RE-PRINTS

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Thermo-Optic behaviour of solids. I. Diamond. II. Fused Quartz. III. Flurospar
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THERMO-OPTIC BEHAVIOUR OF SOLIDS

I. Diamond

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1. Introduction

A STUDY of the temperature-variation of the refractive indices of solids is interesting from many points of view. On the experimental side, optical measurements are capable of very high precision and thus it is possible to obtain accurate data. Theoretically, a satisfactory theory of the variation has not been forthcoming so far. In fact, it is found that many crystals like rocksalt, fluorspar and quartz exhibit a diminution of their refractive indices for visible light on heating, while others like diamond (Sella, 1891) and zinc-blende (Maria Mell, 1923) show an increase. Also, some of the crystals of the former type show the reverse type of behaviour, namely an increase in the refractive index with temperature, in the extreme ultra-violet. An adequate theory of the phenomenon must be capable of explaining all these facts.

The experimental methods of measurement are also capable of improvement. The usual procedure in finding the variation of refractive index with temperature (dn/dt) is to determine the absolute index (n) at various temperatures and then to deduce dn/dt from these measurements. It would, of course, be much more accurate if one could devise a method in which dn/dt is directly measured as a function of temperature. Such a method has been designed by the author and is discussed fully in a later section of this paper. The method has been applied to the case of diamond and dn/dt has been measured over the range of temperatures from $-180°$ C. to $+450°$ C. for three wavelengths in the visible region.

A phenomenological theory of the temperature-variation of the refractive index has also been developed in this paper. It is based on the idea that the refractive index can be expressed in terms of the number of dispersion centres per unit volume and the polarisabilities of these centres. The latter again is dependent on the dispersion frequencies of the system. The variation in the refractive index of the solid can thus be represented

by two terms, one arising from the change in the number of dispersion centres and another from the variation in the spectral position of the dispersion frequencies. The idea is applied to the case of diamond in this paper and it is shown that the rate of change of the dispersion frequencies with temperature is correlated to the rate of change of other electronic and lattice frequencies observed for the crystal. The application of the formulæ to the case of fused silica enables one to calculate dn/dt over the whole spectral range, which are found to fit remarkably well with the experimental data. This will be reported in Part II of these series.

2. EXPERIMENTAL PROCEDURE

The principle of the method may be described as follows. One employs a plate of thickness l and obtains interference fringes by the light obtained from the two surfaces of the plate at normal incidence. (Either the transmitted or the reflected system may be employed.) The path difference between the two interfering beams is $x = 2nl$, where n is the refractive index. Suppose one measures the change in this path, Δx for a known change of temperature Δt. Then,

$$\Delta x/\Delta t = 2n . \Delta l/\Delta t + 2l . \Delta n/\Delta t,$$

so that

$$\frac{\Delta n}{\Delta t} = \frac{1}{2l} \cdot \frac{\Delta x}{\Delta t} - n \cdot \frac{1}{l}\frac{\Delta l}{\Delta t}$$

$$= (1/2l)(\Delta x/\Delta t) - n\alpha, \tag{1}$$

where α is the coefficient of linear expansion at temperature t. Thus, if α is known, then by measuring Δx and Δt, dn/dt can be accurately obtained. Of course, n has also to be known, but only to 3 significant figures for getting an accuracy of 1% and not 5 or 6 significant figures as are necessary with the usual prism methods. Another advantage of the interference methods is that the value of dn/dt obtained is for the absolute refractive index and that no corrections are required for the change in the index of air as is necessary with the prism methods.

In practice, two types of experimental arrangement can be visualised employing the above principle, one or the other being suitable for a particular case. Suppose that one is able to obtain plane-parallel plates of the specimen, as is for instance possible with mica. It is best in this case to form Haidinger rings with monochromatic light with the plate kept in a suitable furnace. When heated, the rings expand or contract and a measurement of the expansion or contraction gives one the alteration in path. One method of obtaining $\Delta x/\Delta t$ is to accurately measure Δx for

a known difference of temperature Δt. But if one is interested in measuring dn/dt over a whole range of temperatures it is much more convenient to make a continuous observation. The temperature of the furnace is raised steadily at a very slow rate and the temperature corresponding to the passage of successive fringes across a fiduciary cross-wire can be noted.

If optically parallel plates are not available, another method can be used, which was in fact employed with diamond in the present experiment. The crystal used for the purpose was N.C. 73 from the collection of Sir C. V. Raman, which was a rectangular plate with a thickness of 0·670 mm. The surfaces of the plate were deposited with a thin layer of aluminium by the evaporation process in order to increase the reflecting power. When viewed by transmission in a parallel beam of monochromatic light, localised interference fringes were observed, which consisted of sharp bright almost circular rings. These were produced because of the variations in the thickness of the specimen. A fine line on the surface of the crystal formed a reference mark across which the fringes shifted as the crystal was heated. It may be mentioned that this method of observation is the same as was employed by the author in determining variations of the absolute path of a ray of light through the crystal plate for calculating the photo-elastic constants of diamond (Ramachandran, 1947).

The diamond was kept in a suitable furnace and the fringes were observed by means of a microscope. The continuous observation method mentioned in connection with the Haidinger rings was employed with these fringes also. The rate of heating was so slow that it took 6 hours to heat the crystal from room temperature to 400° C. The temperature was measured by a standardised thermocouple and the readings of the measuring instrument were such that an accuracy of $\pm 1°$ C. could be obtained even at the highest temperatures. The experiments were performed with three different wavelengths, viz., the 4358 and 5461 Å.U. radiations of the mercury arc and the yellow radiations of 5893 Å.U. from the sodium lamp. In the first case, more than 40 fringes shifted across the reference mark in heating from room temperature to 400° C. and in the last, nearly 30. The observations were repeated with the cooling crystal, this also taking roughly 6 hours. The temperature readings taken during heating and cooling never differed by more than one unit in the last decimal place, i.e., nearly 1° near about 400° C. and less at lower temperatures. For each wavelength, the experiments were also repeated reversing the positions of the source of light and of the observing microscope. This was done in order to correct for any movement of the crystal or of the whole furnace due to heating. Actually, no difference could be noticed between the two readings. Six

independent experiments were performed with each wavelength and the finally calculated values were the means of these.

The values of α at various temperatures were available from the measurements of R. S. Krishnan (1946 a). Knowing Δt corresponding to each wavelength shift, dn/dt was calculated for the mean temperature t. When these values were plotted and a smooth curve drawn through them, it was found that the points appreciably diverged from the mean. This was obviously due to the restricted accuracy of the temperature measurement. Consequently, the values of dn/dt were later calculated from the temperature difference corresponding to a shift of 3, 4 or 5 fringes. These fell very well on a smooth curve, as will be seen from the curves reproduced in Fig. 1. Here, the continuous curves represent the mean value of all the experiments for each wavelength. The points denote the values from a single experiment calculated in the above manner.
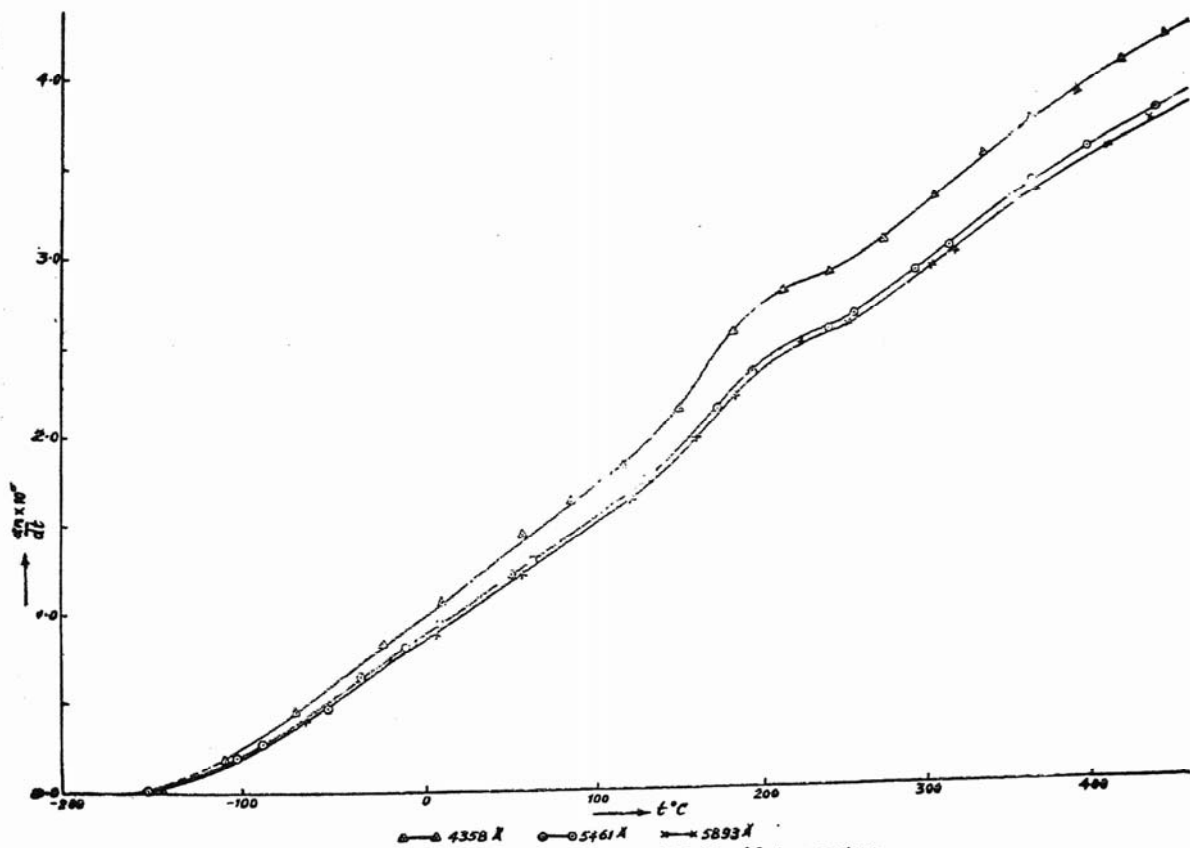

FIG. 1. Curves showing the variation of dn/dt with temperature.

The measurement of *dn/dt* was also made for temperatures down to — 180° C. Here, the accuracy was not as high as at higher temperatures, since the rate of variation was small and only 4 fringes shifted over the whole range and also since measurement could be made only during warming and not during cooling. *dn/dt* was calculated from the temperature difference for the shift of one fringe at a time. The crystal was kept in a copper block which was screwed on to the bottom of a brass tube in which was kept liquid air. The tube with the crystal was enclosed in an outer jacket of glass and the intervening space was kept evacuated. The thermocouple was kept in intimate contact with the bottom of the brass tube. The whole arrangement was first cooled to the temperature of liquid air and then allowed to warm up. It took nearly 3 hours for the system to attain the room temperature. During this period, temperatures were measured corresponding to the passage of each fringe across the reference mark. It was noticed that upto about — 150° C. or so there was no shift at all of the fringes, showing that the rate of variation of the refractive index was extremely small at these temperatures.

An obvious disadvantage of the method described here is that it is not very convenient for work in the ultra-violet; but this may be remedied by the use of photography. The method is, however, particularly useful when one requires to find *dn/dt* accurately over a range of temperatures.

3. RESULTS OF THE EXPERIMENT

The experimental values of *dn/dt* at various temperatures for the three wavelengths are shown by the continuous curves in Fig. 1. The values read off from these ($\times 10^5$) are shown in Table I and will be useful for reference. These are probably accurate to 1%.

TABLE I

$t°$ C.	4358	5461	5893	$t°$ C.	4358	5461	5893
−150	0·02	0·01	0·01	160	2·33	2·04	2·00
−140	0·05	0·03	0·03	180	2·60	2·26	2·22
−120	0·13	0·10	0·09	200	2·78	2·45	2·41
−100	0·24	0·21	0·19	220	2·88	2·57	2·53
− 80	0·38	0·32	0·30	240	2·96	2·66	2·62
− 60	0·53	0·45	0·43	260	3·06	2·76	2·72
− 40	0·68	0·59	0·57	280	3·20	2·88	2·84
− 20	0·83	0·73	0·70	300	3·35	3·03	2·98
0	0·99	0·87	0·84	320	3·50	3·17	3·12
20	1·14	1·01	0·98	340	3·65	3·30	3·25
40	1·29	1·15	1·12	360	3·80	3·43	3·38
60	1·44	1·29	1·26	380	3·94	3·56	3·50
80	1·59	1·43	1·40	400	4·08	3·68	3·62
100	1·75	1·57	1·54	420	4·20	3·80	3·74
120	1·91	1·71	1·68	440	4·31	3·91	3·84
140	2·07	1·85	1·82				

The most interesting fact that comes out of the investigation is that dn/dt is positive for diamond over the whole range of temperatures. This has been observed by Sella (*loc. cit.*) from room temperature to 90° C. His value of $+1 \cdot 86 \times 10^{-5}$ for a mean temperature of 50° C. and 5893 Å.U. is however too large, the present experiment indicating a value of about $+1 \cdot 20 \times 10^{-5}$. It is found that dn/dt is extremely small for temperatures below $-150°$ C. and that it increases practically linearly with temperature from about $-100°$ to 450° C. However, a slight hump is observed in the graph of dn/dt *vs.* t in the neighbourhood of 210° C., as may be seen from Fig. 1. Very accurate and repeated sets of readings have been taken in this range of temperatures and it has been verified that the hump is a genuine effect. The deviation of dn/dt is however only of the order of 10%. In fact when the values of n calculated from the data for dn/dt are plotted against t, it is practically impossible to detect the kink in the curve, even when plotted on a highly magnified scale. The author is not in a position to give a definite explanation for the hump at 210° C. It may however be pointed out that a similar variation, though in a much more pronounced manner, is shown by the refractive index of fused silica in the neighbourhood of 575° C., the temperature of $\alpha-\beta$ transformation of quartz. Here, the kink is observable in the graph of refractive index against temperature. It is not clear what kind of transformation, if any, occurs in diamond near about 200° C. It has however been observed (Chandrasekharan, 1946) that diamond exhibits very bright thermoluminescence at about this temperature. Similarly, Nayar (1941) found that the intensity of luminescence diminishes rapidly at these temperatures and practically vanishes at 300° C. The particular diamond that was studied exhibited a feeble blue luminescence. It would be interesting to repeat the dn/dt measurements with highly luminescent and non-luminescent diamonds to discover if the magnitude of the hump has any relation to luminescence. Another interesting fact is that a particularly low value for the Raman frequency of diamond has been observed near this temperature (R. S. Krishnan, 1946*b*). In Fig. 1 of this reference, it will be noticed that the two values at temperatures 213° C. and 242° C. fall well below the continuous curve through the other points.

Leaving aside such minor differences, it has been calculated that the refractive index of diamond n_t at temperature t can be represented by a formula of the type

$$n_t = n_0 (1 + \alpha t + \beta t^2) \qquad (2)$$

from about $-100°$ C. to 400° C. The values of α and β for the three wavelengths studied are given in Table II.

TABLE II

Wavelength Å. U.	$\alpha \times 10^6$	$\beta \times 10^8$
4358	9·9	7·8
5461	8·7	7·0
5893	8·4	7·0

4. THEORY OF THE THERMAL VARIATION OF REFRACTIVE INDEX

Pockels (1902) has recognized that the rate of change of refractive index with temperature (dn/dt) can be divided into two parts, namely, a pure temperature change which we may denote by $\partial n/\partial t$ and another part due to the change in density which accompanies the temperature change, $(\partial n/\partial \rho)_t \cdot d\rho/dt$. Thus,

$$\frac{dn}{dt} = \left(\frac{\partial n}{\partial \rho}\right)_t \cdot \frac{d\rho}{dt} + \left(\frac{\partial n}{\partial t}\right)_\rho = A + B \text{ say} \tag{3}$$

Of these, the quantity A may be calculated from photo-elastic data. For a cubic crystal,

$$A = -\frac{2}{n^3} \cdot \frac{(p_{11} + 2p_{12})}{3} \cdot \gamma, \tag{4}$$

where γ is the coefficient of cubic expansion and p_{11} and p_{12} are the elasto-optic constants. The same relation is true for isotropic solids like glasses, while similar relations hold for crystals of other classes. When A is actually calculated in this manner, it is found that it is not in general equal to dn/dt. Pockels, in the paper cited above, has shown that A is always algebraically less than dn/dt so that B is a positive quantity for a number of glasses of varying composition. In Table III below, dn/dt, A and B are given for a number of crystals. The data have been collected from the *Handbuch der Physik*, Vol. XXI, 1929, Ch. 19, except for diamond for which the data are taken from a paper by the author (1947).

TABLE III

Substance		$dn/dt \cdot 10^6$	$A \cdot 10^6$	$B \cdot 10^6$
Rocksalt	..	−37·4	−37·2	− 0·2
Fluorspar	..	−12·1	−13·5	+ 1·4
Quartz–ord	..	− 6·50	−12·80	+ 6·30
,, −ext	..	− 7·54	−14·10	+ 6·56
Calcite–ord	..	+ 0·69	− 8·9	+ 9·6
,, −ext	..	+10·57	− 1·9	+12·5
Topaz–α	..	+ 8·1	− 0·38	+ 8·5
,, −β	..	+ 9·0	− 0·713	+ 9·7
,, −γ	..	+ 8·0	− 0·684	+ 8·7
Diamond	..	+10·5	+ 3·8	+ 6·7

It will be seen that, in all the cases except rocksalt, B is positive. Even for rocksalt one cannot say that the negative value, which is less than 1% of the observed dn/dt is not spurious. We may thus say that, in general, *crystals and glasses exhibit a pure thermal coefficient of variation of refractive index which is positive.*

This picture does not however go deep enough into the problem except for separating the density and temperature effects. In fact, one can give a quantitative theory of the thermo-optic behaviour by considering the dispersion of solids and its origin. It has been the attempt of many workers to fit the dispersion data of solids into a formula of one of the following types :—

$$n^2 = C' + \Sigma_r A_r/(\lambda^2 - \lambda_r^2) - K\lambda^2 \tag{5}$$

$$n^2 = C + \Sigma_r B_r \lambda^2/(\lambda^2 - \lambda_r^2) - K\lambda^2 \tag{6}$$

where the term $K\lambda^2$ may sometimes be absent. These two forms are really equivalent and can be converted one into the other by merely changing the constants. Also, the last term arises from the presence of an infra-red frequency or frequencies whose positions are not known, so that in general we may write (6) in the form

$$n^2 = C + \Sigma_r a_r \lambda^2 \lambda_r^2/(\lambda^2 - \lambda^2) = C + \Sigma_r a_r/(\bar{\nu}_r^2 - \bar{\nu}^2) \tag{7}$$

where $\bar{\nu}$ is the wave number of a radiation of wavelength λ. Now, the Ketteler-Helmholtz theory (and also the more recent Kramers-Heisenberg theory) of dispersion leads to a formula of the type

$$n^2 = 1 + \Sigma_r a_r/(\nu_r^2 - \bar{\nu}^2) \tag{8}$$

where all the dispersion frequencies are taken into account. Usually, the empirical formula is derived from observations in the ultra-violet, visible and infra-red regions of the spectrum. If there is a dispersion frequency in the remote ultra-violet, it will contribute a constant term to the right-hand side of the formula, which will then be of the type (7). We shall, however, consider only a formula of the type (8) in our theory since it is of the most general type. It is obvious that the quantities a_r in the numerator are proportional to the number of dispersion centres per unit volume and to the oscillator strength of each centre.

Now, if such a formula is true for a particular temperature, then a similar formula with slightly different constants must hold for a slightly different temperature, so that one can obtain an expression for dn/dt by

differentiating these expressions with respect to t. One thus obtains from (8)

$$2n \frac{dn}{dt} = \sum_r \left[-\frac{2a_r \bar{\nu}_r}{(\bar{\nu}_r^2 - \bar{\nu}^2)^2} \frac{d\nu_r}{dt} + \frac{1}{(\bar{\nu}_r^2 - \nu^2)} \cdot \frac{da_r}{dt} \right] \tag{9}$$

Since a_r is proportional to ρ, the density of the substance, $da_r/dt = (a_r/\rho) \cdot (d\rho/dt) = - a\gamma$, where γ the coefficient of cubical expansion.* Thus, the second term in the right-hand side of (9) becomes

$$\sum_r - \gamma \cdot a_r/(\bar{\nu}_r^2 - \bar{\nu}^2) = - \gamma (n^2 - 1) \qquad \text{from (8)}.$$

$$\frac{dn}{dt} = - \frac{\gamma (n^2 - 1)}{2n} - \frac{1}{n} \sum_r \frac{a_r \bar{\nu}_r}{(\bar{\nu}_r^2 - \bar{\nu}^2)} \cdot \frac{d\bar{\nu}_r}{dt} \tag{10}$$

This is a general expression for dn/dt in terms of known constants of the substance. $\bar{\nu}_r$ is known from the dispersion formula, but $d\bar{\nu}_r/dt$ is not known in many cases. But it may be calculated from the values of dn/dt for a particular wavelength and then formula (10) can be verified to hold over the whole range of wavelengths. It will be convenient to express $d\bar{\nu}_r/dt$ in the form $- \chi_r \bar{\nu}_r$, where χ_r is just a constant expressing the rate of change of wavenumber as so many per wavenumber of the dispersion frequency. It may be noted that χ_r is also equal to $(1/\lambda_r) (d\lambda_r/dt)$. Then,

$$\begin{aligned} \frac{dn}{dt} &= - \frac{\gamma (n^2 - 1)}{2n} + \frac{1}{n} \sum_r \frac{a_r \bar{\nu}_r^2}{(\bar{\nu}_r^2 - \bar{\nu}^2)^2} \chi_r \\ &= - \frac{\gamma (n^2 - 1)}{2n} + \frac{1}{n} \sum_r \frac{a_r \lambda^4 \lambda_r^2}{(\lambda^2 - \lambda_r^2)^2} \chi_r \end{aligned} \right\} \tag{11}$$

In this expression, dn/dt has been split up into two parts, one due to a change in the number of dispersion centres per unit volume and another due to the changes in the dispersion frequencies. We may denote these by P and X respectively. The term X arises from the change in the dispersion frequency with temperature; but it is not at all necessary that this change should be a pure temperature effect. It is necessary to distinguish between the change that is produced by the accompanying change in volume (or density) and the change due to temperature alone. In symbols,

$$\mathbf{X} = \frac{\partial n}{\partial \bar{\nu}} \cdot \frac{\partial \bar{\nu}}{\partial v} \cdot \frac{\partial v}{dt} + \frac{\partial n}{\partial \bar{\nu}} \cdot \frac{\partial \bar{\nu}}{dt}$$

$$= \mathbf{Q} + \mathbf{R} \text{ (say)} \tag{12}$$

Obviously, P arises completely from the change in density, so that one gets immediately,

$$\mathbf{A} = \mathbf{P} + \mathbf{Q}, \qquad \mathbf{B} = \mathbf{R} \tag{13}$$

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* This implies the assumption that the oscillator strengths, *i.e.*, the transition probabilities of the dispersion centres, do not alter with temperature.

These considerations are, of course, purely formal, but they are yet interesting. It is seen that one has to take into account a possible shift of the dispersion frequencies even to explain the alteration of refractive index with pressure. The shift of the frequencies with pressure is not negligible. In fact, for diamond at 25° C. and 5893 Å.U., we have from (11) $P = -3 \cdot 1 \times 10^{-6}$ and combining this with the data in Table I, we have

$$P = -3 \cdot 1 \times 10^{-6}, \quad Q = +6 \cdot 9 \times 10^{-6}, \quad R = +6 \cdot 7 \times 10^{-6} \tag{14}$$

Here, the shift in frequency, due to the change in volume is as much as that due purely to change of temperature.

The considerations put forward above refer strictly only to the behaviour of cubic crystals or of isotropic bodies. In other crystals, the linear thermal expansion is not the same in all directions and the refractive indices in different directions are influenced differently. We shall not go into these questions in this paper.

5. DISCUSSION OF THE RESULTS OBTAINED WITH DIAMOND

We shall now apply the considerations put forward in the previous section to the case of diamond. The dispersion of diamond can be represented by the formula

$$n^2 - 1 = \sum_{1, 2} \frac{a_r \lambda_r^2 \lambda^2}{\lambda^2 - \lambda_r^2}, \quad \begin{aligned} a_1 &= 3 \cdot 859 \times 10^{10}, \quad a_2 = 1 \cdot 080 \times 10^9 \\ \lambda_1 &= 1060 \text{ Å.U.,} \quad \lambda_2 = 1750 \text{ Å.U.} \end{aligned} \tag{15}$$

(Peter, 1923). Consequently, dn/dt is given by Eq. (11). It will be noticed that both the dispersion frequencies are in the extreme ultra-violet and that one of them at 1060 Å.U. is nearly 40 times as strong as the other at 1750 Å.U. We shall make the assumption that $\chi_1 = \chi_2$, in other words that both of them vary in proportion to their frequencies. It will be seen presently that this assumption is not unjustified. Besides, since λ_2 is very weak, slight differences in the value of χ_2 will not matter. Thus, putting $\chi_1 = \chi_2 = \chi$ its value calculated from the measurements of dn/dt for the green and yellow radiations comes out to be $7 \cdot 6 \times 10^{-6}$ at 50° C. It is interesting to note that this is of the same order as the value of χ for the fundamental lattice vibration of 1332 cm.$^{-1}$. From the data of R. S. Krishnan (1946 b), it has been calculated that χ at 50° C. is $9 \cdot 8 \times 10^{-6}$ for this frequency. It is thus found that the rate of variation of the ultra-violet dispersion frequencies is nearly the same as that of the lattice frequency in the infra-red provided the rate is taken as so many wave-numbers per wave-number per degree. In fact, this behaviour is exhibited by practically all the electronic lines found in the absorption and emission spectrum of diamond. In Table III the wavelengths of various such lines are given both at liquid air and room

temperatures and the total change is calculated and given as so many wavenumbers per 1000 wavenumbers (1000 $\Delta \bar{v}/\bar{v}$) in the third column.

TABLE IV

λ at liquid air temperature	λ at room temperature	1000 $\Delta\bar{v}/\bar{v}$	Reference
Disperson	Frequencies	0·6	This paper
2306	2308	0·9	
2309	2312	1·3	K. G. Ramanathan (1946)
2355·9	2359	1·3	
2360	2364	1·8	
3034	3037	1·0	
3064	3067	1·0	
3154	3157	1·0	Robertson, Fox and Martin (1934)
3201	3204	1·0	
3298	3302	1·3	
3447	3450	0·83	
4152	4156	0·83	
5032	5038	1·2	
5115	5123	1·6	
5198	5204	1·2	
5286	5292	1·1	A. Mani (1944)
5359	5367	1·5	
5451	5455	0·7	
5695	5701	1·0	
5758	5768	1·7	
1333·2cm.$^{-1}$	1331·8cm.$^{-1}$	1·1	R. S. Krishnan (1946 b)

The approximate constancy of the numbers in the third column is significant. It shows that the behaviour of the electronic lines is similar to that of the lattice frequency. This is not surprising when one remembers that the electronic lines arise from transitions of the very electrons that are responsible for the binding forces in the lattice.

The refractive indices at various temperatures were calculated from the data for dn/dt by numerical integration assuming the values at 20° C. given by Peter (loc. cit.). In Fig. 2 the course of the refractive index-temperature curve has been plotted from these calculations. It will be noticed that the refractive index does not at all change at very low temperatures. In fact below — 100°, the change does not even amount to one unit in the fourth decimel place, which is the accuracy to which absolute indices are known. Extrapolating to the absolute zero and taking Peter's value for the refractive indices at 20° C., the indices at absolute zero for the three wavelengths have been calculated to be

2·4490 at λ 4358, 2·4225 at λ 5461, 2·4165 at λ 5893.

An attempt was made to calculate the course of the refractive index-temperature curves, assuming that the dispersion frequencies vary in the
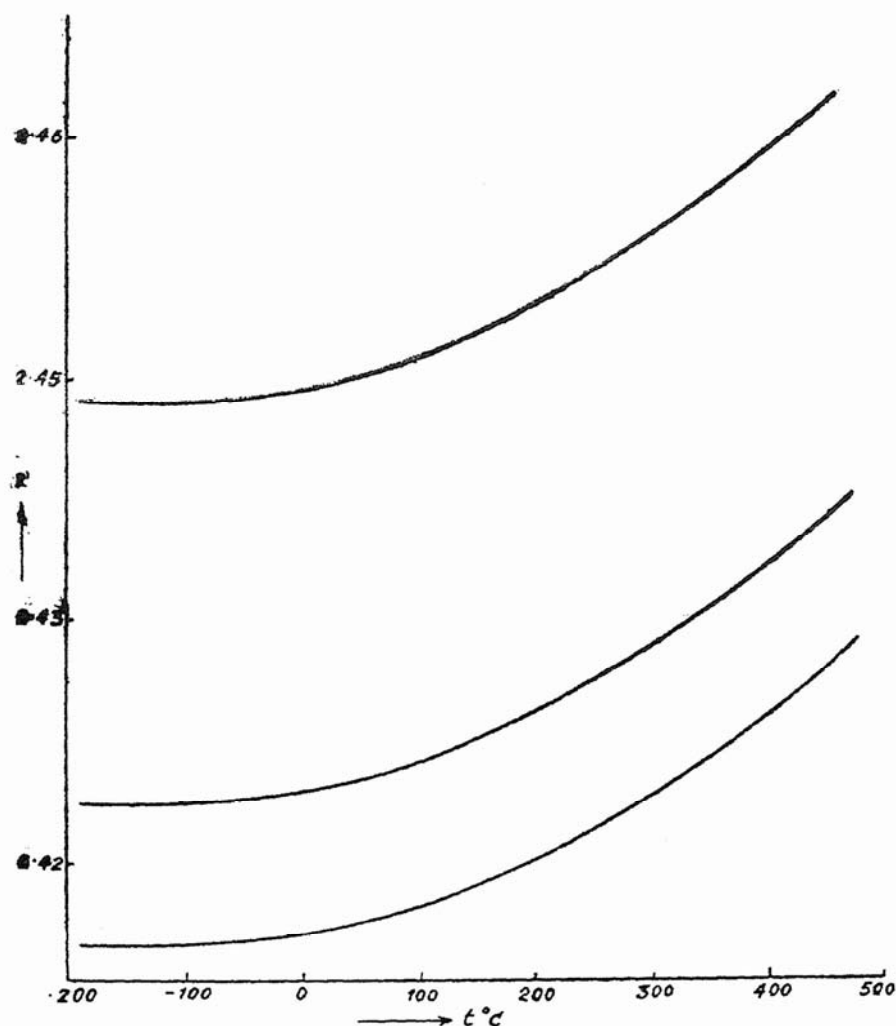

FIG. 2. The variation of refractive index of diamond with temperature. The three curves are from top to bottom for wavelengths 4358, 5461 and 5893 A.U. respectively.

same way as (a) the lattice frequency or (b) the electronic line at 4152 Å.U. Data for the temperature variation of these are available from R. S. Krishnan (1946 b) and P. G. N. Nayar (1941) respectively. The experimental values of $(n_t - n_{25})$ are shown along with those calculated from assumptions (a) and (b) in Table V below. It will be seen that although the general trend of the curve is shown by the calculated values, the numerical agreement with experiment is not very satisfactory. This only shows that the variation with temperature of the dispersion frequency does not exactly follow that of the lattice frequency or the other electronic frequency at 4152 Å.U. although it is of the same order.

TABLE V

Temperature °C.	−180	25	100	200	300	400
$n_t - n_{25}$ (Exp.) ..	−0·0008	0	+0·0009	+0·0026	+0·0055	+0·0098
do from (a)..	−0·0021	0	+0·0015	+0·0038	+0·0063	+0·0082
do from (b)..	−0·0014	0	+0·0017	+0·0052	..	..

It was mentioned above that χ was found to be $7\cdot6 \times 10^{-6}$ at $50°$ C. A recalculation of dn/dt from this value of χ showed that it fitted with experimental values for 5893 and 5461 Å.U., but was too small for 4358 Å.U. The calculated values were $1\cdot20$, $1\cdot22$ and $1\cdot27 \times 10^{-6}$, while experiment gave values of $1\cdot19$, $1\cdot22$ and $1\cdot36 \times 10^{-6}$ respectively for the three wavelengths. The author is of the opinion that the discrepancy for 4358 Å.U. is due to the presence of a weak absorption at 4156 Å.U. in the diamond. It may be pointed out that on account of its proximity, the contribution to dn/dt by this frequency at 4358 Å.U. is nearly 20 times those at 5461 and 5893 Å.U. It will be interesting to see whether the discrepancy is larger with a diamond having a stronger absorption at 4156 Å.U. and also to actually detect the presence of anomalous dispersion of refractive index near this wavelength.

My sincere thanks are due to Prof. Sir C. V. Raman for the kind interest that he took in the investigation and for the many discussions I had with him.

SUMMARY

A phenomenological theory has been put forward for the variation of the refractive indices of solids with temperature, based on the idea that the refractive index can be expressed in terms of the number of dispersion centres and the polarizabilities of these centres, which are again dependent on the dispersion frequencies. The refractive index variation can then be represented as the sum of two terms, one arising from the change in the number of dispersion centres and the other from the variation of the frequencies. Accurate data of the thermal variation of the refractive index of diamond have been obtained for the first time from − 180° C. to 450° C. for three wavelengths, 4358, 5461 and 5893 Å.U. A new method was employed for this purpose which measures dn/dt directly and is capable of general application. When applied to diamond, the theoretical ideas bring out the interesting fact that the rate of change of the dispersion frequencies with temperature is correlated to the rate of change of the fundamental lattice frequency of the crystal.

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THERMO-OPTIC BEHAVIOUR OF SOLIDS

II. Fused Quartz

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1. INTRODUCTION

IN Part I of these series, some general considerations were put forward indicating how a phenomenological theory can be developed for the variation of refractive indices of solid substances with temperature. In this paper, a quantitative application of the theory is made to the case of fused quartz. It is shown that the theory can account satisfactorily for the variation of the refractive index with temperature over the whole spectral range from the extreme ultra-violet up to the red, and also for the course of the refractive index-temperature curve for a particular wavelength.

Fused quartz is particularly interesting in these studies because its thermal coefficient of expansion is extremely small. As is well known, the density of quartz falls down on fusing, but thereafter, it undergoes very little change with temperature when the vitreous silica is heated or cooled. Consequently, the variation of refractive index with temperature is mainly caused by the variation in the dispersion frequencies, the contribution due to the variation in the number of dispersion centres being comparatively small. On the analogy of the result obtained with diamond, one may assume that the dispersion frequencies of silica also move to increasing wavelengths with rise of temperature. This has in fact been verified for the lattice frequencies (Nedungadi, 1940). Then, the contribution to dn/dt by this cause is positive and since the volume change is small, the negative contribution to dn/dt from this cause will be much smaller than the positive component. Consequently, one would expect that vitreous silica would exhibit a resultant positive dn/dt. This is in fact found to be the case over the whole spectrum (Sosman, 1927).

In crystalline quartz, on the other hand, the thermal expansion is appreciable, and there is the possibility of the negative component of dn/dt being the larger one. In fact, both the ordinary and extraordinary indices

of α-quartz diminish with rise of temperature in the visible and near ultra-violet (Sosman, *loc. cit.*). In the far ultra-violet they increase with rise of temperature, since the positive component of *dn/dt* becomes large owing to the approach to the dispersion frequencies.

2. CALCULATION OF THE THERMAL VARIATION OF REFRACTIVE INDEX FOR DIFFERENT WAVELENGTHS

The dispersion of vitreous silica has been studied by Martens and Micheli (1904) who have fitted their data to the following formula with one dispersion frequency in the ultra-violet:

$$n^2 = 1 \cdot 36112 + 0 \cdot 74655 \, \lambda^2/\lambda^2 - (0 \cdot 107044)^2 - 0 \cdot 01350\lambda^2 \qquad (1)$$

the wavelength being expressed in microns. The author has verified that this formula fits the refractive index data from 1850 Å.U. to 6500 Å.U. It may be noticed that the dispersion frequency is at 1070 Å.U., which is very close to that used for crystalline quartz by other workers (Cocde-Adams, 1928; Radhakrishnan, 1947). In the work of Radhakrishnan, two frequencies at 1060 Å.U. and 1190 Å.U. are employed, the latter being much weaker. These frequencies have actually been observed for quartz by Tousey (1940) as reflection maxima analogous to the *Reststrahlen* in the infra-red. For fused quartz, Tousey (*loc. cit.*) found two bands in very nearly the same positions as for crystalline quartz, but very much broader. Considering the relative strengths of the two frequencies, the representation of their total effect at regions of the spectrum not close to them by a single term employing a frequency of 1070 Å.U. appears justifiable. The infra-red term in the above formula (1) is represented by a term of the type $-K\lambda^2$ and does not explicitly involve the frequency. However, there are reasons to believe that none of the frequencies in the infra-red are nearer than 8μ. In the dispersion formula of quartz (Rubens and Nichols, 1897; Radhakrishnan, *loc. cit.*), there is a weak term with the dispersion wavelength in the neighbourhood of 8μ and a strong one at about 21μ. Upto 8μ, the absorption of fused quartz follows very closely that of crystalline quartz, except that the peaks are broader (Drummond, 1936). Also, the Raman spectrum of fused quartz exhibits a great similarity to that of crystalline quartz, the lines in the latter being replaced by broad bands in the former (Gross and Romanova, 1929; Kujumzelis, 1935). These show that the infra-red dispersion wavelength λ_2 of vitreous silica is not less than 8μ. Using a value of $\lambda_2 = 8\mu$ and 12μ, it has been calculated that its contribution to *dn/dt* over the range of wavelengths we are interested in is extremely small compared with that of the ultra-violet frequency and that the contribution progresssively diminishes as λ_2 is taken further away in the infra-red. One

need not therefore be disturbed at the non-occurrence of λ_2 explicitly in the dispersion formula.

Eq. (1) may be put in the form

$$n^2 = C + a_1\lambda_1{}^2 \lambda^2/(\lambda^2 - \lambda_1{}^2) - K\lambda^2 \tag{2}$$

where $C = 1\cdot36112$, $a_1\lambda_1{}^2 = 0\cdot74655$, $\lambda_1 = 0\cdot107044$, $K = 0\cdot01350$.

Differentiating (2) with respect to t, and putting $da/dt = -\gamma a$,

$$\frac{dn}{dt} = -\frac{\gamma}{2n}\frac{a_1\lambda_1{}^2\lambda^2}{(\lambda^2 - \lambda_1{}^2)} + \frac{1}{n}\frac{a_1\lambda_1{}^2\lambda^4}{(\lambda^2 - \lambda_1{}^2)^2}\chi + \frac{1}{2n}\frac{dC}{dt} \tag{3}$$

where χ and γ have the same significance as in Part I, viz., $\chi = (1/\lambda_1)\,(d\lambda_1/dt)$ and γ is the coefficient of cubical expansion. The only unknown quantities in the right-hand side of (3) are χ and dC/dt, which we may denote by β.

Measurements of dn/dt for fused silica at a mean temperature of 60° have been made by Martens (1904) for a series of wavelengths from 1850 Å.U. to 6000 Å.U. Using any two measurements, χ and β can be calculated and then the values of dn/dt for a series of wavelengths can be calculated. In this way, the continuous curve in Fig. 1 has been plotted showing
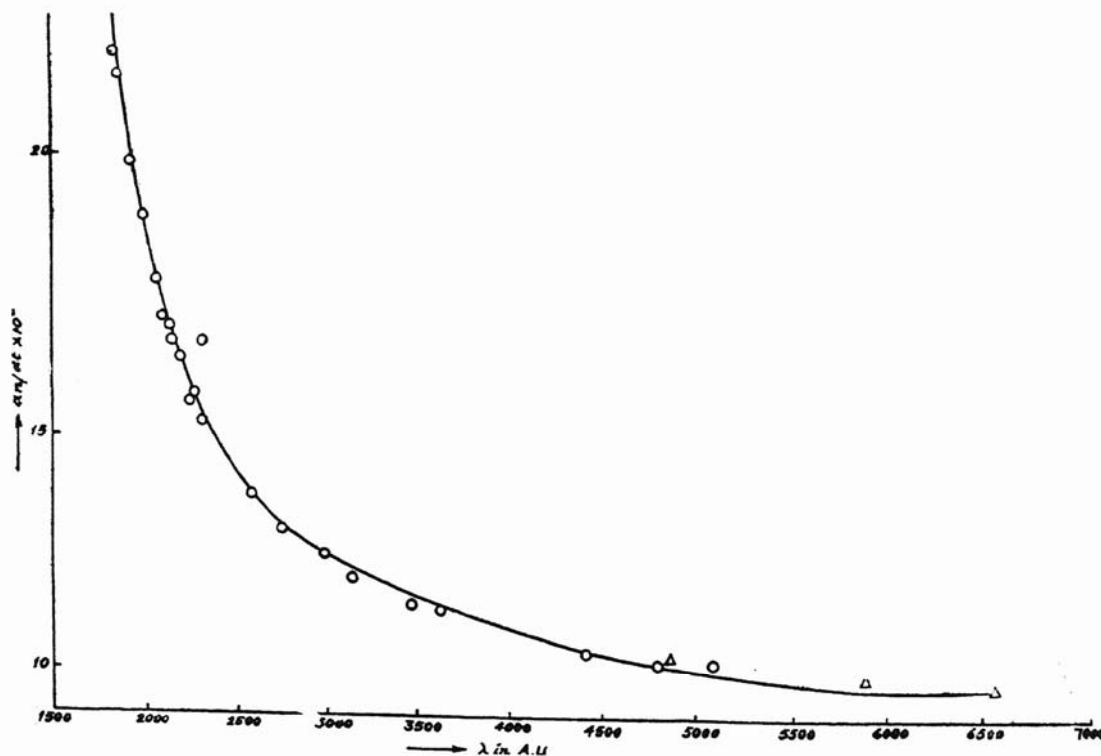

FIG. 1. Variation of dn/dt with wavelength

how dn/dt would vary with wavelength according to theory. The values used for χ and β were $\chi = 24 \cdot 77 \times 10^{-6}$ and $\beta = -10 \cdot 8 \times 10^{-6}$. The circles in Fig. 1 represent the experimental data of Martens (*loc. cit.*). The triangles represent the data of Tilton and Tool (1929). It will be seen that the theoretical curve fits the data well over the whole range of wavelengths.

3. CALCULATION OF THE COURSE OF THE REFRACTIVE INDEX-TEMPERATURE CURVE

As in the case of diamond, one may attempt to compare the value of χ for the dispersion frequency with that for other characteristic frequencies. As already mentioned, the Raman spectrum of fused quartz consists of broad bands but in general these bands are in the same positions as the sharp lines in the Raman spectrum of crystalline quartz. For α-quartz, the sharp and intense line at 465 cm.$^{-1}$ stands out prominently in the Raman spectrum. The variation of the frequency of this line with temperature has been studied by Nedungadi (1940) from $-180°$ upto $500°$ C. From his data, χ at $60°$ C. has been calculated to be $3 \cdot 2 \times 10^{-5}$. It is seen that this is of the same order as the value of χ for the dispersion frequency of fused quartz. In fact, the latter is 77% of the former.

One may attempt an extrapolation and assume that this relation between the χ's of the two frequencies is true at other temperatures, *i.e.*, that the proportionate change in frequency of the 1070 Å.U. band of fused quartz is $0 \cdot 77$ times that of the 465 cm.$^{-1}$ line in crystalline quartz. Then, it is possible to calculate the variation of refractive index with temperature over a range of temperatures, using (3). Here, γ is known at various temperatures and χ can be calculated from the above assumption. For dC/dt, some further consideration is necessary. As mentioned in Part I, the term C arises from the constant contribution to refraction of frequencies in the very remote ultra-violet. dC/dt thus arises from the variation in the number of centres and frequency in this term. It may be shown that the contribution to dn/dt due to a dispersion frequency at wavelength λ_ν, where $\lambda_\nu << \lambda$ is $(a_\nu \lambda_\nu^2/n)(\chi_\nu - \gamma/2)$. Since dC/dt is negative, it follows that χ_ν is less than $\gamma/2$ *i.e.*, less than $0 \cdot 6 \times 10^{-6}$ at $60°$ C. Thus χ_ν is less than 2% of the value of χ for the 1070 Å.U. dispersion frequency. This is not unexpected for these remote ultra-violet frequencies arise from transitions of the inner electrons and are not likely to change with temperature. In calculating dC/dt therefore χ_ν was put equal to zero and dC/dt was taken to vary as γ.

If Δn is the change in refractive index for a change of temperature Δt, then from (3) one has

$$\Delta n = \left[-\frac{1}{2n} \cdot \frac{a_1 \lambda_1^2 \lambda^2}{(\lambda^2 - \lambda_1^2)} \cdot \frac{\Delta V}{V} + \frac{1}{n} \cdot \frac{a_1 \lambda_1^2 \lambda^4}{(\lambda^2 - \lambda_1^2)^2} \cdot \frac{\Delta \bar{v}}{v} + \frac{1}{2n} \frac{dC}{dt} \right] \Delta t \quad (4)$$

Δn was calculated successively between the temperatures — 150°, 0°, 150°, 300° and 450°. $\Delta V/V$ was calculated from the data on thermal expansion. $\Delta \bar{v}/\bar{v}$ was taken to be 0·77 times the corresponding value for the Raman line 465 cm.⁻¹, which was determined from Nedungadi's data (*loc. cit.*). Since the accuracy of these data was only 1 cm.⁻¹, a smooth curve was drawn through them and the change in the wave-number determined from the curve. The change from the value at 0° to various temperatures found in this way were: for — 150°, — 1·9 cm.⁻¹; 150°, 2·5 cm.⁻¹; 300°, 5·3 cm.⁻¹;
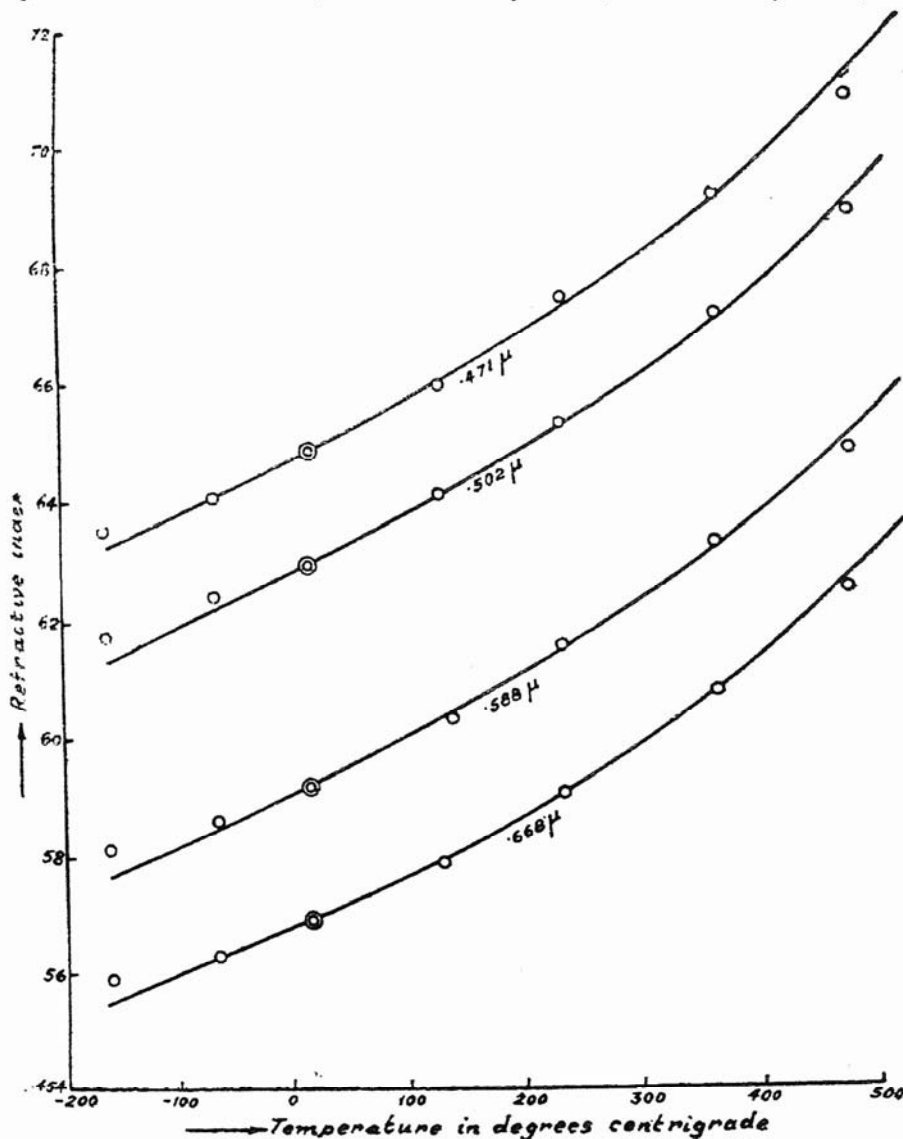

FIG. 2. Refractive index-temperature curves for four wavelengths. The continuous curves are from theory and the circles represent the experimental data.

450°, 8·7 cm.$^{-1}$ The last term was calculated with the assumption just mentioned. In this way, refractive index-temperature curves have been computed and plotted as continuous curves in Fig. 2 for four wavelengths. Experimental data for these are available from the work of Rinne (1914) computed to absolute indices by Sosman (*loc. cit.*). These are shown by circles in Fig. 2. The theoretical curves have in every case been made to pass through the measured value at 18° C. It will be seen that the theory fits the data for higher temperatures upto 500° C. Below 0° C., however, theory gives systematically a lower value than experiment. The discrepancy may be due to the fact that the dispersion frequency varies less in proportion to the infra-red frequency than the ratio 0·77 at these temperatures. It may be mentioned that the error may also be partly due to the fact that Nedungadi's data do not include any measurements in between — 190° and 0° C.

In conclusion, I wish to thank Prof. Sir C. V. Raman for the encouragement he gave me during the investigation.

SUMMARY

The theory outlined in Part I of these series has been applied to calculate the thermal variation of refractive index of fused silica. It is found that the theory can account quantitatively for the experimental values of *dn/dt* over the range of wavelengths from 1850 Å.U. to 6000 Å.U. Using the fact that the frequencies of vitreous silica are practically the same as those of crystalline quartz, the variation of the refractive index with temperature from — 130° C. to 500° C. has been calculated and found to fit well with the experimental data.

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THERMO-OPTIC BEHAVIOUR OF SOLIDS

III. Fluorspar

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1. INTRODUCTION

IN Parts I and II of these series (Ramachandran, 1947), a general theory has been developed for the variation of refractive index of solids with temperature and has been applied to the cases of diamond and vitreous silica. As shown in these papers, the temperature variation of refractive index (dn/dt) can be supposed to consist of two parts, one due to the change in density of the solid and the other due to the changes in the dispersion frequencies, the former being negative and the latter positive, in general. The thermal expansion of both diamond and fused quartz is very small, so that dn/dt for these is positive over the whole spectrum from the far ultra-violet to the red. Fluorspar, on the other hand, has an appreciable thermal expansion and exhibits a negative dn/dt throughout this region. The value is about -5×10^{-6} at 1850 Å.U., which increases numerically to about -12×10^{-6} at 6000 Å.U. (Micheli, 1902) and then again diminishes to about -9×10^{-6} at $6 \cdot 5 \mu$ (Liebreich, 1911). It will be interesting to see how far the theory can explain these variations.

The dispersion of fluorspar has been studied by various workers, and a number of dispersion formulæ have been suggested (Jaffé, 1928). The following formula given in the *International Critical Tables,* Vol. VII, p. 12, is said to fit the experimental data from $0 \cdot 185 \mu$ to $9 \cdot 4 \mu$:

$$n^2 = 6 \cdot 09104 + \frac{0 \cdot 00612093}{\lambda^2 - 0 \cdot 008884} + \frac{5099 \cdot 15}{\lambda^2 - 1258 \cdot 47} \tag{1}$$

This makes use of an ultra-violet frequency at $\lambda 942 \cdot 6$ Å and an infra-red one at $\lambda 35 \cdot 48 \mu$. The ultra-violet frequencies of fluorspar have recently been investigated by Tousey (1936) using a technique analogous to that used for the *Reststrahlen* in the infra-red. It is found that there are two absorption bands, a narrow one with a half-width of roughly 100 Å.U. with its centre at $\lambda 1115$ Å.U. and a stronger and more diffuse band at wave-lengths shorter than 1060 Å.U. and having its maximum at about 900 Å.U. or slightly shorter wave-lengths. In view of Tousey's observations, it will be seen that the above formula (1) can at best only be an

approximation. In fact, it is found that below 1850 Å.U., the formula progressively departs more and more from the experimental values of refractive index as one goes into the ultra-violet. The transmission limit of fluorspar is about 1250 Å.U. and refractive index data down to 1311 Å.U. are available from the work of Handke reported by Martens (1923) in the Landolt-Bornstein Tables. The author has been able to fit these data as well as the data in the visible by a single formula of the form

$$n^2 = C + \sum_{1}^{3} A_r \lambda^2 / (\lambda^2 - \lambda_r^2) \tag{2}$$

with two ultra-violet frequencies at $\lambda\,1115$ Å.U. and 820 Å.U. and an infra-red frequency at $\lambda\,35\cdot48\,\mu$. In fact, a formula of the type

$$(n^2 - 1) = \sum_{1}^{4} A_r \lambda^2 / (\lambda^2 - \lambda_r^2) \tag{3}$$

can also be derived having four dispersion frequencies at $\lambda\,450$ Å, 888 Å, 1115 Å and $35\cdot48\,\mu$. Details of these will be given in later sections.

The question now arises as to which of these formulæ has to be used for calculating dn/dt. It will be evident that as long as a certain formula fits the data for refractive index in the range of wave-lengths in which one is interested, then the theory developed in Part I can be used with that formula for that same range. Consequently, formula (1) has been used for the purpose, which has the advantage of simplicity. It is found that it explains quite well the variations in dn/dt described earlier. Later, formulæ (2) and (3) have been applied, and they lead to certain interesting results. It is found that the extreme ultra-violet frequency at $\lambda\,450$ Å does not vary with temperature, the one at $\lambda\,888$ Å varies only slightly, while the one at $\lambda\,1115$ Å varies much more with temperature.

2. DISPERSION FORMULÆ FOR FLUORSPAR

Formula (1) mentioned in the previous section can be put in the form:

$$\text{F I:}\quad n^2 = 1\cdot35020 + \frac{0\cdot68898\,\lambda^2}{\lambda^2 - 0\cdot008884} + \frac{4\cdot05186\,\lambda^2}{\lambda^2 - 1258\cdot47} \tag{4}$$

Two new formulæ have been developed by the author of the types (2) and (3). They are:

$$\text{F II:}\quad n^2 = 1\cdot25910 + \frac{0\cdot61667\,\lambda^2}{\lambda^2 - 0\cdot0067240} + \frac{0\cdot16404\,\lambda^2}{\lambda^2 - 0\cdot012432} + \frac{4\cdot05186\,\lambda^2}{\lambda^2 - 1258\cdot47} \tag{5}$$

$$\text{F III:}\quad n^2 - 1 = \frac{0\cdot45848\,\lambda^2}{\lambda^2 - 0\cdot0020250} + \frac{0\cdot42824\,\lambda^2}{\lambda^2 - 0\cdot0078925} + \frac{0\cdot15297\,\lambda^2}{\lambda^2 - 0\cdot012432}$$

$$+ \frac{4\cdot05186\,\lambda^2}{\lambda^2 - 1258\cdot47} \tag{6}$$

and are meant to represent the refractive indices n with respect to vacuum at λ, the wave-length in vacuum. In Table I, the difference between the values calculated from the above formulæ and the experimental data are given as the number of units in the fourth decimal place. (In Marten's Table quoted earlier, the refractive indices have been given only to 4 decimal places.) It may be mentioned that F I refers only to refractive indices in air. Making correction for the refractive index of air, the errors are shown in brackets under F I. It will be seen that the error becomes larger and larger as one progresses into the ultra-violet beyond $0 \cdot 185 \mu$. F II and F III on the other hand fit very well down to $0 \cdot 16 \mu$ beyond which both show a peculiar type of error. The difference between experiment and theory is first positive, becomes larger and larger, reaching a maximum at about $0 \cdot 145 \mu$, then diminishes and becomes negative. The author found that no manipulation with the frequencies below $\lambda 1115$ Å.U. can improve the fit in this region. In fact, when the experimental dispersion curve is plotted, an anomalous rise in refractive index is found down to about $0 \cdot 145 \mu$ and then an anomalous fall is found. A similar variation is found in Tousey's reflection curve also (*loc. cit.*). All these suggest that there is an extremely weak absorption band with its centre at about $0 \cdot 134 \mu$ (at which wave-length the error passes from positive to negative values), which is the cause for the anomalous dispersion in its neighbourhood.

TABLE I

λ_{vac} in microns	n_{vac} exp.	$n_{exp} - n_{th}$		
		FI	FII	FIII
0·76845	1·4313		0	0
0·58947	1·4342	+3 (−1)	0	0
0·394524	1·4427		0	0
0·308314	1·4530		0	0
0·257392	1·4653	+4 (−1)	0	0
0·219527	1·4821		0	0
0·199057	1·4969	+8 (+2)	0	0
0·185477	1·5107	+10	0	0
0·176420	1·5227	+14	0	0
0·164455	1·5438		0	0
0·15692	1·5615		−1	−1
0·15234	1·5751	+46	+1	+1
0·14817	1·5896		+2	+2
0·14363	1·6089	+88	+6	+5
0·13940	1·6305		+4	+3
0·13536	1·6565		+1	+1
0·13192	1·6844	+237	−3	−2
0·13111	1·6921		−4	−3

3. CALCULATION OF dn/dt FOR VARIOUS WAVE-LENGTHS

A. Using F I.—As was mentioned earlier, formula F I represents the refractive index sufficiently well for wave-lengths larger than 1850 Å.U. One may therefore calculate dn/dt from it in the same manner as was done for fused quartz. If one writes

$$n^2 = C + \Sigma_r a_r \lambda^2_r \lambda^2/(\lambda^2 - \lambda_r^2), \tag{7}$$

then

$$\frac{dn}{dt} = \frac{\beta}{2n} - \frac{\gamma(n^2 - C)}{2n} + \frac{1}{n} \Sigma_s \frac{a_r \lambda_r^2 \lambda^4 \chi_r}{(\lambda^2 - \lambda_r^2)^2} \tag{8}$$

where $\beta = (dC/dt)$, $\chi_r = (1/\lambda_r)(d\lambda_r/dt)$ and γ is the coefficient of cubical expansion. The value of χ_2 for the infra-red frequency is available from the unpublished work of D.C. Press carried out in this laboratory on the temperature variation of the principal Raman frequency at 320 cm.⁻¹ It is
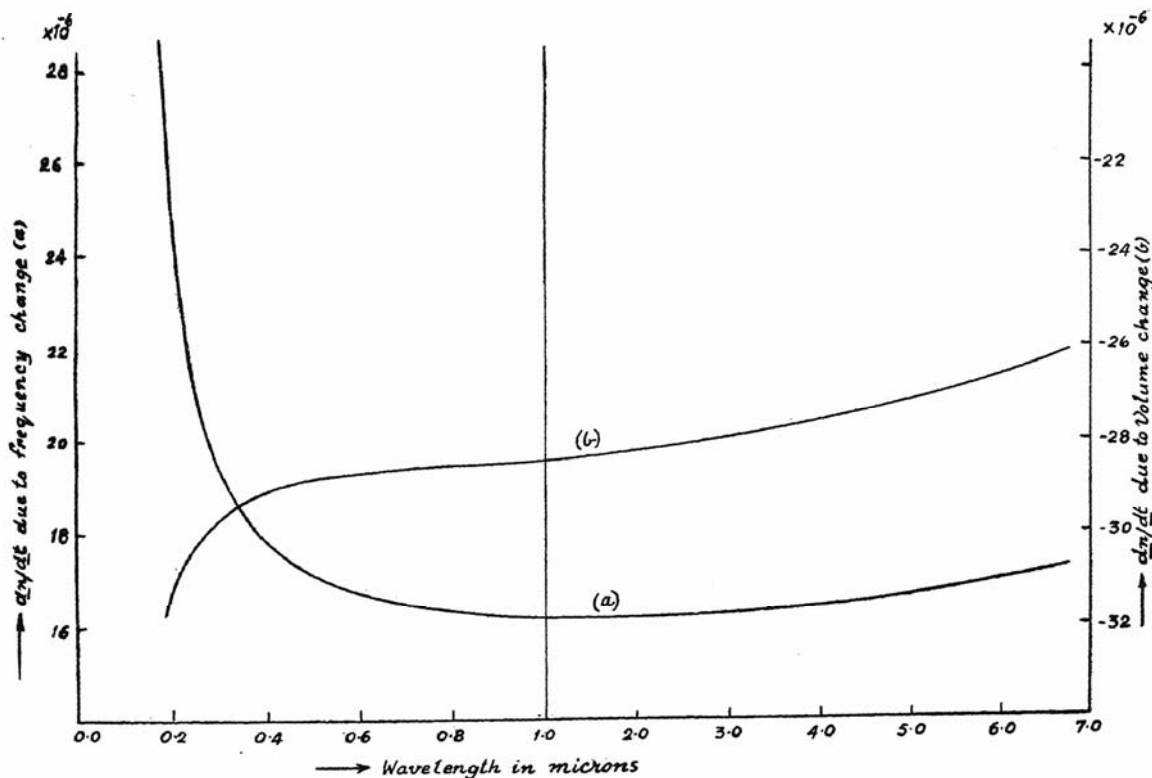

FIG. 1. Curves showing the variation with wavelength of the contributions to dn/dt due to volume and frequency changes. The abscissæ have been reduced five-fold after 1 μ to facilitate the whole range from 0·2 μ to 7 μ being shown in the same diagram. The scale of the ordinates for both the curves is the same, but the origins have been shifted.

found that the contribution to dn/dt due to the change in the infra-red frequency is negligible for the visible and ultra-violet regions of the spectrum, being less than 1% at $0·8\mu$ and less at shorter wave-lengths.

The calculations were done for 60° C. for which temperature the dn/dt data are all available. γ was obtained from the unpublished work of D. C. Press in this laboratory. There are only two unknown quantities, χ_1 and β, which were calculated to have the values

$$\chi_1 = 33·1 \times 10^{-6} \text{ and } \beta = -37·6 \times 10^{-6} \tag{9}$$

As mentioned earlier, dn/dt can be supposed to be composed of two parts, due respectively to the change in density and change in dispersion frequency, which we may denote by P and X, following the notation in Part I. Thus,

$$P = \frac{\partial n}{\partial \rho} \cdot \frac{d\rho}{dt}, \quad X = \frac{\partial n}{\partial \lambda} \cdot \frac{d\lambda}{dt}. \tag{10}$$

Now, in the expression (8) above, the term $\beta/2n$ is the contribution due to the alteration of the constant C, which is negative. Following the reasoning advanced in Part II with respect to vitreous silica, one may conclude that this part is wholly due to the change in volume. In other words, it is assumed that the extreme ultra-violet frequency which gives rise to a constant term in dispersion does not vary with temperature, which is a reasonable assumption. Thus,

$$P = -\gamma(n^2 - C)/2n + \beta, \quad X = (1/n)\sum_r a_r \lambda_r^2 \lambda^4 \chi_r/(\lambda^2 - \lambda_r^2)^2 \tag{11}$$

In Fig. 1, these two parts are shown separately by the curves (a) and (b). The calculations for drawing the curves were made with the values for γ, χ_1 and β given above. For the infra-red, χ_2 was taken from Press's work, which at 60° C. has the value 159×10^{-6}. The curves show interesting variations of P and X. The contribution due to volume change follows a course similar to the refractive index, diminishing (algebraically) as one approaches the ultra-violet frequency and increasing towards longer wave-lengths in the infra-red. The other contribution, however, increases on approaching a dispersion frequency, the increase taking place on either side of it. This is because it is inversely proportional to $(\lambda^2 - \lambda_r^2),^2$ and for the same reason, the increase in X preponderates over the diminution in P as one progresses into the ultra-violet. Thus, dn/dt increases on approach-ing both the ultra-violet and the infra-red dispersion bands. In Fig. 2 the course of the $(dn/dt) - \lambda$ curve is shown, which will illustrate this fact. The continuous curve has been calculated from theory, while the points are the experimental data of Micheli (1902) and Liebreich (1911), the former

being shown by circles and the latter by triangles. It will be seen that the agreement with Micheli's data is remarkably good. Liebreich's data exhibit an appreciable algebraic increase in *dn/dt* from 0.8μ to 2μ and a relatively smaller increase thereafter than indicated by theory. In this region, theory gives systematically lower values, although it agrees with the data at longer wave-lengths. The author is unable to conceive of any reason as to why *dn/dt* should quickly increase (algebraically) upto 2μ. In fact, as will be seen later in this section, the use of other dispersion formulæ like F II and F III does not alter the theoretical curve sensibly and that the discrepancy is still present. It would appear that the discrepancy between theory and experiment in this region must be attributed to experimental errors, which are likely to be large since *dn/dt* is only obtained indirectly from the difference in the refractive indices at two temperatures and also since the latter measurements themselves are less accurate than in the visible because no photographic method can be used.
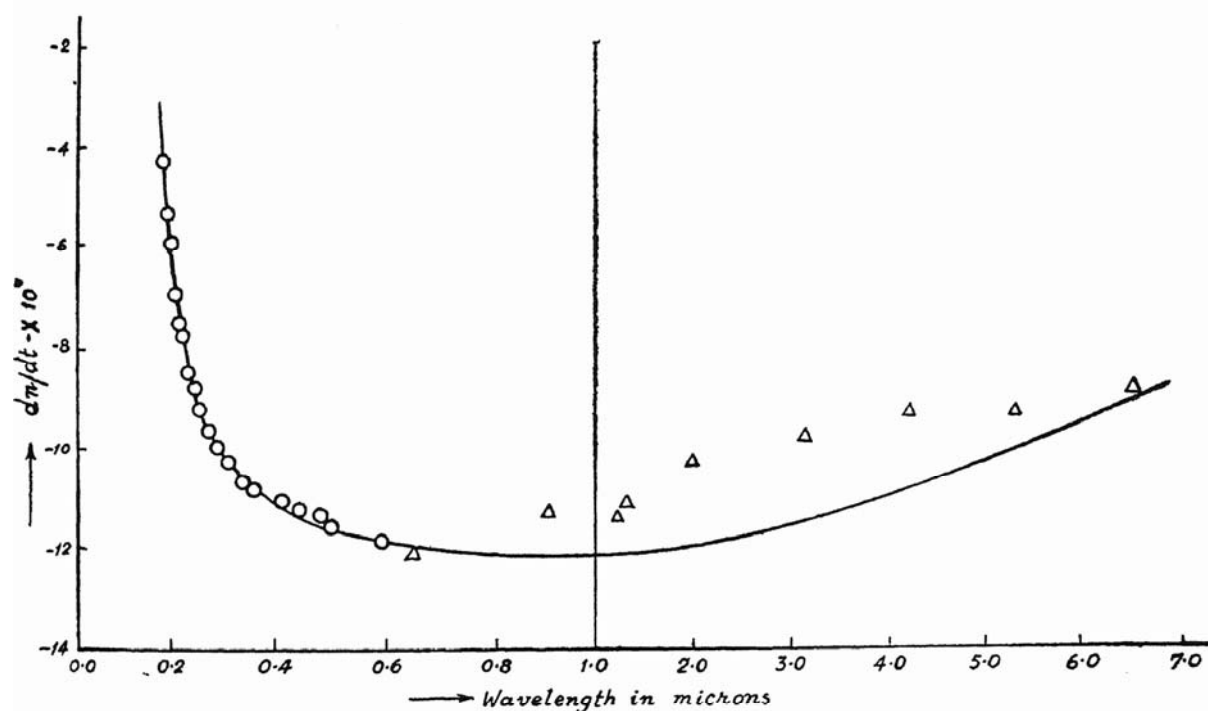

FIG. 2. Variation of *dn/dt* with wavelength. The circles are the experimental data of Micheli and the triangles those of Liebreich. The scale has been compressed five-fold above 1.0μ.

B. Using F II and F III.—We have thus seen how a relatively approximate formula like F I is sufficient to explain the variations in *dn/dt*. We shall now apply the new formula F II, which is also of the form (7), so

that dn/dt is given by (8). Now, there are two ultra-violet frequencies at λ 1115 Å.U. and 820 Å.U. For convenience, we shall assume that both of them vary with temperature to the same extent in proportion to their frequency, in other words that both have the same value of χ. Then, it is found that β and χ have the values:

$$\chi = 33 \cdot 0 \times 10^{-6}, \quad \beta = -37 \cdot 6 \times 10^{-6} \tag{12}$$

The resulting formula fits the data for dn/dt very well. In Table II below, the calculated values of dn/dt for a few wave-lengths from F I, F II and F III are given together with the experimental values. It will be seen that there is little to choose between the three formulæ.

However, F III is interesting because it is of the standard type given by the Ketteler-Helmholtz theory with the constant $C = 1$ in (7). Consequently, dn/dt does not involve an arbitrary constant β, but depends only on the values of χ_r for the dispersion frequencies. Denoting the four frequencies at $\lambda\lambda$ 450 Å.U., 888 Å.U., 1115 Å.U. and $35 \cdot 47 \mu$ respectively by the subscripts 1, 2, 3 and 4, one finds that the χ_r's have the values:

$$\chi_1 = 0, \quad \chi_2 = 11 \cdot 3 \times 10^{-6}, \quad \chi_3 = 70 \cdot 2 \times 10^{-6} \tag{13}$$

χ_4 was taken to have the value 159×10^{-6} obtained from Press's measurements (*loc. cit.*).

TABLE II

Wavelength in microns	dn/dt calculated from			dn/dt from experiment
	FI	FII	FIII	
0·199057	− 6·07	− 5·92	− 5·93	− 5·89
0·257392	− 9·26	− 9·19	− 9·39	− 9·24
0·308314	−10·45	−10·36	−10·44	−10·32
0·58947	−11·84	−11·91	−11·78	−11·93
1·3	−12·23	−12·16	−11·91	−11·21
3·16	−11·63	−11·55	−11·28	− 9·83
6·5	− 9·15	− 9·05	− 8·78	− 8·84

It will be seen the proportionate rate of change of the ultra-violet frequencies becomes less and less as one proceeds further into the ultra-violet. Thus the remote dispersion frequency at λ 450 Å.U. is unaffected by temperature while between the two at λ 888 Å and λ 1115 Å., the latter increases much more than the former. It may be mentioned that the actual numerical values given in (13) can be altered slightly and yet fit the experimental data. However, it will be found that always $\chi_3 > \chi_2 > \chi_1$, the last one being very small.

3. Discussion of the Results

The result just mentioned is what one would expect from other considerations. Of the various ultra-violet frequencies, those having higher frequencies should arise from the deeper levels of the atoms, while those with lower frequencies arise from transitions between the levels of the outer electrons. Since the outer electrons take part principally in the binding of the crystal, a change in temperature would be expected to affect the levels of the outer electrons much more than those of the inner ones.

Another interesting fact emerges when one compares the value of χ for the ultra-violet frequencies with that for the characteristic infra-red frequency of the lattice. It was shown in Parts I and II that these two are of the same order in diamond, and that in fused quartz χ of the dispersion frequency is of the same order as χ of the intense Raman line at 465 cm.⁻¹ of α-quartz. For fluorspar, although the temperature variation of the infra-red active lattice frequency has not been studied, data on the Raman frequency at 320 cm.⁻¹ (which lies close to the former) are available (Press, *loc. cit.*). If one takes F I or F II, then χ for the ultra-violet frequencies is about 33×10^{-6} which is only about 1/5 of χ for the infra-red, *viz.*, 159×10^{-6}. If we denote by χ_V and χ_R the values of χ for the ultra-violet and infra-red frequencies, then χ_V/χ_R is 78% for diamond and 77% for fused quartz while it is only 21% for fluorspar. Even if one takes F III and considers χ_3, the variation of the frequency at $\lambda 1115$ Å.U., then also, χ_3/χ_R is only 45%. Thus, the ultra-violet frequencies vary much less relatively in fluorspar than in diamond and fused quartz when compared with the variation of the lattice frequency of the respective crystals. The interpretation of this difference is not far to seek. Both diamond and quartz are typical covalent solids, in which the binding is essentially produced by the sharing of the outer electrons. One would therefore expect the changes in the binding energy and changes in the electronic states of the outer electrons to correspond closely in these solids. In fluorspar, the binding is not so highly covalent as in diamond or quartz, but is partly electrovalent. It is therefore not surprising that the ultra-violet electronic transitions are relatively less affected by temperature than the infra-red lattice frequency.

One may also consider what happens to χ_V at elevated temperatures. For this, one can make use of the work of Reed (1898) who has determined dn/dt for sodium light for various temperatures above the room temperature. γ can be obtained from the data of Press mentioned earlier. It is assumed that the component of dn/dt produced by change of volume varies in the

same proportion as γ. This means that β is taken to vary as γ, which is true since β is due only to a change in volume, the extreme ultra-violet frequency not altering with temperature. The important values used in the calculation, as well as the values of χ_V (calculated with F I) and χ_R (calculated from Press's data) are shown in Table III.

TABLE III

Temperature °C	$dn/dt \times 10^6$	$\gamma \times 10^6$	$\chi_V \times 10^6$	$\chi_R \times 10^6$
60	−11·9	63·24	33·1	159
100	−12·4	64·17	32·8	131
150	−13·1	65·58	32·7	110
200	−13·7	67·50	33·2	94
250	−14·3	70·35	34·4	90

It will be noticed that χ_V is practically a constant upto 200° C. after which it rises slightly. χ_R on the other hand shows an appreciable decline with rise of tempearture. In both diamond and fused quartz, χ_V increases with temperature. Although the precise reason for the difference in the case of fluorspar is not clear, one may reasonably attribute it to the differences in the nature of binding in the crystal.

SUMMARY

Making use of the dispersion formula given in the International Critical Tables, with absorption bands at $\lambda\lambda\,0\cdot0942$ and $35\cdot48\,\mu$, and using the theory developed in Part I, the course of the variation of dn/dt with wave-length has been satisfactorily explained from $0\cdot185$ to $6\cdot5\,\mu$. The dispersion formula however fails below $0\cdot185\,\mu$, and consequently two new formulæ have been developed holding down to $1300\,\text{Å.U.}$, one of which uses dispersion frequencies at $\lambda\lambda\,0\cdot082,\ 0\cdot1115$ and $35\cdot48\,\mu$ together with a non-unity constant in the expression for n^2, while the other is of the Ketteler-Helmholtz type with four frequencies at $\lambda\lambda\,0\cdot045,\ 0\cdot088,\ 0\cdot1115$ and $35\cdot48\,\mu$. All the formulæ explain the variations of dn/dt, in particular, as to why it increases algebraically as one proceeds both into the ultra-violet and the infra-red. The interesting fact emerges that the extreme ultra-violet frequency at $\lambda\,0\cdot045\,\mu$ does not vary with temperature, while the proportionate variation of the one at $0\cdot0888\,\mu$ is much less than that of the

one at 0.1115μ. This result becomes intelligible when one remembers that the deeper levels in the crystal would be less affected by temperature than the low-lying ones. Even the last one, although it is of the same order, is only one half of the proportionate variation of the infra-red lattice frequency. It is also found that the rate of variation of the ultra-violet frequencies is constant at different temperatures. In these respects, fluorspar differs from diamond and vitreous silica. The difference has been attributed to the fact that the binding in fluorspar is not purely covalent, but is also partly electrovalent.

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