PHOTOELASTIC CONSTANTS OF DIAMOND

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1. Introduction

ALTHOUGH the photoelastic constants of various cubic crystals have been determined (Pockels, 1889, 1890, 1906), there appears to be only one observation made on the birefringence produced by pressure in diamond. was made as early as 1851 by Wertheim (quoted in their book on Photoelasticity by Coker and Filon, 1931). Unfortunately, however, the crystallographic orientation of Wertheim's specimen is unknown. There seems to have been no other attempts at investigating the photoelastic behaviour of diamond. This is probably due to the difficulty of obtaining suitable specimens in the form of rectangular parallelepipeds and also fairly free from natural birefringence. The present investigation has been facilitated by the availability of such specimens in Sir C. V. Raman's collection. experiments were carried out with three different specimens in each of which different directions of pressure and observation were employed. In this way, it has been possible to determine all the three piezo-optic constants that occur in the theory of photoelasticity (Pockels, 1906) for a cubic crystal. The interesting fact comes out that, for both pressures along the cubic and the octahedral axes, the strained crystal behaves optically as a positive uni-axial crystal. Also, it is found that the refractive index should decrease when subjected to a hydrostatic pressure. In both these respects, diamond stands unique among the cubic crystals that have been studied so far.

2. General Theory of Photoelasticity

Since the notation of the general theory of photoelasticity will have to be used often in later sections, it will be useful to give a brief resumé of its results here.

It is assumed that Fresnel's laws hold good in a homogeneously deformed crystal and that the differences between the optical parameters of the crystal in the deformed and the original states are linear functions of the six deformation components x_x , y_y , z_z , y_z , z_x , x_y or of the six stress components X_x , Y_y , Z_z , Y_z , Z_x , Z_x , Z_y . Thus, if a_{11} , a_{22} , a_{33} , a_{23} , a_{31} , a_{12} are the optical polarisation 208

constants of the deformed crystal according to an arbitrarily chosen co-ordinate system and if the original values of these are denoted by a superscript, then we have the following relations:

The first group of constants p_{ij} are called the elasto-optic constants and the second group q_{ij} the piezo-optic constants. Between them, there are the relations:

$$p_{ij} = \sum_{n=1}^{6} q_{ik} c_{kj};$$
 $q_{ij} = \sum_{n=1}^{6} p_{ik} s_{kj},$ (3)

where $c_{kj} = c_{jk}$ are the elastic constants and $s_{kj} = s_{jk}$ are the elastic moduli. The set of 36 constants composed of the p_{ij} 's or the q_{ij} 's completely define the photoelastic behaviour of a crystal when subjected to known strains or stresses respectively. All the constants are, however, not independent if the crystal possesses elements of symmetry, so that the total number of independent constants is reduced (Pockels, 1906; Bhagavantam, 1942). Thus, in a cubic crystal, there are only three independent constants, e.g., p_{11} , p_{12} and p_{44} , and the scheme of 36 constants will be as follows:

The piezo-optic constants all follow an exactly similar scheme with only three independent constants, q_{11} , q_{12} and q_{44} . [In isotropic bodies like glasses, we have additional relations $p_{44} = \frac{1}{2}(p_{11} - p_{12})$ or $q_{44} = q_{11} - q_{12}$, so that there are only two independent constants.]

From the above formulæ, the following relations are readily derived for the polarisation constants of a cubic crystal made doubly refracting by an arbitrary stress:

$$a_{11} = a^{\circ 2} - q_1 X_x - q_2 (X_x + Y_y + Z_z); \quad a_{23} = -q_3 Y_z$$

$$a_{22} = a^{\circ 2} - q_1 Y_y - q_2 (X_x + Y_y + Z_z); \quad a_{31} = -q_3 Z_x$$

$$a_{33} = a^{\circ 2} - q_1 Z_z - q_2 (X_x + Y_y + Z_z); \quad a_{12} = -q_3 X_y$$

$$(5)$$

where $q_1 = q_{11} - q_{12}$, $q_2 = q_{12}$, $q_3 = q_{44}$ and a° is the velocity of light in the unstrained medium on the basis that the velocity of light in vacuo is unity, i.e., $a^{\circ} = 1/n$, where n is the refractive index of the natural crystal.

From equations (5), it can be shown that, in general, the crystal behaves as a biaxial crystal when subjected to a linear compression or dilatation, except when the stress direction is parallel to a cubic or an octahedral axis, when it behaves as a uniaxial crystal with the optic axis parallel to the direction of the stress. However, for an arbitrary stress direction, the directions of the principal axes of polarisations, and consequently those of the two optic axes and the value of the optic axial angle, are independent of the magnitude of the pressure. They depend only on the value of the constant q_3/q_1 , which may be denoted by χ . Thus, in so far as one is interested in the direction of the principal axes of polarisation and of the optic axes of a deformed cubic crystal, the phenomena can be described in terms of a single constant χ .

Further, the magnitude of the birefringence, *i.e.*, the path difference between the two polarised waves propagated in any direction along the deformed crystal, is a linear function of the pressure and of two constants q_1 and q_2 , the constant q_2 not being involved at all. Thus, no observations made on the relative retardation of the rays propagated through the compressed crystal can enable one to determine the value of q_2 . For this purpose, one requires also measurements on the absolute retardations of the two components, *i.e.*, the variations in the optical path of a beam of light when the crystal is subjected to strain.

The experimental work thus falls naturally into two stages: (1) the determination of q_1 and q_3 on the basis of measurements made on the relative retardations of the polarised components, for various directions of pressure and of observation and

(2) the determination of q_2 , and thus of q_{11} and q_{12} separately, from the measurement of absolute retardations.

3. Determination of the Constants q_1 and q_3

Three specimens of diamond, N.C. 73, N.C. 85 and N.C. 60 from Sir C. V. Raman's collection, were employed for the present studies. Of these, N.C. 73 and N.C. 85 were opaque to the ultra-violet below 3000 Å.U., while N.C. 60 was transparent down to 2250 Å.U. N.C. 73 was particularly suited for the investigation since it exhibited very little natural birefringence. The orientations and the magnitudes of the length, breadth and thickness of the three diamonds are given in Table I below. The orientations were determined by X-rays and are correct to within 1°.

TABLE I

No. of diamond	Length		Breadth		Thickness	
	mm.	Parallel to	mm.	Parallel to	mm.	Parallel to
N. C. 73	8.05	[011]	5.08	[211]	0.67	[111]
N. C. 85	7-46	[211]	2.70	[011]	1.03	[111]
N. C. 60	9.77	[011]	6.32	[111]	1.27	[211]

A simple apparatus, shown diagrammatically in Fig. 1, was used for subjecting the crystal to a linear compressive stress. The crystal in the form of a rectangular block was placed on a firm plane horizontal support A and the load was applied by means of a horizontal movable bar B. This bar had two circular holes by which it could be fitted and made to slide smoothly along two cylindrical upright pillars P fixed to the base. It rested freely on the crystal and the crystal was compressed by adding weights to two pans hanging from the ends of the bar, the weights in the two pans being always adjusted to be the same. To uniformise the pressure, lead washers about 2 mm. in thickness were placed both above and below the crystal. prevent any damage to the crystal from the heavy bar falling on it in case it slips and falls flat, two supporting screws S were included having locknuts. These could be adjusted such that their height is a little less than that of the crystal, so that normally the loaded bar B rested on the crystal, while if the crystal fell down it rested on the supporting screws. No lever arrangement, such as was employed by Pockels, was used in the author's apparatus, for the crystals were all sufficiently small and the requisite stresses of 50 to 100 kg./ sq. cm. could be obtained by applying directly loads of the order of 1 to 4 kg. The measurement of the double refraction generated by pressure was carried out by means of a Babinet compensator for three wavelengths, viz., the radiations of wavelengths 4358 and 5461 Å.U. from the mercury

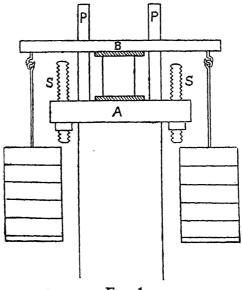


Fig. 1

arc and that of wavelength 5893 Å.U. from the sodium vapour lamp. The experimental set up may be described as follows. The direction of the pressure in the loading apparatus was vertical and this was made parallel to the length, breadth or thickness of the specimen as was necessary. The light from the source was first rendered parallel by means of a lens, and then polarised with its vibration vector exactly at 45° to the vertical, *i.e.*, to the pressure direction. This parallel polarised beam of light then passed through the crystal parallel to one of its two edges at right angles to the direction of the pressure. The emerging light was analysed by the Babinet compensator, which was kept with its principal axes exactly in the horizontal and vertical directions and the analyser at 45° to the vertical, but at right angles to the polariser.

Under these conditions it is obvious that, when the crystal is unstrained and if it possesses no natural birefringence, the central dark fringe of the compensator will be exactly in the zero position. When the load is applied, the fringes should shift and this shift was accurately measured. It is clear that the measured quantity represented the path difference between the two polarised rays having their vibration directions respectively horizontal and vertical. In general, the directions of vibration in the compressed crystal are parallel to these directions so that the measurement directly gives the magnitude of the birefringence. However, there occurred one case where this was not so, viz., with N.C. 85 when the pressure direction was along [211] and observation along [011], in which the vibration directions of the two waves in the crystal were inclined to the vertical. The same arrangement

of the Babinet compensator was used in this case also and the shift was measured. The meaning of this shift will be clear when one remembers that the elliptically polarised light emerging from the crystal is resolved into vertical and horizontal components by the compensator itself, and that the difference in phase of these two is what is indicated by the shift. In fact, this measurement served as a useful check on the others as will be seen a little later.

None of the crystals studied were free from birefringence, although N.C. 73 was very nearly so. Consequently, the compensator fringes were not in the zero position with the unstrained crystal. This was corrected for by bringing the fringes to the zero position both with and without the load and taking the difference to be due to the birefringence produced by the stress. This, of course, implies the asssumption that the optical effects of two arbitrary stresses are the same as if they are applied separately and their effects added up. That this is not far from being true is shown by the experiments themselves. As will be seen from Table II, measurements made on different crystals showing different amounts of natural birefringence agree fairly well. So also, observations made with light going through different regions of the same crystal (showing variations in natural birefringence) gave consistent results.

On account of the variations in natural birefringence, it is necessary that the measurements of path retardation must be performed for light passing through a small area of the crystal. In fact, such measurements could be done at different points on the cross-section of the crystal by employing the technique of obtaining the "Babinet pattern" of the crystal, described by the author in a recent paper (Ramachardran, 1946). It consists in focussing the image of the crystal on the plane of the quartz plates of the compensator. It is then possible by shifting the lens to make the central fringe to pass through any desired point of the image and measure the shift at that point. The aperture of the lens should be made small so that the divergence of the rays reaching the compensator is as small as possible, as otherwise the accuracy of the settings is impaired. The measurements were carried out at a number of points (usually 6 or 9) over the area of the crystal and the average shift taken as the correct value. This was done in order to allow for any non-uniformity in the distribution of stress. It was found that the shifts measured with the three different wavelengths did not differ by more than the experimental errors, so that no attempt was made to measure them separately, but an average was made of the measurements with different wavelengths. Hereafter, in talking of the shift, we shall always mean this final average value.

First, it was verified with N.C. 73 that over the range of stresses employed, viz, upto 120 kg./sq. cm. the birefringence was exactly proportional to the stress. Later, measurements were made with only one value of the load. From these, the shift per unit stress per unit thickness was calculated for different directions of pressure and observation. These are given under the heading β in Table II and are expressed in terms of the number of divisions of the compensator. Theoretically, the expressions for this quantity have been worked out and are given in the last column in the same table. These again are not exactly equal to β , but are proportional to it. The full expression for β should contain a factor $2/n^3$ in addition to what is given in the table. The derivation of these expressions is rather cumbersome, but follow the method given by Pockels (1889), and has been omitted here. As already remarked, the expression for β has been calculated to represent the phase difference between the horizontal and vertical components.

TABLE II

ALMHIN A.					
Diamond	P along	O along	β × 10 ⁴	Expression for β	
N.C. 73					
(1)	[011]	[111]	0.281	$(q_1+2q_3)/3$	
(2)	[211]	[111]	0.279	$(q_1+2q_3)/3$	
N.C. 85					
(3)	[211]	[111]	0.280	$(q_1+2q_3)/3$	
(4)	[011]	[111]	0.272	$(q_1+2q_3)/3$	
(5)	[011]	[211]	0.222	$(q_1 + 5q_3)/6$	
(6)	[111]	[211]	0.178	Q3	
(7)	[111]	[011]	0.169	93	
(8)	[211]	[011]	0.301	$\frac{1}{6}\sqrt{33q_3^2+9q_1^2-6q_1q_3}$	
N.C. 60				•	
(9)	[011]	[111]	0.282	$(q_1+2q_3)/3$	
(10)	[111]	[011]	0.163	93	
(1i)	[011]	[211]	0.226	$(q_1 + 5q_3)/6$	
	l	1	l		

It will be noticed that 5 measurements are available for $(q_1 + 2q_3)/3$, 2 for $(q_1 + 5q_3)/6$ and 3 for q_3 . Of these, two of the first set have been obtained with N.C. 73, which was practically free from natural birefringence. Giving a weightage of 3 for these readings and 1 for the rest, the mean values

for the three quantities come out as 0.279, 0.224 and 0.170. q_1 and q_3 were calculated from these by forming the normal equations from these and solving them. They are $q_1 = 0.503$ and $q_3 = 0.168$. The observed values have been recalculated from these and are compared with the actual data in Table III. The comparison shows that the measurements are consistent. Making use of the observation that 5.39 divisions of the Babinet compensator correspond to 5893 Å.U., the absolute values of q_1 , q_3 and χ have been calculated to be

$$q_1 = q_{11} - q_{12} = 7.8 \times 10^{-11}, \ q_3 = q_{44} = 2.6 \times 10^{-11}, \ \chi = 0.34$$
 (6)
Table III

	Observed	Calculated
$(q_1 + 2q_3)/3$	0.279	0.280
$(q_1 + 5q_3)/6$	0.224	0.224
q_3	0.170	0.168
$(\sqrt{33q_3^2+9q_1^2-6q_1q_3})/6$	0.301	0.305

The corresponding elasto-optic constants have also been calculated from these, using the elastic constants determined by Bhagavantam and Bhimasenachar (1946), viz., $c_{11} = 9.5 \times 10^{12}$, $c_{12} = 3.9 \times 10^{12}$, $c_{44} = 4.3 \times 10^{12}$.

We have

$$p_{11} - p_{12} = (q_{11} - q_{12}) \cdot (c_{11} - c_{12}) = 0.45$$

$$p_{44} = q_{44} \cdot c_{44} = 0.11$$
(7)

4. DETERMINATION OF THE THIRD PHOTOELASTIC CONSTANT

As already remarked, it is necessary to measure the absolute retardations of the two polarised waves separately in order to determine all the three photoelastic constants. The method so far used for this purpose (which was first employed by Pockels, *loc. cit.*) was to use plane parallel plates of the crystal and to measure the variations in the path of each polarised wave, as the crystal is compressed, by means of an interferometer. Optically parallel plates of diamond were not available to the author, and therefore a new method was developed which makes use of the crystal itself as an interferometer. The diamond N.C. 73 was used for the purpose and localised interference fringes of the Newtonian type were produced by the interference of light obtained from the two surfaces of the crystal plate. In this particular specimen, the two faces were such that they together formed a convex lens, so that the fringe system consisted of concentric rings. The

surfaces of the diamond were deposited with aluminium by the evaporation process so as to increase the reflectivity and thus render the rings sharp. The surfaces were normal to [111], so that the light passed along this direction. The pressure direction was along $[01\overline{1}]$. The light was polarised with its vibration direction horizontal and vertical respectively and in either case the fringes were photographed with and without the load. The photographs were taken with three different wavelengths, viz., 4358, 5461 and 5893 Å.U.

The fringes were not exactly circular and their spacings did not correspond to a spherical curvature of the surfaces. Consequently, interpolation formulæ had to be used to obtain the actual path change from the measured shift of the fringes. The widths of the fringes were measured along lines through a marked reference point on the surface of the diamond parallel to its length and breadth. Various types of interpolation formulæ were tried, but the simple Newton's formula was found to be most convenient with the available data. This was used and the path difference Δ was deduced by a method of successive approximations. Since the differences were of the order of 1/20 of a wavelength, the first approximation was generally sufficient. The path difference Δ was calculated from the shifts of the first three fringes and they agreed fairly well showing that the interpolation method was fairly satisfactory. For example, we may mention the calculated Δ 's for the horizontally polarised beam in two experiments which were

$$0.050, 0.059, 0.054;$$
 $0.049, 0.053, 0.062.$

Here again, no differences beyond the limits of experimental error were detected in the values of Δ with the different wavelengths of light and their average was taken. The final mean values of the changes in path for the rays with vibrations in the vertical and horizontal directions respectively were $\Delta_1 = +300$ Å.U. and $\Delta_2 = -333$ Å.U., the relative retardation thus coming out to be 633 Å.U. Actually, the relative retardation as deduced from the Babinet compensator measurements is 632 Å.U. checking very well with the result of the interferometric measurement. The remarkably close agreement must however be considered fortuitous. The accuracy of the interference method is only such as to expect an agreement of within ± 20 Å.U.

The path difference between the interfering beams is 2nt when the crystal is unstrained, where t is the thickness of the crystal and n its refractive index. Hence,

$$\Delta = 2 (n \Delta t + t \Delta n) \tag{8}$$

We are interested in the quantities Δn_1 and Δn_2 , the alterations of the refractive indices for the vertically and horizontally polarised rays. For this

we require to know the change in thickness of the crystal owing to compression. This has been calculated from the theory of elasticity knowing the elastic constants quoted earlier. The contribution to Δ due to the alteration in thickness, viz., $2n\Delta t$ thus comes out to be +67 Å.U. Making this correction, we obtain the changes in path due to variation in the refractive index to be

$$t \triangle n_1 = +233 \text{ Å.U.} \text{ and } t \triangle n_2 = -400 \text{ Å.U.}$$
 (9)

These quantities are respectively proportional to $(3q_1 + 6q_2 + 3q_3)/6$ and $(q_1 + 6q_2 - q_3)/6$. Since q_1 and q_3 are known, $q_2 = q_{12}$ comes out to be -3.6×10^{-11} . Also, $q_{11} = q_1 + q_{12} = 4.2 \times 10^{-11}$.

The values of p_{11} and p_{12} can be calculated from these. They are:

$$p_{11} = c_{11} q_{11} + 2 c_{12} q_{12} = 0.12_5, p_{12} = c_{12} q_{11} + (c_{11} + c_{12}) q_{12} = -0.32_5.$$

5. DISCUSSION OF THE RESULTS

In Table IV below, the piezo-optic and elasto-optic constants of diamond as determined from the present investigation are shown together with the corresponding constants of other cubic crystals that have been studied so far (Pockels, 1906).

Piezo-optic Constants Elasto-optic Constants q1.108 $q_3 \cdot 10^8$ $q_2 \cdot 10^8$ χ $p_{11} - p_{12}$ \$44 *\$*12 *P*11 Rocksalt -1.183-0.833+0.704+1.43-0.0408 | -0.0108 | +0.137 | +0.178+0.0595 |-0.0276|+0.229*|+0.170*Sylvine ...+1.67 -2.525Fluorspar -0.482 + 1.134 - 0.172 + 0.0236 + 0.055 + 0.227-1.420+0.685Potassium alum -0.455 + 0.106-4.30Ammonium alum -4.462|-0.774|+0.173Diamond -0.0036 + 0.45+0.11+0.125 +0.0078 + 0.0026 + 0.34

TABLE IV

It will be noticed from the table that the piezo-optic constants of diamond are roughly a few hundred times less than those for other crystals, while the elasto-optic constants are of the same order. In other words, when subjected to the same strain, the change in the refractive index of diamond is of the same order as that for other cubic crystals; but when

^{*} These were not measured photo-elastically, but were deduced from the variation of the refractive index with temperature.

subjected to the same stress, it is enormously less. This obviously arises from the large values of elastic constants, which are in fact the largest known for any crystal.

Further, both q_1 and q_3 are positive for diamond as distinct from all the other crystals. This means that diamond behaves as a positive uniaxial crystal for unilateral pressures along the cubic and octahedral axes and as a positive biaxial crystal for pressures along the dodecahedral axis or along any other direction.

Another interesting fact follows if we calculate how the refractive index would alter when the crystal is subjected to a uniform hydrostatic pressure. If Δn is the change of the refractive index n, then it can be shown that

$$\Delta n = -\frac{n^3}{2} \cdot \frac{p_{11} + 2p_{12}}{3} \cdot e \tag{10}$$

where e is the volume strain (dv/v), which is positive for a dilatation and negative for a compression. For diamond, $(p_{11}+2p_{12})/3$ is equal to $-0\cdot175$ so that the refractive index decreases when diamond is subjected to a hydrostatic pressure. It will be noticed from Table IV that $(p_{11}+2p_{12})/3$ is positive for all the other crystals which therefore would be expected to show the usual behaviour, viz., an increase of refractive index under compression. Even in these crystals, however, the numerical value of $dn/d\rho$ is appreciably smaller than the value calculated from the Lorentz-Lorenz equation (Mueller, 1935),

viz.,
$$dn/d\rho = (n^2 - 1)(n^2 + 2)/6n\rho$$
 (11)

Mueller has sought to represent this difference by the addition of a factor $(1-\lambda)$ on the right-hand side. The quantity λ may be called the photoelastic anomaly, which has a value roughly 0.4 for glasses and about 0.5 for NaCl, KCl and CaF₂. In diamond, however, $dn/d\rho$ is negative, so that λ is greater than unity. The value calculated from the data of the present investigation is 1.15. As explained by Mueller, the anomaly arises from the alteration in the polarizabilities of the atoms in the crystal accompanying the strain. A fuller discussion of the question is reserved for a later communication.

In conclusion, I wish to express my sincere thanks to Prof. Sir C. V. Raman for the many discussions I had with him during the course of the investigation.

SUMMARY

All the photoelastic constants of diamond have been determined for the first time. The three stress-optic coefficients are $q_{11} = 4.2 \times 10^{-11}$,

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 $q_{12} = -3.6 \times 10^{-11}$, $q_{44} = 2.6 \times 10^{-11}$, from which the elasto-optic coefficients have been deduced to be $p_{11} = 0.12_5$, $p_{12} = -0.32_5$, $p_{44} = 0.11$. It is found that $q_{11} - q_{12}$ and q_{44} are both positive and also that the refractive index of the crystal should decrease when subjected to a hydrostatic pressure, both of which are unique for diamond among the cubic crystals studied so far. In the course of the investigation, a new technique has been developed for determining the absolute path retardation, based on the production of localised interference fringes by the light coming from the two surfaces of the crystal.

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