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Piezo-Optic Birefringence in NaCl Structure Crystals. Part II. Applications

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The theory outlined in Part I is shown to yield the correct values of the strain-optical coefficients P_{11} and P_{12}, the sign reversal of $(P_{11}-P_{12})$, and ionic polarizabilities. In the light of the theory, the following effects have also been examined. (i) The effect of elastic deformation on oscillator strengths and the frequencies of optical electrons, (ii) effect of temperature on ionic polarizability, and (iii) the temperature and wavelength dependence of the strain-polarizability constant under hydrostatic pressure.

1. Introduction

In Part I, the following expressions for the Piezo-optic birefringence in cubic crystals of NaCl structure were developed taking into account the density and polarizability changes of ions in the presence of the dipole, the Coulomb and the continuum fields.

$$(n^3/2)(P_{11}-P_{12})=3M-(1+\sigma)A$$
$$(n^3/2)(P_{11}+2P_{12})=(3L-A)(1-2\sigma)$$

and

$$(n^3/6)(P_{11}+2P_{12})=L(1-\lambda_0)\,, \tag{1}$$

where

$$\lambda_0=2\sigma+A(1-2\sigma)/3L,\ \ M=(n^2-1)^2(n^2+5)/15n\,,$$
$$L=(n^2-1)(n^2+2)/6n\,.$$

$$A=\frac{(n^2+2)^2(n^2+5)}{54n}[1{\cdot}458+2{\cdot}9005\beta(1/f_1+1/f_2)]\theta^2$$
$$-\frac{(n^2-1)(n^2+2)(n^2+5)}{18n}$$
$$\times\left[2{\cdot}916+\frac{4{\cdot}2083\beta}{f_1}+\frac{7{\cdot}5927\beta}{f_2}\right]\theta$$
$$+\frac{(n^2-1)^2(n^2+5)}{3n}\left[0{\cdot}2711+\frac{1{\cdot}6922\beta}{f_2}\right].$$

P_{11} and P_{12} are the strain-optical constants, n the refractive index, σ Poissons' ratio, β the number of valence electrons, f_1, f_2 the oscillator strengths and $\theta=\alpha_j/r^3$.

In this paper it is proposed to employ these expressions to work out some of the consequences of the theory. The following aspects will be considered.

(i) The absolute values of the strain-optical constants.
(ii) The effect of elastic deformation on oscillator strengths and dispersion frequencies of the optical electrons.
(iii) Effect of wavelength on the sign of $(P_{11}-P_{12})$.
(iv) Effect of temperature on the polarizability of the ions.
(v) Ionic polarizabilities as calculated from Piezo-optic data.
(vi) The wavelength and temperature dependence of the strain-polarizability constant under hydrostatic pressure.

2. The absolute strain-optical constants

Expressions in (1) may be used to eliminate A and thus from a knowledge of the difference $(P_{11}-P_{12})$, the absolute values of the strain-optical constants P_{11} and P_{12} may be obtained. The quantity $(P_{11}-P_{12})$ has been experimentally determined by the authors (1958) for a number of cubic crystals over the wave-

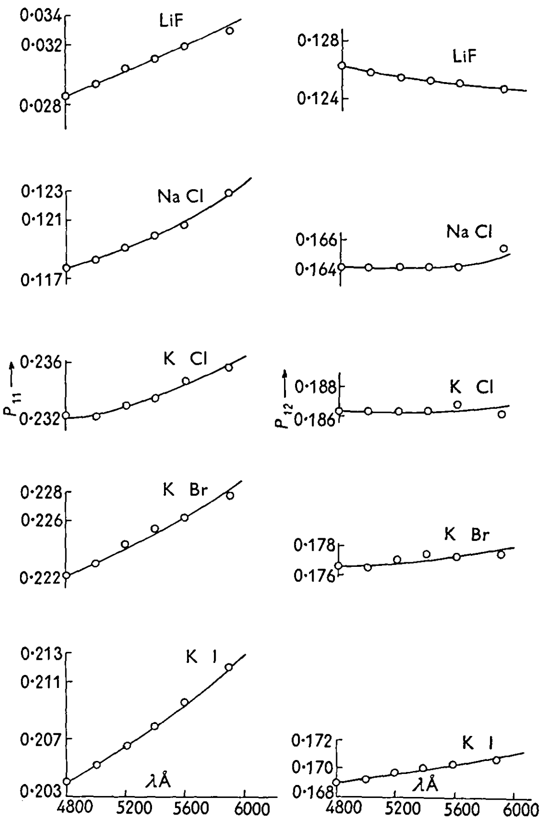

Fig. 1. Absolute strain-optical constant versus wavelength.

Table 1. P_{11}, P_{12} and P_{12}/P_{11}

	P_{11}		P_{12}		P_{12}/P_{11}	
Crystals	Obs. (K)	Calc.	Obs. (K)	Calc.	Obs. (K)	Calc.
KCl	0·21	0·23	0·159	0·186	0·76 ± 0·01	0·79
KBr	0·22	0·228	0·17	0·177	0·77 ± 0·01	0·778
KI	0·21	0·212	0·169	0·170	0·80	0·80
NaCl	0·137	0·123	0·178	0·166	1·35	1·347
LiF	0·02	0·329	0·128	0·125	6·5	3·79
MgO	(BSH) −0·32	−0·0495	−0·08	0·1973	0·25	−3·98
	(GP) −0·21		+0·04		0·20	
NaBr		0·088		0·1176		1·332
AgCl		0·2127		−0·012		−0·057
AgBr		0·1596		−0·0095		−0·0595

(K) = Krishnan, R. S. (BSH) = Burstein, Smith & Henvis. (GP) = Giardini & Poindexter.

length range 4800–6000 Å. The calculated values of P_{11} and P_{12} using these data are shown graphically in Fig. 1. In Table 1, these values together with their ratios for the wavelength of sodium light are shown. The agreement with the values obtained by other workers will be seen to be very close. For LiF and MgO there is a difference between the observed and calculated values. According to Burstein & Smith (1949) such differences may be expected as the presence of homopolar bonding in these crystals are quite pronounced. The strain-optical constants of NaBr, AgCl and AgBr have also been calculated and given in Table 1. The difference $(P_{11}-P_{12})$ for these crystals has been obtained from the experimental work of West & Makas (1951).

3. Effect of elastic deformation on oscillator strengths and dispersion frequencies of optical electrons

The theory of piezo-optic birefringence is simplified if it is assumed that a hydrostatic pressure causes a change in the refractive index of the crystal. Under such a pressure since the crystal symmetry is not destroyed one need consider only the changes in density and the polarizability of the ions. The hydrostatic compression will cause equal strains $\varepsilon_{xx}=\varepsilon_{yy}=\varepsilon_{zz}$ to be set up in the solid and thus change the refractive index by an amount δn. According to the phenomenological theory of Pockels

$$\delta n=(n^3/2)(P_{11}+2P_{12})\varepsilon_{xx}$$

and since $\varepsilon_{xx}=(1/3)(\delta V/V)=-(1/3)\delta\varrho/\varrho$, where δV is the change in volume V and $\delta\varrho$ is the corresponding change in density ϱ,

$$\varrho(dn/d\varrho)=(n^3/6)(P_{11}+2P_{12})\,. \qquad (2{\cdot}1)$$

$\varrho(dn/d\varrho)$ may also be obtained by differentiating a dispersion formula either of *L–L* type

$$(n^2-1)/(n^2+2)=\Sigma a'_r/(v_r^2-v^2) \qquad (2{\cdot}2)$$

or the Drude type

$$n^2-1=\Sigma a_r/(v_r^2-v^2)\,, \qquad (2{\cdot}3)$$

where a'_r and a_r are quantities involving the density of oscillators and their strengths f_r. v is the frequency for which the refractive index is n and v_r are the absorption frequencies. Ramchandran (1947) and Radhakrishnan (1948, 1950) have fitted the observed absorption frequencies v_r of cubic crystals into the Drude form, and obtained expressions for the correct refractive index over a wide wavelength range. Differentiating the Drude expressions with respect to density and remembering that a_r is a function of density, we obtain

$$\varrho\frac{dn}{d\varrho}=\frac{\varrho}{2n}\Sigma\frac{a_r\lambda_r^2\lambda^2}{\lambda^2-\lambda_r^2}\eta_r+2\Sigma\frac{a_r\lambda_r^2\lambda^4}{(\lambda^2-\lambda_r^2)^2}\psi_r\,, \qquad (2{\cdot}4)$$

where λ is the wavelength of the light used and λ_r are the absorption wavelengths corresponding to the absorption frequencies v_r and

$$\eta_r=\frac{1}{a_r}\left(\frac{da_r}{d\varrho}\right)$$

$$\psi_r=\frac{1}{\lambda_r}\left(\frac{d\lambda_r}{d\varrho}\right) \qquad (r=1,2,3 \text{ and } 4)\,.$$

Equating expressions (2·1) and (2·4) and using the known values of $(P_{11}+2P_{12})$ at different wavelengths, η_r and ψ_r have been calculated from the following dispersion formulae:

$$n^2=1{\cdot}243412+\frac{0{\cdot}357362\lambda^2}{\lambda^2-0{\cdot}010}+\frac{0{\cdot}37616\lambda^2}{\lambda^2-0{\cdot}017161}+\frac{0{\cdot}198086\lambda^2}{\lambda^2-0{\cdot}026244}+\frac{2{\cdot}514254\lambda^2}{\lambda^2-4998{\cdot}5}$$

for KCl,

$$n^2=1{\cdot}4725+\frac{0{\cdot}6204\lambda^2}{\lambda^2-0{\cdot}021318}+\frac{0{\cdot}2674\lambda^2}{\lambda^2-0{\cdot}033124}+\frac{2{\cdot}2847\lambda^2}{\lambda^2-7365{\cdot}7}$$

for KBr,

$$n^2=1{\cdot}4532+\frac{0{\cdot}1780\lambda^2}{\lambda^2-(0{\cdot}2190)^2}+\frac{0{\cdot}8027\lambda^2}{\lambda^2-(0{\cdot}1805)^2}+\frac{0{\cdot}2150\lambda^2}{\lambda^2-(0{\cdot}1290)^2}$$

for KI,

$$n^2=1+\frac{0\cdot187895\lambda^2}{\lambda^2-(0\cdot050)^2}+\frac{0\cdot497649\lambda^2}{\lambda^2-(0\cdot10)^2}+\frac{0\cdot384897\lambda^2}{\lambda^2-(0\cdot1280)^2}+\frac{0\cdot25950\lambda^2}{\lambda^2-(0\cdot1580)^2}+\frac{3\cdot470\lambda^2}{\lambda^2-(61\cdot1)^2}$$

for NaCl,

$$n^2=1\cdot3488+\frac{0\cdot57862\lambda^2}{\lambda^2-0\cdot00814}+\frac{7\cdot34258\lambda^2}{\lambda^2-1106\cdot6}$$

for LiF.

The number of parameters in the case of KI and NaCl may be reduced making the following plausible assumptions.

KI: $\psi_2=\psi_3$ and $\eta_2=\eta_3$ for $\lambda=0\cdot1805$ and $\lambda=0\cdot219$

NaCl: $\psi_2=\psi_3$ and $\eta_2=\eta_3$ for $\lambda=0\cdot10$ and $\lambda=0\cdot128$

and the absorption band at 500 Å, being due to the inner level, is not affected due to changes in density.

The results of these calculations are given in Table 2. A negative sign before ψ or η would mean a shift in the absorption band towards the lower wavelength or a decrease in the oscillator strengths with increasing density. A positive sign has the opposite meaning. The only experimental evidence in support of these changes comes from Fesefeldt's work (1930) on the temperature dependence of the absorption band at 0·219 of KI. He found that with decreasing temperature, the absorption band shifts towards shorter wavelength and the intensity of the band increases. Since temperature chiefly influences the density and the pure temperature effect in KI is small, Fesefeldt's observation may be considered to be a density effect on the absorption band.

From the above considerations, one can conclude that the stress-optic dispersion arises due to both a frequency shift and a change in the oscillating strength caused by strain. Such changes in absorption frequencies due to the introduction of a strain have been conceived by earlier workers (Burstein & Smith, 1949; Ramachandran, 1947; Iyengar, 1953) and has actually been experimentally observed in Raman-effect studies by Marie & Mathieu (1947).

4. Effect of wavelength on the sign of (P_{11}-P_{12})

Following Pockels, Mueller (1935) has divided all cubic crystals into four groups according to the sign of $(P_{11}-P_{12})$ and P_{44}. He predicted the classes to which some of the crystals would belong if their photo-elastic nature was explored. The distribution of crystals into groups has been based on the assumption that the sign of the piezo-optic constants is entirely determined by the characteristic property of the ions composing the crystal. However, from the recent work of Srinivasan (1959) it is evident that this conception of the grouping of crystals is not correct. His experiments show that the crystals KCl, KBr and KI which belong to group IV change over to group II in the ultra-violet region. This reversal of sign can be understood on the

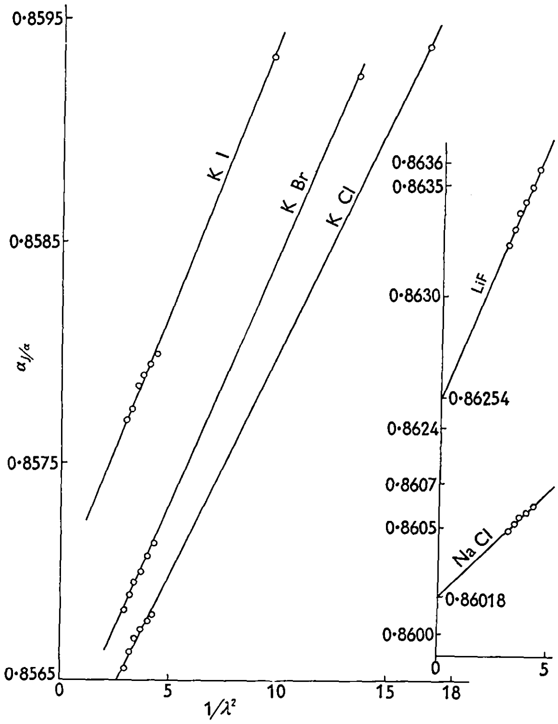

Fig. 2. (α_j/α) versus $1/\lambda^2$.

Table 2. η_r *and* ψ_r

Crystals	ψ_1	η_1	ψ_2	η_2	ψ_3	η_3	ψ_4	η_4
KCl	λ_1^2 = 0·010		λ_2^2 = 0·017161		λ_3^2 = 0·026244		—	—
	−20·78055	−41·0525	−20·78055	−41·0525	−33·30915	+375·0255	—	—
KBr	λ_1^2 = 0·021318		λ_2^2 = 0·033124		—	—	—	—
	+0·42424	−1·68927	−1·205265	+6·13298	—	—	—	—
KI	λ_1^2 = (0·129)^2		λ_2^2 = (0·1805)^2		λ_3^2 = (0·2190)^2		—	—
	−94·1728	−85·9093	−6·73615	+74·2099	−6·73615	+74·2099	—	—
NaCl	λ_1^2 = (0·05)^2		λ_2^2 = (0·100)^2		λ_3^2 = (0·128)^2		λ_4^2 = (0·1580)^2	
	0·0	−357·6529	−35·64385	+158·6560	−35·64385	+158·6560	+19·00835	−74·5275
LiF	λ_1^2 = 0·00814		—	—	—	—	—	—
	−0·0814445	+0·459892	—	—	—	—	—	—

basis of the present theory. Using expressions (1), the ratio of the ionic polarizability to the molecular polarizability (α_j/α) can be calculated at different wavelengths. As shown in Fig. 2, this ratio is found to vary linearly with $1/\lambda^2$ in the visible region. Assuming this relation to hold on either side of the region, the wavelength at which the reversal of sign takes place has been obtained from a knowledge of the ratio at that wavelength. These reversal wavelengths are given in Table 3. The reported values by Srinivasan are in good agreement with these values. For NaCl and LiF this kind of reversal does not appear to be possible as the computed ratio occurs at negative frequencies. Unless there is a sudden fall of the ratio in the infra-red region, one cannot expect a reversal to occur in crystals which belong to the NaCl group of Pockels' classification. The absolute strain-optical constants P_{11} and P_{12} corresponding to the reversal wavelengths are given in Table 3. The variation of P_{11} with wavelength exceeds the variation of P_{12} in all the crystals studied. For KCl, KBr and KI, $P_{11} > P_{12}$ in the visible region. As the wavelength decreases, both coefficients decrease, P_{11} decreasing more rapidly and ultimately overtaking P_{12} at the reversal frequency. This trend is maintained even beyond the reversal frequency.

Table 3. *Reversal wavelengths and absolute strain-optical constants*

Crystal	$(\alpha_j/\alpha)_{\text{reversal}}$	λ (Å) Obs.	λ (Å) Calc.	$P_{11}=P_{12}$
KCl	0·85939	2550	2455	0·1845
KBr	0·85926	2760	2725	0·1715
KI	0·85934	3380	3235	0·1597
NaCl	0·85844	—	—	—
LiF	0·85715	—	—	—
MgO	0·858055	—	—	—
NaBr	0·857412	—	—	—
AgCl	0·856454	—	—	—
AgBr	0·856355	—	—	—

5. Effect of temperature on the polarizability of the ions

When the temperature of an ionic crystal is changed the polarizability of the ion is changed. The factors causing this change are

(i) Density changes which are the result of temperature changes.

(ii) Pure temperature changes.

Assuming, therefore, the polarizability α to be a function of density ϱ and temperature t, we obtain

$$\frac{1}{\alpha}\left(\frac{d\alpha}{dt}\right) = -\gamma\varrho\frac{1}{\alpha}\left(\frac{d\alpha}{d\varrho}\right)_t + \frac{1}{\alpha}\left(\frac{d\alpha}{dt}\right)_\varrho \tag{5·1}$$

where γ is the coefficient of volume expansion, $(d\alpha/d\varrho)_t$ the pure density effect and $(d\alpha/dt)_\varrho$ the pure temperature effect. Differentiating the L–L equation $(n^2-1)/(n^2+2) = N\alpha/3$ with respect to density, we obtain

$$1+\frac{\varrho}{\alpha}\left(\frac{d\alpha}{d\varrho}\right)_t = \frac{6n}{(n^2-1)(n^2+2)}\,\varrho\left(\frac{dn}{d\varrho}\right) \tag{5·2}$$

and since $\varrho\,(dn/d\varrho) = (n^3/6)(P_{11}+2P_{12})$

$$-\frac{\varrho}{\alpha}\left(\frac{d\alpha}{d\varrho}\right)_t = 1-\frac{n^4(P_{11}+2P_{12})}{(n^2-1)(n^2+2)}. \tag{5·3}$$

From equations (5·1) and (5·3), we have for the pure temperature effect

$$\frac{1}{\alpha}\left(\frac{d\alpha}{dt}\right)_\varrho = \frac{1}{\alpha}\left(\frac{d\alpha}{dt}\right) + \gamma\left\{\frac{n^4(P_{11}+2P_{12})}{(n_2-1)(n^2+2)}-1\right\}. \tag{5·4}$$

The first term on the right hand side of the equation may be evaluated using the L–L expression and the thermo-optic data (Ramachandran, 1947). The differential stress optical coefficients have been experimentally determined by Bhagavantam & Krishnamurty (1957) over a range of temperatures for the crystals NaCl, KCl and KBr. Using expressions (1), the quantity $(P_{11}+2P_{12})$ has been evaluated and thus the second term of expression (5·4) has been determined. The pure temperature effect calculated in this manner for NaCl, KCl and KBr at different temperatures is given in Table 4. It will be seen that $(1/\alpha)(d\alpha/dt)_\varrho$ is itself a function of the temperature.

6. Ionic polarizabilities as calculated from piezo-optic data

Employing the expression

$$(P_{11}-P_{12}) = (2/n^3)\{3M-(1+\sigma)A\},$$

of equation (1) the ionic polarizabilities α_j can be calculated from a knowledge of $(P_{11}-P_{12})$ and f_k. Assuming $f_1=f_2=1$, the values of α_j have been calculated for the wavelength 5893 Å. They are given in Table 5 together with the values obtained by other workers. Calculations show that agreement with the

Table 4. $(1/\alpha)(d\alpha/dt)_\varrho \times 10^5$

Pure temperature effect

Crystal	Temperature t °C. 30	100	150	175	200	250
NaCl	+0·404	−0·338	—	−1·13	−1·67	—
KCl	+1·088	+0·701	+0·435	—	+0·184	−0·086
KBr	+0·033	−0·4916	−1·096	—	−1·813	—

Table 5. *Polarizability* α_f
(In cm.$^3 \times 10^{-24}$)

Ion	Authors	Fajans & Joos	Born & Heisenberg	Pauling	Shockley	Shockley, Tessman & Khan
Cl	3·699 KCl 2·899 NaCl 4·557 AgCl	3·53	3·05	3·66	2·92	2·97
Br	4·739 KBr 3·904 NaBr 5·657 AgBr	4·97	4·17	4·77	4·12	4·17
I	6·740 KI	7·55	6·28	7·10	6·41	6·44
O	1·523 MgO	2·75	—	3·88	—	2·4
F	0·8785 LiF	0·98	0·99	1·04	0·86	0·652
Na	0·466 NaCl 0·641 NaBr	0·196	0·21	0·179	0·28	0·40
Li	0·138 LiF	0·087	0·075	0·029	0·045	0·021
Mg	0·266 MgO	0·12	0·12	0·094	—	—
K	0·60 KCl 0·782 KBr 1·106 KI	0·88	0·87	0·83	1·13	1·326
Ag	0·783 AgCl 0·954 AgBr	—	—	—	—	—

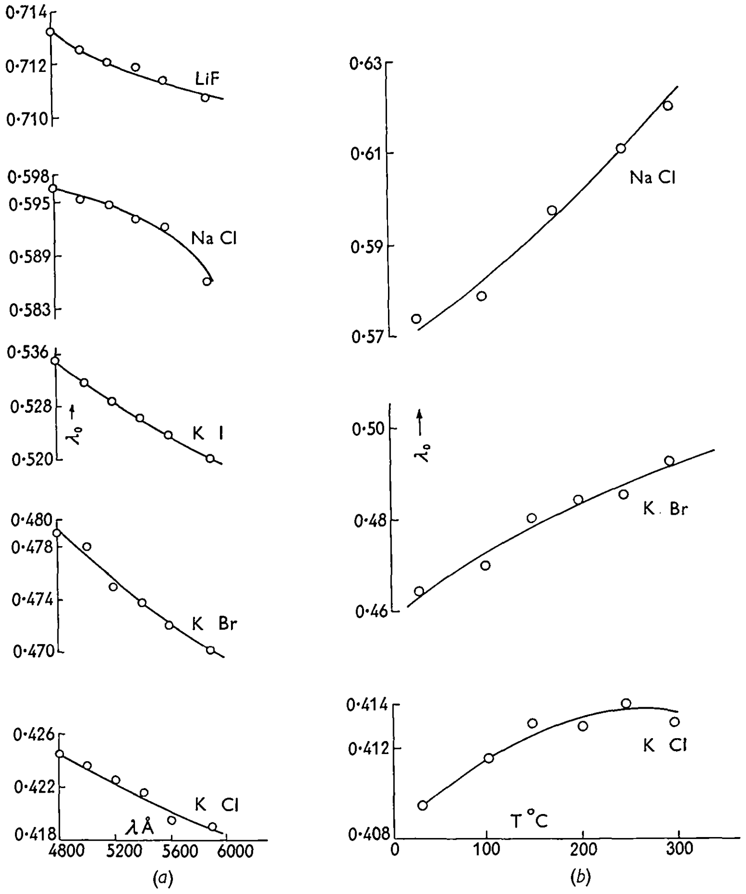

Fig. 3. (*a*) Strain-polarizability constant versus wavelength. (*b*) Strain-polarizability constant versus temperature.

values reported by Shockley (1946), Shockley, Tessman & Khan (Kittel, 1953) is good when $f_1 = f_2 < 1$, and when oscillator strengths are greater than one the agreement is better with those given by Fajans & Joos (1924), Born & Heisenberg (1924) and Pauling (1927).

7. Strain-polarizability constant λ_0

Mueller (1935) introduced a strain-polarizability constant, which he assumed to vary with direction under a unaxial stress. He also introduced the concept of a strain-polarizability constant λ_0 under hydrostatic pressure, and accidentally found that λ_0 was nearly 0·5 for all the three crystals NaCl, KCl and CaF_2.

Subsequently, a number of investigators have reported that λ_0 was not constant but varied from crystal to crystal. While studying the dispersion of piezo-optic constants, Iyengar (1953) observed that λ_0 not only varied from one crystal to another, but also varied with the wavelength of light used. Recently, Srinivasan (1959) has also arrived at a similar conclusion.

Table 6. *Strain polarizability constant* λ_0 *at* 5893 Å

Crystal	Authors	Burstein & Smith
KCl	0·4187	0·61
KBr	0·4701	0·48
KI	0·5201	0·48
NaCl	0·5860	0·63
LiF	0·7108	0·7
MgO	0·7481	1·4
NaBr	0·7048	—
AgCl	0·8406	—
AgBr	0·8744	—

In expression (1), λ_0 is shown to be $2\sigma + A(1-2\sigma)/3L$, where σ is Poissons ratio and A and L are functions of wavelength. In Figs. 3(*a*) and (*b*), plots of λ_0 against wavelength and temperature have been shown. It will be observed that for all the crystals λ_0 increases as the wavelength decreases and the temperature increases. The values of λ_0 at 5893 Å as calculated using expression (1) and also as given by others (Burstein & Smith, 1949), are shown in Table 6. Except in the case of MgO, the agreement is found to be good.

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