

Thermoelasticity of Stressed Materials and Comparison of Various Elastic Constants*

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A general theory of the thermoelasticity of stressed materials is presented. The theory is based on the geometry of strain, Newton's second law of motion, the first and second laws of thermodynamics, and the invariance of the internal energy and Helmholtz free energy with respect to an arbitrary finite rigid rotation of the material. Three different sets of physically significant thermoelastic coefficients are discussed. These are (a) the second-order elastic constants, which contain the rotational invariance conditions and always have the Voigt symmetry, (b) the equation-of-motion coefficients, which govern small-displacement wave propagation and have Voigt symmetry only when the stress vanishes, and (c) the coefficients which relate the variation of stress to the variation of strain from the initial (stressed) configuration. Relations between these sets of coefficients are presented for the case of arbitrary initial stress, and also for initial isotropic pressure. In addition, these second-order elastic coefficients for a stressed material are expressed as series in the second-, third-, and fourth-order elastic constants evaluated at zero stress; the expansion parameters in these series are the parameters which measure the strain from the state of zero stress to the stressed state. All of the general relations are illustrated and tabulated for the example of a cubic material under isotropic pressure. A detailed comparison of the present results with previous theories is given. The two types of elastic constants defined by Fuchs and Voigt are generalized to conditions of initial stress, and compared with the three basic sets of elastic coefficients of the present paper. Finally some comments are made regarding the interpretation of thermoelastic measurements on crystals in terms of static and dynamic calculations based on atomic models.

I. INTRODUCTION

THIS paper presents a general theory of thermoelasticity of stressed materials. The need for such a theory arises from the desire to understand materials from the atomic point of view. For if the atomic interactions are presumed to be known, one can calculate mechanical properties of the material such as the energy levels. This can be done for arbitrary configuration of the atoms in the material, provided only that the configuration satisfies appropriate mechanical equilibrium, invariance, and boundary conditions. Then with the aid of statistical mechanics one can calculate thermodynamic properties such as the Helmholtz free energy; in this way the free energy is naturally a function of configuration and temperature. Through the use of thermodynamic relations involving the free energy, one can finally calculate other thermodynamic quantities for comparison with measurements. In the case of thermoelastic measurements, such as sound velocities in stressed crystals, one therefore needs thermodynamic relations between the elastic constants and the free energy which are valid at arbitrary configuration, or equivalently, at arbitrary stress.

A theory of thermoelasticity for small strains from configurations of zero stress was discussed by Voigt.¹ In addition, many of the results which we find in this paper, for thermoelasticity of stressed materials, have been given previously, but in widely separated places and in many different forms.²⁻¹⁰ We refer to the previous work at appropriate places in the text below.

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¹ W. Voigt, *Lehrbuch der Kristallphysik* (Teubner, Berlin, 1928).

² F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (John Wiley & Sons, Inc., New York, 1951).

Although our motivation originates in the atomic description of materials, the theory to be presented is entirely thermodynamic. We consider a material whose equilibrium states depend only on the configuration, denoted by \mathbf{x} , and the temperature T or the entropy per unit mass S . The traditional state functions are the Helmholtz free energy per unit mass F , and the internal energy per unit mass U . It is convenient to work with functions per unit mass in elasticity theory because mass is conserved, while volume is not generally conserved, during elastic strains. We take the customary functional dependence of U and F :

$$\begin{aligned} U &= U(\mathbf{x}, S), \\ F &= F(\mathbf{x}, T). \end{aligned} \quad (1.1)$$

Thus, the state function F is used when the independent variables are chosen to be \mathbf{x} and T ; in this case the dependent variables are S and the stresses. On the other hand, the function U is appropriate for describing processes in which the independent variables are \mathbf{x} and S , while the dependent variables are T and the stresses. Finally, we consider only states which are obtained by *elastic* deformation from states of zero stress. The requirement that deformations be elastic insures that the state functions are unique (single-valued) functions

³ F. Birch, *Phys. Rev.* **71**, 809 (1947).

⁴ K. Huang, *Proc. Roy. Soc. (London)* **A203**, 178 (1950).

⁵ R. A. Toupin and B. Bernstein, *J. Acoust. Soc. Am.* **33**, 216 (1961).

⁶ A. E. Green, *Proc. Roy. Soc. (London)* **A266**, 1 (1962).

⁷ C. Truesdell and W. Noll, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1965), Vol. III/3, p. 1.

⁸ D. C. Wallace, *Rev. Mod. Phys.* **37**, 57 (1965).

⁹ R. N. Thurston, *J. Acoust. Soc. Am.* **37**, 348 (1965).

¹⁰ T. H. K. Barron and M. L. Klein, *Proc. Phys. Soc. (London)* **85**, 523 (1965).

of the independent variables and hence that reversible thermodynamics may be applied.

The theory is based on the geometry of strain, and on three physical propositions, namely Newton's second law of motion, the first and second laws of thermodynamics, and the rotational invariance of the state functions. In Sec. II we study three physically significant sets of elastic constants for stressed materials: (a) those which contain the rotational invariance requirements, (b) those which govern dynamic thermoelastic motion (wave-propagation coefficients), and (c) those which govern static thermoelastic motion (stress-strain coefficients). These second-order elastic coefficients for a stressed material are expanded in terms of the second-, third-, and fourth-order constants evaluated at zero stress in Sec. III. The various types of coefficients are tabulated and compared in Sec. IV for a cubic material under isotropic pressure. In Sec. V we compare our results with previous theories, including those of Huang, Birch, Fuchs, and Voigt.

II. THERMOELASTICITY OF STRESSED MATERIALS

Basic Equations

We wish to study the thermoelastic motion of a material about the initial configuration. The initial configuration corresponds to applied uniform stress, and hence corresponds to homogeneous elastic strain from a configuration of zero stress. The position of a material particle in the initial configuration is \mathbf{X} , and the position of the same material particle in the final configuration is \mathbf{x} . If the final configuration is obtained by applying a small additional uniform stress, then the strain from \mathbf{X} to \mathbf{x} is homogeneous, i.e., uniform throughout the material. If the final configuration corresponds to a wave propagating in the material, the strain from \mathbf{X} to \mathbf{x} is nonuniform in space and in the time t , and the basic equations derived below are to be considered as equations local in \mathbf{X} and t .

We measure the deformation from \mathbf{X} to \mathbf{x} by either of two different sets of nine independent deformation parameters.

(a) The transformation coefficients α_{ij} , used mostly by classical elasticity theories:

$$x_i = x_i(\mathbf{X}, t); \alpha_{ij} = \partial x_i / \partial X_j. \quad (2.1)$$

(b) The displacement gradients u_{ij} , used mostly by physicists:

$$x_i - X_i = u_i(\mathbf{X}, t); u_{ij} = \partial u_i / \partial X_j. \quad (2.2)$$

The subscripts i, j, \dots indicate Cartesian components and each goes over three values. We always use the Einstein summation convention, implying a sum over repeated indices. The two sets of coefficients are obviously related by

$$\alpha_{ij} = \delta_{ij} + u_{ij}, \quad (2.3)$$

where δ_{ij} is the Kronecker delta. The symmetric finite strain parameters of Murnaghan,² also called Lagrangian strain parameters, are

$$\eta_{ij} = \frac{1}{2}(\alpha_{ki}\alpha_{kj} - \delta_{ij}) = \frac{1}{2}(u_{ij} + u_{ji} + u_{ki}u_{kj}). \quad (2.4)$$

We treat the η_{ij} as nine independent variables, but always make sure the calculations are consistent with $\eta_{ij} = \eta_{ji}$. The density of the material is denoted by $\rho(\mathbf{x})$ or $\rho(\mathbf{X})$, with the abbreviations

$$\rho = \rho(\mathbf{x}), \rho_1 = \rho(\mathbf{X}). \quad (2.5)$$

The symmetric Cauchy stress tensor is

$$T_{ij} = T_{ji}. \quad (2.6)$$

The theory is strongly based on the physical requirement that the internal energy or the Helmholtz free energy should be invariant with respect to arbitrary finite rigid rotation of the material. Thus, U or F depends only on the *relative* positions of all the material particles. Since the relative positions in the configuration \mathbf{x} are completely specified by the initial configuration \mathbf{X} and the η_{ij} , then U and F depend on \mathbf{x} only through \mathbf{X} and η_{ij} :

$$\begin{aligned} U(\mathbf{x}, S) &= U(\mathbf{X}, \eta_{ij}, S), \\ F(\mathbf{x}, T) &= F(\mathbf{X}, \eta_{ij}, T). \end{aligned} \quad (2.7)$$

It should be emphasized that this dependence is necessary and sufficient to insure rotational invariance of U and F , for any initial configuration \mathbf{X} . As an abbreviation, when partial derivatives of the state functions are written, we omit explicit statement of which variables are held constant, with the understanding that all other variables are fixed. For example, $(\partial U / \partial \eta_{ij})$ implies \mathbf{X} , S , and all other η_{kl} are held constant.

The three basic equations of the theory can now be written.

(a) The equation of continuity, or conservation of mass, is based on the geometry of strain, and is well known^{2,7}:

$$\rho_1 / \rho = J = \det[\alpha_{ij}]. \quad (2.8)$$

Here, J is the Jacobian of the transformation from \mathbf{X} to \mathbf{x} , and is the determinant of the transformation matrix.

(b) Equations for the dependent variables are conveniently expressed as follows. From the internal energy,

$$\begin{aligned} T &= (\partial U / \partial S), \\ T_{ij} &= \rho \alpha_{ik} \alpha_{jl} (\partial U / \partial \eta_{kl}). \end{aligned} \quad (2.9)$$

From the Helmholtz free energy,

$$\begin{aligned} S &= -(\partial F / \partial T), \\ T_{ij} &= \rho \alpha_{ik} \alpha_{jl} (\partial F / \partial \eta_{kl}). \end{aligned} \quad (2.10)$$

Both sides of (2.9) and (2.10) are evaluated at \mathbf{x} , with the deformation parameters measured from the arbitrary

trary initial configuration \mathbf{X} . Derivations of these equations are given in the Appendix; the rotational invariance of U and F is used in the derivations.

(c) The equation of motion in the absence of body forces is also well known, and is an expression of Newton's second law of motion.^{2,7}

$$\rho \ddot{x}_i = \partial T_{ij} / \partial x_j. \tag{2.11}$$

Here \dot{x}_i is the second time derivative of x_i , and if the motion is adiabatic or isothermal the right-hand side derivative is evaluated at constant S or T , respectively.

Since the deformation from \mathbf{X} to \mathbf{x} is considered small (but not infinitesimal), it is convenient to expand the state functions about \mathbf{X} .

$$\begin{aligned} \rho_1 U(\mathbf{X}, \eta_{ij}, S) \\ = \rho_1 U(\mathbf{X}, 0, S) + C^S_{ij} \eta_{ij} + \frac{1}{2} C^S_{ijkl} \eta_{ij} \eta_{kl} + \dots, \end{aligned} \tag{2.12}$$

$$\begin{aligned} \rho_1 F(\mathbf{X}, \eta_{ij}, T) \\ = \rho_1 F(\mathbf{X}, 0, T) + C^T_{ij} \eta_{ij} + \frac{1}{2} C^T_{ijkl} \eta_{ij} \eta_{kl} + \dots. \end{aligned} \tag{2.13}$$

By definition, the C coefficients are derivatives of $\rho_1 U$ or $\rho_1 F$, evaluated at \mathbf{X} , and also these coefficients have the complete Voigt symmetry.

$$\begin{aligned} C^S_{ij} &= \rho_1 (\partial U / \partial \eta_{ij}), \\ C^T_{ij} &= \rho_1 (\partial F / \partial \eta_{ij}), \\ C^S_{ijkl} &= \rho_1 (\partial^2 U / \partial \eta_{ij} \partial \eta_{kl}), \\ C^T_{ijkl} &= \rho_1 (\partial^2 F / \partial \eta_{ij} \partial \eta_{kl}), \end{aligned} \tag{2.14}$$

where all derivatives are evaluated at \mathbf{X} . The Voigt symmetry follows from (2.14) and the symmetry of η_{ij} ; for constant S or constant T coefficients this is

$$\begin{aligned} C_{ij} &= C_{ji}, \\ C_{ijkl} &= C_{klij} = C_{jikl} = \dots. \end{aligned} \tag{2.15}$$

We can now interpret the C coefficients. At $\mathbf{x} = \mathbf{X}$, we have $\rho = \rho_1$ and $\alpha_{ij} = \delta_{ij}$, so from (2.9) and (2.10)

$$T_{ij}(\mathbf{X}) = \rho_1 (\partial U / \partial \eta_{ij}) = \rho_1 (\partial F / \partial \eta_{ij}). \tag{2.16}$$

Thus, the leading coefficient in each of the expansions (2.12) and (2.13) is just the stress in the initial configuration

$$T_{ij}(\mathbf{X}) = C^S_{ij} = C^T_{ij}. \tag{2.17}$$

Also, C^S_{ijkl} and C^T_{ijkl} are the usual second-order adiabatic and isothermal elastic constants, respectively, evaluated at \mathbf{X} .

Equation of Motion for Plane Waves

We consider small motions about the initial configuration \mathbf{X} , and linearize the equation of motion (2.11) by keeping only the leading terms in the displacements. The calculation is adequately illustrated by taking the case of adiabatic motion. From (2.8) and

(2.9), the stress may be written

$$T_{ij} = (\rho_1 / J) \alpha_{ik} \alpha_{jl} (\partial U / \partial \eta_{kl}). \tag{2.18}$$

The derivative on the right of (2.11) is simplified by the identity of Euler, Piola, and Jacobi [Truesdell and Toupin,¹¹ Eq. (17.9)]:

$$\frac{\partial}{\partial x_j} \frac{\alpha_{jl}}{J} = 0. \tag{2.19}$$

Then from (2.18) and (2.19), with the definition (2.1) of α_{jl} ,

$$\frac{\partial T_{ij}}{\partial x_j} = \frac{\rho_1}{J} \frac{\partial x_j}{\partial X_l} \frac{\partial}{\partial x_j} \left[\alpha_{ik} \frac{\partial U}{\partial \eta_{kl}} \right] = \frac{\rho_1}{J} \frac{\partial}{\partial X_l} \left[\alpha_{ik} \frac{\partial U}{\partial \eta_{kl}} \right]. \tag{2.20}$$

Also from (2.12) we can write

$$\begin{aligned} \rho_1 (\partial U / \partial \eta_{kl}) &= C^S_{kl} + C^S_{klmn} \eta_{mn} + \dots, \\ &= C^S_{kl} + \frac{1}{2} C^S_{klmn} (\alpha_{pm} \alpha_{pn} - \delta_{mn}) + \dots. \end{aligned} \tag{2.21}$$

The leading term is obtained by carrying out the differentiation $\partial / \partial X_l$ in (2.20), with the aid of (2.21), and evaluating at \mathbf{X} . Since at \mathbf{X} we have $J = 1$, $\eta_{ij} = 0$, $\alpha_{ij} = \delta_{ij}$, the constant entropy stress derivative is

$$(\partial T_{ij} / \partial x_j) = [C^S_{jl} \delta_{ik} + C^S_{ijkl}] (\partial^2 x_k / \partial X_j \partial X_l). \tag{2.22}$$

For the isothermal stress derivative, the C coefficients in (2.22) are replaced by constant T coefficients. Let us introduce the coefficients S_{ijkl} for the square bracket in (2.22) and write the equation of motion for *either* adiabatic or isothermal motion, with all coefficients evaluated at \mathbf{X} .

$$\rho_1 \ddot{x}_i = S_{ijkl} (\partial^2 x_k / \partial X_j \partial X_l), \tag{2.23}$$

where for adiabatic processes one uses

$$S^S_{ijkl} = T_{jl} \delta_{ik} + C^S_{ijkl}, \tag{2.24}$$

and for isothermal processes one uses

$$S^T_{ijkl} = T_{jl} \delta_{ik} + C^T_{ijkl}. \tag{2.25}$$

The stresses have been introduced by means of (2.17).

The equation of motion for a stressed material was obtained in the form (2.23) by Huang.⁴ His calculation was for *mechanical* rather than *thermoelastic* motion, since it was based on a classical Lagrangian; hence the S coefficients of (2.24) and (2.25) are thermoelastic generalizations of the S coefficients of Huang. Although Huang was not able to provide the correct interpretation of his S coefficients, in terms of stresses and elastic constants, the complete interpretation corresponding to (2.24) and (2.25) has been worked out among several

¹¹ C. Truesdell and R. A. Toupin, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1960), Vol. III/1, p. 226.

papers.^{5,6,8-10} Note that only when T_{ij} vanishes do the S_{ijkl} have complete Voigt symmetry.

For a plane wave the displacement may be written

$$\mathbf{x} - \mathbf{X} = \mathbf{u} \exp[i(\mathbf{k} \cdot \mathbf{X} - \omega t)], \quad (2.26)$$

where \mathbf{u} denotes the magnitude and direction of the displacement, \mathbf{k} is the wave vector, ω the circular frequency, and t the time. It is convenient to define $\boldsymbol{\kappa}$ as a unit vector in the direction of propagation and v as the wave velocity.

$$\boldsymbol{\kappa} = \mathbf{k}/|\mathbf{k}|; \quad \omega = v|\mathbf{k}|. \quad (2.27)$$

With the displacement (2.26) the equation of motion then becomes

$$\rho v^2 u_i = S_{ijk\ell\kappa_j\kappa_\ell} u_k. \quad (2.28)$$

Reference to the initial configuration has been omitted in (2.28) since that equation is valid for any initial configuration. Therefore, (2.28) can be used to interpret adiabatic or isothermal plane-wave propagation, with ρ and S_{ijkl} evaluated in the (arbitrary) initial configuration. Because of the sum over j and ℓ in (2.28), only the symmetric combination ($S_{ijkl} + S_{ilkj}$) is observed in wave-propagation experiments.

Stress-Strain Relations and Compressibility

We wish to derive a relation between the variation of stress and the variation of strain from the initial configuration. Here it is convenient to use infinitesimal strain parameters in order to facilitate a direct comparison with previous calculations which have been carried out for special cases (Sec. V below), and also to provide a simple derivation of the compressibility. Again the calculation is illustrated by taking adiabatic variations in particular. From (2.18) and (2.21) the stress components may be written

$$T_{ij} = J^{-1} \alpha_{ik} \alpha_{jl} [C^{ijkl} + \frac{1}{2} C^{klmn} (\alpha_{pm} \alpha_{pn} - \delta_{mn}) + \dots]. \quad (2.29)$$

The first step is to calculate $(\partial T_{ij}/\partial \alpha_{rs})$ for an adiabatic variation. We can use Jacobi's identity [Ref. 11, Eq. (17.8)]:

$$(\partial J/\partial \alpha_{rs}) = (\boldsymbol{\alpha}^{-1})_{rs} J, \quad (2.30)$$

where $\boldsymbol{\alpha}^{-1}$ is the matrix inverse to $\boldsymbol{\alpha}$. The differentiation of (2.29) is straightforward; evaluated at \mathbf{X} the result is

$$(\partial T_{ij}/\partial \alpha_{rs}) = (T_{is} \delta_{jr} + T_{js} \delta_{ir} - T_{ij} \delta_{rs}) + C^{ijrs}. \quad (2.31)$$

The stresses have been introduced by means of (2.17); note that each side of (2.31) is symmetric in i, j .

The symmetric and antisymmetric infinitesimal displacement parameters, ϵ_{ij} measuring pure strain and ω_{ij} measuring pure rotation, are defined as follows:

$$\epsilon_{ij} = \frac{1}{2} (u_{ij} + u_{ji}) = \frac{1}{2} (\alpha_{ij} + \alpha_{ji} - 2\delta_{ij}), \quad (2.32)$$

$$\omega_{ij} = \frac{1}{2} (u_{ij} - u_{ji}) = \frac{1}{2} (\alpha_{ij} - \alpha_{ji}). \quad (2.33)$$

Solving for α_{ij} gives the following relations:

$$\begin{aligned} \alpha_{ij} &= \frac{1}{2} (\epsilon_{ij} + \epsilon_{ji} + \omega_{ij} - \omega_{ji} + 2\delta_{ij}); \\ (\partial \alpha_{ij}/\partial \epsilon_{mn}) &= \frac{1}{2} (\delta_{im} \delta_{jn} + \delta_{jm} \delta_{in}); \\ (\partial \alpha_{ij}/\partial \omega_{mn}) &= \frac{1}{2} (\delta_{im} \delta_{jn} - \delta_{jm} \delta_{in}). \end{aligned} \quad (2.34)$$

Now the derivatives of T_{ij} can be transformed by chain rule differentiation; for example,

$$(\partial T_{ij}/\partial \epsilon_{kl}) = (\partial T_{ij}/\partial \alpha_{rs}) (\partial \alpha_{rs}/\partial \epsilon_{kl}).$$

The results are summarized as follows for adiabatic variations:

$$(\partial T_{ij}/\partial \epsilon_{kl}) = B^S_{ijkl}; \quad (2.35)$$

$$\begin{aligned} B^S_{ijkl} &= \frac{1}{2} (T_{ik} \delta_{jl} + T_{il} \delta_{jk} + T_{jk} \delta_{il} \\ &\quad + T_{jl} \delta_{ik} - 2T_{ij} \delta_{kl}) + C^S_{ijkl}; \end{aligned} \quad (2.36)$$

$$(\partial T_{ij}/\partial \omega_{kl}) = \frac{1}{2} (T_{il} \delta_{jk} - T_{ik} \delta_{jl} + T_{jl} \delta_{ik} - T_{jk} \delta_{il}). \quad (2.37)$$

The symbol B_{ijkl} is introduced because these coefficients are complete generalizations of the coefficients defined by Birch³ for the particular case of isothermal variations for a cubic material under isotropic pressure (see Sec. V). It follows from the derivation that for isothermal variations, B^S_{ijkl} is replaced by B^T_{ijkl} in (2.35), and B^T_{ijkl} is defined by (2.36) with C^S_{ijkl} replaced by C^T_{ijkl} . It also follows that these equations are valid for any initial configuration. The result (2.36) displays the expected symmetry of B_{ijkl} in i, j and in k, l , although the B coefficients do not have complete Voigt symmetry since $B_{ijkl} \neq B_{klij}$ in general. According to (2.37), $(\partial T_{ij}/\partial \omega_{kl})$ has the expected symmetry in i, j and antisymmetry in k, l . In addition, (2.37) shows that even for infinitesimal elastic deformations from \mathbf{X} , the stress depends on the rotation as well as on the pure strain. This is to be expected, since if the material undergoes a pure rotation, with no pure strain, then the stress must also be rotated to maintain zero pure strain. This circumstance has been pointed out in Ref. 7, p. 250. There are, of course, special cases (e.g., isotropic pressure) when the stress does not depend on the rotation.

The relations (2.35)–(2.37) are just the differential form of Hooke's law. In other words, a Taylor-series expansion of the stress about the initial value may be written, for adiabatic or isothermal variations,

$$\begin{aligned} T_{ij}(\mathbf{x}, S) &= T_{ij}(\mathbf{X}, S) + B^S_{ijkl} \epsilon_{kl} \\ &\quad + (\partial T_{ij}/\partial \omega_{kl}) \omega_{kl} + \dots, \end{aligned} \quad (2.38)$$

$$\begin{aligned} T_{ij}(\mathbf{x}, T) &= T_{ij}(\mathbf{X}, T) + B^T_{ijkl} \epsilon_{kl} \\ &\quad + (\partial T_{ij}/\partial \omega_{kl}) \omega_{kl} + \dots, \end{aligned} \quad (2.39)$$

where $+\dots$ indicates terms of second and higher orders in the strain parameters. Part of (2.38) and (2.39) has been given by Barron and Klein.¹⁰

It is now quite simple to calculate the compressibility evaluated at the initial configuration. The adiabatic

compressibility, for example, is given by

$$k_S = -(1/V)(\partial V/\partial P)_S, \tag{2.40}$$

where V is the volume of the material and P is the pressure. In view of (2.8),

$$J = \rho(\mathbf{X})/\rho(\mathbf{x}) = V(\mathbf{x})/V(\mathbf{X}), \tag{2.41}$$

so k_S evaluated at \mathbf{X} is just

$$k_S = -(\partial J/\partial P)_S. \tag{2.42}$$

Now (2.30) evaluated at \mathbf{X} gives

$$(\partial J/\partial \alpha_{rs}) = \delta_{rs}, \text{ at } \mathbf{X}; \tag{2.43}$$

then with the aid of (2.34) we find

$$(\partial J/\partial \epsilon_{ij}) = \delta_{ij}, \quad (\partial J/\partial \omega_{ij}) = 0, \text{ at } \mathbf{X}. \tag{2.44}$$

Therefore, (2.42) can be written

$$k_S = -(\partial J/\partial \epsilon_{ij})(\partial \epsilon_{ij}/\partial T_{kl})_S (\partial T_{kl}/\partial P). \tag{2.45}$$

The term $(\partial \epsilon_{ij}/\partial T_{kl})_S$ is obtained by inversion of the transformation (2.35):

$$(\partial \epsilon_{ij}/\partial T_{kl})_S = \hat{B}^S_{ijkl}, \tag{2.46}$$

where \hat{B}^S is the tensor "inverse" to B^S , i.e.,

$$\hat{B}^S_{ijkl} B^S_{klmn} = \frac{1}{2}(\delta_{im}\delta_{jn} + \delta_{in}\delta_{jm}). \tag{2.47}$$

Finally, if the pressure is varied while the nonisotropic part of the stress is maintained constant, the total stress varies according to

$$dT_{kl} = -dP\delta_{kl}, \text{ or } (\partial T_{kl}/\partial P) = -\delta_{kl}. \tag{2.48}$$

With the aid of (2.44), (2.46), and (2.48), the adiabatic compressibility is

$$\begin{aligned} k_S &= -\delta_{ij} \hat{B}^S_{ijkl} (-\delta_{kl}), \\ &= \hat{B}^S_{iijj}. \end{aligned} \tag{2.49}$$

Note that there are nine terms in the sum in (2.49).

Although the B coefficients do not have complete Voigt symmetry in general, they do have enough symmetry to be written in Voigt notation. This fact allows a practical simplification of the expression (2.49) for the compressibility. We use Greek letter subscripts for Voigt indices, in the usual way:

$$\begin{array}{cccccc} ij = & 11 & 22 & 33 & 32 \text{ or } 23 & 31 \text{ or } 13 & 21 \text{ or } 12 \\ \alpha = & 1 & 2 & 3 & 4 & 5 & 6 \end{array} \tag{2.50}$$

Since B^S_{ijkl} are symmetric in i, j and in k, l , all the independent coefficients can be written as a 6×6 matrix $B^S_{\alpha\beta}$, for $\alpha, \beta = 1, \dots, 6$, and where $B^S_{\alpha\beta} \neq B^S_{\beta\alpha}$ in general. Likewise, from (2.47), \hat{B}^S_{ijkl} have the same symmetry, and all the independent coefficients are contained in the set $\hat{B}^S_{\alpha\beta}$ for $\alpha, \beta = 1, \dots, 6$. Now let $b^S_{\alpha\beta}$ be components of the 6×6 matrix which is inverse to $B^S_{\alpha\beta}$, so that

$$b^S_{\alpha\beta} B^S_{\beta\gamma} = \delta_{\alpha\gamma}. \tag{2.51}$$

Then the $b^S_{\alpha\beta}$ contain all the coefficients $\hat{B}^S_{\alpha\beta}$. In particular, the following relations are easily found:

$$b^S_{\alpha\beta} = \hat{B}^S_{\alpha\beta}; \quad \alpha = 1, 2, 3, \quad \beta = 1, 2, 3. \tag{2.52a}$$

$$\begin{aligned} b^S_{\alpha\beta} &= 2\hat{B}^S_{\alpha\beta}; \quad \alpha = 1, 2, 3, \quad \beta = 4, 5, 6 \\ &\text{and } \alpha = 4, 5, 6, \quad \beta = 1, 2, 3. \end{aligned} \tag{2.52b}$$

$$b^S_{\alpha\beta} = 4\hat{B}^S_{\alpha\beta}; \quad \alpha = 4, 5, 6, \quad \beta = 4, 5, 6. \tag{2.52c}$$

From (2.52a), the nine terms in (2.49) for the adiabatic compressibility are simply

$$k_S = \sum_{\alpha=1}^3 \sum_{\beta=1}^3 b^S_{\alpha\beta}. \tag{2.53}$$

In addition the isothermal compressibility is given by (2.53) with $b^S_{\alpha\beta}$ replaced by $b^T_{\alpha\beta}$, where $b^T_{\alpha\beta}$ is the inverse of $B^T_{\alpha\beta}$ as in (2.51). Therefore, in order to calculate the compressibility, it is only necessary to invert the 6×6 matrix $B^S_{\alpha\beta}$ or $B^T_{\alpha\beta}$.

Case of Initial Isotropic Pressure

We have defined three different sets of thermoelastic coefficients, which have different physical and mathematical significance, namely, the C, S , and B coefficients. In the case of a general initial elastic strain, corresponding to a general initial stress, these three sets are all different. However, if the initial stress is an isotropic pressure P , so that

$$T_{ij}(\mathbf{X}) = -P\delta_{ij}, \tag{2.54}$$

then there is some simplification. The designation of constant S or constant T can be omitted here, since the relations among these coefficients are the same for either case.

The equation of motion coefficients (2.24) and (2.25) are given by

$$S_{ijkl} = -P\delta_{jl}\delta_{ik} + C_{ijkl}. \tag{2.55}$$

These coefficients still do not have complete Voigt symmetry unless P vanishes. The stress-strain coefficients (2.36) and (2.37) simplify to

$$B_{ijkl} = -P(\delta_{jl}\delta_{ik} + \delta_{il}\delta_{jk} - \delta_{ij}\delta_{kl}) + C_{ijkl}, \tag{2.56}$$

$$(\partial T_{ij}/\partial \omega_{kl}) = 0. \tag{2.57}$$

Now the B_{ijkl} have complete Voigt symmetry, for arbitrary P . In addition, the B coefficients are *equivalent* to the equation-of-motion coefficients since the combinations symmetric in j, l are the same for both coefficients. It is easily verified from (2.55) and (2.56)

$$S_{ijkl} + S_{ilkj} = B_{ijkl} + B_{ilkj}. \tag{2.58}$$

This means the coefficients measured in experiments on wave propagation in materials under isotropic pressure may be interpreted to be either S_{ijkl} or B_{ijkl} , since it is only the combination (2.58) which is observed. This

special result for isotropic pressure has been noted previously,^{9,10} and Eq. (2.56) has also been derived.¹²

The result (2.57) is also to be expected: The stress is invariant under pure rotation of the material since the stress itself is rotation-invariant. Alternately, a pure rotation of the material, in the presence of isotropic pressure, induces no pure strain.

If we write (2.56) in the form $B_{\alpha\beta} = C_{\alpha\beta} + \Delta_{\alpha\beta}$, where $\Delta_{\alpha\beta}$ are the terms linear in P , then the 6×6 symmetric matrix Δ has $-P$ for each diagonal element, $+P$ for off-diagonal elements of the upper left 3×3 matrix, and zero elsewhere. The important point is that the matrix $B_{\alpha\beta}$ has the same symmetry as the matrix $C_{\alpha\beta}$, for any of the crystal classes, including an isotropic material. This means the inversion of $B_{\alpha\beta}$ may be accomplished by the usual equations for the inverse of $C_{\alpha\beta}$.¹³ The example of a cubic material is discussed in detail in Sec. IV below.

Since $B_{\alpha\beta}$ have Voigt symmetry, so do the elements $b_{\alpha\beta}$ of the inverse matrix. Then (2.53) for the compressibility becomes

$$k = b_{11} + b_{22} + b_{33} + 2(b_{12} + b_{23} + b_{31}). \quad (2.59)$$

This is valid for adiabatic or isothermal quantities. No sum is implied in (2.59); all nine terms are written out explicitly. Thurston¹⁴ has previously derived the adiabatic compressibility in the form (2.59) for the case of initial isotropic pressure.

III. TRANSCRIPTION TO HIGHER-ORDER ELASTIC CONSTANTS EVALUATED AT ZERO STRESS

Higher-Order Elastic Constants at Zero Stress

In Sec. II we studied the second-order thermoelastic coefficients which govern the motion of a material about the initial configuration. In practical laboratory experiments to which reversible thermodynamics may be applied, the initial stress is usually small. By this we mean that the Lagrangian strain parameters which measure the strain from a configuration of zero stress to the initial stressed configuration are small compared to one. It is therefore reasonable to approximate the second-order thermoelastic coefficients at the initial configuration by means of Maclaurin expansions about a configuration of zero stress. This may be accomplished by expanding the state functions about zero-stress configurations.

We use a superscript bar to denote quantities evaluated at zero stress. In analogy with the notation of Sec. II, the position of a material particle in the zero-stress configuration is \bar{X} , while the position of the same

material particle in the final configuration is still \mathbf{x} . We define

$$\bar{\alpha}_{ij} = \partial x_i / \partial \bar{X}_j, \quad (3.1)$$

$$\bar{\eta}_{ij} = \frac{1}{2}(\bar{\alpha}_{ki}\bar{\alpha}_{kj} - \delta_{ij}). \quad (3.2)$$

The density at \bar{X} is labeled ρ_0 for abbreviation; ρ_0 is a function only of S or T . Keeping rotational invariance in mind, the functional dependence of the state functions is

$$\begin{aligned} U(\mathbf{x}, S) &= U(\bar{\eta}_{ij}, S), \\ F(\mathbf{x}, T) &= F(\bar{\eta}_{ij}, T). \end{aligned} \quad (3.3)$$

In the expansion of U and F , the terms linear in $\bar{\eta}_{ij}$ vanish because the stress vanishes when $\bar{\eta}_{ij} = 0$. We keep terms to fourth order explicitly.

$$\begin{aligned} \rho_0 U(\bar{\eta}_{ij}, S) &= \rho_0 U(0, S) + \frac{1}{2} \bar{C}^S_{ijkl} \bar{\eta}_{ij} \bar{\eta}_{kl} \\ &+ (1/3!) \bar{C}^S_{ijklmn} \bar{\eta}_{ij} \bar{\eta}_{kl} \bar{\eta}_{mn} \\ &+ (1/4!) \bar{C}^S_{ijklmnpq} \bar{\eta}_{ij} \bar{\eta}_{kl} \bar{\eta}_{mn} \bar{\eta}_{pq} + \dots; \end{aligned} \quad (3.4)$$

$$\begin{aligned} \rho_0 F(\bar{\eta}_{ij}, T) &= \rho_0 F(0, T) + \frac{1}{2} \bar{C}^T_{ijkl} \bar{\eta}_{ij} \bar{\eta}_{kl} \\ &+ (1/3!) \bar{C}^T_{ijklmn} \bar{\eta}_{ij} \bar{\eta}_{kl} \bar{\eta}_{mn} \\ &+ (1/4!) \bar{C}^T_{ijklmnpq} \bar{\eta}_{ij} \bar{\eta}_{kl} \bar{\eta}_{mn} \bar{\eta}_{pq} + \dots \end{aligned} \quad (3.5)$$

By definition the \bar{C} coefficients are derivatives $\rho_0 U$ or $\rho_0 F$ evaluated at zero stress, and also these coefficients have complete Voigt symmetry as generalized to higher orders. For example, with all derivatives evaluated at $\bar{\eta}_{ij} = 0$,

$$\begin{aligned} \bar{C}^S_{ijkl} &= \rho_0 (\partial^2 U / \partial \bar{\eta}_{ij} \partial \bar{\eta}_{kl}), \\ \bar{C}^S_{ijklmn} &= \rho_0 (\partial^3 U / \partial \bar{\eta}_{ij} \partial \bar{\eta}_{kl} \partial \bar{\eta}_{mn}), \\ \bar{C}^S_{ijklmnpq} &= \rho_0 (\partial^4 U / \partial \bar{\eta}_{ij} \partial \bar{\eta}_{kl} \partial \bar{\eta}_{mn} \partial \bar{\eta}_{pq}). \end{aligned} \quad (3.6)$$

These are respectively the second-, third-, and fourth-order adiabatic elastic constants evaluated at zero stress and are functions only of S . The isothermal constants are defined similarly in terms of derivatives of F . These definitions agree with those proposed by Brugger.¹⁵

Relation to Second-Order Constants at Nonzero Stress

The second-order elastic constants at the initial configuration are defined by (2.14); we merely need to transform those definitions from the nine independent variables η_{ij} to the nine independent variables $\bar{\eta}_{ij}$. From (2.4) for η_{ij} and (3.2) for $\bar{\eta}_{ij}$, we have

$$(\bar{\eta}_{ij} + \frac{1}{2} \delta_{ij}) = (\eta_{rs} + \frac{1}{2} \delta_{rs}) a_{ri} a_{sj}, \quad (3.7)$$

where

$$a_{ij} = \partial X_i / \partial \bar{X}_j. \quad (3.8)$$

The transformation of variables is then accomplished by

$$(\partial \bar{\eta}_{ij} / \partial \eta_{rs}) = a_{ri} a_{sj}, \quad (3.9)$$

which follows from (3.7). Taking the adiabatic con-

¹² G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 275.

¹³ See, for example, W. Boas and F. K. Mackenzie, in *Progress in Metal Physics*, edited by B. Chalmers (Interscience Publishers, Inc., New York, 1950), Vol. 2, p. 90.

¹⁴ R. N. Thurston, Proc. IEEE 53, 1320 (1965).

¹⁵ K. Brugger, Phys. Rev. 133, A1611 (1964).

TABLE I. Values of ρv^2 for particular plane waves for a cubic material under isotropic pressure. For adiabatic or isothermal propagation, the values of ρv^2 are adiabatic or isothermal coefficients, respectively.

κ	\mathbf{u}	ρv^2
(1,0,0)	(1,0,0)	$S_{1111} = B_{11} = C_{11} - P$
(1,0,0)	(0,1,0)	$S_{1212} = B_{44} = C_{44} - P$
$\frac{1}{\sqrt{2}}(1,1,0)$	$\frac{1}{\sqrt{2}}(1,1,0)$	$\frac{1}{2}(S_{1111} + S_{1122} + S_{1212} + S_{1221}) = \frac{1}{2}(B_{11} + B_{12} + 2B_{44}) = \frac{1}{2}(C_{11} + C_{12} + 2C_{44} - 2P)$
$\frac{1}{\sqrt{2}}(1,1,0)$	$\frac{1}{\sqrt{2}}(1, \bar{1}, 0)$	$\frac{1}{2}(S_{1111} + S_{1212} - S_{1122} - S_{1221}) = \frac{1}{2}(B_{11} - B_{12}) = \frac{1}{2}(C_{11} - C_{12} - 2P)$
$\frac{1}{\sqrt{2}}(1,1,0)$	(0,0,1)	$S_{1212} = B_{44} = C_{44} - P$
$\frac{1}{\sqrt{3}}(1,1,1)$	$\frac{1}{\sqrt{3}}(1,1,1)$	$\frac{1}{3}(S_{1111} + 2S_{1122} + 2S_{1212} + 2S_{1221}) = \frac{1}{3}(B_{11} + 2B_{12} + 4B_{44}) = \frac{1}{3}(C_{11} + 2C_{12} + 4C_{44} - 3P)$
$\frac{1}{\sqrt{3}}(1,1,1)$	$\frac{1}{\sqrt{2}}(1, \bar{1}, 0)$	$\frac{1}{3}(S_{1111} + 2S_{1212} - S_{1122} - S_{1221}) = \frac{1}{3}(B_{11} - B_{12} + B_{44}) = \frac{1}{3}(C_{11} - C_{12} + C_{44} - 3P)$

stants for illustration, (2.14) may be written

$$\begin{aligned}
 C^S_{ijkl} &= \rho_1 (\partial^2 U / \partial \eta_{ij} \partial \eta_{kl}) \\
 &= (\rho_1 / \rho_0) a_{im} a_{jn} a_{kp} a_{lq} \rho_0 (\partial^2 U / \partial \bar{\eta}_{mn} \partial \bar{\eta}_{pq}) \\
 &= (\rho_1 / \rho_0) a_{im} a_{jn} a_{kp} a_{lq} [\bar{C}^S_{mnpq} + \bar{C}^S_{mnpqrs} \bar{\eta}_{rs} \\
 &\quad + \frac{1}{2} \bar{C}^S_{mnpqrst} \bar{\eta}_{rs} \bar{\eta}_{tu} + \dots]. \quad (3.10)
 \end{aligned}$$

The expansion (3.4) has been used to obtain the last form for C^S_{ijkl} in (3.10). The $\bar{\eta}_{ij}$ in (3.10) are to be evaluated at $\bar{\mathbf{X}}$:

$$\bar{\eta}_{ij} = \frac{1}{2}(a_{ki} a_{kj} - \delta_{ij}), \quad \text{at } \bar{\mathbf{X}}. \quad (3.11)$$

We now have a general expression for C^S_{ijkl} evaluated at $\bar{\mathbf{X}}$, in terms of adiabatic second-, third-, and fourth-order elastic constants evaluated at $\bar{\mathbf{X}}$, and the parameters which measure the deformation for $\bar{\mathbf{X}}$ to \mathbf{X} , namely (ρ_1 / ρ_0) and a_{ij} . With the aid of (3.10) and (3.11), the equation-of-motion coefficients S_{ijkl} and the stress-strain coefficients B_{ijkl} can be expressed in terms of the initial stresses and the higher-order elastic constants evaluated at zero stress. A particular example of this is given in Sec. IV.

An important point needs to be emphasized here. In deriving (3.10) and (3.11), all differentiations were carried out at constant S . This implies that ρ_1 / ρ_0 and the a_{ij} in these equations must be evaluated at constant S . By the same token, if (3.10) is used to relate isothermal constants, the parameters measuring the strain from $\bar{\mathbf{X}}$ to \mathbf{X} must be evaluated for a constant T strain. It is possible to consider alternative derivations in which, for example, the strain from $\bar{\mathbf{X}}$ to \mathbf{X} is isothermal while the equation is used to express the adiabatic constant C^S_{ijkl} . We avoid this procedure since it leads to "mixed" higher-order elastic constants such as $(\partial C^S_{ijkl} / \partial \bar{\eta}_{mn})_T$. Although such constants have been

defined,¹⁶ their calculation from atomic models is complicated in an essential way by requiring differentiation with a dependent variable held fixed.

IV. EXAMPLE OF CUBIC MATERIAL UNDER ISOTROPIC PRESSURE

Second-Order Coefficients at Arbitrary Pressure

We assume the material has cubic symmetry under arbitrary pressure P . Then the elastic constants C_{ijkl} , which can always be written in Voigt notation $C_{\alpha\beta}$, reduce to the three independent constants C_{11} , C_{12} , and C_{44} . From (2.28) we calculate the combination of S_{ijkl} which is equal to ρv^2 for a given propagation direction κ and a given displacement direction \mathbf{u} [\mathbf{u} is taken to be a unit vector, since its normalization is arbitrary in (2.28)]. This combination is transformed to a combination of B_{ijkl} by means of (2.58), and to a combination of C_{ijkl} and P by means of (2.55). We drop the designation for constant S or T , the relations among the coefficients being valid for either case, and write C and B coefficients in Voigt notation. The results are listed in Table I.

The relations given in Table I are valid for arbitrary pressure, and the coefficients which give ρv^2 values are functions of P and S or T . In addition, ρv^2 is evaluated in the initial configuration, which is also a function of P and S or T . Even for a cubic material under isotropic pressure, the S_{ijkl} do not have Voigt symmetry and hence cannot be written in Voigt notation. Note that the relations between combinations of $B_{\alpha\beta}$ and combinations of $C_{\alpha\beta}$ are consistent with (2.56).

It is easy to invert the matrix of $B_{\alpha\beta}$ coefficients, since

¹⁶ R. N. Thurston and K. Brugger, Phys. Rev. **133**, A1604 (1964).

these have the same symmetry as the $C_{\alpha\beta}$ for a cubic material. As was noted in Sec. II, this situation holds for any symmetry when the initial stress is isotropic pressure. The three independent $B_{\alpha\beta}$ are B_{11} , B_{12} , and B_{44} , and the corresponding three independent elements of the inverse matrix \mathbf{b} are

$$b_{11} = (B_{11} + B_{12}) / (B_{11} - B_{12})(B_{11} + 2B_{12}), \quad (4.1)$$

$$b_{12} = -B_{12} / (B_{11} - B_{12})(B_{11} + 2B_{12}), \quad (4.2)$$

$$b_{44} = 1/B_{44}. \quad (4.3)$$

From (2.59), the compressibility becomes

$$\begin{aligned} k &= 3(b_{11} + 2b_{12}), \\ &= 3/(B_{11} + 2B_{12}). \end{aligned} \quad (4.4)$$

In terms of the elastic constants $C_{\alpha\beta}$, (4.4) and (2.56) give

$$k = 3/(C_{11} + 2C_{12} + P). \quad (4.5)$$

Again (4.1)–(4.5) are valid either for adiabatic or isothermal coefficients.

Transcription to Third- and Fourth-Order Elastic Constants

If the cubic material remains cubic under arbitrary pressure, the deformation parameters from $\bar{\mathbf{X}}$ (zero-pressure configuration) to \mathbf{X} (configuration at pressure) are simple. We follow the notation of Birch³:

$$X_i = (1 - \alpha)\bar{X}_i; \quad (4.6)$$

$$(1 - \alpha)^3 = (1 + 2\eta)^{3/2}. \quad (4.7)$$

The parameter η is defined by (4.7), and is introduced because of its convenience as an expansion parameter.³ In the following we carry all calculations to second order in α or η ; this is consistent with keeping elastic constants of third and fourth order only. We also drop the designation of constant S or T , but it must be remembered that α and η are to be evaluated along the line of constant S or T , accordingly.

From (3.8) and (4.6) it follows

$$a_{ij} = (1 - \alpha)\delta_{ij}, \quad (4.8)$$

and hence with (3.11) and (4.7), to second order

$$\bar{\eta}_{ij} = \eta\delta_{ij}, \quad \text{at } \mathbf{X}. \quad (4.9)$$

Also from (4.6)

$$\rho_1/\rho_0 = (1 - \alpha)^{-3}. \quad (4.10)$$

We can now evaluate (3.10) for the adiabatic or isothermal case with the aid of (4.8)–(4.10); after carrying out the sums involving Kronecker deltas and transforming to a power series in η , the result is

$$\begin{aligned} C_{ijkl} &= \bar{C}_{ijkl} + \eta[\bar{C}_{ijkl} + \bar{C}_{ijklmm}] \\ &+ \frac{1}{2}\eta^2[-\bar{C}_{ijkl} + 2\bar{C}_{ijklmm} + \bar{C}_{ijklmmp}] + \dots \end{aligned} \quad (4.11)$$

For a cubic material (point groups 0, O_h , T_d) there

are six independent third-order,³ and eleven independent fourth-order,¹⁷ elastic constants; these can, of course, be written in Voigt notation with three and four subscripts, respectively. The explicit expressions obtained from (4.11) for the three independent second-order elastic constants evaluated at η are as follows:

$$\begin{aligned} C_{11} &= \bar{C}_{11} + \eta[\bar{C}_{11} + (\bar{C}_{111} + 2\bar{C}_{112})] \\ &+ \frac{1}{2}\eta^2[-\bar{C}_{11} + (2\bar{C}_{111} + 4\bar{C}_{112}) \\ &+ (\bar{C}_{1111} + 2\bar{C}_{1122} + 2\bar{C}_{1123} + 4\bar{C}_{1112})], \end{aligned} \quad (4.12)$$

$$\begin{aligned} C_{12} &= \bar{C}_{12} + \eta[\bar{C}_{12} + (\bar{C}_{123} + 2\bar{C}_{112})] \\ &+ \frac{1}{2}\eta^2[-\bar{C}_{12} + (2\bar{C}_{123} + 4\bar{C}_{112}) \\ &+ (5\bar{C}_{1123} + 2\bar{C}_{1122} + 2\bar{C}_{1112})], \end{aligned} \quad (4.13)$$

$$\begin{aligned} C_{44} &= \bar{C}_{44} + \eta[\bar{C}_{44} + (\bar{C}_{144} + 2\bar{C}_{166})] \\ &+ \frac{1}{2}\eta^2[-\bar{C}_{44} + (2\bar{C}_{144} + 4\bar{C}_{166}) \\ &+ (\bar{C}_{1144} + 2\bar{C}_{1166} + 2\bar{C}_{1266} + 4\bar{C}_{1244})]. \end{aligned} \quad (4.14)$$

The three independent stress-strain coefficients are given in a convenient form with the aid of (2.56):

$$\begin{aligned} B_{11} &= C_{11} - P, \\ B_{12} &= C_{12} + P, \\ B_{44} &= C_{44} - P. \end{aligned} \quad (4.15)$$

For an adiabatic elastic compression from $\bar{\mathbf{X}}$ to \mathbf{X} , there will be a unique relation between η and P ; likewise for an isothermal compression. In order to calculate this relation, we used a Bridgman¹⁸ equation of state (adiabatic or isothermal)

$$V = V_0(1 - A_1P + A_2P^2),$$

and calculated A_1 and A_2 in terms of $C_{\alpha\beta}$ with the aid of (4.5). Then from (4.12)–(4.14), and noting the relation between η and $V - V_0$, we find to second order in η

$$\begin{aligned} -P &= \eta(\bar{C}_{11} + 2\bar{C}_{12}) + \eta^2[-(\bar{C}_{11} + 2\bar{C}_{12}) \\ &+ \frac{1}{2}(\bar{C}_{111} + 2\bar{C}_{123} + 6\bar{C}_{112})]. \end{aligned} \quad (4.16)$$

It should be emphasized that this result does not depend on the Bridgman equation of state; the Bridgman equation was used merely for convenience in deriving (4.16).

With (4.16) and (4.12)–(4.15) the expansions for $B_{\alpha\beta}$ become

$$\begin{aligned} B_{11} &= \bar{C}_{11} + \eta[2(\bar{C}_{11} + \bar{C}_{12}) + (\bar{C}_{111} + 2\bar{C}_{112})] \\ &+ \frac{1}{2}\eta^2[-3\bar{C}_{11} - 4\bar{C}_{12} + (3\bar{C}_{111} + 2\bar{C}_{123} + 10\bar{C}_{112}) \\ &+ (\bar{C}_{1111} + 2\bar{C}_{1122} + 2\bar{C}_{1123} + 4\bar{C}_{1112})], \end{aligned} \quad (4.17)$$

$$\begin{aligned} B_{12} &= \bar{C}_{12} + \eta[-(\bar{C}_{11} + \bar{C}_{12}) + (\bar{C}_{123} + 2\bar{C}_{112})] \\ &+ \frac{1}{2}\eta^2[2\bar{C}_{11} + 3\bar{C}_{12} - (\bar{C}_{111} + 2\bar{C}_{112}) \\ &+ (5\bar{C}_{1123} + 2\bar{C}_{1122} + 2\bar{C}_{1112})], \end{aligned} \quad (4.18)$$

¹⁷ P. B. Ghatge, *Phys. Status Solidi* **14**, 325 (1966).

¹⁸ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1949), 2nd ed.

$$\begin{aligned}
 B_{44} = & \bar{C}_{44} + \eta[\bar{C}_{44} + \bar{C}_{11} + 2\bar{C}_{12} + (\bar{C}_{144} + 2\bar{C}_{166})] \\
 & + \frac{1}{2}\eta^2[-\bar{C}_{44} - 2\bar{C}_{11} - 4\bar{C}_{12} \\
 & + (\bar{C}_{111} + 2\bar{C}_{123} + 2\bar{C}_{144} + 4\bar{C}_{166} + 6\bar{C}_{112}) \\
 & + (\bar{C}_{1144} + 2\bar{C}_{1166} + 2\bar{C}_{1266} + 4\bar{C}_{1244})]. \quad (4.19)
 \end{aligned}$$

Alternatively one can invert the transformation (4.16), write η as a power series in P , and transform the series for $C_{\alpha\beta}$ and $B_{\alpha\beta}$ to power series in P . We will not write down these expressions, but instead calculate the first pressure derivatives of $B_{\alpha\beta}$, evaluated at $P=0$. The inversion of (4.16) gives

$$\begin{aligned}
 \eta = & -\frac{1}{3}A_1P + O(P^2); \\
 (\partial\eta/\partial P)_{P=0} = & -\frac{1}{3}A_1 = -1/(\bar{C}_{11} + 2\bar{C}_{12}). \quad (4.20)
 \end{aligned}$$

Then from (4.17)-(4.19), the pressure derivatives evaluated at $P=0$ ($\eta=0$) are

$$\partial B_{11}/\partial P = -\frac{1}{3}A_1[2(\bar{C}_{11} + \bar{C}_{12}) + (\bar{C}_{111} + 2\bar{C}_{112})], \quad (4.21)$$

$$(\partial B_{12}/\partial P) = -\frac{1}{3}A_1[-(\bar{C}_{11} + \bar{C}_{12}) + (\bar{C}_{123} + 2\bar{C}_{112})], \quad (4.22)$$

$$(\partial B_{44}/\partial P) = -\frac{1}{3}A_1[\bar{C}_{44} + \bar{C}_{11} + 2\bar{C}_{12} + (\bar{C}_{144} + 2\bar{C}_{166})]. \quad (4.23)$$

These are written as *partial* derivatives because it is implied that either S or T is held constant; then the constants which appear in A_1 of (4.20) and in the square brackets of (4.21)-(4.23) are all adiabatic or isothermal, respectively.

The pressure derivatives of $C_{\alpha\beta}$, evaluated at $P=0$, are easily obtained from (4.21)-(4.23) together with (4.15).

V. COMPARISON WITH OTHER THEORIES

Huang's Expansion of the Mechanical Energy Density

Huang⁴ expanded the mechanical energy density in powers of the displacement parameters u_{ij} of (2.2), for the case of initial homogeneous stress. We generalize the theory of Huang by expanding the state functions U and F , and thus differentiate between adiabatic and isothermal coefficients.

$$\begin{aligned}
 \rho_1 U(\mathbf{X}, u_{ij}, S) = & \rho_1 U(\mathbf{X}, 0, S) + S^s_{ij} u_{ij} \\
 & + \frac{1}{2} S^s_{ijkl} u_{ij} u_{kl} + \dots, \quad (5.1)
 \end{aligned}$$

with a similar expansion for F in terms of isothermal coefficients. These expansions serve as the fundamental definition of the S coefficients. But (5.1) must be equal to (2.12) in each order of the infinitesimal parameters u_{ij} . With the aid of (2.4), (2.12) is transformed to an expansion in u_{ij} .

$$\begin{aligned}
 \rho_1 U(\mathbf{X}, u_{ij}, S) = & \rho_1 U(\mathbf{X}, 0, S) + C^s_{ij} u_{ij} \\
 & + \frac{1}{2} (C^s_{jil} \delta_{ik} + C^s_{ijkl}) u_{ij} u_{kl} + \dots \quad (5.2)
 \end{aligned}$$

Since all nine u_{ij} are independent, the coefficients in

(5.1) and (5.2) must be equal.

$$S^s_{ij} = C^s_{ij} = T_{ij}; \quad (5.3)$$

$$S^s_{ijkl} = T_{jl} \delta_{ik} + C^s_{ijkl}. \quad (5.4)$$

Here we have used (2.17) to introduce $T_{ij}(\mathbf{X})$. The relation (5.4) is the same as (2.24); this is our reason for introducing the S coefficients in Sec. II. Relations analogous to (5.3) and (5.4) hold for the isothermal coefficients S^T_{ij} and S^T_{ijkl} .

Now in (5.1) the u_{ij} are arbitrary, and in particular not necessarily symmetric. Therefore, (5.1) does not contain any information about the rotational invariance of U . But such invariance is completely contained in the expansion (2.12), and hence also in (5.2). Thus the restrictions placed on the S coefficients through (5.3) and (5.4), along with the symmetry properties of T_{ij} and C_{ijkl} , should contain the rotational invariance conditions. For adiabatic or isothermal coefficients, these restrictions are found to be

$$S_{ij} = S_{ji},$$

$$S_{ijkl} - S_{klij} = 0, \quad (5.5)$$

$$S_{ijkl} - S_{jikl} + S_{il} \delta_{jk} - S_{jl} \delta_{ik} = 0.$$

These are just the relations which Huang⁴ found by requiring the energy density to be invariant with respect to infinitesimal rotation.

As was noted in Sec. II, Huang⁴ used his energy expansion [of the form (5.1)] to show that the equation of motion is given by (2.23). He also showed that only when T_{ij} vanishes do the S_{ijkl} have complete Voigt symmetry [this is also obvious from (5.4)]. This lack of Voigt symmetry led Huang to say that elastic constants can only be defined at zero stress⁴; as is evident from Sec. II, this difficulty is now completely removed.

Higher-Order Elastic Constants

Birch³ used the finite strain theory of Murnaghan (see, e.g., Ref. 2) to calculate the elastic coefficients which relate a further infinitesimal stress and strain for a cubic material under isotropic pressure. His calculations were for isothermal variations, since he worked with the Helmholtz free energy per unit mass. The B coefficients of Sec. II are complete generalizations of Birch's coefficients, since they give stress-strain relations for a material of arbitrary symmetry under arbitrary stress. For a cubic crystal under isotropic pressure, Birch wrote the final stress as $T_{ij} = -P\delta_{ij} + T'_{ij}$, where P is the initial pressure. Also the β_{ij} of Birch are the same as our ϵ_{ij} of (2.32). With this notation of Birch, and dropping the rotational dependence of T_{ij} , (2.39) becomes

$$T'_{ij} = B^T_{ijkl} \beta_{kl}, \quad \text{Birch notation.} \quad (5.6)$$

When (5.6) is written out in Voigt notation for T'_{11} , T'_{12} , and T'_{44} , we recover Eqs. (20) and (23) of Birch,

with the identification

$$B^T_{\alpha\beta} = c_{\alpha\beta}' \quad \text{of Birch.} \quad (5.7)$$

Birch wrote the initial pressure P and the $B^T_{\alpha\beta}$ as functions of η and the second- and third-order elastic constants evaluated at $P=0$. His third-order elastic constants are defined with different numerical coefficients than ours; see, e.g., Ghate,¹⁹ footnote 13. When Eqs. (21)–(23) of Birch are expanded in powers of η to second order, and the differences in definitions of third-order constants is taken into account, there is complete agreement with our expansions (4.16)–(4.19), except, of course, for the fourth-order constants, which were not included by Birch.

Ghate¹⁷ has extended the calculations of Birch, for a cubic material under isotropic pressure, to include fourth-order elastic constants. His Eqs. (22)–(24) may be compared directly to our (4.17)–(4.19); the agreement is not complete in terms of order η^2 . The first pressure derivatives of $B_{\alpha\beta}$, evaluated at $P=0$, arise from terms linear in η and are given by Ghate¹⁹ in Eqs. (74)–(76); these agree with our results (4.20)–(4.23).

Thurston and Brugger¹⁶ have studied wave propagation in stressed crystals. They express results in terms of the directly measured quantities $\rho_0 W^2$ and its first pressure derivative, all evaluated at $P=0$, where ρ_0 is the density at $P=0$ and $W=2L_0F$, with L_0 being the specimen length at $P=0$ and F the measured repetition frequency at any pressure. For a cubic material,

$$\rho_0 W^2 = (L/L_0)\rho v^2, \quad (5.8)$$

where L is the specimen length at any pressure. From (5.8) it follows for $P=0$

$$\rho_0 W^2 = \rho v^2, \quad (5.9)$$

$$d(\rho_0 W^2)/dP = -\frac{1}{3}A_1\rho_0 W^2 + d(\rho v^2)/dP, \quad (5.10)$$

where all terms are evaluated at $P=0$ and $\frac{1}{3}A_1$ is given by (4.20). Also, all quantities in (5.9) and (5.10) should be either adiabatic or isothermal. For a cubic material under isotropic pressure and for a [1,0,0] longitudinal wave, Table I gives $\rho v^2 = B_{11}$. Then at $P=0$, (4.15) gives

$$\rho_0 W^2 = \bar{C}_{11}. \quad (5.11)$$

Also, from (4.20) and (4.21), (5.10) is evaluated to give, for $P=0$,

$$d(\rho_0 W^2)/dP = -1 - \frac{1}{3}A_1[2\bar{C}_{11} + \bar{C}_{111} + 2\bar{C}_{112}]. \quad (5.12)$$

In this way we find agreement with all the results of Table I of Thurston and Brugger.¹⁶ There is a difference, however, in that for adiabatic propagation, for example, (5.12) should contain all adiabatic constants in A_1 [see (4.20)] and in the square brackets, while Thurston and Brugger use an isothermal A_1 and mixed

adiabatic and isothermal third-order elastic constants [their Eq. (5.9)]. This difference does not represent an error, but only a difference in expression.

Elastic Constants of Fuchs

Fuchs²⁰ calculated elastic constants for primitive cubic lattices under zero stress, in terms of a particular set of infinitesimal strain parameters. Since several workers have used Fuchs' formulae to interpret ultrasonic measurements for cubic materials under pressure,^{21–23} it is advisable to generalize the calculations of Fuchs to the case of nonvanishing pressure.

Fuchs defined a set of six nonsymmetric deformation parameters $\epsilon_x, \epsilon_y, \epsilon_z, \gamma_{xy}, \gamma_{yz},$ and γ_{zx} ; in terms of these, our u_{ij} of (2.2) are given by

$$\begin{aligned} u_{xx} &= \epsilon_x, & u_{yy} &= \epsilon_y, & u_{zz} &= \epsilon_z; \\ u_{xy} &= \gamma_{xy}, & u_{yz} &= \gamma_{yz}, & u_{zx} &= \gamma_{zx}; \\ u_{yx} &= u_{xy} = u_{zx} = 0. \end{aligned} \quad (5.13)$$

The Huang expansion (5.1) now gives the internal energy in terms of the Fuchs deformation parameters. The S coefficients in (5.1) simplify for a cubic material under isotropic pressure, since

$$S^S_{ij} = -P\delta_{ij}, \quad (5.14)$$

and also since S^S_{ijkl} , given in this case by (2.55), depend on only three independent C^S_{ijkl} . In view of these simplifications, and with the aid of (5.13), the Huang expansion for U becomes

$$\begin{aligned} \rho_1 U(\mathbf{X}, u_{ij}, S) &= \rho_1 U(\mathbf{X}, 0, S) - P(\epsilon_x + \epsilon_y + \epsilon_z) \\ &+ \frac{1}{2}[S^S_{1111}(\epsilon_x^2 + \epsilon_y^2 + \epsilon_z^2) \\ &+ 2S^S_{1122}(\epsilon_x\epsilon_y + \epsilon_y\epsilon_z + \epsilon_z\epsilon_x) \\ &+ S^S_{1212}(\gamma_{xy}^2 + \gamma_{yz}^2 + \gamma_{zx}^2)]. \end{aligned} \quad (5.15)$$

There are no sums implied in (5.15). Note that since γ_{ij} are not symmetric, coefficients such as S^S_{1221} do not appear in (5.15). An expansion of F is analogous to (5.15) and contains isothermal coefficients.

Fuchs expanded the potential energy per atom; this does not differentiate between adiabatic and isothermal variations. The generalization to the expansion of U or F is obvious, and by comparing Eq. (4) of the first paper of Fuchs²⁰ with (5.15) we identify the Fuchs coefficients $F_{\alpha\beta}$ (his $c_{\alpha\beta}$) as follows:

$$F_{11} = S_{1111}, \quad F_{12} = S_{1122}, \quad F_{44} = S_{1212}, \quad (5.16)$$

for adiabatic or isothermal coefficients.

We now calculate the coefficients corresponding to the three choices of deformations which Fuchs labeled deformations (A), (B), and (C).

²⁰ K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1936); **A157**, 444 (1936).

²¹ W. B. Daniels and C. S. Smith, Phys. Rev. **111**, 713 (1958).

²² R. E. Schmunk and C. S. Smith, J. Phys. Chem. Solids **9**, 100 (1959).

²³ W. B. Daniels, Phys. Rev. **119**, 1246 (1960).

¹⁹ P. B. Ghate, Phys. Rev. **139**, A1666 (1965).

(A) Compression in one direction, expansion in another, conserving volume.

$$1 + \epsilon_y = 1 / (1 + \epsilon_x); \quad \epsilon_z \text{ and } \gamma_{ij} = 0. \\ A = \frac{1}{2} \rho_1 (\partial^2 U / \partial \epsilon_x^2). \quad (5.17)$$

It is now necessary to expand ϵ_y to second order in ϵ_x giving

$$\epsilon_y = -\epsilon_x + \epsilon_x^2.$$

With the definition (5.17), we find from (5.15) and (5.16)

$$A = -P + F_{11} - F_{12}. \quad (5.18)$$

(B) Shear in one plane, conserving volume.

$$\epsilon_i = 0; \quad \gamma_{yz} = \gamma_{zx} = 0. \\ B = \frac{1}{2} \rho_1 (\partial^2 U / \partial \gamma_{xy}^2). \quad (5.19)$$

Again from (5.15) and (5.16) we find directly

$$B = \frac{1}{2} F_{44}. \quad (5.20)$$

(C) Uniform volume expansion.

$$\epsilon_x = \epsilon_y = \epsilon_z, \quad \gamma_{ij} = 0. \\ (1 + \epsilon_v) = (1 + \epsilon_x)(1 + \epsilon_y)(1 + \epsilon_z). \quad (5.21) \\ C = \frac{1}{2} \rho_1 (\partial^2 U / \partial \epsilon_v^2).$$

To second order in ϵ_v , the three equal principal strains are given by

$$\epsilon_x = \frac{1}{3} \epsilon_v - \frac{1}{9} \epsilon_v^2;$$

the result is

$$C = \frac{1}{6} (2P + F_{11} + 2F_{12}). \quad (5.22)$$

The above results for $F_{\alpha\beta}$ and the three combinations (A), (B), and (C) are related to the $B_{\alpha\beta}$ and $C_{\alpha\beta}$ for cubic materials under isotropic pressure with the aid of (5.16), (2.55), and (4.15). The relations are summarized in Table II and hold for either adiabatic or isothermal coefficients. It is seen that the quantities (A), (B), and (C) are linear combinations of the $B_{\alpha\beta}$, with no explicit terms in P . Therefore, these combinations may be related directly to the equation of motion coefficients, i.e., directly to ρv^2 values for any pressure, as listed in Table I. This has been the customary procedure.²¹⁻²³ Also, $2C$ is the inverse of the compressibility, at any pressure.

TABLE II. Relations between the Fuchs elastic coefficients $F_{\alpha\beta}$, the stress-strain coefficients $B_{\alpha\beta}$, and the elastic constants $C_{\alpha\beta}$, for adiabatic or isothermal coefficients for a cubic material under isotropic pressure P .

Fuchs	Stress-Strain	Elastic Constants
F_{11}	B_{11}	$C_{11} - P$
F_{12}	$B_{12} - P$	C_{12}
F_{44}	B_{44}	$C_{44} - P$
$A = -P + F_{11} - F_{12}$	$B_{11} - B_{12}$	$C_{11} - C_{12} - 2P$
$2B = F_{44}$	B_{44}	$C_{44} - P$
$2C = \frac{1}{3} (2P + F_{11} + 2F_{12})$	$\frac{1}{3} (B_{11} + 2B_{12})$	$\frac{1}{3} (C_{11} + 2C_{12} + P)$

Voigt-Type Elastic Constants

Following Leibfried,^{24,25} it is convenient to work with the symmetric and antisymmetric infinitesimal displacement parameters ϵ_{ij} and ω_{ij} of (2.32) and (2.33). These two equations can be solved for u_{ij} to give

$$u_{ij} = \frac{1}{2} (\epsilon_{ij} + \epsilon_{ji} + \omega_{ij} - \omega_{ji}). \quad (5.23)$$

With (5.23), the Huang expansion (5.1) becomes

$$\rho_1 U(\mathbf{X}, u_{ij}, S) = \rho_1 U(\mathbf{X}, 0, S) + S^S \epsilon_{ij} \epsilon_{ij} \\ + \frac{1}{2} S^S_{ijkl} [\epsilon_{ij} \epsilon_{kl} + \epsilon_{ij} (\omega_{kl} - \omega_{lk}) \\ + \frac{1}{4} (\omega_{ij} \omega_{kl} - \omega_{ij} \omega_{lk} - \omega_{ji} \omega_{kl} + \omega_{ji} \omega_{lk})] + \dots \quad (5.24)$$

where we have taken account of the symmetry of ϵ_{ij} to simplify (5.24). The adiabatic Voigt elastic constants V^S_{ijkl} are defined by

$$V^S_{ijkl} = \rho_1 (\partial^2 U / \partial \epsilon_{ij} \partial \epsilon_{kl}). \quad (5.25)$$

In view of the symmetry of ϵ_{ij} , only the part of S^S_{ijkl} which has complete Voigt symmetry survives the sum in the term $\frac{1}{2} S^S_{ijkl} \epsilon_{ij} \epsilon_{kl}$. Since $S^S_{ijkl} = S^S_{klij}$ is already satisfied [see (5.5)], then (5.25) is written

$$V^S_{ijkl} = \frac{1}{4} (S^S_{ijkl} + S^S_{jikl} + S^S_{ijlk} + S^S_{jilk}); \quad (5.26)$$

obviously (5.26) always has complete Voigt symmetry, so V^S_{ijkl} can always be written as $V^S_{\alpha\beta}$.

The expansion (5.24) also shows how the internal energy U varies if the material is rotated in the presence of the initial stress. It is easily verified, with the aid of (5.4) and the Voigt symmetry of C^S_{ijkl} , that if the initial stress vanishes or is an isotropic pressure, the terms in ω_{ij} sum to zero in (5.24).

The infinitesimal displacement parameters used by Voigt¹ and others^{26,27} are different from ϵ_{ij} ; in particular they have used e_{ij} given by

$$e_{ij} = e_{\alpha} = (2 - \delta_{ij}) \epsilon_{ij}, \quad (5.27)$$

and they take only six indices α for the set ij (Voigt notation), instead of all nine. It is easily verified that the elastic constants so defined, i.e.,

$$V^S_{\alpha\beta} = \rho_1 (\partial^2 U / \partial e_{\alpha} \partial e_{\beta}), \quad (5.28)$$

are the same as (5.26).

With the aid of (2.24) or (2.25), the Voigt constants for either adiabatic or isothermal cases are

$$V_{ijkl} = \frac{1}{4} (T_{ik} \delta_{jl} + T_{il} \delta_{jk} + T_{jk} \delta_{il} + T_{jl} \delta_{ik}) + C_{ijkl}. \quad (5.29)$$

For a general initial stress, V_{ijkl} are different from any other sets of coefficients which we have considered. For initial isotropic pressure (5.29) simplifies to

$$V_{ijkl} = -\frac{1}{2} P (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) + C_{ijkl}. \quad (5.30)$$

²⁴ G. Leibfried, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. VII/1, p. 104.

²⁵ G. Leibfried and H. Hahn, *Z. Physik* **150**, 497 (1958).

²⁶ A. E. H. Love, *Mathematical Theory of Elasticity* (Cambridge University Press, Cambridge, England, 1927), 4th ed.

²⁷ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954).

For a cubic material under isotropic pressure, there are three independent Voigt coefficients; in Voigt notation these are

$$\begin{aligned} V_{11} &= C_{11} - P, \\ V_{12} &= C_{12}, \\ V_{44} &= C_{44} - \frac{1}{2}P. \end{aligned} \quad (5.31)$$

Even for this simple case, the set $V_{\alpha\beta}$ is different from all the other sets we have considered.

VI. SUMMARY

We have developed a general theory of thermoelasticity of stressed materials, which provides a basis for interpreting measurements on materials of arbitrary symmetry in states of arbitrary homogeneous elastic deformation. In this theory there are three different sets of physically significant thermoelastic coefficients.

(a) The coefficients which contain the rotational invariance requirements placed on the state functions U or F :

$$C^S_{ijkl} = \rho_1 (\partial^2 U / \partial \eta_{ij} \partial \eta_{kl}), \quad (6.1)$$

$$C^T_{ijkl} = \rho_1 (\partial^2 F / \partial \eta_{ij} \partial \eta_{kl}), \quad (6.2)$$

where η_{ij} is measured from the initial configuration and these equations are evaluated at the initial configuration ($\eta_{ij} = 0$). These elastic constants always have complete Voigt symmetry. In addition, if one approximates U or F by the potential energy of the interacting atoms in a simple crystal, the C_{ijkl} are the constants which exhibit Cauchy relations.

(b) The coefficients which govern the adiabatic or isothermal motion of small displacement plane waves according to (2.28):

$$\rho v^2 u_i = S_{ijk} \kappa_j \kappa_k u_k. \quad (6.3)$$

These Huang coefficients have complete Voigt symmetry if and only if the initial stress vanishes; their relation to the elastic constants, for either adiabatic or isothermal cases, is

$$S_{ijkl} = T_{ij} \delta_{ik} + C_{ijkl}. \quad (6.4)$$

(c) The coefficients which relate the variation of strain away from the initial state to the variation of stress, for adiabatic or isothermal processes:

$$(\partial T_{ij} / \partial \epsilon_{kl}) = B_{ijkl}. \quad (6.5)$$

In terms of the elastic constants, these coefficients are

$$B_{ijkl} = \frac{1}{2} (T_{ik} \delta_{jl} + T_{il} \delta_{jk} + T_{jk} \delta_{il} + T_{jl} \delta_{ik} - 2T_{ij} \delta_{kl}) + C_{ijkl}. \quad (6.6)$$

For general initial stress the B_{ijkl} do not have Voigt symmetry. For initial isotropic pressure, however, the B_{ijkl} have Voigt symmetry and also, in view of (2.58), they can replace S_{ijkl} in the equation of motion when the initial stress is isotropic pressure. Since B_{ijkl}

measure stress-strain relations, it is these coefficients which determine the compressibility according to (2.51) and (2.53).

In (3.10) and (3.11), we have given an expression for C_{ijkl} in the initial state, in terms of the strain in the initial state and the second-, third-, and fourth-order elastic constants evaluated at the corresponding state of zero strain. With the aid of this expression, (6.4) and (6.6) can be used to express S_{ijkl} and B_{ijkl} in a similar way. In using (3.10) to relate adiabatic or isothermal elastic constants, one must measure the strain along a line of constant S or constant T , respectively.

Fuchs and Voigt have defined elastic constants as coefficients in the expansion of the energy in powers of particular sets of infinitesimal strain parameters; these are discussed in Sec. V. These two sets of coefficients and the three sets defined above are all different in general. Relations among all five sets for the case of a cubic material under isotropic pressure are listed in Tables I and II and in Eqs. (5.31).

We should like to make some comments regarding the interpretation of thermoelastic measurements on crystals in terms of static and dynamic calculations based on atomic models. We have recently extended the general theory of lattice dynamics to allow the initial configuration to correspond to arbitrary homogeneous applied stress.⁸ This was done by studying the system composed of a finite lattice plus externally applied forces, and the rotational invariance condition was that the energy of the system should be invariant with respect to rotation of the entire system. In such a rotation, the externally applied forces do no work and the lattice configuration changes only by a rotation. Hence, this rotational invariance condition is entirely equivalent to the present treatment, in which the rotational invariance ignores the stresses since they are dependent variables, and requires the energy of the material to be invariant with respect to a rotation of the material. Indeed, we find in Sec. II above that the stresses must rotate with the material if the energy is to remain unchanged. Another point of importance is that if the lattice has more than one atom per unit cell, the strain parameters, say η_{ij} , measure the homogeneous deformation of the primitive lattice, while the relative displacements of the sublattices are dependent variables and must be eliminated.⁸

In the lattice-model calculations, the largest contribution to U or F is usually the potential energy of the interacting atoms; it is therefore customary to approximate either state function by this potential.^{4,20,27-29} One can then use the method of long waves to calculate the coefficients S_{ijkl} in the equation of motion,^{4,27,28} or use the method of homogeneous deformation to calculate the C_{ijkl} constants.²⁹ Of course, the elastic constants

²⁸ K. S. Krishnan and S. K. Roy, Proc. Roy. Soc. (London) **A210**, 481 (1952).

²⁹ G. Leibfried and W. Ludwig, Z. Physik **160**, 80 (1960).

obtained in this way are neither adiabatic nor isothermal, but an approximation to either. We have shown quite generally, regardless of the initial configuration of the lattice, that the two calculations give complete agreement when the relation (6.4) between S and C coefficients is taken into account.⁸ This finding removes a previously encountered difficulty,³⁰⁻³⁴ in which the two methods of calculation were believed to give different results.

In recent years several workers have included approximately the vibrational part of the Helmholtz free energy, in order to calculate isothermal elastic constants.^{19,25,35} The constants so calculated are explicitly temperature-dependent, and in addition the vibrational part introduces departures from the Cauchy relations.

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APPENDIX: DERIVATION OF EQUATIONS FOR THE DEPENDENT VARIABLES

Here we present two different derivations of Eqs. (2.9) and (2.10), which give the dependent variables as derivatives of the state functions with respect to the independent variables. The two derivations have ultimately the same physical basis, but are cast in different languages.

The first derivation is in the language of solid-state physicists, and simply generalizes a derivation of Leibfried and Ludwig¹² to the case of arbitrary initial configuration. The initial configuration is \mathbf{X} , the final configuration is \mathbf{x} , and we proceed to calculate the virtual work done by the stresses $T_{ij}(\mathbf{x})$ when the material undergoes a virtual homogeneous deformation $\Delta\mathbf{x}$ from \mathbf{x} . We write

$$(\mathbf{x} + \Delta\mathbf{x})_i = (\delta_{ij} + \Delta u_{ij})x_j = (\delta_{ij} + \Delta u_{ij})\alpha_{jk}X_k, \quad (\text{A1})$$

and since $\alpha_{ij} = (\partial x_i / \partial X_j)$, it follows from (A1)

$$\Delta\alpha_{ik} = \Delta u_{ij}\alpha_{jk}. \quad (\text{A2})$$

From (2.4), which gives η_{ij} in terms of α_{ij} , and (A2)

³⁰ K. S. Viswanathan, Proc. Indian Acad. Sci. 39A, 196 (1954); 41A, 98 (1955).

³¹ J. Laval, J. Phys. Radium 18, 247 (1957); 18, 289 (1957); 18, 369 (1957).

³² Y. LeCorre, J. Phys. Radium 19, 541 (1958); 19, 704 (1958).

³³ D. Saint-James, J. Phys. Chem. Solids 5, 337 (1958).

³⁴ N. Joel and W. A. Wooster, Nature 180, 430 (1957); 182, 1078 (1958); Acta. Cryst. 14, 571 (1961); Soviet Phys.-Cryst. 7, 423 (1963).

³⁵ T. H. K. Barron and M. L. Klein, Proc. Phys. Soc. (London) 82, 161 (1963).

we have

$$\begin{aligned} \Delta\eta_{mn} &= \frac{1}{2}(\alpha_{pm}\Delta\alpha_{pn} + \alpha_{pn}\Delta\alpha_{pm}) \\ &= \frac{1}{2}(\alpha_{pm}\Delta u_{pq}\alpha_{qn} + \alpha_{pn}\Delta u_{pq}\alpha_{qm}) \\ &= \frac{1}{2}\alpha_{pm}\alpha_{qn}(\Delta u_{pq} + \Delta u_{qp}). \end{aligned} \quad (\text{A3})$$

Define β as the matrix inverse to α , so that

$$\beta_{ij}\alpha_{jk} = \delta_{ik}; \quad (\text{A4})$$

then (A3) can be written

$$\Delta\eta_{mn}\beta_{mi}\beta_{nj} = \frac{1}{2}(\Delta u_{ij} + \Delta u_{ji}). \quad (\text{A5})$$

Let the surface of the material in configuration \mathbf{x} be \mathbf{s} , with surface elements $d\mathbf{s}$. The i component of force on surface element $d\mathbf{s}$, due to the stress applied in the configuration \mathbf{x} , is $F_i = T_{ij}ds_j$. The virtual displacement of $d\mathbf{s}$ in the i direction is $\Delta x_i = \Delta u_{ik}x_k$, evaluated at $d\mathbf{s}$. The virtual work done by the stress acting on $d\mathbf{s}$ is

$$F_i\Delta x_i = T_{ij}ds_j\Delta u_{ik}x_k. \quad (\text{A6})$$

The total virtual work done on the material is ΔW and is just the integral of (A6) over the surface in the configuration \mathbf{x} ; this integral is transformed by Gauss's theorem to a volume integral and is evaluated as follows:

$$\Delta W = \int_{\mathbf{s}} \Delta u_{ik}x_k T_{ij}ds_j = \int_{\tau} T_{ij}\Delta u_{ij}d\tau = T_{ij}\Delta u_{ij}V(\mathbf{x}), \quad (\text{A7})$$

where $V(\mathbf{x})$ is the volume of the material in configuration \mathbf{x} . Since $T_{ij} = T_{ji}$, only the symmetric part of Δu_{ij} survives the sum on ij in (A7); this symmetric part is given by (A5) and we can write

$$\Delta W = V(\mathbf{x})T_{ij}\Delta\eta_{mn}\beta_{mi}\beta_{nj}. \quad (\text{A8})$$

Let us now write the combined first and second laws of thermodynamics in differential form per unit mass:

$$dU = dW + TdS, \text{ per unit mass.} \quad (\text{A9})$$

Multiplying (A9) by the density ρ in the configuration \mathbf{x} , and identifying ρdW with $V^{-1}\Delta W$ of (A8), gives

$$\rho dU = T_{ij}\beta_{mi}\beta_{nj}d\eta_{mn} + \rho TdS. \quad (\text{A10})$$

Also, since $F = U - TS$ per unit mass, (A10) leads to

$$\rho dF = T_{ij}\beta_{mi}\beta_{nj}d\eta_{mn} - \rho SdT. \quad (\text{A11})$$

The equations for the dependent variables follow directly from (A10) and (A11).

For a process at constant S , (A10) gives

$$T_{ij}\beta_{mi}\beta_{nj} = \rho(\partial U / \partial \eta_{mn}),$$

or, in view of (A4),

$$T_{kl} = \rho\alpha_{km}\alpha_{ln}(\partial U / \partial \eta_{mn}). \quad (\text{A12})$$

Similarly for a process at constant T , (A11) gives

$$T_{kl} = \rho\alpha_{km}\alpha_{ln}(\partial F / \partial \eta_{mn}). \quad (\text{A13})$$

For a process at constant η_{ij} , (A10) gives

$$T = (\partial U / \partial S), \quad (\text{A14})$$

while (A11) gives

$$S = -(\partial F / \partial T). \quad (\text{A15})$$

This completes derivation of (2.9) and (2.10).

An alternative derivation is provided in the language of classical elasticity theory. Truesdell and Noll,⁷ in Sec. 82, give the following equations:

$$T_{ij} = \rho \bar{\alpha}_{il} (\partial U / \partial \bar{\alpha}_{jl}) = \rho \bar{\alpha}_{il} (\partial F / \partial \bar{\alpha}_{jl}); \quad (\text{A16})$$

$$T = (\partial U / \partial S), \quad S = -(\partial F / \partial T). \quad (\text{A17})$$

Here $\bar{\alpha}_{ij}$ measures deformation from a configuration of zero stress, as in (3.1). The equations for T and S are

the same as the corresponding parts of (2.9) and (2.10) above, and are valid in any configuration. We transform (A16) from the nine independent variables $\bar{\alpha}_{ij}$ of (3.1) to the nine independent α_{ij} of (2.1); the result is

$$T_{ij} = \rho \alpha_{ik} (\partial U / \partial \alpha_{jk}) = \rho \alpha_{ik} (\partial F / \partial \alpha_{jk}). \quad (\text{A18})$$

Now since U and F depend on α_{ij} only through the η_{ij} , because of rotational invariance, we can transform the derivatives in (A18) to derivatives with respect to η_{ij} .

In view of (2.4),

$$(\partial \eta_{ij} / \partial \alpha_{rs}) = \frac{1}{2} (\alpha_{rr} \delta_{js} + \alpha_{rs} \delta_{is}). \quad (\text{A19})$$

The transformation of (A18) then gives

$$T_{ij} = \rho \alpha_{ik} \alpha_{jl} (\partial U / \partial \eta_{kl}) = \rho \alpha_{ik} \alpha_{jl} (\partial F / \partial \eta_{kl}). \quad (\text{A20})$$

Three-Center Corrections to the NaCl Valence Band*

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The tight-binding method including certain three-center terms has been applied to obtain the structure of the valence bands for NaCl. Two methods have been used. In the first method, which uses the traditional method of applying tight-binding theory, three-center terms are neglected, except those due to the long-range part of the ionic potential. In the second method, a spherical averaging technique is employed to include the three-center terms due to the short-range-potential terms. It is seen that there is a small difference in the band parameters obtained from the two methods; however, the effects on the band structures themselves are rather pronounced. Results are obtained with and without spin-orbit interaction. Some discussion of the different results is included and suggestions are made for future improvement of calculations of this nature.

I. INTRODUCTION

THE tight-binding method has been used successfully to study the valence states of rare gas and ionic solids in recent years.¹⁻⁶ With the exception of the result by Howland for KCl,³ these calculations have found the valence bands to be about 1 eV wide if spin-orbit effects are neglected. Howland's bands tend to be somewhat broader, on the order of 2 eV, and a width of 1.5 eV is achieved only after a considerable number (8) of atomic orbitals are included in the basis set. This calculation differs from the others mentioned in that a more accurate treatment of the lattice potential is used.

Recent calculations on KCl⁷ and KI⁸ by the augmented-plane-wave method indicate that the bands are of the order of 1 eV in width if spin-orbit effects are neglected. In fact there is rather good agreement between the predictions of the augmented-plane-wave method and the predictions of tight-binding theory, excepting those of Howland. Semiempirical band structures have been obtained for the alkali halides by Phillips.⁹ These band structures result in widths for the valence bands which tend to agree with those of Howland.

In this calculation, tight-binding theory is applied to NaCl, and results are obtained with and without the spin-orbit interaction. Results are obtained in two ways. First, the traditional tight-binding method is em-

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¹ W. Beall Fowler, *Phys. Rev.* **133**, A1399 (1963).

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