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## Dispersion of the Stress Optic Coefficient of the Alkali Halides

By

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With 4 Figures in the text

(Received Novembre 28, 1958)

The dispersion of the stress optic coefficient  $C = \frac{n^3}{2}(q_{11} - q_{12})$  of the alkali halides, NaCl, KCl, KBr and KI have been measured from the visible to the ultraviolet region. In general the value of "C" decreases with wavelength for all crystals. While the dispersion is only a few per cent in the visible region of wavelengths, it is enormous in the ultraviolet. NaCl shows a dispersion of about 100% from 5800 to 2400 Å; KCl about 200% from 5000 to 2400 Å; KBr about 300% from 5000 to 2400 Å; and KI about 400% from 5000 to 2800 Å. Also the potassium halides exhibit a change in sign of their "C" values in the ultraviolet. In KCl the sign reversal occurs at about 2550 Å; in KBr at 2760 Å and in KI at 3380 Å. Below these wavelengths, the potassium halides belong to the same class in MUELLER'S classification as sodium chloride. The theory of RAMASESHAN and SIVARAMAKRISHNAN based on the assumption that a stress causes a change in the frequencies and oscillator strengths of atoms is unable to explain the observed behaviour of the alkali halides. On the other hand, the mere variation of the ionic refractivities with wavelength is also unable to explain the observed dispersion on MUELLER'S theory. One is forced to assume that the strain polarisability constant  $K$  in MUELLER'S theory varies with wavelength. When " $K$ " is calculated from the experimentally observed values of "C", it is found to increase with decreasing wavelength for all alkali halides. The variation with wavelength of " $K$ " for all the alkali halides can be fitted up well by a formula of the type given by RAMASESHAN and SIVARAMAKRISHNAN. Hence it appears that the total dispersion of  $C$  can be explained only when we take into account the variation with wavelength of 1. the LORENTZ and COULOMB contributions from MUELLER'S theory and 2. the strain polarisability constant from RAMASESHAN and SIVARAMAKRISHNAN'S theory.

### Introduction

In recent years attempts have been made to measure the dispersion of the stress optic coefficient of a few crystals (POINDEXTER<sup>1</sup>; BANSIGIR and IYENGAR<sup>2</sup>; GIARDINI and POINDEXTER<sup>3</sup>). But in all these cases the dispersion measurements have been confined to the visible region of wavelengths. In all the crystals, the dispersion is only a few per cent up to 4000 Å. In the present investigation, the dispersion of the stress

<sup>1</sup> POINDEXTER, E.: Amer. Mineral. **40**, 1032 (1955).

<sup>2</sup> BANSIGIR, K. G., and K. S. IYENGAR: Proc. Phys. Soc. Lond. **71**, 225 (1958).

<sup>3</sup> GIARDINI, A. A., and E. POINDEXTER: J. Opt. Soc. Amer. **48**, 556 (1958).

optic coefficient  $C = \frac{n^3}{2} (q_{11} - q_{12})$  has been measured for the alkali halides in the visible and ultraviolet region of the spectrum. The alkali halides were chosen because 1. the stress optic coefficient  $C$  is positive for the potassium halides and negative for sodium chloride in the visible region of wavelengths and it would be interesting to find whether this distinction holds in the ultraviolet region of the spectrum also; and 2. the experimental results can be discussed in relation to MUELLER'S<sup>4</sup> theory of photoelasticity.

### Method of measurement

The method of measurement combines the differential feature of BANSIGIR and IYENGAR'S<sup>2</sup> method and the spectroscopic method of JOG<sup>5</sup>. The experimental arrangement is shown in Fig. 1.

Light from an iron or copper arc is focussed on to a slit  $S_1$ . The light emerging from  $S_1$  is focussed by the lens  $L_2$  on to the specimen

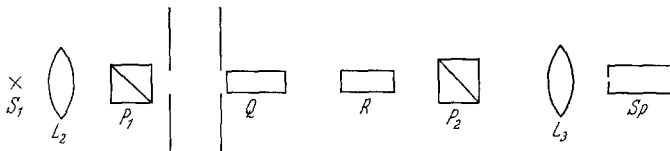


Fig. 1. Schematic diagram of the experimental arrangement

of fused quartz  $Q$  which is stressed with a conventional lever arrangement. A suitably oriented double image prism  $P_1$ , polarises the beam incident on  $Q$  at  $45^\circ$  to the vertical. The other beam is cut out by a suitably placed diaphragm. The light after passing through the fused quartz specimen is incident on the crystal specimen " $R$ ". The emergent light passes through a second Wollaston double image prism  $P_2$  set parallel to  $P_1$ . Two images of " $R$ " are formed on the slit of the spectrograph  $Sp$ . The Intermediate quartz spectrograph of ADAM HILGER is used. Two mirrors are suitably placed after  $P_2$ , to rotate the images of  $R$  through  $90^\circ$  so that the slit of the spectrograph scans a horizontal section of the image. The crystal is compressed by a second lever arrangement.

Initially the crystal  $R$  is removed. The fused quartz specimen  $Q$  is suitably stressed to get the  $n = 1$  band at about  $4900 \text{ \AA}$ . This band arises due to the path difference between the vertically and horizontally polarised light passing through the stressed quartz specimen. The position of the band is determined by the equation

$$\frac{C_1 W_1}{t_1} = n \lambda$$

<sup>4</sup> MUELLER, H.: Phys. Rev. **47**, 947 (1935).

<sup>5</sup> JOG, E. S.: J. Indian Inst. Sci. A **39**, 93 (1957).

( $n$  is integral for one image and half integral for the other) where  $C_1$  = stress optic coefficient of fused quartz at wavelength  $\lambda$ ;  $W_1$  = load in dynes on the specimen  $Q$  and  $t_1$  is its thickness. " $C_1$ " is negative for all wavelengths from 5800 to 2400 Å (JOG<sup>5</sup>). If now the crystal  $R$  is placed in the path of the light beam and compressed, the bands shift their position. The position of the bands is now determined by

$$\frac{C_1 W_1}{t_1} + \frac{C_2 W_2}{t_2} = n \lambda$$

where  $C_2$ ,  $W_2$  and  $t_2$  are the stress optic coefficient the load and the thickness of specimen  $R$ .  $C_1$  and  $C_2$  are the values corresponding to the wavelength  $\lambda$ . So if we know " $C_1$ " as a function of wavelength  $C_2$  can be found at the wavelengths corresponding to the bands. By altering  $W_1$  the bands can be shifted in wavelength and  $C_2$  can be determined at different wavelengths.

The specimen of fused quartz used here was of the *OS* quality kindly presented by the Thermal Syndicate to Professor R. S. KRISHNAN. Its stress optic coefficient " $C$ " was determined from 5600 to 2400 Å employing the method of JOG<sup>5</sup> to an accuracy of 1%. The values were found to be identical with those for the *OG* quality specimen determined by JOG<sup>5</sup>. The specimen was loaded to get bands of order  $n \geq 1$  because the band  $n = \frac{1}{2}$  was not found sharp enough for the work here.

The crystal specimens were prepared in the form of rectangular tablets 2.5 to 3 cms. in length, 1.5 to 2 cms. in height and about 0.4 to 0.6 cms. in thickness. The edges of the rectangular tablet coincided with the cubic axes (100) of the crystal. The pressure was applied along the height of the specimen while the observation was made along its length. As the path difference depends on the load  $W_2$ ,  $W_2$  can be made large by choosing large enough lengths for the crystal so that the stress on the crystal does not exceed that causing plastic deformation (i.e., above 0.2 kg/mm<sup>2</sup>). The stresses were all kept below 0.15 kg/mm<sup>2</sup>; measurements were made at two different stresses for all crystals except potassium iodide. For the lengths chosen and these applied stresses, the path difference due to the crystal amounted to 600 to 1000 Å in the visible region. The sign of  $C_2$  can be determined by observing the direction in which the fringes are shifted. NaCl which has a negative value of " $C$ ", increases the path difference due to the fused quartz specimen and so shifts the  $n = 1$  band to the red while the potassium halides which have a positive value of  $C$  in the visible region, cause an opposite shift. The uniformity of the stress distribution in the crystal is obtained when the bands are parallel to the slit of the spectrograph.

All the crystals examined were melt grown. The sodium chloride crystal was grown and carefully annealed in our laboratory. The potassium halides were obtained from the Harshaw Chemical Company.

These crystals possessed a residual stress which was exhibited by the shift of the  $n = 1$  band when the unstressed crystal specimen was introduced after the fused quartz specimen. The magnitude of this residual stress was determined and allowed for in the following way. After introducing the unstressed crystal in the beam, the shift in the  $n = 1$  band of fused quartz is noted. The weights on the fused quartz specimen  $Q$  are altered to bring back the band to its original position  $\lambda_0$ . Let the new load in the fused quartz be  $W_1'$  and the original load  $W_1$ . Then the residual stress introduces a birefringence at this wavelength (about 4900 Å) of magnitude  $C_1(W_1 - W_1')/t_1$ . Now the crystal  $R$  is stressed with a load  $W_2$ . For the  $n = 1$  band the new position is determined by

$$\frac{C_1 W_1'}{t_1} + C_2 \frac{W_2}{t_2} + \frac{C_1(W_1 - W_1')}{t_1} = \frac{C_1 W_1}{t_1} + \frac{C_2 W_2}{t_2} = \lambda'.$$

Since  $\lambda'$  is also in the visible region and it is known that the dispersion of  $C_2$  is small in the visible region, our tacit assumption that the compensation for the residual stress at  $\lambda_0$  also holds for  $\lambda'$  is justified.  $C_2$  is calculated from the above equation at  $\lambda'$ . Then the residual load  $W_2'$  in the crystal is obtained by putting

$$\frac{C_2 W_2'}{t_2} = \frac{C_1(W - W_1')}{t_1}.$$

This value of  $W_2'$  is correct to a few per cent and as the residual load itself is only a fraction of the applied load  $W_2$ , such an accuracy in the knowledge of  $W_2'$  is enough. Now we can put the actual load on the crystal as  $(W_2 - W_2')$  and for any load  $W_1''$  on the fused quartz specimen, we obtain bands at a wavelength  $\lambda$  given by

$$\frac{C_1 W_1''}{t_1} + \frac{C_2(W_2 - W_2')}{t_2} = n \lambda.$$

This method of correction is necessary because, as our results show the dispersion of  $C_2$  is enormous so that if we compensate for the residual load in the visible region the compensation does not hold in the ultraviolet. The validity of the correction is tested by determining the values of  $C_2$  for two different loads  $W_2$  and  $W_2'$  and concordant results for  $C_2$  have been obtained.

The accuracy of this method depends on the sharpness of the band which in turn depends on the polish of the crystal. The crystal was polished as well as possible and a heater was placed near the crystal so that the polish was not tarnished by atmospheric water vapour. The accuracy also depends on the magnitude of the error in our knowledge of  $C_1$  of the fused quartz specimen. As will be evident from the scatter of the experimental points from a smooth curve, the values of  $C_2$  are accurate only to 10 to 20%.

## Results

In Fig. 2 and 3 are plotted the values of  $C$  as a function of wavelength for the four alkali halides. In the following table the values of  $(q_{11} - q_{12}) = \frac{2}{n^3} C$  in brewsters for the alkali halides are given at 4800 Å

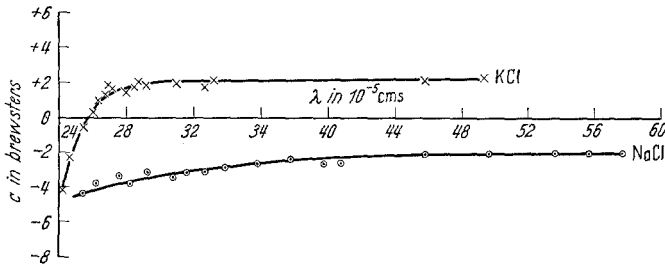


Fig. 2. Stress optic dispersion of KCl and NaCl

and compared with the values in the literature which have been determined at 5893 Å or 5461 Å.

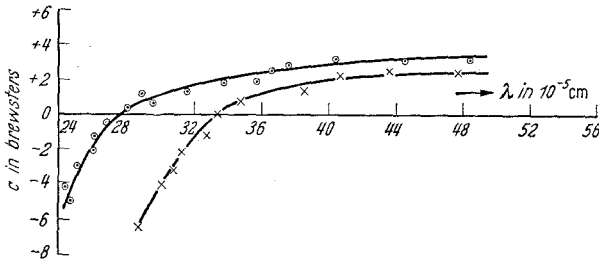


Fig. 3. Stress optic dispersion of KBr and KI

We see that in NaCl, KCl and KBr, the present values are in fair agreement with the values reported by different investigations. On the

Table 1

Substance	$q_{11} - q_{12}$ (author)	Literature values	
		$q_{11} - q_{12}$	author
NaCl	-1.12	-1.17	BANSIGIR and IYENGAR <sup>2</sup>
KCl	+1.42	-1.18	BURSTEIN, SMITH and HENVIS <sup>6</sup>
		+1.47	BANSIGIR and IYENGAR <sup>2</sup>
KBr	+1.76	+1.85	POCKELS <sup>7</sup>
		+1.37	BURSTEIN, SMITH and HENVIS <sup>6</sup>
		+1.76	BANSIGIR and IYENGAR <sup>2</sup>
		+1.70	BURSTEIN, SMITH and HENVIS <sup>6</sup>
KI	+1.00	+1.58	WEST and MAKAS <sup>8</sup>
		+1.83	BURSTEIN, SMITH and HENVIS <sup>6</sup>

<sup>6</sup> BURSTEIN, E., P.L. SMITH and B. HENVIS: Phys. Rev. **73**, 1262 (1948).

<sup>7</sup> POCKELS, F.: Ann. Phys., Lpz. **37**, 51 (1889).

<sup>8</sup> WEST, C.D., and A.B. MAKAS: J. Chem. Phys. **16**, 427 (1948).

other hand in KI, the author's value is found to be nearly half as small as that given by BURSTEIN et al. A similar discrepancy has been noted in diamond, where recent measurements by POINDEXTER<sup>1</sup> and DENNING et al.<sup>9</sup> have indicated a value nearly half that given by BURSTEIN et al.

### Discussion of results

We observe from Fig. 2 and 3 that 1. over the visible range of wavelengths, the dispersion of "C" is small (i.e.), only of the order of a few per cent in agreement with the measurements of BANSIGIR and IYENGAR.

2. As the wavelength is reduced, the value of "C" decreases slowly at first and more rapidly later. When we proceed to the ultraviolet the dispersion becomes enormous. For example, in NaCl "C" varies from  $-1.9$  at  $5800 \text{ \AA}$  to  $-4.5$  brewsters at  $2500 \text{ \AA}$ ; in KCl from  $+2.4$  at  $5000 \text{ \AA}$  to  $-2.0$  at  $2450 \text{ \AA}$ ; in KBr from  $+3.4$  at  $4800 \text{ \AA}$  to  $-4.6$  at  $2450 \text{ \AA}$ ; and in KI from  $+2.5$  at  $4800 \text{ \AA}$  to  $-6.0$  at  $2900 \text{ \AA}$ . In KI, measurements could not be carried out with any certainty below  $2800 \text{ \AA}$  as the bands become crowded together due to the rapid increase in the magnitude of "C". It is to be noted that such large dispersions in C have been observed for the first time.

3. The potassium halides change their sign of  $(g_{11} - g_{12})$  as one proceeds into the ultraviolet. In KCl, the change occurs around  $2550 \text{ \AA}$ ; in KBr at about  $2760 \text{ \AA}$  and in KI at about  $3380 \text{ \AA}$ . Below these wavelengths the potassium halides belong to the same class as NaCl in MUELLER'S<sup>4</sup> classification.

RAMASESHAN and SIVARAMAKRISHNAN<sup>10</sup> have given a phenomenological theory for the dispersion of the stress optic coefficient in a solid making the assumption that a strain alters the frequencies and the oscillator strengths of an atom. They have applied their theory to explain the photoelastic dispersion in glasses over the visible region of the spectrum. Repeated attempts were made to fit a formula of the type suggested by these authors, to the observed dispersion of C in alkali halides; but the attempts ended in failure. While such formulae could be made to fit the curves, they could only be considered as empirical, because no correlation could be discovered between the formulae for the four alkali halides.

On the other hand, MUELLER<sup>4</sup> has explained the photoelastic effect in cubic crystals as arising from three distinct causes: anisotropic

<sup>9</sup> DENNING, R. M., A. A. GIARDINI, E. POINDEXTER and C. B. SLAWSON: Amer. Mineral. **42**, 557 (1957).

<sup>10</sup> RAMASESHAN, S., and V. SIVARAMAKRISHNAN: Current Sci. **25**, 246 (1956).

Lorentz force, anisotropic Coulomb force and change in the optical polarisability of the atoms due to pressure. Defining

$$\hat{p} = \frac{n^4}{(n^2 - 1)^2} (\hat{p}_{11} - \hat{p}_{12}) = \frac{n^4}{(n^2 - 1)^2} \frac{(q_{11} - q_{12})}{(s_{11} - s_{12})} = \frac{2nc}{(n^2 - 1)^2 (s_{11} - s_{12})}$$

where the  $\hat{p}_{ij}$ 's are the elasto-optical constants,  $q_{ij}$  are the piezo-optic constants, the  $s_{ij}$  are the elastic moduli and  $n$  is the refractive index, MUELLER gives the following expression for "p"

$$p = \frac{1}{(1+x)^2} \left[ 0.09(1+x^2) + 5.82x + \frac{2.82}{f_1} \left( 1 - \frac{f_1}{f_2} x^2 \right) \right] - \frac{K}{3} \left( \frac{n^2 + 2}{n^2 - 1} \right).$$

Here  $x = \frac{R_2}{R_1}$  the ratio of the refractivity of the cation to the anion,  $f_1$  and  $f_2$  are the oscillator strengths of the anion and cation respectively and  $K$  is a constant called the strain polarisability constant. The first term in the equation represents the contribution to "p" from the Lorentz and Coulomb fields and is always positive. The second represents the effect of the change in polarisability of the atoms caused by pressure. An interplay of these two nearly equal terms causes the difference in the sign of "p" exhibited by different crystals. The cations in our case have an ultraviolet absorption wavelength at about 500 Å (HERZFELD and WOLF<sup>11</sup>) while the anions have absorption frequencies at longer wavelengths. For chlorine the bands lie at 1000 Å, 1280 Å, and 1580 Å in NaCl and at 1000 Å, 1310 Å and 1620 Å in KCl; in KBr, the bands for bromide lie at 1460 Å and 1820 Å (RADHAKRISHNAN<sup>12</sup>). In KI, the bands for iodine lie at 2190 Å, 1805 Å and 1290 Å (RAMACHANDRAN<sup>13</sup>). So as the wavelength decreases, the anion refractivity  $R_1$  increases much faster than the cation refractivity  $R_2$ . The Lorentz and Coulomb contributions decrease as  $x = R_2/R_1$  decreases. The value of  $x$  at various wavelengths can be calculated from the dispersion formulae proposed (HERZFELD and WOLF<sup>11</sup>; RAMACHANDRAN<sup>13</sup>, RADHAKRISHNAN<sup>12</sup>). Using these values of  $x$  and taking the oscillator strengths  $f_1$  and  $f_2$  as those corresponding to the inert gas atom of the same electronic configuration (HERZFELD and WOLF<sup>14</sup>), the Lorentz and Coulomb contributions to  $\hat{p}$  at various wavelengths can be found. If we assume  $K$  to be a constant independent of wavelength, then we find that the experimental results cannot be explained merely as due to a variation of the Lorentz and Coulomb contributions resulting from a change of  $x$ . For example in KCl, the value of  $x$  varies from 0.256 at 5000 Å to 0.227 at 2600 Å. Taking the experimental values of  $\hat{p}$  and  $n$ , the refractive index, at 5000 Å, the value of  $K$  can be calculated as MUELLER has done in his

<sup>11</sup> HERZFELD, K.F., and K.L. WOLF: Ann. Phys., Lpz. **78**, 35 (1925).

<sup>12</sup> RADHAKRISHNAN, T.: Proc. Ind. Acad. Sci. A **27**, 165 (1948).

<sup>13</sup> RAMACHANDRAN, G.N.: Proc. Ind. Acad. Sci. A **25**, 481 (1947).

<sup>14</sup> HERZFELD, K.F., and K.L. WOLF: Ann. Phys., Lpz. **76**, 71 (1925).

paper.  $K$  comes out to be 1.10. If now the same value of  $K$  is used at 2600 Å, the value of " $p$ " comes from theory to be 0.345 which is nearly ten times the experimental value of 0.03. So one cannot escape the conclusion that " $K$ ", the strain polarisability constant also varies with wavelength.

The variation of  $K$  with wavelength has been determined for all the crystals from the experimentally determined values of " $p$ "\* and the values of the Lorentz and Coulomb contributions. It was found in all the crystals  $K$  increases with wavelength, the increase being 20 to 30%

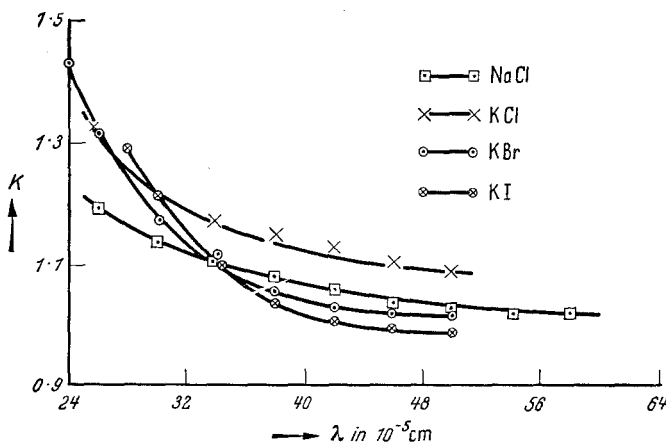


Fig. 4. Variation of the strain polarisability Constant  $K$  with wavelength

over the range of wavelengths investigated. Fig. 4 gives a plot of  $K$  versus  $\lambda$  for the four alkali halides. For all the four curves the following equation could be fitted

$$K = K_0 + \frac{K_1 \lambda^4}{(\lambda^2 - \lambda_0^2)^2}$$

where  $K_0$  and  $K_1$  are constants and  $\lambda_0$  the largest absorption wavelength of the anion (i.e.), 1580 Å for NaCl, 1610 Å for KCl, 1820 Å for KBr and 2190 Å for KI.

The values of  $K_0$  and  $K_1$  are collected in the following table:

	$K_0$	$K_1$
NaCl . .	0.90	0.12
KCl . . .	0.92	0.15
KBr . . .	0.90	0.09
KI . . . .	0.90	0.06

We see now that all the crystals fall in line with one another.

A comparison of the form of the equation for  $K$  with the expression given by RAMASESHAN and SIVARAMAKRISHNAN<sup>10</sup> shows that the dispersion in  $K$  arises due to the splitting of the absorption frequency by the strain. In

\* In calculating " $p$ " from  $C$  the following values of  $(s_{11} - s_{12})$  were used: NaCl 27.6; KCl 29.7; KBr 34.8; (GALT<sup>15</sup>); KI 44.6 (BRIDGMAN<sup>16</sup>) in units of  $10^{-13}$  cm<sup>2</sup>/dyne.

<sup>15</sup> GALT, J. K.: Phys. Rev. **73**, 1262 (1948).

<sup>16</sup> BRIDGMAN, P. W.: Proc. Amer. Acad. Arts Sci. **64**, 19 (1929).



MUELLER'S<sup>4</sup> notation, the constant  $K_1$ , except for a numerical factor of the order of unity, is equal to  $\frac{1}{\lambda_0} \left[ \left( \frac{\partial \lambda_0}{\partial z_z} \right)_{\parallel} - \left( \frac{\partial \lambda_0}{\partial z_z} \right)_{\perp} \right]$ . From the thermo-optic behaviour of crystals one obtains  $\chi = \frac{1}{\lambda_0} \frac{d\lambda_0}{dT}$  and if we assume that the change in  $\lambda_0$  occurs due to the thermal expansion of the specimen then

$$\chi = \frac{1}{\lambda_0} \left[ \left( \frac{\partial \lambda_0}{\partial z_z} \right)_{\parallel} + 2 \left( \frac{\partial \lambda_0}{\partial z_z} \right)_{\perp} \right] \frac{\partial z_z}{dT} = \frac{1}{\lambda_0} \left[ \left( \frac{\partial \lambda_0}{\partial z_z} \right)_{\parallel} + 2 \left( \frac{\partial \lambda_0}{\partial z_z} \right)_{\perp} \right] \alpha$$

where  $\alpha$  is the linear expansion coefficient. In KCl  $\chi$  for 1621 Å is  $90 \times 10^{-6}$  (RAMACHANDRAN<sup>13</sup>). The linear expansion coefficient  $\alpha$  at room temperature is about  $36 \times 10^{-6}$ . So that  $\frac{1}{\lambda_0} \left[ \left( \frac{\partial \lambda_0}{\partial z_z} \right)_{\parallel} + 2 \left( \frac{\partial \lambda_0}{\partial z_z} \right)_{\perp} \right] = 2.5$ . It is gratifying to note that this is of the same order of magnitude but larger than  $K_1$ .

We conclude therefore that the strain polarisability constant  $K$  for the alkali halides increases as the wavelength decreases and RAMASESHAN and SIVARAMAKRISHNAN'S<sup>10</sup> theory applies only to the variation of  $K$  with  $\lambda$ . For the alkali halides the dispersion of the stress optic coefficient  $C$  arises from 1. The dispersion of the Lorentz and Coulomb contribution to 'p' and 2. the dispersion of  $K$ . The large dispersion of "C" in alkali halides arises because "C" occurs as a difference between two nearly equal quantities 1. and 2. Since the behaviour of KI also seems to fall in line with the other alkali halides the present values of "C" for KI seem to be more nearly correct rather than the value of BURSTEIN, SMITH and HENVIS<sup>6</sup>.

My thanks are due to Professor R. S. KRISHNAN for his suggestions and encouragement and to Dr. S. RAMASESHAN for the many helpful discussions I had with him. I am also grateful to the National Institute of Sciences of India for the award of a Junior Research Fellowship which enabled me to carry out this work.