THEORETICAL EVALUATION OF THE ACOUSTIC WAVE-VELOCITIES IN DIAMOND

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1. Introduction

Studies on the scattering of light in crystals yield data of two distinct types which may enable us to evaluate the acoustic wave-velocities in the solid. In the first place, we observe in the scattered light small spectral shifts, which, following L. Brillouin, have been interpreted as Doppler shifts of frequency arising in the reflection of the incident light waves by sound waves of thermal origin. This interpretation, however, ignores the possible influence of the presence of an external boundary in the crystal on the types of stationary elastic vibrations. It has been suggested (Raman, 1948) that the discrepancies noticed between the facts as actually observed and those theoretically expected according to the assumptions of Brillouin (Krishnan, 1947), are to be explained in this manner. The second method available for the evaluation of the acoustic wave-velocities in the crystal is purely theoretical. It is based on the knowledge of the forces acting between the various constituent atoms, the latter being themselves found out from the Raman effect data. A method has been recently worked out (Ramanathan, 1947) which enables these forces to be evaluated from the observed frequencies of the normal modes of vibration of the crystal. Using the force-constants thus evaluated, one may proceed to calculate the frequencies of stationary elastic vibrations of different types and of various wavelengths. When the latter are sufficiently large, the product of the frequency of the vibration and its wavelength reaches a constant value which is the acoustic wave-velocity in the crystal for the particular direction. We shall proceed to find out the acoustic wave-velocities in diamond in different directions using the procedure indicated and compare the same with the experimentally determined sound-velocities.

2. Description of the Method

We shall here consider the three principal directions, *viz.*, cubic, dodecahedral and octahedral, and calculate the velocities of transverse and longitudinal stationary vibrations along these in diamond. In the cubic and dodecahedral directions, the carbon atoms in this crystal are arranged in

equidistant layers spaced at intervals of 0·89 A.U. and 1·259 A.U. respectively. However, the spacing of the layers of atoms perpendicular to any octahedral direction is alternately greater and smaller, the distance between any two equivalent layers being 2·055 A.U. In the two former cases, the nodal planes must necessarily be located in a plane of atoms along the cubic and dodecahedral directions respectively. Consequently, only such vibrations are possible whose wavelengths are even multiples of the lattice spacing d. Further, if the displacements of the atoms in any plane are assumed to vary harmonically with its distance from the nodal plane, it is found that the equations of motion of all the atoms in the entire crystal are simultaneously satisfied, showing thereby that these are possible modes of elastic vibration in the crystal. This result is found to be valid whether the displacements of the planes of atoms are transverse or longitudinal.

Considering now the cube directions, only two distinct types of vibrations are possible, one longitudinal and one transverse. Along any dodecahedral direction however, three distinct types of vibration are possible, in one of which the planes move normal to themselves while in the other two, they move tangentially with respect to themselves, the direction of motion being along a cube axis or along another dodecahedral direction.

In the case of the octahedral planes, if we assume any two nearly-spaced layers to move always with the same phase and further if the displacements of the double-layers (nearly-spaced layers) are supposed to vary harmonically from any nodal plane which is also another double-layer, then, the equations of motion of all the atoms in the crystal are simultaneously satisfied. There will be two kinds of such vibrations, one longitudinal and the other transverse. Here again, as in the cubic case, there is only one distinct transverse vibration.

Let us suppose that the planes of rest are separated by n oscillating planes which vibrate with their phases opposite on either side of a nodal plane. Then, if d denotes the lattice spacing, the wavelength of the stationary vibration is $\lambda = 2d(n+1)$. The phases and amplitudes of motion of all the atoms in a particular plane will be the same, while, it will be different for atoms in different planes. The displacement ξ_k of any atom in plane k at an instant of time t is given by $\xi_k = \xi \sin \frac{\pi k}{n+1}$, where ξ is the displacement at the antinode. The equation of motion of any atom in plane k is

$$m \frac{d^2\xi_k}{dt^2} = a\xi_k + b(\xi_{k-1} + \xi_{k+1}) + c(\xi_{k-2} + \xi_{k+2}) + d(\xi_{k-3} + \xi_{k+3}) + \ldots\ldots(1)$$

where m is the mass of the carbon atom, a represents the sum of the forces

acting on the atom under consideration due to the displacements of all the atoms in the kth layer, b the sum of the forces acting on the atom due to the displacements of all the atoms in the $(k-1)$ st or $(k+1)$ st layer (these two will be equal), c the sum of the forces on the atom due to the displacements of atoms in $(k-2)$ nd or $(k+2)$ nd layer, etc. There will be n equations of motion corresponding to $k = 1, 2, 3, \ldots . n$. All the n equations become identical on eliminating ξ_k and expressing them in terms of ξ, the equation obtained being

$$m\frac{d^2\xi}{dt^2} = \left(a + 2b\cos\frac{\pi}{n+1} + 2c\cos\frac{2\pi}{n+1} + 2d\cos\frac{3\pi}{n+1} + \ldots\ldots\right)\xi \qquad (2)$$

Or, if ν_n, v_n and λ_n represent respectively the frequency of vibration of the atoms, velocity and wavelength of the stationary elastic vibration, then

$$4\pi^2 m\nu_n^2 = \frac{4\pi^2 m v_n^2}{\lambda_n^2} = a + 2b\cos\frac{\pi}{n+1} + 2c\cos\frac{2\pi}{n+1} + 2d\cos\frac{3\pi}{n+1} + \ldots . \qquad (3)$$

3. Evaluation of the Constants

In formula (3), when n becomes large and tends to be infinite, the frequency ν_n tends to be zero and the expression on the right-hand side also tends to be zero. Also, the value of the expression $(a + 2b + 2c + 2d + \ldots)$ which represents a translation of the crystal, is zero. Therefore, an accurate evaluation of the limiting value of the velocity will involve a knowledge of the exact values of the constants a, b, c, d and the other constants representing the series.

In a recent paper already referred to (Ramanathan, 1947), expressions for the frequencies of the nine normal modes of vibration of diamond, were derived in terms of eight force-constants P, Q, R, S, U, W, Σ and Ω, which take account of the influence on each carbon atom of the 28 nearest of its neighbours. A description of these constants and the method of arriving at them by applying the principles of symmetry, are described in the above paper. Also, numerical values for the constants are given there, calculated from the known spectroscopic data.

The constants a, b, c, d, etc., of formula (3) represent, as have been defined already, *the sum of the forces* due to the displacements of *all the atoms* in the plane or planes which they represent. An exact evaluation of these will therefore require also a knowledge of the forces of interaction

between atoms in distant planes as well as distant atoms in neighbouring planes. But, at present, since we have no knowledge of these distant forces of interaction, we shall have to be satisfied with those which we know, *viz.*, P, Q, R, S, U, W, Σ and Ω and evaluate *a*, *b*, *c*, etc., in terms of these. It must be remarked here that the distant forces are not likely to play any sensible part in determining the frequencies of the eigenvibrations of the crystal, because, in these the phases of vibration go on alternating at each successive equivalent layer and so there will be a tendency for these forces to cancel out each other. On the other hand, in the case of elastic vibrations of large wavelengths, there will be mass movements of atoms in a very large number of neighbouring planes all moving in the same direction, and therefore, the distant forces of interaction, though of small magnitude, work together and may be expected to have an appreciable effect on the frequency of vibration.

The constants *a*, *b*, *c*, etc., calculated from P, Q, R, etc., satisfy the condition that a translation involves no energy ($a + 2b + 2c +$ etc. $= 0$) because the latter have been made to satisfy this condition in the paper referred to already.

4. Results

I. Cubic Planes: Longitudinal.

The values of the constants can be easily written down from an examination of a model of diamond.

$a = \mathrm{P} + 4\mathrm{S} = 7{\cdot}33 \times 10^5$ dynes per cm.
$b = 2\mathrm{Q} + 4\Sigma = -3{\cdot}018 \times 10^5$,,
$c = 4\mathrm{U} = -0{\cdot}525 \times 10^5$,,
$d = 2\Sigma = -0{\cdot}12 \times 10^5$,,

The value of the velocity increases gradually as we consider vibrations of larger and larger wavelengths and finally reaches a constant value (v_{lim}) which, in this case, is 15900 metres per second.

II. Cubic Planes: Transverse.

$a = \mathrm{P} + 4\mathrm{U} = 6{\cdot}826 \times 10^5$ dynes per cm.
$b = 2\mathrm{Q} + 4\Sigma = -3{\cdot}018 \times 10^5$,,
$c = 2\mathrm{S} + 2\mathrm{U} = -0{\cdot}272 \times 10^5$,,
$d = 2\Sigma = -0{\cdot}12 \times 10^5$,,

$v_{lim} = 14300$ metres per second.

III. Dodecahedral Planes: Longitudinal.

$a = (\mathrm{P}+2\mathrm{Q}-2\mathrm{R}+2\mathrm{U}-2\mathrm{W}+2\Sigma-2\Omega) = 6{\cdot}122\times10^5$ dynes per cm.
$b = (\mathrm{Q} + \mathrm{R} + 2\mathrm{S} + 2\mathrm{U} + 3\Sigma + 3\Omega) = -2{\cdot}685\times10^5$,,
$c = (\mathrm{U} + \mathrm{W} + 2\Sigma - 2\Omega) = -0{\cdot}375\times10^5$,,

The limiting velocity = 18300 metres per sec.

IV. Dodecahedral Planes: Transverse along cube axis.

$a = (P + 2Q + 2S + 2\Sigma) = 4{\cdot}44 \times 10^5$ dynes per cm.
$b = (Q + 4U + 3\Sigma) = -2{\cdot}094 \times 10^5$,,
$c = (S + 2\Sigma) = -0{\cdot}125 \times 10^5$,,
$v_{lim} = 14300$ metres per sec.

V. Dodecahedral Planes: Transverse along dodecahedral axis.

$a = (P+2Q+2R+2U+2W+2\Sigma+2\Omega) = 2{\cdot}254 \times 10^5$ dynes per cm.
$b = (Q - R + 2S + 2U + 3\Sigma - 3\Omega) = -1{\cdot}00 \times 10^5$,,
$c = (U - W + 2\Sigma + 2\Omega) = -0{\cdot}127 \times 10^5$,,
$v_{lim} = 10900$ metres per sec.

VI. Octahedral: Longitudinal.

$a = (P + 3Q - 2R + 2S + 4U - 4W + 3\Sigma + 6\Omega) = 4{\cdot}668 \times 10^5$ dynes per cm.
$b = \frac{1}{2}(Q + 2R + 2S + 4U + 4W + 9\Sigma - 6\Omega) = -2{\cdot}333 \times 10^5$,,
$v_{lim} = 22300$ metres per sec.

VII. Octahedral: Transverse.

$a = (P + 3Q + R + 2S + 4U + 2W + 3\Sigma - 3\Omega) = 1{\cdot}365 \times 10^5$ dynes per cm.
$b = \frac{1}{2}(Q - R + 2S + 4U - 2W + 9\Sigma + 3\Omega) = -0{\cdot}683 \times 10^5$,,
$v_{lim} = 12100$ metres per sec.

The classical theory of elasticity leads to expressions for the velocities of propagation of longitudinal and transverse waves in a cubic crystal in terms of its three elastic constants C_{11}, C_{12} and C_{44}, and ρ its density. The expressions in the case of the cubic, dodecahedral and octahedral directions are $v = \sqrt{\chi/\rho}$ where χ is the quantity shown in the last column.

Cubic	Longitudinal	C_{11}
Cubic	Transverse	C_{44}
Dodecahedral	Longitudinal	$\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$
Dodecahedral	Transverse	C_{44}
Dodecahedral	Transverse	$\frac{1}{2}(C_{11} - C_{12})$
Octahedral	Longitudinal	$\frac{1}{3}(C_{11} + 2C_{12} + 4C_{44})$.
Octahedral	Transverse	$\frac{1}{3}(C_{11} - C_{12} + C_{44})$.

Theory thus shows that there are two transverse velocities possible for any dodecahedral direction and that one of them is the same as the transverse

velocity along a cube direction. It is gratifying to note that the above calculations lead to two different transverse velocities for any dodecahedral direction, and that one of them in which the direction of motion is along a cube axis is the same as the velocity of transverse vibrations along a cube direction. That this agreement is not accidental is shown by the fact that in spite of the two formulæ being different, the phase-wavelengths of the vibrations also being different, the limiting velocities come out to be the same.

The Table below reproduces the velocities of acoustic waves calculated above together with those calculated from the elastic constants of diamond determined experimentally by Bhagavantam and Bhimasenachar (1946). It will be seen that in the case of the longitudinal vibrations the agreement is best for the cubic planes, the calculated value being only about 3% lower than the experimental. For the dodecahedral planes the value obtained is about 4% higher than the value calculated from experimental data, while for the octahedral planes it is about 25% higher. It was already explained in an earlier section that the distant interactions have to be considered to make accurate calculations of the velocity. As will be seen from the calculations above, we have considered in the cubic case, the interaction of three planes on either side of the one under consideration, while in the dodecahedral case we were obliged to consider only two. In the octahedral case, only one set of double-layers on either side of the double-layer under consideration is taken account of. It is probable that a consideration of the influence of some more layers of atoms might yield better results in the latter two cases.

Acoustic wave-velocities in diamond

Oscillating planes	Direction of oscillation	Velocity from force-constants	Velocity from elastic-constants
		metres per sec.	metres per sec.
(100)	[100]	15900	16400
,,	[001] or [010]	14300	10800
(110)	[110]	18300	17700
,,	[001]	14300	10800
,,	[1$\bar{1}$0]	10900	8900
(11$\bar{1}$)	[111]	22300	17700
,,	[01$\bar{1}$]	12100	9500

The agreement in the case of all the transverse modes is much worse, the discrepancy being nearly 25 to 30% in all the cases. This should also

be not surprising in view of the remarks about distant interactions already made in a previous section and in view of the fact that the interaction between any two atoms is large when the displacement in question involves a change in the distance between the interacting atoms and small when it does not involve a change in the distance. Therefore, a transverse vibration is likely to be much more influenced by the interaction of distant atoms in the plane under consideration and in neighbouring planes, than a longitudinal vibration. On the other hand, a longitudinal vibration will be more and more influenced than the transverse by the more and more distant planes.

It can be seen that the velocities calculated from the interatomic force-constants lead to nearly the correct value for C_{11}, too high a value for C_{44} and too low a value for C_{12}.

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Summary

A dynamical method has been described for evaluating the acoustic wave-velocities in different directions in a crystal, from the interatomic force-constants. The method, applied to the case of diamond, yields two transverse velocities for the dodecahedral directions, one of them coming out to be the same as the transverse velocity in a cubic direction. These facts are in full accordance with theoretical expectations.

References

1. Bhagavantam, S., and Bhimasenachar, J. B. .. *Proc. Roy. Soc.*, A, 1946, **187**, 381.
2. Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, A, 1947, **26**, 399.
3. Raman, C. V. .. *Curr. Sci.*, 1948, **17**, 65.
4. Ramanathan, K. G. .. *Proc. Ind. Acad. Sci.*, A, 1947, **26**, 481.