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# MINERALOGICAL NOTES

## VARIATION OF THE REFRACTIVE INDEX OF DIAMOND WITH HYDROSTATIC PRESSURE TO 7 KILOBARS[1]

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The photoelastic properties of diamond have been studied in the past by a number of workers (Ramachandran, 1950; Poindexter, 1955; Denning, *et al.*, 1957). Due to the inaccuracies existing in the direct measurement of the piezo-optical constants $q_{11}$ and $q_{12}$ much confusion exists concerning the variation of the refractive index with hydrostatic pressure.

Ramachandran (1947) was the first to carry out detailed measurements on the piezo-optic properties of diamond. However, his measurements were subject to an inadvertent error in the sign of the compensator constant. Burstein and Smith (1948) corrected these values and found that the refractive index of diamond should increase when subjected to hydrostatic pressure. Later Ramachandran (1950) redetermined the various piezo-optic constants $q_{ij}$ by more careful interferometric measurements and these new results indicated that the refractive index should decrease with hydrostatic pressure. Subsequently Denning *et al.* (1957) have independently determined the values of $q_{ij}$ by a modified minimum deviation method and found their results to be in essential agreement with the later results of Ramachandran. However very recently Gibbs and Hill (1964) in their analysis of the variation of the dielectric constant with pressure, have computed the strain-optical constants $p_{ij}$ from the values of $q_{ij}$ obtained by Denning *et al.*, and in that process have inadvertently introduced an error, therby leading to the erroneous conclusion that the refractive index increases under hydrostatic pressure.

Recently a method has been developed by the authors which allows the direct measurement of this effect with a high degree of precision to a pressure of about 7 kbars (Vedam and Schmidt, 1966). This method has been used to measure the pressure dependence of the refractive index of some natural diamond samples which have been shown by uv absorption measurements to be of Type I. The samples in the form of thin plates were selected from a large number so that they exhibited good localized interference fringes of Newtonian type across the major face of the samples and thus did not require any further mechanical grinding or polishing.

The data obtained on the variation of refractive index for λ5893 Å

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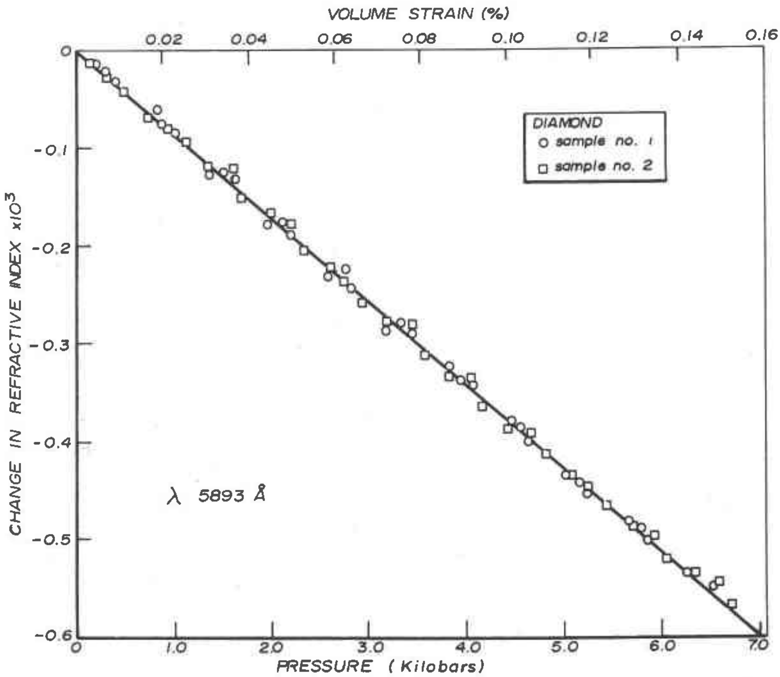


FIG. 1. Variation of the refractive index of diamond with hydrostatic pressure and volume strain. T=22°C.

with hydrostatic pressure is shown in Figure 1. From this we see immediately that the refractive index decreases with pressure with a slope of $0.85\times10^{-4}$/kbar as first deduced by Ramachandran (1950) and later by Denning *et al.* All the earlier techniques required separate measurements of the constants $q_{11}$ and $q_{12}$ by the application of uniaxial stresses. Consequently the refractive index change that can be introduced without plastic deformation or fracture of the crystal is very small. This is not true in the present study since the present method does not employ uniaxial pressures but hydrostatic pressure and hence the upper limit could be increased by nearly a factor of ten. Furthermore the present method does not depend on the measurement of the change in refractive index as a small difference between two large quantities, but measures the change directly. A much greater accuracy can therefore be obtained, as can be seen in Figure 1. It should also be noted that the precision of the direct measurements of $q_{11}$ and $q_{12}$ depend on the accuracy of the elastic modulus $s_{12}$, which, as is well known, is subject to large inaccuracies. This is particularly true in diamond.

It should be remarked that these limitations, however, are not present in the measurement of the piezo-birefringence constants $(q_{11}-q_{12})$ and

TABLE 1. PIEZO- AND ELASTO-OPTIC CONSTANTS OF DIAMOND FOR λ5893 Å

| | Ramachandran | Denning *et al.*[a] | Present Work |
|---|---|---|---|
| $q_{11}$ | $-0.50_5$ | $-0.24$ | $-0.29_5$ |
| $q_{12}$ | $0.21_5$ | $0.06$ | $0.00_6$ |
| $q_{44}$ | $-0.28$ | $-0.14_9$ | — |
| $(q_{11}\text{-}q_{12})$ | $-0.72$ | $-0.30$ | $(-0.30)$ |
| $p_{11}$ | $-0.49$ | $-0.24$ | $-0.31_6$ |
| $p_{12}$ | $0.19_5$ | $0.04$ | $-0.03_0$ |
| $p_{44}$ | $-0.16$ | $-0.08_6$ | — |

All $q_{ij}$ values are given in units of $10^{-13}$ cm$^2$ dyne$^{-1}$.
[a] Values for λ5400 Å.

$q_{44}$ (Vedam and Schmidt, 1966). Thus the value of $(q_{11}-q_{12})$ obtained by Denning *et al.* can be used with confidence for further analysis. Using these values and the present results with hydrostatic pressure where the variation of refractive index is given by

$$\rho\left(\frac{dn}{d\rho}\right) = -\Delta n/\left(\frac{\Delta V}{V_0}\right) = \frac{n^3}{6}(q_{11}+2q_{12})(c_{11}+2c_{12})$$
$$= \frac{n^3}{6}(p_{11}+2p_{12}),$$

we can determine the absolute values of $q_{11}$ and $q_{12}$, and the elasto-optic constants $p_{11}$ and $p_{12}$. This has been done and the results are presented in Table 1′ along with the corresponding values obtained by Ramachandran (1950) and Denning *et al.* The recent values of the elastic constants $c_{11}$ and $c_{12}$, of diamond, as determined by McSkimin and Bond (1957) were employed in the present work, and also to calculate the values of $p_{ij}$ from the values of $q_{ij}$ of Ramachandran and Denning *et al.* It is seen that the results of the present work are in quite good agreement with those of Denning *et al.* and to a lesser extent with those of Ramachandran.

The significance of these values will be discussed elsewhere, along with similar data on other cubic crystals.

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