FURTHER STUDIES ON THE TEMPERATURE VARIATION OF THE REFRACTIVE INDEX OF CRYSTALS

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1. INTRODUCTION

THE temperature coefficient of refraction *dn*/*dt* of a number of crystals has been measured by Reed (1898) over a range of wavelengths in the visible region from room temperature to 500° C. and by Micheli (1902) from λ 2000 to λ 6000 at a single temperature of 60° C. No high temperature measurements are available in the ultra-violet. The present paper describes interferometric measurements of *dn*/*dt* in the ultra-violet and visible regions from room temperature to 400° C. for a number of crystals, namely lithium fluoride, fluorspar, magnesia, quartz and barite. For some of these crystals, additional measurements have been made for the λ 4047, λ 4916 and λ 5790 radiations of mercury at 50° C. The values presented in this paper for the visible region are more accurate than the earlier measurements of the author for some of these crystals. Using these accurate data and the dispersion formulæ for these substances, some of them freshly computed by the author, the rate of shift of the ultra-violet frequencies with temperature is evaluated. This rate is invariably found to increase with temperature.

2. THE METHOD OF MEASUREMENT

The method of measuring *dn*/*dt* in the ultra-violet was a modification of the techniques used earlier for visual studies (Radhakrishnan, 1947 *b*; 1950 *a*, *b*). The wavelengths used were the radiations of the mercury arc at λ 3650 and λ 2537. The former was obtained from a point-source quartz mercury arc, and monochromatized by passing through a Corning glass filter. (A faint trace of the λ 4047 line also remained). The λ 2537 radiation was obtained with great intensity from a water-cooled horizontal quartz mercury arc placed between the poles of an electromagnet. It was monochromatized by passage through an aqueous solution of cobalt and nickel sulphates kept in a cell with fused quartz windows. This filter transmitted a small amount of red light, as well as λ 3100. But these were very feeble in comparison with the λ 2537 radiation.

The monochromatized radiation, limited by a small aperture placed just above the arc, was reflected normally on to the crystal by means of a plate of fused quartz. The interference fringes formed in the crystal were photographed by a camera using a low aperture quartz lens. The fringes were first obtained visually for the λ 5461 radiation. On now altering the focus of the camera, the adjustments were found to be nearly correct for photographing the fringes, and slight shifts of the crystal and the reflecting plate were all that were necessary to obtain the fringes with the maximum clarity. Ilford Process plates were used for photography. These gave good contrast and further, they were insensitive to the red light let through by the filters.

The technique adopted for determining the shift of these fringes was as follows: A number of photographs of the fringes were taken at every two degrees till one complete fringe shift had taken place. With the crystal thicknesses employed, this meant a total temperature shift of about 10° C., or 5 photographs. Sets of photographs like this were taken at 50° intervals up to 400° C. These photographs gave an approximate value of the rate of shift of the fringes with temperature, $\Delta N/\Delta t$. Having obtained these values, it was now easy to take by trial a number of photographs such that a very nearly integral number of fringes (5 or 6) had shifted between two successive photographs. The fractional part of the fringe shift could be estimated to a tenth of a fringe by comparison with the preliminary photographs. In this way $\Delta N/\Delta t$ was accurately determined over the whole range from 50° to 400° C. The temperature coefficient could then be evaluated from the relation

$$\frac{dn}{dt} = \frac{\lambda}{2l}\frac{\Delta N}{\Delta t} - n\alpha_t, \tag{1}$$

where l represents the thickness of the crystal, and α_t its coefficient of thermal expansion perpendicular to the thickness.

In the case of quartz there were two coefficients to be measured corresponding to the ordinary and extraordinary indices. These were obtained by using a plate cut parallel to the optic axis. Polarised light was produced by keeping the quartz plate used for reflecting the light on the crystal at the Brewsterian angle. The crystal was successively mounted with the optic axis parallel and perpendicular to the electric vector of the incident radiation. This method of polarisation was superior to the use of nicols since no intensity was lost by absorption.

In addition to the ultra-violet studies, photographic measurements were also made in the visible region for the wavelengths λ 4047, λ 4916 and λ 5790 of mercury in the case of some of the crystals. These measurements were carried out by allowing the direct light of the mercury arc to fall on the crystal. The light reflected by the crystal was condensed by an achromatic camera lens arranged so as to cast a focussed image of the crystal on the slit of a Fuess spectrograph. The slit was widened to 3 or 4 mm. Under these conditions, the spectrograph served both as a monochromator and as a camera, sorting out the fringe systems due to the several radiations and recording them simultaneously on the plate. There was some overlap between the fringe systems due to the λ 5770 and λ 5790. But this did not affect the measurements. By taking photographs at a number of temperatures, *dn*/*dt* could be evaluated for the various wavelengths.

The results of these studies are presented in the succeeding pages. They are discussed in the light of dispersion formulae for these crystals, some of which have been freshly computed.

3. Results

(*a*) *Lithium Fluoride*

Values of *dn*/*dt* at 100° intervals have been previously given by the author (Radhakrishnan, 1950 *a*) for λ 4358, λ 5461 and λ 5893. The present studies give values at 50° intervals for these lines as well as for the wavelengths λ 2537 and λ 3650 (Table I).

Table I

Temperature (deg. C.)	$10^5 \alpha_t$	$10^5\, dn/dt$				
		2537	3650	4358	5461	5893
50	3·48	−1·10	−1·20	−1·25	−1·27	−1·27
100	3·65	−1·31	−1·37	−1·42	−1·44	−1·44
150	3·83	−1·45	−1·54	−1·60	−1·61	−1·60
200	4·03	−1·67	−1·75	−1·81	−1·81	−1·82
250	4·24	−2·00	−1·95	−2·01	−2·03	−2·03
300	4·46	−2·23	−2·20	−2·25	−2·26	−2·27
350	4·69	−2·44	−2·51	−2·56	−2·56	−2·58
400	4·93	−2·65	−2·78	−2·80	−2·82	−2·85

In a previous paper (Radhakrishnan, 1950 *a*), the author has given a dispersion formula for lithium fluoride employing an ultra-violet frequency at λ 914 and an infra-red frequency at 33 μ. Applying Ramachandran's theory of thermo-optic behaviour to this formula (Ramachandran, 1947 *a*), one obtains the result

$$2n\frac{dn}{dt} + \gamma_t(n^2 - 1) = \frac{17,465}{(122{\cdot}8 - \nu^2)^2}\chi_t \qquad (2)$$

where $$\chi_t = -\frac{1}{\nu_0}\frac{d\nu_0}{dt} \tag{3}$$

is the proportional rate of change of the ultra-violet frequency with temperature and γ_t is the coefficient of volume expansion of the substance at temperature t. The numerical evaluation of x_t from equation (2) gives the results shown below. The values of γ_t have been taken from the work of Eucken and Danöhl (1934).

TABLE II

Temperature (deg. C.)	$10^5\chi_t$		
	2537	3650	5461
50	5·1	5·1	5·0
100	4·9	5·1	5·0
150	5·0	5·1	5·0
200	5·0	5·1	5·1
250	4·8	5·1	5·0
300	4·9	5·1	5·0
350	5·1	4·9	5·1
400	5·1	4·9	4·8

The constancy of χ shows the validity of equation (2) over the whole range of wavelengths. It is further seen that χ_t is practically unchanged with increasing temperature for lithium fluoride.

(*b*) *Fluorspar*

The temperature coefficient of refraction of fluorspar has been studied by Micheli (1902) at 60° C. in the ultra-violet and visible regions and by Reed (1898) at higher temperatures in the visible region. Table III gives

TABLE III

Temperature (deg. C.)	$10^5\alpha_t$	$10^5\, dn/dt$					
		2537	3650	4358	5461	5893	
						Author	Reed
50	1·93	−0·88	−1·08	−1·10	−1·14	−1·18	−1·19
100	2·02	−0·95	−1·10		−1·19	−1·24	−1·24
150	2·12	−1·02	−1·18		−1·25	−1·31	−1·31
200	2·24	−1·13	−1·29		−1·34	−1·39	−1·37
250	2·36	−1·15	−1·46		−1·44	−1·48	−1·43
300	2·49	−1·36	−1·54		−1·55	−1·59	−1·50
350	2·63	−1·44	−1·56		−1·68	−1·71	−1·56
400	2·79	−1·54	−1·73		−1·83	−1·88	

the author's measurements. Although agreeing with Reed's data at the lower temperatures, they differ more and more from it at higher temperatures. It is significant to note in this connection that a comparison of Reed's work on quartz with that of other investigators shows some systematic discrepancy in the measurement of temperature (Sosman, 1927).

Using Micheli's and Reed's measurements of *dn/dt*, as well as the thermal expansion values available at that time, Ramachandran (1947 *c*) calculated the temperature shifts in the ultra-violet absorptions of fluorspar. But the author's present work fails to agree with that of Reed, while the thermal expansion values used by Ramachandran are now known to be slightly in error (Sharma, 1950). Consequently the author has repeated Ramachandran's calculations with the better data. The electronic frequencies of fluorspar are known to be at λ 900 and λ 1115. Ramachandran's analysis of Micheli's data shows that the χ values of these frequencies at 60° C. are respectively $1\cdot1\times10^{-5}$ and $7\cdot0\times10^{-6}$. To calculate χ_t at high temperatures separately for the two frequencies, one requires data on *dn/dt* extending upto λ 2000. In the absence of such data, one can perform an approximate calculation, as was done by Ramachandran, by replacing the terms at λ 900 and λ 1115 by a weighted mean which lies at λ 943. Ramachandran obtained for this term a χ value of $3\cdot3\times10^{-5}$ and found that this value was independent of temperature. But the calculations with the new data on thermal expansion and *dn/dt* show that χ_t does vary with temperature, as seen in Table IV.

TABLE IV

Temperature (deg. C.)	$10^5\chi_t$			
	2537	3650	5461	5893
50	3·0	2·9	2·9	3·1
100	3·1	3·1	3·1	3·2
150	3·2	3·2	3·2	3·3
200	3·3	3·3	3·4	3·5
250	3·4	3·3	3·5	3·7
300	3·5	3·5	3·6	3·8
350	3·7	3·8	3·7	3·9
400	3·9	3·9	3·9	4·1

Again the constancy of χ in each row of the table shows the validity of the theory. The value of χ_t is found to increase with temperature as is the case with most crystals,

(*c*) *Magnesium Oxide*

Observations with magnesia could not be carried out for the 2537 radiation owing to the low transparency of the crystal for this wavelength. The results for the other radiations are set out in Table V. The thermal expansion values have been taken from the work of Thilenius and Holzmann (1930).

TABLE V

Temperature (deg. C.)	$10^5 \alpha_t$	$10^5 dn/dt$				
		3650	4047	4358	5461	5893
50	1·12	1·95	1·85	1·79	1·65	1·60
100	1·16	1·96		1·78	1·64	1·61
150	1·195	1·99		1·80	1·65	1·59
200	1·235	1·99		1·77	1·65	1·61
250	1·29	1·97		1·77	1·64	1·60
300	1·345	1·94		1·78	1·64	1·61
350	1·39	1·95		1·80	1·65	1·60
400	1·41	1·99		1·79	1·65	1·61

A dispersion formula for magnesium oxide has been proposed by the author (Radhakrishnan, 1950 *b*) employing a single ultra-violet term at λ 1180. The formula for χ_t obtained from the dispersion constants is

$$2n\frac{dn}{dt} + \gamma_t(n^2 - 1) = \frac{16{,}940}{(72 \cdot 10 - \nu^2)^2}\,\chi_t. \tag{4}$$

The values of χ_t are displayed in Table VI, which verifies the correctness of this equation at each temperature.

TABLE VI

Temperature (deg. C.)	$10^5 \chi_t$			
	3650	4358	5461	5893
50	3·48	3·50	3·52	3·46
100	3·55	3·56	3·58	3·52
150	3·62	3·63	3·62	3·56
200	3·69	3·67	3·70	3·65
250	3·76	3·76	3·79	3·74
300	3·83	3·86	3·89	3·81
350	3·90	3·95	3·96	3·90
400	3·97	3·97	3·99	3·94

In the author's earlier paper on magnesium oxide, an error had crept into the calculation of χ_t, the values having been divided throughout by $2n$. This mistake has now been rectified. It is seen that χ_t increases slightly with temperature.

(*d*) *Quartz*

The case of quartz has been studied in detail. Previous experimental measurements by Micheli give the values of dn/dt from 2000 Å to 6500 Å at 60° C. At higher temperatures, values in the visible region have been given by Reed and by Rinne and Kolb (1910). The author's measurements in the visible region are, as in the case of fluorspar, slightly different from those of Reed. The necessary data on thermal expansion were taken from Sosman's book "The Properties of Silica". The measured values of dn_ω/dt and dn_ϵ/dt) are shown in Tables VII and VIII.

TABLE VII

Temperature (deg. C.)	$-10^5 dn_\omega/dt$							
	2537	3650	4047	4358	4916	5461	5790	5893
50	0·29	0·54	0·58	0·59	0·60	0·62	0.62	0·63
100	0·32	0·57		0·65		0·68		0·69
150	0·39	0·65		0·70		0·74		0·75
200	0·43	0·71		0·77		0·82		0·84
250	0·50	0·80		0·85		0·92		0·94
300	0·64	0·95		1·00		1·05		1·08
350	0·78	1·10		1·10		1·20		1·23
400	1·00	1·32		1·24		1·44		1·46

TABLE VIII

Temperature (deg. C.)	$-10^5 dn_\epsilon/dt$							
	2537	3650	4047	4358	4916	5461	5790	5893
50	0·40	0·62	0·65	0·66	0·70	0·70	0·71	0·71
100	0·43	0·68		0·74		0·77		0·80
150	0·52	0·77		0·84		0·89		0·91
200	0·55	0·80		0·92		1 00		1·10
250	0·62	0·93		1·01		1·10		1·12
300	0·75	1·12		1·09		1·20		1·23
350	0·89	1·27		1·25		1·35		1·38
400	1·20	1·47		1·58		1·65		1·67

Dispersion formulæ of the Ketteler-Helmholtz form were previously offered by the author for quartz (Radhakrishnan, 1947 *a*), in which the observed infra-red and ultra-violet absorption frequencies were used for the first time. These formulæ fit the data better than any previous formula proposed for quartz. Even this agreement, however, is not as good as could be desired. An additional defect of the formulæ is that they employ a hypothetical ultra-violet term at λ 330 (taken over from previous work by Lowry and Coode-Adams in 1927), the strength of which is very high. On account of this the formulae, when converted to the Drude form, give expressions like

$$n^2 - 1 = -2 + \sum_r \frac{a_r \lambda^2}{\lambda^2 - \lambda_r^2},$$

which is absurd as it leads to a negative strength for some frequency. This defect is now removed by altering the position of the remote ultra-violet term to λ 600. It has then the requisite dispersion with a reasonably low strength. On making this change and reclaculating the oscillator strengths, formulæ have resulted which fit the facts with very good accuracy. These formulæ and their agreement with the facts are given below.

$$n_\omega^2 - 1 = \frac{0{\cdot}663044\,\lambda^2}{\lambda^2 - (0{\cdot}0600)^2} + \frac{0{\cdot}517852\,\lambda^2}{\lambda^2 - (0{\cdot}1060)^2} + \frac{0{\cdot}175912\,\lambda^2}{\lambda^2 - (0{\cdot}1190)^2} + \frac{0{\cdot}565380\,\lambda^2}{\lambda^2 - (8{\cdot}844)^2} + \frac{1{\cdot}675299\,\lambda^2}{\lambda^2 - (20{\cdot}742)^2} \qquad (5)$$

$$n_e^2 - 1 = \frac{0{\cdot}665721\,\lambda^2}{\lambda^2 - (0{\cdot}0600)^2} + \frac{0{\cdot}503511\,\lambda^2}{\lambda^2 - (0{\cdot}1060)^2} + \frac{0{\cdot}214792\,\lambda^2}{\lambda^2 - (0{\cdot}1190)^2} + \frac{0{\cdot}539173\,\lambda^2}{\lambda^2 - (8{\cdot}792)^2} + \frac{1{\cdot}807613\,\lambda^2}{\lambda^2 - (19{\cdot}70)^2} \qquad (6)$$

TABLE IX

Refractive Indices of quartz in air at 18° *C. against I.A.U.*

λ (in μ)	n_ω (calc.)	n_ω (obs.)	n_e (calc.)	n_e (obs.)
0·185467	1·67578	1·67578	1·68997	1·68997
0·193583	1·65995	1·65909	1·67343	1·67343
0·214430	1·63045	1·63039	1·64269	1·64262
0·257304	1·59622	1·59622	1·60714	1·60714
0·325253	1·57091	1·57091	1·58091	1·58095
0·396848	1·55812	1·55813	1·56770	1·56772
0·486133	1·54968	1·54968	1·55898	1·55898
0·546072	1·54617	1·54617	1·55535	1·55535
0·656278	1·54191	1·54190	1·55094	1·55093
0·706520	1·54051	1·54049	1·54919	1·54947

Refractive indices in the infra-red have been omitted from this table, since their representation is the same as in the author's previous paper. It is seen that the terms at λ 600 and λ 1060 are nearly the same for both the indices. Most of the birefringence arises from the term at λ 1190.

Passing now to the consideration of *dn/dt*, the data were previously explained by the author (1947 *b*) as due to a change of density and a shift in the absorption frequency, without specifically taking into account the anisotropy of the crystal. The terms at λ 1190 and λ 1060 were replaced by a weighted mean at λ 1127 having a mean χ of $3 \cdot 0 \times 10^{-5}$ at 60° C. Since rigorous dispersion formulæ have now been evolved, which express the anisotropies of the terms completely, it is possible to calculate the values of the various terms separately, as well as the contribution of the anisotropy factor to *dn/dt*. Ramachandran (1948) has shown that in a uniaxial crystal, *dn/dt* can be expressed for both the rays in a form which is equivalent to the formulæ

$$\left.\begin{aligned} f_\omega &= 2n_\omega \frac{dn_\omega}{dt} + \gamma_t\,(n_\omega{}^2 - 1) = \sum_i \left[\tfrac{1}{2}\,(a_\perp - a_{\parallel})\,\frac{Q_i}{\nu_i{}^2 - \nu^2} + \frac{2b_{\omega i}\,\nu_i{}^4\,\chi_i}{(\nu_i{}^2 - \nu^2)^2}\right] \\ f_\epsilon &= 2n_\epsilon \frac{dn_\epsilon}{dt} + \gamma_t\,(n_\epsilon{}^2 - 1) = \sum_i \left[-\,(a_\perp - a_{\parallel})\,\frac{Q_i}{\nu_i{}^2 - \nu^2} + \frac{2b_{\epsilon i}\,\nu_i{}^4\,\chi_i}{(\nu_i{}^2 - \nu^2)^2}\right] \end{aligned}\right\} \qquad (7)$$

The Q's represent a directional transfer of the strengths of the individual absorptions in such a manner that the total strength remains constant. The constants $b_{\omega i}$ and $b_{\epsilon i}$ are merely the dispersion constants appearing in the numerators of the dispersion formulæ, and χ_i is the proportional rate of change of each electronic frequency with temperature. The infra-red frequencies are neglected in this picture since they offer only slight contributions to *dn/dt* in the ultra-violet and visible regions. On evaluating the Q and χ for the various frequencies at 60° C., using Micheli's data, one obtains the following results:—

$$Q\,(600) \approx 0; \quad Q\,(1060) \approx 0; \quad Q\,(1190) = 62 \cdot 3$$

$$\chi\,(600) \approx 0; \quad \chi\,(1060) \approx 0; \quad \chi\,(1190) = 7 \cdot 8 \times 10^{-6}$$

Thus the terms at λ 600 and λ 1060 undergo practically no directional transfer in strength. This is to be expected since their anisotropies are very slight. But the strongly anisotropic term at λ 1190 has a transfer coefficient of 62·3, which when expressed in Ramachandran's notation leads to a value of 0·882 for his $K = Q/\nu_0{}^2$. The order of this transfer coefficient is the same as in other anisotropic crystals, for example calcite, for which Ramachandran obtains K = 1·006. When there are three Q's and three χ's to fix, it is difficult to assign unambiguous numerical values to all of them. One can assign a small Q and a small χ to the λ 1060 term and still retain a good fit with facts.

The calculated values of the temperature coefficients using Equation (7) are compared with the experimental values in Table X.

TABLE X

Wavelength A.U.	$10^5 dn_\omega/dt$ (calc.)	$10^5 \frac{dn_\omega}{dt}$ (obs.)	$10^5 \frac{dn_\epsilon}{dt}$ (calc.)	$10^5 \frac{dn_\epsilon}{dt}$ (obs.)
2026	+0·12	+0·18	+0·10	+0·13
2063	+0·06	+0·12	+0·03	+0·06
2144	−0·01	−0·01	−0·05	−0·05
2195	−0·07	−0·06	−0·13	−0·11
2265	−0·17	−0·14	−0·19	−0·20
2313	−0·18	−0·18	−0·24	−0·24
2573	−0·31	−0·31	−0·40	−0·39
2981	−0·43	−0·43	−0·53	−0·53
3613	−0·53	−0·53	−0·63	−0·64
4800	−0·59	−0·61	−0·70	−0·72
5893	−0·62	−0·65	−0·73	−0·75
6438	−0·63	−0·66	−0·74	−0·76

The fit with the experimental data appears unsatisfactory at the lowest wavelengths. But it must be remembered that *dn/dt* is really the net effect of two large quantities of opposite sign, namely, contributions due to volume and frequency changes. Our formulæ are developed in a form which expresses not the net effect, but the contribution due to frequency changes alone. Since this quantity has several times the magnitude of *dn/dt*, a small error in its representation results in large errors in the calculated value of *dn/dt*.

To calculate χ_t at higher temperatures, one assumes that Q is the same at different temperatures, *i.e.*, that the transfer is proportional to the difference in the linear thermal expansions parallel and perpendicular to the optic axis. χ_t can then be evaluated from equation (7) using the known values of $\alpha_\perp$, $\alpha_{\parallel}$ and γ_t (Sosman, 1927). The values of χ_t are given below:

TABLE XI

Temperature (deg. C.)	$10^5\gamma_t$	$10^5 \times (\alpha_\perp - \alpha_{\parallel})$	$10^5\chi_t$			$10^5\chi_t$		
			Ordinary Ray			Extraordinary Ray		
			2537	3650	5461	2537	3650	5461
50	3·68	0·65	7·7	7·4	7·4	7·7	7·7	7·7
100	4·00	0·68	8·3	8·2	7·9	8·3	8·3	8·3
200	4·66	0·75	9·4	9·3	9·0	9·4	9·5	8·9
300	5·49	0·82	10·4	10·2	10·1	10·5	10·1	10·2
400	6·74	0·88	11·7	11·6	11·3	11·3	11·5	11·1

The approximate constancy of the value of X shows the validity of the assumptions made in the theory.

The results obtained generally indicate that X_t varies by 50 per cent. from room temperature to 400° C. Taking the weighted mean of the X for the 1190 and 1060 terms, we obtain a value of $2\cdot5\times10^{-5}$ for the electronic absorptions at 50° C. This is precisely the X value obtained by Ramachandran (1947 *b*) for fused quartz, working with a single term at λ 1070. In view of Tousey's observations (1940) of two peaks in the reflection spectrum of both crystal quartz and fused quartz at λ 1060 and λ 1190, the one-term formula used by Ramachandran has to be considered as only a weighted mean. Thus there is a striking similarity between quartz and vitreous silica as regards the positions and the temperature shifts of the electronic lines. This similarity also holds at higher temperatures.

(*e*) *Barite*

Barite is an orthorhombic crystal having three principal refractive indices n_α, n_β and n_γ. These three indices respectively correspond to the electric vector parallel to the crystallographic axes *c*, *b* and *a*. The temperature coefficients of n_β and n_γ were evaluated from observations on a cleavage plate parallel to the *c* (001) face. The coefficient dn_α/dt was obtained by observations on another cleavage plate parallel to the *m* (110) face and using polarised light with the electric vector parallel to the *c*-axis. The refractive index for light with the electric vector in the plane of the plate and perpendicular to the *c*-axis is given by n_m where

$$n_m^{-2} = \cos^2\theta\cdot n_\beta^{-2} + \sin^2\theta\cdot n_\gamma^{-2}$$

and θ is the angle between the electric vector of n_m and the *b*-axis. On differentiating this with respect to temperature and neglecting the small correction caused by the change in θ with temperature, one obtains

$$dn_m/dt = 0\cdot60\, dn_\beta/dt + 0\cdot39\, du_\gamma/dt\,. \tag{8}$$

This formula provided a check on the internal accuracy of the experiment, since dn_m/dt could be measured and compared with the values calculated from dn_β/dt and dn_γ/dt. The relevant thermal expansion data were taken from the work of Sharma (1950) (under publication). The four coefficients in the case of the λ 5461 radiation are given in Table XII:

The dispersion of barite has been measured only in the visible region. Consequently, accurate dispersion formulæ cannot be constructed for this

TABLE XII

Temperature (deg. C.)	$10^5\alpha_c$	$10^5\alpha_m$	$-10^3\, dn/dt$				
			α	β	γ	m (obs.)	m(calc.)
50	1·49	1·84	2·13	1·82	2·53	2·05	2·07
100	1·57	1·91	2·19	1·90	2·62	2·13	2·16
150	1·66	1·98	2·23	2·00	2·73	2·20	2·27
200	1·76	2·07	2·29	2·12	2·83	2·30	2·37
250	1·86	2·16	2·35	2·23	2·93	2·37	2·44
300	1·96	2·26	2·44	2·35	3·04	2·50	2·59
350	2·07	2·36	2·52	2·46	3·14	2·60	2·69
400	2·19	2·48	2·67	2·60	3·25	2·78	2·83

crystal. One-term formulæ can, however, be obtained with a dispersion frequency at λ 1000. These formulæ are of the type

$$n_i^2 - 1 = a_i + \frac{b_i\,\lambda^2}{\lambda^2 - 0{\cdot}0100}, \tag{9}$$

where the constants a_i and b_i are given below. The fit is fairly good as seen from Table XIII:

Ray	a_i	b_i
α	0·1982	1·4362
β	0·1828	1·4549
γ	0·1361	1·5354

TABLE XIII

Wavelength		n_α (calc.)	n_α(obs.)	n_β (cal.)	n_β(obs.)	n_γ(calc.)	n_γ(obs.)
a	0·71890	1·6318	1·6318	1·6329	1·6329	1·6437	1·6437
C	0·65628	1·6337	1·6336	1·6347	1·6346	1·6456	1·6456
D	0·58959	1·6362	1·6361	1·6373	1·6373	1·6483	1·6484
F	0·48613	1·6425	1·6427	1·6442	1·6442	1·6551	1·6551
G	0·43079	1·6481	1·6481	1·6494	1·6494	1·6610	1·6607
H	0·39685	1·6528	1·6528	1·6542	1·6543	1·6660	1·6660

With such elementary formulæ, it is not possible to make a detailed analysis of the temperature coefficient in terms of oscillator transfer and changes in electronic frequencies. But one can obtain an idea of the magnitude of χ by forming the functions

$$f_i = 2n_i \frac{dn_i}{dt} + \gamma_t (n_i^2 - 1); \quad i = \alpha,\ \beta,\ \gamma \tag{10}$$

From Ramachandran's theory, the sum of these functions is

$$f_\alpha + f_\beta + f_\gamma = \frac{2\,(b_\alpha + b_\beta + b_\gamma)}{(\nu_0^2 - \nu^2)^2} \frac{\nu_0^4}{} \chi_t \tag{11}$$

and the transfer term becomes identically equal to zero. The values of χ_t obtained in this way are given in Table XIV:

TABLE XIV

Temp. (deg. C.)	$10^5\gamma_t$	$10^5\chi_t$
100	2·24	0·80
200	2·41	0·92
300	2·61	1·05
400	2·84	1·19

As usual, χ_t is found to increase with temperature.

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SUMMARY

The temperature coefficients of refraction of lithium fluoride, fluorspar, magnesia and quartz have been determined interferometrically for wavelengths between λ 2500 and λ 6000, from room temperature to 400° C. The values have been utilised, in conjunction with dispersion formulæ mostly proposed by the author, to calculate the temperature dependence of the ultra-violet frequencies, using Ramachandran's theory of thermo-optic behaviour. The theory is found to account successfully for the variation of *dn/dt* with wavelength and temperature. Similar results have been obtained in the visible region alone for the three refractive indices of barite.

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