

Thermoelastic properties of perfect crystals with nonprimitive lattices. I. General theory

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Following general ideas proposed by C. Feldman *et al.* and extended by D. C. Wallace in his book on the thermodynamic properties of crystals, we have derived detailed expressions for both external and internal strain derivatives of the Helmholtz free energy of a perfect crystal. The thermodynamic functions are calculated in the quasiharmonic approximation though the present theory can be straightforwardly extended for an arbitrary order of anharmonicity. The formalism developed in this paper is similar, but not equal, to those proposed by previous authors. We have made several important generalizations of the existing theory and, besides, have obtained equations which are much simpler. It makes it possible to consider an arbitrary shell-model crystal with nonprimitive lattice (including piezoelectric crystals) and to pay special attention to the numerical implementation of the formulas obtained. Moreover, by careful consideration, we have corrected a physically doubtful conclusion existing in a particular piece of the literature, namely that microscopic and macroscopic expressions for the crystal energy may not coincide. We prove rigorously that a proper microscopic consideration does lead to the same macroscopic expression. In the second part of this work the theory developed here will be applied to KCl and NaCl crystals.

I. INTRODUCTION

Thermoelastic properties of perfect crystals are of great value in studying general thermal properties of solids.¹⁻⁶ Experimental information concerning equations of states of a solid, its elastic, dielectric, and (if any) piezoelectric properties over a wide range of temperatures and stress conditions (pressure, for example), allows one to find realistic interatomic potentials which should work well over a wide range of interatomic distances. The latter property is of great importance, particularly in studying polymorphic phase transitions,^{7,8} thermal expansion, elastic behavior, etc.

There exists a detailed literature concerning theoretical calculations of zero-temperature dielectric and elastic constants of general nonprimitive crystal lattices when arbitrary external stress is applied to the crystal.^{1-6,9-16} However, there are only a few papers which are devoted to theoretical calculation of these properties at nonzero temperatures, although the corresponding experimental information is available for many crystals. Nevertheless, a number of methods have been developed by different workers for calculating temperature dependencies of elastic and dielectric constants of crystals subjected to arbitrary stress.

In the simplest static approach^{17,18} the vibrational contribution to the elastic constants is neglected, whereas the quasiharmonic approximation^{2,4-6} was used in optimizing the crystal structure. In the method proposed in Ref. 1 (see also Ref. 6) the crystal free energy is considered as a direct function of the elastic strains and temperature. This method was successfully used for NaCl,¹⁹ NaI, KBr,²⁰ and SrTiO₃.²¹ However, this method does not take directly into account the dependence of the phonon frequencies on the strains resulting in a rather slow convergence of the thermodynamic perturbation theory.

The direct dependence of phonon frequencies on the strains was approximately considered in the Einstein model^{2,9} (see also Ref. 22), as well as in the anisotropic-continuum^{23,24} and finite-mode²⁵ models (see also Ref. 26). A more consistent method based on the numerical differentiation of the free energy calculated in the quasiharmonic approximation, was developed and tested for alkali halides in Ref. 22. The same numerical method was used in Refs. 27-29 within the self-consistent phonon formalism.^{2,5,30} The Monte Carlo method has also been developed to study elastic properties of NaCl-type crystals in Ref. 29.

However, the numerical differentiation approaches suffer from some important drawbacks. First of all, they cannot be easily automatized in order to be used for an arbitrary crystal: a special analysis is necessary in every case to avoid time-consuming calculations of the whole Hessian matrix of the second-order free-energy derivatives.¹⁴ Besides, as our experience shows, the numerical differentiation of complicated functions is both a very expensive and a very delicate problem which generally yields rather large and heavy controlled numerical errors even if special numerical algorithms are implemented.

Another approach which is free from these deficiencies was proposed as long as 25 years ago in Ref. 31. Analytical derivatives of the quasiharmonic phonon frequencies over six external strains of fcc rare gas solids were derived and expressed through the corresponding derivatives of the dynamical matrix, i.e., through several lattice sums which are a little more complicated than those used for the dynamical matrix itself. This method appears to be quite general and cheap because the whole Hessian matrix is obtained from one calculation. This method has been extended for the case of nonprimitive lattices by Wallace in his book on the thermodynamic properties of crystals.⁵ Unfortunately, the method used by Wallace to

eliminate the internal strains appeared to be approximate (static energy was used instead of free energy).

In the present paper we have made a further development and generalization of the method of Feldman *et al.*³¹ and of Wallace⁵ mainly in the following directions: (i) any ionic crystal, i.e., a careful treatment of the Coulomb long-range interactions; (ii) an incorporation of the electronic contribution to the lattice distortion via further generalization of the shell model; (iii) arbitrary non-primitive crystal including piezoelectric ones, i.e., the effect of internal strains (sublattice displacements) is rigorously involved since from the beginning we use the free energy; besides, our method in eliminating internal strains leads to comparatively simple and well-observed formulas which can be implemented in practice; (iv) finally, special attention is paid to the numerical implementation of the formulas obtained in the general case of arbitrary structure and symmetry of a crystal.

The plan of the paper is the following. In the next section we describe in some detail our model for the crystal energy and set up our notations. In addition, we show that the proper microscopic consideration leads to the correct expression for the free-energy density of an arbitrary piezoelectric crystal which coincides with corresponding macroscopic expression. Section III contains the most important results of the present paper. The derivatives of phonon frequencies over both external and internal strains are derived in the general case. Then the free energy is considered in the quasiharmonic approximation. Some final comments will be given in Sec. IV. Details of the calculations as well as all our numerical results are considered in the following paper.

II. ELASTIC PROPERTIES OF PERFECT CRYSTALS: A BRIEF OUTLINE OF THE RELEVANT RESULTS

A. Definition of strains

Let us define the positions of atoms in a crystal by specifying the vector

$$\mathbf{R} \begin{pmatrix} l \\ s \end{pmatrix} = \mathbf{R}(l) + \mathbf{X}(s) = \left\| R_\alpha \begin{pmatrix} l \\ s \end{pmatrix} \right\|.$$

Here l numerates unit cells (UC) and $\mathbf{R}(l)$ is used for the corresponding direct lattice vector connecting the 0-th and the l th UC's. The index $s=1, \dots, n$ runs over different atoms in the UC, n being the total number of atoms in the UC. The relative vector linking any two atoms

$$\mathbf{R} \begin{pmatrix} l \\ s \end{pmatrix}$$

and

$$\mathbf{R} \begin{pmatrix} l' \\ s' \end{pmatrix}$$

will be denoted hereafter by

$$\mathbf{R} \begin{pmatrix} ll' \\ ss' \end{pmatrix} = \mathbf{R} \begin{pmatrix} l \\ s \end{pmatrix} - \mathbf{R} \begin{pmatrix} l' \\ s' \end{pmatrix}.$$

The atomic positions in the homogeneously deformed lattice are given by¹

$$\hat{\mathbf{R}}_\alpha \begin{pmatrix} l \\ s \end{pmatrix} = (\delta_{\alpha\beta} + u_{\alpha\beta}) \mathbf{R}_\beta \begin{pmatrix} l \\ s \end{pmatrix} + \mathbf{u} \begin{pmatrix} s \\ \alpha \end{pmatrix}, \quad (1)$$

where

$$\mathbf{u} \begin{pmatrix} s \\ \alpha \end{pmatrix}$$

is the so-called internal strain which (if nonzero) gives rise to some additional displacements of the crystal Bravais lattices with respect to each other in order to maintain thermodynamic equilibrium of the crystal under external stress. $u_{\alpha\beta}$ is the elastic tensor (or external strain). Alternatively, we shall use the so-called Lagrangian strain tensor⁵

$$\eta_{\alpha\beta} = \frac{1}{2}(u_{\alpha\beta} + u_{\beta\alpha} + u_{\gamma\alpha}u_{\gamma\beta}) = \eta_{\beta\alpha}. \quad (2)$$

When symmetric, the elastic tensor $\{u_{\alpha\beta}\}$ appears to be more convenient during algebraic derivations because of the simple expression (1). However, final expressions should be given in the rotational-invariant form, i.e., through the Lagrangian strains. This transformation is easily done by solving Eq. (2) over $u_{\alpha\beta}$ for small $\eta_{\alpha\beta}$.^{4,5,9} We must stress here that the assumption of small strains is quite general since there is one-to-one correspondence between six independent components of $\{\eta_{\alpha\beta}\}$ and the basic vectors \mathbf{a}_i of the direct lattice.

Note that throughout this paper Greek indices will be used to indicate the Cartesian components of vectors and tensors, and, for the sake of simplicity of notation, the Einstein convention will be widely used, i.e., the summation over repeated Greek indices is implied unless otherwise stated.

B. The Helmholtz free energy and a model of the lattice dynamics

It is necessary to distinguish between adiabatic and isothermal thermoelastic properties.⁵ Theoretical calculations appear to be more convenient in the latter case since it is easier to work with the temperature, T , than with the entropy. Transformation to the adiabatic quantities can be done afterwards using well-established thermodynamic expressions.^{4,5,32}

At any microscopic configuration (η, \mathbf{u}) the free-energy density (per UC) is as follows:^{4,5,6,9,33}

$$\begin{aligned} \mathfrak{F} &= \frac{1}{N} U_0 + \frac{1}{N} \sum_{\mathbf{k}j} \mathfrak{F}_{\mathbf{k}j} + \mathfrak{F}_{\text{AH}}(\{\omega_{\mathbf{k}j}\}, T) \\ &= \frac{1}{N} U_0 + \mathfrak{F}_{\text{vibr}}, \end{aligned} \quad (3)$$

where N is the number of UC's in the main region of the crystal, U_0 is a static part of the energy, i.e., potential energy of the crystal. The second term in Eq. (3) represents the quasiharmonic contribution

$$\mathfrak{F}_{\mathbf{k}j} = \frac{1}{2} \hbar \omega_{\mathbf{k}j} + k_B T \ln \left[1 - \exp \left[- \frac{\hbar \omega_{\mathbf{k}j}}{k_B T} \right] \right]. \quad (4)$$

Here k_B is Boltzmann's constant and \hbar Planck's constant. The last term, \mathfrak{V}_{AH} , in Eq. (3) represents anharmonic contributions to the free-energy density resulting from third-, fourth-, etc., order force constants and obtained using the thermodynamic perturbation theory.^{2,5,6} These terms are quite cumbersome and will be omitted here for the sake of simplicity. They do not affect the formal derivation which we are going to perform. We should note, however, that these terms are some well-defined functions of T , $\omega_{\mathbf{k}j}$, phonon eigenvectors and interatomic distances and therefore can be taken into account (at least in principle).

In Eqs. (3) and (4), $\{\omega_{\mathbf{k}j}\}$ are the quasi-harmonic phonon frequencies (\mathbf{k} the wave vector, j a phonon branch, $j=1, \dots, n$). Together with associated eigenvectors, $\mathbf{e}(\mathbf{k}j) = \|e_{s\alpha}(\mathbf{k}j)\|$, they are defined in solving the lattice dynamics secular problem

$$\sum_{s'} \Omega_{\alpha\alpha'}^{ss'}(\mathbf{k}) e_{s'\alpha'}(\mathbf{k}j) = \lambda_{\mathbf{k}j} e_{s\alpha}(\mathbf{k}j), \quad (5)$$

where $\lambda_{\mathbf{k}j} = \omega_{\mathbf{k}j}^2$ and $\Omega(\mathbf{k}) = \|\Omega_{\alpha\alpha'}^{ss'}(\mathbf{k})\|$ is the dynamical matrix. Although the theory of lattice dynamics is well known,^{1,2,5,6} we must summarize it here since we need detailed expressions for the dynamical matrix, $\Omega(\mathbf{k})$, which will be widely used throughout this paper.

It is well understood that in order to take into consideration electronic polarization effects, obtain reasonable phonon curves, and dielectric properties (especially for ionic crystals), it is necessary to go beyond the simple rigid-ion model and account for atomic polarization. In this paper we use something similar to the usual shell model, namely the theory of deformable dipoles developed by K. B. Tolpygo *et al.*^{6,34,33,35} (it was generalized for arbitrary multipole moments of atoms in Ref. 36 and the detailed discussion of the main physical assumptions made there was provided in Ref. 37 from the viewpoint of the theory of electronic separability³⁸). This lattice-dynamics model is attractive since it gives a consistent quantum-mechanical justification of the shell-like models.^{34,35} Note that the theory of deformable dipoles was successfully applied to a wide range of atomic, ionic, and covalent crystals (see Ref. 39 and references therein).

It can be rigorously shown based on arguments of the theory of electronic separability that in the strong orthogonality approximation (keeping only first leading diagrams in the decomposition of the total crystal energy, see Ref. 40 and references therein) and, assuming the crystal atoms are spherically symmetric in the static non-vibrating lattice (the model of spherical balls³⁷), the total potential energy of the crystal in the dipole approximation can be written as follows:³⁵⁻³⁷

$$\begin{aligned} U_0 = & \frac{1}{2} \sum_{ll's's'} \left[V^{ss'}(R) + \frac{q_s q_{s'}}{R} \right] \\ & + \frac{1}{2} \sum_{ll's's'} Q_\alpha \begin{bmatrix} l \\ s \end{bmatrix} D_{\alpha\alpha'}^{ss'}(\mathbf{R}) Q_{\alpha'} \begin{bmatrix} l' \\ s' \end{bmatrix} \\ & + \sum_{ll's's'} Q_\alpha \begin{bmatrix} l \\ s \end{bmatrix} \left[\Gamma^{ss'}(R) - \frac{q_{s'}}{R^2} \right] \frac{R_\alpha}{R}, \quad (6) \end{aligned}$$

where the prime on the lattice sums excludes the term $l=0$ from the summation to remove the self-action of the atoms (if $s=s'$). The first term in Eq. (6) describes core-core-type interactions between atoms, \mathbf{R} being the relative position of displaced atoms

$$\begin{bmatrix} l \\ s \end{bmatrix}$$

and

$$\begin{bmatrix} l' \\ s' \end{bmatrix}.$$

This term contains the usual Coulomb (q_s is the charge of the s th atom in the UC) and central short-range part, $V^{ss'}(R)$. The second term in Eq. (6) is responsible for the shell-shell-type of the interatomic potential,

$$\mathbf{Q} \begin{bmatrix} l \\ s \end{bmatrix} = \left\| \left\| Q_\alpha \begin{bmatrix} l \\ s \end{bmatrix} \right\| \right\|$$

is the vector of the dipole moment on the atom

$$\begin{bmatrix} l \\ s \end{bmatrix}.$$

The following matrix is associated with this term:

$$D_{\alpha\alpha'}^{ss'}(\mathbf{R}) = \delta_{ll'} \delta_{ss'} \delta_{\alpha\alpha'} \frac{1}{A_s} + Z_{\alpha\alpha'}^{ss'}(\mathbf{R}) + Q_{\alpha\alpha'}(\mathbf{R}), \quad (7)$$

where A_s is the s th atom polarizability and

$$Q_{\alpha\alpha'}(\mathbf{R}) = \frac{\delta_{\alpha\alpha'}}{R^3} - \frac{3R_\alpha R_{\alpha'}}{R^5} \quad (8)$$

is the usual dipole tensor.¹ We have also added some general short-range terms,

$$Z_{\alpha\alpha'}^{ss'}(\mathbf{R}) = \delta_{\alpha\alpha'} Z_1^{ss'}(R) + R_\alpha R_{\alpha'} Z_2^{ss'}(R) \quad (9)$$

in order to further generalize the model and allow for a comparison with the usual shell model.³⁴ This short-range term was justified microscopically in Ref. 41. Note that it is implied in Eq. (7) that both $\mathbf{Z}(\mathbf{R})$ and $\mathbf{Q}(\mathbf{R})$ are zero, when $s=s'$ and $l=l'$.

Finally, the third term in Eq. (6) describes interactions between cores and shells and also contains both long-range and short-range, $\Gamma^{ss'}(R)$, parts. The special form of this contribution follows rigorously from the model adopted [spherical structure elements (i.e., atoms), dipole approximation, and the exchange interaction between atoms up to the first order]. For the same reasons,³⁷ all the short-range potentials in all the terms considered have central character and three-body forces are absent (they appear, however, in the next, quadrupole, approximation). Note also that $V^{ss'}(R) = V^{s's}(R)$, but $\Gamma^{ss'}(R) \neq \Gamma^{s's}(R)$ because in the latter case indices s, s' belong to different physical subsystems: the first and second indices correspond to a shell and a core, respectively.

By making use of the usual manipulations, the following expression for the dynamical matrix $\Omega(\mathbf{k})$ is obtained:

$$\Omega(\mathbf{k}) = \mathbf{M}^{-1/2} [\mathbf{A}(\mathbf{k}) - \mathbf{B}(\mathbf{k})^\dagger \mathbf{D}^{-1}(\mathbf{k}) \mathbf{B}(\mathbf{k})] \mathbf{M}^{-1/2}, \quad (10)$$

where $\mathbf{M} = \|\delta_{ss'} \delta_{\alpha\alpha'} \mathbf{M}_s\|$ is the diagonal matrix of atomic masses, the dagger means Hermitian conjugate, and Fourier transforms of the core-core, $\mathbf{A}(\mathbf{k})$, shell-core, $\mathbf{B}(\mathbf{k})$, and shell-shell, $\mathbf{D}(\mathbf{k})$, matrices have been introduced in the following way:

$$D_{\alpha\alpha'}^{ss'}(\mathbf{k}) = \sum_l D_{\alpha\alpha'}^{ss'}(\mathbf{R}) e^{i\mathbf{k}\mathbf{R}} \\ = \delta_{ss'} \delta_{\alpha\alpha'} \frac{1}{A_s} + Z_{\alpha\alpha'}^{ss'}(\mathbf{k}) - Q_{\alpha\alpha'}^{ss'}(\mathbf{k}), \quad (11)$$

$$A_{\alpha\alpha'}^{ss'}(\mathbf{k}) = \delta_{ss'} \Delta \tilde{A}_{\alpha\alpha'}^s - q_s q_{s'} Q_{\alpha\alpha'}^{ss'}(\mathbf{k}) - V_{\alpha\alpha'}^{ss'}(\mathbf{k}), \quad (12)$$

$$B_{\alpha\alpha'}^{ss'}(\mathbf{k}) = \delta_{ss'} \Delta \tilde{B}_{\alpha\alpha'}^s - q_s q_{s'} Q_{\alpha\alpha'}^{ss'}(\mathbf{k}) - \Gamma_{\alpha\alpha'}^{ss'}(\mathbf{k}), \quad (13)$$

where from now on

$$\mathbf{R} = \mathbf{R} \begin{pmatrix} l & 0 \\ s & s' \end{pmatrix}$$

indicates the relative position of undisplaced atoms

$$\begin{pmatrix} l \\ s \end{pmatrix}$$

and

$$\begin{pmatrix} 0 \\ s' \end{pmatrix}.$$

The following notations have been made:

$$V_{\alpha\alpha'}^{ss'}(\mathbf{k}) = \sum_l e^{i\mathbf{k}\mathbf{R}} [\delta_{\alpha\alpha'} V_1^{ss'}(\mathbf{R}) + R_\alpha R_{\alpha'} V_2^{ss'}(\mathbf{R})] \\ = \sum_l e^{i\mathbf{k}\mathbf{R}} V_{\alpha\alpha'}^{ss'}(\mathbf{R}), \quad (14)$$

$$\Gamma_{\alpha\alpha'}^{ss'}(\mathbf{k}) = \sum_l e^{i\mathbf{k}\mathbf{R}} [\delta_{\alpha\alpha'} \Gamma_1^{ss'}(\mathbf{R}) + R_\alpha R_{\alpha'} \Gamma_2^{ss'}(\mathbf{R})] \\ = \sum_l e^{i\mathbf{k}\mathbf{R}} \Gamma_{\alpha\alpha'}^{ss'}(\mathbf{R}), \quad (15)$$

and $Z_{\alpha\alpha'}^{ss'}(\mathbf{k})$ is the Fourier transform of $Z_{\alpha\alpha'}^{ss'}(\mathbf{R})$ given by Eq. (9). The functions $\Gamma_i^{ss'}$, $Z_i^{ss'}$ [see Eq. (9)], and $V_i^{ss'}$ can be expressed quite usefully in the equivalent manner as follows: $X_i^{ss'} = (d/Rd\mathbf{R})X_{i-1}^{ss'}$, where $i=1, 2, \dots$, and $X_i^{ss'}$ is either $\Gamma_i^{ss'}$, $Z_i^{ss'}$, or $V_i^{ss'}$, and $\Gamma_1^{ss'} = \Gamma^{ss'}(\mathbf{R})/R$, but $Z_0^{ss'} = Z^{ss'}(\mathbf{R})$ and $V_0^{ss'} = V^{ss'}(\mathbf{R})$. Note that we have used only $i=1, 2$ in the expressions given above. However, as will be clear later, this more general definition appears to be very convenient for further consideration.

The Coulomb part, $Q_{\alpha\alpha'}^{ss'}(\mathbf{k})$, is defined analogously as the Fourier transform of $(-Q_{\alpha\alpha'}(\mathbf{R}))$ and, as is well known, may be calculated by means of the Ewald method¹ leading to the result

$$Q_{\alpha\alpha'}^{ss'}(\mathbf{k}) = -\frac{4\pi}{v_c} \frac{k_\alpha k_{\alpha'}}{k^2} \exp\left[-\frac{k^2}{4G^2}\right] + \tilde{Q}_{\alpha\alpha'}^{ss'}(\mathbf{k}), \quad (16)$$

where we have separated out the well-recognized macroscopic field part which is irregular in the macroscopic ($\mathbf{k}=\mathbf{0}$) limit, and the regular part, distinguished by the tilde,

$$\tilde{Q}_{\alpha\alpha'}^{ss'}(\mathbf{k}) = \delta_{\alpha\alpha'} \delta_{ss'} \frac{4G^3}{3\pi^{1/2}} + G^3 \sum_l Q_{\alpha\alpha'}(\rho) e^{i\mathbf{k}\mathbf{R}} \\ - \frac{4\pi}{v_c} \sum_{\mathbf{g}} \kappa_\alpha \kappa_{\alpha'} \chi(\kappa^2) e^{i\mathbf{g}\mathbf{X}}, \quad (17)$$

where G is the Ewald parameter, the vector $\rho = G\mathbf{R}$, and v_c is the UC volume. The second sum runs over the nonzero reciprocal-lattice vectors \mathbf{g} and $\kappa = \mathbf{k} - \mathbf{g}$; $\mathbf{X} = \mathbf{X}(s) - \mathbf{X}(s')$ indicates the relative position of the s, s' sublattices, and the function $\chi(x) = (1/x) \exp(-x/4G^2)$. Lastly, the function $Q_{\alpha\alpha'}(\rho)$ can be written as

$$Q_{\alpha\alpha'}(\rho) = \delta_{\alpha\alpha'} Q_1(\rho) + \rho_\alpha \rho_{\alpha'} Q_2(\rho), \quad (18)$$

where the functions $Q_i(\rho)$ are defined completely in the same fashion as above, i.e., $Q_i(\rho) = (d/\rho d\rho) Q_{i-1}(\rho)$ with $Q_0(\rho) = \text{erfc}(\rho)/\rho$.

The contributions $\Delta \tilde{A}_{\alpha\alpha'}^s$ and $\Delta \tilde{B}_{\alpha\alpha'}^s$ in Eqs. (12) and (13) ensure correct behavior of the phonon curves in the long-wavelength limit ($\mathbf{k} \rightarrow \mathbf{0}$) and are given by

$$\Delta \tilde{A}_{\alpha\alpha'}^s = \sum_{s''} [q_s q_{s''} \tilde{Q}_{\alpha\alpha'}^{ss''}(\mathbf{k}=\mathbf{0}) + V_{\alpha\alpha'}^{ss''}(\mathbf{k}=\mathbf{0})], \quad (19)$$

$$\Delta \tilde{B}_{\alpha\alpha'}^s = \sum_{s''} [q_{s''} \tilde{Q}_{\alpha\alpha'}^{ss''}(\mathbf{k}=\mathbf{0}) + \Gamma_{\alpha\alpha'}^{ss''}(\mathbf{k}=\mathbf{0})]. \quad (20)$$

In the quasiharmonic approximation the lattice dynamics problem, Eq. (5), is solved for every crystal configuration given by the whole strain vector

$$\left\{ \eta_{\alpha\beta}, u \begin{pmatrix} s \\ \alpha \end{pmatrix} \right\}.$$

In thermodynamic equilibrium, the following conditions should be satisfied:⁵

$$\frac{\partial \mathfrak{F}}{\partial u \begin{pmatrix} s \\ \alpha \end{pmatrix}} = 0 \quad \text{for every } s=2, \dots, n, \\ \frac{1}{v_c} \frac{\partial \mathfrak{F}}{\partial \eta_{\alpha\beta}} = \tau_{\alpha\beta}^0, \quad (21)$$

where the first equation simply means that the free-energy density \mathfrak{F} is at a minimum with respect to the internal coordinates of the crystal (internal strains). The second equation says that the crystal structure should be balanced with external mechanical forces imposed on the crystal; $\tau_{\alpha\beta}^0$ is the corresponding (initial) external stress tensor. Equations (21) give the complete description of the equation of state of the crystal in the general case of arbitrary external stress and temperature^{5,32} and, therefore, are much more general than those derived under the usual requirement that "Gibbs energy shall be the minimum."⁵

C. Definition of the material properties of crystals in terms of the free-energy derivatives over strains

In order to consider thermoelastic and dielectric (material) properties of a crystal, we have to start from the isothermal case and expand the free-energy density, \mathfrak{F} , in power series over both external, $\eta_{\alpha\beta}$, and internal,

$$u \begin{pmatrix} s \\ \alpha \end{pmatrix},$$

strains about the equilibrium configuration for every desired temperature. Since the free energy consists of two parts, namely, the static part, U_0/N , and the vibrational part [see Eq. (3)], we evidently get two contributions to the corresponding coefficients of the decomposition. In order to simplify the whole picture and avoid cumbersome derivations and notations, it is convenient to consider these two parts separately. In this subsection we give a short survey of the elastic, piezoelectric, and dielectric properties of an arbitrary crystal, considering only the static part of the free-energy density. Our method of separating out the macroscopic field is similar, but not identical, to those existing in the literature (see especially Refs. 9, 13, and 16). However, while we obtained the same expressions for the elastic, dielectric, and piezoelectric constants, we have found a different result for the microscopic energy density of the deformed piezoelectric crystal from that found in Ref. 13. Our expression leads to the correct macroscopic limit.

Let us start again from Eq. (6). We shall use the method of homogeneous deformation.^{1,9,12,13} In order to eliminate the surface effect,^{5,9} we should notice that the l' summation in Eq. (6) counts equivalent terms due to the periodic symmetry of the crystal. Therefore, we can put $l'=0$ and introduce instead the factor N . Then,

$$Q_\alpha \begin{pmatrix} l \\ s \end{pmatrix} = Q_\alpha(s)$$

since under a homogeneous deformation all UC's are identical. Besides, we substitute the vector R of relative position of two atoms

$$\begin{pmatrix} l \\ s \end{pmatrix}$$

and

$$\begin{pmatrix} 0 \\ s' \end{pmatrix}$$

by the vector

$$\hat{\mathbf{R}} = \hat{\mathbf{R}} \begin{pmatrix} l \\ s \end{pmatrix} - \hat{\mathbf{R}} \begin{pmatrix} 0 \\ s' \end{pmatrix} = \hat{\mathbf{R}} \begin{pmatrix} l & 0 \\ s & s' \end{pmatrix}$$

[see Eq. (1)] in the deformed lattice and decompose the expression for $U_0 = U_0(\{\hat{\mathbf{R}}\})$ thus obtained into a power series over both $u_{\alpha\beta}$ and

$$u \begin{pmatrix} s \\ \alpha \end{pmatrix}$$

up to the second-order terms (the higher-order terms result in higher-order properties which are outside the scope of the present paper though they may be considered analogously). We thus get the following result for the change of the crystal potential energy (per UC) caused by the elastic deformation:

$$\begin{aligned} \frac{\Delta U_0}{N} = & \{\alpha\beta\} u_{\alpha\beta} + \sum_s \left[\begin{pmatrix} s \\ \alpha \end{pmatrix} u \begin{pmatrix} s \\ \alpha \end{pmatrix} + \begin{pmatrix} s \\ \alpha \end{pmatrix} Q_\alpha(s) \right] + \frac{1}{2} \{\alpha\beta \ \gamma\delta\} u_{\alpha\beta} u_{\gamma\delta} \\ & + \sum_s \left[u \begin{pmatrix} s \\ \alpha \end{pmatrix} \left\{ \begin{matrix} s \\ \alpha \ \beta\gamma \end{matrix} \right\} + Q_\alpha(s) \begin{pmatrix} s \\ \alpha \ \beta\gamma \end{pmatrix} \right] u_{\beta\gamma} \\ & + \frac{1}{2} \sum_{ss'} \left[u \begin{pmatrix} s \\ \alpha \end{pmatrix} \left\{ \begin{matrix} s & s' \\ \alpha & \alpha' \end{matrix} \right\} u \begin{pmatrix} s' \\ \alpha' \end{pmatrix} + Q_\alpha(s) \begin{pmatrix} s & s' \\ \alpha & \alpha' \end{pmatrix} Q_{\alpha'}(s') + 2Q_\alpha(s) \begin{pmatrix} s & s' \\ \alpha & \alpha' \end{pmatrix} u \begin{pmatrix} s' \\ \alpha' \end{pmatrix} \right], \end{aligned} \quad (22)$$

where the brackets defined above have transparent physical meaning which will be clarified later on. All the brackets except the last three have no singularities and can be easily calculated. After some simple though long algebra they can be expressed through lattice sums over the interatomic potentials:

$$\{\alpha\alpha'\} = \frac{1}{2} \sum_{ss'} \left[-q_s q_{s'} \mathfrak{E}_{\alpha\alpha'}^{ss'} + \sum_l R_\alpha R_{\alpha'} V_l^{ss'}(R) \right], \quad (23)$$

$$\begin{pmatrix} s \\ \alpha \end{pmatrix} = \sum_{s'} \left[-q_s q_{s'} \mathfrak{E}_\alpha^{ss'} + \sum_l R_\alpha V_l^{ss'}(R) \right], \quad (24)$$

$$\begin{pmatrix} s \\ \alpha \end{pmatrix} = \sum_{s'} \left[-q_s \mathfrak{E}_\alpha^{ss'} + \sum_l R_\alpha \Gamma_l^{ss'}(R) \right], \quad (25)$$

$$\{\alpha\beta\gamma\delta\} = \frac{1}{2} \sum_{ss'} \left[q_s q_{s'} \mathfrak{E}_{\alpha\gamma, \beta\delta}^{ss'} + \sum_l R_\beta R_\delta V_l^{ss'}(\mathbf{R}) \right], \quad (26)$$

$$\begin{pmatrix} s \\ \alpha\beta\gamma \end{pmatrix} = \sum_{s'} \left[q_s q_{s'} \mathfrak{E}_{\alpha\beta, \gamma}^{ss'} + \sum_l R_\gamma V_l^{ss'}(\mathbf{R}) \right], \quad (27)$$

$$\left\{ \begin{matrix} s \\ \alpha \end{matrix} \beta \gamma \right\} = \sum_{s'} \left[q_{s'} \mathfrak{E}_{\alpha\beta,\gamma}^{ss'} + \sum_l R_\gamma \Gamma_{\alpha\beta}^{ss'}(\mathbf{R}) \right], \quad (28)$$

where $\mathfrak{E}_{\alpha}^{ss'}$, $\mathfrak{E}_{\alpha\alpha'}^{ss'}$, etc. are Coulomb lattice sums of different types. They can be calculated by means of the Ewald method in the usual way^{1,11} and are given by

$$\mathfrak{E}_{\alpha}^{ss'} = -G^2 \sum_l \rho_\alpha Q_1(\rho) + \frac{4\pi}{v_c} \sum_g g_\alpha \chi(g^2) \sin(\mathbf{g}\mathbf{X}), \quad (29)$$

$$\mathfrak{E}_{\alpha\beta}^{ss'} = -G \sum_l \rho_\alpha \rho_\beta Q_1(\rho) + \frac{4\pi}{v_c} \sum_g [\delta_{\alpha\beta} \chi(g^2) + 2g_\alpha g_\beta \chi'(g^2)] \cos(\mathbf{g}\mathbf{X}), \quad (30)$$

$$\mathfrak{E}_{\alpha\beta,\gamma}^{ss'} = G^2 \sum_l \rho_\gamma Q_{\alpha\beta}(\rho) + \frac{4\pi}{v_c} \sum_g [(\delta_{\alpha\gamma} g_\beta + \delta_{\beta\gamma} g_\alpha) \chi(g^2) + 2g_\alpha g_\beta g_\gamma \chi'(g^2)] \sin(\mathbf{g}\mathbf{X}), \quad (31)$$

$$\begin{aligned} \mathfrak{E}_{\alpha\beta,\gamma\delta}^{ss'} = & G \sum_l \rho_\gamma \rho_\delta Q_{\alpha\beta}(\rho) + \frac{4\pi}{v_c} \sum_g [(\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\beta\gamma} \delta_{\alpha\delta}) \chi(g^2) \\ & + 2(\delta_{\alpha\gamma} g_\beta g_\delta + \delta_{\beta\gamma} g_\alpha g_\delta + \delta_{\alpha\delta} g_\beta g_\gamma + \delta_{\delta\beta} g_\alpha g_\gamma + \delta_{\gamma\delta} g_\alpha g_\beta) \chi'(g^2) \\ & + 4g_\alpha g_\beta g_\gamma g_\delta \chi''(g^2)] \cos(\mathbf{g}\mathbf{X}). \end{aligned} \quad (32)$$

Here χ' and χ'' are the first- and second-order derivatives of the function $\chi(x)$ [it was introduced earlier, see Eq. (17)] via $x = g^2$.

In contrast, the remaining three brackets in Eq. (22) do not contain summations over indices of the sublattices s, s' . That is why they do have special divergent contributions in their Coulomb parts. They result from the $\mathbf{g} = \mathbf{0}$ terms in the corresponding reciprocal-lattice sums, arising while using the Ewald method:

$$\left\{ \begin{matrix} s & s' \\ \alpha & \alpha' \end{matrix} \right\} = [\delta_{ss'} \Delta \bar{A}_{\alpha\alpha'}^s - q_s q_{s'} \bar{Q}_{\alpha\alpha'}^{ss'}(\mathbf{k} = \mathbf{0}) - V_{\alpha\alpha'}^{ss'}(\mathbf{k} = \mathbf{0})] + \frac{4\pi}{v_c} q_s q_{s'} \frac{k_\alpha k_{\alpha'}}{k^2}, \quad (33)$$

$$\left\{ \begin{matrix} s & s' \\ \alpha & \alpha' \end{matrix} \right\} = [\delta_{ss'} \Delta \bar{B}_{\alpha\alpha'}^s - q_s \bar{Q}_{\alpha\alpha'}^{ss'}(\mathbf{k} = \mathbf{0}) - \Gamma_{\alpha\alpha'}^{ss'}(\mathbf{k} = \mathbf{0})] + \frac{4\pi}{v_c} q_s \frac{k_\alpha k_{\alpha'}}{k^2}, \quad (34)$$

$$\left\{ \begin{matrix} s & s' \\ \alpha & \alpha' \end{matrix} \right\} = [\delta_{ss'} \delta_{\alpha\alpha'} \frac{1}{A_s} - \bar{Q}_{\alpha\alpha'}^{ss'}(\mathbf{k} = \mathbf{0}) + Z_{\alpha\alpha'}^{ss'}(\mathbf{k} = \mathbf{0})] + \frac{4\pi}{v_c} \frac{k_\alpha k_{\alpha'}}{k^2}, \quad (35)$$

where the limit $\mathbf{k} \rightarrow \mathbf{0}$ is implied in the last term of each of the expressions. Evidently these divergent terms lead to the well-known macroscopic electric field and, hence, to a description of macroscopic dielectric and piezoelectric properties.^{9,13} Note that some brackets satisfy a number of identities which reflect the invariance of the crystal energy under an arbitrary rigid displacement of the lattice as a whole:¹

$$\begin{aligned} \sum_{s'} \left\{ \begin{matrix} s & s' \\ \alpha & \alpha' \end{matrix} \right\} &= \sum_s \left\{ \begin{matrix} s & s' \\ \alpha & \alpha' \end{matrix} \right\} \\ &= \sum_s \left\{ \begin{matrix} s & s' \\ \alpha & \alpha' \end{matrix} \right\} = \sum_s \left\{ \begin{matrix} s \\ \alpha \end{matrix} \right\} = 0. \end{aligned} \quad (36)$$

In addition, the brackets (33), (34), and (35) are symmetric with respect to the permutation of α, α' and of s, s' [except

$$\left\{ \begin{matrix} s & s' \\ \alpha & \alpha' \end{matrix} \right\},$$

Eq. (34), for the latter case]. It should be stressed also that the bracket $\{\alpha\beta \ \gamma\delta\}$ given by Eq. (26) does not

have the complete Voigt symmetry since we did not assume zero stresses here (cf. Refs. 1 and 11).

Then, following the method developed in Refs. 9, 11, 13, and 15, we introduce the dipole moment per UC,

$$\mathfrak{p}_\alpha = \frac{1}{v_c} \sum_s \left[Q_\alpha(s) + q_s u \left\{ \begin{matrix} s \\ \alpha \end{matrix} \right\} \right] \quad (37)$$

and the corresponding macroscopic electric field,¹

$$\mathfrak{E}_\alpha = -4\pi \frac{k_\alpha k_{\alpha'}}{k^2} \mathfrak{p}_{\alpha'}, \quad (38)$$

where $\mathbf{k} \rightarrow \mathbf{0}$, which satisfies the condition $\text{div}(\mathfrak{E} + 4\pi\mathfrak{p}) = 0$. Starting from this point, our derivation differs from that published in Ref. 13.

In order to find expressions for the elastic, dielectric, and piezoelectric tensors of the crystal as well as for the crystal energy density, we substitute the brackets given by Eqs. (33), (34), and (35) into the expression for the crystal energy, Eq. (22), considering separately their regular and irregular parts. The same notations will be used for the regular part of these brackets. In order to proceed, let us collect all the internal variables together

into one vector of internal coordinates,

$$\mathfrak{S} = \left\| \left\| \mathfrak{S} \begin{pmatrix} m \\ \alpha \end{pmatrix} \right\| \right\| = \begin{pmatrix} u \\ \mathbf{Q} \end{pmatrix}, \quad (39)$$

where $m = (s, \mu)$ and $\mu = 1, 2$ corresponds to

$$u \begin{pmatrix} s \\ \alpha \end{pmatrix}$$

and $Q_\alpha(s)$, respectively. By the same fashion, we can gather all other brackets: those given by Eqs. (24) and (25), into a vector $\mathbf{Y} = \|Y_\alpha^m\|$; the brackets (27) and (28), into a matrix

$$\mathbf{L} = \left\| \left\| L \begin{pmatrix} m \\ \alpha \beta \gamma \end{pmatrix} \right\| \right\|.$$

Lastly, the regular parts of the brackets (33), (34), and (35) are compiled into a square symmetric matrix

$$\mathbf{S} = \left\| \left\| S \begin{pmatrix} m & m' \\ \alpha & \alpha' \end{pmatrix} \right\| \right\|.$$

Since the first three rows and columns of \mathbf{S} are linearly

dependent [see Eq. (36)], we adopt the same method for the calculation of its inverse, \mathbf{S}^{-1} , as in Ref. 1. The convention of summing over the repeated indices m, m' will be adopted throughout this section.

First we notice that all the irregular contributions to the brackets represented by the second terms on the right-hand sides of Eqs. (33), (34), and (35) can be gathered together in the energy (22) leading to the following contribution: $2\pi v_c (\mathbf{k}\mathbf{p})^2 / \mathbf{k}^2 = v_c \mathfrak{E}^2 / 8\pi$. Equation (38) has been used in the last step here. Then, the change of the energy given by (22) can be rewritten as

$$\begin{aligned} \frac{\Delta U_0}{N} = & \{\alpha\beta\} u_{\alpha\beta} + \frac{1}{2} \{\alpha\beta \ \gamma\delta\} u_{\alpha\beta} u_{\gamma\delta} + v_c \frac{\mathfrak{E}^2}{8\pi} \\ & + \mathfrak{S} \begin{pmatrix} m \\ \alpha \end{pmatrix}^\dagger Y \begin{pmatrix} m \\ \alpha \end{pmatrix} + \mathfrak{S} \begin{pmatrix} m \\ \alpha \end{pmatrix}^\dagger L \begin{pmatrix} m \\ \alpha \ \beta \gamma \end{pmatrix} u_{\beta\gamma} \\ & + \frac{1}{2} \mathfrak{S} \begin{pmatrix} m \\ \alpha \end{pmatrix}^\dagger S \begin{pmatrix} m & m' \\ \alpha & \alpha' \end{pmatrix} \mathfrak{S} \begin{pmatrix} m' \\ \alpha' \end{pmatrix} \end{aligned} \quad (40)$$

and is found to be a quadratic form over the internal variables, \mathfrak{S} . The search for a minimum with respect to these internal variables yields the unknown vector \mathfrak{S} in a closed form:

$$\mathfrak{S} \begin{pmatrix} m \\ \alpha \end{pmatrix} = -S^{-1} \begin{pmatrix} m & m' \\ \alpha & \alpha' \end{pmatrix} \left\{ Y \begin{pmatrix} m' \\ \alpha' \end{pmatrix} + L \begin{pmatrix} m' \\ \alpha' \ \beta \gamma \end{pmatrix} u_{\beta\gamma} - q(m') \mathfrak{E}_{\alpha'} \right\}, \quad (41)$$

where $q(m)$ is the vector of charges (the unit charge is attached to shells), i.e., $q(s, 1) = q_s$ while $q(s, 2) = 1$. Note that the electrostatic energy $\mathfrak{E}^2 / 8\pi$ in Eq. (40) must be differentiated also with the help, successively, of Eqs. (38) and (37).

Now, let us express the elastic strain tensor, $u_{\alpha\beta}$, through the Lagrangian strain tensor, $\eta_{\alpha\beta}$. Employing the solution for

$$\mathfrak{S} \begin{pmatrix} m \\ \alpha \end{pmatrix}$$

found above and the definition of the total UC polarization, Eq. (37), we can calculate the change of the dipole moment of the UC because of the deformation as

$$p_\alpha - p_\alpha^0 = \frac{1}{v_c} q(m) \mathfrak{S} \begin{pmatrix} m \\ \alpha \end{pmatrix} = e_{\alpha, \beta\gamma}^{(1)}(0) \eta_{\beta\gamma} + \chi_{\alpha\beta}(0) \mathfrak{E}_\beta \quad (42)$$

and the elastic energy density of the crystal, Eq. (40). The following result was obtained for the latter in the general case of an arbitrary (piezoelectric) crystal:

$$\frac{\Delta U_0}{V} = \tau_{\beta\gamma}^0 \eta_{\beta\gamma} + \frac{1}{2} C_{\beta\gamma, \beta'\gamma'}^T \eta_{\beta\gamma} \eta_{\beta'\gamma'} + \frac{1}{2} \chi_{\alpha\beta}(0) \mathfrak{E}_\alpha \mathfrak{E}_\beta + \frac{\mathfrak{E}^2}{8\pi}, \quad (43)$$

where $V = N v_c$ is the volume of unstrained crystal. In Eq. (42), $e_{\alpha, \beta\gamma}^{(1)}(0)$ is the direct (static) piezoelectric tensor, given microscopically by

$$e_{\alpha, \beta\gamma}^{(1)}(0) = -\frac{1}{v_c} q(m) S^{-1} \begin{pmatrix} m & m' \\ \alpha & \alpha' \end{pmatrix} L \begin{pmatrix} m' \\ \alpha' \ \beta \gamma \end{pmatrix}_S. \quad (44)$$

The static dielectric susceptibility tensor which appeared in Eqs. (42) and (43) is given as

$$\chi_{\alpha\alpha'}(0) = \frac{1}{v_c} q(m) S^{-1} \begin{pmatrix} m & m' \\ \alpha & \alpha' \end{pmatrix} q(m'). \quad (45)$$

The initial stress tensor is found to be

$$\tau_{\beta\gamma}^0 = \frac{1}{V} \left[\frac{\partial \Delta U}{\partial \eta_{\beta\gamma}} \right]_0 = \frac{1}{v_c} \left[\{\beta\gamma\} - Y \begin{pmatrix} m \\ \alpha \end{pmatrix}^\dagger S^{-1} \begin{pmatrix} m & m' \\ \alpha & \alpha' \end{pmatrix} L \begin{pmatrix} m' \\ \alpha' \end{pmatrix} \beta\gamma \right]_S \quad (46)$$

and the Brugger-type elastic constants are

$$C_{\beta\gamma, \beta'\gamma'}^T = \frac{1}{v_c} \left[\{\beta\gamma \beta'\gamma'\}_S - L \begin{pmatrix} m & m' \\ \alpha & \alpha' \end{pmatrix}^\dagger S^{-1} \begin{pmatrix} m & m' \\ \alpha & \alpha' \end{pmatrix} L \begin{pmatrix} m' \\ \alpha' \end{pmatrix} \beta'\gamma' \right]_S - \frac{1}{4} (\tau_{\beta\gamma}^0 \delta_{\gamma\beta'} + \tau_{\gamma\gamma'}^0 \delta_{\beta\beta'} + \tau_{\beta\beta'}^0 \delta_{\gamma\gamma'} + \tau_{\gamma\beta'}^0 \delta_{\beta\gamma'}) . \quad (47)$$

The subscript S on some brackets related to the external strains means their symmetrization over their indices following the recipe: $\{\beta\gamma\}_S = \frac{1}{2}(\{\beta\gamma\} + \{\gamma\beta\})$, etc. This circumstance provides that the elastic constants, Eq. (47), have the complete Voigt symmetry, i.e., $C_{\beta\gamma, \beta'\gamma'}^T = C_{\beta'\gamma', \beta\gamma}^T = C_{\beta\gamma, \gamma'\beta'}^T$. At last, completing our macroscopic relations, we can calculate the instantaneous stress in the deformed crystal as

$$\begin{aligned} \tau_{\beta\gamma} &= \frac{1}{V} \frac{\partial \Delta U}{\partial \eta_{\beta\gamma}} \\ &= \tau_{\beta\gamma}^0 + C_{\beta\gamma, \beta'\gamma'}^T \eta_{\beta'\gamma'} - e_{\alpha, \beta\gamma}^{(2)}(0) \mathcal{E}_\alpha \end{aligned} \quad (48)$$

where the converse (static) piezoelectric tensor, $e_{\alpha, \beta\gamma}^{(2)}(0)$, has been introduced. It was found to be the same as the direct one, Eq. (44).

Equations (42)–(48) complete the macroscopic description of the elastic and dielectric properties of arbitrary crystal. Our derivation generalizes the result of Refs. 12 and 13 because we did not assume that the crystal is unstressed (i.e., that the initial stress $\tau_{\beta\gamma}^0 = 0$) and, in addition, the electronic polarization has also been included. The latter was also considered in Refs. 11 and 16 by means of the method of long waves and in Ref. 15 by using a formal approach based on (numerical) energy derivatives with respect to strains. However, in the papers quoted above the corresponding energy expression was not derived.

Let us now discuss our expression for the elastic crystal energy, Eq. (43). Using the macroscopic relations given by Eqs. (42) and (48), it can be shown easily by simple comparison that the microscopic result (43) is the same as that which follows directly from purely macroscopic considerations.⁴² A somewhat similar, but not identical, derivation made in Ref. 13 led the authors to another expression for the microscopic energy. The explanation for this disagreement lies in the fact that in Ref. 13 the irregular part of the bracket

$$\begin{Bmatrix} s & s' \\ \alpha & \alpha' \end{Bmatrix}$$

was separated out only in finding the dipole moment, but not while deriving the energy expression. This is why their energy results in the correct macroscopic limit, Eq. (43), only under some special assumptions. This fact allowed the authors of Ref. 13 to affirm that “there is not an *a priori* guarantee for the agreement between the microscopic and macroscopic expressions.” Our result

clearly demonstrates, however, that their conclusion is incorrect, and that correct microscopic considerations do lead to the same result as the macroscopic one, as should be so.⁴³

Now we are quite prepared to consider the vibrational part of the free energy. For this purpose we have to obtain corresponding contributions to the brackets $\{\beta\gamma\beta'\gamma'\}$,

$$\begin{Bmatrix} s & s' \\ \alpha & \alpha' \end{Bmatrix},$$

$$\begin{Bmatrix} s \\ \alpha \end{Bmatrix} \beta\gamma,$$

$$\begin{Bmatrix} s \\ \alpha \end{Bmatrix},$$

and

$$\{\beta\gamma\}.$$

Note that all other brackets are unaffected by the vibrational part since the latter (being directly expressed only through the frequencies) depends on the external and internal strains but does not depend on the shell coordinates. It is important to emphasize that the final expressions for elastic, piezoelectric, and dielectric constants obtained above as well as for the energy (the Helmholtz free energy in this case) would be still valid.

III. CALCULATION OF THE FREE-ENERGY DERIVATIVES OVER EXTERNAL AND INTERNAL STRAINS

A. General expressions for the brackets

In order to calculate the temperature-dependent part of the brackets $\{\beta\gamma \beta'\gamma'\}$,

$$\begin{Bmatrix} s & s' \\ \alpha & \alpha' \end{Bmatrix},$$

$$\begin{Bmatrix} s \\ \alpha \end{Bmatrix} \beta\gamma,$$

$$\begin{Bmatrix} s \\ \alpha \end{Bmatrix},$$

and $\{\beta\gamma\}$ (which will be indicated by the subscript T), we have to calculate the following derivatives of the vibra-

tional part $\tilde{\mathcal{F}}_{\text{vibr}}$ of the free energy, Eq. (3), over strains:

$$\begin{aligned} \left\{ \begin{array}{c} s \\ \alpha \end{array} \right\}_T &= \left[\frac{\partial \tilde{\mathcal{F}}_{\text{vibr}}}{\partial u \left\{ \begin{array}{c} s \\ \alpha \end{array} \right\}} \right]_0 \\ &= \frac{1}{N} \sum_{kj} \left[\frac{\partial \tilde{\mathcal{F}}_{kj}}{\partial u \left\{ \begin{array}{c} s \\ \alpha \end{array} \right\}} \right]_0 + \left[\frac{\partial \tilde{\mathcal{F}}_{\text{AH}}}{\partial u \left\{ \begin{array}{c} s \\ \alpha \end{array} \right\}} \right]_0 \end{aligned} \quad (49)$$

and all other brackets are expressed in the same manner. We shall omit the anharmonic part in what follows. We shall make, however, one additional comment concerning the $\tilde{\mathcal{F}}_{\text{AH}}$ contribution later. Thus, we have

$$\{\beta\gamma\}_T = \frac{1}{N} \sum_{kj} \left[\frac{\partial \tilde{\mathcal{F}}_{kj}}{\partial u_{\beta\gamma}} \right]_0, \quad (50)$$

$$\{\beta\gamma \beta'\gamma'\}_T = \frac{1}{N} \sum_{kj} \left[\frac{\partial^2 \tilde{\mathcal{F}}_{kj}}{\partial u_{\beta\gamma} \partial u_{\beta'\gamma'}} \right]_0, \quad (51)$$

$$\left\{ \begin{array}{c} s \\ \alpha \end{array} \beta\gamma \right\}_T = \frac{1}{N} \sum_{kj} \left[\frac{\partial^2 \tilde{\mathcal{F}}_{kj}}{\partial u_{\beta\gamma} \partial u \left\{ \begin{array}{c} s \\ \alpha \end{array} \right\}} \right]_0, \quad (52)$$

$$\left\{ \begin{array}{c} s \ s' \\ \alpha \ \alpha' \end{array} \right\}_T = \frac{1}{N} \sum_{kj} \left[\frac{\partial^2 \tilde{\mathcal{F}}_{kj}}{\partial u \left\{ \begin{array}{c} s \\ \alpha \end{array} \right\} \partial u \left\{ \begin{array}{c} s' \\ \alpha' \end{array} \right\}} \right]_0, \quad (53)$$

where the subscript zero means that all these derivatives should be calculated at zero strains (when both

$$u \left\{ \begin{array}{c} s \\ \alpha \end{array} \right\}$$

and $u_{\beta\gamma}$ are equal to zero). Making use of the detailed expression, Eq. (4), for the quasi-harmonic term, $\tilde{\mathcal{F}}_{kj}$, we have for the first- and second-order derivatives the following general expression (cf. Ref. 31):

$$\begin{aligned} \left[\frac{\partial \tilde{\mathcal{F}}_{kj}}{\partial x} \right]_0 &= \frac{\hbar}{2\omega_{kj}} \left[\bar{n}_{kj} + \frac{1}{2} \right] \left[\frac{\partial \lambda_{kj}}{\partial x} \right]_0 \\ &= \varphi_2(\omega_{kj}) \left[\frac{\partial \lambda_{kj}}{\partial x} \right]_0, \end{aligned} \quad (54)$$

$$\begin{aligned} \left[\frac{\partial^2 \tilde{\mathcal{F}}_{kj}}{\partial x \partial x'} \right]_0 &= \varphi_1(\omega_{kj}) \left[\frac{\partial \lambda_{kj}}{\partial x} \right]_0 \left[\frac{\partial \lambda_{kj}}{\partial x'} \right]_0 \\ &\quad + \varphi_2(\omega_{kj}) \left[\frac{\partial^2 \lambda_{kj}}{\partial x \partial x'} \right]_0, \end{aligned} \quad (55)$$

where

$$\bar{n}_{kj} = \left[\exp \left[\frac{\hbar\omega_{kj}}{k_B T} \right] - 1 \right]^{-1}$$

is the average number of the \mathbf{kj} phonons, and

$$\varphi_1(\omega_{kj}) = -\frac{\hbar}{4\omega_{kj}^3} \left\{ \frac{1}{2} + \bar{n}_{kj} \left[1 + \frac{\hbar\omega_{kj}}{k_B T} (1 + \bar{n}_{kj}) \right] \right\}. \quad (56)$$

In Eqs. (54) and (55) the variable x means either external, $u_{\beta\gamma}$, or internal,

$$u \left\{ \begin{array}{c} s \\ \alpha \end{array} \right\},$$

strains. Note also that it appears to be more convenient to use the derivatives of $\lambda_{kj} = \omega_{kj}^2$ than those of the usual frequencies, ω_{kj} , since, as will be clarified below in detail, the former can be directly related to the corresponding derivatives of the dynamical matrix, $\Omega(\mathbf{k})$. The latter idea is of major importance for the present derivation and was developed for the first time (although for a simple particular case) in Ref. 31 and then it was further extended in Ref. 5 in order to cover the case of an arbitrary lattice.

B. Formal general expressions for the derivatives of the eigenvalues over external parameter (strains)

It was suggested in Refs. 5 and 31 to apply the first- and second-order perturbation theory for deriving expressions for the first- and second-order derivatives of λ_{kj} over x , respectively. At the same time, their derivation cannot be considered as sufficient because of several reasons which should be clarified.

First of all, we found the method of Wallace⁵ for eliminating internal strains, to be approximate. Indeed, this elimination was proposed to be done before the application of the perturbation method, i.e., before the derivatives of the frequencies over strains are calculated. However, the phonon frequencies depend both on the external and internal strains, being together just geometrical parameters of the lattice. Thus, the Wallace method violates the first condition of thermodynamic equilibrium, Eq. (21): the unknown internal strains should be calculated from the minima of the Helmholtz free energy, not from the minima of the potential energy of the crystal as in Ref. 5. Moreover, final formulas published in Ref. 5 are very lengthy and cumbersome since, due to the derivation made there, the knowledge of the internal strains up to the second-order over external strains were found to be necessary. We overcome this difficulty by the elimination of internal strains quite rigorously based on the same algebra as described in some detail in the preceding section. Namely, due to our method, the complete set of derivatives of the free energy over the whole set of geometrical variables should be calculated making use of the perturbation method. And only after that, the elimination of the internal coordinates must be performed. As a result, only first-order terms of the internal strains are necessary, Eq. (41), and our final formulas do not appear to be very complicated.

Besides, in employing the perturbation method, the case of degenerate eigenvalues of the phonon problem has still not been considered. However, we found it to be quite important for the problem in question, especially

for high-symmetry crystals. Indeed, as is clear from the equations given in the preceding section, in order to calculate every bracket, the integration over the Brillouin zone (BZ) should be performed. It is known that the method of special points⁴⁴ is very useful for that purpose producing sets of points distributed over the irreducible part of the BZ. In the cases of high-symmetry crystals, many points lie along high-symmetry axes or on symmetry planes and therefore give rise to degenerate eigenvalues. Though it seems to be possible to choose such sets of special points which contain \mathbf{k} points entirely in general positions, in many cases it is expected that these sets would have too many points. Hence, we have to regard them as impractical for actual calculations. Good-quality sets involving as small a number of points as possible usually contain several high-symmetry points.^{44,45} That is why we must generalize the corresponding derivation. Furthermore, the inclusion of electronic coordinates is still lacking and we shall consider this complexity as well.

Let us decompose the dynamical matrix $\Omega(\mathbf{x})$ into a power series over $\mathbf{x} = \{\text{external, internal strains}\} = \{x_i\}$ up to second order:

$$\Omega(\mathbf{x}) = \Omega_0 + \left[\sum_i \left[\frac{\partial \Omega}{\partial x_i} \right]_0 x_i + \frac{1}{2} \sum_{ii'} \left[\frac{\partial^2 \Omega}{\partial x_i \partial x_{i'}} \right]_0 x_i x_{i'} + \dots \right]. \quad (57)$$

(Note that in Ref. 5 the corresponding decomposition was made only with respect to external strains assuming that the internal strains had already been eliminated and included in a proper expression for the dynamical matrix; see p. 203 in Ref. 5.) In order to simplify the notations, we remove in this section the indication of both the vector \mathbf{k} and the indices like s , α , etc., inherent to the dynamical matrix Ω . However, the latter in the above written expression should be understood as a matrix (with respect to these indices) at some (fixed) $\mathbf{k} \in \text{BZ}$. The matrix $\Omega_0 = \Omega(\mathbf{x} = 0)$ corresponds to an unstrained crystal whereas $\Omega = \Omega(\mathbf{x} \neq 0)$ corresponds to a strained one. Our task is to calculate first- and second-order derivatives of the eigenvalues $\lambda_j(\mathbf{x})$ of the Hermitian matrix $\Omega(\mathbf{x})$ at $\mathbf{x} = 0$ using both eigenvalues, $\lambda_j^0 = \lambda_{jr}^0 = \lambda_{jr}(0)$, and eigenvectors, $\mathbf{e}^0(jr)$, of the unstrained matrix Ω_0 :

$$\Omega_0 \mathbf{e}^0(jr) = \lambda_{jr}^0 \mathbf{e}^0(jr). \quad (58)$$

We assume for the moment (until otherwise stated) that j , j' , etc., run over states having different eigenvalues while additional indices like r , r' , etc., run over degenerate states.

Following the usual perturbation theory for the degenerate states,⁴⁶ we can consider the first- and second-order

terms inside the square brackets in the right-hand side of Eq. (57) as the first- and second-order perturbations, respectively (\mathbf{x} is chosen as a small parameter).

Let us consider one bunch of the degenerate states, say, all states (jr) with fixed j . In zeroth-order perturbation theory, we get the first-order correction $\lambda_{jr}^{(1)}(\mathbf{x})$ to $\lambda_{jr}(\mathbf{x})$ in the form of eigenvalues of the following secular problem formulated on the subspace $\{jr\}$ of the degenerate states (j is fixed):

$$\sum_{r''} W_{r'r''}^{jj(1)}(\mathbf{x}) C_{r''}^{(jr)}(\mathbf{x}) = \lambda_{jr}^{(1)}(\mathbf{x}) C_{r'}^{(jr)}(\mathbf{x}), \quad (59)$$

where $W_{r'r''}^{jj(1)}(\mathbf{x})$ is defined as the diagonal ($j = j'$) element of a more general matrix, which will turn out to be useful later:

$$W_{r'r''}^{jj(1)}(\mathbf{x}) = \mathbf{e}^0(jr')^\dagger \left[\sum_i \left[\frac{\partial \Omega}{\partial x_i} \right]_0 x_i \right] \mathbf{e}^0(j'r''). \quad (60)$$

Of course, the coefficients $C_{r'}^{(jr)}(\mathbf{x})$ depend on \mathbf{x} , but their derivatives tend to zero as $\mathbf{x} = 0$:

$$\left[\frac{\partial C_{r'}^{(jr)}(\mathbf{x})}{\partial \mathbf{x}} \right]_0 = 0 \quad (61)$$

because $W_{r'r''}^{jj(1)}(\mathbf{x})$ is a homogeneous polynomial of the first order in \mathbf{x} . Performing standard manipulations, we get the following expression for the eigenvalues $\lambda_{jr}(\mathbf{x})$ (for arbitrary \mathbf{x}) up to second order in \mathbf{x} :

$$\lambda_{jr}(\mathbf{x}) = \lambda_j^0 + \lambda_{jr}^{(1)}(\mathbf{x}) + \sum_{r''} C_{r''}^{(jr)}(\mathbf{x})^* W_{r'r''}^{jj(2)}(\mathbf{x}) C_{r''}^{(jr)}(\mathbf{x}) + \sum_{j' \neq j} \sum_{r' r''} \frac{\xi_{r'r'}^{j'j} \xi_{r''r}^{j'j*}}{\lambda_j^0 - \lambda_{j'}^0} \quad (62)$$

where

$$W_{r'r''}^{jj(2)}(\mathbf{x}) = \mathbf{e}^0(jr')^\dagger \left[\frac{1}{2} \sum_{ii'} \left[\frac{\partial^2 \Omega}{\partial x_i \partial x_{i'}} \right]_0 x_i x_{i'} \right] \mathbf{e}^0(j'r''), \quad (63)$$

$$\xi_{r'r}^{j'j} = \sum_{r''} W_{r'r''}^{j'j(1)}(\mathbf{x}) C_{r''}^{(jr)}(\mathbf{x}). \quad (64)$$

Now, we must obtain first- and second-order derivatives of $\lambda_{jr}(\mathbf{x})$, Eq. (62), with respect to components x_i , $x_{i'}$ of the vector \mathbf{x} in the limit $\mathbf{x} = 0$. Since, as was already mentioned above, the first derivatives of the coefficients $C_{r''}^{(jr)}(\mathbf{x})$ over arbitrary x_i are zero, as far as the limit is concerned, we need to differentiate only $W_{r'r''}^{jj(1)}(\mathbf{x})$ and $W_{r'r''}^{jj(2)}(\mathbf{x})$. Besides, both $W_{r'r''}^{j'j(1)}(\mathbf{x})$ and $W_{r'r''}^{j'j(2)}(\mathbf{x})$ tend to zero under the same limit. Thus, we have from Eq. (62):

$$\left[\frac{\partial \lambda_{jr}(\mathbf{x})}{\partial x_i} \right]_0 = \left[\frac{\partial \lambda_{jr}^{(1)}(\mathbf{x})}{\partial x_i} \right]_0, \quad (65)$$

$$\left[\frac{\partial^2 \lambda_{jr}(\mathbf{x})}{\partial x_i \partial x_{i'}} \right]_0 = \sum_{r''} C_{r''}^{(jr)}(0)^* \left\{ \Delta_{r'r''}^{jj}(x_i, x_{i'}) + 2 \operatorname{Re} \sum_{j' \neq j} \sum_{r'''} \frac{\Delta_{r''r'''}^{j'j}(x_i) \Delta_{r'r''}^{j'j*}(x_{i'})}{\lambda_j^0 - \lambda_{j'}^0} \right\} C_{r''}^{(jr)}(0), \quad (66)$$

where

$$\Delta_{j'r''}^{jj'}(x_i) = e^{0(j'r')\dagger} \left[\frac{\partial \Omega}{\partial x_i} \right]_0 e^{0(j'r'')}, \quad (67)$$

$$\Delta_{j'r''}^{jj'}(x_i, x_{i'}) = e^{0(j'r')\dagger} \left[\frac{\partial^2 \Omega}{\partial x_i \partial x_{i'}} \right]_0 e^{0(j'r'')}. \quad (68)$$

In order to calculate the derivatives remaining on the right-hand side of Eq. (65), let us differentiate both sides of the secular problem, Eq. (59), over x_i and then approach the limit $\mathbf{x} \rightarrow \mathbf{0}$. Because of Eq. (61), we get the desired result—an equation written directly for the derivatives of $\lambda_{jr}^{(1)}(\mathbf{x})$:

$$\sum_{r''} \Delta_{j'r''}^{jj'}(x_i) C_{r''}^{(jr)}(\mathbf{0}) = \left[\frac{\partial \lambda_{jr}^{(1)}(\mathbf{x})}{\partial x_i} \right]_0 C_{r''}^{(jr)}(\mathbf{0}). \quad (69)$$

Thus, in the general case the first-order derivatives of the phonon eigenvalues $\lambda_{jr}(\mathbf{x})$ for every x_i should be calculated as the eigenvalues of the matrix $\Delta^{jj}(x_i) = \|\Delta_{j'r''}^{jj'}(x_i)\|$ defined on a subspace spanned by the functions $e^{0(jr)}$ of the degenerate states (the index j is fixed). Note that under an infinitesimal distortion of the crystal along x_i the degeneracy can be removed and the derivatives $(\partial \lambda_{jr}(\mathbf{x})/\partial x_i)_0$ may not still be the same for different r [though $\lambda_{jr}(\mathbf{0})$ are the same for different r].

Now, let us consider the second-order derivatives given by Eq. (66). We are going to show that we do not need to know the coefficients $C_{r''}^{(jr)}(\mathbf{0})$ of the secular problem, Eq. (69), for that purpose. Indeed, owing to the orthogonality of the eigenvectors of the problem (69), and to the fact that in Eqs. (51)–(53) we have the complete sum over all states including the complete bunch of those in the degenerate case (when $j = \{jr\}$), we can sum up the second-order derivatives given by Eq. (66) over all the degenerate states r (j is still fixed). The final contribution to every degenerate state is found to be

$$\left[\frac{\partial^2 \lambda_j(\mathbf{x})}{\partial x_i \partial x_{i'}} \right]_0 = \Delta^{jj}(x_i, x_{i'}) + 2 \operatorname{Re} \sum_{j'(\neq j)} \frac{\Delta^{jj'}(x_i) \Delta^{j'j}(x_{i'})^*}{\lambda_j - \lambda_{j'}}, \quad (70)$$

where we have returned to our initial notations (i.e., j runs over all states including degenerate ones) and the summation over j' runs over all states which have distinct eigenvalues, $\lambda_{j'} \neq \lambda_j$.

Our derivation shows that in the general case the expression for the second-order derivatives of the squares of the phonon frequencies is the same as that obtained earlier in Refs. 5 and 31 except the note made above for the sum over j' . However, a new expression for the first-order derivatives was derived here, Eq. (69), instead of that obtained previously basing on the Hellmann-Feynman theorem.^{5,26} It results in an ambiguous result for the first-order derivatives in the general case of degenerate states since the eigenvectors $e^{0(j)}$ are defined up to arbitrary unitary transformation. This problem is easily avoided in solving, instead, the problem (69): any unitary similarity transformation of the matrix $\Delta^{jj}(x_i)$ (on the

subspace of the degenerate states) does not affect the corresponding eigenvalues, i.e., the derivatives $(\partial \lambda_{jr}(\mathbf{x})/\partial x_i)_0$ sought for.

Thus, as follows from Eqs. (67)–(70), in order to calculate the derivatives of the quasiharmonic eigenvalues, λ_{kj} , we have to calculate those of the dynamical matrix, Eq. (10). This is the most powerful result of this section which shows that in the most general case it is nevertheless possible (at least in principle) to link the derivatives of the phonon eigenvalues with those of the dynamical matrix and therefore represent the former through some lattice sums. This provides a basis for the further consideration and for a numerical implementation.

C. Derivatives of the dynamical matrix

Now we must calculate all derivatives of the dynamical matrix, Eq. (10), with respect to external and internal strains (all x_i). First of all we note that a set of matrices $\Delta(x_i) = \|\Delta^{jj'}(x_i)\|$ of the first-order derivatives contributes to the second-order derivatives as well as is clear from Eq. (70). Besides, while calculating the second-order derivatives, $\Delta^{jj}(x_i, x_{i'})$, we should meet products of pure first-order derivatives. It was found to be convenient, however, to separate out all the contributions to $\Delta^{jj}(x_i, x_{i'})$ which come from pure second-order derivatives of the counterparts of the dynamical matrix $\Omega(\mathbf{k})$, i.e., from its blocks $\mathbf{A}(\mathbf{k})$, $\mathbf{B}(\mathbf{k})$, and $\mathbf{D}(\mathbf{k})$, see Eqs. (12), (13), and (11). This simplifies the final expressions and saves computer time considerably. That is why the following additional definitions were found to be useful already at the stage of the first-order derivatives:

$$\Psi(j) = \mathbf{D}^{-1} \mathbf{B} \bar{\mathbf{e}}(j) = \mathbf{D}^{-1} \mathbf{B} \mathbf{e}(j) \mathbf{M}^{-1/2} \quad (71)$$

and

$$\mathbf{f}_j(x_i) = \mathbf{B}(x_i) \bar{\mathbf{e}}(j) - \mathbf{D}(x_i) \Psi(j) \quad (72)$$

where $\Psi(j) = \|\Psi_{s\alpha}(j)\|$, $\mathbf{f}_j(x_i) = \|f_{s\alpha,j}(x_i)\|$, and $\mathbf{e}(j) = \|e_{s\alpha}(j)\|$ is the quasiharmonic eigenvector. Besides, $\mathbf{B}(x_i) = \partial \mathbf{B} / \partial x_i$ is the corresponding derivative of the matrix \mathbf{B} over x_i . The same notations will be used in all other cases, for instance, $\mathbf{A}(x_i)$, $\mathbf{D}(x_i, x_{i'})$, etc. In this section the direct indication of the common BZ vector \mathbf{k} will be omitted for the sake of simplicity of the notations. Using a well-known matrix identity, namely, $d\mathbf{D}^{-1} = -\mathbf{D}^{-1}(d\mathbf{D})\mathbf{D}^{-1}$, and the definitions (71) and (72), we can differentiate the dynamical matrix given by Eq. (10) and then rewrite Eqs. (67) and (68) in the form

$$\Delta^{jj'}(x_i) = \tilde{\Delta}^{jj'}(x_i) - [\Psi(j)^\dagger \mathbf{f}_{j'}(x_i) + \mathbf{f}_j(x_i)^\dagger \Psi(j')], \quad (73)$$

$$\Delta^{jj}(x_i, x_{i'}) = \tilde{\Delta}^{jj}(x_i, x_{i'}) + 2 \operatorname{Re} \left\{ \sum_{j'(\neq j)} \frac{\Delta^{jj'}(x_i) \Delta^{j'j}(x_{i'})^*}{\lambda_j - \lambda_{j'}} - \mathbf{f}_j(x_i)^\dagger \mathbf{D}^{-1} \mathbf{f}_{j'}(x_{i'}) \right\}, \quad (74)$$

where the sum over j' in the last equation runs over all

states which have eigenvalues $\lambda_{j'}$ which differ from λ_j . The contributions marked by the wavy lines in the above given formulas, are the following:

$$\begin{aligned}\tilde{\Delta}^{jj'}(x_i) &= \tilde{\epsilon}(j)^\dagger \mathbf{A}(x_i) \tilde{\epsilon}(j') - \Psi(j)^\dagger \mathbf{D}(x_i) \Psi(j'), \quad (75) \\ \tilde{\Delta}^{jj'}(x_i, x_{i'}) &= \tilde{\epsilon}(j)^\dagger \mathbf{A}(x_i, x_{i'}) \tilde{\epsilon}(j) \\ &\quad + \Psi(j)^\dagger \mathbf{D}(x_i, x_{i'}) \Psi(j) \\ &\quad - 2 \operatorname{Re}[\Psi(j)^\dagger \mathbf{B}(x_i, x_{i'}) \tilde{\epsilon}(j)]. \quad (76)\end{aligned}$$

Thus, all the derivatives under consideration can be directly expressed through the corresponding derivatives of the blocks \mathbf{A} , \mathbf{B} , and \mathbf{D} of the dynamical matrix. Therefore, we have to consider these derivatives in detail.

The corresponding derivation is rather lengthy, though it is similar for every matrix \mathbf{A} , \mathbf{B} , and \mathbf{D} , and so we shall consider only \mathbf{B} here as a simple example. Recalling its definition, Eqs. (13) and (20), we obtain for an external strain derivative [i.e., when $x_i = u_{\beta\gamma} \equiv (\beta\gamma)$]:

$$\begin{aligned}B_{\alpha\alpha'}^{ss'}(\beta\gamma) &= \delta_{ss'} \sum_{s''} \{ q_{s''} \tilde{Q}_{\alpha\alpha'}^{ss''}(\beta\gamma)_0 + \Gamma_{\alpha\alpha'}^{ss''}(\beta\gamma)_0 \} \\ &\quad - q_s Q_{\alpha\alpha'}^{ss'}(\beta\gamma) - \Gamma_{\alpha\alpha'}^{ss'}(\beta\gamma), \quad (77)\end{aligned}$$

where the subscript 0 means that $\mathbf{k}=\mathbf{0}$ [cf. Eq. (20)]. Here $Q_{\alpha\alpha'}^{ss'}(\beta\gamma)$ and $\Gamma_{\alpha\alpha'}^{ss'}(\beta\gamma)$ are the derivatives over $u_{\beta\gamma}$ of $Q_{\alpha\alpha'}^{ss'}(\mathbf{k})$ and $\Gamma_{\alpha\alpha'}^{ss'}(\mathbf{k})$, respectively. Note that $\tilde{Q}_{\alpha\alpha'}^{ss'}(\beta\gamma)$ coincides with $Q_{\alpha\alpha'}^{ss'}(\beta\gamma)$ except that a contribution from the zero reciprocal-lattice vector $\mathbf{g}=\mathbf{0}$ is absent, see Eq. (16). That is why we can consider only $Q_{\alpha\alpha'}^{ss'}(\beta\gamma)$ in the following. Similar expressions are obtained for $A_{\alpha\alpha'}^{ss'}(\beta\gamma)$ and $D_{\alpha\alpha'}^{ss'}(\beta\gamma)$, as well as for external strain second-order derivatives like $A_{\alpha\alpha'}^{ss'}(\beta\gamma, \beta'\gamma')$, etc.

Let us consider now the first-order derivatives over internal strain, when

$$x_i = u \begin{Bmatrix} p \\ \sigma \end{Bmatrix}.$$

One hint was recognized to be useful for the derivation and we would like to pay a special attention to it: examining Eqs. (13), (15), (16), and (17), we can find that lattice sums such as $Q_{\alpha\alpha'}^{ss'}(\mathbf{k})$ or $\Gamma_{\alpha\alpha'}^{ss'}(\mathbf{k})$ depend only upon the difference

$$\hat{X}_\alpha = \hat{X}_\alpha(s) - \hat{X}_\alpha(s') = X_\alpha + u \begin{Bmatrix} s \\ \alpha \end{Bmatrix} - u \begin{Bmatrix} s' \\ \alpha \end{Bmatrix}.$$

Therefore, we can write down, for example, that for the derivative over any internal strain:

$$\begin{aligned}\frac{\partial}{\partial u \begin{Bmatrix} p \\ \sigma \end{Bmatrix}} Q_{\alpha\alpha'}^{ss'} &= (\delta_{sp} - \delta_{s'p}) \frac{\partial Q_{\alpha\alpha'}^{ss'}}{\partial u \begin{Bmatrix} s \\ \sigma \end{Bmatrix}} \\ &= (\delta_{sp} - \delta_{s'p}) Q_{\alpha\alpha'}^{ss'}(\sigma). \quad (78)\end{aligned}$$

The same is true for any other matrix, such as $V_{\alpha\alpha'}^{ss'}$, $\Gamma_{\alpha\alpha'}^{ss'}$ and $D_{\alpha\alpha'}^{ss'}$. Making use of this identity, we can derive all other derivatives of interest containing internal strains. The final relations are rather cumbersome and are omitted.

Thus, as follows from the above, we must calculate (for every $\mathbf{k} \in \text{BZ}$) a set of five derivatives of $V_{\alpha\alpha'}^{ss'}$, namely, $V_{\alpha\alpha'}^{ss'}(\beta\gamma)$, $V_{\alpha\alpha'}^{ss'}(\sigma)$, $V_{\alpha\alpha'}^{ss'}(\beta\gamma, \sigma)$, $V_{\alpha\alpha'}^{ss'}(\sigma, \sigma')$, and $V_{\alpha\alpha'}^{ss'}(\beta\gamma, \beta'\gamma')$ for external, internal, external-internal, internal-internal, and external-external strains, respectively. The same set of derivatives should be derived for $\Gamma_{\alpha\alpha'}^{ss'}$, $Z_{\alpha\alpha'}^{ss'}$, and $Q_{\alpha\alpha'}^{ss'}$. All these derivatives have been calculated by direct differentiation of the corresponding direct and reciprocal- (in the case of $Q_{\alpha\alpha'}^{ss'}$) lattice sums over strains. The zero strain is assumed to be set at the end of the calculations. We give here only the final formulas.

(i) First-order external strain derivatives:

$$V_{\alpha\alpha'}^{ss'}(\beta\gamma) = \sum_l' e^{i\mathbf{k}\mathbf{R}} V_{\alpha\alpha'\beta}^{ss'} R_\gamma, \quad (79)$$

$$Q_{\alpha\alpha'}^{ss'}(\beta\gamma) = G^3 \sum_l' e^{i\mathbf{k}\mathbf{R}} Q_{\alpha\alpha'\beta}^{ss'} + \frac{4\pi}{v_c} \sum_g e^{i\mathbf{g}\mathbf{X}} [\chi(\kappa^2)(\kappa_\alpha \kappa_\alpha' \delta_{\beta\gamma} + \kappa_\alpha \kappa_\beta \delta_{\gamma\alpha} + \kappa_\alpha \kappa_\beta \delta_{\gamma\alpha'}) + 2\chi'(\kappa^2) \kappa_\alpha \kappa_\alpha' \kappa_\beta \kappa_\gamma]. \quad (80)$$

(ii) First-order internal strain derivatives:

$$V_{\alpha\alpha'}^{ss'}(\sigma) = \sum_l' e^{i\mathbf{k}\mathbf{R}} V_{\alpha\alpha'\sigma}^{ss'} + ik_\sigma V_{\alpha\alpha'}^{ss'}, \quad (81)$$

$$Q_{\alpha\alpha'}^{ss'}(\sigma) = G^4 \sum_l' e^{i\mathbf{k}\mathbf{R}} \left[Q_{\alpha\alpha'\sigma}^{ss'} + \frac{ik_\sigma}{G} Q_{\alpha\alpha'}^{ss'} \right] - \frac{4\pi i}{v_c} \sum_g e^{i\mathbf{g}\mathbf{X}} g_\sigma \kappa_\alpha \kappa_\alpha' \chi(\kappa^2). \quad (82)$$

(iii) Second-order external strain derivatives:

$$V_{\alpha\alpha'}^{ss'}(\beta\gamma, \beta'\gamma') = \sum_l' e^{i\mathbf{k}\mathbf{R}} V_{\alpha\alpha'\beta\beta'}^{ss'} R_\gamma R_{\gamma'}, \quad (83)$$

$$\begin{aligned}
Q_{\alpha\alpha'}^{ss'}(\beta\gamma, \beta'\gamma') = & G^3 \sum_l e^{ikR} Q_{\alpha\alpha'\beta\beta'} \rho_\gamma \rho_{\gamma'} \\
& - \frac{4\pi}{v_c} \sum_g e^{igX} \left\{ \kappa_\alpha \kappa_{\alpha'} \left\{ \chi(\kappa^2) [(1 + \delta_{\beta\beta'}) \delta_{\beta\gamma} \delta_{\beta'\gamma'} + (1 - \delta_{\beta\gamma}) \delta_{\beta\gamma'} \delta_{\beta'\gamma}] \right. \right. \\
& \quad + 2\chi'(\kappa^2) (\delta_{\beta\gamma} \kappa_\beta \kappa_{\gamma'} + \delta_{\beta'\gamma'} \kappa_\beta \kappa_\gamma + \delta_{\beta\gamma'} \kappa_\beta \kappa_{\gamma'} + \delta_{\beta'\gamma} \kappa_\beta \kappa_\gamma + \delta_{\gamma'\gamma} \kappa_\beta \kappa_\beta) \\
& \quad + 4\chi''(\kappa^2) \kappa_\beta \kappa_{\beta'} \kappa_\gamma \kappa_{\gamma'} \left. \right\} + \kappa_\beta \kappa_{\beta'} \chi(\kappa^2) (\delta_{\gamma\alpha} \delta_{\gamma'\alpha'} + \delta_{\gamma\alpha'} \delta_{\gamma'\alpha}) \\
& \quad + \left[[2\chi'(\kappa^2) \kappa_\gamma \kappa_{\beta'} \kappa_{\beta'} + \chi(\kappa^2) (\delta_{\beta'\gamma'} \kappa_\beta + \delta_{\beta\gamma'} \kappa_{\beta'})] (\delta_{\gamma\alpha} \kappa_{\alpha'} + \delta_{\gamma\alpha'} \kappa_\alpha) \right. \\
& \quad \left. + \left[\begin{array}{l} \gamma \Rightarrow \gamma' \\ \beta \Rightarrow \beta' \end{array} \right] \right] \left. \right\}. \tag{84}
\end{aligned}$$

(iv) Second-order internal strain derivatives:

$$V_{\alpha\alpha'}^{ss'}(\sigma, \sigma') = \sum_l e^{ikR} V_{\alpha\alpha'\sigma\sigma'}^{ss'} + k_\sigma k_{\sigma'} V_{\alpha\alpha'}^{ss'} + i[k_\sigma V_{\alpha\alpha'}^{ss'}(\sigma') + k_{\sigma'} V_{\alpha\alpha'}^{ss'}(\sigma)], \tag{85}$$

$$Q_{\alpha\alpha'}^{ss'}(\sigma, \sigma') = G^5 \sum_l e^{ikR} \left[Q_{\alpha\alpha'\sigma\sigma'} - \frac{k_\sigma k_{\sigma'}}{G^2} Q_{\alpha\alpha'} + \frac{i}{G} (k_\sigma Q_{\alpha\alpha'\sigma'} + k_{\sigma'} Q_{\alpha\alpha'\sigma}) \right] + \frac{4\pi}{v_c} \sum_g e^{igX} g_\sigma g_{\sigma'} \kappa_\alpha \kappa_{\alpha'} \chi(\kappa^2). \tag{86}$$

(v) Second-order external-internal strain derivatives:

$$V_{\alpha\alpha'}^{ss'}(\beta\gamma, \sigma) = \sum_l e^{ikR} V_{\alpha\alpha'\beta\sigma}^{ss'} R_\gamma + ik_\sigma V_{\alpha\alpha'}^{ss'}(\beta\gamma) - i\delta_{\gamma\sigma} k_\beta V_{\alpha\alpha'}^{ss'}, \tag{87}$$

$$\begin{aligned}
Q_{\alpha\alpha'}^{ss'}(\beta\gamma, \sigma) = & \sum_l e^{ikR} \left[\left[Q_{\alpha\alpha'\beta\sigma} + \frac{ik_\sigma}{G} Q_{\alpha\alpha'\beta} \right] \rho_\gamma - \delta_{\gamma\sigma} \frac{ik_\beta}{G} Q_{\alpha\alpha'} \right] \\
& + \frac{4\pi i}{v_c} \sum_g e^{igX} \left\{ \kappa_\alpha \kappa_{\alpha'} [\chi(\kappa^2) (\delta_{\gamma\sigma} g_\beta + \delta_{\gamma\beta} g_\sigma) + 2\kappa_\beta \kappa_\gamma g_\sigma \chi'(\kappa^2)] + g_\sigma \kappa_\beta \chi(\kappa^2) (\delta_{\gamma\alpha} \kappa_{\alpha'} + \delta_{\gamma\alpha'} \kappa_\alpha) \right\}. \tag{88}
\end{aligned}$$

Here

$$\mathbf{R} = \mathbf{R} \begin{pmatrix} l & 0 \\ s & s' \end{pmatrix}$$

and the following tensor notations have been introduced:

$$V_{\alpha\alpha'\beta}^{ss'} = R_\alpha R_{\alpha'} R_\beta V_3^{ss'} + (\delta_{\alpha\beta} R_{\alpha'} + \delta_{\alpha'\beta} R_\alpha + \delta_{\alpha\alpha'} R_\beta) V_2^{ss'}, \tag{89}$$

$$\begin{aligned}
V_{\alpha\alpha'\beta\beta'}^{ss'} = & R_\alpha R_{\alpha'} R_\beta R_{\beta'} V_4^{ss'} + (\delta_{\alpha\beta} \delta_{\alpha'\beta'} + \delta_{\alpha\beta'} \delta_{\alpha'\beta} + \delta_{\alpha\alpha'} \delta_{\beta\beta'}) V_2^{ss'} \\
& + (\delta_{\alpha\beta} R_{\alpha'} R_{\beta'} + \delta_{\alpha'\beta} R_\alpha R_{\beta'} + \delta_{\alpha\alpha'} R_\beta R_{\beta'} + \delta_{\alpha\beta'} R_{\alpha'} R_\beta + \delta_{\alpha'\beta'} R_\alpha R_{\beta'} + \delta_{\beta\beta'} R_\alpha R_{\alpha'}) V_3^{ss'}. \tag{90}
\end{aligned}$$

$Q_{\alpha\alpha'\beta}$ and $Q_{\alpha\alpha'\beta\beta'}$ are defined in the same fashion except that $V_i^{ss'}$ is substituted for Q_i for $i=1, \dots, 4$. All other derivatives of interest, namely those of $\Gamma_{\alpha\alpha'}^{ss'}$ and $Z_{\alpha\alpha'}^{ss'}$ are written analogously with reasonable substitution of $V_i^{ss'}$ by $\Gamma_i^{ss'}$ and $Z_i^{ss'}$, respectively. Recall that all definitions of these quantities, $V_i^{ss'}$, $\Gamma_i^{ss'}$, etc., were given previously, in Sec. II B for any integer i , though we need here only i up to 4 (higher values are needed for third, etc., derivatives of the phonon frequencies).

Concluding this section, we should emphasize that the complete (i.e., built from both the static and vibrational parts) internal-strain-related brackets must show some properties which follow from the invariance of the crystal subjected to a rigid translation as a whole. In other words, the identities given by Eqs. (36) must be also

fulfilled separately for the vibrational contributions. It was checked that this is really so. Thus, the formulas derived here do not violate this important physical property.

Another point is that, in spite of the first row in Eq. (21), for noncentrosymmetric crystals the complete bracket

$$\begin{Bmatrix} p \\ \sigma \end{Bmatrix} = \begin{Bmatrix} p \\ \sigma \end{Bmatrix}_{st} + \begin{Bmatrix} p \\ \sigma \end{Bmatrix}_T$$

may not be equal to zero in the thermodynamic equilibrium. The same is true for the shell component of the "force,"

$$Y \begin{pmatrix} m \\ \alpha \end{pmatrix}.$$

This is especially so for piezoelectric crystals when atoms are located away from points of high symmetry. In this case the first equation in (21) is satisfied by a special combination of the brackets which can be easily found by careful elimination of the shells in Eq. (40), the final linear term with respect to

$$u \begin{pmatrix} s \\ \sigma \end{pmatrix}.$$

For the same reason, the second term in Eq. (46) which gives the internal strains contribution to the stresses does not vanish for these crystals.

IV. CONCLUDING REMARKS

The method developed here is quite general and may be used to derive corresponding expressions for high-order elastic and dielectric constants as well. For that purpose we must consider additionally only higher-order derivatives of the squares of phonon frequencies, λ_{kj} , over both internal and external strains which can be done

without problems in the same way as was done above, though, clearly, the derivation would be rather lengthy. At the same time, our method can be very easily generalized in order to take into account any order of the anharmonicity [in a line of Eq. (49)]: \mathfrak{F}_{AH} is a well-defined function of quasi-harmonic phonon frequencies, eigenvectors, and interatomic distances. Therefore, except for some additional terms, this modifies the detailed expressions for the functions $\varphi_1(\omega_{kj})$ and $\varphi_2(\omega_{kj})$, but does not affect the derivatives of phonon frequencies derived here.

In the second part of this paper we consider in more detail the numerical implementation of our formulas. Two alkali halide crystals are investigated in the quasi-harmonic approximation employing several sets of pair potentials (including *ab initio* and empirical ones) for a rather wide range of temperatures and pressures. We also make a detailed comparison with results obtained experimentally.

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