indices occur in pairs so that $V^{(4)}$ vanishes unless the polarization indices $(\sigma_1,\sigma_2,\sigma_3,\sigma_4)$ occur in pairs.

APPENDIX D

Consider the symmetry of $U_{j_1\mathbf{p}_1\ldots j_6\mathbf{p}_6}{}^{(6)}$ which is the coefficient of sixth-order terms in F. From the definition of $U^{(6)}$ in Sec. II of the text we find when $b_1\cdots b_6$ are each optical branches,

$$U_{\substack{b_1\sigma_1\mathbf{p}_1;\,\ldots,\,b_6\sigma_6\mathbf{p}_6\\ \lim p_1,\cdots,\,p_6\to 0}}{}^{(6)}=\hat{e}_{\alpha_1}(\sigma_1)\cdots\hat{e}_{\alpha_6}(\sigma_6)\{N^{-3}\Phi_{\alpha_1\alpha_2\ldots\alpha_6}(l_1k_1;\cdots l_6k_6)v_{k_1}(b_1)v_{k_2}(b_2)\cdots v_{k_6}(b_6)\}\,. \qquad \text{(A17)}$$

The quantity in the curly bracket is a sixth-rank tensor. In a cubic crystal the only nonvanishing components of a sixth-rank tensor are those whose indices occur in pairs so that $U^{(6)}$ vanishes unless the polarization indices occur in pairs.