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The Electro-Optic Effect in Uniaxial Crystals of the Type XH_2PO_4 . I. Theoretical

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When voltage is put across a crystal of the type XH_2PO_4 , the index ellipsoid in the crystal is rotated and the length of the axes changes. Two electro-optic coefficients are necessary to describe the effect in the most general plate of the crystal. The necessity for two coefficients is shown from consideration of the crystal symmetry. The behavior of Z-cut and X-cut plates are treated in detail. For Z-cut plates with the voltage in the Z direction the crystal becomes biaxial with the plane of the optic axes at 45° to the X and Y crystallographic axis. The retardation along the normal to the plate is directly proportional to the voltage and independent of the thickness. The characteristics of the polarization interference pattern for excited X and Z plates are discussed.

INTRODUCTION

THERE are many places where an electric light valve or shutter has useful applications. One of the most obvious forms of light valve is the Kerr cell. This cell contains a liquid between a pair of parallel plate electrodes. When an electric field is applied, the liquid becomes birefringent. If the cell is placed between crossed polarizers, light will not pass through the combination until voltage is applied. There are many difficulties associated with the ordinary liquid Kerr cell. This liquid cell uses nitrobenzene which has a high Kerr constant only when it is extremely pure. The operation of the cell tends to decompose the material and the most successful cells have been those in which the nitrobenzene is continuously redistilled as the cell is used. In addition, the liquid has a disagreeable odor and is intensely poisonous.

A solid electro-optic shutter avoids many of these difficulties. As a result, such a device becomes a practical solution for many different problems and should be a useful scientific tool.

The Kerr effect in most solids is extremely small. In certain crystals, however, there is a large electro-optic effect which requires voltage no higher than those required in the liquid cell. This effect varies with first power of the electric field rather than with the square of the field as does the normal Kerr effect.

During the last few years several papers^{1,2,3,4} have appeared discussing the electro-optic effect in tetragonal scalenohedral crystals of the type XH_2PO_4 . Now that some of these crystals such as $NH_4H_2PO_4$ or ADP ⁵ are available as light valves, it seems appropriate to give a more complete treatment of the useful effect than is available in any of these papers.

THEORETICAL

The birefringence of a crystal can be described in terms of its index ellipsoid. The index ellipsoid has axes which are equal to the three crystal indices. If a plane is passed through the center of this ellipsoid at right angles to the direction in which a ray of light is going, it will cut the ellipsoid in an ellipse whose major and minor axes are the two indices associated with that particular direction in the crystal. In the case of a biaxial crystal the equation for this ellipsoid can be written

$$a^2x^2 + b^2y^2 + c^2z^2 = 1 \quad (1)$$

where a , b and c are the three reciprocal indices of

¹ G. D. Gottschall, J. Soc. Mot. Pict. Eng. 51, 13 (1948).

² Hans Jaffe, Phys. Rev. 73, 95 (1948).

³ B. Zwicker and P. Scherrer, Helv. Phys. Acta 16, 214 (1943).

⁴ B. Zwicker and P. Scherrer, Helv. Phys. Acta 17, 346 (1944).

⁵ This crystal is grown under the trademark "PN" by the Brush Development Company, 3405 Perkins Avenue, Cleveland, Ohio.

refraction. In a uniaxial crystal two of the coefficients become equal and the equation reduces to

$$o^2(x^2 + y^2) + e^2z^2 = 1 \quad (2)$$

where o is the ordinary reciprocal index and e the extraordinary reciprocal index. The electro-optic effect in crystals is a change in crystalline birefringence which occurs when a crystal is placed in an electric field. The first general treatment of the effect was given by Pockels.^{6,7} He showed the number of constants to be expected in the different crystal classes and made experimental measurements in the case of quartz, NaClO_3 and rochelle salts. This change can be described in terms of a change of the orientation and the dimensions of the index ellipsoid. The numerical constants involved in this change can be considered as small corrections to be applied to the index ellipsoid constants. In order to write them it is necessary to put the equation of the index ellipsoid in its most general form. Crystallographers commonly refer the faces of a crystal to a cartesian coordinate system. The directions of these crystallographic axes are prescribed for each crystal class. Instead of referring the ellipsoid to its own principal axes it is referred instead to these crystallographic symmetry axes. The equation of the ellipsoid then becomes

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

The new constants, a_{11} , a_{12} , etc., are called the polarization constants. If the a 's are all known, it is possible

to find the orientation of the axes of the ellipsoid with respect to the crystallographic axes.

The direction cosines connecting the two sets of axes may be described in the matrix

$$\begin{array}{c|ccc} & X' & Y' & Z' \\ \hline X & \alpha_1 & \alpha_2 & \alpha_3 \\ Y & \beta_1 & \beta_2 & \beta_3 \\ Z & \gamma_1 & \gamma_2 & \gamma_3 \end{array} \quad (4)$$

where the primed axes are the crystallographic axes, the unprimed axes are the axes of the index ellipsoid, and α_i is the cosine of the angle between x and x' , etc. When an electric field is applied, the polarization constants can be written

$$\begin{aligned} a_{11} - a_0^2 &= r_{11}E_x + r_{12}E_y + r_{13}E_z \\ a_{22} - b_0^2 &= r_{21}E_x + r_{22}E_y + r_{23}E_z \\ a_{33} - c_0^2 &= r_{31}E_x + r_{32}E_y + r_{33}E_z \\ a_{23} &= r_{41}E_x + r_{42}E_y + r_{43}E_z \\ a_{31} &= r_{51}E_x + r_{52}E_y + r_{53}E_z \\ a_{12} &= r_{61}E_x + r_{62}E_y + r_{63}E_z \end{aligned} \quad (5)$$

where the r_{ij} are the electro-optic coefficients and E_x , E_y , E_z are the components of the field along the three crystallographic axes. These equations have been written for a crystal in which the crystallographic axes coincide with the polarization axes. They differ from the equations of Pockels by referring to the field instead of the electrical polarization. The constants r_{ij} are thus related to Pockels' constants e_{ij} by the equation

$$r_{ij} = \frac{K_j - 1}{4\pi} e_{ij}$$

where K_j is the dielectric constant in the direction in which the field is applied. The symbol r_{ij} is used in accordance with Cady's⁸ suggestion that the Mueller⁹ convention be used. If no field were applied the constants would reduce to the three coefficients given in Eq. (1).

The most striking characteristic of a crystal is its symmetry. This symmetry is described by a set of operations sometimes called "covering operations" which can be performed on the crystal without altering its appearance or physical behavior. For example, if a cube is rotated 90° about an axis normal to any face the cube will not appear to have been moved. If the cube is isotropic with respect to all its other physical properties, the operations which leave its external appearance unchanged will be the characteristic symmetry operations. If the cube is made of wood which has a grain perpendicular to one face, the tensile strength would not be the same in the case of the 90° rotation about an axis parallel to this face. In general the physical characteristics of a crystal possess the same or higher symmetry as the symmetry of its form. This is.

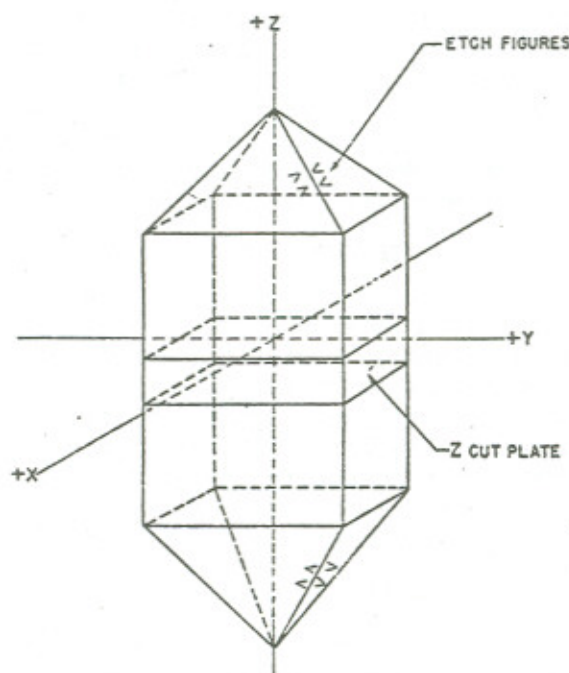


FIG. 1. Sketch of an $\text{NH}_4\text{H}_2\text{PO}_4$ crystal with its crystallographic axes labelled.

⁶ F. Pockels, *Abhandlungen der Gesellschaft der Wissenschaften zu Göttingen*, 39, 1 (1893).

⁷ F. Pockels, *Lehrbuch der Kristalloptik* (Leipzig, 1906).

⁸ W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946).

⁹ H. Mueller, *Phys. Rev.* 58, 805-811 (1940).

of course, true only for an ideal crystal of any material.

Since many readers are perhaps rusty in their crystallography, it seems apropos to carry through the actual reduction of the constants in Eq. (4). In Fig. 1 is a sketch of an $\text{NH}_4\text{H}_2\text{PO}_4$ crystal with its crystallographic axes labeled. At first glance the crystal appears to possess a center of symmetry, i.e., it looks as though every point in the crystal could be reflected through the center to an equal distance on the other side and the resulting crystal would be identical. This turns out not to be the case. It is most simply demonstrated by etch figures. If one of the end faces is slightly moistened and dried, a series of little pits appear. These pits are triangular in shape and are oppositely oriented on opposite faces. There are two main symmetry operations which can be performed on the crystal. The first is a rotation through $\pi/2$ about the z axis followed by an inversion through the center. This, of course, does not mean that the crystal has a center of symmetry because the inversion must always be preceded by the $\pi/2$ rotation about z . The second operation is a rotation of π about either the x or y axis. Crystals whose characteristics are unchanged after these operations are said to belong in the class V_d or $42m$. If these operations are now performed on Eq. (5) the constants must remain unchanged. The operation of rotating through an angle π about the x axis leaves x unchanged and changes y to $-y$ and z to $-z$. The field E_x is unchanged whereas E_y becomes $-E_y$ and E_z becomes $-E_z$. When these substitutions are made in Eq. (5) and Eq. (3) the coefficients a_{11} through a_{12} must change sign in such a way that Eq. (3) is unchanged. The effect on the electro-optic coefficients may be simply shown by writing Eq. (5) in matrix form. For further aid the multiplier of the a_{ij} 's in Eq. (3) is placed in the a_{ij} vector.

$$\begin{bmatrix} a_{11}(x^2) \\ a_{22}(y^2) \\ a_{33}(z^2) \\ a_{23}(yz) \\ a_{31}(xz) \\ a_{12}(xy) \end{bmatrix} = \begin{bmatrix} r_{11} & r_{12} & r_{13} \\ r_{21} & r_{22} & r_{23} \\ r_{31} & r_{32} & r_{33} \\ r_{41} & r_{42} & r_{43} \\ r_{51} & r_{52} & r_{53} \\ r_{61} & r_{62} & r_{63} \end{bmatrix} \begin{bmatrix} E_x(x) \\ E_y(y) \\ E_z(z) \end{bmatrix}$$

If the substitutions $x \rightarrow x$, $y \rightarrow -y$, $z \rightarrow -z$ are made in this matrix equation, it is apparent that a_{11} , a_{22} and a_{33} will not change signs. Since E_y and E_z do change sign, this means that all the r_{ij} 's in the first three rows are zero with the exception of r_{11} , r_{21} , and r_{31} . The operation of rotating the crystal through an angle π about the y axis changes the sign of x and z but leaves y unchanged. This operation makes these the remaining three coefficients in the first three rows vanish. The final array of elements in the matrix becomes

$$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ r_{41} & 0 & 0 \\ 0 & r_{41} & 0 \\ 0 & 0 & r_{63} \end{bmatrix} \quad (7)$$

The constants a_{ij} thus reduce to

$$\begin{aligned} a_{11} &= a_{22} = o^2 & a_{23} &= r_{41} E_x \\ a_{33} &= e^2 & a_{31} &= r_{41} E_y \\ & & a_{12} &= r_{63} E_z. \end{aligned} \quad (8)$$

FIELD IN Z DIRECTION

The crystal section which is most useful as a shutter is the Z-cut or basal plate with field applied in the Z direction and the light traveling in the same direction. For light thus parallel to the optic axis the plate has no retardation and appears isotropic. The analysis below shows that in this direction the electrically induced retardation is also highest for a given voltage.

For this case the fields E_x and E_y become zero and the only non-zero coefficients are thus a_{11} , a_{22} , a_{33} and a_{12} .

These values can be inserted into Eq. (3) to give

$$e^2 z^2 + o^2 (x^2 + y^2) + 2r_{63} E_z xy = 1. \quad (9)$$

From this equation it is apparent that the Z and Z' axes coincide. This shows that $\gamma_1 = \gamma_2 = \alpha_3 = \beta_3 = 0$ and $\gamma_3 = 1$.

To find the remaining cosines and hence the angle by which the ellipsoid is rotated, Eq. (9) is transformed to the coordinate system which has its axes along the ellipsoid axes. This equation connecting the two sets can be written down directly from the matrix (4) which represents the direction cosines between them.

$$\begin{aligned} x' &= \alpha_1 x + \beta_1 y \\ y' &= \alpha_2 x + \beta_2 y. \end{aligned}$$

Since the rotation is in a plane

$$-\alpha_2 = \beta_1; \quad \alpha_1 = \beta_2.$$

These equations can now be put in Eq. (9) and the cross terms set equal to zero so that the axes will coincide with the ellipsoid axes.

$$2r_{63}C(\alpha_1^2 - \alpha_2^2)xy = 0. \quad (10)$$

The expression for the angle then becomes

$$\cos 2\alpha = 0 \quad \alpha = \pm 45^\circ. \quad (11)$$

Since this rotation is independent of the field it is possible at this stage of the analysis to say what will be the appearance between polarizers of a z -cut slab of PN when a field is applied in the z direction. The crystal becomes biaxial and the characteristic uniaxial fringe pattern of circles is replaced by a series of ovals. The long axis of the oval lies at 45° to the crystallographic axis. The length of the long axes of the ovals in the pattern will change as the field is changed. The direction, however, remains constant. To find how the axis length changes with the field it is necessary to compute the actual value of the crystal indices.

It is necessary now to find the new reciprocal indices, a , b and c . These are related to the polarization constants by formulas which can be written directly

from Eq. (3) and the matrix (4)

$$\begin{aligned} a^2 &= a_{11}\alpha_1^2 + a_{22}\alpha_2^2 + a_{33}\alpha_3^2 + 2a_{23}\alpha_2\alpha_3 \\ &\quad + 2a_{31}\alpha_3\alpha_1 + 2a_{12}\alpha_1\alpha_2 \\ b^2 &= a_{11}\beta_1^2 + a_{22}\beta_2^2 + a_{33}\beta_3^2 + 2a_{23}\beta_2\beta_3 \\ &\quad + 2a_{31}\beta_3\beta_1 + 2a_{12}\beta_1\beta_2 \\ c^2 &= a_{11}\gamma_1^2 + a_{22}\gamma_2^2 + a_{33}\gamma_3^2 + 2a_{23}\gamma_2\gamma_3 \\ &\quad + 2a_{31}\gamma_3\gamma_1 + 2a_{12}\gamma_1\gamma_2 \end{aligned} \quad (12)$$

Since the only rotation is ϕ_z in the xy plane,

$$\begin{aligned} a^2 &= a_{11}\cos^2\phi + a_{22}\sin^2\phi + 2a_{12}\sin\phi\cos\phi \\ &= o^2\cos^2\phi + o^2\sin^2\phi + 2r_{63}E_z\sin\phi\cos\phi \\ b^2 &= a_{11}\sin^2\phi + a_{22}\cos^2\phi - 2a_{12}\sin\phi\cos\phi \\ &= o^2\sin^2\phi + o^2\cos^2\phi - 2r_{63}E_z\sin\phi\cos\phi \\ c^2 &= a_{33} = e^2 \end{aligned} \quad (13)$$

since $\phi_z = -45^\circ$

$$\begin{aligned} a^2 &= o^2 - 2r_{63}E_z \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} = o^2 - r_{63}E_z \\ b^2 &= o^2 + 2r_{63}E_z \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} = o^2 + r_{63}E_z \end{aligned} \quad (14)$$

One can write

$$\begin{aligned} c^2 &= e^2 = \frac{1}{\epsilon^2} = \frac{1}{\alpha^2} \\ a^2 &= \frac{1}{\gamma^2} \quad b^2 = \frac{1}{\beta^2} \end{aligned} \quad (15)$$

Since the only field is in the Z direction, E_z can be replaced by V/d when V is the applied voltage and d is the plate thickness. The value of r_{63} then includes the dielectric constant.

The retardation which will appear along the normal to the basal section after the voltage is applied can be written:

$$\Gamma = \frac{d}{\lambda} \left(\frac{1}{a} - \frac{1}{b} \right). \quad (16)$$

This can be rewritten:

$$\begin{aligned} \Gamma &= \frac{d}{\lambda} \frac{a^2 - b^2}{(a+b)ab} \\ &= \frac{d}{2\lambda} (a^2 - b^2) \omega^3. \end{aligned} \quad (17)$$

If Eq. (13) is inserted in this final equation, one gets the equation:

$$\Gamma = \frac{r_{63}V\omega^3}{\lambda} = pV. \quad (18)$$

This shows that in this particular cut of crystal the retardation along the normal is a function of the voltage rather than the field strength. In other words, the

retardation for a given voltage is independent of the thickness of the plate.

The value for r_{63} becomes:

$$r_{63} = \lambda\Gamma/\omega^3V \quad (19)$$

The value of this constant has been determined for $\text{NH}_4\text{H}_2\text{PO}_4$ or "PN" under a variety of conditions by Dr. Hans Jaffe of The Brush Development Company.

The value of the new indices can now be calculated from Eq. (13):

$$\gamma = \frac{1}{a} = \frac{1}{\left(o^2 - \frac{\lambda\Gamma}{\omega^3d} \right)^{1/2}} \quad (20)$$

or

$$\gamma = \omega + \frac{\lambda\Gamma}{2d} \quad (21)$$

Similarly,

$$\beta = \omega - \frac{\lambda\Gamma}{2d} \quad (22)$$

One of the striking things about these two index values is the small change which occurs with the application of voltage. A half-wave retardation requires nearly 10,000 volts for PN and this retardation is the result of index changes of only a few parts in a million for plate thicknesses of the order of a centimeter.

Although this value seems small, it is larger in ADP than in other crystals which have been previously studied. The coefficient r_{63} in ADP is 8.2×10^{-7} whereas the largest coefficients for quartz and rochelle salts are $r_{11}(\text{quartz}) = 4.67 \times 10^{-8}$ cm/kv and $r_{32}(\text{Rochelle}) = -36.0 \times 10^{-8}$ cm/kv.

When voltage is applied to the crystal it becomes biaxial with an axial angle Ω . The retardation along the normal which was expressed in Eq. (14) can be written in terms of this axial angle. The expression for the retardation as a function of angle of incidence in a Z-cut slab of biaxial crystal can be written:

$$\frac{\Gamma}{kd} = \sin\theta_1 \sin\theta_2 / \cos r \quad (23)$$

where θ_1 and θ_2 are the angles made by the ray with the two axes; r is the angle of incidence of the ray; d is the thickness of the slab, k is a constant. When $r=0$, this equation becomes:

$$\Gamma = kd \sin^2\Omega \quad (24)$$

where Ω is the angle between the optic axes and the Z axis. In combination with Eq. (14) this becomes:

$$kd \sin^2\Omega = pV \quad (25)$$

where p is a constant and V is the voltage across the crystal plate.

It is apparent from these equations that the value of the axial angle is inversely proportional to the square

root of the thickness and directly proportional to the square root of the voltage.

FIELD IN X OR Y DIRECTIONS

Since the equations are symmetrical, the effect produced by a field in the X direction is the same as a field in the Y direction. Accordingly, this section will be limited to a discussion of the effect of a field along X . In this case the only non-zero coefficients are a_{11} , a_{22} , a_{32} and a_{23} . These values can be inserted into Eq. (3) to give

$$o^2(x^2 + y^2) + e^2z^2 + 2r_{41}E_x yz = 1. \quad (26)$$

From this equation it is apparent that the X and X' axes coincide and the only rotation is in the yz plane. From an analysis similar to that used in the case of the basal section it can be shown that the axes are rotated through an angle

$$\tan 2\xi = -\frac{2r_{41}E_x}{e^2 - o^2}. \quad (27)$$

This differs from the previous case in that the angle is dependent on the field and that it is quite small. Its size can, of course, only be stated with a knowledge of r_{41} . This coefficient will be discussed in a later paper. For $\text{NH}_4\text{H}_2\text{PO}_4$ it is of such a size that the rotation is only a few minutes.

The reciprocal indices can be found from Eq. (11) which can be rewritten

$$\begin{aligned} b^2 &= o^2 \\ a^2 &= o^2 \cos^2 \xi + e^2 \sin^2 \xi + 2r_{41}E_x \cos \xi \sin \xi \\ c^2 &= o^2 \sin^2 \xi + e^2 \cos^2 \xi - 2r_{41}E_x \cos \xi \sin \xi. \end{aligned} \quad (28)$$

As in the first case this represents a biaxial crystal. To go from Eq. (12) to Eq. (28) it is necessary to interchange a and b . This is because b is by definition intermediate between a and c . If the field had been applied in the Y direction, no such interchange would have been necessary. Since the axial plane is always at right angles to b and since the direction of b is independent of the field, the plane of the axis is again independent of the field as in the Z case. By inspection of Eq. (26) it is apparent that the section of the ellipsoid perpendicular to Z is a circle, and the position of this circular section is independent of the field. This indicates that one of the optic axes of the crystal coincides with the original optic axis and is independent of the field. The other axis moves from this first axis as the field is applied. The axial angle which is the angle between the ellipsoid axis and the optic axis is exactly ξ . This can also be checked by using the equation

$$\sin^2 \Omega = b^2 - c^2 / a^2 - c^2. \quad (29)$$

Observation in the Z direction thus does not give a useful effect when field is applied in the X direction. Furthermore, the axial angle of the new biaxial crystal

is only a few minutes as opposed to several degrees which is obtained when the field is applied in the Z direction.

In the Z -cut case the retardation was zero in the Z direction until the field was applied in this direction. In the X -cut case the retardation in the X direction is already large. For practical use the change in retardation for a reasonable voltage must be large. The retardation without field is:

$$\Gamma = (e - o)d/\lambda. \quad (30)$$

The change in retardation may be calculated to be

$$\Delta\Gamma = \frac{1}{2}r_{41}^2 \frac{V^2 \omega^2 \epsilon^2 (\omega^2 + e^2)}{d (\omega^2 - e^2)}. \quad (31)$$

This turns out to be of the order of 10^{-3} for a PN crystal 1-cm thick with 25 kv applied in the x direction. Even in an isotropic medium such low induced birefringence would not be particularly useful.

CONCLUSIONS

The conclusions of these analyses can be summarized as follows:

For the field in the Z direction:

1. Uniaxial crystals of the form $X \text{ H}_2\text{PO}_4$ become biaxial.
2. The plane of the optic axes is independent of the magnitude of the voltage and is inclined at 45° to the crystallographic axis.
3. For rays parallel to the field and at a given wavelength the retardation through the plate depends only on the voltage and is independent of the plate thickness.

For a field in the X direction:

4. The crystal again becomes biaxial.
5. The plane of the axes is independent of the magnitude of the voltage and is perpendicular to the X axis.
6. The retardation change through the plate for rays parallel to the field depends on the square of the applied voltage and the inverse first power of the plate thickness.
7. If the r_{41} and r_{63} coefficients are of the same order of magnitude a 1-cm plate of ADP gives a retardation change of the order of 10^{-3} for 25 kv applied voltage.

The problem of measuring the coefficients and of determining experimentally the properties of the specific crystal ADP will be discussed in the next paper.

In conclusion the author wishes to express appreciation to Miss Elizabeth Weichel of this laboratory for her help during the preparation of this paper.

