Lattice Dynamics and Elasticity of Stressed Crystals

DUANE C. WALLACE

Sandia Laboratory, Albuquerque, New Mexico

A conservative system composed of a collection of interacting ions plus externally applied forces is considered. The mechanical problem of motion is defined for such a system, and the equilibrium and the translational and rotational invariance conditions discussed. It is shown that the second equilibrium condition of Born and Huang, namely that the stresses must vanish in the equilibrium configuration for the infinite lattice model, is not a requirement of the theory. The dynamical matrices, whose eigenvalues are simply related to the phonon frequencies, are shown to be of the same form for a homogeneously strained crystal as for an ideal unstrained crystal. The elastic constants of a homogeneously strained crystal are calculated by the method of homogeneous deformation, and also by the method of long waves. The quantities which are observed in the measurement of sound velocities in strained crystals are the effective elastic constants, which differ from the elastic constants by terms involving the stress components. These effective elastic constants are also calculated in the lattice theory, and their properties are discussed.

I. INTRODUCTION

The theory of lattice dynamics has not been developed for a crystal which has applied stresses. The difficulties which have prevented this development are intimately associated with the problem of calculating the elastic constants of a stressed crystal.[1,2] Leibfried and Ludwig[3,4] have derived the elastic constants for a primitive lattice in the presence of isotropic pressure. They used the method of homogeneous deformation, and showed how surface effects are to be eliminated.[5] Here, the method of homogeneous deformation and lattice dynamics are extended to the case of a crystal in a homogeneously strained initial configuration, by explicitly including externally applied forces in the formulation of the problem.

In order to define the stresses and elastic constants for a crystal, the lattice treatment is compared with thermoelastic theory. This theory has been developed for homogeneously strained elastic media,[6-9] and the appropriate results are reviewed in Sec. II. In Sec. III, the mechanical problem of motion of a collection of ions in the presence of externally applied forces is defined, and equilibrium and invariance conditions are obtained. In Sec. IV the method of homogeneous deformation is applied to a finite crystal with externally applied forces, and the stresses and elastic constants are derived. Section V outlines the extension of well-known results of lattice dynamics to the case of a stressed crystal, and applies the method of long waves to the calculation of the elastic constants. In Sec. VI, the effective elastic constants, which are directly observed in ultrasonic experiments, are derived in the lattice theory, and their symmetry properties are discussed.

II. THERMOELASTICITY

Elastic Medium with Zero Initial Strain

This brief outline is based primarily on the work of Thurston[8] and Thurston and Brugger.[9] Their notation has been changed so as to mesh smoothly with that used in lattice theory. Throughout Sec. II, the Einstein summation convention is used.

Let the position of a material particle in the ideal unstrained configuration (zero stress) be **a**, and the position in a strained configuration be **x**, where the Cartesian components are indicated by a_i, x_i, respectively, $i = 1$, 2, 3. The displacement vector is **u** and the symmetric finite strain parameters are s_{ij}[10]:

$$u_i = x_i - a_i, \tag{2.1}$$

$$s_{ij} = \tfrac{1}{2}\left(\frac{\partial x_k}{\partial a_i}\frac{\partial x_k}{\partial a_j} - \delta_{ij}\right) = \tfrac{1}{2}\left(\frac{\partial u_i}{\partial a_j} + \frac{\partial u_j}{\partial a_i} + \frac{\partial u_k}{\partial a_i}\frac{\partial u_k}{\partial a_j}\right). \tag{2.2}$$

Now the following definitions are made:

$$t_{ij} = \rho_0\left(\frac{\partial E}{\partial s_{ij}}\right)_S = \rho_0\left(\frac{\partial F}{\partial s_{ij}}\right)_T, \tag{2.3}$$

$$c^S{}_{ijkl} = \left(\frac{\partial t_{ij}}{\partial s_{kl}}\right)_S = \rho_0\left(\frac{\partial^2 E}{\partial s_{kl}\partial s_{ij}}\right)_S, \tag{2.4}$$

$$c^T{}_{ijkl} = \left(\frac{\partial t_{ij}}{\partial s_{kl}}\right)_T = \rho_0\left(\frac{\partial^2 F}{\partial s_{kl}\partial s_{ij}}\right)_T, \tag{2.5}$$

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

[2] K. Huang, Proc. Roy. Soc. (London) **A203**, 178 (1950).

[3] G. Leibfried and W. Ludwig, Z. Physik **160**, 80 (1960).

[4] 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.

[5] G. Leibfried, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. VII/1, p. 104.

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

[7] A. E. Green, Proc. Roy. Soc. (London) **A266**, 1 (1962).

[8] R. N. Thurston, in *Physical Acoustics*, edited by W. P. Mason (Academic Press Inc., New York, 1964), Vol. 1A, p. 1.

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

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

where E and F are, respectively, the internal energy and Helmholtz free energy per unit mass, S and T are entropy and temperature, and $\rho_0=\rho(\mathbf{a})$ is the density of the medium in the unstrained configuration. The t_{ij} are thermodynamic tensions conjugate to the variables (s_{ij}/ρ_0), and the $c^S{}_{ijkl}$, $c^T{}_{ijkl}$ are, respectively, the adiabatic and isothermal elastic constants. As a result of their definitions, the tensions and elastic constants must have the complete "Voigt symmetry."[11]

$$t_{ij}=t_{ji}, \qquad (2.6)$$

$$c^S{}_{ijkl}=c^S{}_{jikl}=c^S{}_{ijlk}=c^S{}_{klij}; \quad \text{similarly for } c^T{}_{ijkl}. \qquad (2.7)$$

The stresses are then given by

$$\tau_{ij}=\frac{1}{J_0}\frac{\partial x_i}{\partial a_k}\frac{\partial x_j}{\partial a_l}t_{kl}, \qquad (2.8)$$

where J_0 is the Jacobian of the strain

$$J_0= \mid \partial x_i/\partial a_j \mid =\rho_0/\rho(\mathbf{x}). \qquad (2.9)$$

The equation of motion for adiabatic propagation, in the presence of body forces f_i, is

$$\rho_0\ddot{u}_i- J_0 f_i=c^S{}_{ijkl}(\partial^2 u_k/\partial a_j\partial a_l), \qquad (2.10)$$

and the expansions for E and F are

$$\rho_0 E(s_{ij},\ S) =\rho_0 E(0,\ S)+t_{ij}s_{ij}+\tfrac{1}{2}c^S{}_{ijkl}s_{ij}s_{kl}+\cdots, \qquad (2.11)$$

$$\rho_0 F(s_{ij},\ T) =\rho_0 F(0,\ T)+t_{ij}s_{ij}+\tfrac{1}{2}c^T{}_{ijkl}s_{ij}s_{kl}+\cdots, \qquad (2.12)$$

where the coefficients $(t_{ij},\ c^S{}_{ijkl},$ etc.) are evaluated at zero strain $(s_{ij}=0)$.

Homogeneously Strained Elastic Medium

Let the medium undergo a homogeneous strain from the positions $\mathbf{a}$ to new initial positions $\mathbf{r}$. If the definitions (2.1)–(2.5) are retained, the equation of motion for adiabatic propagation through the strained medium becomes[8,9]

$$\rho_0\ddot{u}_i- J_0 f_i=\tilde{A}^S{}_{ijkl}(\partial^2 u_j/\partial a_k\partial a_l), \qquad (2.13)$$

where

$$\tilde{A}^S{}_{ijkl}=\tilde{t}_{kl}\delta_{ij}+d_{im}d_{jn}\tilde{c}^S{}_{km\,ln}. \qquad (2.14)$$

Here the tilde means to evaluate at the initial state $\mathbf{r}$, and

$$d_{ij}=(\partial r_i/\partial a_j). \qquad (2.15)$$

Change of Reference Configuration

Up to now the motion of the material points in the elastic medium has been defined with respect to the positions of these points in the unstrained medium.

[11] It is understood that all derivatives are taken symmetrically, after the manner of Green (Ref. 7), so as not to violate the condition $s_{ij}=s_{ji}$.

In the lattice theory (Secs. III–V), the crystal is considered to be in an initial state of strain, and the motion of the material points with respect to their initial positions is studied. This circumstance, whose necessity is discussed further in Sec. VII, requires that the above results of thermoelasticity be expressed in terms of motion with respect to the initial strained configuration $\mathbf{r}$.

Therefore, make the following definitions, where $\rho_1=\rho(\mathbf{r})$ is the density of the strained medium.

$$U_i=x_i-r_i, \qquad (2.16)$$

$$S_{ij}=\tfrac{1}{2}\left(\frac{\partial x_k}{\partial r_i}\frac{\partial x_k}{\partial r_j}-\delta_{ij}\right)=\tfrac{1}{2}\left(\frac{\partial U_i}{\partial r_j}+\frac{\partial U_j}{\partial r_i}+\frac{\partial U_k}{\partial r_i}\frac{\partial U_k}{\partial r_j}\right), \qquad (2.17)$$

$$T_{ij}=\rho_1\left(\frac{\partial E}{\partial S_{ij}}\right)_S =\rho_1\left(\frac{\partial F}{\partial S_{ij}}\right)_T, \qquad (2.18)$$

$$C^S{}_{ijkl}=\left(\frac{\partial T_{ij}}{\partial S_{kl}}\right)_S =\rho_1\left(\frac{\partial^2 E}{\partial S_{kl}\partial S_{ij}}\right)_S, \qquad (2.19)$$

$$C^T{}_{ijkl}=\left(\frac{\partial T_{ij}}{\partial S_{kl}}\right)_T =\rho_1\left(\frac{\partial^2 F}{\partial S_{kl}\partial S_{ij}}\right)_T. \qquad (2.20)$$

According to these definitions, the coefficients T_{ij}, $C^S{}_{ijkl}$, etc., must again have the complete Voigt symmetry, (2.6) and (2.7), and the expansions for E and F are

$$\rho_1 E(S_{ij},\ S) =\rho_1 E(0,\ S)+T_{ij}S_{ij}+\tfrac{1}{2}C^S{}_{ijkl}S_{ij}S_{kl}+\cdots, \qquad (2.21)$$

$$\rho_1 F(S_{ij},\ T) =\rho_1 F(0,\ T)+T_{ij}S_{ij}+\tfrac{1}{2}C^T{}_{ijkl}S_{ij}S_{kl}+\cdots, \qquad (2.22)$$

where the coefficients $(T_{ij},\ C^S{}_{ijkl},$ etc.) are evaluated at zero strain from the initial configuration $(S_{ij}=0)$.

It is possible to relate t_{ij}, etc., to T_{ij}, etc., and also to convert the equation of motion (2.13) to an equation of motion with respect to the initial strained configuration. In order to do this, it is helpful to use the relations

$$\partial^2 U_i/\partial r_j\partial r_k=\partial^2 u_i/\partial r_j\partial r_k, \qquad (2.23)$$

$$\partial S_{ij}/\partial s_{kl}=b_{ki}b_{lj}, \qquad (2.24)$$

$$b_{ij}=(\partial a_i/\partial r_j)=(1/d_{ji}). \qquad (2.25)$$

It then follows

$$t_{ij}= (\rho_0/\rho_1) b_{ik}b_{jl}T_{kl}, \qquad (2.26)$$

$$c^S{}_{ijkl}= (\rho_0/\rho_1) b_{im}b_{jn}b_{kp}b_{lq}C^S{}_{mnpq}, \qquad (2.27)$$

and (2.13) becomes

$$\rho_1\ddot{U}_i- J_1 f_i=[T_{jl}\delta_{ik}+C^S{}_{ijkl}](\partial^2 U_k/\partial r_j\partial r_l), \qquad (2.28)$$

where J_1 is the Jacobian

$$J_1= \mid \partial x_i/\partial r_j \mid =\rho_1/\rho(\mathbf{x}), \qquad (2.29)$$

and in (2.28) the coefficients T_{jl}, C^S_{ijkl} are evaluated at $S_{ij}=0$. When body forces are neglected, (2.28) is of the same form as that given by Toupin and Bernstein,[6] and also by Green,[7] for a homogeneously strained elastic medium. Finally the stresses (2.8) may be written

$$\tau_{ij}=\frac{1}{J_1}\frac{\partial x_i}{\partial r_k}\frac{\partial x_j}{\partial r_l}T_{kl};\qquad(2.30)$$

$$\tau_{ij}=T_{ij}\quad\text{when}\quad S_{ij}=0.\qquad(2.31)$$

Alternative Definition of Elastic Constants

It is physically reasonable to consider the problem of the motion, with respect to the initial configuration, of a homogeneously strained elastic medium as completely analagous to the motion of an unstrained elastic medium. An equation of motion for adiabatic propagation may then be written down by analogy with (2.10)[7]:

$$\rho_1\ddot{U}_i-J_1f_i=E^S_{ijkl}(\partial^2U_k/\partial r_j\partial r_l).\qquad(2.32)$$

By comparison with (2.28), it is seen that these "effective" elastic constants are related to those defined by (2.19) according to

$$E^S_{ijkl}=T_{jl}\delta_{ik}+C^S_{ijkl}.\qquad(2.33)$$

It is the effective elastic constants which are observed in the measurements of sound velocities in strained crystals,[12–14] while the constants C^S_{ijkl} are derivatives of the internal energy. For general nonisotropic initial strains, the constants E^S_{ijkl} do not have the complete Voigt symmetry (2.7); this point is discussed further in Sec. VI.

III. BASIS FOR LATTICE THEORY WITH EXTERNALLY APPLIED FORCES

Definition of the Problem

The system to be considered is a collection of interacting atoms or ions plus that part of the external world which exerts forces on these ions. Let the ions be labeled by the index ν. In the presence of the interactions among the ions, and also the externally applied forces $\mathbf{f}_\nu$ (each $\mathbf{f}_\nu$ is applied to the ion ν), the ions assume an equilibrium configuration, with positions $\mathbf{r}_\nu$, in which the net force on each ion vanishes. The problem to be studied is the motion of the system about this initial equilibrium configuration; this motion is conveniently described in terms of the displacements $\mathbf{U}_\nu$ of the ions from the positions $\mathbf{r}_\nu$. Throughout this paper, the $\mathbf{f}_\nu$ are considered to be independent of time,

and the $\mathbf{U}_\nu$ are always considered to be small, but not infinitesimal.

In order to define the energy of the system as a function of the $\mathbf{U}_\nu$, two assumptions are made.

(a) The potential energy of the collection of ions, due only to interaction among the ions, is a continuous function of the variables $\mathbf{U}_\nu$ (and only these variables) in the region of small $\mathbf{U}_\nu$. Thus the potential due only to interactions among the ions may be expanded as

$$P(\mathbf{r}_\nu+\mathbf{U}_\nu)=P(\mathbf{r}_\nu)+\sum_{\nu,i}X_{\nu i}U_{\nu i}$$
$$+\tfrac{1}{2}\sum_{\nu\nu',ii'}A_{\nu i,\nu'i'}U_{\nu i}U_{\nu'i'}+\cdots,\qquad(3.1)$$

where i represents a Cartesian coordinate.[15] This expansion defines the potential energy coefficients $X_{\nu i}$, $A_{\nu i,\nu'i'}$, etc., as functions of the *initial configuration*. The coefficients $A_{\nu i,\nu'i'}$ are symmetric in the index pairs $(\nu i,\nu'i')$.

(b) All forces, including those applied by external sources, are derivable from potential functions. If $W(\mathbf{r}_\nu)$ is the work done on the ions by external forces, the total potential of the system in the equilibrium configuration is

$$Q(\mathbf{r}_\nu)=P(\mathbf{r}_\nu)-W(\mathbf{r}_\nu).\qquad(3.2)$$

Then $Q(\mathbf{r}_\nu)$ is conserved in any real variation of the $\mathbf{r}_\nu$ which is brought about by a change in the $\mathbf{f}_\nu$.

Now if the ions undergo a virtual displacement $\mathbf{U}_\nu$, i.e., a displacement in which the $\mathbf{f}_\nu$ remain fixed, the work done by external forces is $-\sum_{\nu i}f_{\nu i}U_{\nu i}$, and the potential of the system is given by[16]

$$Q(\mathbf{r}_\nu+\mathbf{U}_\nu)=Q(\mathbf{r}_\nu)+\sum_{\nu,i}(X_{\nu i}-f_{\nu i})U_{\nu i}$$
$$+\tfrac{1}{2}\sum_{\nu\nu',ii'}A_{\nu i,\nu'i'}U_{\nu i}U_{\nu'i'}+\cdots.\qquad(3.3)$$

The Hamiltonian for the initial system (ions plus initial external forces) is

$$\mathcal{H}=T(\dot{U}_{\nu i})+Q(\mathbf{r}_\nu+\mathbf{U}_\nu),\qquad(3.4)$$

$$T(\dot{U}_{\nu i})=\tfrac{1}{2}\sum_{\nu,i}M_\nu(\dot{U}_{\nu i})^2,\qquad(3.5)$$

where M_ν is the mass of ion ν, and $\dot{U}_{\nu i}$ is the time derivative of $U_{\nu i}$.

The Equilibrium Condition

The equilibrium condition for the static configuration is that the net force on each ion vanishes. The total force on ion ν in direction i, when all $\mathbf{U}_\nu=0$, is

$$-(\partial Q/\partial U_{\nu i})\ (\text{at all }U_{\nu i}=0)=-X_{\nu i}+f_{\nu i}.$$

[12] D. Lazarus, Phys. Rev. **76**, 545 (1949).
[13] R. E. Schmunk and C. S. Smith, Phys. Chem. Solids **9**, 100 (1959); W. B. Daniels and C. S. Smith, Phys. Rev. **111**, 713 (1958); W. B. Daniels, *ibid.* **119**, 1246 (1960).
[14] H. J. McSkimin, J. Acoust. Soc. Am. **30**, 314 (1958); H. J. McSkimin and P. Andreatch, Jr., J. Appl. Phys. **34**, 651 (1963).

[15] In the remainder of the paper, the Einstein summation convention is not used, and Cartesian indices are always denoted by $i, i', \cdots$.
[16] Equations (3.1) and (3.3) imply that the potential energy does not depend explicitly on other coordinates of the ions, such as spin direction; Ref. 4, footnote 26a.

Thus

$$X_{\nu i} - f_{\nu i} = 0, \quad \text{all } (\nu, i); \quad \text{equilibrium condition.} \quad (3.6)$$

As a result of this condition, $Q(\mathbf{r}_\nu + \mathbf{U}_\nu)$ is a stationary function (and presumably a relative minimum) with respect to arbitrary virtual displacements of the ions from equilibrium. Neither $P(\mathbf{r}_\nu + \mathbf{U}_\nu)$ nor $W(\mathbf{r}_\nu + \mathbf{U}_\nu)$ is stationary in general.

The translational and rotational equilibrium of the collection of ions as a whole requires the conditions[3]

$$\sum_\nu f_{\nu i} = 0, \quad \text{all } i; \quad (3.7)$$

$$\sum_\nu f_{\nu i} r_{\nu i'} \text{ is symmetric in } (i, i'), \quad \text{all } (i, i'). \quad (3.8)$$

These conditions are contained in (3.6), since for physical reasons a collection of ions should not experience a net force or torque as a result of the interactions among the ions, i.e.,

$$\sum_\nu X_{\nu i} = 0, \quad \text{all } i; \quad (3.7\text{a})$$

$$\sum_\nu X_{\nu i} r_{\nu i'} \text{ is symmetric in } (i, i'), \quad \text{all } (i, i'). \quad (3.8\text{a})$$

In view of (3.6), these equations are identical with (3.7) and (3.8).

When application is to be made to a crystalline lattice, it is convenient to eliminate surface effects. This may be done by considering the interior of a finite crystal, as in the present paper (Secs. IV and V), or with the aid of the idealization of the infinite lattice. Born and Huang[1] have stated that in addition to the requirement that the net force on each ion vanishes, a second equilibrium condition is required for the infinite lattice model, namely that the equilibrium configuration corresponds to vanishing stresses. This second condition is equivalent to requiring that $P(\mathbf{r}_\nu + \mathbf{U}_\nu)$ per unit volume be stationary with respect to a homogeneous deformation of the lattice. To show this, $P(\mathbf{r}_\nu + \mathbf{U}_\nu)$ per unit volume can be written as a series in the strains $S_{ii'}$, when the displacements $\mathbf{U}_\nu$ are taken to be a homogeneous deformation [see (4.4) below].

$$V^{-1}P(\mathbf{r}_\nu + \mathbf{U}_\nu) = V^{-1}P(\mathbf{r}_\nu) + \sum_{ii'} C_{ii'} S_{ii'} + \cdots, \quad (3.9)$$

where V is the volume of the crystal. In (3.9), the $C_{ii'}$ are components of the stress tensor in the equilibrium configuration, and the requirement that $C_{ii'}$ vanish is equivalent to the requirement that $P(\mathbf{r}_\nu + \mathbf{U}_\nu)$ be stationary with respect to a homogeneous deformation from the equilibrium configuration. As an example, it is easily shown that for the central force model of Born and Huang (Ref. 1, article 29), the condition that $P(\mathbf{r}_\nu + \mathbf{U}_\nu)$ per unit volume is stationary with respect to arbitrary $S_{ii'}$ is identical with their condition (29.17) for vanishing stresses.

An essential point of the present paper is that the second equilibrium condition of Born and Huang is not a requirement of the theory. The Hamiltonian (3.4) is valid in the presence of externally applied forces, and the elimination of surface effects is carried out below. The only equilibrium condition is (3.6), and this guarantees that Q is stationary at equilibrium, while in general P is not required to be stationary.

Translational and Rotational Invariance Conditions

The potential energy of the system (ions plus externally applied forces) is invariant with respect to translation or rotation of the system or the coordinate system. It is possible to carry out a simple extension of the derivations of Leibfried and Ludwig,[3,4] whose treatment is valid for a collection of ions without externally applied forces, or with an isotropic pressure. If the ions undergo displacements $\mathbf{Y}_\nu$, the potential energy coefficients vary according to[3,4]

$$X_{\nu i}(\mathbf{r}_\nu + \mathbf{Y}_\nu) = X_{\nu i}(\mathbf{r}_\nu) + \sum_{\nu' , i'} A_{\nu i, \nu' i'} Y_{\nu' i'} + \cdots, \quad (3.10)$$

etc. for higher order coefficients. These are the coefficients which appear in the expansions for $P(\mathbf{r}_\nu + \mathbf{Y}_\nu + \mathbf{U}_\nu)$ or $Q(\mathbf{r}_\nu + \mathbf{Y}_\nu + \mathbf{U}_\nu)$, where the displacements $\mathbf{U}_\nu$ are still given in the same coordinates as before.

Now let the system undergo a translation $\boldsymbol{\varepsilon}$ ($Y_{\nu i} = \epsilon_i$, all ν, with arbitrary ϵ_i). In this case each $f_{\nu i}$ remains the same. Now each coefficient in the expansion for $Q(\mathbf{r}_\nu + \mathbf{Y}_\nu + \mathbf{U}_\nu)$ must equal the corresponding coefficient in the expansion (3.3) for $Q(\mathbf{r}_\nu + \mathbf{U}_\nu)$, since the $\mathbf{U}_\nu$ are arbitrary. This gives rise to the relations

$$\sum_{\nu'} A_{\nu i, \nu' i'} = \sum_{\nu} A_{\nu i, \nu' i'} = 0, \quad \text{all } (\nu i, \nu' i'), \quad (3.11)$$

etc. for higher order coefficients.

To obtain the rotational invariance conditions, carry out the following two operations on the initial configuration.

(a) Rotate the coordinate system through the infinitesimal angle $\omega(\omega_{ii'} = -\omega_{i'i})$, and express (3.3) in terms of the displacements $\tilde{U}_{\nu i}$, where the components $\tilde{U}_{\nu i}$ are given in the rotated coordinate system.

$$Q(\mathbf{r}_\nu + \mathbf{U}_\nu) = Q(\mathbf{r}_\nu) + \sum_{\nu, i} (\tilde{X}_{\nu i} - \tilde{f}_{\nu i}) \tilde{U}_{\nu i} + \cdots, \quad (3.12)$$

$$\tilde{X}_{\nu i} = \sum_{i'} (\delta_{ii'} + \omega_{i'i}) X_{\nu i'}, \quad (3.13)$$

$$\tilde{f}_{\nu i} = \sum_{i'} (\delta_{ii'} + \omega_{i'i}) f_{\nu i'}, \quad \text{etc.} \quad (3.14)$$

(b) Rotate the initial system of ions plus externally applied forces through the infinitesimal angle $-\omega$, and express (3.3) in terms of the displacements $U_{\nu i}$ in the original coordinate system. In this operation each force component $f_{\nu i}$ is rotated through $-\omega$, but is still applied to the ion ν. The rotation of the collection of ions is accomplished by the displacements[4]

$$Y_{\nu i} = -\sum_{i'} \omega_{ii'} r_{\nu i'}. \quad (3.15)$$

Then with the aid of (3.10), there follows

$$Q(\mathbf{r}_\nu + \mathbf{U}_\nu) = Q(\mathbf{r}_\nu) + \sum_{\nu,i} (\bar{X}_{\nu i} - \bar{f}_{\nu i}) U_{\nu i} + \cdots, \quad (3.16)$$

$$\bar{X}_{\nu i} = X_{\nu i} - \sum_{\nu',i'i''} A_{\nu i,\nu' i'} \omega_{i'i''} r_{\nu' i''} + \cdots, \quad (3.17)$$

$$\bar{f}_{\nu i} = \sum_{i'} (\delta_{ii'} - \omega_{ii'}) f_{\nu i'}, \text{ etc.} \quad (3.18)$$

Since the $\mathbf{U}_\nu$ are arbitrary, the corresponding coefficients in (3.12) and (3.16) must be the same. In particular

$$\tilde{X}_{\nu i} - \tilde{f}_{\nu i} = \bar{X}_{\nu i} - \bar{f}_{\nu i}. \quad (3.19)$$

Equation (3.19) is to be satisfied to first order in $\omega_{ii'}$; in view of the antisymmetry of ω, this leads to the condition

$$\sum_{\nu'} A_{\nu i,\nu' i''} r_{\nu' i'} + f_{\nu i} \delta_{ii''} \text{ is symmetric in } (i', i''). \quad (3.20)$$

Since $f_{\nu i}$ can be replaced by $X_{\nu i}$, according to (3.6), then (3.20) is the same as (2.9b) of Leibfried and Ludwig.[4] The higher order equations of Leibfried and Ludwig are obtained exactly as in their treatment, since the $f_{\nu i}$ do not enter in these conditions. Their zero-order equation (2.9a) is the same as (3.8a) above. These conditions apply to the initial equilibrium configuration.

Method of Eliminating Surface Effects

In the case that the collection of ions is supposed to represent a crystal, the ion index ν is written as the pair (n, j), where n labels a unit cell and j labels an ion in the unit cell $(j = 1, 2, \cdots, J)$. The equilibrium position of ion (n, j) is $\mathbf{r}_{nj} = \mathbf{r}_n + \mathbf{r}_j$. In the present work, the crystal is presumed to depart from perfect periodicity (with constant lattice parameters) only near the surface. This implies that the externally applied forces $\mathbf{f}_{nj}$ are the same for each equivalent ion in the interior. The "interior" of the crystal is defined as those cells n for which sums such as

$$\sum_{n',j'} A_{nji,n'j'i'}, \qquad \sum_{n',j'} A_{nji,n'j'i'} (r_{n'j'i''} - r_{nji''})^2$$

converge in the region of perfect periodicity, i.e., the sum need not be carried out over cells n' which are near the surface. The calculations of this paper are restricted to cases in which these sums do converge in the interior for an arbitrarily large (but finite) crystal.

It is convenient to take the origin of coordinates at a cell in the interior, so that $\mathbf{r}_n = 0$ for $n = 0$. The lattice symmetry in the interior gives rise to the following relations with respect to this origin of coordinates.[5]

For every $\mathbf{r}_n$ there is a $-\mathbf{r}_n = \mathbf{r}_{-n}$; (3.21)

$A_{0i,ni'} = A_{0i',ni}$, primitive lattice; (3.22)

$A_{0ji,nj'i'} = A_{0j'i',-nji}$, nonprimitive lattice. (3.23)

The method of eliminating surface effects from a

quantity is to write the quantity so that it is the same for each cell n in the interior, and evaluate at $n = 0$. For example, (3.11) can be written

$$\sum_{n'} A_{0i,n'i'} = 0, \quad \text{all } (i, i'), \text{ primitive lattice};$$

$$\sum_{n',j'} A_{0ji,n'j'i'} = 0, \quad \text{all } (ji, i'), \text{ nonprimitive lattice.}$$

$$(3.24)$$

In addition, with the aid of (3.11), it is obvious that

$$\sum_{nn',jj'} A_{nji,n'j'i'} (r_{n'j'i''} - r_{nji''}) = 0. \quad (3.25)$$

This expression is the same for all cells n in the interior, and evaluating at $n = 0$ with $\mathbf{r}_n = 0$ gives

$$\sum_{n',jj'} A_{0ji,n'j'i'} (r_{n'j'i''} - r_{ji''}) = 0. \quad (3.26)$$

IV. THE STATIC LATTICE AND ELASTIC CONSTANTS

The Method of Homogeneous Deformation

The system is now specialized to a collection of ions representing a finite crystal of initial volume V, plus initial externally applied forces. Thus the crystal is in a state of strain. From the initial equilibrium configuration, let the lattice points (ions) undergo a homogeneous deformation given by the displacements

$$U_{nji} = Y_{ji} + \sum_{i'} Y_{ii'} r_{nji'}. \quad (4.1)$$

This deformation is explicitly assumed to be brought about by additional forces $\mathbf{g}_{nj}$ applied to the ions only in the surface region, while all initial forces $\mathbf{f}_{nj}$ are held constant.[17] The $Y_{ii'}$ are independent elastic strain parameters; the Y_{ji} represent displacements of the sublattices, and must be considered as dependent parameters. After the Y_{ji} are eliminated, the elastic energy per unit volume can be expressed as

$$V^{-1} P(\mathbf{r}_{nj} + \mathbf{U}_{nj}) = V^{-1} P(\mathbf{r}_{nj}) + \sum_{ii'} D_{ii'} Y_{ii'}$$

$$+ \tfrac{1}{2} \sum_{ii'i''i'''} D_{ii'i''i'''} Y_{ii'} Y_{i''i'''} + \cdots. \quad (4.2)$$

This equation defines the D coefficients in terms of the coefficients in the expansion (3.1). Henceforth, the present work is restricted to terms no higher than quadratic in strain parameters.

Now transform to the symmetric finite strain parameters (2.17).

$$S_{ii'} = \tfrac{1}{2} [Y_{ii'} + Y_{i'i} + \sum_{i''} Y_{i''i} Y_{i''i'}]. \quad (4.3)$$

The elastic energy can be expressed in terms of the

$S_{ii'}$ as

$$V^{-1}P(\mathbf{r}_{nj}+\mathbf{U}_{nj}) = V^{-1}P(\mathbf{r}_{nj}) + \sum_{ii'}C_{ii'}S_{ii'}$$

$$+\tfrac{1}{2}\sum_{ii'i''i'''}C_{ii'i''i'''}S_{ii'}S_{i''i'''}. \quad (4.4)$$

This equation defines the C coefficients, and accordingly these coefficients must have the complete Voigt symmetry [analogous to (2.6) and (2.7)]. By comparing (4.2) and (4.4), and using the symmetry of the C coefficients, Leibfried and Ludwig[3] have shown

$$C_{ii'} = D_{ii'}, \quad (4.5)$$

$$C_{ii'i''i'''} = D_{ii'i''i'''} - C_{i'i'''}\delta_{ii''}. \quad (4.6)$$

A fundamental approximation in the interpretation of (4.4) is to equate the elastic energy with either the Helmholtz free energy or the internal energy. Thus, when the $\mathbf{U}_{nj}$ are a homogeneous deformation,

$$V^{-1}P(\mathbf{r}_{nj}+\mathbf{U}_{nj})\approx\rho_1 F(S_{ii'}, T)\approx\rho_1 E(S_{ii'}, S). \quad (4.7)$$

Since the temperature does not enter into P, there is no difference between differentiation of P at constant T or constant S. According to this interpretation,

$$C_{ii'}\approx T_{ii'}, \quad (4.8)$$

$$C_{ii'i''i'''}\approx C^{S}_{ii'i''i'''}\approx C^{T}_{ii'i''i'''}, \quad (4.9)$$

where the quantities in (4.8) and (4.9) are all evaluated in the initial configuration ($S_{ii'}=0$).

Primitive Lattice

In view of the equilibrium and invariance conditions (3.6), (3.8a), and (3.20), the treatment of the primitive lattice for the present case of arbitrary initial stress follows exactly that of Leibfried and Ludwig[3] for the case of isotropic pressure. The more general derivation is outlined here to serve as a foundation for the complicated nonprimitive lattice problem.

The homogeneous deformation is

$$U_{ni} = \sum_{i'}Y_{ii'}r_{ni'}, \quad (4.10)$$

and the D coefficients are

$$D_{ii'} = V^{-1}\sum_{n}X_{ni}r_{ni'}, \quad (4.11)$$

$$D_{ii'i''i'''} = V^{-1}\sum_{nn'}A_{ni,n'i''}r_{ni'}r_{n'i'''}. \quad (4.12)$$

It may appear that the D coefficients depend on the origin of coordinates, but this is not the case, since in view of (3.7a),

$$\sum_{n}X_{ni}r_{ni'} = \sum_{n}X_{ni}(r_{ni'} - R_{i'}),$$

where $\mathbf{R}$ is an arbitrary vector. Similarly, with the aid of (3.11), it is seen that $D_{ii'i''i'''}$ is independent of $\mathbf{R}$.

With the aid of (3.8a), and noting that $A_{ni,n'i''} = A_{n'i'',ni}$, it follows that

$$D_{ii'} = D_{i'i}, \quad (4.13)$$

$$D_{ii'i''i'''} = D_{i''i'''ii'}. \quad (4.14)$$

In the following, $D_{ii'}$ is replaced by $C_{ii'}$.

It is not possible to eliminate surface effects from $C_{ii'}$; the sum (4.11) must be carried out over the entire crystal. Physically this is because for a given state of initial strain, the $C_{ii'}$ are fixed regardless of the volume of the crystal. This point gives no difficulty, however, since by (4.8) the $C_{ii'}$ are components of the observable initial stresses. Surface effects can be eliminated from the $D_{ii'i''i'''}$ by taking the combination symmetric in (i', i''').[3,4]

$$\tfrac{1}{2}(D_{ii'i''i'''}+D_{ii'''i''i'})$$

$$=\tfrac{1}{2}V^{-1}\sum_{nn'}A_{ni,n'i''}\times(r_{ni'}r_{n'i'''}+r_{ni'''}r_{n'i'})$$

$$=-\tfrac{1}{2}V^{-1}\sum_{nn'}A_{ni,n'i''}(r_{n'i'}-r_{ni'})(r_{n'i'''}-r_{ni'''})$$

$$=-\tfrac{1}{2}V_c^{-1}\sum_{n'}A_{0i,n'i''}r_{n'i'}r_{n'i'''}$$

$$=\bar{D}_{ii''i'i'''}. \quad (4.15)$$

The second equality follows by (3.11), the third equality represents the elimination of surface effects, with V_c = volume of one unit cell in the interior, and $\mathbf{r}_n = 0$ for $n=0$, and the fourth equality defines the $\bar{D}$ coefficients. The $\bar{D}$ coefficients satisfy the following symmetry properties.

$$\bar{D}_{ii''i'i'''} = \bar{D}_{ii''i'''i'}, \quad (4.16)$$

$$\bar{D}_{ii''i'i'''} = \bar{D}_{i'i''ii'''}, \quad (4.17)$$

$$\bar{D}_{ii''i'i'''}+C_{ii''}\delta_{i'i'''} = \bar{D}_{i'i''ii'''}+C_{i'i''}\delta_{ii''}. \quad (4.18)$$

The first symmetry is obvious from the definition (4.15), and (4.17) follows with the aid of (3.22). The third symmetry is proved as follows.[3,4] Multiply (3.20) by a component of $\mathbf{r}_n$, sum over n, and relabel Cartesian indices to obtain the condition

$$\sum_{nn'}A_{ni,n'i''}r_{ni'}r_{n'i'''}+\sum_{n}X_{ni''}r_{ni'}\delta_{ii'''}$$

$$\text{is symmetric in } (i'', i'''). \quad (4.19)$$

This may be written

$$D_{ii'i''i'''}+C_{i'i''}\delta_{ii'''} = D_{ii'i'''i''}+C_{i'i'''}\delta_{ii''}. \quad (4.20)$$

From (4.20), (4.14), (4.13), and the definition (4.15) of the $\bar{D}$ coefficients, (4.18) may be proved directly.

Finally, from (4.6), (4.13), and (4.15), the elastic constants are given by

$$\tfrac{1}{2}(C_{ii'i''i'''}+C_{ii'''i''i'}) = \bar{D}_{ii''i'i'''} - C_{i'i'''}\delta_{ii''}. \quad (4.21)$$

With the aid of symmetries of all these quantities, (4.21) may be solved for the elastic constants.[3]

$$C_{ii'i''i'''} = \bar{D}_{ii''i'i'''} + \bar{D}_{i'i''ii'''} - \bar{D}_{ii'i''i'''} - C_{i'i''}\delta_{ii''}$$

$$- C_{ii'''}\delta_{i'i''} + C_{i''i''}\delta_{ii'}. \quad (4.22)$$

The right-hand side of (4.22) must have the complete Voigt symmetry of the left-hand side, and the relations (4.16)–(4.18) are just the necessary and sufficient conditions to insure this symmetry.

Nonprimitive Lattice

The crystal undergoes a homogeneous deformation from the initial state, with displacements (4.1), as a result of additional forces $\mathbf{g}_{nj}$ applied to the ions in the surface region. A complication arises if the initial externally applied forces $\mathbf{f}_{nj}$ are allowed to penetrate throughout the crystal, as would be the case for an applied electric field. For such a case, the energy density associated with the additional displacement (4.1) includes polarization effects (e.g., piezoelectric and magnetostrictive effects), as well as elastic stress-strain effects, due to the motion of the ions in the presence of the initial field.[18] This paper does not consider polarization effects[19]; therefore let

$$\mathbf{f}_{nj} = \mathbf{X}_{nj} = 0, \quad \text{all } (n, j) \text{ in the interior.} \quad (4.23)$$

The initial state of the crystal is thus one of arbitrary *elastic* strain, due to the initial forces $\mathbf{f}_{nj}$ which are applied to ions in the surface region.

When (4.1) is used in (3.1), the elastic energy per unit volume becomes

$$V^{-1}P(\mathbf{r}_{nj} + \mathbf{U}_{nj}) = V^{-1}P(\mathbf{r}_{nj})$$

$$+ V^{-1}\sum_{n,j,i} X_{nji}[Y_{ji} + \sum_{i'} Y_{ii'}r_{nji'}]$$

$$+ \tfrac{1}{2}V^{-1}\sum_{nn',jj',ii'} A_{nji,n'j'i'}$$

$$\times [Y_{ji}Y_{j'i'} + 2Y_{ji}\sum_{i''}Y_{i'i''}r_{n'j'i''}$$

$$+ \sum_{i''i'''} Y_{ii''}Y_{i'i'''}r_{nji''}r_{n'j'i'''}], \quad (4.24)$$

where two cross terms linear in Y_{ji} have been combined by interchanging indices to yield the middle term in the last square bracket. Surface effects can be eliminated at once from three of the terms in (4.24). Thus

$$V^{-1}\sum_{n,j,i} X_{nji}Y_{ji} = V_c^{-1}\sum_{j,i}X_{0ji}Y_{ji} = 0, \quad (4.25)$$

---

[18] See, for example, W. P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1958).

[19] The present treatment, with nonvanishing $\mathbf{X}_{nj}$ in the interior, serves as a starting point for the study of the polarization effects in crystals from the atomic point of view. However, with a nonvanishing contribution to the energy density of the form of (4.25), it is necessary to solve (4.27) for the Y_{ji} to second order in the $Y_{ii'}$.

where the expression vanishes by (4.23). By using the methods which were used in writing (3.25), and transforming to (3.26), the first two terms in the sum involving A coefficients in (4.24) may be written

$$\tfrac{1}{2}V_c^{-1}\sum_{n',jj',ii'} A_{0ji,n'j'i'}[Y_{ji}Y_{j'i'}$$

$$+ 2Y_{ji}\sum_{i''}Y_{i'i''}(r_{n'j'i''} - r_{ji''})], \quad (4.26)$$

where the origin of coordinates is at $n = 0$ as usual.

The parameters Y_{ji} are eliminated by requiring that the net force on each ion vanish in the final configuration, i.e., that Q is again stationary with respect to arbitrary virtual displacements of the ions from their final configuration (as in Sec. III above). With the aid of (3.10), and (4.1) and noting that $\mathbf{f}_{nj}$ remain constant while $\mathbf{g}_{nj}$ are applied, this condition is written

$$f_{nji} + g_{nji} = X_{nji} +$$

$$+ \sum_{n',j',i'} A_{nji,n'j'i'}[Y_{j'i'} + \sum_{i''}Y_{i'i''}r_{n'j'i''}] + \cdots. \quad (4.27)$$

This is to be satisfied for all (n, j, i). Since the energy density is required only to second order in the strain parameters $Y_{ii'}$, and in view of (4.25), (4.27) need only be solved to first order in the $Y_{ii'}$. From (3.6), it is seen that the f_{nji} and X_{nji} may be canceled from (4.27). It is advantageous to eliminate surface effects from (4.27); since $g_{nji} = 0$ in the interior the result is

$$\sum_{n',j',i'} A_{0ji,n'j'i'}Y_{j'i'} = - \sum_{n',j',i'i''} A_{0ji,n'j'i'}$$

$$\times (r_{n'j'i''} - r_{ji''})Y_{i'i''}. \quad (4.28)$$

This is a set of inhomogeneous equations for the Y_{ji}, and the solution has been discussed previously.[1,5] Since the homogeneous equations have solutions $Y_{i'}$ [with arbitrary $Y_{i'}$; the proof follows from (3.24)], the sublattice motion is arbitrary to within a vector $\mathbf{Y}$. Thus (4.28) determines only the relative motion of the sublattices; this is a direct consequence of eliminating the surface effects from (4.27). The solubility condition for (4.28) is just the equation (3.26), and thus is satisfied with the neglect of surface effects. The matrix of coefficients on the left-hand side of (4.28), $\sum_{n'}A_{0ji,n'j'i'}$, is symmetric in the index pairs $(ji, j'i')$, by virtue of (3.21) and (3.23). The solution is therefore given in terms of a (real) symmetric matrix $R_{ji,j'i'}$[1,5]:

$$Y_{ji} = - \sum_{n'',j'j'',i'i''i'''} R_{ji,j'i'}A_{0j'i',n''j''i''}$$

$$\times (r_{n''j''i'''} - r_{j'i'''})Y_{i''i'''}, \quad (4.29)$$

$$R_{ji,j'i'} = R_{j'i',ji}. \quad (4.30)$$

In (4.29) the particular solution Y_i has been dropped; this part of the solution always gives a vanishing contribution in the subsequent calculations. The $R_{ji,j'i'}$ do not contain surface effects, and also these coeffi-

cients do not form a matrix inverse to $\sum_{n'} A_{0ji,n'j'i'}$. For abbreviation, make the definition

$$Y_{ji} = \sum_{i''i'i'''} N_{ji,i''i'''} Y_{i''i'''}. \qquad (4.31)$$

It is now possible to eliminate the Y_{ji} from (4.24). First if (4.28) is used directly in (4.26), the term quadratic in Y_{ji} exactly cancels half of the term linear in Y_{ji}. Then, with the aid of (4.31), (4.25), and (4.26), Eq. (4.24) is transformed to the form (4.2), with

$$D_{ii'} = V^{-1} \sum_{n,j} X_{nji} r_{nji'}, \qquad (4.32)$$

$$D_{ii'i''i'''} = V_c^{-1} \sum_{n',jj',i^{iv}} A_{0ji^{iv},n'j'i}(r_{n'j'i'} - r_{ji'})$$

$$\times N_{ji^{iv},i''i'''} + V^{-1} \sum_{nn',jj'} A_{nji,n'j'i''} r_{nji'} r_{n'j'i'''}. \qquad (4.33)$$

Again it is not possible to eliminate surface effects from $D_{ii'}$, but this causes no difficulty. By (3.8a), $D_{ii'} = D_{i'i}$; in the following $D_{ii'}$ is replaced by $C_{ii'}$, according to (4.5). As in the case of the primitive lattice, surface effects are eliminated from the last term in $D_{ii'i''i'''}$ by taking the combination symmetric in (i', i''').

$$\tfrac{1}{2}(D_{ii'i''i'''} + D_{ii'''i''i'}) = \bar{D}_{ii'i''i'''}, \qquad (4.34)$$

$$\bar{D}_{ii'i''i'''} = \tfrac{1}{2} V_c^{-1} \sum_{n',jj',i^{iv}} A_{0ji^{iv},n'j'i}$$

$$\times [(r_{n'j'i'} - r_{ji'}) N_{ji^{iv},i''i'''} + (r_{n'j'i'''} - r_{ji'''}) N_{ji^{iv},i''i'}]$$

$$- \tfrac{1}{2} V_c^{-1} \sum_{n',jj'} A_{0ji,n'j'i''}(r_{n'j'i'} - r_{ji'})(r_{n'j'i'''} - r_{ji'''}). \qquad (4.35)$$

It is now possible to show that the $\bar{D}$ coefficients of (4.35) satisfy the relations (4.16)–(4.18). This involves a lot of algebra, and the procedure will only be sketched. Equation (4.16) again follows from the definition (4.35). To prove (4.17), write out the $N_{ji^{iv},i''i'''}$, etc., according to their definition [(4.31) and (4.29)] and use (4.30) along with the symmetry of the A coefficients in their index sets. To prove (4.17) for the last term in $\bar{D}$, use (3.21) and (3.23). In proving (4.18), it is convenient to eliminate surface effects directly from (3.20) to get the condition, with the aid of (4.23),

$$\sum_{n',j} A_{0ji,n'j'i'}(r_{n'j'i''} - r_{ji''}) \text{ is symmetric in } (i', i''). \qquad (4.36)$$

This condition can be used to show that

$$N_{ji,i'i''} = N_{ji,i''i'}. \qquad (4.37)$$

Equation (4.18) may be proved for the last term in $\bar{D}$ by a procedure analogous to the proof for the primitive lattice.

From (4.6), (4.13), and (4.34), the elastic constants

are given by the same expressions as for the primitive lattice, namely (4.21) and (4.22), and are again shown to have the Voigt symmetry as a result of (4.16)–(4.18).

V. LATTICE DYNAMICS AND LONG-WAVELENGTH ACOUSTIC MODES

The Dynamical Matrix

The problem of lattice dynamics is to find the normal coordinates of the Hamiltonian (3.4). The usual harmonic approximation is made by dropping terms in (3.3) which are of higher order than quadratic in the displacements. Higher order terms have been extensively discussed in perturbation treatments.[4,20–23] In view of (3.6), the harmonic Hamiltonian is written

$$\mathcal{H}_H = Q(r_{nj}) + \tfrac{1}{2} \sum_{n,j,i} M_j (\dot{U}_{nji})^2$$

$$+ \tfrac{1}{2} \sum_{nn',jj',ii'} A_{nji,n'j'i'} U_{nji} U_{n'j'i'}, \qquad (5.1)$$

where the A coefficients are evaluated at the initial configuration. The virtual displacements and their time derivatives satisfy the commutation relations

$$[M_j \dot{U}_{nji}, U_{n'j'i'}] = -i\hbar \delta_{nn'} \delta_{jj'} \delta_{ii'}, \qquad (5.2)$$

$$[\dot{U}_{nji}, \dot{U}_{n'j'i'}] = [U_{nji}, U_{n'j'i'}] = 0. \qquad (5.3)$$

This problem has been treated in detail for the case $f_{nj} = 0$, all (n, j).[1,24–26] These treatments have, quite naturally, carried the restriction $X_{nj} = 0$, all (n, j). The elimination of surface effects is essentially simpler in lattice dynamics than in the method of homogeneous deformation. This is because in the small vibration problem (lattice dynamics), the equilibrium positions remain fixed. Thus the normal coordinates of the harmonic Hamiltonian are found by applying the cyclic boundary condition to macrocrystals in the interior of a large finite crystal, or in an infinite lattice.[1,26]

The Hamiltonian (5.1) is a homogeneous quadratic form in U_{nji}, $\dot{U}_{nji}$, and the standard procedures[1,24–26] can be applied directly to the present case. With the cyclic boundary condition applied to macrocrystals con-

[20] M. Born and E. Brody, Z. Physik 6, 132 (1921).
[21] W. Ludwig, Phys. Chem. Solids 4, 283 (1958).
[22] A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (N. Y.) 15, 337, 360 (1961); A. A. Maradudin, A. E. Fein, and G. H. Vineyard, Phys. Stat. Solidi 2, 1479 (1962); A. A. Maradudin, ibid. 2, 1493 (1962); P. A. Flinn and A. A. Maradudin, Ann. Phys. (N. Y.) 22, 223 (1963).
[23] J. M. Keller and D. C. Wallace, Phys. Rev. 126, 1275 (1962); D. C. Wallace, Phys. Rev. 131, 2046 (1963); 133, A153 (1964).
[24] G. H. Begbie and M. Born, Proc. Roy. Soc. (London) A188, 179 (1947).
[25] R. E. Peierls, Quantum Theory of Solids (Clarendon Press, Oxford, England, 1955).
[26] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3.

taining N unit cells, the results are as follows:

$$a_{k,ji,j'i'} = \sum_{n'} A_{0ji,n'j'i'} \exp[i\mathbf{k}\cdot(\mathbf{r}_{n'j'}-\mathbf{r}_j)], \quad (5.4)$$

$$\sum_{j'i'} a_{k,ji,j'i'} v_{ks,j'i'} = M_j(\omega_{ks})^2 v_{ks,ji}, \quad (5.5)$$

$$\sum_{ji} M_j v_{ks,ji} v_{-ks',ji} = M_c \delta_{ss'}, \quad (5.6)$$

$$M_j \sum_s v_{ks,ji} v_{-ks,j'i'} = M_c \delta_{jj'} \delta_{ii'}, \quad (5.7)$$

$$M_c = \sum_j M_j, \quad (5.8)$$

where $v_{-ks} = v_{ks}^*$ is taken.

The dynamical matrix a_k, defined by (5.4), is Hermitian and of order $3J$ (J is the number of ions per unit cell). The eigenvectors of a_k are v_{ks}, $s = 1, 2, \cdots,$ $3J$, and the eigenvalues are $M_c(\omega_{ks})^2$, where ω_{ks} is the circular frequency of the normal mode with wave vector $\mathbf{k}$ and polarization s. There are N values of $\mathbf{k}$ distributed in the first Brillouin zone. Equations (5.6) and (5.7) are orthonormality and completeness relations, respectively, for the eigenvectors.[27]

The solution is identical in form to that for the case $f_{nji} = X_{nji} = 0$. However, the dynamical matrices now depend explicitly on the initial configuration through the $\mathbf{r}_{nj}$ vectors, and implicitly through the dependence of the A coefficients on the initial configuration.

Long Waves and Elastic Constants

Born's method of long waves[1,24] can be applied to the dynamical matrices to give the secular equation for long-wavelength acoustic modes. In the present notation, this is

$$(M_c/V_c)\omega_s^2 v_{si} = \sum_{i'i''i'''} \bar{G}_{ii''i'i'''} k_{i'} k_{i'''} v_{si''}, \quad s = 1, 2, 3.$$
$$(5.9)$$

Here the polarization index s is restricted to acoustic modes only, and the (orthonormal and complete) eigenvectors v_s give the directions of the displacements during the propagation of the wave. This equation is valid in the limit of small $|\mathbf{k}|$, and for a given direction of $\mathbf{k}$ (i.e., ω_s, v_s depend on the direction of $\mathbf{k}$). For a primitive lattice,

$$\bar{G}_{ii''i'i'''} = \bar{D}_{ii''i'i'''}; \quad (5.10)$$

for a nonprimitive lattice,

$$\bar{G}_{ii''i'i'''} = V_c^{-1} \sum_{n',jj',i^{iv}} A_{0ji^{iv},n'j'i}(r_{n'j'i'}-r_{ji'})$$

$$\times N_{ji^{iv},i''i'''} - \tfrac{1}{2} V_c^{-1} \sum_{n',jj'} A_{0ji,n'j'i''}(r_{n'j'i'}-r_{ji'})$$

$$\times (r_{n'j'i'''}-r_{ji'''}). \quad (5.11)$$

---

[27] Begbie and Born (Ref. 24) refer to the a_k of (5.4) as the Fourier transform of the dynamical matrix. Also, Refs. 1, 24, and 26 include M_j in the definition of the a_k matrices.

Equation (5.9) is an equation of motion with respect to the initial strained configuration, and is therefor to be compared with the thermoelastic equation of motion (2.28). But (5.9) is a solution to the mechanical problem of motion; statistics have not yet been taken into account. In comparing (5.9) with (2.28), the same approximation is made as in the interpretation of the elastic energy density due to a homogeneous deformation (Sec. IV above), namely that the difference between adiabatic and isothermal propagation is neglected. An equation similar to (2.28) can be written for isothermal propagation, and contains isothermal elastic constants.

Consider solutions to (2.28) of the form of plane elastic waves:

$$U_{si} = v_{si} \exp[i(\mathbf{k}\cdot\mathbf{r}-\omega_s t)], \quad s = 1, 2, 3. \quad (5.12)$$

The body forces in (2.28) are presumed to be time-independent, and do not enter explicitly into the wave solution. Dropping the distinction between adiabatic and isothermal propagation, replacing $T_{ii'}$ by $C_{ii'}$ according to (4.8), and writing Cartesian indices as $i, i', \cdots$, (5.12) and (2.28) give

$$\rho_1 \omega_s^2 v_{si} = \sum_{i'i''i'''} [C_{i'i''i'''}\delta_{ii'''}+C_{ii'i''i'''}]k_{i'}k_{i'''}v_{si''}. \quad (5.13)$$

Since (M_c/V_c) is just ρ_1, the density in the initial configuration, (5.9) and (5.13) are identical for each s and for arbitrary k_i if

$$\tfrac{1}{2}(C_{ii'i''i'''}+C_{ii'''i''i'})+C_{i'i''i'''}\delta_{ii''}$$
$$= \tfrac{1}{2}(\bar{G}_{ii'''i'i''}+\bar{G}_{ii'''i''i'}). \quad (5.14)$$

From the definitions (5.10), (5.11), (4.35), and with the aid of (4.16), it follows that

$$\tfrac{1}{2}(\bar{G}_{ii'''i'i''}+\bar{G}_{ii'''i''i'}) = \bar{D}_{ii'''i'i''}. \quad (5.15)$$

Thus (5.14) is the same as (4.21), and again leads to the expression (4.22) for the elastic constants. The method of long waves leads to identical results for the elastic constants as does the method of homogeneous deformation, when the same approximations are made in each treatment.

VI. EFFECTIVE ELASTIC CONSTANTS

From Homogeneous Deformation

The present section gives some of the physical significance of the effective elastic constants, which were defined in (2.33) above.

Consider the initial system of a collection of interacting ions, representing a finite crystal, plus externally applied forces. If now an elastic deformation is carried out, represented by the displacements (4.1), by the application of additional surface forces g_{nj}, while the initial forces f_{nj} are held constant, then the directly observable energy is the increase in elastic

energy of the system as a whole. In other words, the directly observable additional stress and additional strain are properties of the initial system as a whole. From (3.1), (3.3), (3.6), and (4.2), the elastic energy per unit volume of the system is

$$V^{-1}Q(\mathbf{r}_{nj}+\mathbf{U}_{nj}) = V^{-1}Q(\mathbf{r}_{nj})$$
$$+\tfrac{1}{2}\sum_{ii'i''i'''} D_{ii'i''i'''}Y_{ii'}Y_{i''i'''}+\cdots, \quad (6.1)$$

when the U_{nji} are given by (4.1).

The last term in (6.1) cannot, in general, be written as a quadratic form in the symmetric strain parameters $S_{ii'}$ of (4.3). This can be done only if the $D_{ii'i''i'''}$ have the complete Voigt symmetry, and this is generally not the case. Nevertheless, the D coefficients might be considered as elastic constants, since they enter a generalized stress–strain relation in the appropriate way:

$$\partial[V^{-1}Q(Y_{ii'})]/\partial Y_{ii'} = \sum_{i''i'''} D_{ii'i''i'''}Y_{i''i'''}, \quad (6.2)$$

where the higher order terms have been dropped. The generalized stresses, i.e., the left-hand side of (6.2), are not symmetric.

Within the framework of the method of homogeneous deformations, where the specification of the motion as being either adiabatic or isothermal does not appear, the D coefficients are just the effective elastic constants. Thus, make the identification

$$D_{ii'i''i'''} = E_{ii'i''i'''}. \quad (6.3)$$

Surface effects are now eliminated as in Sec. IV. In view of the definitions (4.15) and (4.34), (6.3) gives

$$\tfrac{1}{2}(E_{ii'i''i'''}+E_{ii'''i''i'}) = \bar{D}_{ii'i''i'''}. \quad (6.4)$$

By comparing (6.4) with (4.21), the explicit relation between the elastic constants and the effective elastic constants is seen to be

$$\tfrac{1}{2}(E_{ii'i''i'''}+E_{ii'''i''i'}) = \tfrac{1}{2}(C_{ii'i''i'''}+C_{ii'''i''i'})$$
$$+C_{i'i''i'''}\delta_{ii''}. \quad (6.5)$$

Equation (6.5) agrees with the definition (2.33) of the effective elastic constants; this justifies (6.3).

From Long Waves

The physical reason for interpreting elastic waves on the basis of the equation of motion (2.32) is exactly the same as for interpreting stress–strain relations on the basis of the energy density (6.1). When elastic waves are propagated through a medium (with or without initial stress), the directly observable property is the set of E coefficients of (2.32). Certain combinations of these coefficients are observed in ultrasonic experiments. In these experiments, the ultrasonic waves are presumed to be adiabatic, and are thus to be identi-

fied with adiabatic E coefficients. In the interpretation of the results of ultrasonic experiments, the distinction between E coefficients and C coefficients, according to (2.33), has not been recognized.[12–14]

If the plane wave (5.12) is used in (2.32), again with time-independent body forces and neglecting the distinction between adiabatic and isothermal propagation, there results

$$\rho_1\omega_s^2 v_{si} = \sum_{i'i''i'''} E_{ii'i''i'''}k_{i'}k_{i'''}v_{si''}. \quad (6.6)$$

Identification of (6.6) with (5.9), with the aid of (5.15), yields again the relation (6.4) for the effective elastic constants.

Departure from Voigt Symmetry

The symmetry properties of the effective elastic constants $E_{ii'i''i'''}$ follow from (2.33), together with the symmetries of $T_{ii'}$, $C_{ii'i''i'''}$ analogous to (2.6) and (2.7).[28] The fact that these constants do not have the complete Voigt symmetry when $T_{ii'}\neq0$ has been recognized by Toupin and Bernstein[6] and by Thurston.[29] In discussing the symmetries of the effective elastic constants, it is convenient to divide them into two groups, since the stress components may be of arbitrary magnitude.

(a) $\quad i\neq i''\qquad E_{ii'i''i'''}=C_{ii'i''i'''}$:

          54 constants; 18 distinct
          constants.

(b) $\quad i=i''\qquad E_{ii'ii'''}=C_{ii'ii'''}+T_{i'i'''}$:

          27 constants; 18 distinct in
          general.

In general, then, there are 36 distinct effective elastic constants. If the initial stress is a homogeneous pressure p, $T_{ii'}=-p\delta_{ii'}$, and there are 24 distinct effective elastic constants. A general symmetry property which follows directly from (2.33) is

$$E_{ii'i''i'''} = E_{i''i'''ii'}. \quad (6.7)$$

Finally, the results of Sec. IV show that the effective elastic constants calculated from lattice theory, after surface effects are eliminated with (6.4), have the correct symmetry.

The number of independent E coefficients is reduced from the number of distinct coefficients by equations which couple different coefficients and the stress components. For the most general lattice symmetry, there are 27 independent E coefficients for arbitrary stress and 22 for homogeneous pressure.

[28] Here the notation for constant S or constant T is dropped for abbreviation.
[29] R. N. Thurston, J. Acoust. Soc. Am. **36**, 1041 (1964), abstract T11.

VII. DISCUSSION

The lattice theory of Secs. III–V represents the definition and solution of a mechanical problem. In formulating this problem, the initial positions r_ν of the ions, the potentials of interaction between the ions, and the externally applied forces f_ν might all be considered as arbitrary within the restriction that the equilibrium condition (3.6) and the invariance conditions (3.11) and (3.20), and similar higher order invariance conditions, must be satisfied. There is no way to put thermodynamic conditions, such as requiring that the pressure p is zero, into the mechanical problem, although this has been attempted by previous authors.[1,30] This is because it is not possible to evaluate thermodynamic functions on the basis of the solution of the mechanical problem alone. In particular, the externally applied forces f_ν are not thermodynamic forces (although their averages are approximations to observable forces). Furthermore, since the mechanical problem does not contain the temperature T as a parameter, it cannot specify elastic constants as being either adiabatic or isothermal. Finally, the problem of motion may be set up without the previously used requirement that the initial stresses vanish,[1,2] or the equivalent requirement that the energy of interaction among ions, per unit cell, is a minimum.[3,4]

Once the mechanical problem is solved, and the energy levels are found with the aid of boundary conditions, the partition function Z can be evaluated for the initial configuration. Certain thermodynamic properties which are obtained by differentiating Z with respect to T (e.g. the caloric quantities S and E), can be calculated for this configuration. To obtain thermodynamic forces, which depend on the variation of Z with respect to the configuration (e.g., p), it is necessary in principle to find Z for a new configuration which is infinitesimally removed from the old one. In this manner the thermodynamic properties of the system are described as explicit functions of the configuration and the temperature.[31] Such calculations would be impossible in principle if an equilibrium condition were applied which fixed the configuration.

Now the necessity of the change of reference configuration in Sec. II becomes obvious. The theory of statistical mechanics of a solid is based on the motion of the ions about the initial configuration, and the stresses which give rise to this configuration are not known until the partition function has been calculated. Likewise, the observed thermodynamic properties of a solid are functions of the initial configuration.

Observed ultrasonic waves are true thermoelastic waves, and, under the assumption of adiabatic propagation, can be used to obtain the thermoelastic constants (2.19). If these wave velocities are used to obtain the potential energy coefficients for a lattice model, for example by comparing (5.9) with (2.28), it should be recognized that the resulting potential energy coefficients are in error because the mechanical problem has not taken statistics into account.[32]

[30] H. Kaplan, Phys. Rev. 125, 1905 (1962).

[31] See for example R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, Oxford, England, 1938).

[32] Numerical calculations of the vibrational contribution to the compressibility as a function of temperature are presently being carried out for some central-force models.