

The quantum theory of elastic constants

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 2247

(<http://iopscience.iop.org/0953-8984/3/14/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 07:10

Please note that [terms and conditions apply](#).

The quantum theory of elastic constants

A G McLellan

Department of Physics, University of Canterbury, Christchurch, New Zealand

Received 5 November 1990

Abstract. A recent rigorous and rotationally invariant treatment of the theory of a homogeneously deformed material is discussed. It is shown that it leads to different strain perturbation terms in the Hamiltonian from those arrived at in the standard treatment of Born and Huang. These differences are discussed. It is shown also that the Hamiltonian of the deformed system may be directly expressed in terms of the Lagrangian finite strain tensor, with the result, for example, that the correct symmetries for the thermodynamic quantities are apparent at all times. The advantages and simplicity of the finite strain treatment are discussed. It is also shown that the Born–Huang treatment fails a simple test of rotational invariance and so cannot be correct. This accounts for the difference in the two treatments. As an example, it is shown how the soft mode of β quartz, following the method of Axe and Shirane, contributes a logarithmic divergence to the elastic constants in addition to the $(T - T_c)^{-1}$ divergence discussed by these authors. It is weaker than this latter divergence, but it may be of interest further away from the transition.

1. Introduction

Recently, a study (McLellan 1984a, b, 1985a, b and 1988—referred to here as M84a, M84b, etc, respectively) was made of the quantum theory of a homogeneously deformed system. A rigorous treatment was given, an important aspect of which is the recognition that the energy eigenfunctions of the deformed system satisfy boundary conditions different to those satisfied by the eigenfunctions of the undeformed system. Thus, without a particular transformation of coordinates, the usual perturbation methods cannot apply since it is basic to such methods that the perturbed eigenfunctions can be expressed as, usually orthogonal, transformations of the unperturbed eigenfunctions which are regarded as a complete set. This may not be done if they satisfy different boundary conditions.

Emphasis is also placed on the symmetry properties of the indices of the elastic constants and the rotational invariance properties of the potential energy function. It was shown that, in this treatment, the correct symmetries are obtained from the beginning.

In this paper we show that this treatment does not agree with the standard treatment of Born and Huang (1954), (here referred to as BH) even for the case of a harmonic model. It similarly disagrees with other treatments, e.g. that of Barron and Klein (1974), which are variations on the BH treatment. The reasons for this disagreement will be discussed in section 8 where it will be shown that the BH description of a deformed crystal is not rotationally invariant and that this accounts for the different results in the

two treatments. This section, apart from some definitions given in table 1, may be read independently of other parts of this paper.

After a brief discussion of the present treatment, the differences between the formulae for the elastic constants for the two theories will be discussed. It will be shown that while the correct index symmetries of the constants are shown to hold in the present theory as a simple consequence of the rotational invariance condition on the Hamiltonian of the system, such symmetries for the elastic constants on the BH theory would be inconsistent with the well known invariance conditions applied to the lattice potential coefficients (see e.g. Wallace 1972).

The differences in the various contributions to the elastic constants are significant and consist of extra terms in the vertex functions of the diagram perturbation technique. For example, in the discussion of the α - β quartz transition, a term in the elastic constants was discussed by Axe and Shirane (1970) as showing the effect of the soft mode. This term gave a $(T - T_c)^{-1}$ singularity in the elastic constants. One of the two corrections to this term as required in the present treatment would, on following the same mode of analysis as that of these authors, add a logarithmically divergent contribution to this term. Of course, at the transition, the stronger divergence would control effects there. However, this diverging contribution may be of importance in precursor effects; they may also be of importance if the coefficient in the most strongly divergent term became zero for some materials or some conditions. In the light of the current interest in this transition because of the recent elegant experimental and theoretical work leading to the discovery of an incommensurate intermediate phase, it is important that the correct treatment of thermodynamic quantities such as elastic constants and piezoelectric coefficients be given. Quantities, such as these that are related to strain deformations will require corrections.

The elastic constants referred to throughout this paper will be the isothermal constants of finite strain theory, namely those defined by

$$c_{ab\alpha\beta} = (\partial^2 f / \partial \eta_{ab} \partial \eta_{\alpha\beta})_0 \quad (1)$$

where the derivatives are evaluated at the zero-strain reference state, and f is the Helmholtz free energy per unit *reference volume* (see e.g. M84a, table 1). In passing, the use of infinitesimal strain theory has few advantages which are offset by the fact that the Cauchy stress tensor cannot be expressed as a derivative of a free energy *even in the infinitesimal limit*. One result is that, although they are equal to those of equation (1) for a zero-stress state only, the elastic constants of infinitesimal theory are symmetric only when evaluated at a state that is at hydrostatic pressure, not for non-hydrostatic reference states (see e.g. M80, pp 150-7). See e.g. M84a, table 1, for relations between the elastic constants calculated using \mathbf{u} or η .

In applying this treatment to a crystal system, we shall use the well known Hamiltonian formulation appropriate to the adiabatic approximation. However, this treatment is completely general, and could be applied to the case of the full Hamiltonian of nuclei and electrons. Nelson (1988) (see also Pleiner and Brand 1988) has recently studied the crystal system as a non-adiabatic case, and he has arrived at the conclusion that, due to the coupling of optical phonons to acoustic phonons, there may be a small dynamic antisymmetric part of the stress tensor. This would have the consequence that the elastic constants would have 45 independent elements in the most general anisotropic case—instead of the usually accepted number of 21. It should be possible to formulate this possibility using the treatment presented here.

Table 1. Definitions of symbols.

Symbol	Definition
N	Number of particles (atoms or ions)
N_c	Number of cells in lattice
v_c	Volume of a cell
f	Helmholtz free energy per unit reference volume
x^μ	Position vector of particle μ , $\mu = 1, \dots, N$
x	Shorthand for all position vectors x^μ
X	Shorthand for all position vectors X^μ in deformed container
E_3	Unit 3×3 matrix
D	Homogeneous deformation matrix = $\partial X/\partial x$
J	Determinant of D
u	$D - E_3$, finite strain tensor
η	Lagrangian finite strain tensor, defined by $dS^2 - ds^2 = 2\eta_{\alpha\beta}dx_\alpha dx_\beta$ where $dS^2 = dX ^2$, $ds^2 = dx ^2$
\hat{x}^μ	Reference position vector
$v^\mu = x^\mu - \hat{x}^\mu$	Particle displacement from reference position
Lattice notation	
$\hat{x}^\mu \rightarrow$	$x \begin{pmatrix} l \\ \kappa \end{pmatrix}$ reference position vector
$x^\mu \rightarrow$	$x \begin{pmatrix} l \\ \kappa \end{pmatrix} + v \begin{pmatrix} l \\ \kappa \end{pmatrix}$
$\hat{\Phi}_{\alpha\beta}^{\mu_1\mu_2}$	$\Phi_{\alpha\beta} \begin{pmatrix} l_1 & l_2 \\ \kappa_1 & \kappa_2 \end{pmatrix}$
m_κ	Mass of particle of sub-lattice κ
$\lambda, -\lambda$	$qj, -qj = (-q)j$, wave vector and branch
$A(\lambda)$	$a_{-\lambda}^\dagger + a_\lambda$, creation and annihilation operators
$Q(\lambda)$	$A(\lambda)(\hbar/2\omega_\lambda)^{1/2}$
$B(\lambda) = -B^\dagger(-\lambda)$	$a_\lambda - a_{-\lambda}^\dagger$
$\Delta(q)$	1 when q is a reciprocal lattice point, 0 otherwise
$e(\kappa \lambda), e(\kappa qj)$	Normalised polarization vectors, see Maradudin <i>et al</i> (1971), equation (2.1.51)

In the next section we shall discuss the present treatment in order to introduce the corrections.

For convenience a list of definitions of symbols is given in table 1.

2. Theory

The present theory derives rigorously in quantum terms all the contributions to the elastic constants, that is, the kinetic and the potential terms as well as the fluctuation terms. In the original treatment, M84a, the system was considered deformed homogeneously by suitably deforming the container as is done in experimental work. The container was described in terms of a containing potential, but here we shall somewhat more briefly discuss this effect by saying that the container is deformed, thus giving rise to different boundary conditions when different deformations are applied. Reference to the above paper will show that this is satisfactory.

The Schrödinger equation for the system in the reference zero-strain state may be written as

$$H(x)\psi_n(x) = E_n\psi_n(x) \quad (2)$$

where x is shorthand for all the position vectors x^μ , $\mu = 1, \dots, N$ of the N particles of the system.

The Schrödinger equation for the system when in the deformed container is of the same form

$$H(X)\psi'_n(X) = (E_n + \delta E_n)\psi'_n(X) \quad (3)$$

where, for convenience in this case, we use upper case X for the Cartesian position vectors, which span the region enclosed by the deformed container.

The important difference between these two equations is not in their form, but in the fact that the boundary conditions in the two cases are different. This means that we cannot use the ordinary techniques of perturbation theory and regard equation (3) as a perturbed form of equation (2), since it is basic to such methods that it can be assumed that the perturbed eigenfunctions may be taken to be linear combinations of the unperturbed eigenfunctions, and, in fact, when suitably normalized, that they can be taken as orthogonal transformations of them. This certainly cannot be the case when each set of eigenfunctions satisfies different boundary conditions.

This difficulty can be readily overcome by using a non-orthogonal transformation at first, as follows.

In equation (3), we make the mathematical transformation

$$X = \mathbf{D}x \quad (4)$$

where \mathbf{D} is the homogeneous deformation matrix produced by the deformation of the container, that is the container shape is changed so that the system is deformed homogeneously and each point x of the system in the reference state is deformed to the point X such that equation (4) holds true where the matrix \mathbf{D} has the same value everywhere in the system.

When the mathematical transformation is performed, the Schrödinger equation of the deformed state becomes

$$H(\mathbf{D}x)\psi'_n(\mathbf{D}x) = (E_n + \delta E_n)\psi'_n(\mathbf{D}x). \quad (5)$$

We now observe that the eigenfunctions, $\psi'_n(\mathbf{D}x)$, regarded as explicit functions of the vectors denoted by x , obey exactly the same boundary conditions as do the unperturbed eigenfunctions $\psi_n(x)$ (as we may now describe them). Thus when suitably normalized, using the determinant J of the matrix \mathbf{D} as the Jacobian in the integrals, the eigenfunctions $\psi'_n(x)$ may now be expressed as an orthogonal transformation of the unperturbed eigenfunctions of the reference zero-strain state.

It is readily seen that $H(\mathbf{D}x)$ is Hermitian and well behaved with respect to functions which satisfy the boundary conditions of the reference zero-strain state, when regarded as an operator function of the variable x .

Thus, for example, we may write equation (5) in a perturbed form as

$$[H(x) + w(x)]\psi'_n(\mathbf{D}x) = (E_n + \delta E_n)\psi'_n(\mathbf{D}x) \quad (6)$$

where

$$\omega(x) = H(\mathbf{D}x) - H(x). \quad (7)$$

Note that if \mathbf{D} represents a rotation instead of a deformation this perturbation vanishes.

This perturbation may first be expanded as a series in either the finite strain tensor \mathbf{u} , or, as we shall show, as a series in the Lagrangian finite strain tensor η (see table 1, for definitions). The coefficients of these series, which are functions of the x^μ , may then be expanded as series in the displacements v^μ from the reference configuration \hat{x}^μ , to obtain either a double series in the elements of \mathbf{u} and the v^μ , or in those of η and the v^μ .

These expansions and then the kinetic contribution will be discussed in sections 4, 5 and 6, respectively.

However, first we shall show how to treat, in a simple way, the sum over states Z for the deformed strain state, in a manner independent of the treatment of the Schrodinger equation given in this section.

3. The sum over states

We shall briefly show from first principles how the correct thermodynamic approach may be given without directly referring to the treatment of the Schrödinger equation given in the previous section. For diagram and other techniques, we start with the sum over states for the deformed state

$$Z = \text{Trace}(e^{-\beta H}) = \sum_{n'} \langle n' | e^{-\beta H(X)} | n' \rangle \quad (8)$$

where $|n'\rangle$ is the ket notation for the eigenfunction $\psi'_{n'}(X)$; this eigenfunction is considered normalized to unity in the space of the variables X .

If we compare this expression with that for the reference container state, we see that we cannot compare them in the usual manner by taking the trace of an operator with respect to the perturbed eigenfunctions as being equal to its trace with respect to the unperturbed eigenfunctions. This is so since we cannot transform from one to the other by an orthogonal transformation.

Therefore, we must perform the mathematical transformation $X = \mathbf{D}\mathbf{x}$ as in the previous section to obtain the following expression for the sum over states Z for the deformed state,

$$\sum_{n'} \int \psi'^*_{n'}(X) e^{-\beta H(X)} \psi'_{n'}(X) dX = J^N \sum_{n'} \int \psi'^*_{n'}(\mathbf{D}\mathbf{x}) e^{-\beta H(\mathbf{D}\mathbf{x})} \psi'_{n'}(\mathbf{D}\mathbf{x}) d\mathbf{x} \quad (9)$$

where J is the determinant of \mathbf{D} . If we normalize the functions $\psi'_{n'}(\mathbf{D}\mathbf{x})$ to unity with respect to the variables \mathbf{x} , we then see that the factor J^N in this equation is absorbed. The right hand side is now the trace of an operator with respect to a set of orthonormal functions which may be transformed by an orthogonal transformation to the unperturbed eigenfunctions of the reference container state, since they obey the same boundary conditions. We may write the perturbed sum over states as

$$Z = \sum_n \langle n | e^{-\beta H(\mathbf{D}\mathbf{x})} | n \rangle \quad (10)$$

where the basis functions are the unperturbed eigenfunctions. Thus conventional perturbation techniques may be applied.

It is of interest to see that, in the corresponding classical statistical mechanical treatment of Z , a factor J^N is obtained in a similar way. However, it is not absorbed into

the integral as here. In fact, this factor leads to the familiar equation of state $pV = NkT$ in the limit of an ideal classical gas.

We may note that the treatment is very general—for example, it does not need a reference configuration or lattice. It has been applied successfully, for example, see M84a, to the case of a perfect quantum gas.

4. The expansion in terms of \mathbf{u}

If we take $\mathbf{D} = \mathbf{E}_3 + \mathbf{u}$, where \mathbf{E}_3 is the unit 3×3 matrix, we can expand $w(\mathbf{x})$ as a series in the finite strain tensor \mathbf{u} .

The potential part of the perturbation term is

$$\begin{aligned} \Phi(\mathbf{D}\mathbf{x}) - \Phi(\mathbf{x}) = & u_{\alpha\beta} x_{\beta}^{\mu} \frac{\partial \Phi}{\partial x_{\alpha}^{\mu}} + \frac{1}{2!} u_{\alpha_1\beta_1} u_{\alpha_2\beta_2} x_{\beta_1}^{\mu_1} x_{\beta_2}^{\mu_2} \frac{\partial^2 \Phi}{\partial x_{\alpha_1}^{\mu_1} \partial x_{\alpha_2}^{\mu_2}} \\ & + \dots + \frac{1}{n!} \left\{ \prod_{i=1}^n u_{\alpha_i\beta_i} x_{\beta_i}^{\mu_i} \right\} \frac{\partial^n \Phi}{\partial x_{\alpha_1}^{\mu_1} \dots \partial x_{\alpha_n}^{\mu_n}} + \dots \end{aligned} \quad (11)$$

where the partial derivatives are evaluated at the (arbitrary) configuration \mathbf{x}^{μ} , $\mu = 1, \dots, N$, where N is the number of particles. In this equation, for brevity, we use a generalized summation convention for repeated particle indices $\mu_1, \mu_2, \dots, \mu_i, \dots$, as well as for the Cartesian components.

The perturbation term involving the potential energy terms only has been expanded as in equation (11) in powers of the tensor \mathbf{u} . For a crystal lattice, we have a reference configuration C_0 . The coefficient of each term of the expansion of equation (11) may be expanded in powers of the displacements, v^{μ} , of the particles from their reference configuration positions, \hat{x}^{μ} , to obtain a double series in powers of the strain tensor \mathbf{u} and of the particle displacements.

Since

$$\mathbf{v}^{\mu} = \mathbf{x}^{\mu} - \hat{\mathbf{x}}^{\mu} \quad (12)$$

we obtain, on expanding each term of equation (11),

$$\Phi(\mathbf{D}\mathbf{x}) - \Phi(\mathbf{x}) = \sum_{n=1}^{\infty} \frac{1}{n!} (u_{\alpha_i\beta_i})_n \sum_{i=1}^{\infty} \frac{1}{i!} \left\{ \frac{\partial^i}{(\partial x_{\gamma_i}^{\nu_i})_i} \left((x_{\beta_i}^{\mu_i})_n \frac{\partial^n \Phi}{(\partial x_{\alpha_i}^{\mu_i})_n} \right) \right\}_0 (v_{\gamma_i}^{\nu_i})_i \quad (13)$$







where $\{\}_0$ signifies evaluation at the reference configuration, $\hat{\mathbf{x}}^{\mu}$, and the bracket symbols $(\)_n$ are defined by, for example,

$$(f_{\alpha_i\beta_i}^{\mu_i})_n = \prod_{i=1}^n f_{\alpha_i\beta_i}^{\mu_i} \quad (14)$$

Again, we are using the generalized summation convention for all repeated particle indices and those of Cartesian components.

In table 2 are listed some terms, first order and second order in the strain tensor, of the perturbation. It may be noted that the corresponding coefficients of the contributions according to BH, Cowley (1963) and Barron and Klein (1972) are the leading terms in those of the second columns of these tables. As indicated in table 2, the first-order coefficients listed will be shown, in section 5, to be the same as those for the first-order expansion in powers of $\boldsymbol{\eta}$.

Table 2. Some perturbation terms, first order in the strain tensors \mathbf{u} or $\boldsymbol{\eta}$, for the whole crystal, using untransformed lattice potential coefficients; also some quadratic in the tensor \mathbf{u} . Strain lines have arrows, phonon lines do not. The summation convention is to be used for all pairs of repeated indices of whatever type, $\alpha, \beta, \gamma, \dots, \mu, \nu \dots$. In lattice notation, each index of the type μ, ν corresponds to a pair of indices of the type (lk) , the cell origin and sublattice indices respectively.

Factors and vertices	Perturbation functions
$u_{\alpha\beta}$ or $\eta_{\alpha\beta}$	First order in strain
1 $\alpha\beta$ 	$(\dot{x}_{\beta}^{\mu} \dot{\Phi}_{\alpha\gamma}^{\mu\nu} + \delta_{\beta\gamma} \dot{\Phi}_{\alpha}^{\nu}) u_{\gamma}^{\nu}$
2 $\alpha\beta$ 	$\frac{1}{2!} (\dot{x}_{\beta}^{\mu} \dot{\Phi}_{\alpha\gamma}^{\mu\nu} u_{\gamma}^{\nu} + \delta_{\beta\gamma_1} \dot{\Phi}_{\alpha\gamma_2}^{\nu_1\nu_2} + \delta_{\beta\gamma_2} \dot{\Phi}_{\alpha\gamma_1}^{\nu_2\nu_1}) u_{\gamma_1}^{\nu_1} u_{\gamma_2}^{\nu_2}$
3 $\alpha\beta$ 	$\frac{1}{3!} (\dot{x}_{\beta}^{\mu} \dot{\Phi}_{\alpha\gamma_1\gamma_2\gamma_3}^{\mu\nu_1\nu_2\nu_3} + \delta_{\beta\gamma_1} \dot{\Phi}_{\alpha\gamma_2\gamma_3}^{\nu_1\nu_2\nu_3} + \delta_{\beta\gamma_2} \dot{\Phi}_{\alpha\gamma_1\gamma_3}^{\nu_2\nu_1\nu_3} + \delta_{\beta\gamma_3} \dot{\Phi}_{\alpha\gamma_1\gamma_2}^{\nu_3\nu_1\nu_2}) u_{\gamma_1}^{\nu_1} u_{\gamma_2}^{\nu_2} u_{\gamma_3}^{\nu_3}$
$u_{\alpha_1\beta_1} u_{\alpha_2\beta_2}$	Second order in strain
4 $\alpha_1\beta_1$ $\alpha_2\beta_2$ 	$\frac{1}{2!} (\dot{x}_{\beta_1}^{\mu_1} \dot{x}_{\beta_2}^{\mu_2} \dot{\Phi}_{\alpha_1\alpha_2}^{\mu_1\mu_2})$
5 $\alpha_1\beta_1$ $\alpha_2\beta_2$ 	$\frac{1}{2!} (\dot{x}_{\beta_1}^{\mu_1} \dot{x}_{\beta_2}^{\mu_2} \dot{\Phi}_{\alpha_1\alpha_2\gamma}^{\mu_1\mu_2\nu} + \delta_{\gamma\beta_1} \dot{x}_{\beta_2}^{\mu_2} \dot{\Phi}_{\alpha_1\alpha_2}^{\nu\mu_2} + \delta_{\gamma\beta_2} \dot{x}_{\beta_1}^{\mu_1} \dot{\Phi}_{\alpha_1\alpha_2}^{\mu_1\nu}) u_{\gamma}^{\nu}$
6 $\alpha_1\beta_1$ $\alpha_2\beta_2$ 	$(1/2!2!)(\dot{x}_{\beta_1}^{\mu_1} \dot{x}_{\beta_2}^{\mu_2} \dot{\Phi}_{\alpha_1\alpha_2\gamma_1\gamma_2}^{\mu_1\mu_2\nu_1\nu_2} + \delta_{\gamma_1\beta_1} \dot{x}_{\beta_2}^{\mu_2} \dot{\Phi}_{\alpha_1\alpha_2\gamma_2}^{\nu_1\mu_2\nu_2} + \delta_{\gamma_1\beta_2} \dot{x}_{\beta_1}^{\mu_1} \dot{\Phi}_{\alpha_1\alpha_2\gamma_2}^{\mu_1\nu_1\nu_2} + \delta_{\gamma_2\beta_2} \dot{x}_{\beta_1}^{\mu_1} \dot{\Phi}_{\alpha_1\alpha_2\gamma_1}^{\mu_1\nu_2\nu_1} + \delta_{\gamma_2\beta_1} \dot{x}_{\beta_2}^{\mu_2} \dot{\Phi}_{\alpha_1\alpha_2\gamma_1}^{\nu_2\mu_2\nu_1} + \delta_{\gamma_1\beta_1} \delta_{\gamma_2\beta_2} \dot{\Phi}_{\alpha_1\alpha_2}^{\nu_1\nu_2} + \delta_{\gamma_1\beta_2} \delta_{\gamma_2\beta_1} \dot{\Phi}_{\alpha_1\alpha_2}^{\nu_2\nu_1}) u_{\gamma_1}^{\nu_1} u_{\gamma_2}^{\nu_2}$

In table 2, for brevity, we are using indices, such as μ, ν etc, instead of the usual lattice notation

$$\begin{pmatrix} l \\ K \end{pmatrix}.$$

We define

$$\dot{\Phi}_{\alpha_1\alpha_2\dots}^{\mu_1\mu_2\dots} = \Phi_{\alpha_1\alpha_2\dots} \begin{pmatrix} l_1 & l_2 & \dots \\ K_1 & K_2 & \dots \end{pmatrix} \tag{15}$$

the usual lattice potential coefficients, which are derivatives evaluated at the reference configuration (see table 1)

$$\dot{x}^{\mu} = x \begin{pmatrix} l \\ K \end{pmatrix}.$$

With regard to index symmetries, we see that the coefficients of equation (13) are symmetric with respect to interchanges of the type $(\alpha_i\beta_i) \leftrightarrow (\alpha_j\beta_j)$. With regard to interchanges of the type $\alpha_i \leftrightarrow \beta_i$, we see that the terms of this equation that are linear in \mathbf{u} do have this symmetry as a consequence of the rotational invariance of Φ . But for terms quadratic and higher in \mathbf{u} we see, by comparison with equation (19), that in general we do not have this type of symmetry. As an important exception, we see that, for a zero-stress state only, the coefficient of item 4, table 2 does have this symmetry (cf item 4, table 3, which certainly does have this symmetry for any stress state).

In the next section we shall show how to express the perturbed Hamiltonian $H(\mathbf{D}\mathbf{x})$ explicitly in terms of the well known Lagrangian finite strain tensor $\boldsymbol{\eta}$ (see e.g. M84a, table 1).

5. The use of the Lagrangian finite strain tensor

It has been shown (see M88) that a rotationally invariant and parity conserving potential energy function may be taken as a function $\Phi(S^{\mu\nu})$, where $S^{\mu\nu} = \mathbf{x}^\mu \cdot \mathbf{x}^\nu$ is a set of scalar products (often, but not necessarily, all such possible products). If we regard Φ as an explicit function of these scalar products, it may readily be shown (see also M84a, equation (4.9)) that we may write

$$H(\mathbf{D}\mathbf{x}) = (1/2m_\mu)[1/(\mathbf{E}_3 + 2\boldsymbol{\eta})]_{\alpha\beta} p_\alpha^\mu p_\beta^\mu + \Phi(\mathbf{x}^\mu \cdot (\mathbf{E}_3 + 2\boldsymbol{\eta}) \cdot \mathbf{x}^\nu) \quad (16)$$

using the generalized summation convention. The perturbation of equation (7) may now be expanded in powers of $\boldsymbol{\eta}$ and will contain kinetic and potential terms.

At present we shall consider only the potential energy terms arising from the expansion of $\Phi(S^{\mu\nu} + 2\eta_{\alpha\beta}x_\alpha^\mu x_\beta^\nu)$. The derivatives of Φ with respect to the $S^{\mu\nu}$ may be related to the derivatives of Φ with respect to the variables x^μ . The relationships for the derivatives of order 1 to 3 are effectively listed in M88, equations (2.8–10).

Now, if we expand the above function we obtain

$$\Phi(\mathbf{D}\mathbf{x}) - \Phi(\mathbf{x}) = 2\eta_{\alpha\beta}x_\alpha^\mu x_\beta^\nu \Phi^{\mu\nu} + (2^2/2!)\eta_{\alpha_1\beta_1}\eta_{\alpha_2\beta_2}x_{\alpha_1}^{\mu_1}x_{\beta_1}^{\nu_1}x_{\alpha_2}^{\mu_2}x_{\beta_2}^{\nu_2}\Phi^{\mu_1\nu_1\mu_2\nu_2} + \dots \quad (17)$$

where

$$\Phi^{\mu_1\nu_1\dots\mu_n\nu_n} = (\partial^n \Phi / \partial S^{\mu_1\nu_1} \dots \partial S^{\mu_n\nu_n}) \quad (18)$$

are, importantly, *scalar* functions. Again we use the generalized summation convention. We note that the index symmetries of the coefficients of the terms in equation (17) agree with those required of the elastic constants.




Now using the relationships of M88 equations (2.8–10), but for an arbitrary configuration \mathbf{x}^μ , not, as in these equations, for the reference configuration $\bar{\mathbf{x}}^\mu$, we readily obtain

$$\begin{aligned} \Phi(\mathbf{D}\mathbf{x}) - \Phi(\mathbf{x}) &= \eta_{\alpha\beta}x_\beta^\mu (\partial\Phi/\partial x_\alpha^\mu) + (1/2!)\eta_{\alpha_1\beta_1}\eta_{\alpha_2\beta_2}[x_{\beta_1}^{\mu_1}x_{\beta_2}^{\mu_2}(\partial^2\Phi/\partial x_{\alpha_1}^{\mu_1}\partial x_{\alpha_2}^{\mu_2}) \\ &\quad - \delta_{\alpha_1\alpha_2}x_{\beta_1}^{\mu_1}(\partial\Phi/\partial x_{\beta_2}^{\mu_2}) + \dots \end{aligned} \quad (19)$$

using the generalized summation convention. Since $\boldsymbol{\eta}$ is zero if \mathbf{D} represents a rotation, rotational invariance is trivially evident when $\boldsymbol{\eta}$ is used as the strain variable.

If we compare this expansion with that of equation (11) in powers of the strain tensor \mathbf{u} , we see that the first-order coefficients are identical and the second-order coefficients

Table 3. Some perturbation terms, second order in the strain tensor η , for the whole crystal, using untransformed lattice potential coefficients. Strain lines have arrows, phonon lines do not. The summation convention is to be used for all pairs of repeated indices of whatever type, $\alpha, \beta, \gamma, \dots, \mu, \nu \dots$. In lattice notation, each index of the type μ, ν corresponds to a pair of indices of the type $(l\kappa)$, the cell origin and sublattice indices respectively.

Factors and vertices $\eta_{\alpha_1\beta_1}\eta_{\alpha_2\beta_2}$	Perturbation functions Second order in strain
4 $\alpha_1\beta_1$ $\alpha_2\beta_2$ 	$\frac{1}{2!}(\hat{x}_{\beta_1}^{\mu}\hat{x}_{\beta_2}^{\nu}\hat{\Phi}_{\alpha_1\alpha_2}^{\mu\nu} - \delta_{\alpha_1\alpha_2}\hat{x}_{\beta_1}^{\mu}\hat{\Phi}_{\beta_2}^{\nu})$
5 $\alpha_1\beta_1$ $\alpha_2\beta_2$ 	$\frac{1}{2!}(\hat{x}_{\beta_1}^{\mu}\hat{x}_{\beta_2}^{\nu}\hat{\Phi}_{\alpha_1\alpha_2}^{\mu\nu} + \delta_{\gamma\beta_1}\hat{x}_{\beta_2}^{\nu}\hat{\Phi}_{\alpha_1\alpha_2}^{\mu\nu} + \delta_{\gamma\beta_2}\hat{x}_{\beta_1}^{\mu}\hat{\Phi}_{\alpha_1\alpha_2}^{\mu\nu} - \delta_{\alpha_1\alpha_2}\{\hat{x}_{\beta_1}^{\mu}\hat{\Phi}_{\beta_2}^{\nu} + \delta_{\beta_1\gamma}\hat{\Phi}_{\beta_2}^{\nu}\})v_{\gamma}^{\nu}$
6 $\alpha_1\beta_1$ $\alpha_2\beta_2$ 	$\frac{1}{2!2!}(\hat{x}_{\beta_1}^{\mu}\hat{x}_{\beta_2}^{\nu}\hat{\Phi}_{\alpha_1\alpha_2\gamma_1\gamma_2}^{\mu\nu} + \delta_{\gamma_1\beta_1}\hat{x}_{\beta_2}^{\nu}\hat{\Phi}_{\alpha_1\alpha_2\gamma_1\gamma_2}^{\mu\nu} + \delta_{\gamma_2\beta_2}\hat{x}_{\beta_1}^{\mu}\hat{\Phi}_{\alpha_1\alpha_2\gamma_1\gamma_2}^{\mu\nu} + \delta_{\gamma_1\beta_1}\delta_{\gamma_2\beta_2}\hat{\Phi}_{\alpha_1\alpha_2}^{\nu} + \delta_{\gamma_1\beta_2}\delta_{\gamma_2\beta_1}\hat{\Phi}_{\alpha_1\alpha_2}^{\nu} - \delta_{\alpha_1\alpha_2}\{\hat{x}_{\beta_1}^{\mu}\hat{\Phi}_{\beta_2\gamma_1\gamma_2}^{\nu} + \delta_{\gamma_2\beta_1}\hat{\Phi}_{\beta_2\gamma_1}^{\nu}\} + \delta_{\gamma_1\beta_1}\hat{\Phi}_{\beta_2\gamma_1\gamma_2}^{\nu})v_{\gamma_1}^{\nu}v_{\gamma_2}^{\nu}$

are not. In fact, the additional term in the second-order coefficient of equation (19) is proportional to the Cauchy stress tensor at the reference zero-strain state. Thus, these coefficients are related in the same way as the elastic constant tensor \mathbf{c} and the wave propagation tensor \mathbf{A} ($=\partial^2 f/\partial \mathbf{u}\partial \mathbf{u}$, see M84a, table 1).

As we shall be discussing the second-order elastic constants only, the first- and second-order terms are all that we require at present. We have noted that they have the required symmetries. It may readily be seen from the coefficients of equation (17) that all such coefficients will have the symmetry properties required for the elastic constants of any order. Another way of arriving at these symmetries is given in M84a, section 6 (see equation (6.4)).

If we expand the coefficients of equation (19) about the reference configuration \hat{x}^{μ} , just as we did for the series of equation (11), we obtain a double series in η and the particle displacements v^{μ} . In table 3, we list some of the corresponding perturbation terms, second order in the strain, while in table 2 we recognise the identity of the coefficients which are first order in the strain tensor \mathbf{u} or η . All these results are valid for the case of non-zero stress at the zero-strain reference state.

Note that the present treatment can be given completely in terms of η only, if desired. The discussion has been given in terms of \mathbf{u} as well, in order to compare the treatment with that of BH.

The close relationship of the coefficients of the linear terms in table 2 to the well known rotational invariance conditions on the lattice potential coefficients should also be noted (see e.g. Wallace 1972).

6. The kinetic perturbation terms

The kinetic contribution to the perturbation $w(x)$ of equation (7) is given by (see equation (16))

$$(1/2m_\mu)[1/(\mathbf{E}_3 + 2\boldsymbol{\eta}) - \mathbf{E}_3]_{\alpha\beta} p_\alpha^\mu p_\beta^\mu \quad (20)$$

where we use the generalized summation convention.

On converting to lattice notation and normal modes (see table 1 for notation), the kinetic contribution may be written

$$\begin{aligned} (\hbar/4)[2\boldsymbol{\eta} - (2\boldsymbol{\eta})^2 + \dots]_{\alpha\beta} \sum_{\lambda, \lambda_1} \left\{ \sum_{\kappa} e_\alpha(\kappa|\lambda) e_\beta(\kappa|\lambda_1) \right\} \sqrt{\omega_\lambda \omega_{\lambda_1}} \\ \times \Delta(\mathbf{q} + \mathbf{q}_1) B(\lambda) B(\lambda_1) \end{aligned} \quad (21)$$

where we have used the well known expression

$$p_\alpha(i\kappa) = (1/i) \left(\frac{\hbar m_\kappa}{2N_c} \right)^{1/2} \sum_{\lambda} \omega_\lambda^{1/2} e_\alpha(\kappa|\lambda) e^{i\mathbf{q} \cdot \mathbf{x}(\lambda)} B_\lambda \quad (22)$$

for the momentum components in terms of operators of the type B_λ , given in equation (2.3.56b) of Maradudin *et al* (1971).

It is of interest to compare the vertex function here with that of the potential energy perturbation term of item 3, table 4. It may be seen that the harmonic contribution to this potential term has a vertex function which differs from that above only in having the factor $\omega_\lambda^{3/2}/\omega_{\lambda_1}^{-1/2}$ instead of $\sqrt{\omega_\lambda \omega_{\lambda_1}}$. However, the traces of these two terms are identical.

We see that the kinetic perturbation contributes to all orders of strain, with the same vertex function for each order. It always has two phonon lines, no more and no less.

As an example, we shall consider the kinetic contribution to the perturbation terms which are linear in $\boldsymbol{\eta}$, as this is important in considering the internal strain.

We shall limit ourselves to the kinetic terms for which the two modes λ and λ_1 have the same branch. That is, we shall take $\lambda_1 = -\lambda = \bar{\lambda}$, in equation (21).

The vertex function of equation (21) is the same for all orders of $\boldsymbol{\eta}$, and, if we write the complete general term, we have

$$\frac{1}{2} \hbar \omega_\lambda (-2)^{p-1} (\boldsymbol{\eta}^p)_{\alpha\beta} f_{\alpha\beta}(\lambda) B_\lambda B_{\bar{\lambda}} \quad (23)$$

where

$$f_{\alpha\beta}(\lambda) = \sum_{\kappa} e_\alpha(\kappa|\lambda) e_\beta^*(\kappa|\lambda). \quad (24)$$

If we combine this linear strain term with the harmonic term in item 3, table 4, for this case of $\lambda_1 = \bar{\lambda}$, we obtain for the combination,

$$\eta_{\alpha\beta} (\hbar \omega_\lambda) f_{\alpha\beta}(\lambda) [a_\lambda a_{\bar{\lambda}}^\dagger + a_{\bar{\lambda}}^\dagger a_\lambda]. \quad (25)$$

The cubic anharmonic term of item 3, table 4, may be written

$$\frac{1}{2} \eta_{\alpha\beta} V_{(\alpha\beta)(-\lambda\bar{\lambda})} \{ [a_\lambda a_\lambda^\dagger + a_{\bar{\lambda}}^\dagger a_{\bar{\lambda}}] + [a_\lambda a_{\bar{\lambda}} + a_{\bar{\lambda}}^\dagger a_\lambda^\dagger] \}. \quad (26)$$

The first term in the braces commutes with the harmonic Hamiltonian, which we shall take as our zero-order Hamiltonian, and so it does not contribute to the internal strain. It is of interest that it contributes a temperature dependent term

$$\frac{1}{2} V_{(\alpha\beta)(-\lambda\bar{\lambda})} (2\bar{n}_\lambda + 1) \sim V_{(\alpha\beta)}(\dots) (kT/\hbar\omega_\lambda) \quad (27)$$

to $(v_c N_c) \Theta_{\alpha\beta}$, where $\Theta_{\alpha\beta}$ is the Cauchy stress tensor at the zero-strain reference state and \bar{n}_λ is the mean mode occupation number. The last expression in this equation is the high temperature value.

The other terms of item 3 plus the kinetic contribution are

$$\eta_{\alpha\beta} \hbar [(F_{\alpha\beta}(\lambda)/\omega_\lambda) + \omega_\lambda f_{\alpha\beta}(\lambda)] [a_\lambda a_{\bar{\lambda}} + a_\lambda^\dagger a_{\bar{\lambda}}^\dagger] \quad (28)$$

where

$$F_{\alpha\beta}(\lambda) = \Phi_{\alpha\beta}(-|\lambda\bar{\lambda}|) \quad (29)$$

(see item 2, table 5).

We shall apply this result in section 9, when we consider the elastic constants of α - β quartz. In the BH theory, the term in $f_{\alpha\beta}$ does not appear.

7. The elastic constants

Excellent accounts of diagram and Green's function techniques for evaluating the elastic constants have been given by Cowley (1963) and Barron and Klein (1974). We see that the potential energy contributions to the elastic constants are given by simple diagrams containing vertices having one strain line corresponding to, say, $u_{\alpha\beta}$ or two strain lines corresponding to $u_{\alpha_1\beta_1} u_{\alpha_2\beta_2}$, as shown in table 4.

In table 4, we compare the corresponding potential energy perturbation terms, obtained from a BH type of treatment and from the present treatment. The notation used is based on the BH notation, but owes something also to that of Maradudin *et al* (1971), and of Barron and Klein (1974). See tables 1 and 5, for the necessary definitions. In table 5, sufficient typical quantities are defined that the general notation may be readily inferred.

We see that a harmonic contribution occurs in each vertex function of the 3rd and 7th items of table 4 (see item 6 of table 5). Both these vertices make up the quasi-harmonic contributions to the elastic constants, for a crystal where every particle is at a centre of symmetry (see Barron and Klein 1974, p 424, figure 9). Thus for a harmonic model there will still apparently be contributions to the quasi-harmonic expressions for the elastic constants. Such a contribution also occurs in item 6, although it is a different transformation of the harmonic potential coefficients.

Concerning the index symmetries of these terms, since we may prove rigorously that the terms of the present treatment have the required symmetries, we may say, for example, that the BH term of item 7, say, may only have the required symmetries if the expression

$$2V_{(\alpha_1\beta_1)(\alpha_1\beta_1)}(-|\lambda\lambda_1|) + V_{(\alpha_2\beta_2)(\alpha_2\beta_2)}(\lambda\lambda_1) \quad (30)$$

found in item 7 table 4 of the present treatment, has the required symmetries independently of the BH quantity of item 7. There appears to be no proof of this or similar propositions.

8. The Born-Huang treatment

The BH treatment of the thermodynamics of a deformed crystal is given in chapter VI, beginning in section 39. In the first paragraph of section 40 it is stated that the Hamiltonian

Table 4. Comparison of potential energy perturbation terms. Strain lines have arrows, phonon lines do not. Note that the entries must be multiplied by N_c to obtain the perturbation term for the crystal.

Factors and vertices	Vertex functions	
	Born and Huang $\times N_c$	Present theory $\times N_c$
$u_{\alpha\beta}$ or $\eta_{\kappa\beta}$	First order in strain	
1 $\alpha\beta$	$V_{(\alpha\beta)}(-)$	$\left(x_{\beta}^{\alpha} \frac{\partial \Phi}{\partial x_{\alpha}^{\beta}}\right)_0$
2 $A(\lambda)\Delta(q)$ $\alpha\beta$	$V_{(\alpha\beta)}(- \lambda)$	$V_{(\alpha\beta)}(- \lambda)$
3 $A(\lambda)A(\lambda_1)$ $\Delta(q + q_1)$ $\alpha\beta$	$\frac{1}{2!} V_{(\alpha\beta)}(- \lambda\lambda_1)$	$\frac{1}{2!} [V_{(\alpha\beta)}(- \lambda\lambda_1) + 2V_{(\alpha\beta)}(\lambda\lambda_1)]$ $= \frac{1}{2!} [V_{(\alpha\beta)}(- \lambda\lambda_1)$ $+ \hbar\omega_{\lambda_1}^{3/2}\omega_{\lambda}^{-1/2}\sum_{\kappa} e_{\alpha}(\kappa \lambda)e_{\beta}(\kappa \lambda_1)]$
4 $A(\lambda)A(\lambda_1)A(\lambda_2)$ $\Delta(q + q_1 + q_2)$ $\alpha\beta$	$\frac{1}{3!} V_{(\alpha\beta)}(- \lambda\lambda_1\lambda_2)$	$\frac{1}{3!} [V_{(\alpha\beta)}(- \lambda\lambda_1\lambda_2) + 3V_{(\alpha\beta)}(\lambda\lambda_1\lambda_2)]$
$u_{\alpha_1\beta_1}u_{\alpha_2\beta_2}$	Second order in strain	
5 $\alpha_1\beta_1$ $\alpha_2\beta_2$	$\frac{1}{2!} V_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(---)$	$\frac{1}{2!} V_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(---)$
6 $A(\lambda)\Delta(q)$ $\alpha_1\beta_1$ $\alpha_2\beta_2$	$\frac{1}{2!} V_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(--- \lambda)$	$\frac{1}{2!} [V_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(--- \lambda) + 2V_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(- \lambda)]$
7 $A(\lambda)A(\lambda_1)\Delta(q + q_1)$ $\alpha_1\beta_1$ $\alpha_2\beta_2$	$\frac{1}{2!2!} V_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(--- \lambda\lambda_1)$	$\frac{1}{2!2!} [V_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(--- \lambda\lambda_1)$ $+ 4V_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(- \lambda\lambda_1)$ $+ 2V_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(\lambda\lambda_1)]$

of the deformed crystal is to be expressed in terms of internal coordinates and of macroscopic parameters describing the state of strain. The finite strain tensor elements $u_{\alpha\beta}$ are taken as the macroscopic parameters, in the sense that they describe an elastically strained lattice. The internal coordinates are taken to be the displacements

$$v \begin{pmatrix} l \\ \kappa \end{pmatrix}$$

in our notation v^{μ} , of the nuclei from the strained lattice, described in our notation by

Table 5. Definitions. In definitions 2b–6 the summation convention is to be used for any repeated pair of indices whatever, except for the pair labelled 0.

Expression	Definition
1 $T_\gamma(l\kappa, \lambda)$	$(\hbar/2\omega_\lambda N_c m_c)^{1/2} e^{iq \cdot r(l)} e_\gamma(\kappa \lambda)$
2a $V_{(\alpha_1\beta_1)\dots(\alpha_n\beta_n)}(-\dots\lambda_1\dots\lambda_n)$	$\Phi_{(\alpha_1\beta_1)\dots(\alpha_n\beta_n)}(-\dots\lambda_1\dots\lambda_n) \prod_{i=1}^n (\hbar/2\omega_{\lambda_i})^{1/2}$ in the BH notation
2b $V_{(\alpha\beta)}(\lambda\lambda_1)$	$\Phi_{\sigma\gamma_1} \begin{pmatrix} 0 & l_1 \\ \kappa & \kappa_1 \end{pmatrix} T_\beta(0\kappa, \lambda) T_{\gamma_1}(l_1\kappa_1, \lambda_1)$ $= \frac{1}{2} \hbar \omega_{\lambda_1}^{3/2} \omega_\lambda^{-1/2} e_\alpha(\kappa \lambda) e_\beta(\kappa \lambda_1) \Delta(\mathbf{q} + \mathbf{q}_1)$
3 $V_{(\alpha\beta)}(\lambda\lambda_1\lambda_2)$	$\Phi_{\sigma\gamma_1\gamma_2} \begin{pmatrix} 0 & l_1 & l_2 \\ \kappa & \kappa_1 & \kappa_2 \end{pmatrix} T_\beta(0\kappa, \lambda) T_{\gamma_1}(l_1\kappa_1, \lambda_1) T_{\gamma_2}(l_2\kappa_2, \lambda_2)$
4 $V_{(\alpha\beta)}(- \lambda\lambda_1)$	$\Phi_{\sigma\gamma_1\gamma_2} \begin{pmatrix} 0 & l_1 & l_2 \\ \kappa & \kappa_1 & \kappa_2 \end{pmatrix} x_\beta \begin{pmatrix} 0 \\ \kappa \end{pmatrix} T_{\gamma_1}(l_1\kappa_1, \lambda) T_{\gamma_2}(l_2\kappa_2, \lambda_1)$
5 $V_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(- \lambda)$	$\Phi_{\sigma_1\sigma_2\gamma} \begin{pmatrix} 0 & l_1 & l_2 \\ \kappa & \kappa_1 & \kappa_2 \end{pmatrix} x_{\beta_1} \begin{pmatrix} 0 \\ \kappa \end{pmatrix} x_{\beta_2} \begin{pmatrix} l_1 \\ \kappa_1 \end{pmatrix} T_\gamma(l_2\kappa_2, \lambda)$
6 $V_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(\lambda\lambda_1)$	$\Phi_{\sigma_1\sigma_2} \begin{pmatrix} 0 & l_1 \\ \kappa & \kappa_1 \end{pmatrix} T_{\beta_1}(0\kappa, \lambda) T_{\beta_2}(l_1\kappa_1, \lambda_1)$

the configuration $\mathbf{D}\dot{\mathbf{x}}^\mu$. This lattice is obtained by deforming the zero-strain lattice $\dot{\mathbf{x}}^\mu$ homogeneously and without internal strain.

We shall show that this basic description is not adequate to describe a deformed crystal. In fact, we shall show that this description fails a simple test required by the rotational invariance property of the Hamiltonian of the system.

To do this we must first obtain from the BH description an expression for the elastic potential energy, as follows. By elastic potential energy we mean the change in the potential energy function $\Phi(\dot{\mathbf{x}}^\mu + \mathbf{v}^\mu)$ due to the application of the above deformation to the lattice $\dot{\mathbf{x}}^\mu$.

Consider the quantity $\delta\Phi^{\text{def}}$ of their equation (40.4). This may be seen to be given by

$$\delta\Phi^{\text{def}} = \Phi(\mathbf{D}\dot{\mathbf{x}}^\mu + \mathbf{v}^\mu) - \Phi(\mathbf{D}\dot{\mathbf{x}}^\mu) = \Phi(\dot{x}_\alpha^\mu + u_{\alpha\beta} \dot{x}_\beta^\mu + v_\alpha^\mu) - \Phi(\dot{x}_\alpha^\mu + u_{\alpha\beta} \dot{x}_\beta^\mu). \quad (31)$$

That is, as stated explicitly in BH section 39 in the paragraph immediately before equation (39.19), $\delta\Phi^{\text{def}}$ is the potential energy of the configuration $\mathbf{D}\dot{\mathbf{x}}^\mu + \mathbf{v}^\mu$ relative to that of the homogeneously deformed lattice (without internal strain). On this basis we may accept equation (31) as a correct description of the BH expression $\delta\Phi^{\text{def}}$. However, it may be felt desirable to reconcile this description of equation (31) with the explicit

expression for $\delta\Phi^{\text{def}}$ given in BH equation (40.4). This may be done readily by expanding both terms on the right hand side in powers of the two types of displacements, $u_{\alpha\beta}\hat{x}_{\beta}^{\mu}$ and v_{α}^{μ} , about the zero-strain reference configuration \hat{x}^{μ} . Then, in order to compare the result with the expression in BH equation (40.4), it is necessary to carry out the well known transformation to normal mode amplitudes Q .

We should note further that $\delta\Phi^{\text{def}}$ contains terms independent of the $u_{\alpha\beta}$ which add up to

$$\Phi(\hat{x}^{\mu} + v^{\mu}) - \Phi(\hat{x}^{\mu}). \quad (32)$$

This term is clearly not part of the elastic potential energy which should vanish as the strain tensor vanishes. In fact, it is the limit of $\delta\Phi^{\text{def}}$ when the strain tensor is zero.

Taking this into account, we may write equation (31) as

$$\begin{aligned} \delta\Phi^{\text{def}} = & [\Phi(\mathbf{D}\hat{x}^{\mu} + v^{\mu}) - \Phi(\hat{x}^{\mu} + v^{\mu})] + [\Phi(\hat{x}^{\mu} + v^{\mu}) - \Phi(\hat{x}^{\mu})] \\ & - [\Phi(\mathbf{D}\hat{x}^{\mu}) - \Phi(\hat{x}^{\mu})]. \end{aligned} \quad (33)$$

On rearrangement, this equation may be written as

$$\delta\Phi^{\text{def}} + [\Phi(\mathbf{D}\hat{x}^{\mu}) - \Phi(\hat{x}^{\mu})] - [\Phi(\hat{x}^{\mu} + v^{\mu}) - \Phi(\hat{x}^{\mu})] = \Phi(\mathbf{D}\hat{x}^{\mu} + v^{\mu}) - \Phi(\hat{x}^{\mu} + v^{\mu}) \quad (34)$$

where the total elastic potential energy of the BH treatment is given by the left hand side of this equation. That is, to obtain this quantity, we have added to $\delta\Phi^{\text{def}}$ the potential energy gained by deforming the lattice (from \hat{x}^{μ} to $\mathbf{D}\hat{x}^{\mu}$), without internal strain, and this is the second term of the left hand side of the above equation. This is the term to which BH approximated by using the well known square brackets expression. We must further subtract from $\delta\Phi^{\text{def}}$ its limiting value when the strain tensor is zero. This is the third term on the left hand side.

Thus, this expression for the elastic energy vanishes with \mathbf{u} . However—and this provides the test—, it should also vanish if \mathbf{D} is a proper orthogonal matrix \mathbf{O} representing an arbitrary rigid rotation. Thus we must have, from the right hand side of equation (34),

$$\Phi(\mathbf{O}\hat{x}^{\mu} + v^{\mu}) = \Phi(\hat{x}^{\mu} + v^{\mu}) \quad (35)$$

or

$$\Phi(\hat{x}^{\mu} + \mathbf{O}^{-1}v^{\mu}) = \Phi(\hat{x}^{\mu} + v^{\mu}). \quad (36)$$

It is well known that these equations cannot be generally true.

We must therefore conclude that the BH basic description of a deformed crystal is not a rotationally invariant description and so is not correct. We note that, in this respect, the present treatment is consistently rotationally invariant.

The differences in the strain energy perturbation terms of the two treatments are due to

- (i) the presence of the kinetic term of section 6, in the present treatment; and to
- (ii) the present treatment having extra potential energy perturbation terms equal to

$$\Phi(\mathbf{D}\hat{x}^{\mu}) - \Phi(\mathbf{D}\hat{x}^{\mu} + v^{\mu}) = \Phi(\hat{x}^{\mu} + \mathbf{u}\hat{x}^{\mu}) - \Phi(\hat{x}^{\mu} + \mathbf{u}\hat{x}^{\mu} + v^{\mu}).$$

The BH expansion of the potential energy perturbation terms in powers of \mathbf{u} may thus be obtained by replacing the factor $(x_{\beta}^{\mu})_n$ in the right hand side of equation (13) by the factor $(\hat{x}_{\beta}^{\mu})_n$. Thus each coefficient of the BH expansion is the leading term only of the corresponding coefficient of the present treatment (see section 4 and table 2).

9. The elastic constants of β -quartz

In discussing the elastic constants of β -quartz near the α - β quartz transition, Axe and Shirane (1970), addressed the problem of explaining the behaviour of these quantities in the face of the fact that the soft mode appeared to be a B_1 optic mode. The problem arose from the fact that this mode does not transform under the crystal symmetry group like any part of a second rank tensor, which is a requirement for it to contribute to the internal strain part of the elastic constants (see Miller and Axe 1967).

Axe and Shirane introduced an anharmonic contribution to the internal strain part of the elastic constants, and were able to give a satisfactory explanation of their behaviour near the transition temperature. This contribution was based on the BH treatment of a deformed crystal and was of the form

$$c'_{ab\alpha\beta} = (C/N_c v_c) [F_{ab}(\lambda) F_{\alpha\beta}(\bar{\lambda})] (kT/\omega_\lambda^4) \quad (37)$$

where C is a constant. The tensor is defined as in equation (29). It is readily seen that this tensor is based on the diagram of item 3 of table 4, where the correct factor may be found.

From equation (28), we see that in equation (37) the tensors should be replaced by, for example,

$$F_{ab}(\lambda) + \omega_\lambda^2 f_{ab}(\lambda). \quad (38)$$

On substituting these corrected tensors in equation (37), we must write

$$c'_{ab\alpha\beta} = -(C/N_c v_c) [F_{ab} \bar{F}_{\alpha\beta} / \omega_\lambda^4 + (F_{ab} \bar{f}_{\alpha\beta} + \bar{F}_{\alpha\beta} f_{ab}) / \omega_\lambda^2 + f_{ab} \bar{f}_{\alpha\beta}] kT \quad (39)$$

where, for example, $\bar{F}_{\alpha\beta} = F_{\alpha\beta}(\bar{\lambda})$ —abbreviations which should not create confusion.

Axe and Shirane integrated their term over modes on the same branch as the B_1 optic soft mode by using an approximate empirical expression for the frequency as a function of q for q directed close to the c -axis. Their result was a $(1/\omega^2(0j)) \sim (T - T_c)^{-1}$ divergence in the elastic constants—a result which gave good agreement with experiment. If we follow the same integration method for the expression in equation (39) then from the middle term of this equation we find a logarithmic divergence of the form

$$\ln[(\omega^2(0j) + \alpha q_{\max}^2) / \omega^2(0j)]$$

where q_{\max} is a suitably chosen maximum value for $\sqrt{q_x^2 + q_y^2}$ in the empirically chosen expression for $\omega^2(qj)$ as a function of q near the c -axis, and the parameter α occurs in this latter expression.

This new divergence is, of course, not as strong as the Axe and Shirane divergence. However, it will be of some importance in the behaviour of the elastic constants as the transition temperature is approached. The extra terms of equation (39) may also be of interest for some materials where the tensor \mathbf{F} or some of its elements are zero. We should note, however, that, for a rotationally invariant vibrational model, the cubic anharmonic term may not vanish except for the simple rotationally invariant harmonic model, discussed in M85b. Thus, if the tensor \mathbf{F} is small or zero for a material, this indicates that its behaviour may be approximated by such a harmonic model.

Acknowledgments

I am very grateful for some useful discussions with Dr C N Hooker and Professor G E Stedman.

References

- Axe J D and Shirane G 1970 *Phys. Rev. B* **1** 342-8
- Barron T H K and Klein M L 1974 *Dynamical Properties of Solids* vol 1 (Amsterdam: North-Holland) pp 391-449
- Born M and Huang K 1954 *The Dynamical Theory of Crystal Lattices* (Oxford: OUP)
- Cowley R A 1963 *Adv. Phys.* **12** 421-79
- Maradudin A A, Montroll E W, Weiss G H and Ipatova I P 1971 *Solid State Physics* Suppl 3 (New York: Academic)
- McLellan A G 1980 *The Classical Thermodynamics of Deformable Materials* (Cambridge: Cambridge University Press)
- 1984a *J. Phys. C: Solid State Phys.* **17** 1-12
- 1984b *J. Phys. C: Solid State Phys.* **17** 2999-3007
- 1985a *J. Phys. C: Solid State Phys.* **18** 1553-67
- 1985b *J. Phys. C: Solid State Phys.* **18** 5511-30
- 1988 *J. Phys. C: Solid State Phys.* **21** 1177-90
- Miller P B and Axe J D 1967 *Phys. Rev.* **163** 924-6
- Nelson D F 1988 *Phys. Rev. Lett.* **60** 608-10
- Pleiner H and Brand H R 1988 *Phys. Rev. Lett.* **61** 766
- Wallace D C 1972 *Thermodynamics of Crystals* (New York: Wiley)