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Piezo-optic Birefringence in NaCl Structure Crystals. III

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Following the theoretical approach of Bansigir and Iyengar, an expression for the stress–optical coefficient q_{44} is developed. Using experimental values of q_{44}, ionic polarizibilities of some ions are calculated. Also, the wavelengths at which $q_{44}=0$ are evaluated for a few crystals. Both ionic polarizabilities and reversal wavelengths are found to be in good agreement with reported values.

Introduction

Some years ago, an improved theory (Bansigir & Iyengar, 1961*a*) of artificial birefringence observed in cubic crystals with the sodium chloride structure, subject to uniaxial deformation in the direction of a cube axis, was developed. The theory was limited to a discussion of observations made along a cube axis chosen normal to the deformation axis and the birefringence characterized by the elasto-optic coefficients P_{11} and P_{12} and their difference. The consequences following from the theory were separately dealt in Part II of the paper (Bansigir & Iyengar, 1961*b*). During recent years new observations relating to the elasto-optic coefficient P_{44} and the corresponding piezo-optic coefficient q_{44} have been reported (Laiho & Korpela, 1968; Rahman & Iyengar, 1970). In this paper the theory has been extended on the lines of Part I (Bansigir & Iyengar, 1961*a*) to cover the related phenomena.

Phenomenological theory and expression for q_{44}

Let a rectangular bar of cubic crystal with orientation [1$\bar{1}$0], [001], [110] (to be called **x**′, **y**′, **z**′ respectively), be stressed along the **z**′ direction. The induced refractive index changes are related to the strain t', through the following expressions based on the phenomenological theory of Pockels (1906)

$$n_{z'}-n_{x'}=-P_{44}\frac{n^3}{2}t'=-q_{44}C_{44}\frac{n^3}{2}t', \tag{1}$$

where n is the refractive index in the unstrained condition, $n_{z'}$ and $n_{x'}$ are the altered refractive indices for the light vibrating in the **z**′ and **x**′ directions and C_{44}, the relevant elastic coefficient of the crystal.

The alteration in the refractive index is caused by (i) change in the density of the crystal, *i.e.* change in the number of dispersion centres in unit volume, (ii) change in the polarizibility of the ions.

(i) If a unit volume of the crystal is stressed along **z**′, a strain t' along this direction and a corresponding strain $-\sigma_{x'}t'$ and $-\sigma_{y'}t'$ along **x**′ and **y**′ would be produced where $\sigma_{x'}$ and $\sigma_{y'}$ are the Poisson's ratio in the **x**′ and **y**′ directions respectively. Hence the change in the volume would be $t'[1-(\sigma_{x'}+\sigma_{y'})]$. This volume change would bring about a change δN_j in the number of ions per unit volume and is given by $-t'[1-(\sigma_{x'}+\sigma_{y'})]N_j$ where N_j represents the number of ions per unit volume.

(ii) The factors affecting polarizibility are

(*a*) the Lorentz–Lorenz anisotropy due to the material continuum,

(*b*) the Lorentz–Lorenz anisotropy due to dipoles within the cavity,

(*c*) the Coulomb anisotropy due to the presence of +ve as well as −ve ions within the cavity.

Lorentz–Lorenz anisotropy due to the material continuum has been calculated by Mueller (1935) on the lines suggested by Havelock (1908). He has shown that for a medium strained in the **z**′ direction (where the strain ellipsoid has an axial ratio of $1:1:1+t'$), the refractive index for light vibrating in the **x**′ direction is given by (Brayborn, 1953)

$$3(n_{x'}^2-1)=4\pi N_j\alpha_j[(n_{x'}^2+2)+K_{x'}(n^2-1)] \tag{2}$$

with a similar expression for vibration along the **z**′ direction, where $K_{x'}=2t'/5$ and $K_{z'}=-4t'/5$, α_j = polarizibility of the ion under consideration and N_j the number of molecules per unit volume.

The expression for dipole anisotropy if the incident field is polarized in the **z**′ direction, the centre being occupied by a +ve or −ve ion, is given by

$$E_{jz'd}=D_{jkz'}\,(\mu_{kz'})\frac{t'}{\gamma^3} \tag{3a}$$

where j represents the ion occupying the centre of the cavity, k the ion the effect of which is to be calculated at the centre, d indicates that the field is dipole in nature, and γ is the distance between any two ions along the edges of the unit cell.

For light polarized in the **x**′ direction, the corresponding expression is

$$E_{jx'd}=D_{jkx'}\,(\mu_{kx'})\frac{t'}{\gamma^3}\,. \tag{3b}$$

μ_{kz} and $\mu_{kx'}$ in the above expressions are the dipole moments along **z**′ and **x**′ respectively; $D_{jkz'}$ and $D_{jkx'}$ are numerical values of finite lattice sums in the deformed states.

The expression for the field created due to Coulomb anisotropy by the charges present in the cavity, for light polarized in the **z**′ direction is given by

$$E_{jz'c}=(\beta t'/\gamma^3)C_{jkz'}\,(\alpha_k/f_k) \qquad (4a)$$

and for light polarized in **x**′ direction by

$$E_{jx'c}=(\beta t'/\gamma^3)\,C_{jkx'}\,(\alpha_k/f_k) \qquad (4b)$$

where β is the number of valence electrons, α_k is the polarizability of the +ve or −ve ion and f_k is the oscillator strength of the +ve or −ve ion. $C_{jkz'}$ and $C_{jkx'}$ are numerical constants of the lattice. The Coulomb fields are created because, under the influence of the incident field, the −ve and +ve ions are displaced by amounts s_1 and s_2, or s_k in general, giving rise to a dipole whose moment could be expressed as $f_k e^* s_k/\sqrt{4\pi}=\mu_{kz'}$ or $\mu_{kx'}$ where e^* = effective charge (Fröhlich, 1949).

The dipole moment of the jth ion in the presence of the resultant field (arising from continuum, dipole and Coulomb anisotropies) is given by

$$(\mu_{jz'})_{idcp}=\alpha_j F_{jz'} \text{ in the } \mathbf{z}' \text{ direction,} \qquad (5a)$$

$$(\mu_{jx'})_{idcp}=\alpha_j F_{jx'} \text{ in the } \mathbf{x}' \text{ direction,} \qquad (5b)$$

where

$$F_{jz'}=E_{iz'}+E_{jz'd}+E_{jz'c}+K_{z'}P_j\,, \qquad (6a)$$

$$F_{jx'}=E_{ix'}+E_{jx'd}+E_{jx'c}+K_{x'}P_j\,. \qquad (6b)$$

E_i is the incident field and P_j the polarizibility of the medium per unit volume.

Alternatively, the dipole moment in the expressions (6) could be assumed to arise due to the effective polarizabilities $\alpha_{jz'}$ or $\alpha_{jx'}$ in the **z**′ and **x**′ directions under the incident fields $E_{iz'}$ or $E_{ix'}$ according to

$$(\mu_{jz'})_{idcp}=\alpha_{jz'}E_{iz'}\,, \qquad (7a)$$

$$(\mu_{jx'})_{idcp}=\alpha_{jx'}E_{ix'}\,. \qquad (7b)$$

It is assumed that the Lorentz–Lorenz equation for the refractive index n in the form

$$\frac{n^2-1}{n^2+2}=\sum\frac{N_j\alpha_j}{3} \qquad (8)$$

holds good.

Thus equations (5), (6), (7) and (8) yield

$$\alpha_{jz'}=\alpha_j\left[1+\left\{\frac{(n^2+2)}{3}\,(D_{jkz'}\,\alpha_k/\gamma^3+C_{jkz'}\,\beta\alpha_k/\gamma^3 f_k)\right.\right.$$
$$\left.\left.+\frac{K_{z'}}{3}\,(n^2-1)\right\}t'\right], \qquad (9a)$$

$$\alpha_{jx'}=\alpha_j\left[1+\left\{\frac{(n^2+2)}{3}\,(D_{jkx'}\,\alpha_k/\gamma^3+C_{jkx'}\,\beta\alpha_k/\gamma^3 f_k)\right.\right.$$
$$\left.\left.+\frac{K_{x'}}{3}\,(n^2-1)\right\}t'\right]. \qquad (9b)$$

The changes in the polarizabilities in the two directions **z**′ and **x**′ are then as follows:

$$\delta\alpha_{z'}=(D_{12z'}+C_{12z'})\,[(\bar{\alpha})^2+(\overset{+}{\alpha})^2]$$
$$+2(\bar{\alpha})(\overset{+}{\alpha})\,(D_{11z'}+C_{11z'} \qquad (10a)$$

$$\delta\alpha_{x'}=(D_{12x'}+C_{12x'})\,[(\bar{\alpha})^2+(\overset{+}{\alpha})^2]$$
$$+2(\bar{\alpha})(\overset{+}{\alpha})\,(D_{11x'}+C_{11x'})\,. \qquad (10b)$$

The expressions for the D's and C's are evaluated assuming that

$$x'=\sqrt{2}(\gamma-\delta\gamma_2)\,,\quad y'=\gamma-\delta\gamma_1\,,\quad z'=\sqrt{2}(\gamma+\delta\gamma_3)$$

where γ is the distance between any two ions taken along the edges of the unit cell. $\delta\gamma_1$, $\delta\gamma_2$ and $\delta\gamma_3$ are changes brought about in the **y**′, **x**′ and **z**′ directions respectively by the applied stress. Values thus obtained are given in Table 1.

Table 1. *Numerical constants*

$$\begin{aligned}
D_{11z'} &= D_{22z'} = 2\cdot487+7\cdot460\sigma_{x'}-4\cdot974\sigma_{y'}\\
D_{12z'} &= D_{21z'} = -0\cdot530-1\cdot591\sigma_{x'}+1\cdot061\sigma_{y'}\\
D_{11x'} &= D_{22x'} = -7\cdot460-2\cdot487\sigma_{x'}-4\cdot974\sigma_{y'}\\
D_{12x'} &= D_{21x'} = 1\cdot591+0\cdot530\sigma_{x'}+1\cdot061\sigma_{y'}\\
C_{11z'} &= C_{22z'} = 22\cdot617-7\cdot539\sigma_{x'}-7\cdot539\sigma_{y'}\\
C_{12z'} &= C_{21z'} = -4\cdot242\sigma_{x'}-4\cdot242\sigma_{y'}\\
C_{11x'} &= C_{22x'} = 7\cdot539-22\cdot618\sigma_{x'}-7\cdot539\sigma_{y'}\\
C_{12x'} &= C_{21x'} = 4\cdot242-4\cdot242\sigma_{y'}
\end{aligned}$$

Assuming that $\alpha=\overset{+}{\alpha}+\bar{\alpha}$, the changes in polarizabilities along **z**′ and **x**′ are expressed as follows:

$$\delta\alpha_{z'}=\frac{t'}{4\pi\gamma^3}\,[(-51\cdot268-11\cdot508\sigma_{x'}+18\cdot664\sigma_{y'})$$
$$\times[(\bar{\alpha})^2-\alpha(\bar{\alpha})]-(0\cdot530+5\cdot833\sigma_{x'}+3\cdot181\sigma_{y'})\,\alpha^2]\,, \qquad (11a)$$

$$\delta\alpha_{x'}=\frac{t'}{4\pi\gamma^3}\,[(11\cdot508+51\cdot268\sigma_{x'}+18\cdot664\sigma_{y'})$$
$$\times[(\bar{\alpha})^2-\alpha(\bar{\alpha})]+(5\cdot833+0\cdot530\sigma_{x'}-3\cdot181\sigma_{y'})\,\alpha^2]\,. \qquad (11b)$$

Putting $m_1=\dfrac{1}{4\pi}\,[-51\cdot268-11\cdot508\sigma_{x'}+18\cdot664\sigma_{y'}]$,

$$n_1=\frac{-1}{4\pi}\,[0\cdot530+5\cdot833\sigma_{x'}+3\cdot181\sigma_{y'}]\,,$$

$$m_2=\frac{1}{4\pi}\,[11\cdot508+51\cdot270\sigma_{x'}+18\cdot664\sigma_{y'}]\,,$$

$$n_2=\frac{1}{4\pi}\,[5\cdot833+0\cdot530\sigma_{x'}-3\cdot181\sigma_{y'}]$$

and taking into consideration all the anisotropies and density change, the changes in the refractive indices along **z**′ and **x**′ are

$$\delta n_{z'} = \Big[-\{1-(\sigma_{x'}+\sigma_{y'})\}L_1 + M_1K_{z'} + \frac{2m_1O_1u^2N\gamma^3}{3} - 2m_1L_1u + \frac{6n_1M_1}{N\gamma^3}\Big]\, t', \quad (12a)$$

$$\delta n_{x'} = \Big[-\{1-(\sigma_{x'}+\sigma_{y'})\}L_1 + M_1K_{x'} + \frac{2m_2O_1u^2N\gamma^3}{3} - 2m_2L_1u + \frac{6n_2M_1}{N\gamma^3}\Big]\, t', \quad (12b)$$

where

$$u = \frac{4\pi(\overset{+}{\alpha} \text{ or } \bar{\alpha})}{\gamma^3}, \quad L_1 = \frac{(n^2-1)(n^2+2)}{6n},$$

$$M_1 = \frac{(n^2-1)^2}{6n}, \quad O_1 = \frac{(n^2+2)^2}{6n}.$$

Therefore

$$q_{44} = -\frac{(1+\sigma_{x'})}{E'}\,\frac{2}{n^3}\Big[M_1(K_{z'}-K_{x'}) + \frac{2(m_1-m_2)N\gamma^3O_1u^2}{3} - 2(m_1-m_2)L_1u + \frac{6(n_1-n_2)M_1}{N\gamma^3}\Big] \quad (13)$$

or

$$q_{44} = -\frac{(1+\sigma_{x'})}{E'}\,\frac{2}{n^3}\Big[\frac{6M_1}{5} + 3{\cdot}329\,(1+\sigma_{x'})N\gamma^3O_1u^2 - 9{\cdot}986(1+\sigma_{x'})L_1u + 0{\cdot}759(1+\sigma_{x'})\frac{M_1}{N\gamma^3}\Big]. \quad (14)$$

The expressions for Poisson's ratio $\sigma_{x'}$ and Young's modulus E' in terms of elastic constants are given in the Appendix.

Applications

To test the validity of the theory the following aspects are considered:

(1) *Ionic polarizabilities*

Using experimental values of q_{44}, expression (14) was solved for u. Two values, the higher one corresponding to −ve ion and lower one to +ve ion were obtained. (The polarizability of −ve ion $\bar{\alpha} = \bar{u}\gamma^3/4\pi$ and +ve ion $\overset{+}{\alpha} = \overset{+}{u}\gamma^3/4\pi$.) Calculated values of α_j's for various ions are tabulated in Table 2 and comparison with those obtained by other investigators show that they are in good agreement.

Table 2. *Polarizability* α_j *at* = 5890 Å (cm$^3 \times 10^{-24}$)

Ion	Calculated value	Fajans and Joos	Born and Heisen-berg	Paul-ing	Shock-ley
Cl	3·1290 NaCl 3·4126 KCl 2·6613 RbCl	3·53	3·05	3·06	2·92
Br	4·6619 KBr 4·3053 RbBr	4·97	4·17	4·77	4·12
I	6·9018 KI 6·5001 RbI	7·55	6·28	7·10	6·41
Na	0·2526 NaCl	0·196	0·210	0·179	0·280
K	0·8183 KCl 0·8742 KBr 0·8274 KI	0·88	0·87	0·83	1·13
Rb	2·1885 RbCl 1·9916 RbI 1·8571 RbBr	—	—	—	—

(2) *Reversal wavelength*

Putting $q_{44} = 0$ in expression (14) and substituting $u = 4\pi\alpha_j/\gamma^3$ reduces it to the following form

$$a(\alpha_j/\gamma^3)^2N\gamma^3O_1 + b(\alpha_j/\gamma^3)L_1 + c(M_1/N\gamma^3) = 0\,, \quad (15)$$

where a, b, and c are constants. Substituting the values of L_1, O_1 and M_1 and dividing throughout by $(n^2-1)^2$, equation (15) becomes

$$6/5 + 59{\cdot}918(1+\sigma_{x'})\,(\alpha_j/\alpha)^2 - 59{\cdot}918(1+\sigma_{x'})\,(\alpha_j/\alpha) + 0{\cdot}759(1+\sigma_{x'}) = 0 \quad (16)$$

since

$$\frac{n^2-1}{n+2^2} = \frac{N\alpha}{3}.$$

Equation (16) gives the ratio between (i) the polarizibility of the −ve ion to the total polarizability; (ii) the polarizibility of the +ve ion to the total polarizability. Assuming that the polarizability of the +ve ion does not change with the frequency of the incident radiation and taking $\overset{+}{\alpha}$ to be the polarizability of the +ve ion at 5890 Å, the total polarizability α at $q_{44} = 0$ is calculated. This gives the polarizability at reversal.

The wavelength corresponding to polarizability at reversal is calculated from the equation

$$\alpha_{\text{rev}} = \frac{A'\lambda_{\text{rev}}^2}{\lambda_{\text{rev}}^2 - \lambda_t^2}$$

where λ_t is the first exciton peak wavelength and A' a constant.

Values thus obtained for reversal wavelength are given in Table 3. They are found to be in good agreement with observed values.

Table 3. *Reversal wavelengths*

Crystal	$\overset{+}{\alpha}$ 5890 Å	$\overset{+}{\alpha}/\alpha$	α_{rev} $\times 10^{24}$	λ_t	λ Calcu-lated	λ Obser-ved
KI	0·827	0·0618	13·3884	2190	3083	2900 (9)
RbBr	1·857	0·0772	24·0556	1910	2170	2140 (6)
RbI	1·992	0·0799	24·9260	2230	2640	2300 (6)
RbCl	2·188	0·0703	31·1309	1660	1793	—
KBr	0·874	0·0654	13·3670	1870	2360	—
KCl	0·818	0·0618	13·2411	1620	1985	—

This method could also be adopted to determine the reversal wavelengths for $q_{11}-q_{12}$.

APPENDIX

$$E'=\frac{4(C_{11}-C_{12})\,(C_{11}+2C_{12})C_{44}}{C}$$

$$\sigma_{x'}=\frac{2C_{11}C_{44}-(C_{11}-C_{12})\,(C_{11}+2C_{12})}{C}$$

$$\sigma_{y'}=\frac{2C_{12}C_{44}}{C}\,,$$

where

$$C=2C_{11}C_{44}+(C_{11}-C_{12})\,(C_{11}+2C_{12})\,.$$

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Derivation and Experimental Verification of the Normalized Resolution Function for Inelastic Neutron Scattering*

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Based upon the work of Cooper & Nathans, an expression for the normalized resolution function of a triple-axis neutron spectrometer is derived and tested experimentally. The formalism is extended to show the explicit dependence of the integrated intensity of a sharp excitation spectrum on all of the relevant instrumental parameters. Extensive measurements of the integrated intensities of phonons in copper have been carried out for a wide range of all adjustable parameters. The experimentally determined intensities are found to be in good agreement with the calculated values.

1. Introduction

Resolution effects in triple-axis neutron spectrometers were first considered by Caglioti, Paoletti & Ricci (1958) and Collins (1963). These authors considered the effect of horizontal collimations and mosaic spreads for special arrangements of relaxed collimations. Stedman (1968) and Bjerrum Møller & Nielsen (1970) derived expressions for the dependence of the intensity on the horizontal collimation, mosaic spread of the monochromator and analyzer crystals and Bragg angles of those crystals. Expressions for the width of an inelastic peak were derived by Stedman & Nilsson (1966), Cooper & Nathans (1967) and Nielsen & Bjerrum Møller (1969). Though derived by different methods, the expressions for the peak width are in mutual agreement. None of these authors, however, is concerned with the correct normalization of the resolution function since they were interested in line shapes rather than in accurate measurements of scattering intensities.

Although an essentially correct formulation of the resolution-function normalization has existed in our laboratory for several years [see for example Samuelsen, Hutchings & Shirane (1970)], in the course of a study of phonon intensities in zinc we felt it necessary to formalize the derivation and to test experimentally the salient features of the results. To this end, we have extended the resolution-function calculations of Cooper & Nathans (1967)* to give a closed analytic expression for the normalized resolution function of a triple-axis spectrometer. This result is used to derive the inte-

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* See Appendix.