Acta Cryst. (1951). **4**, 237

Tensor Form of Piezo-optic and Electro-optic Equations

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(*Received* 18 *August* 1950)

The relations for piezo-optic and electro-optic phenomena are expressed in tensor form by means of only one equation. The possible existence is shown of refraction of a kind similar to Hamilton's conical refraction which might be observed in a crystal placed in an alternating electric field. The interpretation of this effect is, however, physically essentially different.

1. Introduction

It is convenient to express the classical piezo-optic and electro-optic equations of Pockels (1906) in a tensor form. Piezo-electric phenomena were expressed in a similar form by Mason (1946, 1947).

2. Classical equations of Pockels

Pockels' theory assumes that the electrical field changes both the directions and the magnitudes of the principal axes of the index ellipsoid

$$a_0^2x^2+b_0^2y^2+c_0^2z^2=1, \tag{1}$$

where a_0, b_0, c_0 are the principal velocities. The subscript 0 designates the unstrained state of the crystal.

Transformation of the system of co-ordinates given by

$$\begin{array}{c|ccc} & x' & y' & z' \\ \hline x & \alpha_1 & \alpha_2 & \alpha_3 \\ y & \beta_1 & \beta_2 & \beta_3 \\ z & \gamma_1 & \gamma_2 & \gamma_3 \end{array} \tag{2}$$

changes (1) into

$${}^0a_{11}x^2+{}^0a_{22}y^2+{}^0a_{33}z^2+2{}^0a_{23}yz+2{}^0a_{31}zx+2{}^0a_{12}xy=1. \tag{3}$$

In the case of the piezo-optic effect Pockels assumes that the change of the 'polarization constants' ${}^0a_{ik}$ is a linear function of stresses or strains (Pockels, 1906; Cady, 1946)

$$\left.\begin{aligned} a_{11}-{}^0a_{11}&=p_{11}x_x+p_{12}y_y+p_{13}z_z+p_{14}y_z+p_{15}z_x+p_{16}x_y,\\ a_{22}-{}^0a_{22}&=p_{21}x_x+p_{22}y_y+\dots,\\ &\vdots\\ a_{12}-{}^0a_{12}&=p_{61}x_x+\dots;\end{aligned}\right\} \tag{4}$$

$$\left.\begin{aligned} a_{11}-{}^0a_{11}&=-(\pi_{11}X_x+\pi_{12}Y_y+\pi_{13}Z_z\\ &\qquad+\pi_{14}Y_z+\pi_{15}Z_x+\pi_{16}X_y),\\ a_{22}-{}^0a_{22}&=-(\pi_{21}X_x+\dots),\\ &\vdots\\ a_{12}-{}^0a_{12}&=-(\pi_{61}X_x+\dots).\end{aligned}\right\} \tag{5}$$

Here $x_x, y_y, z_z, y_z, z_x, x_y$ are the strains, and $X_x, Y_y, Z_z, Y_z, Z_x, X_y$ are the stresses. Pockels calls the p_{ik} 'the elasto-optic constants' and the π_{ik} 'piezo-optic constants'.

Similarly, the changes of the polarization constants due to the external electrical field are

$$\left.\begin{aligned} a_{11}-a_0^2&=r_{11}P_x+r_{12}P_y+r_{13}P_z,\\ a_{22}-b_0^2&=r_{21}P_x+r_{22}P_y+r_{23}P_z,\\ a_{33}-c_0^2&=r_{31}P_x+r_{32}P_y+r_{33}P_z,\\ a_{23}&=r_{41}P_x+r_{42}P_y+r_{43}P_z,\\ a_{31}&=r_{51}P_x+r_{52}P_y+r_{53}P_z,\\ a_{12}&=r_{61}P_x+r_{62}P_y+r_{63}P_z.\end{aligned}\right\} \tag{6}$$

Here r_{ik} are the 'electro-optic constants',* and P_x, P_y, P_z are the components of the electric polarization.

3. Tensor form

(1) Let us introduce new symbols adapted to tensor analysis:

$$\left.\begin{aligned} (x, y, z)&\equiv(x^1, x^2, x^3),\\ (x', y', z')&\equiv('x^1, 'x^2, 'x^3),\end{aligned}\right\} \tag{7}$$

$$\begin{pmatrix}\alpha_1 & \alpha_2 & \alpha_3\\ \beta_1 & \beta_2 & \beta_3\\ \gamma_1 & \gamma_2 & \gamma_3\end{pmatrix}\equiv\begin{pmatrix}\alpha_1^1 & \alpha_2^1 & \alpha_3^1\\ \alpha_1^2 & \alpha_2^2 & \alpha_3^2\\ \alpha_1^3 & \alpha_2^3 & \alpha_3^3\end{pmatrix}. \tag{8}$$

From these, $$x^i=\alpha_k^i\,'x^k. \tag{9}$$

Let us confine ourselves in the following to the transformations leaving α_k^i constant in the whole space (orthogonal transformations).

Then $$\frac{\partial x^i}{\partial' x^k}=\alpha_k^i,\quad \frac{\partial' x^k}{\partial x^i}=\alpha_k^i, \tag{10}$$

$$x^i=\frac{\partial x^i}{\partial' x^k}\,'x^k. \tag{11}$$

Identifying $(a_0, b_0, c_0)\equiv(c_1, c_2, c_3)$,

we get from (1) $$\sum_i(c_i x^i)^2=1. \tag{12}$$

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* The more convenient symbols r_{ik} are used instead of Pockels's e_{ik}.

Putting (11) into (12), we have

$$\sum_i (c_i)^2 \frac{\partial x^i}{\partial' x^k} \frac{\partial x^i}{\partial' x^l} {}'x^k\, {}'x^l = 1, \tag{13}$$

whence the equation of the index ellipsoid in the new system of co-ordinates is

$${}'a_{kl}\, {}'x^k\, {}'x^l = 1. \tag{14}$$

Here $${}'a_{kl} = \sum_i (c_i)^2 \frac{\partial x^i}{\partial' x^k} \frac{\partial x^i}{\partial' x^l} = \sum_i (c_i)^2 \alpha^i_k \alpha^i_l; \tag{15}$$

${}'a_{kl}$ is the symmetrical tensor having six independent components.

(2) In what follows let us designate the polarization constants of an unstrained crystal ${}^0a_{ik}$. Then (4) can be written

$$a_{ik} - {}^0a_{ik} = p_{ikmn} S_{mn}, \tag{16}$$

where (Mason, 1946, 1947)

$$\left.\begin{aligned} S_{11} &= S_1 = x_x, & S_{12} &= S_{21} = \tfrac{1}{2}S_6 = \tfrac{1}{2}x_y, \\ S_{22} &= S_2 = y_y, & S_{13} &= S_{31} = \tfrac{1}{2}S_5 = \tfrac{1}{2}z_x, \\ S_{33} &= S_3 = z_z, & S_{23} &= S_{32} = \tfrac{1}{2}S_4 = \tfrac{1}{2}y_z, \end{aligned}\right\} \tag{17}$$

Thus p_{ikmn} are the components of a tensor of fourth order. Transition from double to simple indices is shown in

$$\begin{array}{cccccc} 11 & 22 & 33 & 23 & 31 & 12 \\ \updownarrow & \updownarrow & \updownarrow & \updownarrow & \updownarrow & \updownarrow . \\ 1 & 2 & 3 & 4 & 5 & 6 \end{array} \tag{18}$$

In the general case there are 3^4 components p_{ikmn}. Since the tensors a_{ik}, ${}^0a_{ik}$, S_{ik} are symmetrical, there are two conditions to be satisfied:

$$\left.\begin{aligned} p_{ikmn} &= p_{kimn}, \\ p_{ikmn} &= p_{iknm}. \end{aligned}\right\} \tag{19}$$

Hence there are only 36 independent components, in accordance with Pockels's theory.

Similarly $$a_{ik} - {}^0a_{ik} = -\pi_{ikpq} T_{pq}, \tag{20}$$

where (Mason, 1946, 1947)

$$\left.\begin{aligned} T_{11} &= T_1 = X_x, & T_{23} &= T_4 = Y_z, \\ T_{22} &= T_2 = Y_y, & T_{31} &= T_5 = Z_x, \\ T_{33} &= T_3 = Z_z, & T_{12} &= T_6 = X_y. \end{aligned}\right\} \tag{21}$$

There are also 36 independent components of π_{ikmn}.

From the generalized Hooke's law,

$$S_{ij} = s_{ijkl} T_{kl}, \tag{22}$$

and from (16) and from the comparison with (20) it follows that

$$p_{ikmn} s_{mnpq} = -\pi_{ikpq}. \tag{23}$$

(3) Equation (6) may be written in the more general form

$$a_{ik} - {}^0a_{ik} = r_{ikm} P_m; \tag{24}$$

r_{ikm} are now the components of a tensor of third order. The scheme gives again relations between r_{ik} and r_{ikm}.

It follows from the symmetry of a_{ik} and ${}^0a_{ik}$ that

$$r_{ikm} = r_{kim}. \tag{25}$$

Thus there are only $6 \times 3 = 18$ independent components, in accordance with Pockels.

Choosing $$({}^0a_{ik}) \equiv \begin{pmatrix} a^2 & 0 & 0 \\ 0 & b^2 & 0 \\ 0 & 0 & c^2 \end{pmatrix}$$

we may identify r_{ikm} with Pockels's electro-optical constants.

(4) In the most general case it is possible to strain the crystal both mechanically and electrically. It is to be expected that the resulting change of polarization constants will be given by superposition of both influences. We therefore write

$$a_{ik} - {}^0a_{ik} = p_{ikmn} S_{mn} + r_{ikm} P_m, \tag{26}$$

and $$a_{ik} - {}^0a_{ik} = -\pi_{ikpq} T_{pq} + r_{ikm} P_m. \tag{27}$$

The quantities S_{mn}, T_{pq}, P_m then denote the total values of strains, stresses and polarization.

APPENDIX

(1) Let us choose

$$({}^0a_{ik}) \equiv \begin{pmatrix} (c_1)^2 & 0 & 0 \\ 0 & (c_2)^2 & 0 \\ 0 & 0 & (c_3)^2 \end{pmatrix}.$$

Then $$\begin{aligned} a_{ik} &= {}^0a_{mn} \frac{\partial^0 x^m}{\partial x^i} \frac{\partial^0 x^n}{\partial x^k} \\ &= {}^0a_{mn} \alpha^m_i \alpha^n_k; \end{aligned} \tag{28}$$

and from (8) and

$${}^0a_{ik} = a_{mn} \frac{\partial x^m}{\partial^0 x^i} \frac{\partial x^n}{\partial^0 x^k} = a_{mn} \alpha^i_m \alpha^k_n$$

follow $$\left.\begin{aligned} 0 &= a_{ik} \alpha_i \beta_k, \\ 0 &= a_{ik} \alpha_i \gamma_k, \\ 0 &= a_{ik} \beta_i \gamma_k, \end{aligned}\right\} \tag{29}$$

$$\left.\begin{aligned} (c_1)^2 &= a_{ik} \alpha_i \alpha_k, \\ (c_2)^2 &= a_{ik} \beta_i \beta_k, \\ (c_3)^2 &= a_{ik} \gamma_i \gamma_k. \end{aligned}\right\} \tag{30}$$

Equations (28), (29), (30) contain all Pockels's transformation equations of a_{ik} (see Pockels, 1906).

(2) For vibrating crystals T_{pq} and P_m are periodical functions of time. Hence a_{ik} must also be a periodical function of time, from (26) or (27). This means that the rays falling on the surface of a vibrating crystal at different instants are refracted in different directions.

During a period the tangent lines of the rays emanating from one point on the surface form the surface of a general cone—a phenomenon analogous to Hamilton's internal conical refraction. Of course, the origins of these two phenomena are essentially different. A thorough study of the conditions for this phenomenon and its experimental proof will be the object of our next work. Because there must be a connexion between the form of the 'cone' and the electro-optical constants, the determination of r_{ikm} by means of the observed curves is not excluded.

I wish to thank Prof. Dr V. Petržílka of Charles University, Prague, who has enabled me to work on this problem.

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Acta Cryst. (1951). **4**, 239

Structure Cristalline de l'Acide Nitrique à une Molécule d'Eau

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(*Reçu le* 21 *juillet* 1950)

$HNO_3 . H_2O$ melts at $-37{\cdot}7^{\circ}$ C. The experimental technique adopted for the study of the crystal structure was the same as that used for HNO_3.

The crystals are orthorhombic, symmetry group C_{2v}^{9}–Pna. The unit cell contains 4 molecules and has the dimensions: $a = 5{\cdot}44$, $b = 8{\cdot}69$, $c = 6{\cdot}31$ A.

The structure was determined from the projections of the electron density. All the oxygen and all the hydrogen atoms are involved in hydrogen-bond formation. The hydrogen bonds link the molecules to form infinite two-dimensional aggregates. The configuration of the NO_3 groups and of the oxygen atoms of the water molecules possesses a pseudo-trigonal symmetry.

Introduction

Ce travail fait partie d'une étude entreprise dans le Laboratoire Central des Services Chimiques de l'État sur les phases solides de l'acide nitrique et de quelques composés similaires. N_2O_5 (Grison, Eriks & de Vries, 1950), et HNO_3 (Luzzati, 1951) ont déjà fait l'objet de communications.

Il nous a paru intéressant *a priori* de déterminer la différence entre la structure de l'acide nitrique anhydre et celle de ses hydrates, et d'essayer de comprendre le rôle de l'eau dans les phases solides hydratées.

Pour la partie expérimentale de ce travail, nous avons trouvé une aide précieuse de la part de M. L. Bouttier.

Partie expérimentale

$HNO_3 . H_2O$ cristallise à $-37{,}7^{\circ}$ C. Par la méthode de Bouttier (1949) on obtient des aiguilles formées de blocs monocristallins de petit volume (de 0,1 à 2 mm.^{3}): ces blocs ont en commun l'axe cristallographique **c** et sont décalés les uns par rapport aux autres par des rotations égales approximativement à des multiples de $2\pi/3$ autour de cet axe.

Nous avons enregistré des diagrammes de Weissenberg par rotation autour des trois axes cristallographiques, en isolant chaque fois dans le faisceau de rayons X un seul bloc monocristallin, dont le volume est de 1 à 2 mm.^{3}.

La technique expérimentale et les méthodes de calculs sont identiques à celles employées pour la détermination de la structure de l'acide nitrique anhydre (Luzzati, 1951).

Détermination de la structure

$HNO_3 . H_2O$ cristallise dans le système orthorhombique. Les dimensions de la maille élémentaire sont:

$$a = 5{,}44 \pm 0{,}02, \quad b = 8{,}69 \pm 0{,}02, \quad c = 6{,}31 \pm 0{,}01 \text{ A}.$$

La maille élémentaire contient 4 molécules $HNO_3 . H_2O$.

Les extinctions systématiques conduisent à deux groupes de symétrie possibles: *Pmnc* ou *Pnc*. Les projections de la fonction de Patterson $P(x,y)$ et $P(y,z)$ permettent d'exclure le premier cas. Le groupe de symétrie est donc Pnc-C_{2v}^{9}.

La maille élémentaire n'a pas de centre de symétrie: seule la projection parallèle à **a** possède un centre de symétrie.

Nous avons commencé à étudier la projection $\rho(y,z)$ de la densité électronique, car l'existence d'un centre de symétrie simplifie les calculs. Par l'interprétation de la projection de la fonction de Patterson $P(y,z)$, et par quelques essais, nous avons trouvé les positions approximatives des atomes: par des calculs successifs des signes et des synthèses de Fourier, nous avons amélioré ces positions, jusqu'à obtenir la projection définitive de la densité électronique (Fig. 1). Sur cette projection on ne peut pas déterminer les paramètres y et z des atomes avec précision, car trop d'atomes sont superposés.

Nous avons étudié ensuite la projection $\rho(x,y)$. En partant des coordonnées atomiques y, obtenues sur $\rho(y,z)$, et en tenant compte des indications de la projection $P(x,y)$, nous avons obtenu les positions approximatives des atomes. Quelques calculs des angles des