

TEMPERATURE VARIATION OF REFRACTIVE INDEX AND OPTICAL ROTATION OF SODIUM CHLORATE

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SUMMARY

Measurements of the temperature variation of refractive index of sodium chlorate for the two wavelengths 4358 A.U. and 5461 A.U. of mercury have been made in the temperature region from 55° C. to 200° C. From the data, the values of the proportionate shift with temperature of the ultraviolet dispersion frequencies have been evaluated. The thermal variation of optical rotation ($d\rho/dt$) of sodium chlorate for the wavelengths λ 3650, 4047, 4358, 5461 and 5790 of mercury have been determined for three temperature ranges using a photoelectric polarimeter and the results are explained using Chandrasekhar's theory.

1. INTRODUCTION

A phenomenological theory for the thermal variation of the refractive indices of cubic and birefringent crystals was put forward by Ramachandran (1947), on the basis of which the thermo-optic behaviour of a number of crystals was satisfactorily explained. Recently Chandrasekhar (1952, 1954) presented a theory for the variation of optical rotation of crystals with temperature and applied it successfully to the case of quartz and cinnabar. Both the theories make use of the concept that the effect of temperature on a crystal is not only to change the number of dispersion centres per unit volume but also to alter the magnitudes of the absorption frequencies responsible for the optical properties. Sodium chlorate which crystallises in the cubic system (Class T, 23) and exhibits optical activity would be an ideal substance for verification of both the theories. The thermal variation of the refractive index of this substance has not been investigated up till now. Some data on the variation of its optical activity with temperature were recorded by Sohncke (1878). A detailed study has therefore been made on the temperature variation of refractive index and optical rotation of a single crystal of sodium chlorate.

2. EXPERIMENTAL DETAILS

(i) *Temperature Variation of Refractive Index.*—A clear strain-free crystal of sodium chlorate was grown by the method of slow evaporation from an aqueous solution. A thin plate was cut parallel to the cube faces, ground and polished to give fairly broad interference fringes. The thickness of the plate used was 1.4 mm.

The optical set-up employed for the measurement of the temperature variation of refractive index was similar to the one used in this laboratory by Radhakrishnan (1948) for quartz. The temperature of the furnace enclosing the crystal was measured accurately with the aid of a calibrated thermo-couple. The accuracy of the measurement was $\pm 0.03^\circ \text{C}$. Fringe-shift was observed visually when the crystal was slowly heated. Measurements were carried out for λ 4358 and 5461 of mercury in the range of temperature from 55°C . to 200°C .

From the observations dn/dt was calculated by means of the relation,

$$\frac{dn}{dt} = \frac{\lambda}{2l\Delta t} - n\alpha_t \quad (1)$$

where l = the thickness of the crystal, Δt = the temperature necessary for one fringe-shift at a mean temperature of $t^\circ \text{C}$., λ the wavelength of light used and α_t the coefficient of linear expansion at temperature t . The coefficient of linear expansion α_t was obtained from the equation,

$$\alpha_t = 0.04279 + 0.075973t + 0.0107201t^2 \quad (2)$$

given by Sharma (1950). The calculated values of dn/dt along with the values of α at various temperatures are given in Table I. The values of dn/dt are accurate to 5%.

TABLE I
Values of dn/dt and χ of Sodium Chlorate

Temperature $^\circ \text{C}$.	Coefficient of linear expansion $\times 10^6$	$10^6 (dn/dt)$ 4358	$10^6 (dn/dt)$ 5461	$\chi \times 10^6$ (900)	$\chi \times 10^6$ (1850)
75	47.7	-53.0	-53.0	5.7	55.0
100	49.5	-56.0	-55.5	5.2	60.0
125	51.4	-59.0	-58.5	4.7	61.0
150	53.4	-61.0	-60.5	4.6	63.0
175	55.5	-63.0	-63.0	4.1	73.0

(ii) *Temperature Variation of Optical Rotation.*—As the change in the optical rotation with temperature is small, photoelectric methods for the measurement of temperature variation of optical rotation had to be used. A photoelectric polarimeter constructed and used by Mr. V. Sivaramakrishnan (1956) of this laboratory for his investigations on magneto-optics was suitably modified for the measure-

ment of the temperature variation of optical rotation. A parallel beam of light from a mercury discharge lamp was allowed to pass successively through a polariser, the specimen of sodium chlorate kept in a suitable furnace, an analysing nicol and was focussed on to the slit of a monochromator. A photomultiplier tube (RCA IP 28) received the light emerging from the exit slit of the monochromator. After suitable amplification, the signal was fed to a cathode-ray oscillograph. The "symmetric angles" method was employed for measuring the optical rotation and a calibrated thermocouple for recording the temperature. With this arrangement, rotations could be measured accurate to $\pm 0.01^\circ$ and the temperature within 0.75°C .

Using a strain-free crystal of sodium chlorate of effective optical path 13.5 mm., the rotations were measured for the five wavelengths λ 3650, 4047, 4358, 5461 and 5790 at the three different temperatures, namely, 34.8°C ., 71.5°C . and 103.5°C . The specific rotations (ρ) at these temperatures are given in Table II and the values of $d\rho/dt$ for the five wavelengths for the different temperature ranges are entered in Table III.

TABLE II
Specific Rotations (ρ) Expressed in Degrees per Millimetre

Wavelength	34.8°C .	71.5°C .	103.5°C .
3650 A.U.	8.54	8.87	9.19
4047 ..	6.88	7.12	7.34
4358 ..	5.90	6.07	6.24
5461 ..	3.67	3.77	3.87
5790 ..	3.26	3.34	3.42

Sohncke's values of $d\rho/dt$ for λ 5893, viz., $(0.193 \times 10^{-3}$ and $0.1817 \times 10^{-3})$ at the mean temperatures of 74°C . and 58°C . respectively are in good agreement with the values reported here.

3. DISCUSSION OF RESULTS

The dispersion of refractive index and that of optical rotation are represented by the formulæ

$$n^2 - 1 = \sum_r \frac{a_r \lambda^2}{(\lambda^2 - \lambda_r^2)} \tag{3}$$

and

$$\rho = \sum_r \frac{A_r N_r \lambda^2}{(\lambda^2 - \lambda_r^2)^2} \tag{4}$$

Differentiating (3) with respect to temperature and applying Ramachandran's theory, one gets

$$2n \frac{dn}{dt} = -\gamma(n^2 - 1) + \sum_r \frac{2a_r \lambda^4}{(\lambda^2 - \lambda_r^2)^2} x_r \quad (5)$$

TABLE III

Value of $d\rho/dt$ for different temperature ranges expressed in degrees per cm. per degree C. and of $(d\rho/dt + \gamma\rho)$, Experimental and Calculated

$$E_{(\text{expt.})} = \frac{d\rho}{dt} + \gamma\rho \quad C_{(\text{calc.})} = \frac{4\rho_1 \lambda^2}{(\lambda^2 - \lambda_1^2)} x_1 + \frac{4\rho_2 \lambda^2}{(\lambda^2 - \lambda_2^2)} x_2$$

	$d\rho/dt$ values		$(d\rho/dt + \gamma\rho)$ values calculated and experimental			
Temperature range	71.5–34.8° C.	103.5–71.5° C.	71.5–34.8° C.		103.5–71.5° C.	
Wavelength	Mean temperature 53.3° C. $d\rho/dt \times 10^3$	Mean temperature 87.5° C. $d\rho/dt \times 10^3$	E (Expt.) $\times 10^3$	C (Calc.) $\times 10^3$	E (Expt.) $\times 10^3$	C (Calc.) $\times 10^3$
3650 A.U.	0.888	0.997	1.06	1.06	1.12	1.12
4047 "	0.647	0.688	0.75	0.75	0.79	0.79
4358 "	0.469	0.525	0.55	0.55	0.61	0.63
5461 "	0.277	0.325	0.30	0.31	0.38	0.34
5790 "	0.216	0.250	0.26	0.26	0.30	0.30

where γ = coefficient of cubical expansion,

$$x_r = \frac{1}{\lambda_r} \frac{d\lambda_r}{dt}$$

Neglecting the contribution to dn/dt of the infrared term and using the necessary constants from the following equation given by Chandrasekhar (1953), the values of the proportionate shift with temperature of the dispersion wavelengths 900 A.U. and 1850 A.U. were calculated using (5) and are entered in Table I.

$$n^2 - 1 = \frac{1.1825 \lambda^2}{\lambda^2 - (0.0900)^2} + \frac{0.07992 \lambda^2}{\lambda^2 - (0.1850)^2} - 0.00864 \lambda^2 \quad (6)$$

Differentiating equation (4) and applying the theory of Chandrasekhar, one gets

$$\frac{d\rho}{dt} = \sum_r \frac{4\rho_r \lambda^2}{(\lambda^2 - \lambda_r^2)} x_r - \gamma\rho \quad (7)$$

where γ = coefficient of cubical expansion,

$$\rho_r = \frac{A_r N_r \lambda^2}{(\lambda^2 - \lambda_r^2)^2}; \quad \chi_r = \frac{1}{\lambda_r} \frac{d\lambda_r}{dt}$$

From the experimentally determined values of $d\rho/dt$, the values of the proportionate shift with temperature of the dispersion wavelengths 900 A.U. and 1850 A.U. were calculated, the necessary constants being from Chandrasekhar's (1953) equation

$$\rho = \frac{1.2387 \lambda^2}{[\lambda^2 - (0.0900)^2]^2} - \frac{0.1374 \lambda^2}{[\lambda^2 - (0.1850)^2]^2} - 0.123$$

It was observed that the values of χ evaluated from both the measurements were of the same order of magnitude as in other crystals studied. Further, the value of $\chi_{(1850)}$ is nearly ten times that for λ 900. This is quite in accord with the observations of Ramachandran (1947) who finds that in NaCl and KCl the dispersion wavelengths nearer to the visible region contribute much more to dn/dt than those in the remote ultraviolet. It is seen that the value $\chi_{(1850)}$ evaluated from dn/dt data increases with temperature. This seems to be a common feature of all the cubic crystals studied so far. However, the value of $\chi_{(900)}$ calculated from dn/dt measurements, decreases with increase of temperature. It is not clear whether this decrease is a genuine effect or due to experimental error. The latter possibility is very probable for the following reasons. The actual contribution to dn/dt by $\chi_{(900)}$ is very small compared to $\chi_{(1850)}$. Hence slight errors in dn/dt are liable to affect $\chi_{(900)}$ appreciably. It must also be remembered that the path retardation that is measured in the interference method mainly arises due to thermal dilatation for this particular case. Since the thermal expansion of NaClO_3 is large, dn/dt is evaluated as a small difference between two large quantities and hence is susceptible to an appreciable error. On the other hand it is seen that the values of $\chi_{(900)}$ and $\chi_{(1850)}$ obtained from $d\rho/dt$ data both increase with increase of temperature.

For verifying Chandrasekhar's theory, the values of $\chi_{(900)}$ and $\chi_{(1850)}$ obtained from equation (7) using the data for λ 3650 and 5790, were substituted in the expression

$$\frac{4\rho_1\lambda^2}{(\lambda^2 - \lambda_1^2)} \chi_1 + \frac{4\rho_2\lambda^2}{(\lambda^2 - \lambda_2^2)} \chi_2$$

and this value is compared with the experimental value of $(d\rho/dt + \gamma\rho)$ for the other wavelengths for the two ranges of temperature (71.5°C ., to 34.8°C . and 103.5°C . to 71.5°C .) (see Table III). According to the theory, the value of $(d\rho/dt + \gamma\rho)$ must be equal to

$$\frac{4\rho_1\lambda^2}{(\lambda^2 - \lambda_1^2)} \chi_1 + \frac{4\rho_2\lambda^2}{(\lambda^2 - \lambda_2^2)} \chi_2$$

and from Table III it is seen that they are nearly equal.

A comparison of the values of χ of the lattice lines and of the internal oscillations as obtained from the data on the temperature variation of Raman spectra with those obtained from dn/dt measurements is of interest. In NaClO_3 the temperature variation of Raman spectra has been investigated by Shantakumari (1950) and using her data the value of χ for the lattice lines comes out to be about 360×10^{-6} , while that for the internal oscillations has a value of the order of 27×10^{-6} . Unlike the covalent crystals quartz and diamond, the values of χ for the lattice lines in sodium chlorate are very much higher than the values obtained from dn/dt data. However, it is noticed that in sodium chlorate, the latter are nearly the same as those due to internal oscillations. As both diamond and quartz are typical covalent solids the binding is essentially due to the sharing of the outer electrons. In NaClO_3 which is an ionic crystal the ultraviolet electronic transitions and the internal oscillations of the ClO_3 ions behave in the same manner when the temperature is altered, *i.e.*, they are less affected by temperature than the lattice frequencies.

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