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PIEZOBIREFRINGENCE IN DIAMOND: FURTHER RESULTS*

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Abstract

Further studies of the piezobirefringence effect in diamond have been carried out on a specimen bounded by (100), (011), and $(0\bar{1}1)$ planes. The near-isotropy of the effect has been thus confirmed. The absolute values of the stress-optical constants have been determined approximately; the values obtained lead to a prediction of decline in refractive index in a diamond subjected to uniform hydrostatic stress. The absolute constants also agree somewhat better with considerations based on the Brillouin scattering of light in the crystal.

All previous studies of piezobirefringence in diamond have been carried out with specimens bounded by the (111), $(1\bar{1}0)$, and $(11\bar{2})$ planes. This is a convenient orientation, since the common natural or cleaved octahedral planes form a permanent reference frame of known position. With this orientation, it is possible to measure directly only the constant $2q_{1212}$; the value of the piezobirefringence constant q_{1111}-q_{1122} is deduced by computation. A comparison of the values of $2q_{1212}$ and q_{1111}-q_{1122} reported by Ramachandran (1) shows substantial anisotropy of the stress-optical effect in diamond. Grodzinski (2), however, has reported anisotropy of only 2%; and the earlier results of Poindexter (3) show less than 1% anisotropy for the same orientations. In the present work, a specimen bounded by (100), (011), and $(0\bar{1}1)$ was used to measure directly the constant q_{1111}-q_{1122} and thus to confirm the earlier work (3) based on indirect measurement.

The method used to determine q_{1111}-q_{1122} was essentially that used for the earlier measurement of $2q_{1212}$, with the exception of some modifications introduced by Giardini (4). Stress application was improved by use of a motor-driven weight moving along the compressor lever arm. Ball bearings were installed to reduce friction in the compressor's operating joints. A photomultiplier tube was used instead of a vacuum phototube, for greatly improved signal-noise ratio. The output of the amplifier was connected to a Varian recorder, rather than a meter.

A new rectangular parallelopiped of diamond was prepared from a 3-carat octahedron of nearly perfect shape. The orientation of the prepared faces was held to within 6′ of theoretically perfect orientation. This diamond was not of the excellent quality of the first one (3). It was faintly yellow and had several microscopic flaws. Low order interference colors were seen irregularly distributed about the crystal between crossed

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polars. The new crystal was more brittle than the first one, and eventually shattered, thereby concluding the study.

Measurements were made of the stress necessary to produce a retardation increase of $\frac{1}{2}$ wave length at 5400 Å. Because of the inherent double refraction in the crystal, it was impossible to use the correction formulas for non-uniform loading (3). Any non-uniformity of stress distribution, however, makes the apparent stress-optical constants too high in the photometric-integration method. The derivative of light intensity with respect to applied stress has a higher average value in the segments where the stress is higher; hence the peaks of overall light transmission tend to favor these segments. Accordingly, about 20 experimental runs were made and the lowest value selected as most nearly correct.

TABLE 1. PIEZOBIREFRINGENCE CONSTANTS OF DIAMOND

Specimen	Stress Axis	Observation Axis	Constant	Value
No. 1	[111]	$[1\bar{1}0]$	$2q_{1212}$	$-2.97\times10^{-14}\ \frac{\text{cm}^2}{\text{dyne}}$
No. 1	[111]	$[11\bar{2}]$	$2q_{1212}$	-2.99
A No. 1	$[11\bar{2}]$	[111]	$1/3(q_{1111}-q_{1122}+4q_{1212})$	-3.00
B No. 1	$[11\bar{2}]$	$[1\bar{1}0]$	*	-3.01
No. 1	(calculated)		$q_{1111}-q_{1122}$	-3.04 from A
No. 1	(calculated)		$q_{1111}-q_{1122}$	-3.07 from B
No. 2	[100]	[011]	$q_{1111}-q_{1122}$	-3.08

* $1/6\pm\sqrt{9(q_{1111}-q_{1122})^2-6(q_{1111}-q_{1122})(2q_{1212})+33(2q_{1212})^2}$

The observations were taken with pressure applied to the (100) face and observations directed normal to (011). The appropriate piezobirefringence constant for this situation is q_{1111}-q_{1122}. The value directly measured for this constant is -3.08×10^{-14} cm^2/dyne. In Table 1 this value is compared with the values for constants measured and calculated in the earlier study. (Note that the values are prefixed by a minus sign, instead of a plus, as in the first paper by Poindexter (3). The values are now in accord with Pockels' convention; in the case of the absolute constants, the minus sign indicates a decrease in refractive index under compressive stress.)

It is thus confirmed that diamond is nearly perfectly isotropic in its piezobirefringent behavior. In view of the poorer quality of diamond No. 2, it is reasonable to give greater weight to the values calculated from the results of measurement on No. 1. It is entirely possible that more refined measurements would demonstrate an even closer approach to isotropy.

Since publication of the first article, the results of other measurements have been communicated to the author by Grodzinski. The measurements were made by Fisher. The observations were taken on three different diamond needles subjected to bending. These are shown in Table 2.

TABLE 2. RESULTS FROM OTHER SOURCES

Observation Axis	Grodzinski-Fisher (2)		Ramachandran 1950 (1)
	Average Constant, Brewsters	q	q
[111]	2.76	$-3.85\times10^{-14}\ \frac{\text{cm}^2}{\text{dyne}}$	$-4.2\times10^{-14}\ \frac{\text{cm}^2}{\text{dyne}}$
[$\bar{2}$11]	2.80	$-3.78\times10^{-14}\ \frac{\text{cm}^2}{\text{dyne}}$	$-2.7\times10^{-14}\ \frac{\text{cm}^2}{\text{dyne}}$

Presently, there is no plausible explanation for the magnitudes of Grodzinski's data being approximately 1.3 times those of the present study. The anisotropy, however, is seen to be very slight.

MEASUREMENT OF THE ABSOLUTE VALUES OF q_{1111} AND q_{1122}

Qualitative measurements of the absolute changes in index are essential to determine whether a specific stress increases or decreases the index. The difference constant q_{1111}-q_{1122} might arise from the index increasing in one direction and decreasing in another, or simply from different rates of change of the same algebraic sign.

The quantitative determination of the absolute values of q_{1111} and q_{1122} presents substantially greater difficulties than in the case of the difference constant q_{1111}-q_{1122}. Inequalities in the stress distribution give rise to errors of far greater magnitude than in the case of the simpler piezobirefringence observations; the magnitude of the errors may often exceed the magnitude of the quantity which it is desired to measure.

Great sensitivity is needed for measurement of the stress-induced index change, since the change in index which may be introduced without fracture of the crystal is seldom more than one figure in the fourth decimal place. Two basic techniques are presently available; these are founded on either interference or deviation. In the first method, polarized light is passed through the crystal and allowed to interfere either with an external split beam, or with itself by internal reflection from the crystal faces. In the second method, a prism cut from the crystal is compressed, and the change in deviation of a transmitted beam of light is measured.

The deviation method was chosen for the present study. It was desired to continue making observations photometrically, and at the same time integrating and averaging the light from throughout the crystal. The extreme sensitivity of the emergent wavefront to variation in stress and flaws in the crystal precluded the interference technique.

The diamond was recut in the form of a prism frustum with an included angle of $8\frac{1}{2}°$. The frustum was preferred to a triangular prism because of its greater strength. Furthermore, there is no sharp corner to cut into the compressor pads; and the wider frustum is more stable when clamped in the compressor.

The design of the apparatus was straightforward. The exit slit of the monochromator was imaged at infinity and the beam passed through the prism of diamond placed in the compressor jaws. The deviated beam was focused on a 0.1-mm. slit by a lens of 50-inch focal length. A 931-A photomultiplier received the light through the slit. The slit and lens were assembled as a telescope, pivoted at the objective end. The slit end could be moved horizontally by a micrometer head.

The minimum measurable deviation corresponded to approximately 0.0002 inch micrometer motion, or about 1 second of arc.

Ideally, the deviation method has an advantage over the interference method in that only the stress-optical constants enter into the expression for the change in deviation; the elastic constants are not concerned. As little as a 10% non-uniformity of stress, however, can produce variations in apparent deviation which exceed the magnitude of that due solely to index change. This arises from the fact that the prism forms a very small aperture, and slight distortions of the emergent wave front cause serious shifts in the energy distribution in the slit image. The observed results when it was attempted to stress the prism uniformly were so erratic as to be completely worthless. Accordingly, a modified technique was developed.

In this method the prism was deliberately stressed non-uniformly by concentrating the load almost entirely on one edge. Under such conditions, with the stress at the opposite edge essentially zero, the change in deviation $\Delta\phi$ of the light beam is given by the formula

$$w' \cos\theta\Delta\phi = qn^3Tl_b + sT(n-1)(l_b+l_t)$$

where w' is the hypotenuse of the prism frustum, θ the angle between the hypotenuse and the emergent beam, T the average stress, s the appropriate compliance constant, l_b and l_t the path lengths on the long and short edges of the prism. The light is incident normally (see Fig. 1).

The modified method has the advantage that the deviation produced is about five times that to be expected from uniform loading, and that the portion of the deviation due to the elastic component is only about a third of the total. In practice, substantially more consistent results were obtained with the non-uniform loading technique, and they are at least qualitatively reliable.

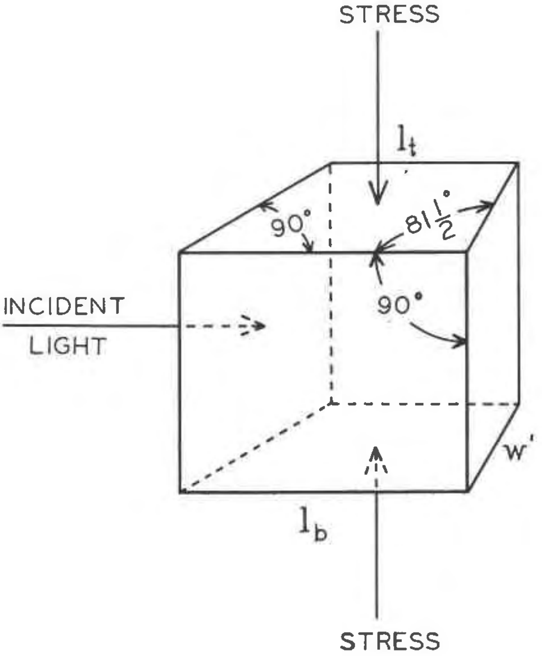

FIG. 1. The diamond prism, showing directions of stress and incident light.

The light distribution in the image of the monochromator slit at the phototube corresponded to a roughly bell-shaped curve. It was found that any noticeable distortion of the intensity curve by the application of stress to the crystal made apparent image shift values entirely useless. The final deviation values were obtained after careful adjustment of the crystal and load to obtain the least image distortion.

The measured values are shown in Table 3. The crystal was stressed on the (110) face, but the piezobirefringent isotropy makes it unnecessary to transform coordinates.

TABLE 3. ABSOLUTE STRESS-OPTICAL CONSTANTS

Constant	Poindexter (3)	Rama-chandran (1)	Burstein-Smith (5)	Avg. reduced
q_{1111}	$-2.4\times10^{-14}\ \frac{\text{cm}^2}{\text{dyne}}$	-5.0	-4.3	-2.0
q_{1122}	$+0.6\times10^{-14}$	$+2.1$	$+3.7$	$+1.0$
$q_{1111}-q_{1122}$	-3.0×10^{-14}			

The agreement between the difference of the absolute values and the measured piezobirefringence constant may be to a considerable extent fortuitous, but the values indicate clearly the sense of the change in the index of refraction. The ratio of the constants q_{1111} and q_{1122} as determined in the present study is $-4:1$. The ratio of the corresponding compliance constants of elasticity theory is $-3.5:1$.

The results of the present study and that of Ramachandran indicate that the index of refraction of diamond would decrease if a crystal were subjected to hydrostatic pressure. Burstein and Smith have found the contrary. The reduced average values shown above were computed after proportionally correcting the absolute constants to conform with a piezobirefringence constant of -3.0×10^{-14} cm^2/dyne. The appropriate constant for the hydrostatic effect is $q_{1111}+2q_{1122}$; it is thus seen that from the averaged values it cannot be predicted with certainty whether the index should increase or decrease.

The significance of the algebraic sign of the hydrostatic effect upon refractive index with respect to the binding electrons has been discussed briefly by Burstein and Smith (5). The present fund of data is unfortunately insufficient to substantiate a general theory, but certain qualitative aspects may be noted. The interaction of the binding electrons in a crystal with incident radiation varies with their degree of freedom from the nuclei. This is evidenced by the somewhat higher refractive indices of covalent crystals as compared to ionic, and the high absorption coefficients of metallic substances. In the hydrostatic compression of a simple ionic crystal, the net effect is largely due to the increase in density, whereas the freedom of the electrons is not directly affected. The refractive index would accordingly be expected to increase.

In more or less covalent crystals, however, the spatial or temporal distribution of the binding electrons may be more drastically altered, though the other electrons are virtually unaffected. Theoretical prediction of the effect of hydrostatic stress on index of refraction involves very lengthy computations. The calculation of the dependence of polarizability on internuclear distance in H_2 has been made by Ishiguro, Arai, Mizushima, and Kotani (6). The variation method was applied to the James and Coolidge wave functions for the H_2 molecule for various values of internuclear distance; it was found that the polarizability of the molecule declines as the distance is reduced. The derivative $d\alpha/dr$ has the value 1.5×10^{-24} cm³/Å for the mean polarizability. In the diamond crystal, the derivative (for each bond) would have to be about 1.0×10^{-24} cm³/Å to offset the Lorentz-Lorenz increase in refractive index with the increase in density. To justify the hydrostatic stress-optical constant value -1.2×10^{-14} cm²/dyne observed in the present study would require a rate of 1.7×10^{-24} cm³/Å.

A less well-known application of stress-optical data lies in the prediction of intensities in the Brillouin or thermal scattering of light. The direct measurements of the scattered light are not of great precision, but they serve as a useful check on the magnitudes of the stress-optical constants.

An exact computation of intensities for a general orientation of the crystal involves a high-order summation. For incident and scattering directions along cube axes, the work is much simpler. Born and Huang (7) give the result for this case. The ratio of the intensities of light scattered by transverse and longitudinal thermal vibrations, respectively, is

$$\frac{(2p_{1212})^2}{2c_{1212}} : \frac{2(2p_{1212})^2 + p_{1122}{}^2}{c_{1111} + c_{1122} + 4c_{1212}},$$

where p_{ijk} are the strain-optical constants and c_{ijk} are the elastic constants.

The strain-optical constants are related to the stress-optical constants by the equations $p_{ijkl} = c_{ijmn}q_{mnkl}$. Using the values (8) $c_{1111} = 9.2\times10^{12}$ dyne/cm², $c_{1122} = 3.9\times10^{12}$, $2c_{1212} = 4.3\times10^{12}$, and the previously determined stress-optical constants, we get $p_{1122} = -1.5\times10^{-2}$ and $2p_{1212} = -12.9\times10^{-2}$. Substitution in the intensity ratio formula gives the value 2.5:1. Ramachandran's ratio, deduced from his stress-optical measurements, is 1.6:1. Chandrasekharan (9) has measured the effect for several directions in diamond other than along cube axes and obtained ratios of 1.8:1, 2.3:1, and 3.3:1.

NOTE

Since publication of the first paper, it has been learned that F. Fumi (10) had earlier confirmed the work of Bhagavantam on the stress-optical tensor.

R. M. Denning and A. A. Giardini were responsible for much of the development of the measurement technique. Edward Poindexter made

the experimental observations and provided the theoretical discussion. C. B. Slawson prepared the diamond parallelopiped. The Office of Naval Research supported the work financially.

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