

THERMO-OPTIC BEHAVIOUR OF CRYSTALS

1. INTRODUCTION

Since the early realisation that with rise of temperature the refractive index of some solids decreased while in others it increased, a large number of investigators have measured the temperature variation of the refractive index, birefringence and optical rotation in numerous crystals. The following review presents the experimental data on this subject and briefly describes the experimental methods used in acquiring them. The phenomenological theories put forward to explain the various thermo-optic phenomena have been summarised and these have been discussed in relation to the observed results.

2. DISPERSION FORMULA FOR REFRACTIVE INDEX

It is quite evident that for the development of a phenomenological theory of thermo-optic behaviour of solids, one has to start with a formula relating the dielectric constant or the refractive index of a substance with the resonant frequencies in it. For the optical range of frequencies the dielectric constant arises entirely from the electronic polarisability. If the substance has a set of oscillators of frequencies ν_1, ν_2, \dots , the incident light vector would induce moments in each one of them. If one does not take into account the mutual interactions between the different oscillators, then according to both the classical theory of electronic polarisability developed by Drude and the more modern Kramers-Heisenberg theory, the refractive index of a substance for light of frequency ν takes the Drude form

$$n^2 - 1 = \sum_i \frac{e^2}{m\pi} \frac{f_i N_i}{\nu_i^2 - \nu^2} \quad (1)$$

where N_i is the number of oscillators per unit volume of frequency ν_i and f_i is the oscillator strength or the transition probability corresponding to that particular frequency.

If, however, the mutual interaction between the different oscillators are taken into account and if p_{ij} represents the polarisation field factor defining the polarisation field acting on any oscillator of type (i) due to all the oscillators of type (j) in the medium, and Ω_i is the frequency of the oscillator in the free state and Ψ_i is the contribution to the polarisation per unit volume per unit field in the medium from oscillators of type (i), then the refractive index is given by

$$n^2 - 1 = 4\pi \sum_i \Psi_i \quad (2)$$

where

$$\Psi_i = \frac{B_i}{\Omega_i^2 - \nu^2} \left(1 + \sum_j p_{ij} \Psi_j \right)$$

where j can take all the values (i), (j), (k) etc. When p_{ij} 's have the same value

p then $\sum_j \rho_{1j} \psi_j = p\psi$ and the equation (2) reduces to

$$\frac{n^2 - 1}{n^2 + \alpha} = \sum_1 \frac{C_1}{(\Omega_1^2 - \nu^2)} \quad (3)$$

where

$$\alpha = \frac{4\pi}{p} - 1 \text{ and } C_1 = \rho B_1$$

Lorentz calculated the magnitude of p in isotropic solids and cubic crystals to be $4\pi/3$ in which case the formula (3) reduces to

$$\frac{n^2 - 1}{n^2 + 2} = \sum_1 \frac{C_1}{(\Omega_1^2 - \nu^2)} \quad (4)$$

This is the traditional Lorentz-Lorenz formula and equation (2) could be termed as the generalised Lorentz formula [Krishnan and Roy (26)].

The assumption implicit in the Lorentz derivation is that the elementary dipoles in the crystals are point dipoles and that the distance of separation of the charges is small in comparison to the interatomic distance. If this condition is not satisfied the polarisation factor would possibly be less than $4\pi/3$.

There has always been considerable difference of opinion amongst investigators in this field as to which of the two dispersion formulae is to be used in optical studies of solids. Krishnan and Roy (*Loc. cit*) point out that the observational data on the dispersion of refractive index of any dense medium can be fitted into a Drude formula or into a generalised Lorentz formula irrespective of the actual nature or magnitude of the polarisation field inside the medium. This equivalence between the two formulae has been shown explicitly by Herzfeld and Wolf (22) for the most general case when the medium has more than one resonant frequency.

The physical meaning of this equivalence is the following. Since the polarisation field has been taken into account in the derivation of the Lorentz formula, the characteristic frequencies Ω_1 's that appear in the formula correspond to those of the *isolated* oscillators, unaffected by the polarisation field. In the Drude formula however the polarisation field is taken into account in a completely different manner. The field may be regarded as changing the frequency Ω_1 of the isolated oscillator into the corresponding frequency ν_1 of the medium and its effect on the dielectric and refractive behaviour of the substance manifests itself through these altered frequencies. It is therefore quite evident that the dispersion data as such cannot give us any information regarding the nature of the polarisation field that actually exists in a medium, *though they enable us to obtain the absorption frequencies directly if the data are expressed in the Drude form*. Conversely if one were to use the experimentally observed frequencies to fit the observational data one must necessarily use the Drude formula.

3. THERMO-OPTIC BEHAVIOUR OF SOLIDS

(a) VARIATION OF REFRACTIVE INDEX WITH TEMPERATURE

(i) **ISOTROPIC CRYSTALS** : Having discussed the type of the dispersion formula to be used, we shall proceed to present the phenomenological theory of thermo-optic behaviour (Ramachandran 51). It is quite evident from what has

been said in the previous section that the dispersion formula of a solid can be written in the form

$$n^2 - 1 = \sum_i \frac{a_i f_i N_i}{\nu_i^2 - \nu^2} \quad (5)$$

where ν_i 's represent the absorption frequencies of the oscillators in the solid state.

The change of temperature could affect the three parameters f_i , N_i and ν_i and each would produce a change in the refractive index, the total change in n being the algebraic sum of the three individual effects. Hence differentiating equation (5) one has

$$2n \frac{dn}{dT} = \sum_i - \frac{2a_i f_i N_i \nu_i}{(\nu_i^2 - \nu^2)^2} \frac{d\nu_i}{dT} + \sum_i \frac{a_i N_i}{\nu_i^2 - \nu^2} \frac{df_i}{dT} + \sum_i \frac{a_i f_i}{\nu_i^2 - \nu^2} \frac{dN_i}{dT} \quad (6)$$

Since N_i is proportional to ρ , the density

$$\frac{dN_i}{dT} = \frac{N_i}{\rho} \frac{d\rho}{dT} = -N_i \gamma \quad (7)$$

where γ is the coefficient of cubical expansion. If one expresses

$$\frac{1}{\nu_i} \frac{d\nu_i}{dT} = -\frac{1}{\lambda_i} \frac{d\lambda_i}{dT} = -X_i \quad (8)$$

and

$$\frac{1}{f_i} \frac{df_i}{dT} = -F_i$$

then

$$\frac{dn}{dT} = \frac{1}{n} \sum_i \frac{a_i f_i N_i \nu_i^2}{(\nu_i^2 - \nu^2)^2} X_i - \frac{1}{2n} \sum_i \frac{a_i N_i f_i}{\nu_i^2 - \nu^2} F_i - \frac{n^2 - 1}{2n} \gamma \quad (9)$$

or in terms of λ

$$\frac{dn}{dT} = \frac{1}{n} \sum_i \frac{a_i f_i N_i \lambda_i^2 \lambda^4}{c^2 (\lambda^2 - \lambda_i^2)^2} X_i - \frac{1}{2n} \sum_i \frac{a_i N_i f_i \lambda^2 \lambda_i^2}{c^2 (\lambda^2 - \lambda_i^2)} F_i - \frac{n^2 - 1}{2n} \gamma.$$

This would represent the variation of the refractive index of a solid with temperature.

Taking an analogy from the phenomenological theory of Magneto-optic rotation Ramchandran (51, 54) assumed that there is no change in the oscillator strength with temperature in cubic crystals. In such a case if $\Lambda_i = \frac{a_i f_i N_i \lambda_i^2}{c^2}$ then equations (5) and (9) reduce to

$$n^2 - 1 = \Lambda + \sum_i \frac{\Lambda_i \lambda^2}{(\lambda^2 - \lambda_i^2)}$$

$$\frac{dn}{dT} = \frac{1}{n} \sum_i \frac{\Lambda_i \lambda^4}{(\lambda^2 - \lambda_i^2)^2} X_i - \frac{n^2 - 1}{2n} \gamma \quad (10)$$

where X_i is the proportionate change of the frequency of the oscillator ν_i with temperature. Measurements of the absorption frequencies at different temperatures by Fesefeldt (19) on KI and RbBr have shown that they shift down in the scale of frequencies with increase in temperature. It is well known from Raman effect studies that lattice frequencies also exhibit a similar variation with temperature. From these observations one could generally conclude that the values of X in most cases would be positive. Since γ is always positive, it is evident from equation (10) that

the volume and the frequency contributions would normally be of opposite signs. The actual sign and the magnitude of these two opposing effects determine the sign and magnitude of dn/dT . We shall present the experimental results and the verification of the formula in a later section.

It may be pointed out that the only assumption made in the case of cubic crystals is that there is no change in the oscillator strength with change in temperature. More accurate experiments on the temperature variation of the absorption frequency of various substances would be most helpful in the establishing whether this assumption is correct or not.

(ii) **BIREFRINGENT CRYSTALS** : For the general case of birefringent crystals, Ramachandran (55) has suggested the following formula for the principal refractive indices n_1 , n_2 and n_3 :

$$n_r^2 - 1 = \sum_i \frac{a_i f_{ri} N_i}{v_i^2 - \nu^2} \quad \text{where } r = 1, 2, 3. \quad (11)$$

This means that for the three refractive indices, the dispersion frequencies are the same, but only their strengths alter with the direction of incident electric vector.

The temperature variation of the refractive indices of the birefringent solid would therefore be governed by three equations similar to equation (9). In fitting up the experimental data, Ramachandran (55) had to modify his assumption as to the invariance of f_1 with temperature. The two new assumptions he made were :

(a) The sum of the three individual strengths does not change with temperature, although the individual strengths might alter, *i.e.*,

$$\sum_{r=1}^3 \frac{df_{ri}}{dT} = 0. \quad (12)$$

(b) The transfer of the oscillator strength for light vibrating along two directions is proportional to the difference in the linear expansion coefficients along them

$$\begin{aligned} \frac{df_{11}}{dT} - \frac{df_{21}}{dT} &= \text{const} (\alpha_1 - \alpha_2) \\ \frac{df_{21}}{dT} - \frac{df_{31}}{dT} &= \text{const} (\alpha_2 - \alpha_3) \\ \frac{df_{31}}{dT} - \frac{df_{11}}{dT} &= \text{const} (\alpha_3 - \alpha_1) \end{aligned} \quad (13)$$

where α_1 , α_2 and α_3 are the three principal linear expansions. Using these ideas Ramachandran (55) obtained the following equations for a uniaxial crystal

$$2n_\omega \frac{dn_\omega}{dT} = -\gamma (n_\omega^2 - 1) + \sum_i \frac{2A_{\omega i} \lambda^4}{(\lambda^2 - \lambda_i^2)^2} X_i - \frac{1}{2} (\alpha_{||} - \alpha_{\perp}) \sum_i \frac{K_i \lambda^2}{(\lambda^2 - \lambda_i^2)} \quad (14)$$

$$2n_\epsilon \frac{dn_\epsilon}{dT} = -\gamma (n_\epsilon^2 - 1) + \sum_i \frac{2A_{\epsilon i} \lambda^4}{(\lambda^2 - \lambda_i^2)^2} X_i + (\alpha_{||} - \alpha_{\perp}) \sum_i \frac{K_i \lambda^2}{(\lambda^2 - \lambda_i^2)}$$

where K_i is a constant, and $A_{ri} = \frac{a_i f_{ri} N_i \lambda_i^2}{c^2}$; $r = \omega$ or ϵ and he was able to explain the thermo-optic behaviour of a few uniaxial birefringent crystals.

The present writers feel that the assumption made by Ramachandran that for all the three refractive indices the dispersion frequencies are the same but only their

strengths alter, presents rather too simplified a picture. This may prove a fair approximation in the case of crystals with highly anisotropic groups like CaCO_3 , NaNO_3 etc. but is bound to fail in the case of crystals like quartz, rutile, SiC etc., where the birefringence is caused mainly by the anisotropy of distribution of the individual units that form the crystal. Following the ideas enunciated by Chandrasekhar (9) for the case of optical activity, recently Ramaseshan and Sivaramakrishnan (57) have suggested that due to the weak coupling of the neighbouring oscillators, which are asymmetrically distributed, the characteristic frequency of each oscillator splits into two or three components depending on whether the crystal is uniaxial or biaxial. Each component is responsible for the dispersion of the corresponding refractive index of the crystal. The oscillator strengths can also alter due to this interaction.

For instance for a uniaxial crystal if the ordinary refractive index is

$$n_{\omega}^2 - 1 = \sum_i \frac{c_i}{v_i^2 - \nu^2} \quad (15)$$

where

$$c_i = a_i f_i N_i \quad (15a)$$

then the birefringence δ is obtained by differentiating (15) as

$$n_{\omega} \delta = n_{\omega} (n_{\epsilon} - n_{\omega}) = \sum_i \frac{c_i v_i^2}{(v_i^2 - \nu^2)^2} R_i' + \frac{1}{2} \sum_i \frac{c_i}{v_i^2 - \nu^2} R_i'' \quad (16)$$

where

$$R_i' = - \frac{[\Delta v_i]}{v_i} \quad \text{and} \quad R_i'' = \frac{[\Delta f_i]}{f_i} \quad (17)$$

where $[\Delta v_i]$ and $[\Delta f_i]$ are the changes in the frequency and oscillator strength due to the anisotropy. One must remember that since the total transition probability must be equal to unity

$$\sum_i R_i'' f_i = 0. \quad (18)$$

Once suitable dispersion formulae for n_{ω} and n_{ϵ} are obtained using these concepts, equation (9) can be directly applied for the computation of the thermal variation of the refractive indices. If, however, one is interested in the temperature variation of birefringence alone then we have from equation (16)

$$n \frac{d\delta}{dT} + \delta \frac{dn}{dT} = \sum_i \left[(\delta n)_{\nu_1} \frac{3v_i^2 + \nu^2}{v_i^2 - \nu^2} + (\delta n)_{f_1} \frac{v_i^2}{v_i^2 - \nu^2} \right] X_i - \delta n Q \quad (19)$$

$$\text{where} \quad Q = \frac{1}{Nf} \frac{d(Nf)}{dT} \quad (20)$$

and $(\delta n)_{\nu_1}$ and $(\delta n)_{f_1}$ are the contributions to δn caused by the frequency change $[\Delta v_i]$ and the oscillator strength change $[\Delta f_i]$. If, however, one assumes a single mean absorption frequency for a substance the formulae are considerably simplified. Using these formulae both the birefringence and its temperature variation in a series of crystals have been explained (70).

(b) VARIATION OF OPTICAL ACTIVITY WITH TEMPERATURE

Before considering the variation of optical activity of crystals with temperature one has again to discuss the nature of the dispersion formula to be used to explain optical activity of crystals. The earlier formulae that were proposed were of the

Drude type and Chandrasekhar (7) showed that all the formulae proposed for crystals did not satisfy the important theoretical condition known as Kuhn's summation rule (28, 14). Chandrasekhar (9) was later able theoretically to derive a formula for the case of substances like quartz, NaClO_3 , HgS , Benzil etc., whose optical activity arises due to the crystal structure alone. He assumed that each oscillator in an optically active medium is feebly coupled to its neighbours. It is found that the structure of the optically active crystal splits the characteristic frequencies of the individual oscillators into two components as a result of the coupling between the neighbouring units in the crystal. Using these principles he obtained a formula

$$\rho = \sum_i \frac{b_i N_i v^2}{(v_i^2 - v^2)^2} \quad (21)$$

where v_i 's are the characteristic frequencies of the substance. This formula was found to fit the data for many crystals. For obtaining the temperature variation of optical activity, differentiating (6), one has (Chandrasekhar 12)

$$\frac{d\rho}{dT} = \sum_i \frac{4 b_i N_i v_i^2 v^2}{(v_i^2 - v^2)^3} X_i - \sum_i \frac{b_i N_i v^2}{(v_i^2 - v^2)^2} \gamma \quad (22)$$

$$\text{or } \frac{d\rho}{dT} = \sum_i \rho_i \frac{4 v_i^2}{v_i^2 - v^2} X_i - \rho \gamma \quad (23)$$

where ρ_i is the contribution of the frequency v_i to the rotation. If however the crystal has only one absorption frequency

$$\frac{1}{\rho} \frac{d\rho}{dT} = \frac{4 v_0^2}{v_0^2 - v^2} X_0 - \gamma \quad (24)$$

One notices that X_i 's in these formulae are the same as the X_i 's in the formulae for the thermal variation of refractive index. Using these formulae it was possible to explain the thermal variation of the optical rotatory power in many crystals.

4. EXPERIMENTAL METHODS

(i) VARIATION OF REFRACTIVE INDEX WITH TEMPERATURE

The temperature coefficient of refractive index of a solid is usually evaluated from the measurement of the refractive index of the substance at different temperatures by the well known prism method. The various details of the experimental technique can be obtained from the following references (32, 42, 62). The disadvantages and limitations of this method are obvious. For instance the requirement of the experimental specimen in bulk, the maintenance of these large non-conducting specimens at uniform temperatures, the making of prisms from crystals like mica which exhibit layer structure are some of the problems one is confronted with. Further the accuracy of the method is also not very high. Since the magnitude of dn/dT is of the order of 10^{-5} , the prism has to be heated by 100°C . to alter its refractive index by one unit in the third place. The value of dn/dT would have altered in this range. In addition the measurements of the refractive index must be correct to the fourth decimal place in order to secure an accuracy of 10% in dn/dT . This is by no means an easy task, when the prism and its supports are heated to 500°C .

A much simpler way of measuring dn/dT is provided by the interference method (51, 47, 45) where the dn/dT is evaluated from the measurements of the shift with temperature of the interference fringes formed between the two surfaces of the crystal,

fashioned in the form of a plate. Either Newtonian fringes or Haidinger fringes could be used. In both cases for normal incidence the bright fringes satisfy the relation

$$2nl = N\lambda \quad (25)$$

where n is the refractive index, l the thickness of the crystal, λ the wavelength and N an integer. On varying the temperature the fringes will move past any reference mark on the crystal. If ΔN is the number of fringes crossing this mark, for a temperature change ΔT from (25) we have

$$2l \frac{\Delta n}{\Delta T} + 2n \frac{\Delta l}{\Delta T} = \lambda \frac{\Delta N}{\Delta T}$$

from which we get

$$\frac{dn}{dT} = \frac{\lambda \Delta N}{2l \Delta T} - n\alpha \quad (26)$$

where $\alpha = \frac{1}{l} \frac{dl}{dT}$, the linear expansion coefficient of the crystal. Hence from a knowledge of the thermal expansion and a measurement of the number of fringes crossing the fiducial mark on the crystal for a small change in temperature one can obtain the value of dn/dT with respect to vacuum. The shift in the fringes can be determined either visually or photographically. Even though the value of $\Delta N/\Delta T$ can be determined to within 1%, the value of dn/dT can usually be obtained to only 5% as the major contribution to the path retardation change arises due to the thermal expansion. The extension of this to birefringent crystals is quite evident.

(ii) VARIATION OF OPTICAL ACTIVITY WITH TEMPERATURE

The method consists of measuring the rotation of the crystal at various temperatures using the well known visual, photographic or photoelectric polarimeters (43, 30, 8). Although in principle these methods are capable of giving very great accuracy, they have not been exploited to the maximum extent for temperature studies.

5. DISCUSSION OF RESULTS

One notices from Table (I) that the value of dn/dT is in general negative except in a few cases (like diamond, MgO, Calcite etc.). This is obviously because the contribution due to the thermal dilatation, in most cases, far exceeds that due to the frequency change. In the discussion that follows we shall have often to refer to the magnitude of X for the different absorption frequencies that exist in various crystals. It is quite clear that the X 's are obtained from a fitting up process and values of any accuracy or significance can only be obtained if experimentally observed absorption frequencies are used and if the values of dn/dT are very precise. For this purpose it is quite essential to extend most of the data on thermo-optics to the far ultraviolet and the infra-red. One is also confronted with another difficulty. This relates to the cubic crystals where an assumption that the oscillator strength f does not change with temperature, has been made. In fact this assumption is quite doubtful as even in the case NaCl and KCl one finds that a considerable change in the oscillator strength has to be assumed to bring about an exact fit with the experimental data, particularly as one proceeds into the infra-red (Ramachandran 54). This of course assumes that the experimental data of Liebreich (29) are reliable.

In NaCl, dn/dT actually becomes positive below λ 2200, for the following reason. As one proceeds into the ultraviolet the effect of the frequency change, due to the nearness of the absorption frequency, increases in magnitude so as to first equalise and later overwhelm the effect due to the opposing density change. The χ values for the different frequencies of NaCl (Ramachandran 54) are

$$\chi_{100} = 0; \chi_{1000} = -33.6 \times 10^{-6}; \chi_{1280} = 33.5 \times 10^{-6}; \chi_{1580} = 110 \times 10^{-6}.$$

This indicates that the nearer absorption wavelengths shift towards longer wavelengths while that at λ 1000 shifts towards the shorter wavelengths. This seems to signify that the polarisability of the negative ion (whose characteristic absorption is believed to occur at longer wavelengths) increases, while that of the positive ion decreases with dilatation. This is quite in accord with the computation of Shockley (68) of the change of the polarisability of the ions when they go over from the solid state to the gaseous state. There are no extensive measurements available for KCl, KBr, and KI but one finds that the numerical magnitude of $(dn/dT)_{KI} > (dn/dT)_{KBr} > (dn/dT)_{KCl}$. Both NaF and LiF have low values of dn/dT . In the case of the Caesium halides also one finds $(dn/dT)_{CsI} > (dn/dT)_{CsBr}$. The dn/dT value of NH_4Cl and NH_4Br show anomalous behaviour at their transition points, $-30^\circ C$ and $-38^\circ C$ respectively. In ammonium chloride dn/dT reaches the phenomenally high value of -550×10^{-6} at the transition temperature. NH_4Br on the other hand exhibits a positive value of dn/dT on approaching the transition temperature (Table I-a). This is quite in tune with the fact that these substances exhibit catastrophic changes in length at these temperatures, (NH_4Cl expands while NH_4Br contracts) (Simon and Bergmann 69).

CaF_2 is one of the few substances that have been studied in great detail, the measurements extending from the infrared (6.5μ) to 0.185μ in the ultraviolet. Since the effect of the thermal expansion is much higher than the frequency contribution, dn/dT throughout this region is found to be negative. One notices that dn/dT tends to increase as one proceeds both into the infrared and the ultraviolet. The explanation of this is as follows (Ramachandran 52). The volume contribution follows a course similar to that of the refractive index, *i.e.*, $1/(\lambda^2 - \lambda_1^2)$ (see equation 10), while the frequency contribution is proportional to $1/(\lambda^2 - \lambda_1^2)^2$. The volume contribution decreases numerically as we go from the extreme ultraviolet to the infrared. The latter effect, due to the square term is symmetrical about the absorption frequencies and increases as we go towards both the ultraviolet and the infrared. The sum of these two would give values of dn/dT which increase as we approach both the ultraviolet and the infrared. This behaviour is not a particular characteristic of CaF_2 . Indeed this should be the behaviour to be expected in all crystals.

We next take up the case of crystals that show a positive value of dn/dT . These crystals are usually known to be covalent. The thermal expansion in these crystals is so small that the volume effect is much less than that due to the frequency change. In ZnS, in spite of its thermal expansion being about twice that of diamond, the dn/dT value is almost five times as large. The positive value for MgO was actually predicted by Burstein and Smith (4) from a study of its photoelastic constants. In the case of diamond the value of χ ($= 7.6 \times 10^{-6}$) calculated from the dn/dT data agrees reasonably well with that obtained from the shift of the lattice frequency ($\chi = 9.8 \times 10^{-6}$).

Diamond also exhibits a rather peculiar anomaly at 210°C. One finds that while the curve dn/dT vs. T is almost a straight line over the temperature range -100°C to 450°C there appears a perceptible hump at 210°C . At this temperature diamond is known to exhibit a very bright thermo-luminescence (Chandrasekharan 13) and even the Raman shift of the lattice line has a particularly low value (R. S. Krishnan 27).

It is seen from Tables I and II that dn/dT is a function of temperature. The numerical magnitude of dn/dT , increases with temperature irrespective of its actual sign and it tends towards zero as one approaches absolute zero. The values of X for various crystals also exhibit a similar variation with temperature, tending towards zero as the temperature decreases. We shall have occasion to refer to this property in the next section.

The variety of extremely beautiful phenomena exhibited by birefringent crystals when they are heated has attracted the attention of a large number of experimenters. We shall now discuss the famous Mitscherlich phenomenon. When a plate of gypsum (which at room temperature is a positive biaxial crystal) is heated, the optical axial angle goes on diminishing and at about 90°C the crystal becomes uniaxial. Above this temperature the crystal again becomes biaxial but with its optic axial plane rotated through a right angle. This phenomenon can be most spectacularly exhibited in the case of crystals whose three refractive indices are very close to each other, for in such a case the optic axial angle would be large. The condition for exhibiting this phenomenon in an orthorhombic crystal is that two of the refractive indices (say $n_1 > n_2$) must be close to each other and $dn_1/dT < dn_2/dT$. In such a case at a particular temperature, n_2 could become equal to n_1 making the crystal uniaxial. At higher temperatures n_2 may even become greater than n_1 . Here special mention should be made of CsSeO_4 (Tutton 79) for which within the narrow range of $0-250^\circ\text{C}$ each of the three axes of the optical ellipsoid becomes in turn the acute bisectrix. In the case of crystals belonging to the monoclinic or triclinic systems this phenomenon is further complicated by the rotation of the axes of the index ellipsoid due to thermal expansion. Indeed the crossed axial dispersion effect in the case of gypsum, which belongs to the monoclinic system, mainly arises due to this effect.

The temperatures at which these biaxial crystals become uniaxial will obviously depend on the wavelength of light. In fact there are a few crystals like Brookite which exhibit crossed axial dispersion at room temperature with change of wavelength. In a similar manner a few uniaxial crystals are known to become optically isotropic at a particular wavelength or temperature. For instance the birefringence of the positive uniaxial crystal benzil progressively decreases as one goes from the red to the blue. At γ 4900 it becomes isotropic and beyond this wavelength the crystal becomes optically negative (Bryant 3).

Quartz is one of the substances whose thermo-optic behaviour has been extensively investigated. The complete data and literature for this substance up to the year 1928 are available in the monograph 'Properties of Silica' by Sosman. It may be remarked that the dn/dT values for both the ordinary and the extraordinary rays are negative up to a wavelength of about γ 2200 below which they both become positive (Michelli 34). This arises, as has been mentioned earlier, due to the large

frequency contribution as these wavelengths are close to the absorption bands. Another exceedingly interesting phenomenon that has been observed is that even fused silica which is amorphous, shows anomalies in optic behaviour at temperatures close to the α - β transformation of quartz and to the crystobalite transformation near 300°C (Narayanan 37).

The comparison of the thermo-optic properties of calcite and aragonite which are structurally and optically similar is of some interest. The dn/dT of calcite is positive while that of aragonite is negative. This difference is due to the much larger thermal expansion of aragonite (70×10^{-6} as compared to 16×10^{-6} for calcite) which gives rise to a large negative component which swamps the positive frequency contribution.

The phenomenological theories for the thermo-optic behaviour of birefringent solids given in Sec. 3 have been successfully applied to the cases of quartz, calcite, aragonite, SiC, and anatase and the χ and K values are included in Table VII.

Very little data are available for the variation of optical activity of crystals with temperature, the only cases being quartz, NaClO_3 , HgS , and Benzil. The $d\rho/dT$ in all these substances have been explained satisfactorily using the theory given in Sec. 3. A point of some significance is that the values of χ obtained from $d\rho/dT$ is approximately the same order as those obtained from dn/dT data. Here again one has to seriously examine whether the oscillator strength also changes with temperature or not.

6. THERMO-OPTIC AND PIEZO-OPTIC CONSTANTS OF CRYSTALS

When a crystal is subjected to hydrostatic pressure its density and hence the number of the dispersion centres per unit volume increases. It is found that the change in the refractive index due to this effect alone cannot explain the observed changes in ' n ' of the crystal. Mueller (36) attributed this difference to the change in the intrinsic polarisability of the atoms due to strain. Let us next consider the change in the refractive index of a crystal whose temperature is lowered. Again the number of dispersion centres and the lattice parameter are altered. In this case, also one finds that these two effects alone cannot completely explain the observed dn/dT . This indicates most clearly the existence of a pure temperature effect. We shall now proceed to derive expression for these three effects and evaluate them from the experimental data.

For doing this one has to start with an equation correlating density with the refractive index of the solid. Here again we have to choose between the Drude form and the Lorentz form. Following Ramachandran and Radhakrishnan (56) we shall use in the following derivation the Drude type of equation. As the procedure adopted when the Lorentz formula is used, is almost identical we shall content ourselves by giving only the final numerical values for this case.

According to the Drude formula

$$n^2 - 1 = 4\pi N\alpha \quad (29)$$

where α is the polarisability. When the density ρ or the temperature is altered

both N and α are altered and since N is proportional to ρ

$$\frac{dN}{d\rho} = \frac{N}{\rho}, \quad \frac{dN}{dT} = \frac{dN}{d\rho} \times \frac{d\rho}{dT} = \frac{N}{\rho} \frac{d\rho}{dT} \quad (30)$$

and since α is a function of both ρ and T

$$\frac{d\alpha}{dT} = \left(\frac{\partial\alpha}{\partial\rho}\right)_T \frac{d\rho}{dT} + \left(\frac{\partial\alpha}{\partial T}\right)_\rho \quad (31)$$

Differentiating equation (29) we have

$$\frac{dn}{d\rho} = \frac{n^2 - 1}{2n\rho} \left[1 + \frac{\rho}{\alpha} \left(\frac{\partial\alpha}{\partial\rho}\right)_T \right] \quad (32)$$

and

$$\frac{dn}{dT} = -\gamma \frac{n^2 - 1}{2n} \left[1 + \frac{\rho}{\alpha} \left(\frac{\partial\alpha}{\partial\rho}\right)_T - \frac{1}{\gamma\alpha} \left(\frac{\partial\alpha}{\partial T}\right)_\rho \right] \quad (33)$$

where the coefficient of cubical expansion γ is given by

$$\frac{1}{\rho} \frac{d\rho}{dT} = -\gamma.$$

Thus it is possible to separate dn/dT as arising from three causes namely (a) the change in the dispersion centres per unit volume (b) the change in the polarisability caused by thermal dilatation and finally (c) the pure temperature effect on the polarisability. Denoting these contributions by P ; Q ; R respectively we have

$$P = \left(\frac{\partial n}{\partial N}\right)_\alpha \left(\frac{dN}{dT}\right) = -\gamma \frac{n^2 - 1}{2n} \quad (34)$$

$$Q = \left(\frac{\partial n}{\partial\alpha}\right)_N \left(\frac{\partial\alpha}{\partial\rho}\right)_T \left(\frac{d\rho}{dT}\right) = -\gamma \left[\rho \frac{dn}{d\rho} - \frac{n^2 - 1}{2n} \right] \quad (35)$$

$$R = \left(\frac{\partial n}{\partial\alpha}\right)_N \left(\frac{\partial\alpha}{\partial T}\right)_\rho = \frac{dn}{dT} + \gamma\rho \frac{dn}{d\rho} \quad (36)$$

and hence

$$\frac{dn}{dT} = P + Q + R. \quad (37)$$

From the measured values of γ , n , dn/dT and $dn/d\rho$ $\left[= \frac{n^2}{6\rho} (\rho_{11} + 2\rho_{12}) \right]$, Ramachandran and Radhakrishnan have evaluated the value of P , Q and R for a number of crystals and these are entered in Table IX.

Equation (31) could be rewritten as -

$$\frac{1}{\alpha} \left(\frac{d\alpha}{dT}\right) = -\gamma \frac{\rho}{\alpha} \left(\frac{\partial\alpha}{\partial\rho}\right)_T + \frac{1}{\alpha} \left(\frac{\partial\alpha}{\partial T}\right)_\rho \quad (31-a)$$

Since γ represents the increase in volume when the temperature of a unit volume of the substance is increased by 1°C . (*i.e.*, the strain introduced per unit rise of temperature), then $-\frac{\rho}{\alpha} \left(\frac{\partial\alpha}{\partial\rho}\right)_T$ and $\frac{1}{\alpha} \left(\frac{\partial\alpha}{\partial T}\right)_\rho$ are the strain and temperature coefficients of polarisability and could, for convenience, be denoted by λ_0 and τ_0 . It may be mentioned that λ_0 is identical with the strain-polarisability constant which Mueller introduced while developing the theory of Photoelasticity (Mueller 36).

The altered value of the polarisability for T°C. rise of temperature can then be written as

$$\alpha_T = \alpha_0 (1 + \lambda_0 \gamma T + \tau_0 T) \quad (38)$$

which to a first degree of approximation gives

$$\frac{dn}{dT} = \frac{n^2 - 1}{2n} \left[-\gamma + \lambda_0 \gamma + \tau_0 \right] \quad (39)$$

A comparison of (37) and (39) yields

$$\lambda_0 = -\frac{Q}{P}; \quad \tau_0 = -\frac{R\gamma}{P} \quad (40)$$

Since polarisability is the fundamental optical property, it is quite clear that while comparing the thermo-optic behaviour of *different substances*, one has to compare the magnitudes of λ_0 , γ and τ_0 . The values of λ_0 , $\lambda_0 \gamma$, τ_0 and τ_0/γ at room temperature for different cubic crystals calculated from the above formulae are given in Table X. The values $\lambda_0 L$ and $\tau_0 L/\gamma$ calculated by using the Lorentz-Lorenz formula are also given in the same table.

It may be noticed that the magnitude and in some cases even the sign of τ_0 depend on the type of dispersion formula used. However since both τ_0 and τ_{0L} show the same trends we may draw some general conclusions regarding the thermo-optic behaviour of various crystals.

The most striking fact one notices on a study of Table X is that τ_0 is very much lower than $\lambda_0 \gamma$ showing that the change in the polarisability due to the pure temperature effect is much smaller than that due to a change in the lattice parameter. In other words the major part of the frequency shift observed (Fesefeldt 19) and calculated (Ramachandran 51 etc.) is due to the change in the lattice parameter rather than the pure temperature effect. The change in the Raman frequencies with temperature would also obviously depend mainly on $\lambda_0 \gamma$.

The first term in equation (39) represents the density contribution and is always negative, $\lambda_0 \gamma$ is in general positive and τ_0 can either be positive or negative; but as τ_0 is much smaller than $\lambda_0 \gamma$, the sign of dn/dT usually depends on $(-1 + \lambda_0)$. Consequently, we could predict the thermo-optic behaviour of many crystals from a knowledge of their photoelastic behaviour. For example in the case of NH_4 -alum, K-alum, Tl-alum and $\text{Pb}(\text{NO}_3)_2$, since λ_0 is negative, dn/dT must necessarily be negative. Conversely, the photoelastic behaviour of a crystal could also be predicted from its thermo-optic behaviour. The case of ZnS is particularly interesting because of its exceptional thermal variation of the refractive index. dn/dT for this crystal is found to be 65×10^{-6} for 5780 Å.U. By a simple calculation using (43) one gets $(\lambda_0 + \tau_0/\gamma) = 4.32$. Hence λ_0 must definitely be more than unity. Therefore the elasto-optic constant $(\rho_{11} + 2\rho_{12})$ must be negative. Photoelastic measurements on ZnS are not available but it would be most interesting to see whether experiments actually support these theoretical conjectures.

From Table (I) it is seen that dn/dT is itself a function of temperature. A complete expression for this can be had by the differentiating equation (29) with the proper values of α substituted from (39). It is found on computation that all the

three parameters $\left(\frac{d\gamma}{dT}\right)$, $\left(\frac{d\lambda_0}{dT}\right)$ and $\left(\frac{d\tau_0}{dT}\right)$ contribute to the observed variation of (dn/dT) with temperature.

It may be remarked that Ramachandran and Radhakrishnan (56) expressing the polarisability α as Taylor series in δr , the changes in the distance r between atoms, find that while the piezo-optic coefficients depend only on $d\alpha/dr$ the pure temperature effect is a function of $\frac{d^2\alpha}{dr^2}$.

7. EXPERIMENTAL DATA

In Tables I to III are collected the temperature variation of refractive index data for isotropic and birefringent crystals at selected values of wavelengths and temperatures. Table I deals with the data on cubic crystals. The values of $dn/dT \times 10^6$ are given for five different wavelengths λ 2537 μ , 3615 μ , 4358 μ , 5461 μ , 5893 μ at various temperatures wherever such data are present. In a few cases the measurements have been carried out at wavelengths different from those mentioned above. These cases are labelled by letters in parentheses and exact values of the wavelengths at which measurements have been carried out can be had from the foot-notes to Tables I and II. Wherever dn/dT data for any particular crystal have been obtained by more than one observer, only those data which cover the widest range of temperature and wavelength are included in the tables. The unbracketed numbers in column (9) give the references to the workers whose data are given in the tables. The numbers in brackets in the last column denote the references to the other workers who have also made observations on the particular crystal.

In Table I (a) the dn/dT values are given for λ 5461 μ for NH_4Cl and NH_4Br at various temperatures including the transition range.

In Tables II and II (a) are given the dn/dT values for the principal refractive indices for some birefringent crystals. The remarks on Table I hold for these tables also. In uniaxial crystals the refractive indices are labelled by the Greek symbols ω and ϵ , while in biaxial crystals they are denoted by n_1, n_2, n_3 .

Table III gives the temperature variation of refractive index data for some minerals. As the measurements are not extensive, only the mean values of dn/dT for the visible region of the spectrum are given over a temperature range.

In Table IV are given the data on the temperature variation of the optical rotation in crystals. The values of $\left(\frac{d\rho}{dT}\right) \times 10^3$ are given for eight different wavelengths wherever such measurements are available. The temperature range over which measurements have been made is also indicated.

The principal refractive index of any crystal at any wavelength λ is usually expressed by the following formula :

$$n^2 - 1 = A + \sum_i \frac{A_i \lambda^2}{\lambda^2 - \lambda_i^2}$$

where A and A_i 's are constants and λ_i 's are the absorption wavelengths for the crystal. In Table V are given the values of these constants as proposed by the various obser-

vers (indicated in the last column of the table) along with the range of wavelengths over which this formula holds. The fit of the formula is also indicated in the table. The absorption wavelengths given in italics in the table have been experimentally observed (22a, 63a). The other wavelengths are hypothetical and have been chosen by different observers to give a good fit with the observed data on refractive index.

Similarly Table VI gives the parameters in the following formula for the dispersion of optical rotation.

$$\rho = B + \sum_i \frac{B_i \lambda^2}{(\lambda^2 - \lambda_i^2)^2}$$

Table VII gives the values of $X_i = \frac{1}{\lambda_i} \frac{d\lambda_i}{dt} \times 10^6$ near room temperature for the different absorption frequencies that are responsible for refractive dispersion indicated in Table V. These X values have been proposed by various workers (indicated in the last column of the table) from the data on dn/dT in crystals.

In Table VIII are given the X values for the different absorption wavelengths in Table VI used in the dispersion formula for optical rotation. These values have been obtained from the $d\rho/dT$ data in crystals.

Table IX gives the values of the constants P (the contribution to dn/dT due to a change in the number of oscillators per unit volume), Q (the contribution to dn/dT due to a change in polarisability caused by thermal dilatation) and R (the contribution to dn/dT due to a pure temperature effect on polarisability). These values have been obtained from the values of γ , n , dn/dT and $dn/d\rho$ (56).

Table X gives the values of λ_0 , γ , τ_0 , λ_0 and τ_0/γ where

λ_0 = Strain coefficient of the polarisability

τ_0 = Temperature coefficient of the polarisability at constant strain and

γ = the coefficient of cubical expansion of the crystal.

In all these tables the wavelengths are given in microns.

TABLE I

TEMPERATURE VARIATION OF REFRACTIVE INDEX OF CUBIC CRYSTALS $dn/dT \times 10^6$

Crystal	T°C.	.2537	.3650	.4358	.5461	.5893	Wavelength range	Author Reference
LiF	50	-11.0	-12.0	-12.5	-12.7	-12.7		47 (23)
	100	-13.1	-13.7	-14.2	-14.4	-14.4		
	200	-16.7	-17.5	-18.1	-18.1	-18.2		
	300	-22.3	-22.0	-22.5	-22.6	-22.7		
	400	-26.5	-27.8	-28.0	-28.2	-28.5		
NaF	49				-10.0			23
NaCl	-180				-26.5			2
	-120				-31.1			
	-60				-37.7			
	0				-38.2			
	61.8	+2.99(a)	-21.05(b)	-35.4(d)		-37.3	.2 to .59	34
KCl	55			-35.6(c)		-36.4	.43 to .21	41
KBr	22			-37.1	-39.2	-39.7(l)	.40 to .71	62 (25)
KI	64				-50			25
CsBr	25		-73.3	-60.0	-63.3	-63.3(l)	.36 to .71	63
CsI	25			-98.2	-99.4	-100 (l)	.4 to .64	61
NaClO ₃	75			-53.2	-53			21
	125			-58.6	-58.4			
	175			-63.5	-63.2			

TABLE I—(continued)

Crystal	T°C.	.2537	.3650	.4358	.5461	.5893	Wavelength range	Author Reference
CaF ₂	-170				- 8.0			
	-110				-11.2			2
	- 10				-13.3			
	68	-9.24(b)		- 11.6(g)		-11.9	.18 to 6.5	34, 29 (58)
	50	-8.8	-10.8	- 11.0	-11.4	-11.8		
	200	-11.3	-12.9		-13.4	-13.9		47
MgO	400	-15.4	-17.3		-18.3	-18.8		
	50		+19.5	+ 17.9	+16.5	+16		46
	400		+19.9	+ 17.9	+16.5	+16.1		
ZnS	-195				+12.5			
	-100				+45.0			2
	- 20				+67.5			
	- 40			+ 98.7	+37.5	53.7(i)	0.41 to 0.73	
	100			+103.5	+68.5	58.0(i)	0.41 to 0.73	
	300			+121.0	+86.5	73.5(i)	"	33
	500			+142.5	+93	84.0(i)	"	
	650			-	+85	-	-	
Diamond	-150			+ 0.2	+ 0.1	+ 0.1		
	-100			+ 2.4	+ 2.1	+ 1.9		
	0			+ 9.9	+ 8.7	+ 8.4		
	100			+ 17.5	+15.7	+15.4		51 (67)
	200			+ 27.8	+24.5	+24.1		
	300			+ 33.5	+30.3	+29.8		
	400			+ 43.1	+39.1	+38.4		
	K alum	21					-14	

TABLE II
TEMPERATURE VARIATION OF REFRACTIVE INDEX OF QUARTZ AND CALCITE $dn/dT \times 10^6$

Crystal	T°C.	.2537	.3650	.4358	.5461	.5893	Wavelength Range	Author Reference	
Quartz ω	-180				-4.1				
	-100				-4.8				
	0				-5.65				
	50	-2.9	-5.4	-5.9	-6.2	-6.3		47	
	200	-4.3	-7.1	-7.7	-8.2	-8.4		(2, 60, 72)	
	400	-10.0	-13.2	-12.4	-14.4	-14.6			
	ϵ	61.4	+1.84 (a)		6.25 (g)		-6.50	0.20 to 0.64	34
		61.4	+1.29 (a)		-7.29 (g)		-7.54	" "	34
		-175				-6.0			
		-75				-7.0			2
		+25				-7.2			
		50	-4.0	-6.2	-6.6	-7.0	-7.1		
		200	-5.5	-8.0	-9.2	-10.0	-11.0		47
	400	-12.0	-14.7	-15.8	-16.5	-16.7		(60, 72)	
Calcite ω	-175				+ 2.6				
	-75				+ 0.6			2	
	9				+ 0.06				
	61.5	+8.1 (b)		+ 1.67 (g)		+ 1.21	0.21 to 0.64	34	
	18					+ 0.71			
	61					+ 0.79		59	
	248					+ 1.32			
	349					+ 1.68			
	ϵ	-175				+10.0			
		-75				+11.6			2
		9				+12.2			
	61.5	+17.6 (b)		+11.27 (g)		+11.06	0.21 to 0.64	34	
	18					+10.05			
	61					+11.0		59	
	248					+13.13			
	349					+14.35			

TABLE II (a)

TEMPERATURE VARIATION OF REFRACTIVE INDEX OF
BIREFRINGENT CRYSTALS

Crystal	T°C	·4358	·5461	·6910	Author Reference	
Aragonite	n_1	150	-12·0 (<i>e</i>)	-11 (<i>q</i>)	31	
		150	-13·0 (<i>f</i>)	-14 (<i>p</i>)	38	
	n_2	150	-25·0 (<i>e</i>)	-27 (<i>q</i>)	31	
		150	-25·0 (<i>f</i>)	-25 (<i>p</i>)	38	
	n_3	150	-29·0 (<i>e</i>)	-30 (<i>q</i>)	31	
		150	-27 (<i>f</i>)	-28 (<i>p</i>)	38	
SiC	ω	240	+75 (<i>e</i>)	+66 (<i>h</i>)	+59 (<i>n</i>)	
		610	+100 (<i>e</i>)	+82 (<i>h</i>)	+74 (<i>n</i>)	83
		955		+97 (<i>h</i>)	+90 (<i>m</i>)	
	ϵ	240	+82 (<i>e</i>)		+63 (<i>n</i>)	83
		610	+115 (<i>e</i>)		+80 (<i>n</i>)	
Anatase (TiO ₂)	ω	162	-18	-25	-26	
		600		-6	-13	66
	ϵ	162	+4	-8	-18	
Rutile (TiO ₂)	ω	600		+6	0	
		162		-51	-45	
	ϵ	375		-27	-30	1 (66)
		162		-89	-77 (<i>j</i>)	
Brookite	n_1	375		-54 (<i>j</i>)		
		162	+51	+24	+20	
		450		+24	+18	
	n_2	162	+53	+21	+14	66
		450		+21	+11	
		162		-91	-89	
Barite	n_1	450		-51	-50	
		50		-25·3		
		400		-32·5		
	n_2	50		-18·2		
		400		-26·0		47 (24)
Mica	n_2	50		-21·3		
		400		-26·7		
	n_3	107	-4·4 (<i>c</i>)		-7·9 (<i>k</i>)	45
		107	-3·8 (<i>c</i>)		-6·8 (<i>k</i>)	

Foot Note to Tables I and II

$a = \lambda \cdot 2020$; $b = \lambda \cdot 2573$; $c = \lambda \cdot 4340$; $d = \lambda \cdot 4450$; $e = \lambda \cdot 4710$;
 $f = \lambda \cdot 4800$; $g = \lambda \cdot 5058$; $h = \lambda \cdot 5540$; $i = \lambda \cdot 6190$; $j = \lambda \cdot 6230$;
 $k = \lambda \cdot 6380$; $l = \lambda \cdot 6438$; $m = \lambda \cdot 6500$; $n = \lambda \cdot 6680$; $p = \lambda \cdot 6710$;
 $q = \lambda \cdot 7060$.

TABLE III
TEMPERATURE VARIATION OF REFRACTIVE INDEX IN SOME MINERALS $dn/dT \times 10^6$

Crystal	Formula	T°C.	Wavelength	$dn/dT \times 10^6$			Reference
				n_1	n_2	n_3	
Sulphur		19	0.535	-170	-230	-280	64
Molybdenite	MoS ₂	-190 to 18	0.705	+16300	—	—	15
Mascagnite	(NH ₄) ₂ SO ₄	15 to 80	Visible	-49	-40	-62	75
	K ₂ SO ₄	20 to 180	Visible	-40	-40	-50	75
	Rb ₂ SO ₄	60 to 180	Visible	-40	-30	-30	75
	Cs ₂ SO ₄	20 to 180	Visible	-40	-30	-30	75
Anhydrite	CaSO ₄	-50 to 560	Visible	-4	-6	-12	24
Celestite	SrSO ₄	-50 to 500	Visible	-16	-14	-19	24
Anglesite	PbSO ₄	-50 to 550	Visible	-28	-23	-37	24
Gypsum	CaSO ₄ .2H ₂ O	12 to 105	Visible	-13	-43	-26	16
Syngenite	CaSO ₄ .K ₂ SO ₄ .H ₂ O	10 to 130	Visible	-26	-26	-35	65
	(NH ₄) ₂ SeO ₄	80 to 100	Visible	-10	-30	-40	78
	Rb ₂ SeO ₄	20 to 80	Visible	-40	-50	-60	76
	Cs ₂ SeO ₄	20 to 80	Visible	-70	-60	-60	76
	R ⁿ R ₂ (SO ₄) ₂ .6H ₂ O*	10 to 80	Visible	≈ -30	≈ -30	≈ -40	80
	R ⁿ R ₂ (SeO ₄) ₂ .6H ₂ O†	10 to 80	Visible	≈ -20	≈ -30	≈ -30	80
Apatite	CaF.Ca ₄ (PO ₄) ₃	0 to 600	Visible	-30	—	-59	17
Phenacite	Be ₂ SiO ₄	0 to 300	Visible	+11	—	+11	38
Beryl	Be ₃ Al ₂ (SiO ₃) ₆	0 to 300	Visible	+13	—	+12	38
Topaz	(AlF) ₂ SiO ₄	0 to 300	Visible	+8.5	+8.5	+8.5	38
Oligoclase	(nNaAlSi ₃ O ₈ .mCaAl ₂ Si ₂ O ₉)	0 to 300	Visible	+3.7	+4.8	+4.6	38
Orthoclase	KAlSi ₃ O ₈	-50 to 400	Visible	+4	+5.4	+3.5	84
Leucite	KAl(SiO ₃) ₂	21 to 585	Visible	-12	—	—	60
Zircon	ZrSiO ₄	25 to 1000	Visible	+18	—	+20	18, 77
Boracite	Mg ₆ B ₁₄ O ₂₆ Cl ₂	290 to 650	Visible	+10	—	—	31
	K ₂ SeO ₄	20 to 50	Visible	-50	-60	-70	76
Rochelle salt	NaKC ₄ H ₄ O ₆ .4H ₂ O	-65 to 40	Visible	-65	-61	-65	81

* Rⁿ = Zn, Cu, Mn, Co, Ni, Mg ; R₂ = (NH₄).

† Rⁿ = Zn, Mn, Fe, Ni ; R₂ = (NH₄)₂, Cs₂, Rb₂.

TABLE IV
TEMPERATURE VARIATION OF OPTICAL ROTATION IN CRYSTALS $d\rho/dT \times 10^3$

Crystal	Temperature	.2537	.3650	.4358	.5085	.5461	.5893	.6438	.6708	Reference
α -Quartz	-188 to 20°C			4.7	3.2	2.8	2.4	1.9	1.7	35 (73)
	31 to 185°C	27.4	10.3	7.0		4.0	3.6(a)			12
	199 to 410°C	34.6	13.0	8.8		5.0	4.4(a)			12
NaClO ₃	53°C		0.089	0.047		0.028	0.022(a)			21 (71)
	69°C		0.094	0.049		0.030	0.023(a)			21
	88°C		0.100	0.053		0.033	0.025(a)			21
Cinnabar	-180 to 20°C							180	120	35
Benzil					-25(b)	-20	-15(a)			

(a) — λ .5790 (b) — λ .4916

TABLE VI

DISPERSION OF OPTICAL ROTATION OF CRYSTALS $\rho = B + \sum \frac{B_1 \lambda^2}{(\lambda^2 - \lambda_1^2)^2} + \sum \frac{B_2 \lambda^2}{(\lambda^2 - \lambda_2^2)^2}$

Crystal	B	B ₁	λ ₁	B ₂	λ ₂	Wavelength range	Fit.	Ref.
α-Quartz		7.186	0.0926			0.15 to 0.80	0.1%	12
NaClO ₃	-0.123	1.2387	0.0900	-0.1374	0.1850	0.23 to 0.87	0.5%	8
Benzil				6.27	0.2400	0.36 to 0.88	*	11
Cinnabar				19.13	0.4930	0.60 to 0.72	2%	10

* anomalous rotation between λ 3900 and λ 4900.

TABLE VII
 χ VALUES OF CRYSTALS (from dn/dT data)

Crystal	$X_1 \times 10^6$	$X_2 \times 10^6$	$X_3 \times 10^6$	$X_4 \times 10^6$	$X_5 \times 10^6$	Remarks	Ref.
LiF	45						21
NaF		79					21
NaCl	0	-33	23.5	110	150		54
KCl	0	-13		90	150		54
KBr			-4.9	81			21
NH ₄ Cl	0	63.6		63.6			21
NaClO ₃		5.7		55.5			21
CaF ₂	0	11.3	70.2		159		52
MgO		35					46
ZnS				70			53
Diamond		7.6		7.6			51
α -Quartz	0	0	78			$K_1 = K_2 = 0, K_3 = 0.88$	47, 50
Calcite	0	10.8	30			$K_1 = K_2 = 0, K_3 = 1.006$	55
Aragonite	0	14.6	29			$K_1 = K_2 = 0, K_3 = 1.3$	55
SiC			35	35			49
Anatase				12.3			48

TABLE VIII

X VALUES OF CRYSTALS (from $d\rho/dT$ data)

Crystal	X_1	X_2	Ref.
α -Quartz	40		12
NaClO ₃	7.5	75	21
Cinnabar		70	10

TABLE IX

Crystal	n_D	$\gamma \times 10^5$	$P \times 10^5$	$Q \times 10^5$	$R \times 10^5$
LiF	1.392	10.2	-3.4	2.4	-0.3
NaCl	1.544	12	-5.4	2.5	-0.9
KCl	1.490	11.4	-4.7	2.1	-1.0
KBr	1.559	12	-5.6	1.4	-0.2
KI	1.667	13.5	-7.2	1.4	+0.8
CaF ₂	1.434	5.7	-2.1	0.7	+0.2
MgO	1.736	3.9	-2.2	3.6	+0.2
Diamond	2.417	1.3	-1.3	1.66	+0.6

TABLE X

STRAIN AND TEMPERATURE COEFFICIENT OF POLARISABILITY

Crystal	Drude Equation				L-L Equation	
	$\lambda_0 \gamma \times 10^5$	$\tau_0 \times 10^5$	λ_0	τ_0/γ	λ_0^L	τ_0^L/γ
LiF	7.1	+0.9	+0.7	-0.09	0.7	-0.06
NaCl	5.6	-2.0	0.47	-0.17	0.63	-0.11
KCl	5.0	-2.4	0.44	-0.21	0.61	-0.14
KBr	2.9	-0.5	0.24	-0.04	0.48	+0.05
KI	2.6	+1.5	0.19	+0.11	0.48	+0.08
CaF ₂	1.8	+0.6	0.32	+0.10	0.50	+0.07
MgO	7.0	+0.35	1.8	+0.09	1.4	-0.02
Diamond	1.7	+0.6	1.28	+0.49	1.1	+0.18

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