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References

- ALLPRESS, J. G. & ROSSELL, H. J. (1975). *J. Solid State Chem.* **15**, 68–78.
- ALLPRESS, J. G., ROSSELL, H. J. & SCOTT, H. G. (1975). *J. Solid State Chem.* **14**, 264–273.
- BATTERMAN, B. W., CHIPMAN, D. R., & DEMARCO, J. J. (1961). *Phys. Rev.* **122**, 68–74.
- BORIE, B. & SPARKS, C. J. (1971). *Acta Cryst.* **A27**, 198–201.
- CARTER, R. E. & ROTH, W. L. (1963). General Electric Research Report No. 63-RL-3479 M.
- CARTER, R. E. & ROTH, W. L. (1968). *Electromotive Force Measurements in High-Temperature Systems*, edited by C. R. ALCOCK, pp. 125–144. New York: The Institute of Mining and Metallurgy.
- CROMER, D. T. (1969). *J. Chem. Phys.* **50**, 4857–4859.
- ETSELL, T. H. & FLENGAS, S. N. (1970). *Chem. Rev.* **20**, 339–376.
- FABER, J. JR, MUELLER, M. H. & COOPER, B. R. (1978). *Phys. Rev. B*, **17**, 4884–4888.
- GRAGG, J. E. JR, BARDHAN, P. & COHEN, J. B. (1971). *Critical Phenomena in Alloys, Magnets and Superconductors*, edited by R. E. MILLS, E. ASHER & R. JAFFEE, pp. 309–337. New York: McGraw-Hill.
- HAYAKAWA, M. & COHEN, J. B. (1975). *Acta Cryst.* **A31**, 635–645.
- HUANG, K. (1947). *Proc. R. Soc. London Ser. A*, **190**, 102–116.
- HUDSON, B. & MOSELEY, P. T. (1976). *J. Solid State Chem.* **19**, 383–389.
- HUDSON, B. & MOSELEY, P. T. (1978). *Inst. Phys. Conf. Ser.* No. 41, pp. 104–108.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KOCH, F. B. & COHEN, J. B. (1969). *Acta Cryst.* **B25**, 275–287.
- MORINAGA, M. (1978). PhD Thesis, Northwestern Univ., Evanston, IL 60201.
- MORINAGA, M. & COHEN, J. B. (1979). *Acta Cryst.* **A35**, 975–989.
- MORINAGA, M., COHEN, J. B. & FABER, J. JR (1979). *Acta Cryst.* **A35**, 789–794.
- ROTH, W. L. (1975). *Crystal Structure and Chemical Bonding in Inorganic Chemistry*, edited by C. J. M. ROOYMANS & A. RABENAN, pp. 85–102. The Netherlands: North-Holland.
- SCHWARTZ, L. H. & COHEN, J. B. (1977). *Diffraction from Materials*, pp. 191–192. New York: Academic Press.
- SCHWARTZ, L. H., MORRISON, L. A. & COHEN, J. B. (1963). *Adv. X-ray Anal.* **7**, 281–301.
- SMITH, D. K. & NEWKIRK, H. W. (1965). *Acta Cryst.* **18**, 983–991.
- STEELE, D. & FENDER, B. E. F. (1974). *J. Phys. C*, **7**, 1–11.
- TERAUCHI, H. & COHEN, J. B. (1979). *Acta Cryst.* **A35**, 646–652.
- TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.
- TEUFER, G. (1962). *Acta Cryst.* **15**, 1187.
- WILLIAMS, R. O. (1972). Report ORNL-4828. Oak Ridge National Laboratory, Tennessee.
- WOLFF, P. M. DE (1956). *Acta Cryst.* **9**, 682–683.

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Theory of Piezo-Optic Birefringence in Mixed Crystals of Equimolar Concentration with NaCl Structure

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Abstract

Following the theoretical approach of Bansigir & Iyengar [*Acta Cryst.* (1961), **14**, 670–674], an expression for $p_{11} - p_{12}$ is developed for a mixed crystal of KCl–KBr with equimolar concentration. It was assumed that among the six nearest neighbours of the K^+ ion, three are Cl^- and the other three Br^- , and that each K^+ is accompanied by Cl^- and Br^- on either side

in all three principal directions. The expression $p_{11} - p_{12}$ is used to evaluate the polarizabilities, reversal wavelength, ratio and absolute values of strain–optical constants p_{11} and p_{12} .

Introduction

Some years ago, an improved theory of piezo-optic birefringence in cubic crystals of NaCl structure was

developed (Bansigir & Iyengar, 1961a; Ethiraj & Bansigir, 1973). The theory was later extended to CsCl-type crystals (Ethiraj, Krishna Murty & Bansigir, 1973, 1978a). In view of the recent studies on the piezo-optic birefringence in mixed crystals of KCl–KBr (Ethiraj, Krishna Murty & Bansigir, 1978b; Kumar, Ethiraj & Krishna Murty, 1979), an attempt is made in this paper to extend the above theory to the mixed crystals of NaCl structure of equimolar concentration with the same cation. The theory is worked out for equimolar concentration of KCl–KBr specifically and is valid for any mixed crystal having the same structure and concentration.

Phenomenological theory

It is well known that when a cubic crystal with edges parallel to [100] [010] [001] is stressed along the Z axis [001], its refractive index changes and varies with direction. Hence the refractive index along the direction of stress [001] will be different from the refractive index along its perpendicular axis [100]. Let the changes in the refractive index in these two directions be dn_z and dn_x respectively. These changes are related to the strain ε [along Z] through the following expressions based on the phenomenological theory of Pockels (1906), the observation being made along the [010] direction,

$$\begin{aligned} dn_z &= n_z - n = -p_{11}(n^3/2) \varepsilon, \\ dn_x &= n_x - n = -p_{12}(n^3/2) \varepsilon, \end{aligned} \quad (1)$$

where n is the refractive index of the crystal in the unstrained condition and n_z and n_x are the refractive indices of the strained crystal for light vibrating in the Z and X directions respectively and p_{11} and p_{12} are the corresponding strain–optical coefficients.

The unequal changes in the refractive indices resulting from the deformation may be attributed to change in the density of the crystal and change in the polarizability of the ion.

(1) *Change in the density of the crystal.* If a unit volume of the crystal is stressed along the Z direction, a strain ε along this direction and a corresponding strain $\sigma\varepsilon$ along the X and Y directions occur, where σ is Poisson's ratio. Hence the change in volume would be $\varepsilon(1 - 2\sigma)$. This volume would bring about a change δN_j in the number of ions per unit volume and is given by $\varepsilon(1 - 2\sigma)N_j$, where N_j represents the number of ions per unit volume.

(2) *Change in the polarizability of the ion.* The change in the polarizabilities of ions may be attributed to the following anisotropies: (a) Lorentz–Lorenz anisotropy due to the material continuum; (b) Lorentz–Lorenz anisotropy due to the dipoles within the cavity;

and (c) Coulomb anisotropy due to the presence of positive and negative charges within the cavity.

The Lorentz–Lorenz anisotropy due to the material continuum has been calculated by Mueller (1935) on the lines suggested by Havelock (1908). He has shown for a medium strained in the Z direction, where the strain ellipsoid has the axial ratio $1:1:1 + \varepsilon$, that the refractive index n_x for light vibrating along the X direction is given by (Brayborn, 1953)

$$3n_x^2 - 1 = 4\pi N_j \alpha_j [(n_x^2 + 2) + K_x(n^2 - 1)], \quad (2)$$

with similar expressions for light vibrating along the Y and Z directions, where $K_x = K_y = (2/5)\varepsilon$ and $K_z = -(4/5)\varepsilon$; α_j is the polarizability of the ion under consideration and N_j the number of ions per unit volume.

To evaluate the other two anisotropies, (b) and (c), we assume a spherical cavity of radius greater than $\sqrt{3}\gamma$ and less than 2γ , where 2γ is the lattice constant. When this cavity is subjected to a uniaxial stress, in the direction of one of the edges of the unit cell, the sphere changes to an ellipsoid. The centre of the cell is chosen as the origin of the coordinate system. In the unit cell of a mixed crystal of equimolar concentration of $\text{KCl}_{0.5}\text{--KBr}_{0.5}$, we have assumed that among the six nearest neighbours of K^+ ion, three are Cl^- ions and the other three Br^- ions, and that each K^+ ion is accompanied by Cl^- and Br^- ions on either side in all three directions (Fig. 1). It may be mentioned that this is one of the possible configurations suggested by Durham & Hawkins (1951).

The expression for the field due to dipole anisotropy if the incident field is polarized in the Z direction, the centre of the cavity being occupied by a positive or either of the negative ions, is given by

$$E_{jzd} = D_{jkz}(\mu_{kz}) \varepsilon/\gamma^3, \quad (3a)$$

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 inter-ionic distance.

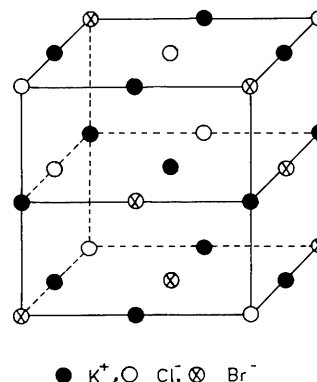


Fig. 1. The unit cell of the mixed crystal $\text{KCl}_{0.5}\text{--KBr}_{0.5}$.

For light polarized in the X direction, the corresponding expression is

$$E_{jxd} = D_{jkk}(\mu_{kx}) \varepsilon / \gamma^3, \quad (3b)$$

where μ_{kx} and μ_{kz} in the above expressions are dipole moments along the X and Z directions respectively; D_{jkk} and D_{jxz} are numerical values of finite lattice sums in the deformed lattice.

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

$$E_{jzc} = \frac{\beta \varepsilon}{\gamma^3} C_{jkk} \frac{\alpha_k}{f_k}, \quad (4a)$$

and for light polarized in the X direction is

$$E_{jxc} = \frac{\beta \varepsilon}{\gamma^3} C_{jkk} \frac{\alpha_k}{f_k}, \quad (4b)$$

where β is the number of valence electrons, α_k is the polarizability of a positive or either of the negative ions and f_k is the oscillator strength of a positive or either of the negative ions; C_{jkk} and C_{jxz} are numerical constants of the lattice. The Coulomb fields are created because, under the influence of the incident field, the excess charges are displaced by S_1 , S_2 , S_3 , or S_k in general, giving rise to a dipole whose moment could be expressed as $f_k e^* S_k / 4\pi = \mu_{kz}$, or μ_{kx} , where e^* is the effective charge (Fröhlich, 1949); S_1 , S_2 and S_3 are the displacements of Cl^- , K^+ and Br^- respectively.

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

$$(\mu_{jz})_{idcp} = \alpha_j F_{jz} \text{ in the } Z \text{ direction}, \quad (5a)$$

$$(\mu_{jx})_{idcp} = \alpha_j F_{jx} \text{ in the } X \text{ direction}, \quad (5b)$$

where

$$F_{jz} = E_{iz} + E_{jzd} + E_{jzc} + K_z P_j, \quad (6a)$$

$$F_{jx} = E_{ix} + E_{jxd} + E_{jxc} + K_x P_j, \quad (6b)$$

E_i is the incident field and P_j is the polarization of the medium.

Alternatively, the dipole moment in (6) could be due to the effective polarizabilities α_{jz} or α_{jx} in the Z and X directions under the incident fields E_{jz} and E_{jx} according to

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

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

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

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

holds good for mixed cubic crystals, where

$$N_j = \left[\frac{N_j}{2} \text{KCl} + \frac{N_j}{2} \text{KBr} \right]$$

for equimolar concentration.

Equations (5), (6), (7) and (8) together yield

$$\alpha_{jz} = \alpha_j \left\{ 1 + \left[\left(\frac{n^2 + 2}{3} \right) \left(D_{jkk} \frac{\alpha_k}{\gamma^3} + C_{jkk} \frac{\alpha_k \beta}{\gamma^3 f_k} \right) + \frac{K_z}{3} (n^2 - 1) \right] \varepsilon \right\}, \quad (9a)$$

$$\alpha_{jx} = \alpha_j \left\{ 1 + \left[\left(\frac{n^2 + 2}{3} \right) \left(D_{jkk} \frac{\alpha_k}{\gamma^3} + C_{jkk} \frac{\alpha_k \beta}{\gamma^3 f_k} \right) + \frac{K_x}{3} (n^2 - 1) \right] \varepsilon \right\}. \quad (9b)$$

The values of the D 's and C 's are calculated by assuming that $z = \gamma + \delta z$, $x = \gamma - \delta x$ and $y = \gamma - \delta y$, where δx , δy and δz are linear deformations caused by the stress and the higher powers of δx , δy and δz are negligible. Values thus obtained for the constants are given in Table 1.

Assuming that $\alpha = \alpha^- + \alpha^+$ (where α^- is taken to be the effective polarizability of the negative ion) and $f_1 = f_2 = f_3 = f$, the change in the polarizabilities along the Z and X directions could be expressed as follows:

$$\begin{aligned} d\alpha_z = & \frac{\varepsilon}{4\pi\gamma^3} [A'(\alpha^{-2} - \alpha\alpha^-) + B'\alpha^2] \\ & + \left(\frac{\gamma - 2\varepsilon\gamma}{\gamma^3} \right) \left[\frac{\alpha^{\text{Cl}}}{S_1 f} - \frac{\alpha^{\text{Br}}}{S_3 f} \right]; \end{aligned} \quad (10a)$$

Table 1. Numerical constants

$$\begin{aligned} D_{11z} = D_{13z} = D_{31z} = D_{33z} &= 0.0844(\sigma + 1) \\ D_{12z} = D_{32z} &= -0.7916(\sigma + 1) \\ D_{21z} = D_{23z} &= -0.3958(\sigma + 1) \\ D_{22z} &= 0.1688(\sigma + 1) \\ D_{11x} = D_{13x} = D_{31x} = D_{33x} &= -0.0422(\sigma + 1) \\ D_{12x} = D_{32x} &= 0.3958(\sigma + 1) \\ D_{21x} = D_{23x} &= 0.1979(\sigma + 1) \\ D_{22x} &= -0.0844(\sigma + 1) \\ C_{11z} = C_{13z} = C_{31z} = C_{33z} &= 0.0844(\sigma + 1) \\ C_{12z} = C_{32z} &= -0.7916(\sigma + 1) \\ C_{21z} = C_{23z} &= -0.3958(\sigma + 1) \\ C_{22z} &= 0.1688(\sigma + 1) \\ C_{11x} = C_{13x} = C_{31x} = C_{33x} &= -0.0422(\sigma + 1) \\ C_{12x} = C_{32x} &= 0.3958(\sigma + 1) \\ C_{21x} = C_{23x} &= 0.1979(\sigma + 1) \\ C_{22x} &= -0.0844(\sigma + 1) \end{aligned}$$

$$d\alpha_x = \frac{\varepsilon}{4\pi\gamma^3} [A''(\alpha\alpha^- - \alpha^2) - B''\alpha^2] - \frac{N(n^2 + 2)^2 (\gamma + 2\sigma\varepsilon\gamma)}{18n\gamma^3} \left[\frac{\alpha^{\text{Cl}}}{S_1 f} - \frac{\alpha^{\text{Br}}}{S_3 f} \right]; \quad (11b)$$

$$- \left(\frac{\gamma + 2\sigma\varepsilon\gamma}{\gamma^3} \right) \left[\frac{\alpha^{\text{Cl}}}{S_1 f} - \frac{\alpha^{\text{Br}}}{S_3 f} \right]; \quad (10b)$$

$$A' = 24 \cdot 1372(\sigma + 1) + 303 \cdot 4391(\sigma + 1)/f,$$

$$B' = 2 \cdot 1214(\sigma + 1) + 26 \cdot 6690(\sigma + 1)/f,$$

$$A'' = 12 \cdot 0686(\sigma + 1) + 151 \cdot 7195(\sigma + 1)/f,$$

$$B'' = 1 \cdot 0607(\sigma + 1) + 13 \cdot 3345(\sigma + 1)/f.$$

Taking into account all the anisotropies and the density change, we obtain the changes in refractive indices along the Z and X directions:

$$dn_z = \left[- \frac{(1 - 2\sigma)(n^2 - 1)(n^2 + 2)}{6n} - \frac{2(n^2 - 1)^2}{15n} + \frac{A'N\gamma^3(n^2 + 2)^2}{226 \cdot 2857n} \theta^2 - \frac{A'(n^2 + 2)(n^2 - 1)}{75 \cdot 4286n} \theta + \frac{B'(n^2 - 1)^2}{25 \cdot 1429N\gamma^3 n} \right] \varepsilon + \frac{N(n^2 + 2)^2 (\gamma - 2\varepsilon\gamma)}{18n\gamma^3} \left[\frac{\alpha^{\text{Cl}}}{S_1 f} - \frac{\alpha^{\text{Br}}}{S_3 f} \right]; \quad (11a)$$

$$dn_x = \left[- \frac{(1 - 2\sigma)(n^2 - 1)(n^2 + 2)}{6n} + \frac{(n^2 - 1)^2}{15n} - \frac{A''N\gamma^3(n^2 + 2)^2}{226 \cdot 2857n} \theta^2 + \frac{A''(n^2 + 2)(n^2 - 1)}{75 \cdot 4286n} \theta - \frac{B''(n^2 - 1)^2}{25 \cdot 1429N\gamma^3 n} \right] \varepsilon$$

where $\theta = \alpha^+/\gamma^3$ or α^-/γ^3 .

From the above expressions for dn_z and dn_x , one can obtain an expression for the birefringence:

$$dn_z - dn_x = \left[- \frac{(n^2 - 1)^2}{5n} + \frac{(A' + A'')N\gamma^3(n^2 + 2)^2}{226 \cdot 2857n} \theta^2 - \frac{(A' + A'')(n^2 + 2)(n^2 - 1)}{75 \cdot 4286n} \theta + \frac{(B' + B'')(n^2 - 1)^2}{25 \cdot 1429N\gamma^3 n} \right] \varepsilon + \frac{N(n^2 + 2)^2 (\sigma - 1)}{9n\gamma^2} \left[\frac{\alpha^{\text{Cl}}}{S_1 f} - \frac{\alpha^{\text{Br}}}{S_3 f} \right] \varepsilon + \frac{N(n^2 + 2)^2}{9n\gamma^2} \left[\frac{\alpha^{\text{Cl}}}{S_1 f} - \frac{\alpha^{\text{Br}}}{S_3 f} \right]. \quad (12)$$

It is interesting to note that the birefringence does not become zero in the undeformed state ($\varepsilon = 0$) but is equal to

$$\frac{N(n^2 + 2)^2}{9n\gamma^3} \left[\frac{\alpha^{\text{Cl}}}{S_1 f} - \frac{\alpha^{\text{Br}}}{S_3 f} \right].$$

However, if we consider an adjacent unit cell to the one considered, the birefringence in the undeformed state is found to be opposite in sign but equal in magnitude. Thus the net birefringence for the crystal as a whole is zero in the undeformed state.

The expression for $(dn_z - dn_x)$ was worked out for all the eight possible arrangements of Cl^- and Br^- ions with the assumed symmetry regarding the distribution

Table 2. Variation of polarizabilities with wavelength

Wavelength (nm)	Refractive index n	Brewster constant $C_{001} \times 10^{12}$ m^2/N	$(p_{11} - p_{12}) \times 10^2$	Polarizability of K^+ $\alpha^+ \times 10^{30}$ m^3	Effective polarizability of the negative ions $\alpha_{\text{eff}}^- \times 10^{30}$ m^3	Ratio of the strain-optical constants p_{12}/p_{11}
560	1.512	2.93	5.1757	0.465	4.471	0.82
520	1.516	2.68	4.6967	0.467	4.498	0.83
480	1.520	2.40	4.1729	0.469	4.535	0.85
450	1.525	2.23	3.8393	0.472	4.569	0.86
400	1.535	1.94	3.2752	0.478	4.643	0.88
360	1.547	1.70	2.8037	0.486	4.731	0.90
320	1.566	1.30	2.0669	0.498	4.866	0.92
290	1.588	0.33	0.5032	0.510	5.023	0.99
270	1.609	-0.70	-1.0261	0.522	5.174	1.05

of these ions in the unit cell, and the birefringence in all cases is given by

$$dn_z - dn_x = \left[-\frac{(n^2 - 1)^2}{5n} + \frac{(A' + A'') N \gamma^3 (n^2 + 2)^2}{226 \cdot 2857n} \theta^2 - \frac{(A' + A'')(n^2 + 2)(n^2 - 1)}{75 \cdot 4286n} \theta + \frac{(B' + B'')(n^2 - 1)^2}{25 \cdot 1429 N \gamma^3 n} \right] \epsilon. \quad (13)$$

From (1) and (13), the expression for $p_{11} - p_{12}$ may be written as

$$p_{11} - p_{12} = (2/n^3)(dn_z - dn_x)/\epsilon. \quad (14)$$

Applications

(1) Polarizabilities of the ions and reversal wavelength

From (14), the polarizability of the positive ion and the effective polarizability of the negative ions are

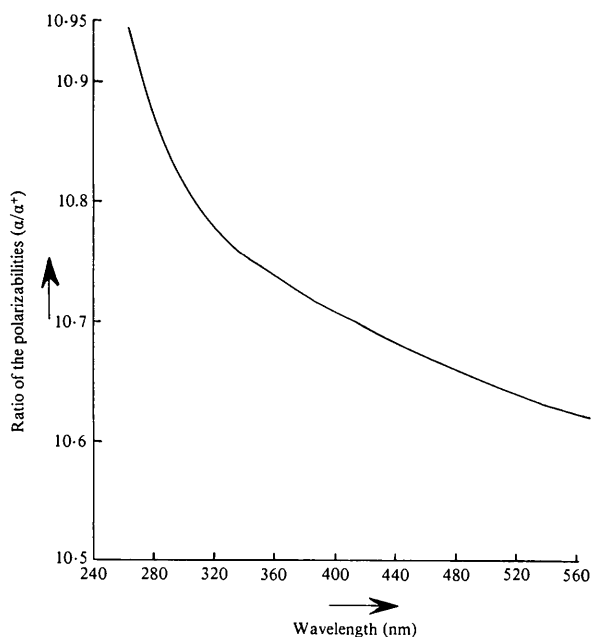


Fig. 2. Ratio of polarizabilities, α/α^+ , versus wavelength.

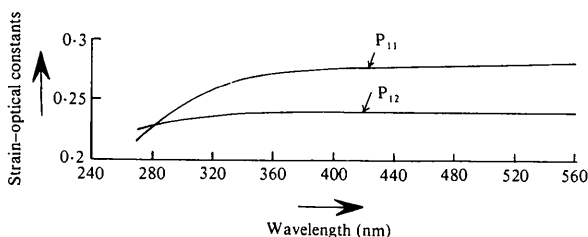


Fig. 3. Variations of p_{11} and p_{12} with wavelength.

evaluated at different wavelengths and are given in Table 2. In evaluating the polarizabilities, the value of the strain-optical constants ($p_{11} - p_{12}$) are calculated using the expression, $C_{001} = (n^3/2)(p_{11} - p_{12})/(C_{11} - C_{12})$. The data on the Brewster constant C_{001} (Kumar, Ethiraj & Krishna Murty, 1979) and the elastic constant ($C_{11} - C_{12}$) (Slagle & McKinstry, 1967) are taken from the literature. The data on the refractive index for the mixed crystal was evaluated using the Lorentz-Lorenz equation (Ethiraj, 1976).

The effective polarizability of the negative ions increases with decrease of wavelength as is observed in the case of pure crystals (Ethiraj, Krishna Murty & Bansigir, 1978a). The variation of the polarizability of the positive ion is, however, small. The polarizabilities of Cl^- and Br^- ions in KCl and KBr for sodium light are 3.694 and 4.739 respectively (Bansigir & Iyengar, 1961b). The effective polarizability of the negative ion obtained in the present investigation is comparable with them.

For evaluating the reversal wavelength (wavelength at which $p_{11} = p_{12}$), the ratio of the polarizabilities, α/α^+ , was plotted against wavelength as shown in Fig. 2. With $p_{11} = p_{12}$ in (14), α/α^+ was calculated and the wavelength corresponding to this value was obtained from Fig. 2. The reversal wavelength so obtained is 282.5 nm which is in good agreement with the experimental value 282 nm (Kumar, Ethiraj & Krishna Murty, 1979).

(2) Ratios of the strain-optical constants and their absolute values

From (1) and the expressions for dn_z and dn_x , the ratio of the strain-optical constants, $p_{12}/p_{11} = dn_x/dn_z$, was evaluated at different wavelengths; the results are given in Table 2. By combining the values of ($p_{11} - p_{12}$) and p_{12}/p_{11} , the absolute values of p_{11} and p_{12} were evaluated and their variation with wavelength is shown in Fig. 3.

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References

- BANSIGIR, K. G. & IYENGAR, K. S. (1961a). *Acta Cryst.* **14**, 670-674.
- BANSIGIR, K. G. & IYENGAR, K. S. (1961b). *Acta Cryst.* **14**, 727-732.
- BRAYBORN, J. E. H. (1953). *Proc. Phys. Soc. London Sect. B*, **66**, 61-63.
- DURHAM, G. S. & HAWKINS, J. A. (1951). *J. Chem. Phys.* **19**, 149-156.

- ETHIRAJ, R. & BANSIGIR, K. G. (1973). *Acta Cryst.* **A29**, 157–160.
- ETHIRAJ, R. (1976). Thesis, Osmania Univ., Hyderabad, India.
- ETHIRAJ, R., KRISHNA MURTY, V. G. & BANSIGIR, K. G. (1973). *Acta Cryst.* **A29**, 636–639.
- ETHIRAJ, R., KRISHNA MURTY, V. G. & BANSIGIR, K. G. (1978a). *Acta Cryst.* **A34**, 318–321.
- ETHIRAJ, R., KRISHNA MURTY, V. G. & BANSIGIR, K. G. (1978b). *Phys. Status Solidi*, **45**, 83–87.
- FRÖHLICH, H. (1949). *Theory of Dielectrics*. Oxford: Clarendon Press.
- HAVELOCK, T. H. (1908). *Proc. R. Soc. London Ser. A*, **80**, 28–44.
- KUMAR, G. S., ETHIRAJ, R. & KRISHNA MURTY, V. G. (1979). *Acta Cryst.* **A35**, 857–858.
- MUELLER, H. (1935). *Phys. Rev.* **47**, 947–957.
- POCKELS, F. (1906). *Lehrbuch der Kristallographie*. Berlin: Teubner.
- SLAGLE, O. D. & MCKINSTRY, H. A. (1967). *J. Appl. Phys.* **38**, 446–451.

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Tensor Properties and Rotational Symmetry of Crystals.

I. A New Method for Group $3(3_2)$ and Its Application to General Tensors up to Rank 8*

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Abstract

A new method is presented to overcome the cumbersome of the existing methods in the derivation and tabulation of the results for general tensors when the elements of the group do not all simply permute coordinates apart from sign; here the method is described for the generator 3_2 . The method uses a conjectured, optimal choice of independent components (verified up to rank 8) and a new procedure to obtain the expressions of the dependent components. The independent components adopted consist of sets of components related by appropriate permutations of component indices: this choice is suggested by the similarity of transformation properties of these components. The procedure for the determination of the expressions of dependent components is based on the representation of all components by suitable numerical vectors. The procedure allows the exploitation of the restrictions on the general form of the expressions which follow from the optimal choice of independent components. The method is applied to the derivation of the schemes of general tensors up to rank 8 in group $3(3_2)$. The simplification provided by the method is considerable.

The method permits, for instance, the complete determination of the scheme for the 2^8 components with only x and y indices of a general eighth-rank tensor by solving five systems of linear inhomogeneous equations, one 7 by 7, two 6 by 6 (with identical matrices of coefficients), one 5 by 5 and one 3 by 3. Furthermore, and perhaps more importantly, the resulting scheme can be completely represented by ten distinct expressions (and their permutations). Several errors are pointed out in the table of Chung & Li [*Acta Cryst.* (1974), **A30**, 1–13] for the (non-tensorial) array for fourth-order elasticity in group $3(3_2)$.

1. A synopsis of the existing methods

The field of tensor properties of crystals is probably the oldest chapter of solid-state physics, and thus the history of the methods used to study the effect of the rotational symmetry of crystals on their tensor properties is a long and involved one. Here we will try to focus on the main ideas of these methods.

A broad distinction can be made between *direct* methods and *indirect* methods. The direct methods work with the tensor as such, while the indirect methods work with the cause-effect relationship defining the tensor or with the expression of a thermodynamic potential involving the tensor.

The typical direct method imposes invariance on each tensor component, *i.e.* imposes equality between each tensor component and its transforms under all the symmetry elements of the crystal. The method, first

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