PIEZOBIREFRINGENCE IN DIAMOND*

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ABSTRACT

In this study the stress-birefringence behavior of diamond has been investigated. The phenomenon has been neglected by both classical and modern crystallographers. A theoretical investigation of the stress-optical tensor for the cubic system confirms Bhagavantam's results. A new and substantially improved method of measurement of the stress-optical effect was developed. A study of the effects of non-uniform loading upon the results of measurement was made. It has been confirmed that the diamond is virtually isotropic in its stress-birefringence effect. The dispersion of the constant q_{1212} throughout the range 4400 Å to 7700 Å is no greater than $\pm 1\%$. The relative retardation varies linearly with stress to pressures of 40,000 psi. No hysteresis was observable upon sudden application or removal of load, nor could permanent deformation be produced by prolonged stresses of the order of 40,000 psi. Diamond becomes negative uniaxial or biaxial under a single linear compression, depending on the direction of force. The stress-birefringent behavior of diamond is found to be compatible with the elastic properties and internal structure of the diamond crystal.

The term *piezobirefringence* is proposed as being more descriptive of the phenomenon than *photoelasticity*.

INTRODUCTION

The phenomenon of stress birefringence was discovered by Sir David Brewster in 1815 (1). His first studies were concerned with the stress-optical effect in jellies, but by 1818 he had investigated the effect in amorphous solids, and in isotropic, uniaxial, and biaxial crystals (2, 3). Brewster was the first to discuss stress birefringence in the diamond. The work of Brewster was entirely qualitative, but it inspired Fresnel (4, 5) and several less well-known scientists, to attempt a theoretical explanation. They contributed little, however, toward any general theory. Neumann in the 1840's (6) founded a mathematical explanation of the observed behavior of non-crystalline substances, based on the strain-dependence of the birefringence. Maxwell in 1852 (7) announced a similar theory, based on the stress dependence. Though developed independently, both theories arrived at analogous results. Both are very useful today in the engineering applications of stress birefringence to the study of stress and strain in materials such as glass and lucite.

Wertheim, in the early 1850's, was the earliest to investigate quantitatively the stress-optical behavior of crystals (8, 9). Despite several omis-

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sions and misinterpretations in his writings, he drew important conclusions regarding the differences in the stress-optical behavior of glasses and crystals. He is credited by Coker and Filon (10) as being the first to measure the effect in diamond.

Pockels developed the original, universally accepted theory describing the stress-birefringence relation for all crystalline and non-crystalline forms of matter. The theory was published as his doctoral dissertation at Göttingen in 1889 (11). With minor corrections, Pockels' work is the basis for all investigations of the effect today. The theory was laid down in the compact notation now described as tensorial, so that a great amount of information was compressed into a few very brief equations. This theory is discussed in the next section.

Bhagavantam in 1942 (12) noted that Pockels has erred in the tabulation of constants for several crystal classes, and Bhagavantam and his associates have confirmed the corrections experimentally. Other than the work of Bhagavantam, there have been no contributions to the geometrical theory for over 60 years. Coker and Filon (10), Mason (13), and others have repeated the errors made by Pockels.

Explanations of the physical mechanism responsible for the stress birefringence are unsatisfactory when any quantitative predictions of the effect are made. Much of the work has been based upon inference from relations not involving pressure effects. The semi-classical work of Mueller (14) is the most comprehensive attempt; it gives a reasonable prediction of the magnitude of the effect, but fails to predict the positive or negative character. Burstein and Smith (15, 16) have more recently added some pertinent speculations on the behavior of the constituent particles in the stressed crystal, but the number of crystals studied is too small to test even the qualitative aspect of their hypothesis. The assumptions necessary to simplify any inclusive analysis of the problem will demand even more observations for their justification.

The number of crystals which have been studied quantitatively is about twenty. Wertheim observed four (9), Pockels seven; Ramachandran (17, 18) and his associates another seven or eight; and West, Makas (19, 20) and Burstein, Smith a few more. Several other crystals were studied qualitatively by Brewster and some lesser investigators of the nineteenth century. Ramachandran also measured the stress-birefringence effect in diamond; his work on this crystal is the only extensive work other than that of the present study. Until the present study, all measurements have been made at relatively low stresses. No previous studies have been made on crystals to determine the dispersion of the stress-optical constants with the wavelength of the light.

The infrared stress-optical effect has recently been studied by Bond

(21) and others interested in the properties of silicon and germanium. No published results are yet available on this work.

The stress-optical effect is commonly termed *photoelasticity* by members of the engineering profession. This term is not properly descriptive of the phenomenon. It is correct in that it implies a sort of optical strain arising from the application of stress; it does not, however, convey any idea of the manner in which the strain reveals itself. The necessity has arisen on several occasions to explain the meaning of *photoelasticity* to investigators completely familiar with many other vectorial properties of crystals. As a result of these considerations, the term *piezobirefringence* is suggested as a name for the birefringence produced by stress. This term describes in itself the nature of the phenomenon. It is compounded of familiar terms and is compatible with the names of other crystal properties, for example, pyro- and piezoelectricity. *Piezobirefringence* will be used throughout this paper in preference to *photoelasticity*.

Piezobirefringence is potentially of considerable importance in the study of the solid state. Several properties of "perfect" crystals can never be measured directly because of the great sensitivity of the properties to minute quantities of imperfections, either chemical or physical. Piezobirefringence effects are not especially sensitive to these quantitatively minor flaws. The effect itself, however, is closely related to several of these types of flaws, which produce a local or a general distortion of the crystal. The phenomenon of piezobirefringence is most obviously of direct application to the study of a general, overall distortion. Most crystals, even the best synthetic ones, show birefringence which is not justified by the idealized internal structure of the crystal. The exact cause of this birefringence is usually not known. Silicon and synthetic corundum are important examples in which "anomalous" double refraction is common; diamond is a familiar natural example. Screw dislocations and twinning are possible explanations; then again, very little systematic research has been done on the problem.

The paucity and inconsistency of available information on piezobirefringence, and the potential value of quantitative results inspired the present study. In the paper by Slawson and Denning (22) in this issue, the application of piezobirefringence studies to an interpretation of double refraction in natural diamond is discussed. The synthesis of the diamond was announced only after the present study was well underway. It can only be supposed that someday the growth of diamond crystals, and imperfections and dislocations in them will be as common topics in industrial discussions as they are for silicon and germanium today. The piezobirefringence investigations should be of assistance in such problems.

Theory of Piezobirefringence

Geometrical Theory

Pockels developed the first geometrical theory of piezobirefringence in a generalized treatment, applicable to crystals of all classes and homogeneous non-crystalline substances. Pockels' theory is analogous to the commonly accepted theories describing all other vectorial properties of crystals. Within the present boundaries of experiment, all evidence has supported the basic assumptions of his theory. Bhagavantam's corrections to the development of the theory for various crystal classes have been partially verified experimentally by Bhagavantam and Suryanarayana (24), and theoretically by Bond (21), Mason (23), and the writer. Pockels' approach is nonetheless fundamentally sound; as modified by the corrections noted above, it is the theory presented here (25).

A non-absorbing triclinic crystal may be characterized optically for any one wavelength of light by specification of six independent quantities called the polarization constants. We designate the principal refractive indices as follows: $\alpha_1=1/\alpha$, $\alpha_2=1/\beta$, $\alpha_3=1/\gamma$. We let α_{ij} represent the cosine of the angle between the jth principal optical direction and the ith coordinate axis of a reference Cartesian frame in the crystal. Then the polarization constants a_{ij} are defined by

$$a_{ij} = \sum_{k=1}^{3} \alpha_{ik}\alpha_{jk}\alpha_k\alpha_k \tag{1}$$

Since $a_{ij}=a_{ji}$, there are in reality only six independent constants a_{ij}.

Pockels postulated that stress is related to the change in optical properties by the equations

$$\Delta a_{ij} = a_{ij} - a^\circ{}_{ij} = q_{ijkl}T_{kl},$$

where a_{ij} are the polarization constants in the stressed crystal, and $a^\circ{}_{ij}$ in the unstressed. The quantities q_{ijkl} compose the stress-optical tensor. A similar set of relations hold for strain; the corresponding quantities p_{ijkl} compose the strain-optical tensor.

In a three-dimensional space the expression q_{ijkl} comprises 81 possible independent quantities. The symmetry of the crystal class in question reduces the number of independent components. In the usual method of approach, the effects upon q_{ijkl} of a transformation of coordinates in accord with crystallographic laws of transformation are compared with the effects in accord with mathematical laws. It will then be found that in order to satisfy both theorems of transformation, certain linear relations must be satisfied by some q's, while others must necessarily vanish. The reduction will be illustrated here for the five cubic classes.

The components q'_{ijkl} of a fourth order tensor in one set of rectangular

Cartesian coordinates are mathematically related to the components of the same tensor in another set by the equations

$$q'_{ijkl} = \frac{\partial x_i'}{\partial x_r}\frac{\partial x_j'}{\partial x_s}\frac{\partial x_k'}{\partial x_t}\frac{\partial x_l'}{\partial x_u} q_{rstu}. \tag{2}$$

The crystallographic transformation laws depend, of course, upon the symmetry of the crystal class. Class 23 will be considered first. The threefold axis suggests a cyclic transformation in which we have $x_3' = x_2$, $x_2' = x_1$, and $x_1' = x_3$. Thus we see that

$$\frac{\partial x_i'}{\partial x_r} = +1 \text{ if } i = r + 1,$$

and

$$\frac{\partial x_i'}{\partial x_r} = 0 \text{ otherwise.}$$

Thus in equation (2) the only q'_{ijkl} which are not zero are those in which each primed subscript is one greater than each unprimed subscript. But crystallographic symmetry requires that $q'_{ijkl} = q_{ijkl}$. By induction, it follows that each q_{ijkl} is equal to the corresponding component with subscript increased by one, and hence by two. The number of independent components is thus reduced from 81 to 27.

The two-fold axis suggests the transformation $x_1' = -x_1$, $x_2' = -x_2$, $x_3' = x_3$. Thus we have

$$\frac{\partial x_i'}{\partial x_r} = -1 \text{ for } i = r = 1 \text{ or } 2.$$

$$\frac{\partial x_i'}{\partial x_r} = +1 \text{ for } i = r = 3,$$

$$\frac{\partial x_i'}{\partial x_r} = 0 \qquad \text{otherwise.}$$

It is seen that in the mathematical transformation of q_{rstu}, equation (2), only one term remains on the right side, that in which the primed subscripts equal the unprimed. Hence we have $q'_{ijkl} = \pm q_{ijkl}$, depending on the values of the subscripts. If an even number of $(ijkl)$ have a value of 3, then we have $q'_{ijkl} = +q_{ijkl}$; if an odd number have a value of 3, then we have $q'_{ijkl} = -q_{ijkl}$. But crystal symmetry requires that $q'_{ijkl} = q_{ijkl}$. Therefore, q_{ijkl} vanishes for the odd case. The threefold axis requires that this result be valid for any other transformation of the same type. Hence the only non-zero components of the earlier 27 are those in which the subscripts occur in pairs. The independent components of the stress-optical tensor remaining at this stage are thus q_{1111}, q_{1122}, q_{1133}, q_{1212}, q_{2121}, q_{1221}, q_{2112}.

It will be remembered that in equation (1), both Δa_{ij} and T_{kl} are symmetric, that is, $\Delta a_{ij} = \Delta a_{ji}$ and $T_{kl} = T_{lk}$. There is thus seen to be no loss

in generality in taking $q_{ijkl}=q_{jikl}$ and $q_{ijkl}=q_{ijlk}$. The seven independent components are thus reduced to four, q_{1111}, q_{1122}, q_{1133}, q_{1212}. These are the stress-optical constants of class 23.

Class 23 is of considerably interest, since it is one of those for which Pockels was in error. Pockels deduced that there should be three independent stress-optical constants for each class in the cubic system. The result above is the first independent confirmation of Bhagavantam's group-theory proof of Pockels' error. Both Bond (21) and Mason (23) have indicated agreement with these more recent results.

The remaining cubic classes will be examined briefly. The next more symmetrical class after 23 is $m3$. The axial planes suggest a transformation $x_1'=-x_1$, $x_2'=x_2$, $x_3'=x_3$. The transformation affords no relations between terms of differing subscripts; and since the non-zero partial derivatives are either $+1$ or -1, and the four q_{ijkl} remaining have subscripts only in pairs, no conflict arises between mathematical and crystallographic transformation. The center corresponds to a transformation $x_i'=-x_i$, and by the same reasoning as above affords no reductions in the number of constants. Hence the scheme of independent constants for class $m3$ is the same as for class 23.

In class $\bar{4}3m$, the diagonal planes make the crystal axes completely equivalent, as compared to their cyclical equivalence in classes 23 and $m3$. In this case the formal transformation is $x_1'=x_1$, $x_2'=x_3$, $x_3'=x_2$. Both the crystallographic and mathematical transformations lead to the same results, $q_{1122}=q_{1133}$. This is the sole effect of the diagonal planes. The independent constants for class $\bar{4}3m$ are then q_{1111}, q_{1122}, q_{1212}.

In class 43, the four-fold axes have the same effect as the diagonal planes; equivalence of crystal axes. The formal transformation is $x_2'=x_3$, $x_3'=-x_2$, $x_1'=x_1$. This leads to the relation $q_{1122}=q_{1133}$. Crystallographic symmetry yields the same result. The independent stress-optical constants remain as q_{1111}, q_{1122}, q_{1212}.

In class $m3m$, to which diamond belongs, the problem is not so much to see what effect the symmetry does have, but rather what it does not have. Complete axial equivalence yields $q_{1122}=q_{1133}$. As is evident by this time, the only transformations of value in the cubic system are those in which the derivatives are either ± 1 or 0. Such transformations make components vanish only if the subscripts do not occur in pairs. Such transformations bring about relations only between components having the same subscript pattern, for example, q_{aaab} and q_{jjjk}. In the three remaining stress-optical constants, all the subscripts occur in pairs, and none of the sets of subscripts follows the same pattern. Hence the independent constants for diamond, and all crystals of class $m3m$, are q_{1111}, q_{1122}, q_{1212}.

The results for the various cubic classes are summarized in Table 1.

TABLE 1. STRESS-OPTICAL CONSTANTS OF CUBIC CRYSTALS

Class	Independent Components of Stress-optical Tensor	
	Pockels	Bhagavantam, Poindexter
23, $m3$	q_{1111}, q_{1122}, q_{1212}	q_{1111}, q_{1122}, q_{1135}, q_{1212}
$\bar{4}3m$, 43, $m3m$	q_{1111}, q_{1122}, q_{1212}	q_{1111}, q_{1122}, q_{1212}

It should be noted here that the constant q_{1111} relates a compression on the (100) face to the change in index of refraction for light polarized perpendicular to that face. The constant q_{1122} relates the same compression to the change in index for light polarized perpendicular to any $(0kl)$ face. The constant q_{1212} relates a shear stress to the orientation of the indicatrix in the stressed crystal.

In the present study, the stress birefringence was measured, not the absolute change in index of refraction. Only two constants are required to characterize completely the birefringence effect in class $m3m$. Exact expressions relating the stress to the resultant change in optical properties are given in a later section.

The stress-optical equations may be solved to give quantitative results, and thus prediction of the optical effect of any stress whatever. It is worthwhile, however, to examine qualitatively the behavior of cubic crystals under a single linear compression. Several simple rules serve to predict the nature of the change in optical properties produced by this stress. No justification other than intuition will be offered here for these rules; all can be rigorously verified by computation.

1. Any symmetry axis in the unstressed crystal which coincides with the axis of compression is also present in the stressed crystal.

2. A two- or four-fold axis normal to the axis of compression is present as a two-fold axis in the stressed crystal.

3. Symmetry planes parallel or normal to the compression axis are unaffected by the stress.

4. A center of symmetry is unaffected by the stress.

5. Any symmetry element not oriented as discussed above is destroyed by the compression.

6. No symmetry elements are created by the compression.

In accord with the above rules, it is seen that a single compression applied to an opposite pair of cube faces of cystals of classes 23 and $m3$ produces in effect orthorhombic crystals of classes 222 and mmm, respectively. A similar stress in classes $\bar{4}3m$, 43, and $m3m$ produces tetragonal

symmetry of classes $\bar{4}2m$, 42, and $4/mmm$. Compression on an octahedron in any class converts the crystal to class 3 hexagonal. Compression in a general direction converts classes 23, $\bar{4}3m$, and 43 into class 1 triclinic, and classes $m3$ and $m3m$ into class $\bar{1}$ triclinic. The modified optical properties correspond, of course, to the modified symmetry of the stressed crystal.

The above rules can be of very real value in selecting the orientation of the crystal to be studied. It is impossible to measure all of the stress-optical constants by a single compression on a cube face; in fact, it is often inconvenient to measure any of them in this manner. A crystal with an easy octahedral cleavage, for example, may split too easily when stressed on the cube face. Furthermore, many substances have naturally occurring faces (or cleavages), not normal to the crystallographic axes, which are desirably left on the crystal specimen as reference planes. It turns out that all the stress-optical or stress-birefringence constants may be measured by simple compressions if the orientation of the specimen is properly chosen.

When a crystal is compressed on any but a cube face, it is necessary to derive stress-optical constants appropriate to the orientation. This procedure is far simpler than an attempt to resolve a general compression into its components along the crystal axes, and to relate these many components to the optical effect. The appropriate derived constants are related to the original constants by the theorem of tensor transformation, equation (2). The procedure will not be illustrated in this paper, but the derived constants for the orientations employed are given in the section on measured results.

Physical Theory

The various physical theories of piezobirefringence have had only a very limited success in the correlation of prediction and experiment. All of the theories have required considerable amounts of data from other sources, often questionable in themselves, in order to translate symbols into measurable predictions. The theoretical work has been hindered by the lack of data on the piezobirefringent behavior of crystals. About twenty crystals have been studied, and they make up a rather heterogeneous lot as far as their stress-optical effects are concerned. It is necessary to postulate different mechanisms for each crystal to explain the observed effects. The most successful attacks have been semi-classical in nature; the quantum-mechanical approaches have been too complicated to permit of any predictions whatever.

The present investigation has included only a brief treatment of the problems of physical theory. Accordingly, only a short discussion of the

factors involved and a short résumé of the principal studies will be presented here.

We consider the crystal as a system of electric charges. When a charge system is subjected to an electrostatic field (it is assumed that magnetic fields have negligible interaction with the crystals concerned here), the energy E put into the charge system is related to the field strength F by the formula $E = -\frac{1}{2}\alpha F^2$. The quantity α is a constant for the system and is called the polarizability. The refractive index is theoretically related to the polarizability by the Lorentz-Lorenz equation,

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \frac{L\alpha\rho}{M},$$

where M is molecular weight, L Avogadro's number, and ρ density. The total polarizability of a crystal is the resultant of three contributions: the electronic component, which arises from the distortion of the electron field around each nucleus; the ionic component, which arises from the movement of oppositely charged ions with respect to each other; and the orientational component, which arises from the rotation of dipolar molecules in certain types of crystals. In the optical range of frequencies, the inertia of ions and molecules prevents any appreciable movement; so the polarizability is almost entirely due to the deformation of the electronic orbits.

The effect of an applied electric field on any one particle in an assemblage of particles, such as a crystal, is modified by the reaction of the other particles. The total displacement of charge under the influence of the external field creates a counter-field in opposition to the applied field, which reduces the effectiveness of the applied field.

A more complete discussion of dielectric phenomena and mechanisms may be found in any text on crystal or solid-state physics.

Attempts to calculate the index of refraction for crystals have not been notably successful, despite the great amount of experimental data available. Empirical formulas can be found which fit certain groups of crystals better than the Lorentz-Lorenz equation, but none presents any striking improvement. The attempts to explain piezobirefringence have been even less successful. Banerjee (28) considered two effects. The first is the modification of the counter-field by the deformation of the crystal; the second is the effect of distortion of the constituent ions in the crystal. Mueller (14) observed, however, that Banerjee made a serious error in his choice of method for adding up the reactions of the particles in the crystal. Banerjee's predictions were compared with the observed behavior of only two substances, NaCl and KCl. Banerjee found found acceptable results for these two; so another error, which compensates for the first,

is present. Banerjee did not attempt to apply his theory to other substances.

Herzfeld (29) and Herzfeld, Lee (30) considered the effect of the crystal deformation on the counter-field, and also considered the resultant modification of the electronic energy levels. The effect on the energy levels, which in turn determine the polarizability, was calculated by a second-order perturbation treatment commonly used in quantum mechanics. A distortion of the potential well around the nucleus was postulated as the perturbation. The method is sound, but Herzfeld concluded that the final equations require too many assumptions regarding the proper values of constants. Furthermore, Mueller pointed out several errors in computation; Herzfeld himself later admitted these.

Mueller (14) included in his calculations the effect of deformation on the counter-field, the effect on inter-ion spacing and the effect on the shape of the ions themselves. Mueller made no final calculations for covalent crystals; he did, however, by proper assumptions make the equations match the behavior of NaCl and KCl. The most unsatisfactory aspect of the theory is its inability to predict whether the refractive index increases or decreases under the effects of compression. His theory is the most complete of any on the topic, and Mueller concluded that it is satisfactory because it is at least not in opposition to the facts.

The extreme difficulties involved are well illustrated by the simplified quantum-mechanical treatment of the problem attempted in the present work. The Lorentz-Lorenz equation may be rearranged and differentiated to give

$$\frac{\partial n^2}{\partial \rho} = \frac{4\pi L\alpha}{M\left(1 - \frac{4\pi L\alpha\rho}{3M}\right)^2}.$$

Since for any real value of n, the quantity $4\pi L\alpha\rho/3M$ must be less than 1, it is seen that an increase in density ρ causes an increase in refractive index. This direct effect is, of course, modified by the change in the nature of the counter-field under the deformation. The counter-field in turn depends not only on the directional alteration of the lattice constant, but upon the directional change in polarizability of the electron systems in the crystal. As far as optical properties are concerned, the density change is a bulk effect for either hydrostatic force or a single linear compression, and thus can produce no anisotropy. Piezobirefringence for any type of stress must be analyzed in terms of the anisotropies of the structure change and the polarizability. For hydrostatic compression, the density change, the modification of the structure, and the change in polarizability all affect the overall index change; but wheth-

er the crystal acquires greater or lesser birefringence again depends solely upon the latter two factors. The effects of polarizability change do not necessarily add to the direct effect of density change; there is some evidence at the present time that the refractive indices of some crystals decrease under hydrostatic pressure.

If we assume a simple one-electron "covalent" bond in a diamond-like crystal, the polarizability of the electron is given by (31)

$$\alpha = \frac{\left(\int\int\int_{-\infty}^{+\infty} \phi^2 z^2 dxdydz\right)^2}{\int\int\int_{-\infty}^{+\infty} \phi z \frac{\partial \phi}{\partial z} dxdydz} \frac{8\pi^2 me^2}{h^2},$$

where ϕ is the appropriate wave function and z is the coordinate in the direction of the applied field. The function ϕ will vary with change in lattice constant; thus the polarizability will be changed. The expression, itself an approximation, would be extremely difficult to evaluate with exactness. The inclusion of the effects of the other charged particles in the crystal increases the difficulties still more. Under a single compression, some bonds will be lengthened, others shortened; bond angles will be changed. The change in polarizability will vary with direction. There is no obvious evidence that the effect of three equal linear compressions at right angles (hydrostatic force) is simply the sum effect of the three compressions applied individually. If such is not the case, Pockels' tensor treatment is incorrect. At the present time the experimental evidence is not sufficiently accurate to enable any conclusions on the latter possibility. In brief, expressions such as the one above are all but useless in a discussion of piezobirefringence.

Further elaboration of the physical theory would be futile at the present stage of understanding of the problem. Qualitative observations on the application of theory to the present work will be presented in a later section.

Measurement Apparatus and Procedure

An interference method of observation was chosen for the present study. The principle may be used in measurements either of the piezobirefringence directly, or of the absolute change in refractive indices. In the first case, the specimen is stressed while in the 45° position between crossed polars, and the change in relative retardation is observed. The birefringence is then computed in the usual way, and the stress-birefringence constants calculated. To measure the absolute index change, the retardation of light polarized in the principal optical directions must be observed. This may be accomplished by splitting an appropriately polarized light beam with a half-silvered mirror, sending half through

and half around the crystal specimen, and observing the interference arising upon recombinations of the two halves of the beam. Localized fringes arising between two surfaces of the crystal may also be employed if the faces are nearly perfectly parallel.

In the present work, only the birefringence was observed. The technique developed for the study entails one important modification, not used heretofore, which increases the precision of the observations. The measurement of retardation was supplanted by measurement of transmitted light intensity; instead of an optical compensator, an electronic

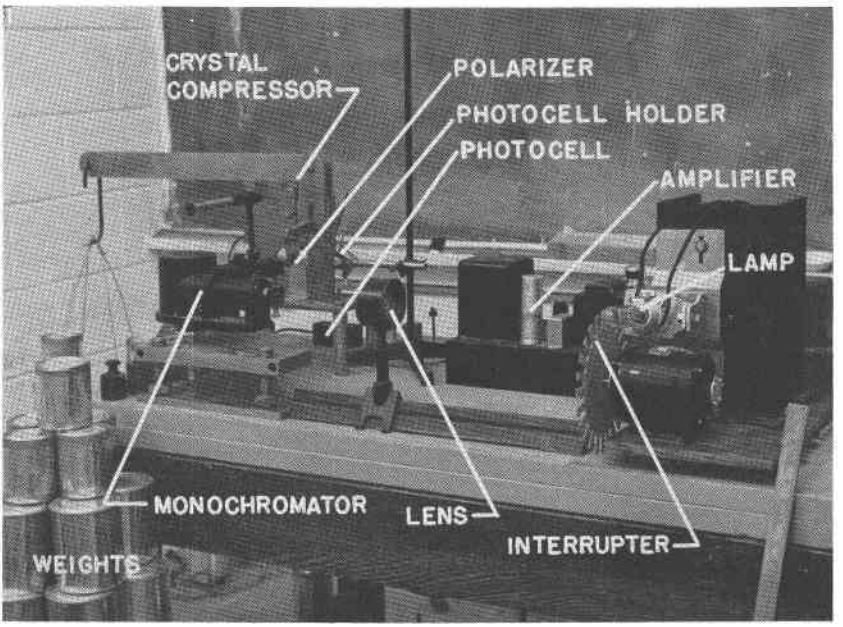

FIG. 1. Overall view of the measurement apparatus.

photometer was used. The advantages of this modification will be discussed shortly.

The measurement apparatus consists of a light source, 750-cps interrupter, monochromator, polarizer, crystal compressor, analyzer, photocell, and tuned amplifier, arranged in that sequence. A photograph of the apparatus is shown in Fig. 1. Note that the analyzer is not visible, and that the photocell is not in position in the clamp directly behind the compressor. Protective covers were removed from the device in order to reveal the component parts. An enlarged view of the compressor is shown in Fig. 2. Both polarizer and analyzer are moved from the light

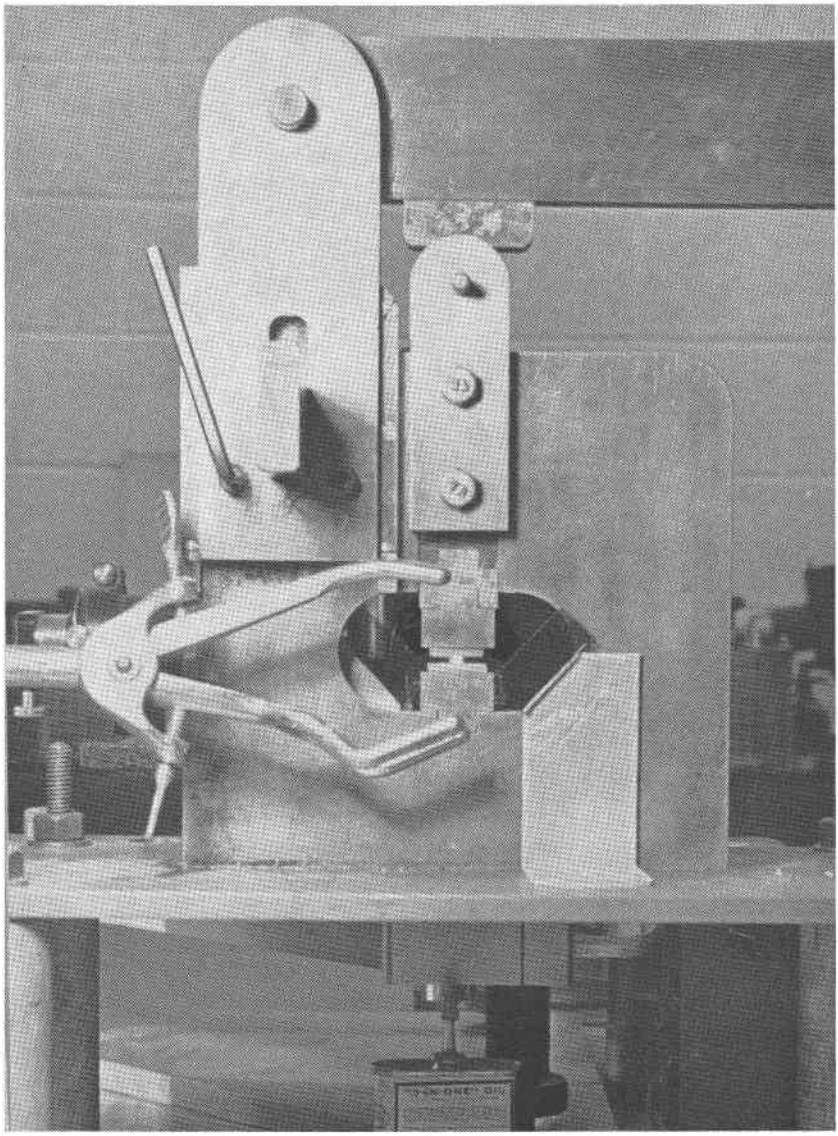

FIG. 2. The crystal compressor. The polaroids and photocell are not in position. The crystal is mounted as in actual measurements.

path, and the photocell is out of sight. The crystal is mounted as in actual measurement, and it may be seen brightly illuminated by the beam from the monochromator directly behind.

The construction of the apparatus is almost self-explanatory from the illustrations, and will not be discussed.

Measurement Technique

The technique employed in the present study requires that the crystal specimen be shaped in the form of a parallelepiped, roughly equidimensional. The specimen is placed between crossed polars, which are in the 45° position, and subjected to a single linear compression on one pair of faces normal to the polars. The relative retardation produced by a known stress is observed. The piezobirefringence constants may then be computed from relations derived later.

The present study initiated a modified method of observing the retardation which has several important advantages. The first difference between the new and the old is that the apparatus measures only the relative intensity of the transmitted light; it is not well adapted for direct measurement of retardation. The second difference is that the crystal is examined over the entire visible area of one face, rather than in selected small regions. The second difference is in one respect a consequence of the first, and it greatly facilitates accurate measurement. In the older method, the results of observation at several points on the crystal face were averaged. This method can present serious difficulties, because of the non-uniformity of the stress distribution in the crystal. In the present method, the observed quantity is light intensity; it is easily possible to obtain an integrated average over the face of the crystal by placing the photocell so that all of the transmitted light is intercepted. There is no way to measure the average retardation directly with such facility. This automatic average is the most significant improvement afforded by the intensity method of observation.

The observation procedure is such as to reduce the effects of instrumental failings and observational misjudgments. Though the instrument was designed to measure intensity of light, only the successive maxima and minima of transmission under increasing stress were recorded. Thus the transfer characteristic of the amplifier has no influence whatever upon the results. The accuracy of the photometric determination of retardation is about as good as that obtainable with a Babinet compensator, that is, about 1/400 wavelength (32).

Obtaining a uniform stress distribution in the crystal is a very critical consideration. The observations were in effect averages over an entire crystal face. Nevertheless, the observed quantity, light intensity, is related to the stress in such a way that any non-uniformity of stress distribution is reflected as an increase in the apparent values of the piezobirefringence constants. It is desirable that the maximum variation in stress not exceed $\pm 20\%$. In such a case, the correction is no greater than 1%, which can be applied with confidence. If the non-uniformity exceeds $\pm 20\%$, the correction increases very rapidly, and soon becomes so sensitive to the distribution as to be useless in application.

Although $\pm 20\%$ may appear a generous tolerance, attainment of such a degree of uniformity is a matter of some difficulty. Simple pads of resilient material inserted between crystal and compressor jaws were not adequate. Rubber and lead tended to spread laterally from beneath the crystal, with the result that the stress was very much higher in the center of the crystal. Cardboard became very compact after a few compressions and thereby lost its value as a pad. Celluloid performed very well, but internal rearrangment in the material destroyed its effectiveness very rapidly. Furthermore, the shape and size of simple pads of any material is so critical that the ideal form is seldom obtained. These difficulties led to abandonment of the simple pad.

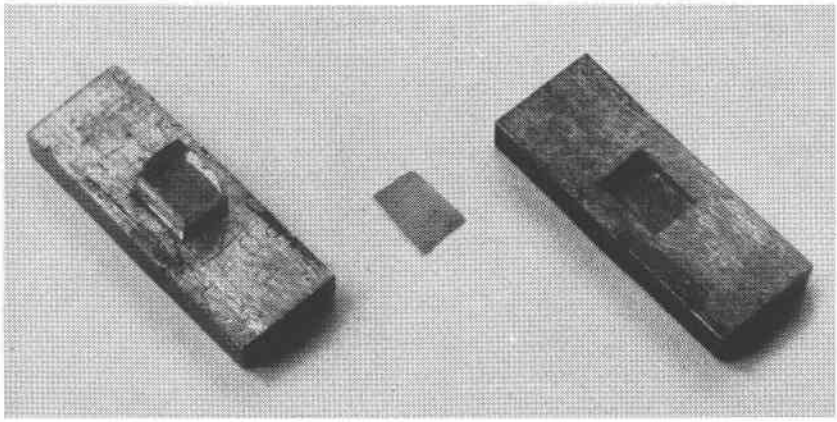

FIG. 3. View of crystal mounting pads. In order from left to right are a pad with the diamond in place, a dental rubber cushion, and the other pad. The rubber is to be placed in the bottom of the well of the empty pad before insertion of the crystal.

A semi-hydrostatic crystal mount was the eventual solution to the problem. Small brass blocks were made which receive the crystal snugly in rectangular wells. A thin layer of soft solder was placed in the bottom of the wells. Under any compression of greater than about 9000 psi, the solder behaves as a viscous fluid and distributes the load evenly over the face of the crystal. To improve the performance below the yield point of solder, an additional pad of dental dam rubber was inserted between the crystal and the solder layer. An enlarged view of the compound pads is shown in Fig. 3.

The performance of the compound pads has been very satisfactory. The effective variation in stress was typically $\pm 15\%$, and at very high stresses, often no worse than $\pm 2\%$.

The range of stresses throughout which measurements were made serves as a valuable check on the performance of the pads and the ac-

curacy of the observations. Previous piezobirefringence studies were limited to stresses of the order of 100 kg/cm.^{2} In the present work, pressures were carried to a maximum of 3000 kg/cm.^{2} The observed linearity of the piezobirefringence effect to these high stresses is very good evidence that the measurement technique is satisfactory.

Errors and Corrections

Three predictable sources of error are present in the measurement process. The first is the non-uniformity of stress distribution in the crystal; the second is the joint effect of the pass-band of the monochromator, the spectral emission curve of the lamp, and the spectral response of the phototubes; the third is the divergence of the light beam passed through the crystal. These three faults cause errors which can be computed to within $\pm 20\%$ of their own true value; so in each case a small correction is applied to the data.

The first source of error is the non-uniformity of stress distribution. It should be noted that variations in stress along any ray of light through the crystal can cause no error as long as the stress-retardation effect is linear. The observed intensity is a function of the total retardation along the path of the ray, regardless of the history of the ray. Variation in total retardation in a direction normal to the ray, however, does produce an error in the measurement. Such variation results in variation in the intensity of the light reaching the photocell from various portions of the crystal. The observed readings may be corrected if the approximate degree of the non-uniformity is known.

If the effective stress non-uniformity is $1 \pm p$ times the mean stress, then it can easily be shown that the stress producing an observed minimum in light transmission is $T = T^0/1+p^2$, where T^0 is the stress producing a minimum if the stress were uniform. The degree of non-uniformity may be noted by scanning the face of the crystal with a narrow slit. The transmission I at a minimum may also be shown to be related to the non-uniformity by the expression

$$T = \frac{T^0}{1 + \frac{2I}{\pi^2}}.$$

Both methods were used as a check on the value of the correction. It is seen that a value for p of 0.1, corresponding to a total variation in stress of about $\pm 20\%$, gives rise to a correction of 1%.

The combination of tungsten radiator and phototube produced virtual sensitivity peaks in the green and infrared. The monochromator was set to have a pass band with half-intensity points 100Å apart. Thus the effective wavelength was not exactly that indicated on the monochroma-

tor scale. This error was evaluated approximately; it was found that the greatest correction to the piezobirefringence constants is 0.15%. This is so small that it is hardly worth consideration.

The light was not collimated before passing through the crystal. The divergence is approximately 1.3° in the diamond. This results in an increase in effective path length in the crystal of about 0.07%, again hardly worthy of notice.

Several unpredictable sources of error were observed. These were friction in the compressor, inaccuracies in the loading weights, rapid shifts in line voltage, and non-uniformity of the phototube cathode surface. No attempt was made to correct for any of these.

Results and Conclusions

In the section on theory it was shown that the diamond requires three constants to enable complete description of the optical effect produced by a general stress. These three constants, the stress-optical constants, are designated as q_{1111}, q_{1122}, q_{1212}. The physical interpretation of these constants should be reviewed at this time. The constant q_{1111} relates the compression on a pair of crystallographic cube faces to the change in refractive index for light whose vibration direction is normal to those faces. The constant q_{1122} relates the same stress to the change in index for light whose vibration direction is parallel to those faces. The constant q_{1212} relates a shear stress to the orientation of the resultant indicatrix.

In the present study, the birefringence was investigated, not the absolute change in index of refraction. Since birefringence is a difference in indices, fewer constants are needed to specify the birefringence effect. For compression on a cube, the birefringence is related to the stress by the constant $q_{1111} - q_{1122}$. The constant q_{1212} has, of course, the same significance as before. These two constants have been called the piezobirefringence constants in previous sections.

The piezobirefringence constants may be measured conveniently with a rectangular parallelepiped of a single crystal of the substance. If both constants are to be measured, the orientation of the parallelepiped must not coincide with a crystallographic cube. For diamond, a suitable form is bounded by the (111), $(1\bar{1}0)$, and $(11\bar{2})$ faces. The specimen used in the present study was prepared in that form.

The diamond parallelepiped was cut from an octahedron of exceptional quality. The uncut crystal weighed 3.6 carats. The natural (111) faces were left on the crystal untouched, since they were very smooth and flat. Artificial $(1\bar{1}0)$ and $(11\bar{2})$ faces were ground and given an optical polish. The orientations of the artificial faces were held to within 10′ of the theoretical position by frequent checks on an optical goniometer during the cutting. The finished specimen is 3.31mm by 3.91mm by

4.57mm and weighs slightly over one carat. The largest face is the dodecahedron and the smallest the octahedron. The crystal is colorless, and unusually free of inherent double refraction, flaws, and twinning. The crystal appears "perfect" under 100× magnification.

The choice of orientation enables both piezobirefringence constants to be measured by stressing the crystal on the different faces. The piezobirefringence effect is most conveniently described by secondary constants, derived from the two constants given earlier, and appropriate to the orientation of the crystal. The computation of these constants will not be given here; the secondary constants are related to the original two by the law of tensor transformation. The constants for the orientations employed in the present study are given in Table 2.

TABLE 2. PIEZOBIREFRINGENCE CONSTANTS FOR VARIOUS ORIENTATIONS

Direction of Compression	Direction of Observation	Piezobirefringence Constant, Q
[111]	$[11\bar{2}]$ or $[1\bar{1}0]$	$2q_{1212}$
$[11\bar{2}]$	[111]	$\frac{1}{3}(q_{1111}-q_{1122}+4q_{1212})$
$[11\bar{2}]$	$[1\bar{1}0]$	$\frac{1}{6}\sqrt{9(q_{1111}-q_{1122})^2-6(q_{1111}-q_{1122})(2q_{1212})+33(2q_{1212})^2}$

The piezobirefringence constant is related to the observed retardation R and the stress T by the equation

$$Q = \frac{2\lambda R}{dn_0^3 T},$$

where Q represents the appropriate constant, selected from the table, and d is optical path length.

MEASURED RESULTS

Both primary piezobirefringence constants were measured for only one wavelength, 5400 Å. The sensitivity of the apparatus is greatest at this wavelength. Furthermore, this wavelength is approximately the average of the wavelengths employed by other investigators. The values recorded for $2q_{1212}$ were obtained by inspection of the trend of observed results in the neighborhood of 5400 Å. The values for the other constants are the averages of eight measurements at 5400 Å. These results are shown in Table 3.

The significant fact to be drawn from the results of the present study is the very slight deviation from piezobirefringent isotropy. Wertheim (10) made the first determination of the piezobirefringence constant for diamond in the early 1850's. He has been discredited by most later in-

TABLE 3. OBSERVED AND COMPUTED VALUES OF PIEZOBIREFRINGENCE CONSTANTS

	Direction of Compression	Direction of Observation	Q	Average Value	Observed
	[111]	[1$\bar{1}$0]	$2q_{1212}$	2.97×10^{-14}	cm²/dyne
	[111]	[11$\bar{2}$]	$2q_{1212}$	2.99	
(*A*)	[11$\bar{2}$]	[111]	$\frac{1}{3}(q_{1111}-q_{1122}+4q_{1212})$	3.00	
(*B*)	[11$\bar{2}$]	[1$\bar{1}$0]	(see Table 2)	3.01	
			Computed Results		
	[100]	[010]	$q_{1111}-q_{1122}$	3.04	from (*A*)
				3.07	from (*B*)

vestigators because he reported only one value, and did not specify the orientation of the crystal studied. The results of the present study imply that there is no great need to specify orientation.

The measurements by the three principle investigators are summarized in Table 4.

TABLE 4. COMPARISON OF PIEZOBIREFRINGENCE MEASUREMENTS BY DIFFERENT INVESTIGATORS

Q	Wertheim c. 1850 (10)	Ramachandran		Poindexter 1955
		1947 (47)	1948 (18)	
$q_{1111}-q_{1122}$	3.3	7.8	7.2	3.04
$2q_{1212}$		2.6	2.7	2.98
$\frac{1}{3}(q_{1111}-q_{1122}+4q_{1212})$			4.2	3.00

The factor 10^{-14} cm²/dyne has been omitted from all values.

Ramachandran's results show pronounced anisotropy.

The difference between his results and those of the other two studies is at first inspection suggestive of gross errors in technique or arithmetic. Ramachandran performed his measurements on specimens oriented the same as those used in the present study. For such specimens, the constant $2q_{1212}$ may be observed directly, but $q_{1111}-q_{1122}$ must be computed from a relation which tends to mangify errors in the values of the observed data. Ramachandran used simple pads of lead to distribute the stress on the crystal. It was found in the present study that such pads do not distribute the stress satisfactorily. Furthermore, Ramachandran did not carry his stresses to much beyond 100 kg/cm², which does not produce even $\frac{1}{2}$ wavelength of retardation. In view of these facts, his observed results for two of the Q's are not unreasonable; the value derived from these, $q_{1111}-q_{1122}$, is necessarily far more inaccurate.

There are several arguments favoring near-isotropy of the piezobirefringence effect in diamond. If it is assumed that the birefringence is in reality a strain-dependent phenomenon, then the elastic and piezobirefringence effects should be analogous. A comparison of the two properties for several cubic crystals is shown in Table 5. It is seen that in general,

TABLE 5. CRYSTAL ELASTICITY AND PIEZOBIREFRINGENCE PROPERTIES

Crystal	Compliance		Ref.	Piezobiref.		Ref.
	s_1	s_3		q_1	q_3	
Diamond	1.8	2.3	(26)	3.0	3.0	—
NaCl	29	78	(26)	12	8	(25)
LiF	13.6	15.9	(32)	14	7	(19)
MgO	4.9	6.4	(32)	12	6	(19)
CaF_2	8.4	29.6	(32)	14	−7	(25)
KBr	36	161	(32)	−16	47	(19)
KCl	28	156	(32)	−17	42	(25)

The abbreviated symbols designate the following constants:

$$s_1 = s_{1111} - s_{1122},\ s_3 = 2s_{1212},\ q_1 = q_{1111} - q_{1122},\ q_3 = 2q_{1212}.$$

The units for the compliance constants are 10^{-13}cm²/dyne; for the piezobirefringence constants 10^{-14}cm²/dyne.

crystals showing greater elastic anisotropy also show greater piezobirefringent anisotropy.

Another argument favoring near-isotropy for diamond may be based on the internal structure of the crystals. In the case of ionic crystals, the atoms are effectively in contact. A distortion of the crystal structure produces a distortion of the electron shells of these ions, which in turn causes a considerable directional difference in polarizability of the ions. It is easily visualized how the nature of the ion distortion will vary with the direction of the applied compression. In KBr, for example, which has the halite structure, a compression on (100) forces the ions directly against each other. A compression on (111), however, tends to force the ions between neighboring ions. The nature of the distortion introduced and the resultant effect on polarizability of the ions is thus markedly different for different directions of stress.

In the case of diamond, an entirely different disposition of particles prevails. Individual ions are not in contact at all. The structure is essentially an array of very compact C^{+4} nuclei relatively widely separated, but bound by electrons which move around two adjacent nuclei. A distortion of the crystal does not affect the nuclei at all. Bond distances are altered, and bond angles changed. These changes bring about modifi-

cations of the polarizabilities of the bonding electrons. The sum of polarizabilities in one direction no longer equals the sum in another; so the crystal has become birefringent. Regardless of the direction of compression, the effect is much the same.

The near isotropy of the piezobirefringence effect in diamond has been observed by Slawson and Denning (23). The same isotropy has been predicted for silicon (which has the same structure as diamond) by Bond (21).

The values of the constant $2q_{1212}$ observed at various wavelengths are shown in Fig. 4. No dispersion of the constant can be deduced with certainty from the data. The variation is at most $\pm 1\%$ throughout the

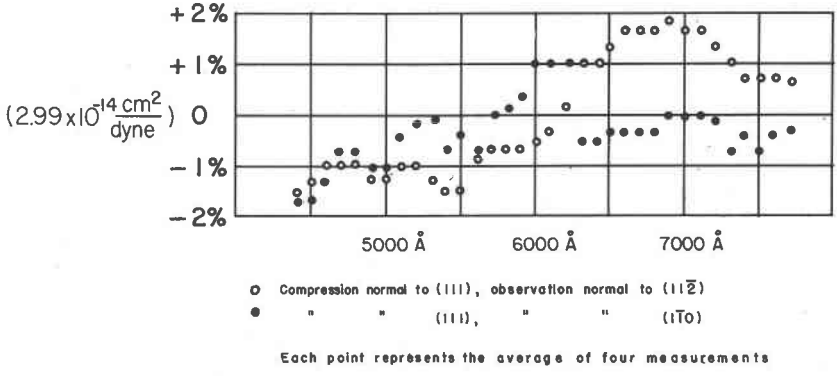

FIG. 4. Dependence of $2q_{1212}$ upon wavelength.

range of wavelengths studied. The limit of accuracy of the observations is of this order. It should be remembered that the retardation is proportional to the stress and the cube of the reciprocal of the refractive index. For diamond, the quantity n^3 is nearly 10% greater for light of wavelength 4400 Å than for light of 7700 Å. The first impression upon inspection of the observed data is that the piezobirefringence effect does vary substantially with wavelength. No theoretical explanation is currently available to justify either dispersion or non-dispersion of the property. The present work marks the first time the wavelength dependence of the piezobirefringence effect has been studied for any crystal.

The piezobirefringent behavior at increasing values of stress for several wavelengths is shown in the next series of graphs, Fig. 5. The plotted points are not averages in this case, but represent values observed with crystal mounts producing the most nearly uniform stress distribution at the higher stresses. This is the first time that the piezobirefringence of diamond, or any crystal, has been studied at such high stresses. Ramachandran employed pressures of about 100 kg/cm². The observed linearity of the stress-retardation effect to pressures of nearly 3000 kg/cm²

(40,000 psi) yields very valuable information. The combined effects of the pass band of the monochromator, the sensitivity curve of the lamp-phototube combination, and the non-uniformity of stress distribution become increasingly troublesome at higher stresses. The close agreement of measurements at both high and low stresses is very good evidence of the accuracy of the determinations.

No hysteresis or permanent deformation could be observed in the piezobirefringence of the diamond. The crystal was left stressed for

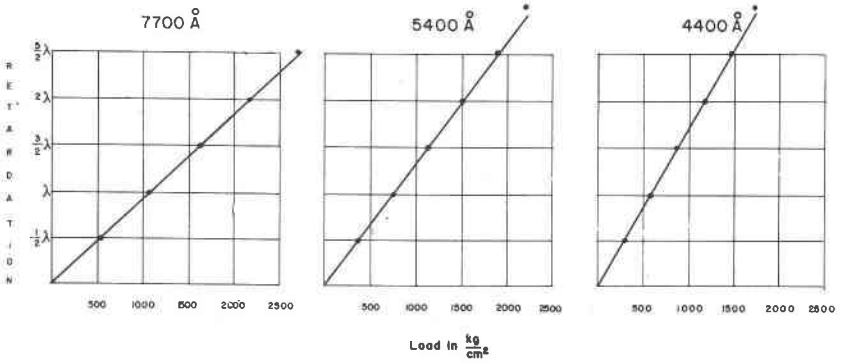

FIG. 5. Retardation versus applied load.

periods of up to one week at pressures of 30,000 psi. Upon removal of the load, a process requiring about a second, the transmitted light returned as fast as the milliammeter could indicate to the original no-load value. The original diamond octahedron was stressed very non-uniformly between v-shaped jaws at maximum concentrated loads of 45,000 psi, and likewise showed neither hysteresis upon application or removal of load, nor permanent deformation under prolonged stress. This behavior is to be expected because of the very great structural strength of the diamond.

The diamond behaves as a negative uniaxial crystal when compressed on (100) or (111); the short axis of the indicatrix is parallel to the axis of compression. For compression in any other direction, the crystal becomes negative biaxial. This is deduced by noting that the index for light vibrating along the stress axis is always less than that for light polarized perpendicular to the stress axis, and that the indices for the perpendicular waves are nearly identical. In fact, the maximum difference in indices for light vibrating normal to the compression axis is so slight that the crystal is virtually uniaxial for any compression. The behavior of diamond in these respects for visible light is similar to the behavior of silicon in the near infrared (21).

Acknowledgments

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References

1. Brewster, D., *Phil. Trans.*, 60 (1815).
2. Brewster, D., *Phil. Trans.*, 156 (1816).
3. Brewster, D., *Trans. Roy. Soc. Edin.*, **8,** 281, 369 (1818).
4. Fresnel, A., *Ann. Chim. Phys.*, **15,** 379 (1820).
5. Fresnel, A., *Ann. Chim. Phys.*, **20,** 376 (1822).
6. Neumann, F., E. *Abh. Kon. Akad. Wiss. Berlin*, II, 1 (1841).
7. Maxwell, J., *Trans. Roy. Soc. Edin.*, **20,** part 1, 87 (1853).
8. Wertheim, G., *Compt. rend.*, **33,** 576 (1851).
9. Wertheim, G., *Ann. Chim. Phys.*, **40,** ser. III, 156 (1854).
10. Coker, E. G., and Filon, L. N. G., *A Treatise on Photoelasticity*, Cambridge University Press (1931).
11. Pockels, F., *Ann. Phys.*, **37,** 151 (1889).
12. Bhagavantam, S., *Proc. Ind. Acad. Sci.*, **15,** 97 (1942).
13. Mason, W. P., *Bell System Tech. J.*, **29,** 161 (1950).
14. Mueller, H., *Phys. Rev.*, **47,** 947 (1935).
15. Burstein, E., and Smith, P., *Phys. Rev.*, **74,** 229 (1948).
16. Burstein, E., and Smith, P., *Phys. Rev.*, **74,** 1880 (1948).
17. Ramachandran, G. N., *Proc. Ind. Acad. Sci.*, **25,** 208 (1947).
18. Ramachandran, G. N., *Proc. Ind. Acad. Sci.*, **32,** 171 (1950).
19. West, C. D., and Makas, J., *J. Chem. Phys.*, **16,** 427 (1948).
20. West, C. D., and Makas, J., *Am. Mineral.*, **35,** 130 (1950).
21. Bond, W. L., personal communication.
22. Slawson, C. B., and Denning, R. M., this issue, p. 1135.
23. Mason, W. P., personal communication.
24. Bhagavantam, S., and Suryanarayana, D., *Proc. Ind. Acad. Sci.*, **25,** 97 (1947).
25. Pockels, F., Lehrbuch der Krystalloptik, B. G. Teubner, Leipzig-Berlin (1906).
26. Kittel, C., Introduction to Solid State Physics, John Wiley and Sons, New York (1953).
27. Mott, N. F., and Gurney, R. W., Electronic Processes in Ionic Crystals, Oxford University Press (1948.)
28. Banerjee, K., *Ind. J. Phys.*, **2,** 190 (1927).
29. Herzfeld, K. F., *J. Opt. Soc. Am.*, **17,** 26 (1928).
30. Herzfeld, K. F., and Lee, R. H., *Phys. Rev.*, **44,** 625 (1933).
31. Poindexter, E., thesis, University of Michigan (1955).
32. Jerrard, H. G., *J. Opt. Soc. Am.*, **38,** 35 (1948).
33. Birch, F., Schairer, J. F., and Spicer, H. C., editors, Handbook of Physical Constants, *Geological Society of America* (1942).