

BIREFRINGENCE OF CRYSTALS AND ITS TEMPERATURE-VARIATION

Part I. Calcite and Aragonite

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1. INTRODUCTION

CALCITE is a common mineral and exhibits strong birefringence, and it is therefore not surprising that the phenomenon of double refraction was first observed in it. The origin of the phenomenon has naturally been the subject of inquiry ever since its discovery. As early as 1690, Huygens suggested that it arises from the form and arrangement of the particles of which the crystal is built up. A clearer explanation had however to wait till the structure of the crystal was more fully elucidated. Following his determinations of the structures of calcite and aragonite, W. L. Bragg (1924) put forward a theory of the origin of birefringence in these crystals. The theory is based on the idea that, as a result of the mutual influence of the oxygen atoms, the carbonate ion is much more polarisable in its plane than at right angles to it. Since all the CO_3 ions are orientated in the same plane throughout the crystal, the latter also exhibits a strong birefringence. Bragg also considered the mutual influences of neighbouring ions, and the method was also successfully used to calculate the birefringence of other carbonates and nitrates. However, refraction and birefringence form only part of a larger subject, namely the theory of dispersion. In this paper, an attempt is made to apply dispersion theory to explain the birefringence of crystals, and in particular dispersion formulæ have been developed both for calcite and aragonite.

In a series of papers on thermo-optic behaviour (Ramachandran, 1947 *a* to *f**), the author has given a theory of the temperature-variation of refractive index (dn/dt) of an isotropic solid, and has applied it to a number of cases. The theory is based on the idea that the refractive index variation is due to two effects, one arising from the change in the number of dispersion centres and the other from the shift of the dispersion frequencies. The theory, in this form, has been applied by Radhakrishnan (1947 *b*) to successfully

* These will be referred to as A 1,, A 6 in this paper.

explain dn/dt data for quartz, a feebly birefringent crystal. It is obvious that the theory needs modifications, if it is to be applied to strongly birefringent crystals. These have also been considered in this paper, and the modified theory has been applied to the cases of calcite and aragonite.

2. DISPERSION OF BIREFRINGENT CRYSTALS

According to the quantum mechanical theory of dispersion, developed by Kramers and Heisenberg, the refractive index n of a substance for light of frequency ν is given by the expression

$$n^2 - 1 = \sum_r \frac{e^2}{m\pi} \cdot \frac{N_r f_r}{\nu_r^2 - \nu^2}, \quad (1)$$

where N_r is the number of oscillators per unit volume of frequency ν_r and f_r is the oscillator-strength or transition probability corresponding to the particular frequency, the summation being performed over all the natural frequencies of the system. In a gas composed of optically isotropic molecules, the transition probability and frequency will be independent of the direction of the electric vector. If, however, the molecules are anisotropic, then there is no *a priori* reason for supposing that this would be the case. In particular, along the three principal directions, the transition probabilities may be different. In a gas, however, such differences will not result in any anisotropy in the refractive index, since the molecules are orientated at random. Actually, the gas will exhibit an isotropic refractive index which will correspond to a mean transition probability obtained by averaging over all orientations. The inherent anisotropy of the molecule is however exhibited in light-scattering, as shown by depolarisation measurements of the scattered light.

In crystals, on the other hand, the situation is different, since the various atoms are all situated in fixed positions (thermal agitation apart), and the different ions are also orientated in definite directions. Consequently, one would expect a specific correlation between the refractive index and the direction of the electric vector. In the particular case when the atoms occupy positions in a cubic lattice, the optical properties are isotropic. In all other cases, anisotropy is present, with the crystal exhibiting uniaxial or biaxial optical properties. Following the analogy of anisotropic molecules mentioned above, one may say that such anisotropy arises from differences in the electronic transition probabilities (for each frequency) along the three principal directions. Thus, if n_1, n_2, n_3 are the refractive indices along the three directions, they would be given by formulæ of the type:

$$n_i^2 - 1 = \sum_r \frac{e^2}{m\pi} \cdot \frac{N_r f_{ir}}{\nu_r^2 - \nu^2}, \quad i = 1, 2, 3. \quad (2)$$

The differences in the three directions arise only in the factor f_{ir} ; in particular, it may be zero for a particular direction.

In applying these ideas to a practical case, it will be necessary to know the quantities N_r , f_{ir} and ν_r for calculating the refractive indices. Our present knowledge is, however, not sufficient to calculate these purely from theory. ν_r can be obtained from experiment by studying the absorption spectrum of the crystal, and probably f_{ir} could also be obtained from a study of the relative strengths of absorption for different directions of the electric vector. For cubic crystals, the procedure usually adopted is to determine the quantity $N_r f_r$ in Eq. (1) empirically from the measured values of refractive indices for different wavelengths. Where the absorption frequencies ν_r are known, they are incorporated in the dispersion formula; otherwise they are also deduced from the measured refractive indices. One can employ similar methods for anisotropic solids, using Eq. (2) as the basis for the calculations. Putting $(e/m\pi) \cdot N_r f_{ir} = a_{ir}$, and using the wavelengths λ_r of the dispersion frequencies, this takes the form:

$$n_i^2 - 1 = \sum_r \frac{a_{ir} \lambda_r^2 \lambda^2}{\lambda^2 - \lambda_r^2}, \quad i = 1, 2, 3. \quad (3)$$

In this, one has only to find the λ_r 's and a_{ir} 's. For calcite and aragonite, the ultra-violet absorption frequencies have not been measured, so that they also have to be obtained from the data. It is found that by using three ultra-violet frequencies with wavelengths 1535, 1000 and 500 Å.U., both the ordinary and extraordinary indices of calcite can be fitted over the whole range of wavelengths from 2000 Å.U. to 2μ . The a_{ir} 's are different for the ordinary and the extraordinary rays, and the interesting fact comes out that the frequency at 1535 Å.U. is practically inactive in the extraordinary, the strength for this being only about 1/20 of that for the ordinary. The same frequencies also suffice for fitting the refractive indices of aragonite from 4000 to 7000 Å.U., and the oscillator strengths in this case show a close analogy to those for calcite.

3. DISPERSION FORMULÆ FOR CALCITE

For calcite, which is a uniaxial crystal, there are only two principal refractive indices, *viz.*, ordinary (n_ω) and extraordinary (n_ϵ), dispersion formulæ for which will have the forms:

$$n_\omega^2 - 1 = \sum_r a_{\omega r} \lambda_r^2 \lambda^2 / (\lambda^2 - \lambda_r^2), \quad (4)$$

$$n_\epsilon^2 - 1 = \sum_r a_{\epsilon r} \lambda_r^2 \lambda^2 / (\lambda^2 - \lambda_r^2), \quad (5)$$

in which the λ_r 's are the same in both the equations, but $a_{\omega r}$ and $a_{\epsilon r}$ are

different. As already mentioned, no studies have been made of the ultra-violet absorptions of calcite, but the infra-red absorptions are well known (Nyswander, 1909; Liebisch and Rubens, 1919). For the ordinary ray, reflection maxima are found at 6.46, 6.96, 14.17, 80.3 and 94 μ , while for the extraordinary ray, the maxima are at 11.3, 28.0 and 94 μ . Of these, the one at 14.17 μ is very weak. Also, the frequencies near 30 and 90 μ are sufficiently far away for their effects to be neglected in the region (0.2 to 2 μ) in which we are interested. Hence, in the dispersion formula, only the nearer infra-red frequencies at 6.7 μ (mean of 6.46 and 6.96 μ) and 11.3 μ respectively are employed for the two rays, a_e being zero for 6.7 μ and a_w for 11.3 μ . For the ultra-violet, three frequencies are employed, which were found by trial and error to be at 500, 1000 and 1535 Å.U. the dispersion formulæ for the ordinary and extraordinary are:

$$n_{\omega}^2 - 1 = \frac{0.43257 \lambda^2}{\lambda^2 - (0.500)^2} + \frac{0.82932 \lambda^2}{\lambda^2 - (0.1000)^2} + \frac{0.43376 \lambda^2}{\lambda^2 - (0.1535)^2} + \frac{0.61855 \lambda^2}{\lambda^2 - (6.7)^2} \quad (6)$$

$$n_{\epsilon}^2 - 1 = \frac{0.45899 \lambda^2}{\lambda^2 - (0.500)^2} + \frac{0.69835 \lambda^2}{\lambda^2 - (0.1000)^2} + \frac{0.02680 \lambda^2}{\lambda^2 - (0.1535)^2} + \frac{0.30018}{\lambda^2 - (11.3)^2} \quad (7)$$

The fit of the formulæ can be judged from Table I, in which the values calculated from these formulæ are compared with the measured values. The refractive indices of calcite have been measured by many workers (for references, see Landolt-Bornstein Tables, 1923). For comparison here, the values of Martens are taken from 0.19898 μ to 0.65628 μ and those of Carvallo beyond. The measurements of other workers lie close to these. In the ultra-violet, below 0.3 μ , Martens' values slightly depart from other workers', but since only Martens' data are available below 0.214 μ , his data are taken for the whole range. Also, the measurements upto 0.656 μ are at 18° C., while those in the infra-red are at 20° C. The difference is however not of serious consequence, for this would affect the indices in the 6th decimal place for the ordinary ray and by 2 units in the 5th decimal place for the extraordinary, as deduced from the dn/dt data of Micheli (1902). The present formulæ are expected to hold for 18° C. The errors (experiment—theory) are also given in Table I from which it will be seen that they are mostly less than 1 unit in the 4th decimal place, which is the order of fit found for various cubic crystals (*cf.* A 2, A 3, A 4, A 5).

TABLE I

Wavelength in microns	Ordinary			Extraordinary		
	<i>n_{exp.}</i>	<i>n_{th.}</i>	Diff. × 10 ⁴	<i>n_{exp.}</i>	<i>n_{th.}</i>	Diff. × 10 ⁴
0.19898	1.57796	1.57809	-1.3
0.20006	1.90284	1.90289	-0.5	1.57649	1.57656	-0.9
0.214439	1.84558	1.84558	0.0	1.55976	1.55970	+0.6
0.219462	1.83075	1.83068	+0.7	1.55496	1.55493	+0.3
0.231288	1.80233	1.80229	+0.4	1.54541	1.54537	+0.4
0.257304	1.76038	1.76038	0.0	1.53005	1.53005	0.0
0.274867	1.74139	1.74141	-0.2	1.52261	1.52261	0.0
0.340365	1.70078	1.70079	-0.1	1.50562	1.50560	+0.2
0.394403	1.68374	1.68373	+0.1	1.49810	1.49801	+0.9
0.441568	1.67423	1.67422	+0.1	1.49373	1.49368	+0.5
0.486133	1.66785	1.66783	+0.2	1.49074	1.49074	0.0
0.58929	1.65835	1.65836	-0.1	1.48640	1.48638	+0.2
0.656278	1.65437	1.65439	-0.2	1.48459	1.48461	-0.2
1.0417	1.64276	1.64276	0.0	1.47985	1.47976	+0.9
1.3958	1.63637	1.63638	-0.1	1.47789	1.47784	+0.5
1.8487	1.62800	1.62799	+0.1
2.0998	1.47492	1.47492	0.0
2.1419	1.62099	1.62078	+2.1

The formulæ bring out the interesting fact that the differences in the two refractive indices are to a large extent due to differences in the activity of the frequency at 1535 Å.U. in the ordinary and extraordinary rays. As shown by the formulæ, the strength of this frequency is nearly 20 times larger for the former than for the latter. The remoter frequencies, although practically isotropic, still show small differences for the two polarised rays.

The question arises as to how accurately the dispersion frequencies are determinable by the empirical method used here. It is obvious that the numerators in Eqs. (6) and (7) depend on the position of the dispersion frequencies. To fit the data for the ordinary index, it was found that the nearest frequency at 1535 Å.U. could not be altered by more than about ± 15 Å.U. without seriously affecting the accuracy of the fit—this in spite of changing the second frequency at 1000 Å.U. by nearly 50 Å.U. either way and the remote one by 100 Å.U. If these two are fixed, the nearest one could be determined correct to 5 Å.U. So also, the fit of both the indices was appreciably affected if the frequency at 1000 Å.U. was altered by more than 60 to 80 Å.U. either way. On the other hand, the exact position of the remote frequency does not appear to be important, for a good fit to be obtained. It may lie anywhere from about 300 to 600 Å.U.

It is obvious that one should expect more than just three absorption frequencies in the ultra-violet, considering that, in various halides, a large

number have been observed (Hilsch and Pohl, 1930; Schneider and O'Bryan, 1937). The three frequencies employed here are only a representation of these. However, it may be stated with confidence that the first absorption would be found near 1535 Å.U. and that it would exhibit a large difference in strength between the ordinary and extraordinary rays.

4. DISPERSION FORMULÆ FOR ARAGONITE

The three principal refractive indices of aragonite have been measured by various workers, but all for the visible region of the spectrum only. (Rudberg, 1829; Pulfrich, 1887; Mühlheims, 1888; Offret, 1890; Scouvert, 1912; Marbach, 1913). It is therefore not possible to obtain accurate dispersion formulæ in this case. The measurements of different workers (though individually accurate to 1×10^{-4}) often differ by 2 to 3×10^{-3} , since different specimens were used by them. Consequently, one must use the measurements of a single worker in calculating the dispersion formula. The data, which cover the largest range of wavelengths, are by Rudberg (*loc. cit.*), which are used in this section.

We denote the three principal refractive indices by n_1, n_2, n_3 , where $n_1 < n_2 < n_3$. These three will correspond to the directions of the electric vector parallel to the c, a and b crystallographic axes. As has been pointed out by Bragg (1924), there is a close resemblance between the optical properties of calcite and aragonite, as will be seen from below:

Calcite	Aragonite
$n_e = 1.486$ (to trigonal axis)	$n_1 = 1.530$ (c , the pseudo-hexagonal axis)
$n_\omega = 1.658$ (\perp to axis)	$n_2 = 1.681$ (a)
	$n_3 = 1.686$ (b)

The infra-red behaviour of the two substances also show a close similarity. The nearer infra-red absorptions for light with electric vectors parallel to the three axes are as follow (Nyswander, 1901):

a 6.65 μ ,	14.06 μ (weak)
b 6.46 μ , 6.70 μ ,	14.17 μ (,)
c 11.55 μ .	

A comparison with calcite shows that n_1 corresponds to n_e and that n_2 and n_3 correspond to n_ω . Since the dispersion data are not extensive enough to obtain the frequencies, and since the infra-red frequencies are close to those of calcite, the ultra-violet frequencies of aragonite were taken to be the same as those of calcite. In the infra-red, however, a frequency at 6.6 μ

was used for n_2 and n_3 , and one at 11.55μ for n_1 . The dispersion formulæ obtained were of the form

$$n_i^2 - 1 = \frac{c_{i1} \lambda^2}{\lambda^2 - (0.500)^2} + \frac{c_{i2} \lambda^2}{\lambda^2 - (0.1000)^2} + \frac{c_{i3} \lambda^2}{\lambda^2 - (0.1535)^2} + \frac{c_{i4} \lambda^2}{\lambda^2 - \lambda_4^2} \quad (8)$$

in which the constants for the three directions are given in Table II.

TABLE II

i	1	2	3
c_{i1}	0.51143	0.51091	0.49082
c_{i2}	0.77665	0.88367	0.89499
c_{i3}	0.02250	0.37976	0.40139
c_{i4}	0.33671	0.54277	0.53266
λ_4	11.55 μ	6.6 μ	6.6 μ

The fit of the formulæ can be judged from Table III where the values calculated from them are compared with the measurements of Rudberg (*loc. cit.*). A comparison of the values of the constants with those of calcite reveals again the close similarity between calcite and aragonite. The frequency at 1535 Å.U. is very weakly active in n_1 , while strongly so in n_2 and n_3 , so that the strong birefringence of aragonite is also produced principally by the highly polarised electronic transition corresponding to this frequency.

TABLE III

Wavelength in microns	n_1		n_2		n_3	
	Measured	Calculated	Measured	Calculated	Measured	Calculated
0.39685	1.54226	1.54226	1.70509	1.70509	1.71011	1.71011
0.43078	1.53882	1.53884	1.69836	1.69840	1.70318	1.70320
0.48613	1.53479	1.53479	1.69053	1.69054	1.69515	1.69515
0.52701	1.53264	1.53260	1.68634	1.68633	1.69084	1.69082
0.58929	1.53013	1.53013	1.68157	1.68152	1.68589	1.68589
0.65628	1.52820	1.52820	1.67779	1.67776	1.68203	1.68204
0.68700	1.52749	1.52749	1.67631	1.67637	1.68061	1.68061

5. THERMAL VARIATION OF THE REFRACTIVE INDICES

(a) *General.*—We shall now apply the dispersion formulæ considered in Section 2 to calculate dn/dt of anisotropic crystals. Differentiating Eq. (2) one obtains

$$2n_i \frac{dn_i}{dt} = \frac{e^2}{m\pi} \sum_r \left[\frac{f_{ir}}{\nu_r^2 - \nu^2} \cdot \frac{dN_r}{dt} + \frac{N_r}{\nu_r^2 - \nu^2} \cdot \frac{df_{ir}}{dt} - \frac{2N_r f_{ir} \nu_r}{(\nu_r^2 - \nu^2)^2} \cdot \frac{d\nu_r}{dt} \right] \quad (9)$$

Obviously, $dN_r/dt = -\gamma N_r$, where γ is the coefficient of cubical expansion. In A 1 to A 6, it was assumed that, for isotropic solids, the oscillator strength did not alter with temperature. For anisotropic solids also, one would expect an analogous result to hold, *viz.*, that the total oscillator strength does not change with temperature. This does not however preclude the possibility that the individual strengths f_{ir} along the three principal directions can alter. Thus, Eq. (9) can be written in terms of the a_{ir} 's and λ_r 's in the form

$$2n_i \frac{dn_i}{dt} = -\gamma (n_i^2 - 1) + \sum_r \frac{2a_{ir} \lambda_r^2 \lambda^4}{(\lambda^2 - \lambda_r^2)^2} \chi_r + \sum_r \frac{\lambda_r^2 \lambda^2}{\lambda^2 - \lambda_r^2} \cdot \frac{da_{ir}}{dt}, \quad i=1, 2, 3, \quad (10)$$

where $\chi_r = (1/\lambda_r)(d\lambda_r/dt)$, following the notation of A 1 to A 6. It will be noticed that this equation differs from that for isotropic solids (*cf.* Eq. 11 of A 1) only in the presence of the last term, which is absent in the other case. However, the assumption of invariability of the total strength with change of temperature gives the condition

$$\sum_{i=1}^3 \frac{da_{ir}}{dt} = 0. \quad (11)$$

A possible explanation of the changes that occur in the individual oscillator strengths is furnished by the following considerations. Taking the special cases of calcite and aragonite, the planar CO_3 ions will undergo tilting oscillations, which will increase in amplitude with rise of temperature. As a result, a certain amount of polarisability will be transferred from the plane to the perpendicular direction. It is also possible to conceive of other factors, which would result in a 'transfer' of oscillator strength from one direction to another. Taking a phenomenological view, the transfers may be correlated with the differences in the linear thermal expansions along the three directions. Thus, one may take that the transfer of oscillator strength between two directions is proportional to the difference in the expansions along those directions, *i.e.*,

$$\frac{da_{1r}}{dt} - \frac{da_{2r}}{dt} \propto (a_1 - a_2) \quad (12)$$

with two other similar equations, where a_1, a_2, a_3 are the coefficients of linear expansion along the three principal directions. Solving the three equations of (12), subject to proviso (11), one obtains

$$\left. \begin{aligned} \lambda_r^2 \frac{da_{1r}}{dt} &= K_r \left(a_1 - \frac{a_2 + a_3}{2} \right) \\ \lambda_r^2 \frac{da_{2r}}{dt} &= K_r \left(a_2 - \frac{a_3 + a_1}{2} \right) \\ \lambda_r^2 \frac{da_{3r}}{dt} &= K_r \left(a_3 - \frac{a_1 + a_2}{2} \right) \end{aligned} \right\} \quad (13)$$

where K_r is a constant. Thus, the problem of evaluating the dn/dt 's along the three directions reduces to the evaluation of two constants, viz., χ_r and K_r for each of the dispersion frequencies. It may be mentioned that the number of constants are in no way larger than for isotropic solids. For, if there are r dispersion frequencies, r constants (χ_r) have to be determined to explain the dispersion of dn/dt of one index, while here $2r$ constants have to be found out to explain the variations of dn/dt of three indices.

(b) *Calcite*.—Calcite being a uniaxial crystal, has only two principal refractive indices, $n_\omega (= n_2 = n_3)$ and $n_\epsilon (= n_1)$. Using Eqs. (10), (11) and (13), one may obtain the following expressions for the thermal variations of the two indices:

$$2n_\omega \frac{dn_\omega}{dt} = -\gamma (n_\omega^2 - 1) + \sum_r \frac{2a_{\omega r} \lambda_r^2 \lambda^4}{(\lambda^2 - \lambda_r^2)^2} \cdot \chi_r - \frac{1}{2} (\alpha_{||} - \alpha_{\perp}) \sum_r \frac{K_r \lambda^2}{\lambda^2 - \lambda_r^2}, \quad (14)$$

$$2n_\epsilon \frac{dn_\epsilon}{dt} = -\gamma (n_\epsilon^2 - 1) + \sum_r \frac{2a_{\epsilon r} \lambda_r^2 \lambda^4}{(\lambda^2 - \lambda_r^2)^2} \cdot \chi_r + (\alpha_{||} - \alpha_{\perp}) \sum_r \frac{K_r \lambda^2}{\lambda^2 - \lambda_r^2}, \quad (15)$$

where $\alpha_{||}$ and α_{\perp} are the coefficients of thermal expansion parallel and perpendicular to the optic axis.

dn/dt from 2000 to 6000 Å.U. for both ordinary and extraordinary indices have been measured by Micheli (1902) for a mean temperature of 61.5°C . Reed (1898) has measured dn/dt from room temperature to 350°C . for the sodium D line. We shall base all our calculations on these measurements.

As will be seen presently, the contribution to dn/dt due to the shift (if any) of the infra-red frequency will be very small and is therefore neglected. γ has the value, 15.77×10^{-6} and $\alpha_{||} - \alpha_{\perp}$, 31.91×10^{-6} (Fizeau's data from Liebisch, 1891). The values of the K_r 's and the χ_r 's, found so as to get a good fit with the dn/dt data are:

$$\left. \begin{aligned} K(500) = 0, \quad K(1000) = 0, \quad K(1535) = 1.006 \\ \chi(500) = 0, \quad \chi(1000) = 10.8 \times 10^{-6}, \quad \chi(1535) = 30.2 \times 10^{-6} \end{aligned} \right\} \quad (16)$$

Following the procedure in A 1 to A 6, the remote ultra-violet frequency was taken not to change with temperature. It was found that small values of the order of 1% of that of $K(1535)$ could be given to $K(500)$ and $K(1000)$, without upsetting the fit of the dn/dt values. However, since they were very small, they were put as zero. A probable explanation of the small values of these K 's is given below under aragonite.

The values of dn_ω/dt and dn_ϵ/dt , calculated with equations (14) and (15), using the constants given in (16) are shown as continuous curves in Fig. 1.

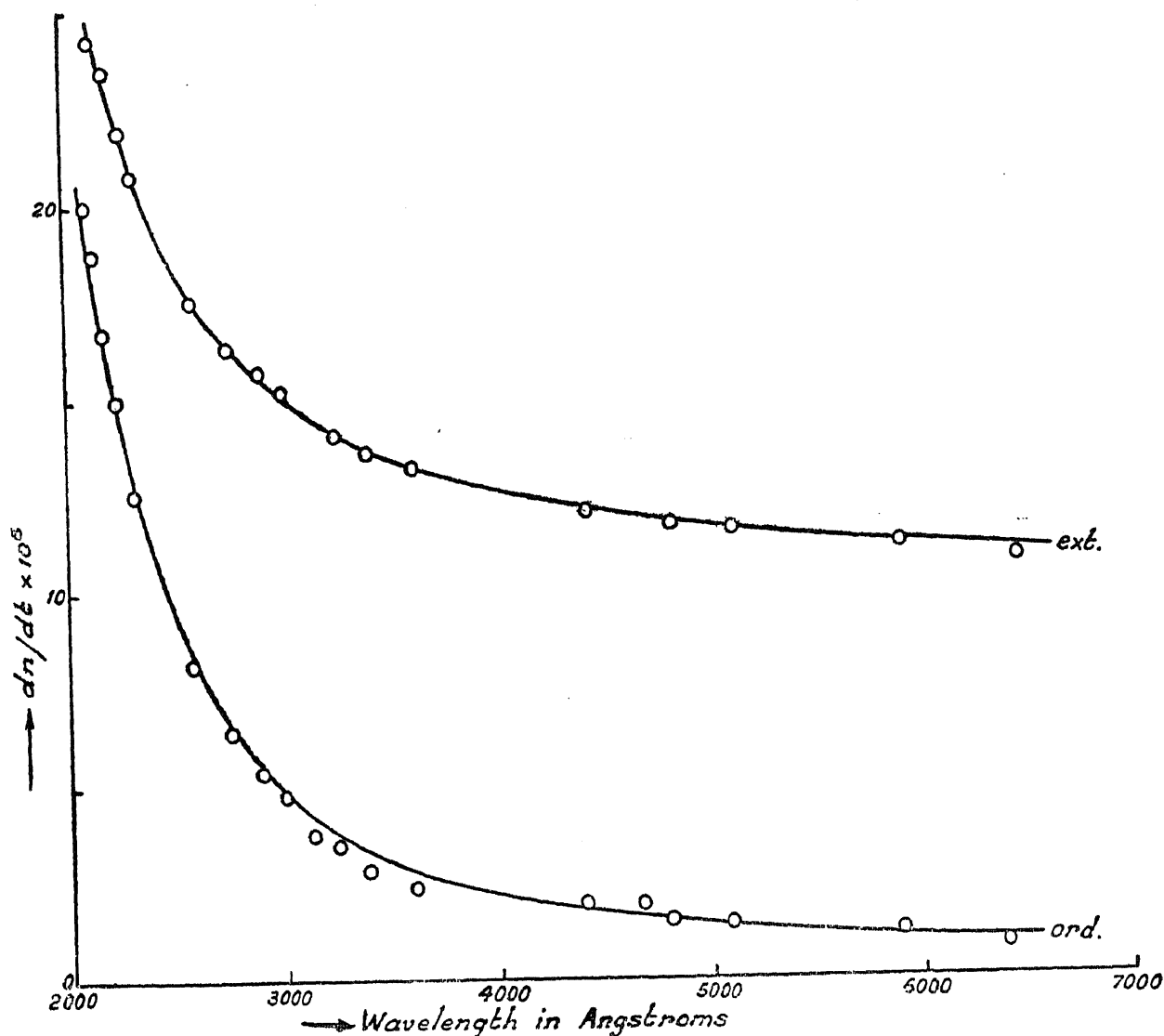


FIG. 1. Variation of dn/dt of calcite with wavelength for the ordinary and extraordinary rays. The continuous curves are from theory. The circles represent the measurements of Micheli.

The circles are the experimental data of Micheli (*loc. cit.*). It will be noticed that, with only three arbitrary constants, *viz.*, χ (1000), χ (1535) and K (1535), the whole range of data from 2000 to 6000 Å.U. for both the rays are satisfactorily explained.

Considering now the refractive index variations at higher temperatures, Reed's data are confined only to one wavelength, so that they cannot be used to verify the theory. However, some interesting deductions can be obtained from them. We shall assume that K_r is the same at all temperatures, so that the transfer of oscillator strength is proportional to $(a_{11} - a_{\perp})$, *i.e.*, the rate of change of the axial ratio. The values of both this quantity and that of γ at higher temperatures can be obtained by extrapolating Fizeau's formulæ for the coefficients of expansion. Then, using Eqs. (14) and (15), χ (1000) and χ (1535) can be calculated for different temperatures.

Their values calculated in this way from Reed's data as given in the International Critical Tables, Vol. VII, p. 24, are given in Table IV. The χ 's show a peculiar variation, the one for the 1535 Å.U. absorption being practically independent of temperature, while the other one rapidly increases with temperature. It may be mentioned that too much importance should not be attached to these finer details, both because of the assumptions in the calculations and also because Reed's temperature measurements are not very reliable (*cf.* Sosman, 1927, where Reed's measurements of dn/dt for quartz are compared with those of other workers).

TABLE IV

Temperature °C.	χ (1000) $\times 10^6$	χ (1535) $\times 10^6$	Based on measurements of
61.5	10.8	30.2	Micheli
61.5	10.6	26.9	Reed
152.1	14.6	28.7	"
248.5	19.3	27.5	"
349	24.0	26.6	"

It will be interesting to compare the χ -values of the ultra-violet frequencies with those of the infra-red frequencies as deduced from Raman effect data (Ornstein and Went, 1935; Kopcewicz, 1937; Venkateswarulu, 1942). Calcite has two low frequency lines at 155 and 282 cm.^{-1} , due to the tilting and transverse oscillations of the CO_3 ions, which have large χ values of 400×10^{-6} and 250×10^{-6} respectively. This, as well as the fact that they become broader at higher temperatures, suggest that they are highly temperaturesensitive, and support the idea mentioned earlier that the transfer of oscillator strength is at least partly due to the increase in amplitude of the tilting oscillations. The CO_3 ion has 4 internal oscillations of higher frequency, two perpendicular and two in the plane of the ion. One of the first and both of the second type appear in the Raman effect as fundamentals (1087, 714, 1432 cm.^{-1}), while the fourth one occurs as the octave ($1749 = 2 \times 874 \text{ cm.}^{-1}$). The results of different workers regarding the temperature-shift of these frequencies show discrepancies. Kopcewicz has, however, found that the degenerate vibrations shift with χ 's of about 18×10^{-6} and 8×10^{-6} , which, as is to be expected, are of the same order as the χ 's of the ultra-violet frequencies. He finds the shift of frequency in the other two oscillations to be much smaller. However, in the analogous case of NaNO_3 , Nedungadi (1939), using a Hartmann diaphragm method, found χ to be of the order of 15×10^{-6} for the symmetric planar vibration. It will be useful to make more exact studies of the temperature-variation of the Raman lines of calcite, using the same method.

It may be mentioned that even if χ of the infra-red frequencies is about 30×10^{-6} , the contribution to dn/dt by them for wavelengths below 6000 Å.U. is less than 0.001×10^{-6} , so that its neglect in the calculations made above is justified.

(c) *Aragonite*.—The thermal variation of all the three principal indices of aragonite have been measured by two workers (Offret, 1890; Marbach, 1913) over the temperature range from 0° to 300° C. Their data are shown in Table V. It will be noticed that their measurements are not sufficiently accurate for any conclusions to be drawn regarding the variation of dn/dt with wavelength. One can only get approximate values for the three principal variations, corresponding to a mean wavelength, which are shown in the last row. The mean wavelength, 0.582μ , is so close to the D line, 0.589μ , that the calculations can be carried out for the latter.

TABLE V

Wavelength in microns	$\frac{dn_1}{dt} \cdot 10^5$	$\frac{dn_2}{dt} \cdot 10^5$	$\frac{dn_3}{dt} \cdot 10^5$	Reference
0.471	- 1.2	- 2.5	- 2.9	Marbach
0.480	- 1.3	- 2.5	- 2.7	Offret
0.671	- 1.4	- 2.5	- 2.8	Offret
0.706	- 1.1	- 2.7	- 3.0	Marbach
0.582	- 1.25	- 2.55	- 2.85	Mean

Eq. (10) with the values of da_{ir}/dt given by (13) can be used directly to calculate the refractive index variations. On account of the fact that the dispersion frequencies are the same as those of calcite, one may take the χ 's also to be the same as for calcite at the same mean temperature of 150° C., viz., $\chi(500) = 0$, $\chi(1000) = 14.6 \times 10^{-6}$, $\chi(1535) = 28.7 \times 10^{-6}$. But, one is not justified in assuming the values of K_r to be the same as for calcite. However, the following consideration will show that K_r will be significant only for the nearest ultra-violet frequency. It is obvious that, if an oscillator is isotropic with $a_{1r} = a_{2r} = a_{3r}$, then there will be no transfer at all with change of temperature, i.e., K_r will be zero. Also, it is reasonable to suppose that the less anisotropic the oscillator is, the less will be the magnitude of the transfers in oscillator strength. One may take the following function Ω_r as defining the anisotropy of an oscillator:

$$\Omega_r = \frac{\Sigma (a_{1r} - a_{2r})^2}{(a_{1r} + a_{2r} + a_{3r})^2} \quad (17)$$

In this, the denominator is proportional to the mean oscillator strength, and the numerator vanishes only when $a_{1r} = a_{2r} = a_{3r}$, i.e., when the oscilla-

tor is isotropic. In Table VI are given the values of Ω_r for the three ultra-violet frequencies with both calcite and aragonite.

TABLE VI

Calcite		Aragonite	
Wavelength	Anisotropy	Wavelength	Anisotropy
Å.U.		Å.U.	
1535	0.4144	1535	0.4208
1000	0.0062	1000	0.0024
500	0.0008	500	0.0004

It will be seen from the table that the anisotropy of the second frequency at 1000 Å.U. is only of the order of 1% of the first one, and that for the remote frequency it is negligibly small. So, if one takes the transfer of oscillator strength to be proportional to the anisotropy, it would explain the fact found with calcite, *viz.*, that the transfer is very small, except for the nearest frequency. It may be mentioned that, in applying the author's thermo-optical theory to the case of quartz, Radhakrishnan (*loc cit.*) did not assume any transfer in the oscillator strength, but was yet successful in explaining the data. This is because the anisotropies of all the oscillators in quartz are very small, the largest being 0.00231, so that, just as with the remoter ultra-violet frequencies of calcite, one may put the transfer to be zero without committing a serious error.

For aragonite also, therefore, we shall take K (1000) and K (500) to be zero, so that only one constant has to be determined, *viz.*, K (1535). This was found to have the value 1.30 as compared with 1.01 for calcite. The rates of change of the three indices, calculated with this and the values of χ mentioned above, are $dn_1/dt = -1.31 \times 10^{-5}$, $dn_2/dt = -2.40 \times 10^{-5}$, $dn_3/dt = -2.97 \times 10^{-5}$, which may be compared with the experimental values given in Table VI, *viz.*, -1.25 , -2.55 and -2.85×10^{-5} respectively. The agreement between the two must be taken to be reasonably good, considering the approximate nature of the calculations.

6. GENERAL DISCUSSION

The theory of thermo-optic behaviour of an anisotropic crystal given in the previous section hold only for biaxial crystals of the orthorhombic system and for all uniaxial crystals. In the case of crystals of lower symmetry, not only do the principal refractive indices alter with temperature, but the directions of the principal axes also undergo changes. A theory of thermo-optic behaviour of the type developed by the author becomes too complicated for such cases.

The explanation of birefringence as arising from the existence of (partially) polarised electronic transitions should, however, be capable of being extended to all birefringent crystals. In particular, it will be interesting to see whether it is applicable to the case of nitrates, which have a structure very similar to that of the carbonates. So also, many aromatic organic compounds exhibit marked anisotropy in their optical properties, due no doubt to the presence of planar rings, and their birefringence must also be capable of being explained on the basis of polarised electronic transitions. It is expected to consider these in a later publication.

It might be noticed that the idea of an inner Lorentz field has not been explicitly assumed in this paper, and that the dispersion formulæ have been written in the $(n^2 - 1)$ form. The problem of evaluating the magnitude of the Lorentz field in an anisotropic crystal is a complicated one and depends on the anisotropy of the particular crystal. Besides, even the necessity for introducing the Lorentz field in dispersion theory for isotropic crystals is not very clear. As has been pointed out by the author (A5), the dispersion formula for a crystal lattice, developed by Ewald (1916) and Born (1918, 1922) are of the $(n^2 - 1)$ form. Besides, for the alkali halides, the frequencies used in the dispersion formula agree with the observed absorption frequencies only in the $(n^2 - 1)$ form and not in the $(n^2 - 1)/(n^2 + 2)$ form (A 5). Also, Kurtz and Ward (1937) have given some reasons to believe that the Lorentz field is probably non-existent. Because of these considerations, we shall leave the theoretical question, whether the Lorentz-Lorenz form is to be used for dispersion formulæ or not, an open one. The $(n^2 - 1)$ form has been used in this paper, because it has been successful for various cubic crystals such as diamond, fluorspar, zinc-blende and the alkali halides (cf. A 1 - A 5) and also for quartz (Radhakrishnan, 1947) using the observed frequencies.

In conclusion, I should like to express my sincere thanks to Prof. Sir C. V. Raman for the deep interest that he took in this investigation.

SUMMARY

It is suggested that the birefringence of crystalline bodies can be explained as arising from the existence of polarised electronic transitions, so that the probability of transition is different for different directions of the incident electric vector. As a result, in the dispersion formulæ for the three principal refractive indices of a biaxial crystal, the oscillator-strengths will be different, although the dispersion frequencies are the same. The application of the idea to the cases of calcite and aragonite (two strongly birefringent crystals) enables one to construct dispersion formulæ involving

three ultra-violet frequencies at 1535, 1000 and 500 Å.U. The formulæ, which fit the dispersion data for both rays of calcite from 0·2 to 3 μ , show that a large part of the birefringence arises from the large anisotropy in the strength of the nearest ultra-violet frequency at 1535 Å.U. A similar result is also found for aragonite.

The dispersion formulæ are also successful in explaining the thermo-optic behaviour of both calcite and aragonite, when they are utilised in the author's theory of thermo-optic behaviour, which has so far been applied only for isotropic solids. For anisotropic solids, an additional principle has to be used, *viz.*, that, while the total oscillator strength does not alter with temperature, the individual strengths along the three principal directions can change, resulting in a mutual transfer. It is suggested that this transfer is related to the differences in thermal expansion along the three directions, which finds some support in the case of aragonite. A physical explanation of the transfer can be found, wholly or partly, in the tilting oscillations of the CO₃ ion.

The theory is successful in explaining the remarkable fact that, while dn/dt for both indices of calcite is positive, that for all the indices of aragonite is negative, the difference being attributable to the much larger coefficient of thermal expansion of the latter.

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Note added in proof.

It is a remarkable fact that while dn/dt 's for both the indices of calcite are positive, those for aragonite are negative for all the three indices. It may be noticed that we have used the same dispersion frequencies with nearly the same weights for both the crystals and also taken the frequencies to change with temperature to the same extent. Nevertheless, the theory is able to explain quantitatively the positive and negative values of dn/dt in the two cases. The difference arises principally because of the much larger coefficient of thermal expansion of aragonite, the coefficient of cubical expansion for which is 70×10^{-6} as compared with 16×10^{-6} for calcite. This gives rise to a large negative contribution to dn/dt and makes it negative for *all* the indices of aragonite. The small difference in the value of K (1535) assumed in the two cases, *viz.*, 1.0 and 1.3 respectively, is not of serious consequence. The value 1.3 was taken for aragonite to get the best fit with the data. Even if it were taken as 1.0, the dn/dt 's would have values -1.50 , -2.35 and -2.80×10^{-6} , which do not differ much from the observed ones.