

## THE THEORY OF THE ELASTICITY OF CRYSTALS

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### I. INTRODUCTION

THE subject of the elasticity of crystals has from its very early stages of development been approached from two distinct view-points which have resulted respectively in the phenomenological and the atomistic theories. The phenomenological theory was initiated by Green and Kelvin, and is founded on the continuum hypothesis of matter in solids. It is further built on the basis that the total energy of the solid is obtainable as the sum of the energies of the individual volume elements into which it can be subdivided. Each such volume element is supposed to possess a uniform density and the forces acting on it are assumed to be conservative, being derivable from a potential function. These remarks concerning the hypotheses underlying the phenomenological theory have been made here, in order to emphasize the limitations of the theory and to bring out the range of applicability of its results to any actual crystal composed of discrete atoms. It is obvious that these conditions can be incorporated for a crystal with a lattice structure only if the volume elements under consideration are large in comparison to the interatomic distances in the solid. The range of applicability of the phenomenological theory is therefore limited for crystals and its results can be expected to be sustainable only in relation to phenomena involving large volume elements, such as the propagation of non-dispersive waves of large wavelengths and low frequencies in the medium.

A fundamental problem of solid state physics is to interpret the macroscopic behaviour of crystals in terms of the constants characterising the lattice structure and the mutual interactions between pairs of atoms of the crystal. The importance of such an atomistic theory is mainly three-fold. Firstly, it enables us to examine the question whether the two theories would lead to identical results even in the range wherein the phenomenological theory is expected to be applicable. Secondly, it elucidates the nature of the vibrations in a crystal in regions that fall definitely outside the scope of the ordinary theory of elasticity, as in the case of dispersive waves in the medium. Finally, it holds out the hope of computing theoretically the

numerical values of the macroscopic constants. This is rendered possible because every crystal possesses a set of stationary normal modes of vibration whose frequencies are obtainable from spectroscopic data. The frequencies of these vibrations are also expressible in terms of the force-constants of the crystal. By a comparison of these two, the numerical values of at least a few of the force-constants can be ascertained and thus a possibility is opened up whereby the numerical values of the elastic constants become accessible to theoretical calculations as well.

The earliest attempt to provide an atomistic theory of elasticity is due to Cauchy. The investigations of Cauchy were however based on a somewhat outdated model of a solid, in which each atom is a centre of symmetry for the structure and the interatomic forces are strictly central. A direct consequence of these assumptions is that only fifteen among the twenty-one elastic constants emerging from Green's theory are independent, this reduction being effected by means of six relations that are generally known after Cauchy's name. Recent experiments have however proved that the Cauchy relations<sup>2</sup> are violated by a great number of crystals, even by most of the simplest variety of them, *viz.*, the cubic crystals. The failure of the Cauchy relations is clearly due to the assumption of central interactions among the atoms of the crystal, which might be true if each atom is simply an ion attracting the others in accordance with a law of force of the Coulomb type. But in any solid, the nuclei are all surrounded by clouds of electronic charges and any deformation of the substance would tend to change the energy of the electron cloud as well, thus producing forces that are non-central in character.

In order to be able to arrive at results that are in agreement with experimental data, it is therefore essential to start with a system of forces more general than a central force-scheme to represent the interatomic force-field inside crystals. An atomistic theory of elasticity based on such general system of forces was first provided by Begbie and Born<sup>6, 7</sup> and by Kun Huang.<sup>5</sup> By comparing the equations of long acoustic waves of low frequencies obtained from the atomistic theory with the equations of wave-propagation of the elasticity theory, these authors deduced expressions for the elastic constants of the crystal in terms of the force-constants. But the process of identification of the two sets of equations in their theories necessitated the assumption of a few relations among the force-constants which would be strictly true for central force systems only. Thus in spite of the formalism using a general force-scheme, the theories so far provided are reliable only for central interactions among the atoms of the crystal and do not adequately take account of the force-field existing inside crystals.

In this review, an attempt is made to present coherently the facts relating to the nature of the atomic vibrations inside crystals, and the general character of elastic deformations and wave-propagation inside crystals. A substantial part of the review is drawn from material contained in two papers already published by the author but it is made self-contained as far as possible. The contents of it are arranged in seven sections. Section one describes the notation adopted in the paper and introduces the basic concepts regarding wave-propagation in crystal structures. In Section II, we consider the state of movements of the atoms of the crystal arising from a disturbance confined initially to a small region of it. It is shown here that any arbitrary disturbance resolves itself into a superposition of the  $(24p-3)$  harmonic vibrations predicted by the theory of Sir C. V. Raman, and an elastic wave-motion that moves away from the region of the initial disturbance. In any region, the former modes are the only vibrations that possess significant amplitudes after a long time, and further these are independent of the conditions of the boundary of the crystal. Section III is devoted to a discussion of the long waves of low frequency inside the crystal, which are the analogue of the non-dispersive waves contemplated in the elasticity theory. Section IV concerns itself with the evaluation of the strain-energy function in the atomistic theory. An important fact emerging from this section is that the strain-energy function derived from the atomistic theory differs from the energy function of Green in that the former contains terms in the three rotational components of the strain also and thus involves forty-five independent elastic constants. A comparison of the two theories is possible only for the case of static strains which are strictly homogeneous or strictly irrotational. In these circumstances, expressions for the elastic constants as defined in the phenomenological theory can be obtained in terms of the atomic force-constants. Section VI deals again with wave-propagation inside crystals and it is shown here that except in the case of longitudinal waves, the equations of wave motion and the velocities of propagation of the elastic waves would be different in the two theories. Finally, the consequences of the forty-five constant theory as regards the stress-strain relations inside the crystal are discussed in Section VII.

### I. PRELIMINARY CONCEPTS

We shall suppose that an unit cell of the crystal contains  $p$  atoms, and denote the three primitive translational vectors of the lattice by  $\mathbf{d}_1$ ,  $\mathbf{d}_2$  and  $\mathbf{d}_3$ . If the positions of the  $p$  atoms, which we can number as  $1, 2, 3, \dots, p$ , are all known inside any unit cell, then the structure of the crystal is completely specified. We denote by  $\mathbf{b}_1$ ,  $\mathbf{b}_2$  and  $\mathbf{b}_3$  the three primitive translational

vectors which generate the reciprocal lattice of the crystal. These are then determined from the relations

$$\mathbf{b}_i \cdot \mathbf{d}_j = \delta_{ij} \quad (1)$$

where  $\delta_{ij}$  is the Kronecker delta symbol. Any vector  $\mathbf{a}$  of the reciprocal lattice is therefore expressible as

$$\mathbf{a} = \theta_1 \mathbf{b}_1 + \theta_2 \mathbf{b}_2 + \theta_3 \mathbf{b}_3 \quad (2)$$

Further, we use in the sequel the letters  $r$  and  $\rho$  as general symbols to represent any of the  $p$  atoms in the unit cell, and likewise denote by  $s$  and  $\sigma$  a general cell of the crystal lattice.

Taking any three mutually orthogonal axes  $x$ ,  $y$  and  $z$  we represent the components of the displacements of the atom ( $r$ ,  $s$ ) from its equilibrium position by  $q_{xrs}$ ,  $q_{yrs}$  and  $q_{zrs}$ . If however the letters  $x$  or  $y$  occur under a summation sign in any expression, they should be understood as general summational indices that cover all the three directions of the co-ordinate axes of the system.

The expressions for the kinetic and potential energies of the crystal can now be written down. Denoting by  $m_1, m_2, \dots, m_p$  the masses of the  $p$  different atoms in the unit cell, we can write them as

$$2T = \sum_{rs} m_r \dot{q}^2_{xrs} \quad (3)$$

and

$$2V = \sum_{rs} \sum_{y\rho\sigma} k_{rs}^{y\rho\sigma} q_{xrs} q_{y\rho\sigma} \quad (4)$$

The equations of motion of the atoms of the crystal can be derived from (3) and (4) by means of a Lagrangian formulation. They are given by

$$-m_r \ddot{q}_{xrs} = \sum_{y\rho\sigma} k_{rs}^{y\rho\sigma} q_{y\rho\sigma} \quad (5)$$

The force-constants occurring in the above equations are not all entirely independent, but are connected to each other by means of a few relations which express the invariance conditions of the potential energy under pure translations. If the entire crystal is translated by an amount specified by the vector  $\mathbf{u} = (u_x, u_y, u_z)$ , then the left-hand side of the equation (5) should vanish and one therefore gets

$$\sum_{y\rho\sigma} u_y k_{rs}^{y\rho\sigma} = 0 \quad (6)$$

As the vector  $\mathbf{u}$  is arbitrary it follows that

$$\sum_{\rho\sigma} k_{rs}^{\nu\rho\sigma} = 0 \quad (x, y = x, y, z) \quad (7)$$

Substituting the relations (7) in (5) we can rewrite the latter as

$$-m_r \bar{q}_{xrs} = \sum_{\nu\rho\sigma} k_{rs}^{\nu\rho\sigma} (q_{y\rho\sigma} - q_{yrs}) \quad (5')$$

The above equation expresses the fact that the total force acting in the  $x$ -direction on the atom  $(r, s)$  is a linear sum of the forces due to the displacements of its neighbours, the force exerted by  $(\rho, \sigma)$  alone being equal to  $-\sum_{\nu} k_{rs}^{\nu\rho\sigma} (q_{y\rho\sigma} - q_{yrs})$ . The force-constant  $k_{rs}^{\nu\rho\sigma}$  can therefore be interpreted as the  $x$ -component of the force exerted by  $(\rho, \sigma)$  on the atom  $(r, s)$  per unit relative displacement of these two atoms parallel to the  $y$ -direction.

Since the crystal is composed of  $p$  different homogeneous lattices, we shall suppose that a wave of given frequency and wave-length is propagated with different amplitudes inside the different Bravais lattices and that no damping of the waves occurs anywhere inside the crystal. The displacement of any atom caused by the propagation of a wave of frequency  $\nu$  and wave-length  $\lambda$  travelling in the direction of the vector  $\mathbf{e}$  through it is then expressible in the form

$$\begin{aligned} \mathbf{q}_{rs} &= A_r e^{2\pi i \left( \nu t - \frac{\mathbf{e} \cdot \mathbf{s}}{\lambda} \right)} \quad \text{or} \\ \mathbf{q}_{rs} &= A_r e^{i(\omega t - \mathbf{a} \cdot \mathbf{s})} \end{aligned} \quad (8)$$

where

$$\omega = 2\pi\nu \quad \text{and} \quad \mathbf{a} = \frac{2\pi}{\lambda} \mathbf{e}$$

By substituting these wave solutions in the equations of motions of the atoms of the crystal, we can now obtain a set of  $3p$  linear equations in the  $3p$  amplitudes  $A_r^x, A_r^y, A_r^z$  ( $r = 1, 2, \dots, p$ ). A process of elimination of these amplitudes from these homogeneous equations then leads to the determinantal equation

$$|\mathbf{A} - \mathbf{M}\omega^2| = 0 \quad (9)$$

in which the elements of the matrix  $(\mathbf{A})$  composed of  $3p$  rows and columns are the coefficients of the  $3p$  amplitudes in the  $3p$  sets of equations.

Equation (9) can also be rewritten in the form

$$s_0 \omega^{6p} + s_1 \omega^{6p-2} + \dots + s_{3p} = 0 \quad (9')$$

The coefficients  $s_1, s_2, \dots, s_{3p}$  are functions of the wave vector  $\mathbf{a}$ . The frequencies of the waves in the crystal are therefore dependent on their wavelengths, or the waves are dispersive. Further, there are  $3p$  waves with a given wavelength, whose frequencies are the roots of (9) which correspond to this wave-vector.

## II. EFFECT OF AN ARBITRARY DISTURBANCE

This section deals with the spreading of a disturbance, initially confined to a small region of the crystal, into its undisturbed portions at later instants of time. In view of the interaction among the atoms of the crystals, any local disturbance will gradually spread into the other regions of the lattice also, the rate of spreading depending on the strength of coupling between the various atoms of the crystal. To make the problem specific, we shall suppose that initially all the atoms in the cell  $(0, 0, 0)$  with index zero are displaced by small amounts and that the velocities of all other atoms are zero. In other words, the initial state of movements of the atoms is described by

$$\mathbf{q}_{rs}(0) = \frac{1}{8\pi^3c} \int_{\Delta} \mathbf{u}_r e^{i\mathbf{a}\cdot\mathbf{s}} dV = \mathbf{u}_r \delta_{s0} \quad (10)$$

and

$$\dot{\mathbf{q}}_{rs}(0) = 0 \quad (11)$$

Here  $dV$  denotes the element of volume in the reciprocal space. If  $a_1, a_2, a_3$  are the components of the wave vector in any three orthogonal directions and if  $c$  denotes the determinant of the transformation  $a_i = \sum_j c_{ij}\theta_j$  ( $i, j = 1, 2, 3$ ) where  $\theta_1, \theta_2, \theta_3$  are the components of the wave vector along the directions of the axes of the primitive vectors of the reciprocal lattice, then  $dV = da_1 da_2 da_3 = c d\theta_1 d\theta_2 d\theta_3$ . Further  $\Delta$  denotes the volume of the parallelepiped whose corners are given by  $\pi (\pm \mathbf{b}_1 \pm \mathbf{b}_2 \pm \mathbf{b}_3)$ .

The displacements of the atoms of the crystal from their equilibrium positions at a later instant can be determined by superposing waves of type (8) for all possible wavelengths and frequencies so that the final result reduces to the equations (10) and (11) for the case  $t = 0$ . If therefore we denote by  $\omega_1^2, \omega_2^2, \dots, \omega_{3p}^2$  the  $3p$  different roots of (9) and their associated amplitudes by  $A_{r,1}, A_{r,2}, \dots, A_{r,3p}$  ( $r = 1, 2, \dots, 3p$ ), then by choosing the amplitude functions so as to satisfy the relation

$$\sum_{k=1}^{3p} \mathbf{A}_{r,k} = \mathbf{u}_r \quad (12)$$

we can represent the state of movements of the atoms of the crystal at any later instant by

$$q_{rs}(t) = \frac{1}{16\pi^3 c} \sum_{k=1}^{3p} \int_{\Delta} A_{r,k} \left( e^{i\omega_k t} + e^{-i\omega_k t} \right) e^{ia \cdot s} dV \quad (13)$$

A discussion of the above sum of  $3p$  integrals for different values of  $t$  and  $s$  would reveal the nature of the disturbance at different instants and in the different regions of the crystal. We here consider only a simple and interesting case, namely the value of the above sum for large values of  $t$ .

This is done with the aid of the method of stationary phases introduced by Kelvin. The principle of Kelvin asserts that the value of an integral of the type

$$I = \int_{\Delta} f(\mathbf{x}) \exp i \{ \omega(\mathbf{x}) t - \mathbf{s} \cdot \mathbf{x} \} dV \quad (14)$$

for large values of  $t$  arises only from the neighbourhood of points at which the function  $\omega(\mathbf{x})$  is stationary. Such points are known as *saddle points*. We shall denote the stationary points of the function  $\omega$  in the region of integration by  $x_0, x_1, \dots, x_i$ . If the matrix whose elements are  $a_{rs} = \left( \frac{\partial^2 \omega}{\partial x_r \partial x_s} \right)_{x=x_0}$  is denoted by  $\Delta(x_0)$  and  $k$  denotes the difference between the number of positive eigenvalues of  $\Delta(x_0)$  and the number of its negative eigenvalues, then the asymptotic value itself is given by

$$I \sim \left( \frac{2\pi}{t} \right)^{3i/2} \sum_{x_0} \frac{f(x_0)}{|\Delta(x_0)|^{1/2}} \exp i \{ \omega(x_0) t - \mathbf{s} \cdot \mathbf{x}_0 + k\pi/4 \} \quad (15)$$

the summation being over all the stationary points of the function  $\omega$  inside the region of integration.

The above expression in fact denotes the first term in the asymptotic expansion of (14) in inverse powers of  $t$  and will represent integral (14) very closely if  $t$  is sufficiently large. It can be supposed to provide a fairly good estimate of (14) for all values of  $t$  greater than or equal to  $K |s|^2$ , where  $K$  is a constant of the dimensions of Time, for in this case  $\omega(\mathbf{x}) t$  is a quantity of second-order in largeness compared to the factor  $\mathbf{s} \cdot \mathbf{x}$  occurring in the exponential of the integral.

The saddle points for the  $3p$  integrals occurring in equation (13) are clearly the solution of the equations  $\frac{d\omega_k}{da} = 0$  ( $k = 1, 2, \dots, 3p$ ). In any

dispersive medium, the expression  $\frac{d\omega}{da}$  represents the group velocity of the waves traversing it. Thus the saddle points correspond to waves for which the group velocity is identically equal to zero. It has now been shown elsewhere<sup>10</sup> that there are eight points in the reciprocal space for which the group velocities of waves traversing the crystal are equal to zero and for these, the components  $\theta_1$ ,  $\theta_2$  and  $\theta_3$  of the wave-vector  $\mathbf{a}$  are all equal to either zero or  $\pi$ . Explicitly, these points are given by  $\mathbf{a}^1 = (0, 0, 0)$ ;  $\mathbf{a}^2 = (\pi, 0, 0)$ ;  $\mathbf{a}^3 = (0, \pi, 0)$ ;  $\mathbf{a}^4 = (0, 0, \pi)$ ;  $\mathbf{a}^5 = (0, \pi, \pi)$ ;  $\mathbf{a}^6 = (\pi, 0, \pi)$ ;  $\mathbf{a}^7 = (\pi, \pi, 0)$ ; and  $\mathbf{a}^8 = (\pi, \pi, \pi)$ .

Considering first the vector  $\mathbf{a}^1 = (0, 0, 0)$ , it is readily observed from (8) that this corresponds to waves of infinite wave-length inside the lattice. It can be shown that for this case three of the roots of (9) vanish and that  $\frac{d\omega_k}{da} \neq 0$  for these three frequency branches. Long waves associated with these three branches correspond to the elastic vibrations of the crystal and will be discussed later. For the remaining  $(3p - 3)$  frequencies associated with this vector, as also for the  $21p$  frequencies that are yielded by the seven other points listed above, the expression  $\frac{d\omega_k}{da}$  vanishes. Thus we see that for a crystal containing  $p$  atoms in each of its unit cells, there are  $(24p - 3)$  frequencies for which the group velocity of the waves vanishes.

Returning to the evaluation of (13) for large values of  $t$ , we note that the functions  $A_{r,k}$  and  $\omega_k$  occurring in the  $3p$  integrals are all periodic functions of the wave-vector  $\mathbf{a}$  with periods equal to  $2\pi$  for their components  $\theta_1$ ,  $\theta_2$  and  $\theta_3$  in the reciprocal lattice, and the region of integration of the integrals can therefore be slightly shifted about the origin without affecting their values so that it completely encloses all these eight saddle points. Then, denoting by  $\Delta^{\alpha k}$ ,  $v^{\alpha k}$  and  $A_{r,k}^{\alpha}$  the values of the functions  $\Delta_k$ ,  $\omega_k$  and  $A_{r,k}$  at the eight saddle points, we can write the asymptotic value of the displacement of the atom  $(r, \mathbf{s})$  as

$$\begin{aligned} \mathbf{q}_{r\mathbf{s}}(t) = & \frac{1}{c(2\pi t)^{3/2}} \sum_{k=1}^{3p} \frac{A_{r,k}(1)}{|\Delta^1 k|^{\frac{1}{2}}} \cos(v^1 k t + k^1 \pi/4) \\ & + \frac{1}{c(2\pi t)^{3/2}} \sum_{\alpha=2}^8 \sum_{k=1}^{3p} \frac{A_{r,k}^{(\alpha)}}{|\Delta^{\alpha} k|^{\frac{1}{2}}} \cos(v_k^{\alpha} t + \mathbf{a}^{\alpha} \cdot \mathbf{s} + k^{\alpha} \pi/4) \end{aligned} \quad (16)$$



The above expression can be considered to give a good approximation of  $q_{rs}(t)$  for all values of  $t$  greater than or equal to  $K|s|^2$  where  $K$  is a constant characteristic of the medium having the dimensions of (Time).

Equation (16) suggests that in any region for which the above approximation is applicable, the vibrations of the atoms are all obtainable as a superposition of a set of harmonic vibrations which are characteristic of the crystal and hence may be appropriately called the characteristic vibrations of the crystal lattice. In the  $(3p - 3)$  modes represented by the first sum, equivalent atoms in successive cells all vibrate with the same phase and amplitude. In the remaining  $21p$  modes equivalent atoms in successive cells vibrate with the same amplitude but with opposite phases along one, two or three of the Bravais axes of the crystal, as each term in the second sum contains a factor  $\cos a^\alpha \cdot s$  which is equal to *plus* or *minus* unity. Thus these modes are exactly identical with the stationary normal modes of vibration discussed in the dynamics of crystal lattices proposed by Sir C. V. Raman.<sup>3-5</sup> *Our theory therefore shows that the asymptotic nature of the vibrations of the atoms of the crystal arising from an arbitrary disturbance, confined initially to a small region of the lattice is a summation of the  $(24p - 3)$  normal modes of vibrations recognised in Raman's theory.*

With the aid of the above results, it is possible to visualise at least qualitatively the nature of the vibration of the atoms at different instants of time and in different regions. In and very near the region of initial disturbance, the displacements of the atoms are representable by (16) even for small values of  $t$  and the disturbance therefore resolves itself into a superposition of the  $(24p - 3)$  characteristic vibrations of the crystal almost immediately. In the farther off regions the disturbance spreads in the form of waves of which the fastest groups correspond to the elastic vibrations of the crystal. Since no atom can acquire a sensible amplitude until the fastest group reaches that lattice point, the maximum amplitude of any atom is attained only after a certain instant of time which depends on the velocity of propagation of the elastic waves in the medium. The value of the maximum amplitude can further be estimated to be of the order of  $t^{-1}$ , if we consider the elastic vibrations as surface waves divulging from a point whose energy is concentrated in a thin spherical shell only. The amplitudes of the atom thereafter fall away and for sufficiently large values of time comparable in magnitude with the square of the distance of any atom in a given region from the origin, the vibration of the atoms in this region consist of a superposition of the characteristic vibrations of the crystal with time-dependent amplitudes. At these instants, the elastic waves would have

completely moved away from the region under consideration, and their effects on the vibration of the atoms is therefore negligible, as can otherwise also be seen from the fact that the contributions of the elastic waves to the displacements of the atoms are infinitesimals of order higher than  $t^{-3/2}$  and are therefore ignorable. Thus asymptotically in any region the characteristic modes of the crystal are the only vibrations that possess physically significant amplitudes, and the elastic waves which form a low frequency residue to them contribute none other than second order perturbation terms to the actual displacements of the atoms.

If the characteristic vibrations are assumed to settle in any region after an interval of time of the order  $r^2$  where  $r$  is the distance of the region from the origin, then the rate of spreading of the disturbance  $\frac{dr}{dt}$  at any point is inversely proportional to its distance from the centre. The vibrations therefore spread rapidly in the regions near the centre of disturbance but their rate of spreading diminishes for points in the farther off regions of the crystal. Another significant result that deserves mention is the dependence of the amplitudes of these vibrations on time, which indicates that these modes diffuse slowly into the volume of the crystal and do not travel outwards like elastic wave propagation in a medium. Further by the time these vibrations take to reach the external boundary of the crystal, their amplitudes would have become insignificant infinitesimals. Hence the characteristic vibrations are entirely uninfluenced by the boundary conditions of the crystal, and in discussing them all reference to its size and shape can be completely left out of account.

### III. THE ELASTIC WAVES IN THE CRYSTAL LATTICE

We have already mentioned that three roots of equation (9) tend to zero in the limiting case of waves of infinite wave-length. Vibrations associated with these three roots of the secular equation (9) represent the elastic wave-motions inside the lattice and are propagated without any dispersion. For such vibrations, since  $\text{Lt}_{a \rightarrow 0} \frac{\omega_k}{a} = \frac{d\omega_k}{da}$  the group and wave velocities become identical with the velocity of propagation of the elastic waves inside the crystal.

As in the classical elasticity theory, there can progress in any direction three types of elastic waves whose vibration directions are mutually orthogonal. Denoting by  $y$  and  $e$  the velocity and direction of propagation of sound waves, it can be shown<sup>11</sup> that the velocity of the three different waves

travelling in the direction of the unit vector  $e$  are given by the roots of the cubic equation

$$720 a_0 y^3 + 360 a_1 y^2 + 30 a_2 y + a_3 = 0 \quad (17)$$

The coefficients  $a_0$ ,  $a_1$ ,  $a_2$  and  $a_3$  in the above equation are functions of the force-constants and are equal to the derivatives of  $s_{3p-3}$ ,  $s_{3p-2}$ ,  $s_{3p-1}$  and  $s_{3p}$  with respect to the variable  $a$  of orders 0, 2, 4 and 6 respectively. The velocities of the sound waves in crystals are therefore functions of the force-constants, which are the roots of the equation (17).

#### IV. THE DEFORMATION ENERGY FOR CRYSTALS

To obtain an expression for the deformation energy of the crystal, we first try to calculate the mutual energy between pairs of atoms of the crystal. The energy stored in any unit cell can then be obtained by summing up the mutual energy of interactions of the atoms in that cell with all the atoms of the crystal. We have already shown in Section I that the force exerted on the atom  $(r, s)$  in the  $x$ -direction by the displacement of the atom  $(\rho, \sigma)$  is equal to  $-\sum_y k_{ars}^{y\rho\sigma} (q_{y\rho\sigma} - q_{yrs})$ . The mutual energy of this pair ( $V_{rs}^{\rho\sigma}$ ) is obtained by multiplying the force by the relative displacement of the atoms, and dividing the result by two. Hence we have

$$V_{rs}^{\rho\sigma} = -\frac{1}{2} \sum_{xy} k_{ars}^{y\rho\sigma} (q_{y\rho\sigma} - q_{yrs}) (q_{x\rho\sigma} - q_{xrs}) \quad (18)$$

If  $\Delta$  denotes the volume of the unit cell, the deformation energy stored in the cell  $s$  is given by

$$\Delta U = \frac{1}{2} \sum_r \sum_{\rho\sigma} V_{rs}^{\rho\sigma}$$

or

$$-4 \Delta U = \sum_{ar} \sum_{y\rho\sigma} k_{ars}^{y\rho\sigma} (q_{y\rho\sigma} - q_{yrs}) (q_{x\rho\sigma} - q_{xrs}) \quad (19)$$

Now each atom of the crystal should be in equilibrium in the deformed state also and hence one gets

$$\sum_{y\rho\sigma} k_{ars}^{y\rho\sigma} q_{y\rho\sigma} = 0 \quad (20)$$

With the aid of (20) we can rewrite (19) also in the form

$$-4 \Delta U = \sum_{ar} \sum_{y\rho\sigma} k_{ars}^{y\rho\sigma} q_{x\rho\sigma} q_{y\rho\sigma} \quad (21)$$

Any deformation of the crystal can be analysed into two parts: a part which denotes the mutual displacements with respect to each other of the  $p$

interpenetrating Bravais lattices and which is thus the same for all the atoms in the same lattice of the crystal; and another part which corresponds to the usual elastic deformations, denoting the continuous change in the relative displacements of the points of the body due to the strain. The former are generally known as the *inner displacements*.

Denoting now by  $k_{xr}, k_{yr}, k_{zr}$  the components of the inner displacements of the  $r$ th lattice, by  $x_{rs}, y_{rs}, z_{rs}$  the co-ordinates of the atom ( $r, s$ ) in the underformed state and by  $u_{xy}$  ( $= \frac{\partial u_x}{\partial y}$ ) the components of the strain, we can represent displacement components of the atoms due to the deformation by

$$q_{xrs} = k_{xr} + \sum_{\bar{x}} u_{x\bar{x}} \bar{x}_{rs} \quad (22)$$

Substituting (22) in (21) we can rewrite the energy expression as

$$-2U = \sum_{x\rho} \sum_{y\bar{y}} \left\{ \begin{matrix} \rho \\ xy\bar{y} \end{matrix} \right\} k_{x\rho} u_{y\bar{y}} + \sum_{x\bar{x}} \sum_{y\bar{y}} [x\bar{x}, y\bar{y}] u_{x\bar{x}} u_{y\bar{y}} \quad (23)$$

where

$$\left\{ \begin{matrix} \rho \\ xy\bar{y} \end{matrix} \right\} = \frac{1}{\Delta} \sum_{r\sigma} k_{rs}^{y\rho\sigma} \bar{y}_{r\sigma}$$

and

$$[x\bar{x}, y\bar{y}] = \frac{1}{2\Delta} \sum_{r\rho\sigma} k_{rs}^{y\rho\sigma} \bar{x}_{r\rho} \bar{y}_{r\sigma} \quad (24)$$

The inner displacements can now be eliminated from the energy expression which can thus be expressed as a function of the strain variables only. The equations determining them are obtained by substituting (22) in (20) and are given by

$$\sum_{y\rho\sigma} k_{rs}^{y\rho\sigma} k_{y\rho} = - \sum_{y\bar{y}} u_{y\bar{y}} \left( \sum_{\rho\sigma} k_{rs}^{y\rho\sigma} \bar{y}_{r\sigma} \right) \quad (25)$$

These are a set of  $3p$  equations in the  $3p$  unknowns  $k_{y\rho}$ , etc., of which only  $(3p - 3)$  can be linearly independent since the matrix multiplying them in the left-hand side is singular and is of rank  $(3p - 3)$ . Assuming that these equations are consistent and solvable and denoting by  $\Gamma$  the matrix that would multiply the column vector on the right-hand side in the solution of these equations, we can find the expressions for the inner displacements as

$$k_{xr} = - \sum_{y\rho} \sum_{\sigma'y'} \sum_{\rho'\sigma'} u_{x'y'} \Gamma_{\sigma'r}^{y\rho} k_{y\rho\sigma'}^{s'\rho'\sigma'} y'_{\rho'\sigma'} \quad (26)$$

Substituting (26) in (23) one gets

$$2U = \sum_{x\bar{x}} \sum_{y\bar{y}} d_{x\bar{x}, y\bar{y}} u_{x\bar{x}} u_{y\bar{y}} \quad (27)$$

where

$$d_{x\bar{x}, y\bar{y}} = - [x\bar{x}, y\bar{y}] + (x\bar{x}, y\bar{y}) \quad (28)$$

with

$$(x\bar{x}, y\bar{y}) = \frac{1}{\Delta} \sum_{\sigma'\rho} \sum_{\tau\sigma} \sum_{\nu'\rho'} \sum_{\rho_1\sigma_1} k_{\sigma'\rho_1}^{\nu\rho\sigma} \bar{y}_{\rho\sigma} \Gamma_{\sigma'\rho'}^{\nu'\rho'} k_{\nu'\rho_1}^{\sigma_1\rho_1} \bar{x}_{\rho_1\sigma_1} \quad (29)$$

Equation (27) gives the energy expression in the atomistic theory, and the constants multiplying the various quadratic terms in it are functions of the force-constants and the lattice parameters. We note that both the bracket expressions in (28) are symmetric in the pairs  $x\bar{x}$ ,  $y\bar{y}$ . The round brackets are further invariant under a permutation of the symbols  $x$  and  $\bar{x}$ , or of  $y$  and  $\bar{y}$ , while the square brackets do not possess such a symmetry except in the special case of a central force system.

#### V. THE ELASTIC CONSTANTS OF CRYSTALS<sup>12</sup>

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 the notation of Voigt in which the numbers (1, 2, 3, 4, 5, 6) replace respectively the symbols ( $xx$ ,  $yy$ ,  $zz$ ,  $yz$ ,  $zx$ ,  $xy$ ) the strain energy function of the elasticity theory can be written in either of these two forms

$$2U = \sum_{r,s} \sum_{r=1}^6 c_{rs} e_r e_s \quad (30)$$

$$= \sum_{x\bar{x}} \sum_{y\bar{y}} c_{x\bar{x}, y\bar{y}} u_{x\bar{x}} u_{y\bar{y}}$$

The second form of the energy expression contains forty-five terms and the constants  $c_{x\bar{x}, y\bar{y}}$  are therefore subjected to the symmetry relations

$$c_{x\bar{x}, y\bar{y}} = c_{x\bar{x}, \bar{y}y} = c_{\bar{x}x, y\bar{y}} = c_{\bar{x}x, \bar{y}y} \quad (31)$$

so that it might become identical with the first one.

The expression (27) for the energy expression obtained from the atomistic theory can also be written in the form (30) provided the constants  $d_{x\bar{x}, y\bar{y}}$  also satisfy the same symmetry laws as the elastic constants, *i.e.*, if they are invariant under a permutation of the letters  $x$  and  $\bar{x}$  or  $y$  and  $\bar{y}$ . But this is by no means the case, for these constants are functions of the force-

constants defined in accordance with the relations (24) and (29), and any assumption of such symmetry requirements can be shown to be equivalent to the assumption of a central force scheme for the interactions among the atoms of the crystal. As a central force interaction is not obeyed by a number of crystals, there is no justification whatsoever to suppose that these constants are also governed by relations (31) with the  $c$ 's replaced by the  $d$ 's.

The atomistic theory thus involves 45 independent constants for the case of a general strain\* as had been stressed recently by Laval<sup>9</sup> and the present writer.<sup>10</sup> In order to derive expressions for the elastic constants in terms of the force-constants, it is therefore necessary to investigate the circumstances or conditions of strains under which expression (27) might reduce to the same mathematical form as that of (30) and which might thus enable us to identify the two. Obviously both these expressions reduce to the same form if

$$u_{xy} = u_{yx} \quad (32)$$

The above relation is clearly satisfied by irrotational strains. There is another type of strain which is important from the experimental standpoint, and which conforms to the above condition. These are the infinitesimal homogeneous deformations for which all the nine strain components are constants throughout the volume of the crystal. Any small homogeneous strain can now be analysed into a pure strain followed by a rotation about a suitable axis. By a proper choice of the co-ordinate axes it is always possible to make the rotational part of the strain vanish, and thus the relation (32) holds good for homogeneous strains also. By substituting (32) in (27) and comparing it with (30) we can now obtain expressions for the elastic constants determined by static homogeneous strains in terms of the force-constants, and they are given by

$$c_{x\bar{x}, y\bar{y}} = \frac{1}{4} [d_{x\bar{x}, y\bar{y}} + d_{\bar{x}x, y\bar{y}} + d_{\bar{x}x, \bar{y}y} + d_{x\bar{x}, \bar{y}y}] \quad (33)$$

The constants appearing on the right-hand side of the above equation reduce to a fewer number than forty-five for crystals possessing symmetry. We shall consider the explicit relations following from (33) for crystals possessing the symmetry of the cubic class. If, as before, we introduce the convention of replacing the letter pairs ( $xx$ ,  $yy$ ,  $zz$ ,  $yz$ ,  $zy$ ,  $zx$ ,  $xz$ ,  $xy$ ,  $yx$ )

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\* Cases in which the energy function is a quadratic expression in the nine strain components have been considered in the phenomenological theory also, as can be inferred from a reference to a paper by Macdonald (*London Math. Soc. Proc.*, 1900, 32, 311) given in Chapter VII of Love's book. Since this paper is not available to the author, it has not been possible to discuss the results contained therein in this article.

wherever they occur into the numbers (1, 2, 3, 4, 5, 6, 7, 8, 9), it can be shown that there are only four independent constants  $d_{11}$ ,  $d_{12}$ ,  $d_{44}$  and  $d_{45}$  for cubic crystals. The relations (33) reduce in this case to

$$\begin{aligned} c_{11} &= d_{11}; \\ c_{12} &= d_{12}; \\ c_{44} &= \frac{1}{2} (d_{44} + d_{45}) \end{aligned} \quad (34)$$

## VI. WAVE-PROPAGATION INSIDE CRYSTALS

In this section we consider the nature of wave-propagation inside the crystal assuming that the strain produced by the propagation of a wave-front inside the crystal is very general and that the energy of the wave motion involves all the nine components of strain being given by the function (27).

We shall assume all the nine strain components  $u_{xy} = \frac{\partial u_x}{\partial y}$  are linearly independent functions of variables  $x$ ,  $y$  and  $z$ . Then the equations of motions of the various elements of the crystal can be derived from the variational principle

$$\delta \int (T - U) dt + \int \delta W dt = 0 \quad (35)$$

in which  $U$  stands for the potential energy function (27) and  $T$  and  $W$  denote respectively the total kinetic energy of the solid and the work done by the external forces on the solid.

In the absence of body forces,  $W$  is given by

$$\delta W = \sum_x \int (T_{x\nu} \delta u_x) dS \quad (36)$$

if  $T_{x\nu}$  denotes the normal component of the surface traction of the body, and the kinetic energy  $T$  is given by the expression

$$T = \int \rho (\dot{u}_x^2 + \dot{u}_y^2 + \dot{u}_z^2) dV \quad (37)$$

where  $\rho$  is the density of the medium.

The variational equations of (35) can now be written down and they are given by

$$\rho \frac{\partial^2 u_x}{\partial t^2} = \sum_{\bar{x}} \frac{\partial}{\partial \bar{x}} \left( \frac{\partial U}{\partial u_{x\bar{x}}} \right) \quad (x \rightarrow x, y, z) \quad (38)$$

for interior points of the solid, and

$$T_{x\nu} = \sum_y \frac{\partial U}{\partial u_{xy}} \cos(y, \nu) \quad (39)$$

for points on the surface of the crystal.

We now seek to find out solutions of the above equations which are in the form of plane waves of the type

$$u_x = A^x \exp. \frac{2\pi i}{\lambda} (vt - e.r) \quad (x \rightarrow x, y, z) \quad (40)$$

Substituting (40) in (38) one gets

$$\rho v^2 A^x = \sum_x \sum_{y\bar{y}} d_{x\bar{x}, y\bar{y}} e_{\bar{x}} e_{\bar{y}} A^y \quad (x \rightarrow x, y, z) \quad (41)$$

If we write  $A = (A^x, A^y, A^z)$  and  $D_{xy} = \sum_{\bar{x}\bar{y}} d_{x\bar{x}, y\bar{y}} e_{\bar{x}} e_{\bar{y}}$  then the above equations can be rewritten as  $(D - \rho v^2) A = 0$ . The matrix  $D = (D_{xy})$  is symmetric and hence its eigenvalues are real. If they are distinct, the corresponding eigenvectors are mutually orthogonal. Thus there are three types of elastic waves progressing in any direction of the crystal. Their vibrations directions are mutually perpendicular to each other, but they may be obliquely inclined to their direction of propagation.

Equations (41) are the equations of wave-propagation inside a crystal lattice and were first deduced by Begbie and Born. They had subsequently been used by several authors to obtain expressions for the elastic constants in terms of the force-constants. The first set of expressions were given by Begbie and Born, who obtained the relations

$$c_{x\bar{x}, y\bar{y}} = d_{x\bar{x}, y\bar{y}} \quad (42)$$

This relation is clearly untenable in a general force-scheme, for it amounts to assuming a central force-scheme, and would lead to the Cauchy relations for crystals possessing a centre of symmetry. For such crystals, the round brackets vanish and therefore  $d_{x\bar{x}, y\bar{y}} = -[x\bar{x}, y\bar{y}]$ . If further the relation (42) is satisfied, then the suffixes  $x$  and  $y$  are interchangeable in the expression for  $d_{xx, yy}$ , and similarly  $x$  and  $y$  or  $z$  are interchangeable in  $d_{xx, yz}$ . Therefore it follows from (33) that

$$\begin{aligned} c_{12} &= c_{66}; & c_{23} &= c_{44}; & c_{31} &= c_{55}; \\ c_{14} &= c_{56}; & c_{25} &= c_{46}; & c_{45} &= c_{36} \end{aligned} \quad (43)$$



which are the Cauchy relations. Thus the expressions of Begbie and Born are true in a central force scheme only and are not valid for the case of a general force system. A second set of relations for the elastic constants were later obtained by Kun Huang whose method also consists in identifying the lattice wave equations with the wave equations of the elasticity theory. But such an identification could be done only with the aid of a few additional relations such as  $[x\bar{x}, y\bar{y}] = [\bar{x}x, \bar{y}y]$  which were assumed in Kun Huang's theory, and these were interpreted as the conditions for the vanishing of the initial stresses in an infinite lattice. We may mention that there is no justification for the assumption of these relations in a general force scheme which would hold good for central interactions between the atoms only. The expressions of Kun Huang are also not reliable in a general force scheme and can be expected to hold good for the case of central force systems only.

The real difficulty or source of error in identifying the lattice wave equations with those of the elasticity theory lies in the fact that they owe their origin to different potential functions in the variational method of deriving them. The former are derived from a potential function that contains the rotational part of the strain as well thus involving 45 independent constants, whereas the latter are derived from an energy expression involving 21 constants only. These two are not in general mathematically equivalent and are therefore not identifiable. For those cases of wave-propagation in which longitudinal waves moving in a certain direction alone are excited, the energy of the solid due to the wave motion will not involve the three rotational components of the strain, and in such cases both the theories would lead to identical results. But in general the equations of wave-motion and hence velocities of propagation of the waves are different in the two theories that involve twenty-one and forty-five constants respectively.

## VII. THE STRESS-STRAIN RELATIONS

A natural question that arises in a forty-five constant theory is as regards the nature of the stress-strain relations in the solid. Since the potential energy of deformation in this case is a function of the nine strain variables, one can form nine quantities  $T_{xy} = \frac{\partial U}{\partial u_{xy}}$  obtained by differentiating the energy expression partially with respect to the strain variables  $u_{xy}$ . If these are called the stresses acting on the body, then a striking property of the forty-five constant theory is that the stress tensor *does not* satisfy the symmetry property

$$T_{xy} = T_{yx} \quad (44)$$

If the surface tractions are the only forces acting on any volume element of the body, the result  $T_{xy} = T_{yx}$  holds good at every point inside an elastic body which is under a state of stress. This is easily shown by considering the equilibrium of any small cube of volume  $l^3$  with its centre at the origin and edges parallel to the axes and equating the total angular momentum parallel to the three axes to zero. In order to reconcile ourselves to the circumstance in which the nine stresses do not form a symmetric tensor, we shall assume that each volume element is being acted upon by a couple which tends to rotate it relative to its neighbouring elements in the solid, in addition to the surface tractions acting on it. Denoting by  $lW_x, lW_y, lW_z$  the components of the moment of the couple parallel to the three co-ordinate axes, we can obtain the equilibrium conditions of this element by equating the total angular momentum of the system to zero. This leads to

$$(T_{yx} - T_{xy}) + W_z = 0 \quad (45)$$

We shall now write

$$e_{xy} = \frac{1}{2}(u_{xy} + u_{yx})$$

and

$$\omega_z = \omega_{xy} = -\omega_{yx} = \frac{1}{2}(u_{xy} - u_{yx}).$$

Then obviously

$$T_{xy} = \frac{\partial U}{\partial u_{xy}} = \frac{1}{2} \left( \frac{\partial U}{\partial e_{xy}} + \frac{\partial U}{\partial \omega_z} \right) \text{ and } T_{yx} = \frac{1}{2} \left( \frac{\partial U}{\partial e_{xy}} - \frac{\partial U}{\partial \omega_z} \right).$$

Hence

$$(T_{yx} - T_{xy}) + \frac{\partial U}{\partial \omega_z} = 0 \quad (46)$$

Comparing (45) and (46) we see that the quantities  $\frac{\partial U}{\partial \omega_x}, \frac{\partial U}{\partial \omega_y}, \frac{\partial U}{\partial \omega_z}$  denote respectively the components of the couple  $W_x, W_y, W_z$  acting on any small element of unit volume in the body.

We have already shown in Section IV that the quantities  $d_{11}, d_{12}$  and  $\frac{1}{2}(d_{44} + d_{45})$  denote respectively the three elastic constants of cubic crystals for static homogeneous strains. A physical interpretation of the four constants occurring in the general theory will therefore be complete if it is possible to give a meaning to the quantity  $(d_{44} - d_{45})$  which is independent of the above three. It then follows as a consequence of (45) applied to the case of cubic crystal that the constant  $2(d_{44} - d_{45})$  is equal to the ratio of the magnitude of the couple acting on any volume element of the crystal to the magnitude of the rotation suffered by it due to the strain.

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