

EVALUATION OF THE ELASTIC CONSTANTS OF DIAMOND FROM ITS RAMAN FREQUENCIES

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Received May 8, 1951

(Communicated by Sir C. V. Raman)

1. INTRODUCTION

THE frequencies of the normal modes of vibration of the structure of diamond admit of very precise determination from its Raman spectrum. According to the theoretical formulation of the dynamics of crystal lattices by Sir C. V. Raman (1943), a crystal with p atoms in its unit cell is capable of $(24p-3)$ normal modes of vibration. In the case of diamond, the vibration spectrum consists of eight discrete monochromatic frequencies of which one is triply degenerate, two are fourfold degenerate, three are sixfold degenerate and two are eightfold degenerate. The triply degenerate oscillation is active in the first order and manifests itself as a single very sharp and intense frequency shift of 1332 cm.^{-1} (C. Ramaswamy, 1930). The remaining seven frequencies are inactive in the first order, but may be expected to manifest themselves as octaves and combinations in the second order Raman spectrum.

The investigations of R. S. Krishnan (1947) have shown that this is actually the case and that the octaves and combinations of the frequencies manifest themselves as sharply defined frequency shifts capable of being measured with high accuracy. A rigorous method of calculating the eight fundamental frequencies of the diamond lattice taking into consideration the interactions between each atom and its 28 nearest neighbours has been developed by K. G. Ramanathan (1947). The identification of the spectroscopic frequencies actually observed with the respective modes to which they refer presents no difficulty, since the eight frequencies arrange themselves in the correct order even in the first approximation where only the four nearest neighbours alone are considered. The identification is further confirmed by a consideration of the intensity relations between the different lines in the second order spectrum (C. V. Raman, 1947). Ramanathan's formulæ show that the eight fundamental frequencies are expressible in terms of eight force constants. The latter can therefore be completely evaluated.

The object of the present paper is a rigorous treatment of the problem of the evaluation of the three elastic constants of diamond, taking into account the interaction between each atom and its 28 nearest neighbours. Utilising the values for the force constants derived from K. G. Ramanathan's investigation of the second-order Raman spectrum, it is shown to be possible to determine the elastic constants from the spectroscopic data alone. A gratifying measure of agreement with the experimental values of the elastic constants emerges (Bhagavantam and Bhimasenachar, 1946).

2. THE ENERGY OF DEFORMATION

The deformation energy can be represented as the sum of the changes in mutual energy of pairs of points. The strain energy W can be calculated in terms of the force constants and the relative displacements u, v, w of an atom i with respect to the atom o at the origin. The force components are:

$$\left. \begin{aligned} F_x &= u F_{xi}^{x0} + v F_{yi}^{x0} + w F_{zi}^{x0} \\ F_y &= u F_{xi}^{y0} + v F_{yi}^{y0} + w F_{zi}^{y0} \\ F_z &= u F_{xi}^{z0} + v F_{yi}^{z0} + w F_{zi}^{z0} \end{aligned} \right\} \quad (1)$$

where F_{yi}^{z0} represents the force constant acting in the z direction on atom o due to the displacement of the atom i along the y direction. Hence the deformation energy for this pair is given by

$$\phi_i = -\frac{1}{2} [u F_x + v F_y + w F_z]. \quad (2)$$

The relative displacement of the atom i is made up of two parts. The first part consists of the relative displacement of the two interpenetrating lattices with respect to each other. The second part consists of a uniform expansion or contraction along the three directions which is the same for both lattices. Hence u, v, w are given by

$$\left. \begin{aligned} u &= k_x + \left(x_i \frac{\partial u}{\partial x} + y_i \frac{\partial u}{\partial y} + z_i \frac{\partial u}{\partial z} \right) \\ v &= k_y + \left(x_i \frac{\partial v}{\partial x} + y_i \frac{\partial v}{\partial y} + z_i \frac{\partial v}{\partial z} \right) \\ w &= k_z + \left(x_i \frac{\partial w}{\partial x} + y_i \frac{\partial w}{\partial y} + z_i \frac{\partial w}{\partial z} \right) \end{aligned} \right\} \quad (3)$$

where k_x, k_y, k_z represent the relative inner displacement between the two atoms. In the case of a pair of points belonging to the same lattice $k_x = k_y = k_z = 0$. x_i, y_i, z_i represent the position of the atom i in the undeformed state. The terms $\frac{\partial u}{\partial y}, \frac{\partial v}{\partial x}$, etc., are the components of a tensor

which can be presumed to be symmetrical since a simple rotation is of no significance.

We may remark that the displacements u, v, w increase proportionately with the distance of the atoms from the origin and the number of such atoms to be taken into account increases even more rapidly at the same time. Hence even if the force constants diminish rapidly with increasing distance—as they should—the expression for the deformation energy may be expected to converge rather slowly. The numerical values for the force constants deduced by Ramanathan fall off very quickly with increasing distance. Even so, as we shall see, the outermost 12 of the 28 neighbours considered by him play a far from negligible role in determining the magnitude of the elastic constants of diamond.

3. THE FORCE CONSTANTS

The force constants introduced by Ramanathan can be defined by using the notation given above.

$$P = F_{x0}^{x0} = F_{y0}^{y0} = F_{z0}^{z0}$$

$$Q = F_{xi}^{x0} = F_{yi}^{y0} = F_{zi}^{z0}$$

$$R = F_{yi}^{x0} = F_{xi}^{x0} = F_{xi}^{y0} = F_{yi}^{y0} = F_{xi}^{z0} = F_{yi}^{z0}$$

where i represents the atom at (1, 1, 1). The unit used for co-ordinates is $d/4$, where d is the lattice constant = 3.56 A.U.

For the second neighbours we have

$$S = F_{xi}^{x0}; \quad T = F_{yi}^{x0} = F_{zi}^{x0}$$

$$U = F_{yi}^{y0} = F_{xi}^{z0}$$

$$V = F_{xi}^{y0} = F_{xi}^{z0} \text{ and } W = F_{xi}^{y0} = F_{yi}^{z0}$$

where i represents the atom at (0, 2, 2).

For the third neighbours we have

$$\alpha = F_{xi}^{x0} = F_{xi}^{z0}$$

$$\beta = F_{yi}^{x0} = F_{yi}^{z0}$$

$$\gamma = F_{xi}^{x0} = F_{xi}^{z0}$$

$$\delta = F_{yi}^{y0} \text{ and } \epsilon = F_{xi}^{y0} = F_{xi}^{z0}$$

where i represents the atom at (1, -3, 1).

Due to the symmetry of the structure of diamond, the force constants for the other atoms can be got by considering the position of the atom and the

nature of its displacement. The actual constant involved in a particular case can be found from the table given by Ramanathan.

In the case of second neighbours, there is a plane of reflection perpendicular to the yz plane bisecting the line joining the origin to the atom $(0, 2, 2)$ and hence it can be shown that $T = -V$.

In the case of third neighbours, there is a centre of inversion between the two atoms which involve the constants β and ϵ . By inverting about the centre it can be proved that $\beta = \epsilon$. These two relations considerably simplify the calculations.

4. ELIMINATION OF THE INNER DISPLACEMENTS

In the deformed state each lattice point should be in equilibrium. Due to the relative displacement of each of the 28 surrounding neighbours, forces act on the atom at the origin. These forces should be in equilibrium. The relative displacement of each atom is known from equation (3), and the forces can be computed from equation (1) by substituting the proper force constants. In the summation of the forces due to all the atoms it is found that the effect of the second neighbours add up to zero. Due to the symmetry of the crystal, the final expression gets considerably simplified and we have

$$k_x \{4Q + 8\alpha + 4\delta\} + \left\{ \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \right\} (4R + 8\beta - 12\gamma) = 0$$

$$\text{i.e., } k_x (Q + 3\Sigma) + \left\{ \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \right\} (R + 2\beta - 3\gamma) = 0,$$

where $3\Sigma = 2\alpha + \delta$,

$$\begin{aligned} \text{Hence } k_x &= - \frac{(R + 2\beta - 3\gamma)}{(Q + 3\Sigma)} \left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \right) \\ k_y &= - \frac{(R + 2\beta - 3\gamma)}{(Q + 3\Sigma)} \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \\ k_z &= - \frac{(R + 2\beta - 3\gamma)}{(Q + 3\Sigma)} \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \end{aligned}$$

It is important to remark that the inner displacements are of considerable magnitude and that the equilibrium condition is not satisfied if we assume that the inner displacements do not exist.

5. CALCULATION OF THE DEFORMATION ENERGY

The deformation energy of the 28 typical pairs of points can be written down and the final summation made. For the nearest neighbours we have,

$$\begin{aligned} 2\phi_1 &= -\{Q(u^2 + v^2 + w^2) + 2R(uv + vw + wu)\} \\ 2\phi_2 &= -\{Q(u^2 + v^2 + w^2) + 2R(-uv + vw - wu)\} \\ 2\phi_3 &= -\{Q(u^2 + v^2 + w^2) + 2R(-uv - vw + wu)\} \\ 2\phi_4 &= -\{Q(u^2 + v^2 + w^2) + 2R(uv - vw - wu)\} \end{aligned}$$

For the second neighbours we have,

$$\begin{aligned} 2\phi_5 &= -\{Su^2 + U(v^2 + w^2) + 2W(vw)\} \\ 2\phi_9 &= -\{Sv^2 + U(u^2 + w^2) + 2W(wu)\} \\ 2\phi_{13} &= -\{Sw^2 + U(u^2 + v^2) + 2W(uv)\} \\ 2\phi_6 &= -\{Su^2 + U(v^2 + w^2) + 2W(vw)\} \\ 2\phi_{11} &= -\{Sv^2 + U(u^2 + w^2) + 2W(uw)\} \\ 2\phi_{16} &= -\{Sw^2 + U(u^2 + v^2) + 2W(uv)\} \\ 2\phi_7 &= -\{Su^2 + U(v^2 + w^2) - 2W(vw)\} \\ 2\phi_{12} &= -\{Sv^2 + U(u^2 + w^2) - 2W(uw)\} \\ 2\phi_{15} &= -\{Sw^2 + U(u^2 + v^2) - 2W(uv)\} \\ 2\phi_8 &= -\{Su^2 + U(v^2 + w^2) - 2W(vw)\} \\ 2\phi_{10} &= -\{Sv^2 + U(u^2 + w^2) - 2W(uw)\} \\ 2\phi_{14} &= -\{Sw^2 + U(u^2 + v^2) - 2W(uv)\} \end{aligned}$$

For the third neighbours we have

$$\begin{aligned} 2\phi_{17} &= \delta u^2 + \alpha(v^2 + w^2) + uv(2\beta) + vw(2\gamma) + wu(2\beta) \\ 2\phi_{18} &= \delta v^2 + \alpha(u^2 + w^2) + uv(2\beta) + vw(2\beta) + wu(2\gamma) \\ 2\phi_{19} &= \delta w^2 + \alpha(u^2 + v^2) + uv(2\gamma) + vw(2\beta) + wu(2\beta) \\ 2\phi_{20} &= \delta u^2 + \alpha(v^2 + w^2) - uv(2\beta) + vw(2\gamma) - wu(2\beta) \\ 2\phi_{24} &= \delta v^2 + \alpha(u^2 + w^2) - uv(2\beta) - vw(2\beta) + wu(2\gamma) \\ 2\phi_{28} &= \delta w^2 + \alpha(u^2 + v^2) + uv(2\gamma) - vw(2\beta) - wu(2\beta) \\ 2\phi_{26} &= \delta u^2 + \alpha(v^2 + w^2) + uv(2\beta) - vw(2\gamma) - wu(2\beta) \\ 2\phi_{21} &= \delta v^2 + \alpha(u^2 + w^2) - uv(2\beta) + vw(2\beta) - wu(2\gamma) \\ 2\phi_{25} &= \delta w^2 + \alpha(u^2 + v^2) - uv(2\gamma) - vw(2\beta) + wu(2\beta) \\ 2\phi_{23} &= \delta u^2 + \alpha(v^2 + w^2) - uv(2\beta) - vw(2\gamma) + wu(2\beta) \\ 2\phi_{27} &= \delta v^2 + \alpha(u^2 + w^2) + uv(2\beta) - vw(2\beta) - wu(2\gamma) \\ 2\phi_{22} &= \delta w^2 + \alpha(u^2 + v^2) - uv(2\gamma) + vw(2\beta) - wu(2\beta) \end{aligned}$$

6. EXPRESSIONS FOR THE ELASTIC CONSTANTS

If we consider the unit cube in the case of diamond lattice, it is found that there are four similar pairs of points of each kind. Hence the total deformation energy is four times the summation over all the different types of pairs of points. The force constant P does not enter the discussion here since only the change in the mutual energy of pairs of points is considered. Carrying out the summation over all pairs and dividing by the volume of the unit cube, the energy density W is found to be given by

$$\begin{aligned}
 W = & (e_{xx}^2 + e_{yy}^2 + e_{zz}^2) \left\{ -\frac{1}{d} (Q + 8U + 9\delta + 2\alpha) \right\} \\
 & + (e_{xx}e_{yy} + e_{yy}e_{zz} + e_{zz}e_{xx}) \left\{ -\frac{1}{d} (R + 4W - 6\beta + \gamma) \right\} \\
 & + (e_{xy}^2 + e_{yz}^2 + e_{zx}^2) \left\{ -\frac{1}{2d} [Q + R + 4(U + S + W) \right. \\
 & \qquad \qquad \qquad \left. + \delta + 10\alpha - 6\beta + \gamma] \right\} \\
 & + (e_{xy}^2 + e_{yz}^2 + e_{zx}^2) \left\{ \frac{1}{d} \frac{(R + 2\beta - 3\gamma)^2}{Q + 3\Sigma} \right\}
 \end{aligned}$$

here $e_{xx} = \frac{\partial u}{\partial x}$ and $e_{xy} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}$.

The strain energy W in terms of the elastic constants is given by

$$\begin{aligned}
 W = & \frac{1}{2} C_{11} (e_{xx}^2 + e_{yy}^2 + e_{zz}^2) + C_{12} (e_{xx}e_{yy} + e_{yy}e_{zz} + e_{zz}e_{xx}) \\
 & + \frac{1}{2} C_{44} (e_{xy}^2 + e_{yz}^2 + e_{zx}^2)
 \end{aligned}$$

Identifying the two expressions for W

$$\begin{aligned}
 C_{11} = & - \left\{ \frac{Q + 8U + 9\delta + 2\alpha}{d} \right\} \\
 C_{12} = & - \left\{ \frac{R + 4W - 6\beta + \gamma}{d} \right\} \\
 C_{44} = & - \left\{ \frac{Q + R + 4(U + S + W) + \delta + 10\alpha - 6\beta + \gamma}{2d} \right\} \\
 & + \frac{(R + 2\beta - 3\gamma)^2}{(Q + 3\Sigma)} \times \frac{1}{d}.
 \end{aligned}$$

We may remark that the effect of the third neighbours is of the same order of magnitude as that of the second neighbours. Ramanathan has obtained the following values for the constants.

$$Q = -1.39 \times 10^5; \quad R = -0.858 \times 10^5; \quad S = -0.005 \times 10^5$$

$$U = -0.131 \times 10^5; \quad W = -0.114 \times 10^5; \quad \Sigma = -0.06 \times 10^5$$

and $\Omega = 0.005 \times 10^5$ dynes per cm. where $3\Sigma = 2\alpha + \delta$ and $3\Omega = \beta + \epsilon + \gamma$.

7. NUMERICAL EVALUATION

In the expressions for C_{11} , C_{12} and C_{44} the constants α , β , γ , δ , ϵ appear separately. But Ramanathan has evaluated only the constants $(2\alpha + \delta)$ and $(\beta + \epsilon + \gamma)$. Hence there arises a slight difficulty in the numerical computation of the values of the elastic constants. α and δ are the force constants for the two atoms that are at the same distance from the origin and whose x co-ordinates are in the ratio 1:3. With the help of a model of diamond, it can be seen from the position of the two atoms and the nature of the displacement that α and δ would be of the same sign and that α would be definitely less than δ . As regards the magnitude of α , we may surmise that it would be somewhere between $\frac{1}{2}\delta$ and $\frac{1}{3}\delta$.

TABLE I

Elastic constants		$\alpha = \delta$	$2\alpha = \delta$	$3\alpha = \delta$
		$\beta = -2\gamma$	$\beta = -2\gamma$	$\beta = -2\gamma$
$C_{11} \times 10^{-12}$	..	8.7	9.38	9.77
$C_{12} \times 10^{-12}$	..	3.88	3.88	3.88
$C_{44} \times 10^{-12}$	..	4.37	4.20	4.11

It will be seen from Table I that changes in α produce considerable changes in the values of the elastic constants deduced from the formulæ.

The constants β and γ represent forces acting in a perpendicular direction to that of the displacement and they are, in consequence, of small magnitude. Considerations similar to those stated in respect of α and δ indicate that γ and β are of opposite sign and that $|\gamma| < |\beta|$. We assume $\beta = -2\gamma$ as a near enough approximation.

The most probable values of the elastic constants of diamond deduced from the present investigation, may be given as

$$C_{11} = 9.6 \times 10^{12}; \quad C_{12} = 3.9 \times 10^{12}; \quad C_{44} = 4.2 \times 10^{12} \text{ dynes/cm}^2.$$

These values show satisfactory agreement with the values experimentally determined by the ultrasonic method by Bhagavantam and Bhimasenachar (1946) who get the following values.

$$C_{11} = 9.5 \times 10^{12}; \quad C_{12} = 3.9 \times 10^{12}; \quad C_{44} = 4.3 \times 10^{12} \text{ dynes/cm}^2.$$

The bulk modulus of diamond $K = \frac{1}{3}(C_{11} + 2C_{12})$ comes out as 5.8×10^{12} if the theoretical values are substituted. This result agrees with the value obtained by Williamson who gets 5.6×10^{12} . Adams obtained a value 6.3×10^{12} for K and this is rather high.

In conclusion, the author wishes to express his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for suggesting this problem and for the many illuminating discussions he had with him. He also thanks Dr. G. N. Ramachandran for his kind interest in this work.

8. SUMMARY

Expressions for the elastic constants of diamond have been derived in terms of the force constants calculated by Ramanathan which express the interaction of any atom with its 28 neighbours. The calculated values are: $C_{11} = 9.6 \times 10^{12}$; $C_{12} = 3.9 \times 10^{12}$; $C_{44} = 4.2 \times 10^{12}$ dynes/cm.² while the values experimentally determined by Bhagavantam and Bhimasenachar are:

$$C_{11} = 9.5 \times 10^{12}; C_{12} = 3.9 \times 10^{12}; C_{44} = 4.3 \times 10^{12} \text{ dynes/cm.}^2$$

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