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Piezo-Optic Birefringence in CsCl-Structure Crystals

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Following the theoretical approach of Bansigir and Iyengar, expressions for $p_{11}-p_{12}$ and p_{12}/p_{11} are developed for crystals of the CsCl type. Using experimental values of $p_{11}-p_{12}$, the polarizabilities of some of the ions are evaluated. From the calculated values of the polarizabilities, the ratios of the strain-optical constants are evaluated.

Introduction

Expressions for the change in the refractive index due to strain in NaCl-type crystals, were developed by Bansigir & Iyengar (1961). However no such study was made on crystals belonging to the CsCl type. In this paper an attempt has been made to develop the theory for CsCl-type crystals on the lines suggested by Bansigir & Iyengar. Using experimental values of $p_{11}-p_{12}$, (Laiho & Korpela, 1968) the polarizabilities of various ions are calculated and compared with observed values. From the calculated values of α 's the ratios of strain-optical constants of a few crystals are evaluated.

Theory

It is well known that when a cubic crystal is stressed, its refractive index changes and varies with direction.

This change can be expressed in the following manner.

Let a rectangular bar of the crystal with edges parallel to [100], [010], [001] (to be called X, Y and Z respectively) be stressed along the Z direction. The changes dn_x and dn_z in the refractive index n are related to strain ϵ (along Z) through the following expressions based on the phenomenological theory of Pockels (1906), the observation being made along the Y direction

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

where n_x and n_z are the refractive indices of the stressed crystal for light vibrating in the X and Z directions respectively; n is the refractive index of the crystal in its unstrained condition and p_{12} & p_{11} are the respective strain-optical coefficients.

The change in the refractive index is caused by

- (i) change in the density of the crystals, *i.e.* the change in the number of dispersion centres per unit volume,
- (ii) change in the polarizability of the ion.

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 the Poisson's ratio. Hence the change in volume would be $\varepsilon(1-2\sigma)$. This volume change 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.

The factors affecting polarizability are

- (a) Lorentz-Lorentz anisotropy due to the material continuum,
- (b) Lorentz-Lorentz anisotropy due to dipoles within the cavity,
- (c) Coulomb anisotropy due to the presence of positive and negative charges within the cavity.

The Lorentz-Lorentz 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+ ε , the refractive index for light vibrating in the **X** direction is given by (Brayborn, 1953),

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

with a similar expression for light vibrating in the **Z** direction, 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.

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 a negative ion, is given by

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

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 lattice constant.

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

$$E_{jxd} = D_{jkx}(\mu_{kx}) \frac{\varepsilon}{\gamma^3}. \quad (3b)$$

μ_{kx} and μ_{kz} in the above expressions are dipole moments along the **X** and **Z** directions respectively; D_{jkz} and D_{jkx} 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 given by

$$E_{jzc} = \left[\frac{\beta\varepsilon}{\gamma^3} \right] C_{jkz} \left[\frac{\alpha_k}{f_k} \right] \quad (4a)$$

and for light polarized in **X** direction by

$$E_{jxc} = \left[\frac{\beta\varepsilon}{\gamma^3} \right] C_{jkx} \left[\frac{\alpha_k}{f_k} \right] \quad (4b)$$

where β is the number of valence electrons, α_k = the polarizability of a positive or negative ion and f_k the oscillator strength of a positive or negative 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 excess charges are displaced by an amount s_1 and s_2 , or s_k in general, giving rise to a dipole whose moment could be expressed as $f_k e^* s_k / 4\pi = \mu_{kz}$ or x where e^* is the effective charge (Fröhlich, 1949).

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

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

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

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 per unit volume.

Alternatively, the dipole moment in expression (6) could be due to the effective polarizabilities α_{jz} or α_{jx} in the **Z** and **X** directions under the incident field 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-Lorentz 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 cubic crystals.

The equations, (5), (6), (7) and (8) together yield

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

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

The expressions for the D 's and C 's are evaluated by taking the radius of the cavity to be equal to $(\frac{2}{3})\gamma$ and assuming that $z = \gamma/2 + \delta z$, $x = \gamma/2 - \delta x$, $y = \gamma/2 - \delta y$ where δx , δy , and δz are linear deformations caused by the stress. The higher powers of δx , δy , and δz are neglected in the evaluation. Values thus obtained are given in Table 1.

Table 1. Numerical constants

$$D_{12z} = D_{21z} = \frac{\mu_z}{4\pi\gamma^3} [14.1608(1 + \sigma)]\epsilon$$

$$D_{11z} = D_{22z} = -\frac{\mu_z}{4\pi\gamma^3} [9.8784(1 + \sigma)]\epsilon$$

$$D_{12x} = D_{21x} = -\frac{\mu_x}{4\pi\gamma^3} [7.0804(1 + \sigma)]\epsilon$$

$$D_{11x} = D_{22x} = \frac{\mu_x}{4\pi\gamma^3} [4.9390(1 + \sigma)]\epsilon$$

$$C_{11z} = C_{22z} = \left[(13.1961 - 8.7920\sigma) \frac{s_1 \text{ or } 2}{f_1 \text{ or } 2\gamma^3} \right] \epsilon$$

$$C_{11x} = C_{22x} = \left[(4.3960 - 17.5921\sigma) \frac{s_1 \text{ or } 2}{f_1 \text{ or } 2\gamma^3} \right] \epsilon$$

$$C_{12z} = C_{21z} = \left[(16.7296 - 20.4864\sigma) \frac{s_1 \text{ or } 2}{f_1 \text{ or } 2\gamma^3} \right] \epsilon$$

$$C_{12x} = C_{21x} = \left[(10.2432 - 26.9720\sigma) \frac{s_1 \text{ or } 2}{f_1 \text{ or } 2\gamma^3} \right] \epsilon$$

Assuming that $\alpha = \bar{\alpha} + \alpha^+$ and $f_1 = f_2 = f$, the change in the polarizabilities along the Z and X directions could be expressed as follows:

$$d\alpha_z = \frac{\epsilon}{4\pi\gamma^3} [A'(\bar{\alpha}^2 - \alpha\bar{\alpha}) + B'\alpha^2] \quad (10a)$$

$$d\alpha_x = \frac{\epsilon}{4\pi\gamma^3} [A''(\bar{\alpha}^2 - \alpha\bar{\alpha}) + B''\alpha^2], \quad (10b)$$

where

$$A' = [48.0784(1 + \sigma) + (-7.0670 + 23.3888\sigma)/f]$$

$$B' = [-9.8784(1 + \sigma) + (13.1961 - 8.7920\sigma)/f]$$

$$A'' = [24.0392(1 + \sigma) + (-11.6944 + 18.7614\sigma)/f]$$

$$B'' = [4.9392(1 + \sigma) + (4.3960 - 17.5921\sigma)/f].$$

Taking into consideration all the anisotropies and the density change, the changes in refractive indices along the Z and X directions are given as follows:

$$dn_z = \left[\frac{(1 - 2\sigma)(n^2 - 1)(n^2 + 2)}{6n} - \frac{2(n^2 - 1)^2}{15n} \right. \\ \left. + \frac{A'N\gamma^3(n^2 + 2)^2}{226.29n} u^2 - \frac{A'(n^2 - 1)(n^2 + 2)}{75.43n} u \right. \\ \left. + \frac{B'(n^2 - 1)^2}{25.143nN\gamma^3} \right] \epsilon \quad (11a)$$

$$dn_x = \left[\frac{(1 - 2\sigma)(n^2 - 1)(n^2 + 2)}{6n} + \frac{(n^2 - 1)^2}{15n} \right. \\ \left. + \frac{A''N\gamma^3(n^2 + 2)^2}{226.29n} u^2 - \frac{A''(n^2 - 1)(n^2 + 2)}{75.43n} u \right. \\ \left. + \frac{B''(n^2 - 1)^2}{25.143nN\gamma^3} \right] \epsilon \quad (11b)$$

where

$$u = \frac{4\pi}{\gamma^3} (\bar{\alpha} + \text{or } \alpha^+).$$

$$p_{11} - p_{12} = \frac{2}{n^3} \left[\frac{(n^2 - 1)^2}{15n} + \frac{(A'' - A')N\gamma^3(n^2 + 2)^2}{226.29n} u^2 \right. \\ \left. - \frac{(A'' - A')(n^2 - 1)(n^2 + 2)}{74.43n} u \right. \\ \left. + \frac{(B'' - B')(n^2 - 1)^2}{25.143nN\gamma^3} \right]. \quad (12)$$

1. Ionic polarizabilities as calculated from the present theory

Using the experimental values of $p_{11} - p_{12}$ (Krishna Rao & Krishna Murty, 1961; Laiho & Korpela, 1963) and assuming the oscillator strength to be unity, the polarizabilities of the various ions for the wavelength 5893 Å are evaluated and compared with those obtained by other workers. The results are given in Table 2.

2. Ratios of strain-optical constants

Equation (1) and (11) yield, $p_{12}/p_{11} = (dn_z/dn_x)$, the ratio of strain-optical constants. Using the calculated

Table 2. Polarizabilities α_i ($\text{cm}^3 \times 10^{-24}$)

Ion	Present work	Fajans & Joos (1924)	Born & Heisenberg (1924)	Pauling (1927)	Shockley (1946)	Shockley, Tessman & Khan (Kittel, 1953)
Cl	3.701 NH ₄ Cl	3.53	3.05	3.66	2.92	2.97
	4.505 CsCl	—	—	—	—	—
Br	5.582 CsBr	4.97	4.17	4.77	4.12	4.17
	7.604 CsI	7.55	6.28	7.10	6.41	6.44
NH ₄	1.274	—	—	—	—	—
	1.470 CsCl	—	—	—	—	—
Cs	1.670 CsBr	—	—	—	—	—
	2.017 CsI	—	—	—	—	—

values of α 's (Table 2), the ratios of strain-optical constants are obtained and given in Table 3. The experimental data on p_{12}/p_{11} is available only for NH_4Cl .

Table 3. Ratios of strain-optical constants

Crystal	Calculated p_{12}/p_{11}	Observed p_{12}/p_{11}
NH_4Cl	1.217	1.560*
CsCl	1.225	—
CsBr	1.267	—
CsI	1.099	—

* Krishna Rao & Krishnamurty (1961).

Both polarizabilities and strain-optical constants are found to be in satisfactory agreement with the observed values.

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Groupes Magnétiques Associés aux Groupes d'Espace de Réseau Non Primitif

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In order to enumerate the magnetic groups with a non-primitive lattice, the real one-dimensional representations of space groups G_e with a non-primitive lattice are sought; it is possible to come back to primitive lattices by considering the factor group $G' = G_e/P$, where P is the subgroup of primitive translations of G_e . The introduction of G' makes it possible to simplify the construction of the irreducible representations of G_e .

Introduction

Dans un travail récent (Sivardière, 1969a), nous avons indiqué une méthode nouvelle d'énumération des groupes magnétiques, basée sur la correspondance suivante déjà signalée par d'autres auteurs (Indenbom, 1960; Niggli, 1960; Bertaut, 1968): soit Γ_{kj} une représentation réelle de dimension 1 d'un groupe d'espace G_e ; si on remplace les éléments de G_e ayant le caractère -1 par les antiopérateurs correspondants, on obtient un groupe magnétique isomorphe de G_e .

La méthode des représentations, équivalente à celle d'Opechowsky & Guccione (1961), a été développée seulement pour les groupes d'espace de réseau primitif: elle est étendue ici aux groupes d'espace de réseau non primitif. En principe, cette méthode est applicable quel que soit le type de réseau; nous avons cherché cependant à nous ramener au cas plus simple d'un réseau primitif.

Nous utilisons les notations suivantes:

- G_e : groupe d'espace,
 G : groupe ponctuel, d'ordre $g: G = G_e/T$;
 T : translations du réseau;
 P : translations entières;
 t_i : translations C, I, F non entières;
 $(\alpha|\tau_\alpha)$: rotation de G_e ;
 k : vecteur de l'espace réciproque (maille primitive);
 k' : vecteur de l'espace réciproque (maille multiple).

I. Structure algébrique des groupes d'espace de réseau non primitif

Les translations P forment un sous-groupe invariant de T et de G_e ; on peut donc définir les groupes facteurs: