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Classification

*Physics Abstracts*

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## Elastic moduli of TiO<sub>2</sub> up to 13 GPa (\*)

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**Résumé.** — TiO<sub>2</sub> a été étudié par diffusion Brillouin jusqu'à des pressions de 13 GPa. La transition de phase à 9 GPa ne provoque pas de changement marqué dans les propriétés élastiques mesurées. Une faible non-linéarité est observée en-dessous de la transition. La biréfringence des échantillons ne varie que peu avec la pression.

**Abstract.** — TiO<sub>2</sub> has been studied by Brillouin scattering up to pressure of 13 GPa. The phase transition at 9 GPa produces no marked changes in the measured elastic properties and only a very small nonlinearity is observed below the transition. The birefringence of the sample is also found to change only slightly under pressure.

### 1. Introduction.

TiO<sub>2</sub> is a prominent member of the important di-oxide class of materials, and hence it has received considerable attention. Many members of this di-oxide family: SiO<sub>2</sub>, PbO<sub>2</sub>, GeO<sub>2</sub>, TeO<sub>2</sub>, etc., are known to exist as various polymorphs and TiO<sub>2</sub> itself has three stable structures at atmospheric pressure. Given the technological and geological importance of many of these materials it is not surprising that much is known about the various phases common to this class of materials.

Since pressure is one of the most important variables associated with the various phases, there have been many studies on the stability of these materials under pressure. The results previously obtained on TiO<sub>2</sub> (D<sub>4h</sub>) under pressure show a wide spread in the transition pressures to a D<sub>2h</sub> phase: Jamieson and Olinger [1] found the transition at ~ 7 GPa using X-rays, Nicol and Fong [2] using Raman spectroscopy found evidence of this phase at 2.6 GPa and also that it was highly dependent on shear stress inhomogeneities. Further Raman work by Mammone and Sharma [3] and Mammone, Sharma and Nicol [4] confirmed the work of reference [1] in finding the phase transition at ~ 7 GPa and consistent with the X-ray work up to 5 GPa by Hazen and Finger [5] who find no evidence of the high pressure phase. Raman studies at higher

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pressure [6, 7] starting from  $\text{TiO}_2$ -II shows a sluggish and reversible phase transition between phases II and III, starting at 20 GPa and completed at 37 GPa. Recent X-ray work by Ming and Manghnani [8] up to 35 GPa shows the rutile  $\rightarrow$   $\text{TiO}_2$ -II phase transition to be at 9 GPa and the subsequent phase transition to begin at 18 GPa.

For the above reasons we considered it worthwhile to investigate  $\text{TiO}_2$  (rutile) using the relatively novel technique of Brillouin scattering from samples inside diamond anvil cells [9-15]. In references [11] and [14] phase transitions from liquid to solid were observed and references [14] and [15] deal with solid-solid phase transitions.

## 2. Experiment.

The equipment used in these experiments is identical to that described in reference [14], except that a 5 + 2 pass tandem interferometer was used. The  $\text{TiO}_2$  samples were prepared by grinding and polishing an oriented crystal down to a thickness of  $\sim 25$  micrometers. These slabs were later broken into small fragments and an adequate sample chosen from the chips thus obtained. Three orientations were chosen *viz.* (100), (110), and (001) surfaces. These orientations and the backscattering geometry used in these experiments allowed us to obtain information on the  $C_{11}$ ,  $1/2(C_{11} + C_{12} + 2C_{66})$ , and  $C_{33}$  elastic moduli. The pressure was measured using the linear ruby fluorescence scale (*viz.*  $-7.53 \text{ cm}^{-1}/\text{GPa}$ ).

Our spectra were recorded using  $\sim 100$  mW of 531 nm radiation from a  $\text{Kr}^+$  laser. All measurements were taken at room temperature.

## 3. Results.

In figure 1 we present the spectrum obtained at 11.4 GPa on a  $\text{TiO}_2$  sample. The lines labelled D and M are due to the diamonds and to the 4:1 methanol-ethanol mixture respectively. The orientation of the  $\text{TiO}_2$  sample in this spectrum was such that the phonon wavevector was along

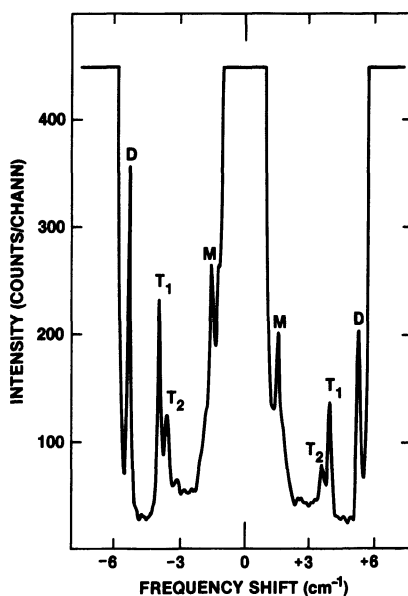


Fig. 1. — Brillouin spectrum of  $\text{TiO}_2$  in a diamond anvil cell at 11.4 GPa. The lines from  $\text{TiO}_2$  are labelled  $T_1$  and  $T_2$  while D and M label the lines from the diamonds and methanol-ethanol mixture respectively.

the [110] direction. Two peaks due to TiO<sub>2</sub> are observed because of birefringence, T<sub>1</sub> and T<sub>2</sub> label these peaks and correspond to the extraordinary and ordinary rays respectively.

The frequency shifts obtained for the three orientations studied are shown in figure 2. The crosses are points obtained in this investigation, the squares are obtained from previous Brillouin results [16] and the refractive indices [17]. The systematic offset of our results compared to values in the literature at zero pressure can be traced to misorientations of our polished platelets of about 4°.

The relatively large scatter in our results at pressures above ~ 6 GPa are probably due to nonhydrostatic pressures. It was found that in all cases where the gasket came into contact with the sample, the sample would visibly change its colour and « texture » and the measured frequency shifts would differ markedly from the results shown in figure 2. Hence, we included in figure 2 only the results of runs in which no such visible effects occurred. These observations are consistent with the reported effects of shear stress on the phase transition [2].

Due to the errors just described it is unreasonable to extract a precise value for the transformation pressure. However, our results (especially those for  $q \parallel [001]$ ) are consistent with the results of reference [8] where the transition was found to be at ~ 9 GPa.

In order to compare our results with previous investigations on TiO<sub>2</sub> we have performed the following analysis : the frequency shift ( $\nu$ ) in our backscattering geometry is related to the sound velocity ( $v$ ) and refractive index ( $\eta$ ) through

$$\nu = \frac{2 v_L}{c} \eta v \tag{1}$$

where  $v_L$  is the frequency of the exciting radiation and  $c$  is the velocity of light. Hence, the ratio of  $\nu_e$  to  $\nu_o$ , where the subscripts e and o refer to the extraordinary and ordinary rays, is

$$\frac{\nu_e}{\nu_o} = \frac{\eta_e}{\eta_o} \tag{2}$$

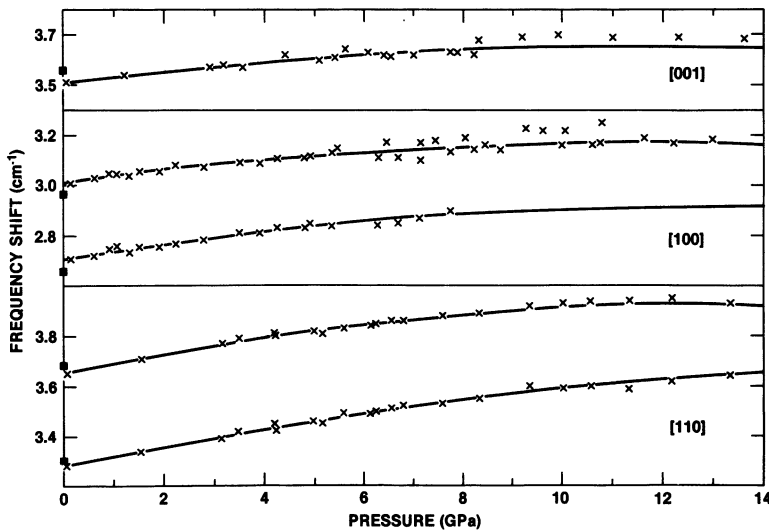


Fig. 2. — Frequency shifts vs. pressure obtained for three orientations. The lines are calculated from Eq. (6) with the parameters given in table I.

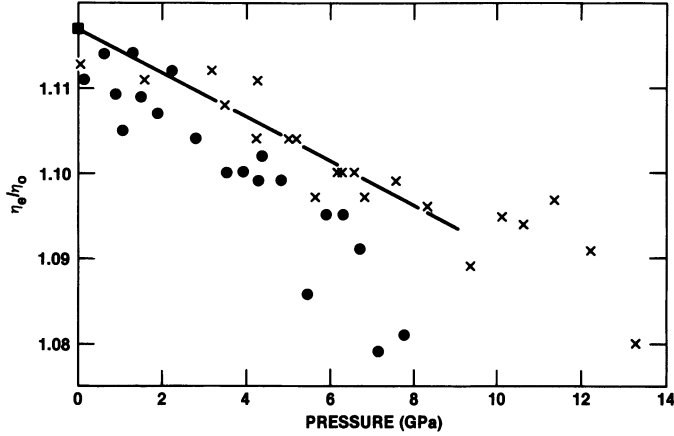


Fig. 3. — Ratio of the extraordinary to ordinary refractive indices vs. pressure.

In figure 3 we plot the value of  $\eta_e/\eta_o$  obtained from our measurements (crosses,  $q \parallel [110]$  and dots,  $q \parallel [100]$ ) and compare it with the value from reference [17] (square). Furthermore, we can calculate the pressure ( $P$ ) dependence of  $\eta_e/\eta_o$  using the piezo-optic constants

$$\frac{\eta_e}{\eta_o}(P) = \frac{2 \eta_e(0) + \eta_e^3(0) (\pi_{33} + 2 \pi_{31}) P}{2 \eta_o(0) + \eta_o^3(0) (\pi_{11} + \pi_{12} + \pi_{13}) P} \quad (3)$$

where  $P$  is the applied pressure. Using the elasto-optic constants from reference [16] we obtain the full line in figure 3 in reasonably good agreement with the experimental results.

Using equation (1) it is easy to show that the pressure dependence of the frequency shift is given by

$$\frac{1}{v(0)} \frac{\Delta v}{\Delta P} = \left[ \frac{1}{\eta} \frac{\Delta \eta}{\Delta P} + \frac{1}{v} \frac{\Delta v}{\Delta P} \right]. \quad (4)$$

Using the elasto-optic constants from [16], we have  $\frac{1}{\eta_e} \frac{\Delta \eta_e}{\Delta P} = -0.0020 \text{ GPa}^{-1}$  and  $\frac{1}{\eta_o} \frac{\Delta \eta_o}{\Delta P} = +0.0003 \text{ GPa}^{-1}$ . Furthermore, since  $\Delta v/\Delta P$  is related to the pressure dependence of the elastic moduli through

$$\frac{2}{v} \frac{dv}{dP} = \frac{1}{C^*} \frac{dC^*}{dP} - \frac{1}{B} \quad (5)$$

where  $C^*$  is the appropriate combination of elastic constants and  $B$  is the bulk modulus, we can compare our results with those of references [18] and [19] (Table II). For this purpose we have performed a least-squares fit to our data up to 9 GPa to a quadratic function (a fit to a linear function was found inadequate).

$$v = v(0) + \alpha P + \beta P^2. \quad (6)$$

The values of  $v(0)$ ,  $\alpha$ , and  $\beta$  thus obtained are given in table I. The fits are shown as full lines in figure 2. From a comparison of the fits (made to the data below 9 GPa) and the experimental points above 9 GPa it can be concluded that either no significant change takes place in the elastic properties at the phase transition or, due to the fact that the rutile  $\rightarrow$  TiO<sub>2</sub>-II phase

Table I. — *Results of a least squares fit of  $\nu = \nu(0) + \alpha P + \beta P^2$  to the experimental results of figure 2.*

| $q$ | $\eta$   | $\nu(0)$ (cm <sup>-1</sup> ) | $\alpha$ (cm <sup>-1</sup> /GPa) | $\beta$ (cm <sup>-1</sup> /GPa <sup>2</sup> ) |
|-----|----------|------------------------------|----------------------------------|---|
| 001 | $\eta_o$ | 3.51                         | 0.025                            | - 0.0011                                      |
| 110 | $\eta_o$ | 3.28                         | 0.041                            | - 0.0010                                      |
| 110 | $\eta_e$ | 3.65                         | 0.042                            | - 0.0016                                      |
| 100 | $\eta_o$ | 2.71                         | 0.032                            | - 0.0012                                      |
| 100 | $\eta_e$ | 3.02                         | 0.026                            | - 0.0011                                      |

Table II. — *Pressure dependence of elastic moduli.*

|                      | Present study | Ref. [18] | Ref. [19] |
|----------------------|---------------|-----------|-----------|
| $\frac{dC_{11}}{dP}$ | 7             | 6.29      | 6.47      |
| $\frac{dC_{33}}{dP}$ | 9             | 8.13      | 8.34      |
| $\frac{dC'}{dP}$ (*) | 12            | 13.57     | 14.22     |

$$(*) C' = \frac{1}{2}(C_{11} + C_{12} + 2 C_{66})$$

transition is sluggish only a small portion of the rutile has transferred to TiO<sub>2</sub>-II, no Brillouin shift from the high pressure phase was observed. There are a few indications, however, that are consistent with a phase change at  $\sim 9$  GPa : (i) a discontinuity of  $\Delta\nu \cong 0.05$  cm<sup>-1</sup> at around 8.5 GPa for  $q \parallel [001]$ , (ii) for  $q \parallel [100]$  there is a spread in the measured frequency shift of the « extraordinary » phonon above 6.5 GPa while the « ordinary » one disappears above 8 GPa. (This latter point however must be viewed with care since the intensity of this line decreases monotonically with pressure). (iii) for  $q \parallel [110]$  there is a small variation in slope above 9 GPa.

Using our values of  $\alpha$  (Table I) and equations (4) and (5) we obtain the values of  $dC/dP$  given in table II. We estimate the error of our  $dC/dP$  values to be  $\pm 1.0$  which puts our results in reasonable agreement with previous determinations also shown in table II.

#### 4. Conclusions.

Brillouin scattering from TiO<sub>2</sub> under pressures up to 13 GPa (i) is consistent with previous reports of a phase transition between 6.5 and 9 GPa ; (ii) shows a slight non-linear behaviour of certain elastic constants up to  $\sim 9$  GPa ; (iii) the elastic properties of the high pressure phase are almost identical to those in the low pressure phase ; (iv) the birefringence decreases slightly with pressure but the sample remains strongly birefringent in the high pressure phase.

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