THE THEORY OF ELASTICITY AND OF WAVE-PROPAGATION IN CRYSTALS FROM THE ATOMISTIC STANDPOINT

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Introduction

The earliest attempt to formulate the theory of elasticity on the basis of the discrete atomic structure of matter was due to Cauchy who, assuming central interactions between pairs of atoms of a homogeneous body, deduced his well-known relations among the elastic constants. Recent developments, however, have shown that a central force-scheme is inadequate to describe correctly the interatomic interactions in solids and that the Cauchy relations[1] are violated by many crystals. The later theory of Green has the merit of resulting directly in all the 21 independent elastic constants which have since then been found to be innately essential for an adequate description of the elastic behaviour of crystals in general.

There are two principal methods for determining the values of the elastic constants experimentally for crystals. The first is the static procedure in which the solid is subjected to external stress and the resulting deformation is measured. When the deformation is homogeneous, the elastic constants can be calculated from the stress-strain relations implied in Hooke's law. In the second one, which is the dynamic method, the velocities of propagation of specific types of waves are observed and the elastic constants are evaluated therefrom. It is essential in the latter procedure to restrict attention to waves of large wavelengths and low frequencies. For, waves inside crystals are dispersive and are of a much more general character than the ordinary elastic waves. The validity[2] of the elasticity theory will thus break down for stationary vibrations of high frequencies and it can be sustained only over those regions of the frequency spectrum wherein the frequencies of the waves vary inversely as their wavelengths. Conversely, as the long waves of the three acoustic branches satisfy this criterion, the elastic behaviour of crystals could be expected to be determined by these low frequency vibrations involving mass movements of their lattice cells. This enables one to write quantitative identities between the elastic constants

and the force constants of the atomistic theory. In the process of comparing the two theories, however, it is essential beforehand to reduce the mathematical framework of both the formulations to identical forms. Thus, it is necessary to set up as many equations in lattice theory as in the continuum theory, with their variables possessing identical significance and further to ensure that these two sets of equations are of the same form. When this condition is complied with, the scope and physical implications of both the formulations become identical and one can compare the two sets of equations to derive relations between the parameters involved in them.

It was shown by Born[3] that the macroscopic elastic properties of crystals could be deduced from an atomistic lattice theory in terms of a few parameters which are the force constants of the potential energy expression and the lattice constants. As this theory is based on the assumption of central forces, the problem was reconsidered again by Begbie[4] and Born,[4] using a general force scheme. By comparing the lattice equations of the long acoustic waves with the elastic wave equations, they obtained expressions for the elastic constants in terms of the force-constants. But, in spite of the use of a general force-scheme, these expressions still continue to hold good for central force systems only, as the validity of a symmetry relation used by them could be realised only for central interactions among the atoms. A second set of relations for the elastic constants were later given by Kun Huang. Again, his theory also restricts the generality of the force-scheme by introducing new compatibility conditions among the force constants. Since the validity of these relations can be realised strictly for central force systems only, the results of Kun Huang also are not in general reliable.

It is shown in this paper that it is possible to derive an expression for the strain-energy function characterising the deformation of the lattice, from general dynamical considerations. This function is a quadratic in all the nine strain components, unlike the classical theory in which the deformation energy is a quadratic in the six strain components only. From the Lagrangian obtained in this way, the variational equations describing the nature of waves traversing the crystal can be written down and these are identical with the equations of Born and Begbie. But since these equations are not in the same mathematical form as the wave-equations of the elasticity theory, it is clearly not justifiable to identify these two sets of equations to obtain identities between the constants involved in them. Expressions for the elastic constants can nevertheless be derived by comparison, as the two strain energy functions assume the same form for irrotational strains or for homogeneous deformations. It is shown that the numerical values of the elastic constants calculated

from the expressions obtained in this way agree well with the experimental values for the case of diamond, whereas significant deviations from the experimental results arise from the relations derived by comparing directly the elastic wave equations with the lattice wave-equations of Begbie and Born.

The paper is divided into two parts. In Part I, the static method of finding the strain energy function for a general deformation is developed and expressions for the elastic constants are given in terms of the force constants. Part II deals with the propagation of acoustic waves inside crystals.

PART I. THE STATIC METHOD

I. The Deformation energy

We choose the state in which all the atoms of the crystal (assumed to be very large compared to the dimensions of its unit cell, but still finite) are at their lattice sites, as the zero configuration for the potential energy of the lattice. The total potential energy of the crystal for small nuclear displacements is then given by

$$2V = \sum_{xrs} \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\, q_{xrs}\, q_{y\rho\sigma} \tag{1}$$

where q_{xrs} denotes the displacement of the atom (r, s) from its equilibrium position. The equations of motion of the atoms of the cell (s) of the crystal are given by

$$-m_r \ddot{q}_{xrs} = \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\, q_{y\rho\sigma} \tag{2}$$

The force constants satisfy the following relations, which express the invariance conditions of the potential energy under pure translations.

$$\sum_{\rho\sigma} k^{y\rho\sigma}_{xrs} = 0 \qquad (x, y = x, y, z) \tag{3}$$

With the help of (3), we can rewrite (2) as

$$-m_r \ddot{q}_{xrs} = \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs} (q_{y\rho\sigma} - q_{yrs}) \tag{4}$$

The total force on the atom (r, s) in the x-direction is therefore a linear sum of the forces due to the displacements of its neighbours, the force exerted by the atom (ρ, σ) on (r, s) being equal to $\sum_{y} k^{y\rho\sigma}_{xrs}\, (q_{y\rho\sigma} - q_{yrs})$. The force constant $k^{y\rho\sigma}_{xrs}$ denotes the force on (r, s) in the x-direction due to (ρ, σ) per unit relative displacement of these two atoms parallel to the y-direction

The work done by (ρ, σ) on (r, s) is given by

$$\sum_{\nu\rho} k^{\nu\rho\sigma}_{xrs} (q_{y\rho\sigma} - q_{yrs}) q_{xrs} \qquad (5\,a)$$

Similarly the work done by (r, s) on (ρ, σ) is given by

$$\sum_{\nu\rho} k^{\nu\rho\sigma}_{yrs} (q_{yrs} - q_{y\rho\sigma}) q_{x\rho\sigma} \qquad (5\,b)$$

The sum of $(5\,a)$ and $(5\,b)$ gives twice the contribution of the atoms (r, s) and (ρ, σ) to the total intrinsic energy of the crystal in a potential field caused by the vibrations of the remaining atoms; it is equivalent to twice the mutual potential energy $V^{\rho\sigma}_{rs}$ of this pair of atoms. Hence if Δ is the volume of the unit cell, the energy of deformation (U) stored in the cell (s) is given by

$$\Delta U = \frac{1}{4} \sum_{r} \sum_{\rho\sigma} V^{\rho\sigma}_{rs} \qquad (6)$$

or

$$4\Delta U = \sum_{sr} \sum_{\nu\rho\sigma}{}' \{k^{\nu\rho\sigma}_{xrs} (q_{y\rho\sigma} - q_{yrs}) q_{xrs} + k^{\nu\rho\sigma}_{yrs} (q_{yrs} - q_{y\rho\sigma}) q_{x\rho\sigma}\} \qquad (6\,a)$$

the accent indicating that the term $(r, s) = (\rho, \sigma)$ is omitted in the summation of the above term.

If

$$k^{\nu\rho\sigma}_{xrs} = k^{\nu\rho\sigma}_{yrs} \qquad (7)$$

then (6) can be rewritten as

$$4\Delta U = \sum_{sr} \sum_{\nu\rho\sigma}{}' k^{\nu\rho\sigma}_{xrs} (q_{y\rho\sigma} - q_{yrs}) (q_{x\rho\sigma} - q_{xrs}) \qquad (8)$$

It can easily be verified that the sum of (6) for all values of the cell index s is identical with the expression (1) for the total potential energy of the crystal. The relation (7) will hold good for any atomic system under the assumptions (*a*) that the total potential energy of the system can be expressed as the sum of the mutual energies between pairs of atoms and (*b*) the mutual energy between any two atoms can be expanded as a quadratic in their relative displacements. In this case, (7) will easily follow because of the commutative property of the Taylor coefficients.

Now each lattice point of the crystal should be in equilibrium in the deformed state also and hence the resultant force acting on any atom vanishes. This leads to

$$\sum_{\nu\rho\sigma}{}' k^{\nu\rho\sigma}_{xrs} q_{y\rho\sigma} = 0 \qquad (9)$$

The first term in $(6\,a)$ now drops out in view of the relation (9). Also,

$$\sum_{sr} \sum_{\nu\rho\sigma}{}' k^{\nu\rho\sigma}_{yrs} q_{yrs} q_{x\rho\sigma} = -\sum_{sr} \sum_{r} k^{srs}_{yrs} q_{xrs} q_{yrs}$$

Hence, the deformation energy (U) of the cell (s) is given by

$$-4\Delta U=\sum_{xr}\sum_{y\rho\sigma}k^{y\rho\sigma}_{xrs}\,q_{x\rho\sigma}\,q_{y\rho\sigma} \tag{10}$$

II. The strain energy function

The displacement components q_{xrs}, q_{yrs}, q_{zrs} of the atom (r, s) under a general deformation are given by

$$q_{xrs}=k_{xr}+\sum_{\bar{x}}u_{x\bar{x}}\,\bar{x}_{rs} \tag{11}$$

where x_{rs}, y_{rs}, z_{rs} are the co-ordinates of the atom (r, s) in the undeformed state and $\mathbf{k}_r=(k_{xr},\ k_{yr},\ k_{zr})$ $(r=1, 2, \ldots\ p)$ are the inner displacements of the p interpenetrating Bravais lattices. $u_{x\bar{x}}$ .. etc., are the components of the strain which is assumed to be linear, as the applied external stresses to determine experimentally the elastic behaviour of a crystal generally lie within its elastic limits.

Substituting (11) in (10), we get

$$-4\Delta U=\sum_{xr}\sum_{y\rho\sigma}k^{y\rho\sigma}_{xrs}\left(k_{x\rho}+\sum_{\bar{x}}u_{x\bar{x}}\,\bar{x}_{\rho\sigma}\right)\left(k_{y\rho}+\sum_{\bar{y}}u_{y\bar{y}}\,\bar{y}_{\rho\sigma}\right) \tag{12}$$

or

$$-2\,U=\sum_{x\rho}\sum_{y\bar{y}}\begin{Bmatrix}\rho\\ xy\bar{y}\end{Bmatrix}k_{x\rho}\,u_{y\bar{y}}+\sum_{x\bar{x}}\sum_{y\bar{y}}[x\bar{x},\,y\bar{y}]\,u_{x\bar{x}}\,u_{y\bar{y}} \tag{13}$$

where

$$\begin{Bmatrix}\rho\\ xy\bar{y}\end{Bmatrix}=\frac{1}{\Delta}\sum_{r\sigma}l^{y\rho\sigma}_{xrs}\,\bar{y}_{\rho\sigma};$$

$$[x\bar{x},\,y\bar{y}]=\frac{1}{2\Delta}\sum_{\rho\sigma}l^{y\rho\sigma}_{xrs}\,\bar{x}_{\rho\sigma}\,\bar{y}_{\rho\sigma};\ \text{and} \tag{14}$$

$$l^{y\rho\sigma}_{xrs}=\tfrac{1}{2}\,(k^{y\rho\sigma}_{xrs}+k^{x\rho\sigma}_{yrs})$$

The term involving the product of $k_{x\rho}\,k_{y\rho}$ in (12) vanishes in view of the relations (3).

The inner displacements can be eliminated from (13) and the deformation energy can be expressed as a function of the strain components only. The equations determining them are obtained by substituting (11) in (9). They are:

$$\sum_{y\rho\sigma}k^{y\rho\sigma}_{xrs}\,k_{y\rho}=-\sum_{y\bar{y}}u_{y\bar{y}}\left(\sum_{\rho\sigma}k^{y\rho\sigma}_{xrs}\,\bar{y}_{\rho\sigma}\right) \tag{15 a}$$

or

$$\sum_{t'}(a^{\circ}_{s't'})\,k_{t'}=\mathrm{B}_{s'} \tag{15}$$

where

$$a^{\circ}_{s't'} = \sum_{\sigma} k^{y\rho\sigma}_{xrs}$$

$B_{s'}$ denotes the quantity on the right-hand side of (15 *a*). By setting up a correspondence between the number-pairs $y\rho$ ($y = x, y, z$; $\rho = 1, 2, \ldots . p$) and the numbers t' ($t' = 1, 2, \ldots 3p$) where $t' = 3(\rho - 1) + y$ [$s' = 3(r-1) + x$] we could reduce (15 *a*) to the form (15).

The matrix $(a^0_{s't'})$ is now singular and is of rank $(3p - 3)$. We shall assume that the above equations are consistent and solvable. Then a solution of (15) is given by

$$k = \Gamma \mathrm{B} + \mathrm{B}' \qquad (16\,a)$$

where k is the column matrix $\{k_{t'}\}$ and B′ denotes the solution of the homogeneous equations of (15). As only the relative inner displacements of the p lattices are of physical significance, we can assume without loss of generality that the inner displacement of one of the atoms (say k_n) is zero. In this case $\{\mathrm{B}'\} = \{0\}$.

Further, if we partition $(a^0_{s't'})$ in the form $\begin{pmatrix} \mathrm{C}_1 & \mathrm{C}_2 \\ \mathrm{D}_1 & \mathrm{D}_2 \end{pmatrix}$ where C_1 is a matrix containing $(3p - 3)$ rows and columns, then[7] Γ is the matrix $\begin{pmatrix} \mathrm{C}_1^{-1} & 0 \\ 0 & 0 \end{pmatrix}$. Hence, the inner displacements are given by

$$k_{xr} = -\sum_{y\rho} \sum_{x'y'} \sum_{\rho'\sigma'} u_{x'y'} \Gamma^{y\rho}_{xr} k^{x'\rho'\sigma'}_{y\rho s} y'_{\rho'\sigma'} \qquad (16)$$

Substituting (16) in (13), we get

$$2\mathrm{U} = \sum_{x\bar{x}} \sum_{y\bar{y}} d_{x\bar{x}, y\bar{y}}\, u_{x\bar{x}}\, u_{y\bar{y}} \qquad (17)$$

where

$$d_{x\bar{x}, y\bar{y}} = -[x\bar{x},\ y\bar{y}] + (x\bar{x},\ y\bar{y}) \qquad (18)$$

and

$$(x\bar{x}, y\bar{y}) = \frac{1}{\Delta} \sum_{x'\rho} \sum_{r\sigma} \sum_{y'\rho'} \sum_{\rho_1\sigma_1} l^{y\rho\sigma}_{x'rs}\, \bar{y}_{\rho\sigma}\, \Gamma^{y'\rho'}_{x'\rho}\, k^{r_1\rho_1\sigma_1}_{y'\rho's}\, \bar{x}_{\rho_1\sigma_1} \qquad (19)$$

Both the bracket expressions are symmetric in the pairs $x\bar{x}$, $y\bar{y}$. The symmetry $(x\bar{x}, y\bar{y})$ follows directly from the invariance conditions of the potential energy of the lattice under rigid rotations.[5]

The bracket expressions $[\bar{x}x, y\bar{y}]$ and $(\bar{x}x, y\bar{y})$ are defined in the papers of Born and Kun Huang in terms of relative displacement co-ordinates. When the relation (7) is satisfied, one can easily verify that both the forms are identical.

III. The elastic constants

If we write $e_{x\bar{x}}=(u_{x\bar{x}}+u_{\bar{x}x})$ for $\bar{x}\neq x$ and $e_{xx}=u_{xx}$, then the deformation energy obtained from the elasticity theory is a general quadratic in the six strain components e_{xx}, e_{yy}, e_{zz}, e_{yz}, e_{zx} and e_{xy}. Using Voigt's notation in which the indices (1, 2, 3, 4, 5, 6) replace respectively the symbols (xx, yy, zz, yz, zx, xy), the energy density could be written in either of these two forms.[8]

$$2U_1=\sum_r\sum_s c_{rs}\,e_r\,e_s$$

$$=\sum_{x\bar{x}}\sum_{y\bar{y}} c_{x\bar{x},\,y\bar{y}}\;e_{x\bar{x}}\,e_{y\bar{y}} \tag{20}$$

where the summation in the second expression is over the six different pairs given above for the indices $x\bar{x}$. The elastic constants satisfy the following symmetry relations

$$c_{x\bar{x},\,y\bar{y}}=c_{x\bar{x},\,\bar{y}y}=c_{\bar{x}x,\,y\bar{y}}=c_{y\bar{y},\,x\bar{x}} \tag{21}$$

The expression (17) can be written in the form (20), if the coefficients $d_{x\bar{x},\,yy}$ also satisfy the symmetry conditions (21) (*i.e.*) if

$$d_{x\bar{x},\,y\bar{y}}=d_{x\bar{x},\,\bar{y}y}=d_{\bar{x}x,\,y\bar{y}}=d_{y\bar{y},\,x\bar{x}} \tag{22}$$

The coefficient $d_{x\bar{x},\,y\bar{y}}$ is no doubt invariant under an interchange of the pairs $(x\bar{x})$ and $(y\bar{y})$, but its value is definitely altered under any interchange of either x and $\bar{x}$ or y and $\bar{y}$. Further, any assumption of the symmetry conditions (22) would introduce new relations among the force constants, which will lead directly to a central force-scheme, thereby spoiling the generality of the force system with which we have started. Hence, when all the nine strain components are linearly independent functions of x, y and z as in the case of heterogeneous deformations, the deformation energy is a general quadratic in all the *nine* strain components $u_{x\bar{x}}\,(x,\,\bar{x}=x,\,y,\,z)$ and not in the six components $e_{x\bar{x}}\ldots$ only.

For a homogeneous deformation, the strain components $u_{x\bar{x}}$, etc., are independent of the space co-ordinates x, y, z of any point and are constants throughout the volume of the crystal. In this case, the strain can be analysed into a pure strain, followed by a rotation about an axis. By a suitable choice of the co-ordinate axes, it is possible to make the rotational part of the deformation vanish and the strain matrix will consequently become symmetric. The relations[1] $u_{x\bar{x}}=u_{\bar{x}x}$ $(x,\,\bar{x}=x,\,y,\,z)$ are satisfied for all homogeneous deformations and irrotational strains. In both these cases, the expression (17) reduces to the form of the strain energy function of the

elasticity theory and one can therefore compare the coefficients of $e_{x\bar{x}}$, $e_{y\bar{y}}$ in both these expressions to obtain relations between the elastic and force constants of the crystal. The expressions for the elastic constants are therefore given by

$$c_{x\bar{x}, y\bar{y}} = \tfrac{1}{4}\,[d_{x\bar{x}, y\bar{y}} + d_{\bar{x}x, y\bar{y}} + d_{\bar{x}x, \bar{y}y} + d_{x\bar{x}, \bar{y}y}] \tag{23}$$

IV. Symmetry

The displacement components q_x, q_y, q_z of a vector $\mathbf{r} = (x, y, z)$ under any small deformation are given by

$$q_x = \sum_{\alpha} u_{x\alpha}\, x \quad \text{or} \quad \mathbf{q} = U\mathbf{r} \tag{24}$$

where U is the matrix $(u_{x\alpha})$ of the strain components and x, y, z are the components of $\mathbf{r}$ in the unstrained state.

Let the co-ordinate axes be changed to a new set of axes according to the transformation law

$$\mathbf{r}' = S\mathbf{r} \tag{25}$$

Then the deformation in the new frame of reference is represented by

$$\mathbf{q}' = U'\mathbf{r}' \text{ where } U' = SUS^{-1} \tag{26}$$

Let S now be a symmetry operation of the crystal transforming any configuration of the crystal into another one observationally indistinguishable from it. The potential energy should be covariant under all the operations of the symmetry group of the crystal. Hence,

$$\begin{aligned} 2U &= \sum_{\alpha\beta} \sum_{\gamma\delta} d_{x\alpha, y\beta}\, u_{x\alpha}\, u_{y\beta} \\ &= \sum_{\alpha\beta} \sum_{\gamma\delta} d_{x\alpha, y\beta}\, u'_{x\alpha}\, u'_{y\beta} \\ &= \sum_{\alpha\beta} \sum_{\gamma\delta} \sum_{ij} \sum_{kl} d_{x\alpha, y\beta}\, S_{xi}\, S_{yk}\, \tilde{S}_{j\alpha}\, \tilde{S}_{l\beta}\, u_{ij}\, u_{kl} \end{aligned} \tag{27}$$

where we write $\tilde{S} = S^{-1}$.

From the above, it follows

$$2d_{ij, kl} = \sum_{\alpha\beta} \sum_{\gamma\delta} d_{x\alpha, y\beta}\, (S_{xi}\, S_{yk}\, S_{l\alpha}\, \tilde{S}_{l\beta} + S_{xk}\, S_{yl}\, \tilde{S}_{l\alpha}\, \tilde{S}_{j\beta}) \tag{28}$$

These relations reduce the number of independent constants in (17) considerably

PART 2. THE DYNAMIC METHOD

I. The velocity of the long acoustic waves

Long waves associated with the three acoustic branches are propagated without any damping or dispersion inside the crystal. It was shown in an earlier paper[6] that the frequencies (say ω_1, ω_2, ω_3) corresponding to long waves of these three branches tend to zero and that their wave and group velocities become identical in the limit. But the expression for $\frac{d\omega}{da}$ for these three roots given there as $(-s''^{(0)}_{3p}/2s^{(0)}_{3p-1})^{\frac{1}{2}}$ is an error. We here derive a cubic equation whose roots give the values of the limiting velocities of the acoustic waves travelling in any direction of the crystal.

Differentiating the equation (10, I)

$$\sum_{t=0}^{3p} s_t z_k^{3p-t} = 0 \tag{29}$$

six times with respect to a, one obtains by Leibnitz's theorem

$$\sum_{t=0}^{3p}\sum_{s=0}^{m}\binom{m}{s}(\mathrm{D}^{m-s}s_t)\,\mathrm{D}^s(\omega_k{}^{6p-2t}) = 0 \tag{30}$$

where we write $m=6$. With the help of equation (1) of Appendix I the above equation becomes

$$\sum_{t=0}^{3p}\sum_{s=0}^{m}\sum_{r=0}^{s}\binom{m}{s}(\mathrm{D}^{m-s}s_t)\,a_{s,r}\,(6p-2t)_r\,\omega_k{}^{6p-2t-r} = 0 \tag{31}$$

where $(n)_r = n(n-1)\ldots(n-r+1)$ and $(n)_m = 0$ if $m > n$.

Now s_{3p}, s_{3p-1}, s_{3p-2} are equal to the sums of products of the roots of (29) taken respectively $3p$, $(3p-1)$, $(3p-2)$ times and therefore are zero for $\mathrm{a}=0$. By direct differentiation of these expressions, it can be verified that the first non-vanishing derivatives of these three coefficients for $\mathrm{a}=0$ are $s^{(6)}_{3p}{}^{(0)}$, $s^{(4)}_{3p-1}{}^{(0)}$ and $s''_{3p-2}{}^{(0)}$ respectively, as the derivatives of lesser orders of s_{3p}, s_{3p-1}, and s_{3p-2} are expressible as sums of terms, each containing at least one factor ω_k $(k=1, 2, 3)$ or products and squares of them. Again, as the terms in the left-hand side of (31) are continuous functions of the variable a, the limit for $\mathrm{a}=0$ could be obtained by writing $\omega_k = 0$; $s^{(i)}_{3p}{}^{(0)} = 0$ $(i = 0, 1, 2\ldots.5)$; $s^{(i)}_{3p-1}{}^{(0)} = 0$ $(i = 0, 1, 2, 3)$ and $s^{(i)}_{3p-2}{}^{(0)} = 0$ for $i=0, 1$. In proceeding to the limit, we note that all terms excepting those for which $r=s=(6p-2t)$ $(3p-t=0, 1, 2, 3)$ on the L.H.S. of (31) contain either powers of ω_k or $(n)_m$ with $m > n$ or derivatives of s_{3p},

$s_{3p,1}$ and $s_{3p,2}$ with respect to a of order less than 6, 4 and 2 respectively. Equating the sum of these four terms to zero, we obtain

$$720\, a_0 y^3 + 360\, a_1 y^2 + 30\, a_2 y + a_3 = 0 \tag{32}$$

where

$$a_0 = s_{3p,0}^{(0)}; \quad a_1 = s''_{3p,0}{}^{(0)}; \quad a_2 = s_{3p,1}^{(4)}{}^{(0)}; \quad a_3 = s_{3p,0}^{(6)}{}^{(0)}; \text{ and}$$

$$y = \left(\frac{d\omega}{da}\right)^2.$$

If $\mathbf{a} = e a$, then y denotes the square of the limiting group velocity of the acoustic waves in the direction of the vector e. a_0 is independent of e and is the same for all directions, but a_1, a_2 and a_3 are clearly functions of the vector e. The roots of (32) therefore give the three possible velocities of sound waves of thermal origin travelling in the direction e of the crystal.

For the actual numerical evaluation of the coefficients of the various powers of y in (32), we observe that the elements of the matrix[6] $A = (a_{s's})$ can be expanded as a power series in a as they involve only sine and cosine terms. Hence a_1, a_2, a_3 are equal to the coefficients of $\frac{a^2}{2!}$, $\frac{a^4}{4!}$ and $\frac{a^6}{6!}$ in the Maclaurin expansion of $s_{3p,2}$, $s_{3p,1}$ and $s_{3p,0}$ respectively.

II. Wave propagation in crystals

The equations determining the velocities and direction of vibration of the elastic waves in terms of their direction of propagation can be obtained from the variational equations derived from Hamilton's principle. The total kinetic energy of the body is given by

$$2T = \int \rho (\dot{u}_x^2 + \dot{u}_y^2 + \dot{u}_z^2)\, dV \tag{33}$$

and the work done by the external forces for a small displacement is expressed by

$$\delta W_1 = \sum_x \int \rho (T_x\, \delta u_x)\, dV + \sum_x \int (T_{xv}\, \delta u_x)\, dS \tag{34}$$

Here T_x, T_y, T_z are the body forces per unit volume acting on the element dV and T_{xv} $(T_{\bar{x}x}, T_{\bar{x}y}, T_{\bar{x}z})$ $(\bar{x} = x, y, z)$ are the surface tractions acting on the surface element dS. We shall assume that all the nine strain components $u_{x\bar{x}} = \frac{\partial u_x}{\partial \bar{x}}$ $(x, \bar{x} = x, y, z)$ are linearly independent functions of the space co-ordinates x, y, z and further take the relation (7) to be true. The potential energy of deformation is given by (17) so that we have,

$$\delta \int_{t_0}^{t_1} \mathrm{V}\, dt = \delta \int_{t_0}^{t_1} dt \int \mathrm{U}\, d\mathrm{V}$$

$$= \int_{t_0}^{t_1} \left\{ \int \sum_{x\bar{x}} \left(\frac{\partial \mathrm{U}}{\partial u_{x\bar{x}}} \delta u_{x\bar{x}} \right) d\mathrm{V} \right\} dt \tag{35}$$

We have now from Hamilton's principle

$$\delta \int (\mathrm{T} - \mathrm{V})\, dt + \int \delta\, \mathrm{W}_1 dt = 0 \tag{36}$$

The Euler variational equations can be set up in the usual way and these are expressed by

$$\rho \frac{\partial^2 u_x}{\partial t^2} = \rho \mathrm{T}_x + \frac{\partial \mathrm{T}_{xx}}{\partial x} + \frac{\partial \mathrm{T}_{xy}}{\partial y} + \frac{\partial \mathrm{T}_{xz}}{\partial z} \tag{37}$$

$$= \rho \mathrm{T}_x + \sum_{\bar{x}} \frac{\partial}{\partial \bar{x}} \left(\frac{\partial \mathrm{U}}{\partial u_{x\bar{x}}} \right) \qquad (x = x,\ y,\ z)$$

together with the equations

$$\mathrm{T}_{x\nu} = \sum_{y} \frac{\partial \mathrm{U}}{\partial u_{xy}} \cos(y,\ \nu) \tag{38}$$

determining the state of motion at the surface of the body. A set of functions $(u_x,\ u_y,\ u_z)$ satisfying the equations (37) and (38) represent the possible components of vibration of the elements of the elastic body.

If we assume plane wave solutions for the above equations of the form

$$u_x = \mathrm{A}^x e^{i(wt - a.r)} \tag{39}$$

then substitution of (39) in (37) leads to [for the case $(\mathrm{T}_x = \mathrm{T}_y = \mathrm{T}_z = 0)$]

$$\rho v^2 \mathrm{A}^x = \sum_{\bar{x}} \sum_{y\bar{y}} d_{x\bar{x},\, y\bar{y}}\, \mathrm{e}_{\bar{x}}\, \mathrm{e}_{\bar{y}}\, \mathrm{A}^y \tag{40}$$

Writing $\mathrm{A} = (\mathrm{A}^x,\ \mathrm{A}^y,\ \mathrm{A}^z)$ and $\mathrm{D}_{xy} = \sum_{\bar{x}\bar{y}} d_{x\bar{x},\, y\bar{y}}\, \mathrm{e}_{\bar{x}} \mathrm{e}_{\bar{y}}$, we can rewrite the above equations as $(\mathrm{D} - \rho v^2)\, \mathrm{A} = 0$. The matrix D (D_{xy}) is symmetric and hence its eigenvalues are real. If they are distinct, the corresponding eigenvectors are mutually orthogonal. Hence the vibration directions of the three wavefronts moving in any direction are mutually perpendicular to each other, but they may be obliquely inclined to their direction of propagation.

Equations (40) are the Begbie-Born equations for the long acoustic waves of the crystal. Born and Begbie held the relations (22) to be true, even for a general force system and derived the expressions $c_{x\bar{x},\, y\bar{y}} = d_{x\bar{x},\, y\bar{y}}$

for the elastic constants. Clearly, their contention is untenable, as the Cauchy relations can be shown to be a direct consequence of the relations (22) for crystals with a centre of symmetry. For such crystals, the round brackets in (18) vanish[5] and so $d_{x\bar{x},\ y\bar{y}} = -\ [x\bar{x},\ y\bar{y}]$. In view of the interchangeability of x and y or $\bar{x}$ and $\bar{y}$ in the square brackets, we have now from (22)

$$d_{xx,\ yy} = d_{yx,\ xy} = d_{xy,\ xy}, \cdots .$$

and

$$d_{xx,\ yz} = d_{xz,\ yx} = d_{zx,\ xy}$$

The Cauchy relations are now a matter for mere verification. Hence the expressions of Begbie and Born for the elastic constants are not valid for a general force-scheme and are true for central force systems only. A second attempt to derive expressions for the elastic constants by a comparison of (40) with the elastic wave equations was made of Kun Huang, but he could do so only after the explicit introduction of certain additional conditions like $[x\bar{x},\ y\bar{y}] = [\bar{x}x,\ \bar{y}y]$, etc., which he interpreted as the conditions for the vanishing of the initial stresses in an infinite lattice. That such additional conditions had to be imposed is not surprising, for equations (40) involve 45 independent constants whereas the equations of the elasticity theory contain only 21 constants. Further, the equations (40) are derived from a potential function containing the rotational components of the strain also, while the equations of the elasticity theory are derived from a potential involving the six strain components only and hence these two cannot generally be reduced to the same form. As mentioned earlier, any assumption of new relations—other than those supplied by the invariance conditions of the potential energy under translations and rigid rotations—has no theoretical justification. So, the expressions given by Kun Huang for the elastic constants are also not reliable and correct.

The equations (40) fail to hold good for the case $u_{x\bar{x}} = u_{\bar{x}x}$ ($x,\ \bar{x} = x,\ y,\ z$). In this case, the deformation energy is a function of the six strain components only and the equations obtained by the variational method are identical with the equations of the elasticity theory. The latter can always be used to find the velocities of any disturbance generated inside the crystal, provided the stresses produced by the wave-fronts are uniform throughout its volume and their wavelengths are large compared to the dimensions of the unit cell. As longitudinal waves are strictly irrotational, their velocities can be deduced from the elastic wave equations only. The vibration directions and velocities of quasi-torsional waves, on the other hand, are determined by the equations (40).

III. The elastic constants of diamond

The elastic constants and vibration spectrum of diamond has recently been a subject of numerous investigations by various authors.[9, 10, 11] We here briefly sketch the application of the preceding sections to the evaluation of the elastic constants of diamond. For the notation used and other details, the reader is referred to the papers of Krishnamurti and Ramanathan.[9, 10]

The symmetry operations which we use to reduce (17) to its simplest form are:

(*a*) S_1: a rotation by $\frac{2\pi}{3}$ about the line $x = y = z$.

(*b*) S_2: a reflection in the plane $x = y$.

(*c*) S_3: a rotation by $\frac{\pi}{2}$ about a line parallel to the x-axis through the point $\left(\frac{d}{4}, \frac{d}{4}, \frac{d}{4}\right)$ followed by another rotation through $\frac{\pi}{2}$ about an axis through the same point parallel to the x-axis.

The matrix $\bar{U} = (u_{x\bar{x}})$ transforms under these three operations into

$$(a)\ \bar{U}_1' = S_1 \bar{U} S_1^{-1} = \begin{pmatrix} u_{yy} & u_{yz} & u_{yx} \\ u_{zy} & u_{zz} & u_{zx} \\ u_{xy} & u_{xz} & u_{xx} \end{pmatrix}$$

$$(b)\ \bar{U}_2' = S_2 \bar{U} S_2^{-1} = \begin{pmatrix} u_{yy} & u_{yx} & u_{yz} \\ u_{xy} & u_{xx} & u_{xz} \\ u_{zy} & u_{zx} & u_{zz} \end{pmatrix} \qquad (41)$$

$$(c)\ \bar{U}_3' = S_3 \bar{U} S_3^{-1} = \begin{pmatrix} u_{yy} & u_{yz} & -u_{yx} \\ u_{zy} & u_{zz} & -u_{zx} \\ -u_{xy} & -u_{xz} & u_{xx} \end{pmatrix}$$

We have used in the above the matrix forms for S_1, S_2 and S_3 given in Smith's paper.[11]

By setting up a correspondence between the symbols (xx, yy, zz, yz, zy, zx, xz, xy, yx) and the numbers (1, 2, 3, 4, 5, ... 9), we can conveniently write the constants $d_{x\bar{x}, y\bar{y}}$ in the form d_{ij} with two indices only.

From (41) we obtain with the help of (27) the following relations:

$$d_{11}=d_{22}=d_{33};\quad d_{12}=d_{23}=d_{31};\quad d_{45}=d_{67}=d_{89}.$$

$d_{44}=d_{55}=d_{66}=d_{77}=d_{88}=d_{99}$. All other constants in (17) are zero. Thus for cubic crystals of the O_h class, the number of independent constants in (17) is four.

The values of the above constants expressed in terms of the force constants are given by

$$\begin{aligned}
d_{11}&=d_{xx,\,xx}=-\frac{(Q+8U+2\alpha+9\delta)}{d}\\
d_{12}&=d_{xx,\,yy}=-\frac{(R+4W-6\beta+\gamma)}{d}\\
d_{45}&=d_{yz,\,zy}=-\frac{(R+4W-6\beta+\gamma)}{d}+\frac{(R+2\beta-3\gamma)^2}{(Q+3\Sigma)}\times\frac{1}{d}\\
d_{44}&=d_{yz,\,yz}=-\frac{1}{d}(Q+4S+4U+10\alpha+\delta)+\frac{1}{d}\frac{(R+2\beta-3\gamma)^2}{(Q+3\Sigma)}
\end{aligned}\tag{42}$$

Hence from (23) the expressions for the elastic constants are:

$$\begin{aligned}
c_{11}&=d_{11};\\
c_{12}&=d_{12};\\
c_{44}&=\tfrac{1}{2}(d_{44}+d_{45});\\
&=-\frac{1}{2d}\{Q+R+4(S+U+W)+10\alpha+\delta+\gamma-6\beta\}\\
&\qquad+\frac{(R+2\beta-3\gamma)^2}{d(Q+3\Sigma)}
\end{aligned}\tag{43}$$

which are identical with the expressions of Krishnamurti.

To arrive at an estimate of the discrepancies in the values of the elastic constants calculated by the two different procedures, we shall next express the elastic-force constant relations by comparing the lattice wave-equations (40) with the elastic wave equations. The former are given by

$$\rho v^2 A^x=A^x\{d_{11}l^2+d_{44}(m^2+n^2)\}+(d_{12}+d_{45})(A^y lm+A^z ln)\tag{44}$$

and two similar equations obtained by cyclic permutation of the letters x, y, z and l, m, n. Comparing (44) with the equation

$$\rho v^2 A^x=A^x\{c_{11}l^2+c_{44}(m^2+n^2)\}+(c_{12}+c_{44})(A^y lm+A^z ln)\tag{45}$$

we obtain*

$$c_{11}=d_{11};$$

$$c_{44}=d_{44};\ \text{and}$$

$$c_{12}=d_{12}+d_{45}-d_{44} \qquad (46)$$

$$=\frac{(Q+4S+4U+10\alpha+\delta)}{d}-\frac{2(R+4W+6\beta+\gamma)}{d}$$

These expressions are different from those of (43). The expression for c_{11} is the same in both the cases. The numerical values of the force constants were obtained by Ramanathan from spectroscopic data. If these values are substituted in (43) and (46), we get the following numerical values for the elastic constants of diamond, calculated by the two different procedures.

$$c_{11}=9\cdot6\times10^{12}\ (9\cdot6\times10^{12});\ c_{12}=3\cdot9\times10^{12}\ (1\cdot49\times10^{12});$$

$$c_{44}=4\cdot2\times10^{12}\ (5\cdot39\times10^{12})\ \text{dynes/cm.}^2$$

The elastic constants of diamond were determined experimentally by Bhagavantam and Bhimasenachar who get the following values:

$$c_{11}=9\cdot5\times10^{12};\ c_{12}=3\cdot9\times10^{12};\ c_{44}=4\cdot3\times10^{12}\ \text{dynes/cm.}^2$$

While the expressions of Krishnamurti show a very good fit with the experimental data of Bhagavantam and Bhimasenachar, the values calculated from (46) show significant divergences from these results.

Finally, the author wishes to express his deep gratitude to Professor Sir C. V. Raman, F.R.S., N.L., for his inspiring guidance and valuable criticisms during the course of this work.

SUMMARY

The static method of obtaining the strain energy function of a crystal has been developed for the case where the potential energy of the entire lattice is a general quadratic in the nuclear displacements of the atoms of the crystal. It is shown that for heterogeneous strains, the deformation energy of the crystal is a quadratic in all the nine strain components. For small homogeneous deformations, the strain energy function reduces to the form of the corresponding function in the elasticity theory. The wave equations obtained from this energy function by the variational procedure are

* These expressions for diamond based on the dynamic method were obtained by Mr. D. Krishnamurti and independently by Dr. J. Callaway, R. C. A. Laboratories, Princeton, N.J. I am indebted to Mr. D. Krishnamurti for pointing out the discrepancies in the expressions arising out of these two theoretical procedures and for the general discussions on the subject.

APPENDIX I

Lemma.—If ω is a continuous function of the variable a with continuous derivatives with respect to a of order upto N in (α, β) and D denotes the operator $\left(\frac{d}{da}\right)$, then $D^n = \sum_{r=0}^{n} a_{n,r} \left(\frac{d}{d\omega}\right)^r$ in (α, β) $(n \leqslant N)$ (1)

where

$$a_{n,r} = \sum \frac{n!\,(D^{r_1}\omega)^{a_1}(D^{r_2}\omega)^{a_2}\ldots(D^{r_s}\omega)^{a_s}}{(r_1!)^{a_1}a_1!\,(r_2!)^{a_2}a_2!\ldots(r_s!)^{a_s}a_s!} \text{ for } (r>0); \quad (2)$$

$a_{n,0} = \delta_{n0}$;

$n = a_1r_1 + a_2r_2 + \ldots + a_sr_s$ and

$r = a_1 + a_2 + \ldots + a_s$; the summation in (2) is over all the partitions of n into r non-zero integral parts.

Proof.—$D_1, D_2, \ldots D_r$ being r mutually commuting operators, we first define the symbol $(D_1^{p_1}D_2^{p_2}\ldots D_r^{p_r})\,\omega$ as equivalent to the scalar expression $(D_1^{p_1}\omega)\,(D_2^{p_2}\omega)\ldots(D_r^{p_r}\omega)$. With this convention, consider the multinomial expansion $\frac{1}{r!}(D_1+D_2+\ldots+D_r)^n\omega = \frac{1}{r!}\sum \frac{n!}{n_1!\,n_2!\ldots n_r!}$ $(D_1^{n_1}\omega)\ldots(D_r^{n_r}\omega)$ where $\sum_{s=1}^{r} n_s = n$. $a_{n,r}$ can now easily seen to be the expression obtained by writing $D_1 = D_2 = \ldots\ldots = D_r = D$ in the sum of all the terms of the above expansion which arise from a partition of n into r non-zero integral parts. We have now for $n=1$ and $n=2$,

$$D = \frac{d\omega}{da} \times \frac{d}{d\omega} \text{ and}$$

$$D^2 = (D^2\omega)\frac{d}{d\omega} + (D\omega)^2 \cdot \frac{d^2}{d\omega^2}$$

Evidently D^n is of order n in $\left(\frac{d}{d\omega}\right)$ and hence can be expressed by a series of the form (1). Again, by differentiating (1) with respect to a and comparing the result with

$$D^{n+1} = \sum_{r=1}^{n+1} a_{n+1,r}\left(\frac{d}{d\omega}\right)^r,$$

we obtain

$$a_{m+1,r} = a_{m,r-1}\left(\frac{d\omega}{da}\right) + \frac{da_{m,r}}{da} \quad (3)$$

If therefore (3) can be proved on the assumption that (2) is valid for all values of n upto m, then the lemma will easily follow by induction as it is true for $n=1$ and $n=2$.

By definition $a_{m+1,r}$ is the sum of all the terms involving the products of *all* the r operators in the expression

$$(D_1+D_2+\ldots+D_r)\frac{1}{r!}(D_1+D_2+\ldots+D_r)^m \tag{4}$$

if in the final result D is substituted in the place of all the D_i's. Such terms arise in two ways. (*a*) They could for example be obtained by multiplying D_i with the terms containing $(r-1)$ factors in the expansion of $\frac{1}{r!}(D_1+D_2+\ldots+D_{i-1}+D_{i+1}+\ldots D_r)^m\omega$ and as i takes r values, the sum of all such terms reduces to $a_{m,r-1}\frac{d\omega}{da}$ when in the final result we write $D_i=D$. (*b*) They can arise by multiplying the first (linear) term in (4) with the terms involving the products of all the D_i's in the expansion of $\left(\sum_{i=1}^{r} D_i\right)^m\omega$. Taking a typical term $k\,(D_1^{p_1}D_2^{p_2}\ldots D_r^{p_r})\omega$ where $k=\frac{m!}{\Pi p_r!}$ arising out of this partition of m into r factors, the result of multiplying this term with $\left(\sum_{i=1}^{r} D_i\right)$ is evidently

$$k\sum_{i=1}^{r}(D_1^{p_1}\omega)\ldots(D_i^{p_i+1}\omega)\ldots(D_r^{p_r}\omega) \tag{5}$$

As the expression obtained by writing $D_i=D$ $(i=1, 2, \ldots r)$ in (5) is the differential coefficient of $k\,(D^{p_1}\omega)\ldots(D^{p_r}\omega)$, the sum of all the terms under consideration is clearly $\frac{da_{n,r}}{da}$. This establishes the result (3) and consequently the lemma by induction.

In particular, we note that $a_{n,n}=\left(\frac{d\omega}{da}\right)^n$.