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Variation of the Refractive Indices of Calcite, with Pressure to 7 kbar¹⁾

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The variation of the ordinary and extraordinary refractive indices of calcite for $\lambda = 5893$ Å with hydrostatic pressure to 7 kbar has been measured from the shift of the localized interference fringes across the sample which was kept in a fluid pressure medium. The change in the thickness of the sample under pressure was considered by utilizing the non-linear theory of elasticity. The ordinary and the extraordinary refractive indices were found to increase linearly with pressure with slopes of $0.50 \times 10^{-3}/\text{kbar}$ and $0.44 \times 10^{-3}/\text{kbar}$ respectively in the entire region investigated. The results are compared with the theoretical values evaluated from Bragg's theory, and are also interpreted according to Mueller's theory of photoelasticity.

Die Abhängigkeit des ordentlichen und außerordentlichen Brechungsindex von Kalkspat vom hydrostatischen Druck wurde bis 7 kbar für $\lambda = 5893$ Å durch die Verschiebung der Interferenzringe gemessen. Die Kristalle wurden durch ein flüssiges Einbettmedium beobachtet. Die durch den Druck entstandene Veränderung der Dicke der Probe wurde durch die nichtlineare Theorie der Elastizität berücksichtigt. Es wurde festgestellt, daß der ordentliche, sowie der außerordentliche Brechungsindex linear mit einem Anstieg von $0,50 \times 10^{-3}/\text{kbar}$, bzw. $0,44 \times 10^{-3}/\text{kbar}$ mit dem Druck ansteigt. Die Resultate werden mit den theoretischen Werten der Braggschen Theorie verglichen und nach der Muellerschen Theorie der Photoelastizität ausgewertet.

1. Introduction

It is of interest to examine the relationship between pressure and the refractive indices of calcite in order to study the effect of varying interatomic distance upon the polarizability of the ions. The only complete investigation of this property to date is that of Pockels [1] whose measurements were confined to uniaxial stress, as were all photoelastic investigations until recently. Thus all of these measurements were limited to low stress levels and hence susceptible to possible large errors for reasons given by Vedam and Schmidt [2].

Bragg [3] has made a theoretical calculation of the indices of refraction for calcite at standard room temperature and pressure. These calculations can be made at various pressures and thus extended to give a theoretical value of dn/dP .

The present paper describes measurements made using hydrostatic pressure to about seven kilobars and reports the piezo-optic behavior of CaCO_3 at these pressures. These results are compared with the theoretical values evaluated from Bragg's theory and finally interpreted in the light of Mueller's theory of photoelasticity.

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2. Experimental Method

The experimental arrangement used is essentially the same as has been described earlier [4, 5] in connection with the measurement of dn/dP of α -quartz and vitreous silica. In brief, the high pressure vessel was of conventional design with an alumina window, and sovasol, an optically transparent fluid marketed by Socony Mobil Oil Company was used as the pressure medium. Natural calcite specimens of very good optical quality were cut, ground and polished such that the localized Newtonian interference fringes could be easily observed through a telemicroscope. As the crystal was subjected to hydrostatic pressure, both the thickness and the refractive indices changed, with a resulting shift of the fringe pattern across a fiducial mark on the crystal. The change in the refractive index was evaluated from the formula

$$\Delta n = \frac{p\lambda - 2n\Delta t}{2t_0}, \quad (1)$$

where p is the number of fringes shifted, t_0 is the initial thickness of the crystal, Δt is the change in thickness of the crystal under pressure and λ the wavelength of the light employed.

3. Results

Table 1 lists the variation of the refractive indices n_o and n_e for Calcite at $\lambda = 5893 \text{ \AA}$ for various pressures up to about 7 kbar, as well as the observed fringe shift at these pressures, for one of the specimens used. Since the pressure employed was quite large, the change in the thickness of the sample and the corresponding volume strain were calculated from the non-linear theory of elasticity developed by Murnaghan [6], Hearmon [7] and others [8]. The elastic constants data of Voigt [9] were used in these calculations.

Bridgman [10] has measured the linear compressibility perpendicular to the c -axis and the volume compressibility of calcite. Using his values we calculated the linear and volume strains and evaluated the corresponding changes in the thickness of the sample and refractive indices. The latter are given in Table 1. The uncertainty in Δn is ± 3 in the third figure.

4. Discussion

The values of strain computed from the elastic constants data of Voigt were found to be consistently larger than the values computed from the compressibility data of Bridgman. This difference is about 15%. This is understandable since a calculation of the volume compressibility from the elastic data gives a value about 15% higher than that reported by Bridgman. This occurs even though both the elastic constants as determined by Voigt and the compressibility measurements as obtained by Bridgman were carried out under isothermal conditions. In our following discussion we shall be concerned with the values computed from Bridgman's data because he includes a nonlinear term as well in his strain data.

Fig. 1 and 2 represent respectively the variation of the ordinary and the extraordinary refractive indices of Calcite with pressure and volume strain. They are both seen to be linear with pressure and volume strain in the region investigated. The slopes are $0.50 \times 10^{-3}/\text{kbar}$ and $0.44 \times 10^{-3}/\text{kbar}$ respectively.

Table 1
 Calcite: variation of the refractive indices with pressure
 ($\lambda = 5893 \text{ \AA}$, $t_0 = 0.2057 \text{ cm}$, $T = 22 \text{ }^\circ\text{C}$)

Pressure (kbar)	$\eta_{11} \times 10^2$	Strain ($\Delta V/V_0 \times 10^2$)	$n_o = 1.658$				$n_e = 1.486$			
			Fringe shift	$\Delta n_o \times 10^2$	A_o^{LL}	A_o^D	Fringe shift	$\Delta n_e \times 10^2$	A_e^{LL}	A_e^D
0.552	-0.015	-0.08	0.27	0.028	0.54	0.56	0.10	0.027	0.45	0.48
1.103	-0.030	-0.15	0.45	0.056	0.55	0.57	0.22	0.051	0.44	0.48
1.655	-0.045	-0.22	0.82	0.086	0.54	0.56	0.39	0.075	0.44	0.47
2.201	-0.060	-0.30	1.21	0.116	0.53	0.56	0.53	0.099	0.44	0.47
2.758	-0.075	-0.37	1.33	0.143	0.54	0.56	0.69	0.122	0.43	0.47
3.309	-0.089	-0.45	1.54	0.170	0.54	0.56	0.73	0.147	0.44	0.47
3.861	-0.104	-0.52	1.74	0.198	0.55	0.57	0.86	0.172	0.44	0.47
4.412	-0.119	-0.59	1.99	0.226	0.55	0.57	1.00	0.196	0.44	0.47
4.964	-0.134	-0.67	2.25	0.254	0.55	0.57	1.19	0.220	0.43	0.47
5.515	-0.149	-0.74	2.43	0.282	0.55	0.57	1.41	0.245	0.43	0.46
6.067	-0.164	-0.81	2.70	0.310	0.55	0.57	1.58	0.270	0.43	0.46
6.619	-0.178	-0.88	2.92	0.338	0.55	0.57	1.72	0.293	0.43	0.46
6.894	-0.186	-0.92	3.03	0.352	0.55	0.57	1.79	0.305	0.43	0.46

If the data based on Voigt's elastic constants were plotted the shape of the graphs would have been exactly the same but with a slope larger by about 15%.

The above values obtained by us compare well with the values of $0.58 \times 10^{-3}/\text{kbar}$ and $0.51 \times 10^{-3}/\text{kbar}$ calculated from the strain-optical data of Pockels [1]. The agreement is very good when we realize that Pockels used the elastic constants data of Voigt in his calculations and hence we should expect his values to be larger than ours by about 15%.

The theoretical calculation by W. L. Bragg for the indices of refraction of calcite at room temperature and pressure, can be extended to the region of high pressure and the value of dn/dP evaluated therefrom. For these calculations we assumed the more recent value of Sass et al. [11] for the C-O distance, as 1.294 Å. The anisotropy of the oxygen polarizability was also taken into account by using the values given by Lawless and Devries [12] $\alpha_z = 1.384 \text{ Å}^3$ and $\alpha_x = 1.328 \text{ Å}^3$. The polarizability of the calcium ion was taken as 1.1 Å^3 [13]. The polarizability of the carbon was taken to be zero [3].

The index of refraction was then calculated with the help of the relation [3]

$$n^2 - 1 = \frac{4\pi \sum C_i N_i \alpha_i}{1 - \frac{4\pi}{3} \sum C_i N_i \alpha_i}, \quad (2)$$

where N_i is the number of atoms of type i per cm^3 , C_i are constants not differing greatly from unity depending on the type of atom, and α_i is the polarizability of atom i in the appropriate direction. This type of calculation was carried out, taking the sum over only the oxygen atoms in one CO_3 group, and the values for the respective indices agree with the measured values within 1 to 2%. This is about the same order of agreement that Bragg obtained using earlier data. Bragg in an effort to obtain better agreement extended his sum to include up to 42 neighboring dipoles. However the theoretical value for the index

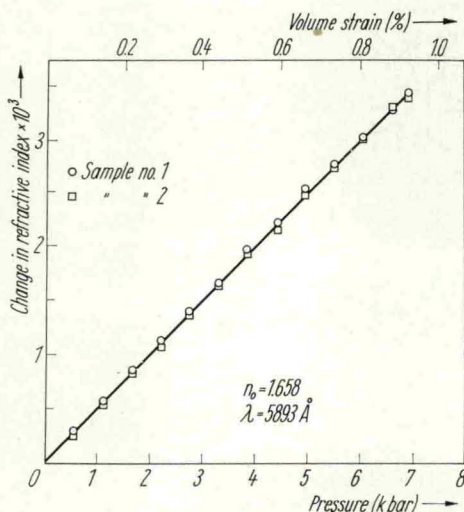


Fig. 1. Variation of the ordinary refractive index of calcite with pressure and volume strain. $T = 22^\circ\text{C}$

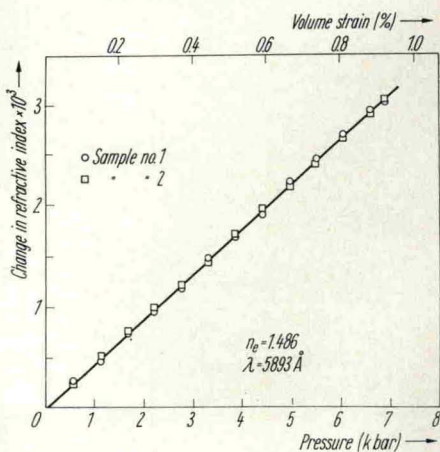


Fig. 2. Variation of the extraordinary refractive index of calcite with pressure and volume strain. $T = 22^\circ\text{C}$

depends upon just where the sum is discontinued in the lattice and agreement better than 1 to 2% could not be obtained. We did not extend our calculations beyond neighboring dipoles because there are other unknown factors which affect the indices much more than terms due to next nearest dipoles in the sum in (2). Chief among these is the polarizability and its anisotropy of the calcium atom. Its effect on the indices of refraction is much less than that of the oxygen atoms but it is far from negligible. Its contribution to the index of refraction is about 20 to 30% that of the oxygen. The anisotropy of its polarizability is also unknown. The value used for its polarizability was the one reported by Tessman et al. [13] from an examination of the indices of refraction of two alkaline earth-halide crystals namely, CaF_2 and CaCl_2 . The difference between the Ca^{2+} polarizability in these two crystals was found to be about 20%. We used the reported average value of 1.1 which is probably at best $\pm 10\%$. Following through the calculation with these values in the manner described above we find $dn_e/dP = +0.64 \times 10^{-3}/\text{kbar}$ and $dn_o/dP = +1.23 \times 10^{-3}/\text{kbar}$ respectively. These values are of the correct order of magnitude and of the proper sign. This is perhaps all that can be expected since we are essentially taking the difference between two quantities which are uncertain themselves in the second decimal place.

According to Mueller's [14] theory of photoelasticity, the change of the refractive indices of a crystal under stress depends upon (i) the change in the Coulomb field, (ii) the change in the Lorentz-Lorenz field, and (iii) the variation of the intrinsic polarizability of the ions. The calculations of these, for crystals with a symmetry lower than cubic, are extremely complicated and have not as yet been carried out. But in the present case of calcite under hydrostatic pressure, some general conclusions can be reached regarding the variation of the polarizability with strain.

The well-known Lorentz-Lorenz condition is:

$$\frac{n^2 - 1}{n^2 + 2} = A N \alpha, \quad (3)$$

where A has a value $4\pi/3$ for cubic D lattices but for a trigonal crystal like calcite A has different value ($\neq 4\pi/3$) for both indices, N is the number of molecules per cubic volume and α is the molecular polarizability.

As an approximation we shall assume that the contribution of Ca^{++} to the refractive indices of CaCO_3 is negligible and that A does not vary with hydrostatic pressure. Differentiating the above equation with respect to density, we obtain

$$\frac{dn}{d\rho} = [(n^2 - 1)(n^2 + 2)/6n\rho][1 - A_0], \quad (4)$$

where

$$A_0 = -\frac{\rho}{\alpha} \left(\frac{\partial \alpha}{\partial \rho} \right) = \frac{1}{\alpha} \frac{\Delta \alpha}{(\Delta V/V_0)} \quad (5)$$

is taken as the strain-polarizability parameter. With the help of (4) and the observed values of $dn/d\rho$, the values of A_0 were calculated at various pressures for both the ordinary and extra-ordinary indices, and are entered in Table I. The fact that A_0 is positive in every case implies that the polarizability of the oxygen ions decreases as the crystal is compressed, quite in accordance with the observations of Fajans and Joos [15] and also the recent conclusions

of Tessman et al. [13]. These authors have shown that the polarizability of cations decreases and the polarizability of the anions increase upon going from the free-ion gaseous state to the solid state. So a further change in the polarizabilities of the ions is expected, in the same direction, when the crystal is subjected to hydrostatic pressure. The above results are similar to those found for α -quartz [4].

From the table it is seen that the value of A_0 for the ordinary ray is larger than that for the extraordinary ray. This is as expected for a negative crystal like calcite since we expect the change in polarizability for the ordinary ray to be larger than the change for the extraordinary ray. We also note that A_0 for the ordinary ray seems to increase while A_0 for the extraordinary ray seems to decrease. No special significance should be attached to this since our uncertainty in A_0 is 5% at the lower pressures and about 1 to 2% at 7 kbar, thus the observed variation is within our experimental error.

The last column in Table I gives values of A_0^D , the strain-polarizability constant, but derived from the Drude-equation instead of the Lorentz-Lorenz equation. The values of A_0^D and A_0^{LL} are almost equal indicating that A_0 is not very sensitive to the type of dispersion relation used to derive it.

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