THE DYNAMICAL THEORY OF THE DIAMOND LATTICE.

Part II. The Elastic Constants of Diamond.

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1. *Introduction.*

In Part I,[1] it has been pointed out that the vibration of the two cubic face-centered lattices composing the diamond lattice relative to one another is Raman-active but infra-red inactive and that it has the frequency 1332 cm.$^{-1}$ In this note, the expressions for the elastic constants of diamond have been found in terms of the molecular force constants and their values have been evaluated *approximately*.

M. Born[2] was the first to calculate the elastic constants of diamond from theoretical considerations. He obtained the value $1 \cdot 59 \times 10^{12}$ dyn./cm.^{2} for the bulk-modulus of diamond. This is of the same order of magnitude as the experimental value 2×10^{12} dyn./cm.^{2} obtained by Richards[3] in 1907. The latter determination has not however been confirmed by later work. As was pointed out by Landé[4] Richard's value for the bulk-modulus of diamond is less than the value $2 \cdot 6 \times 10^{12}$ dyn./cm.^{2} obtained for corundum by Madelung and Fuchs[5] and its correctness is therefore highly improbable. Adams[6] and Williamson[7] determined the bulk-modulus of diamond experimentally as $6 \cdot 25 \times 10^{12}$ dyn./cm.^{2} and $5 \cdot 56 \times 10^{12}$ dyn./cm.^{2} respectively. These later determinations are in close agreement with the value $5 \cdot 6 \times 10^{12}$ dyn./cm.^{2} calculated theoretically by Sir J. J. Thomson.[8] Frenkel[9] has also made a theoretical calculation of the bulk-modulus of diamond and has found it to be 14×10^{12} dyn./cm.^{2} which

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[1] N. S. Nagendra Nath, *Proc. Ind. Acad. Sci.*, 1934, **1**, 333.

[2] Max Born, *Ann. der Phys.*, 1914, **44**, 605.

[3] Th. W. Richards, *Zeit. f. Phys. Chem.*, 1907, **61**, 183.

[4] A. Landé, *Zeit. f. Phys.*, 1920, **4**, 410, and 1921, **6**, 10.

[5] E. Madelung and R. Fuchs, *Ann. der Phys.*, 1921, **65**, 288.

[6] L. H. Adams, *Jour. Wash. Acad. Sci.*, 1921, **11**, 45.

[7] E. D. Williamson, *Jour. Franklin Inst.*, 1922, **193**, 491.

[8] Sir J. J. Thomson, *Phil. Mag.*, 1922, **44**, 657.

[9] J. Frenkel, *Zeit. f. Phys.*, 1924, **25**, 1.

is rather too far out from the experimental values. In the present note, we investigate the values of all the three elastic constants of diamond on the basis of the known crystal structure of diamond and the binding forces operative between the atoms in it.

2. *The Calculation of the Elastic Constants.*

A general homogeneous distortion[10] of a crystal lattice can be represented at the point $\mathfrak{r}^l_k$ where k is the 'basis-index' and l is the 'cell-index' by the distortion vector $\mathfrak{U}^l_k$ whose cartesian components are given by

$$\mathfrak{U}^l_{kx} = \mathfrak{U}_{kx} + \sum_y u_{xy}\, y^l_k \qquad y = x,\ y,\ z. \quad \cdots \quad (1)$$

where $\mathfrak{U}_{kx}$ corresponds to the inner distortion and $\sum\limits_y u_{xy}\, y^l_k$ corresponds to the homogeneous distortion of the lattice from the continuum standpoint.

The change in the energy density of the homogeneously distorted lattice from its original undistorted configuration can be represented by second order terms in the distortion components. In the case of a regular diatomic lattice it is given by

$$\left.\begin{aligned} \mathrm{U}_2 = \frac{\mathrm{A}}{2} \sum_x u^2_{xx} + \frac{\mathrm{B}}{2} \sum_{\substack{xy \\ x \neq y}}{}' \left\{u_{xx}\, u_{yy} + \tfrac{1}{2}\,(u_{xy} + u_{yx})^2\right\} \\ + \mathrm{C} \sum (\mathfrak{U}_{1x} - \mathfrak{U}_{2x})\ (u_{yz} + u_{zy}) + \frac{\mathrm{D}}{2} \sum_x (\mathfrak{U}_{1x} - \mathfrak{U}_{2x})^2 \end{aligned}\right\} \quad (2)$$

where the suffixes 1 and 2 refer to the two types of atoms. The forces at the atoms ('*Einzelkrafte*') 1 and 2 and the stresses per unit area are given by

$$\left.\begin{aligned} \mathfrak{k}_{1x} &= -\,\mathrm{D}\,(\mathfrak{U}_{1x} - \mathfrak{U}_{2x}) - \mathrm{C}\,(u_{yz} + u_{zy}) \\ \mathfrak{k}_{2x} &= \mathrm{D}\,(\mathfrak{U}_{1x} - \mathfrak{U}_{2x}) + \mathrm{C}\,(u_{yz} + u_{zy}) \\ K_{xy} &= -\,\mathrm{C}\,(\mathfrak{U}_{1z} - \mathfrak{U}_{2z}) - \mathrm{B}\,(u_{xy} + u_{yx}) \qquad x \neq y \\ K_{xx} &= -\,\mathrm{A}\, u_{xx} \qquad\qquad\qquad - \mathrm{B}\,(u_{yy} + u_{zz}) \end{aligned}\right\} \quad (3)$$

In the case of the pure elastic deformation of the lattice, the forces at all the atoms are zero. Hence

$$K_{xy} = -\,(\mathrm{B} - \mathrm{C}^2/\mathrm{D})\ (u_{xy} + u_{yx}) \quad \cdots \quad (3)$$

The various elastic constants of the crystal are given by

$$\left.\begin{aligned} c_{11} &= c_{22} = c_{33} = \mathrm{A} \\ c_{12} &= c_{13} = c_{23} = \mathrm{B} \\ c_{44} &= c_{55} = c_{66} = \mathrm{B} - \mathrm{C}^2/\mathrm{D} \end{aligned}\right\} \quad \cdots \quad \cdots \quad (4)$$

The remaining elastic constants are all zero.

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[10] Max Born and M. Göppert-Mayer, *Handbuch der Physik,* 1933, Vol. **24** (2), p. 623.

Now, let us first calculate the elastic constants c_{11} and c_{12} in the case of diamond. Let the stresses K_{xx}, K_{yy} and K_{zz} act on the crystal and let $K_{xy} = K_{yz} = K_{zx} = 0$. From this it follows from (3) that

$$u_{yz} + u_{zy} = u_{zx} + u_{xz} = u_{xy} + u_{yx} = 0$$

$$\text{and} \quad \mathfrak{A}_{1x} = \mathfrak{A}_{2x}, \quad \mathfrak{A}_{1y} = \mathfrak{A}_{2y} \text{ and } \mathfrak{A}_{1z} = \mathfrak{A}_{2z}.$$

Without any loss of generality we can consider here all $\mathfrak{A}$'s to be zero.

Let the origin of the axes of reference be at an atom 1. In the following table, the co-ordinates of the nearest atoms of the origin-atom, the direction cosines of the lines joining them to the origin-atom and the components of the distortion vectors at those atoms calculated according to (1) are given.

TABLE I.

Co-ordinates	Direction cosines	Distortion components
(0) $0, \ 0, \ 0$		$0, \ 0, \ 0$
(1) $l, \ l, \ l$	$a, \ a, \ a$	$\lambda, \ \mu, \ \nu$
(2) $l, -l, -l$	$a, -a, -a$	$\lambda, -\mu, -\nu$
(3) $-l, -l, \ l$	$-a, -a, \ a$	$-\lambda, -\mu, \ \nu$
(4) $-l, \ l, -l$	$-a, \ a, -a$	$-\lambda, \ \mu, -\nu$

where $a = 1/\sqrt{3}$ and $u_{xx} = 4\lambda/d$, $u_{yy} = 4\mu/d$ and $u_{zz} = 4\nu/d$ where d $(d = 4l)$ is the length of the cubic cell.

The above table shows that all the primary valence bonds are extended by $a\,(\lambda+\mu+\nu)$. Let d_{rs} denote the change in the internuclear distance between the atoms r and s $(r, s = 0, 1, 2, 3, 4)$ and let θ_{rs} denote the change in the valence angle bound by the atoms r and s at the origin-atom from the equilibrium configuration $(r, s = 1, 2, 3, 4)$. Then

$$d_{01} = d_{02} = d_{03} = d_{04} = a\,(\lambda+\mu+\nu)$$

Similarly one can find that

$$\begin{aligned} d_{12} &= d_{34} = 2\,\beta\,(\mu + \nu) \\ d_{23} &= d_{41} = 2\,\beta\,(\nu + \lambda) \qquad \beta = \frac{1}{\sqrt{2}} \\ d_{31} &= d_{42} = 2\,\beta\,(\lambda + \mu) \end{aligned}$$

Also,

$$\begin{aligned}\theta_{12} = \theta_{34} &= \frac{1}{p}\{2\,\beta\,\sqrt{3}\,(\mu+\nu) - 2\,\alpha\,\sqrt{2}\,(\lambda+\mu+\nu)\}\\ \theta_{23} = \theta_{41} &= \frac{1}{p}\{2\,\beta\,\sqrt{3}\,(\nu+\lambda) - 2\,\alpha\,\sqrt{2}\,(\lambda+\mu+\nu)\}\\ \theta_{31} = \theta_{42} &= \frac{1}{p}\{2\,\beta\,\sqrt{3}\,(\lambda+\mu) - 2\,\alpha\,\sqrt{2}\,(\lambda+\mu+\nu)\}\end{aligned}$$

$$4\,p = \sqrt{3}\,d$$

where p is the distance between the atom at the origin and any of its nearest neighbours.

Referring to Part I (page 339), the change V_2 in the energy of a *unit cell* due to the primary valence forces, the directed valence forces, the repulsive forces and the intra-valence forces can be shown to be given by

$$\begin{aligned}2\,V_2 = {} & 8\,K\cdot\tfrac{1}{2}\cdot\{4\,\alpha^2\,(\lambda+\mu+\nu)^2\}\\ & + 8\,K''\cdot\tfrac{1}{2}\cdot\left[\frac{16}{2}\{(\lambda+\mu)^2+(\mu+\nu)^2+(\nu+\lambda)^2\}\right]\\ & + \frac{8\,(K'+K''')}{p^2}\,[2\,\{6\,\Sigma\,(\mu+\nu)^2 + 8\,(\lambda+\mu+\nu)^2\\ & \qquad - \tfrac{8}{3}\,(\lambda+\mu+\nu)\,\Sigma\,(\mu+\nu)\}]\end{aligned}$$

Now it is easy to see that the change U_2 in the energy density of the crystal per unit volume is given by

$$\left.\begin{aligned}2\,U_2 = {} & \frac{1}{3d}\left[K + 12\,K'' + \frac{12\,(K'+K''')}{p^2}\right]\Sigma\,u^2_{xx}\\ & + \frac{1}{3d}\left[K + 6\,K'' - \frac{6\,(K'+K''')}{p^2}\right]\sum_{\substack{xy\\ x\neq y}}{}'\,u_{xx}\,u_{yy}\end{aligned}\right\} \quad \cdots \quad (5)$$

By comparing the coefficients of (2) and (5) with the help of (4), it follows that

$$\begin{aligned}c_{11} &= \frac{1}{3d}\left[K + 12\,K'' + \frac{12\,(K'+K''')}{p^2}\right]\\ c_{12} &= \frac{1}{3d}\left[K + 6\,K'' - \frac{6\,(K'+K''')}{p^2}\right]\end{aligned}$$

The bulk-modulus which is the reciprocal of the compressibility κ is given by

$$\frac{1}{\kappa} = \frac{c_{11}+2\,c_{12}}{3} = \frac{1}{3d}\,\{K + 8\,K''\}$$

We shall now calculate the third elastic constant c_{44}. To do this let us consider all the stresses in the lattice to be zero except K_{xy}. Then it can be shown from (3) that

$$\begin{aligned}& u_{xx} = u_{yy} = u_{zz} = 0,\\ & u_{yz} + u_{zy} = u_{zx} + u_{xz} = 0,\\ & \mathfrak{U}_{1x} = \mathfrak{U}_{2x} \text{ and } \mathfrak{U}_{1y} = \mathfrak{U}_{2y}.\end{aligned}$$

Without loss of generality we can have $\mathfrak{U}$'s in the above as zero. In the case of the pure elastic deformation, the relation

$$C\,(u_{xy} + u_{yx}) + D\,(\mathfrak{U}_{1z} - \mathfrak{U}_{2z}) = 0$$

holds good. The resulting energy expression is

$$2\,U_2 = (B - C^2/D)\ (u_{xy} + u_{yx})^2$$

The analogous table of Table I in this case can be easily constructed.

TABLE II.

Co-ordinates	Direction Cosines	Distortion Components
(0) $0,\ 0,\ 0$		$0,\ 0,\ z_1$
(1) $l,\ l,\ l$	$a,\ a,\ a$	$\lambda,\ \mu,\ z_2$
(2) $l,\ -l,\ -l$	$a,\ -a,\ -a$	$-\lambda,\ \mu,\ z_2$
(3) $-l,\ -l,\ l$	$-a,\ -a,\ a$	$-\lambda,\ -\mu,\ z_2$
(4) $-l,\ l,\ -l$	$-a,\ a,\ -a$	$\lambda,\ -\mu,\ z_2$

where $u_{xy} = 4\,\lambda/d$ and $u_{yx} = 4\,\mu/d$. $(d = 4l)$.

It can be easily seen that

$$d_{01} = d_{03} = a\,(\lambda + \mu + z_2 - z_1)$$
$$d_{02} = d_{04} = -\,a\,(\lambda + \mu + z_2 - z_1)$$

If the primary valence forces should cause no net resultant force at any atom, it follows from the above that

$$\lambda + \mu + z_2 - z_1 = 0$$
$$\text{or}\quad d_{01} = d_{02} = d_{03} = d_{04} = 0$$

Also it can be found that

$$d_{12} = d_{34} = 0$$
$$d_{23} = d_{41} = 0$$
$$d_{31} = -\,d_{42} = 2\,\beta\,(\lambda+\mu)$$

and

$$\theta_{12} = \theta_{34} = 0$$
$$\theta_{23} = \theta_{41} = 0$$
$$\theta_{31} = -\,\theta_{42} = 2\,\sqrt{3}\,\beta\,(\lambda+\mu)/p$$

It can be seen that the repulsive forces, the directed valence forces and the intravalence forces do not cause any inner forces for the distortions given in Table II.

Now, the change U_2 in the energy density of the crystal is given by

$$2\,U_2 = \frac{2}{d}\left[\mathrm{K}'' + \frac{3\,(\mathrm{K}'-\mathrm{K}''')}{p^2}\right](u_{xy}+u_{yx})^2$$

Hence $$c_{44} = \frac{2}{d}\left[\mathrm{K}'' + \frac{3\,(\mathrm{K}'-\mathrm{K}''')}{p^2}\right]$$

c_{44} is the rigidity modulus for any pair of the axes of reference.

Collecting our formulæ for the elastic constants, we have

$$\left.\begin{aligned} c_{11} &= \frac{1}{3d}\left[\mathrm{K} + 12\,\mathrm{K}'' + \frac{12\,(\mathrm{K}'+\mathrm{K}''')}{p^2}\right] \\ c_{12} &= \frac{1}{3d}\left[\mathrm{K} + 6\,\mathrm{K}'' - \frac{6\,(\mathrm{K}'+\mathrm{K}''')}{p^2}\right] \\ c_{44} &= \frac{2}{d}\left[\mathrm{K}'' + \frac{3\,(\mathrm{K}'-\mathrm{K}''')}{p^2}\right] \\ \frac{1}{\kappa} &= \frac{1}{3d}\{\mathrm{K} + 8\,\mathrm{K}''\} \end{aligned}\right\} \quad \cdots \quad \cdots \quad (6)$$

It will be noticed that a relation between the elastic constants

$$c_{11} \simeq c_{12} + c_{44}$$

exists when K'''/p^2 *the intravalence constant is negligibly small.*

In calculating the lattice frequency of diamond, we assumed $\mathrm{K} \simeq 4 \times 10^5$ dyn./cm. and $(\mathrm{K}'-\mathrm{K}''')/p^2 \simeq 0\cdot 2 \times 10^5$ dyn./cm. On this assumption the contribution of the primary valence forces towards the bulk-modulus of diamond is $3\cdot 8 \times 10^{12}$ dyn./cm.^{2} using the value $3\cdot 552 \times 10^{-8}$ for d given by Bragg.[11]

Assuming that the remaining portion of the bulk-modulus $6\cdot 25 \times 10^{12}$ dyn./cm.^{2} of diamond is contributed by the repulsive forces we find that $\mathrm{K}'' \simeq 0\cdot 34 \times 10^5$ dyn./cm. With the above values for K, K′ and K″ (*neglecting* K‴), we find that

$$\left.\begin{aligned} c_{11} &\simeq 9\cdot 8 \times 10^{12}\ \text{dyn./cm.}^2 \\ c_{12} &\simeq 4\cdot 5 \times 10^{12}\ \quad ,, \\ c_{44} &\simeq 5\cdot 3 \times 10^{12}\ \quad ,, \end{aligned}\right\} \quad \cdots \quad \cdots \quad (7)$$

where, as remarked above, $c_{11} = c_{12} + c_{44}$

The Poisson constant σ_x for a stress acting along the cubic axis is given by

$$\sigma_x = \frac{c_{12}}{c_{11}+c_{12}} \simeq 0\cdot 31$$

The Debye value of the Poisson constant assuming the crystal to be a homogeneous and isotropic continuum is 0·26.

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[11] W. H. Bragg and W. L. Bragg, *Introduction to Crystal Analysis*, 1928, page 58.

The Young's modulus E along a direction whose direction cosines are (l, m, n) with respect to the axes of reference is given by[12]

$$\frac{1}{\mathrm{E}} = \left(\frac{1}{c_{11}-c_{12}} - \frac{1}{2\,c_{44}}\right)(l^4 + m^4 + n^4) - \left[\frac{c_{12}}{(c_{11}-c_{12})\,(c_{11}+2\,c_{12})} - \frac{1}{2\,c_{44}}\right]$$

$$\approx [\cdot 094\,(l^4 + m^4 + n^4) + \cdot 05] \times 10^{-12}$$

The end point of the radius vector from the origin whose magnitude is $\frac{1}{\mathrm{E}}$ and whose direction cosines are (l, m, n) describes a surface. The sections of the surface perpendicular to a cubic axis and bisecting a pair of cubic axes are drawn in figures (1) and (2). If E_w, E_0 and E_g be the Young's moduli along a cubic axis, a diagonal of the cubic cell and a diagonal of the face of a cube respectively, then we have

$$\mathrm{E}_w \approx 6\cdot 9 \times 10^{12} \text{ dyn./cm.}^2$$
$$\mathrm{E}_0 \approx 12\cdot 3 \times 10^{12} \quad ,,$$
$$\mathrm{E}_g \approx 10\cdot 5 \times 10^{12} \quad ,,$$

Sections of the Elastic Surface of the reciprocal of the Young's modulus.

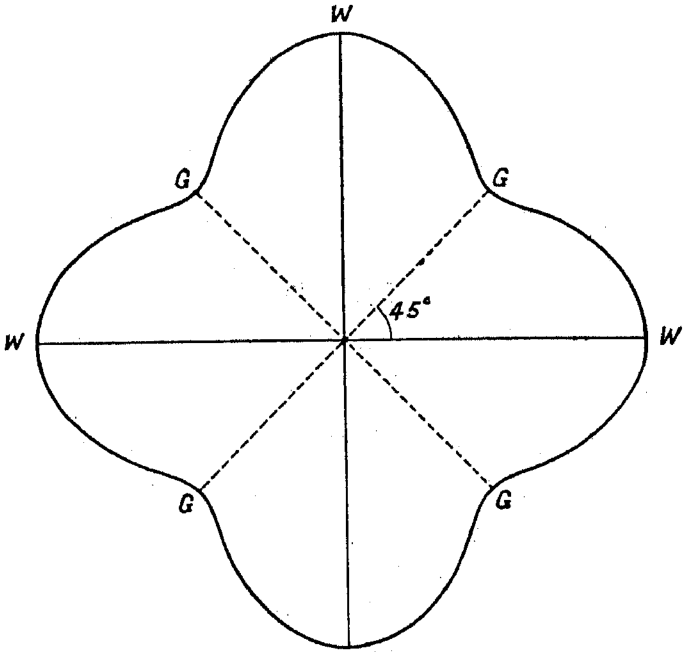

FIG. 1. Section perpendicular to the cubic axis.

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[12] A. E. H. Love, *The Mathematical Theory of Elasticity*, 1927, page 191; and F. Auerbach and W. Hort, *Handbuch der Physikalischen und Technischen Mechanik*, Bd. 3, pages 249 & 254.

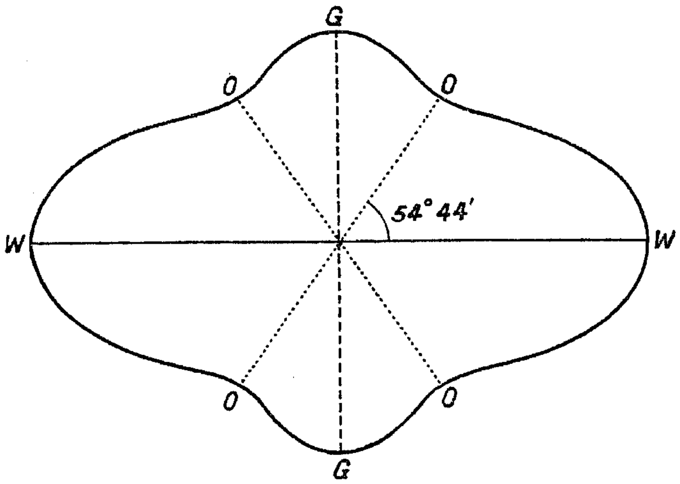


FIG. 2. Section perpendicular to the dodecahedral axis.

The rigidity modulus G for a pair of orthogonal axes whose direction cosines are (l, m, n) and (l_1, m_1, n_1) respectively is given by

$$\frac{1}{G} = \frac{1}{c_{44}} - 4\left(\frac{1}{2c_{44}} - \frac{1}{c_{11}-c_{12}}\right)(l^2 l_1^2 + m^2 m_1^2 + n^2 n_1^2)$$

If we take a rod of the crystal with a circular section with the axial direction cosines (l, m, n), the torsion is given by

$$T = \frac{2}{c_{44}} + 4\left(\frac{2}{c_{11}-c_{12}} - \frac{1}{c_{44}}\right)(m^2 n^2 + n^2 l^2 + l^2 m^2)$$

In the case of diamond

$$T \backsimeq [\cdot 38 + \cdot 75\ (m^2 n^2 + n^2 l^2 + l^2 m^2)] \times 10^{-12}$$
$$\backsimeq [\cdot 75 - \cdot 38\ (l^4 + m^4 + n^4)] \times 10^{-12}$$

Hence

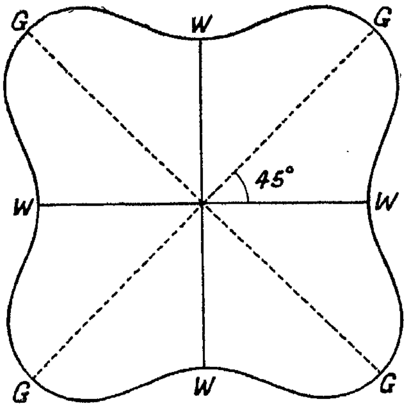
$$1/T_w \backsimeq 2\cdot 7 \times 10^{12} \text{ dyn./cm.}^2$$
$$1/T_0 \backsimeq 1\cdot 6 \times 10^{12} \quad ,,$$
$$1/T_g \backsimeq 1\cdot 8 \times 10^{12} \quad ,,$$

The sections of the torsion surface are drawn in figures (3) and (4).

The foregoing values of the moduli are all only *approximations* as they have been calculated on an inexact knowledge of the values of the force constants. In view of this, the experimental investigation of the elastic constants of diamond would be of the greatest interest as it would enable us to get a correct idea of the magnitudes of the chemical binding forces in diamond.

The author is highly thankful to his professor Sir C. V. Raman for his great interest in this work.

Sections of the Torsion Surface.



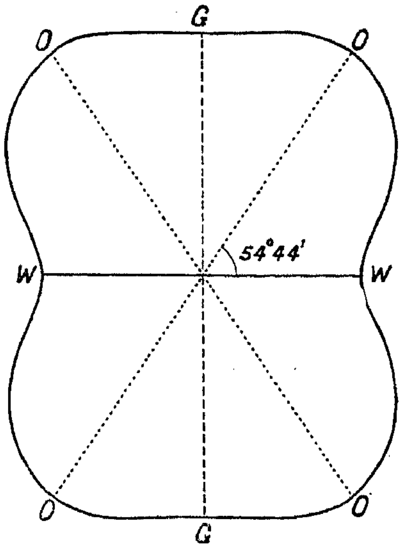


FIG. 3. Section perpendicular to the cubic axis.

FIG. 4. Section perpendicular to the dodecahedral axis.

Note :—The author takes this opportunity of rectifying a remark made in Part I. The author made the remark that Sir Robert Robertson and his collaborators suggest that the normal mode of vibration responsible for the principal Raman line is also responsible for the strong infra-red absorption with the frequency 1289 cm.$^{-1}$. The above statement was based on their remark in their paper (p. 523)—" the strong peak at 1289 cm.$^{-1}$ is near the Raman frequency 1332 cm.$^{-1}$ and differs from it in the same manner as has been observed between the Raman lines and the infra-red bands in other substances "—. From a private communication the author learns that this interpretation was not intended by them. He therefore wishes to withdraw the remark made by him.