PIEZO-ROTATORY COEFFICIENTS AND STRESS-INDUCED OPTICAL ACTIVITY

BY G. S. RANGANATH AND S. RAMASESHAN, F.A.SC.
(*Materials Science Division, National Aeronautical Laboratory, Bangalore-17, India*)

Received April 15 1969

ABSTRACT

This paper reports the methods of obtaining the components of the fourth rank axial piezo-rotatory tensor in different crystal classes. The methods of recovering the two piezo-rotatory coefficients R_{11} and R_{12} of isotropic optically active glasses, the three coefficients R_{11}, R_{12} and R_{44} of cubic crystals belonging to the point group 432 and the four coefficients R_{11}, R_{12}, R_{13} and R_{44} of crystals like $NaClO_3$ (point group 23) have been described in detail. The non-centrosymmetric class $\bar{4}3$ m. which is not optically active has one non-vanishing piezo-rotatory coefficient, showing that stress induces optical activity in it. A method of retrieving this coefficient has also been described. In most of the other point groups, the difficulty of measuring optical activity in directions other than those of the optic axes severely limits the number of coefficients that can be extracted. The paper also touches upon some interesting methods of obtaining the components of the gyration tensor in non-enantiomorphic optically active crystals.

1. INTRODUCTION

THE present authors have, of late, been investigating the effect of stress on the optical rotatory power of crystals (Ramaseshan and Ranganath, 1969). Optical activity can be represented by the second rank symmetric axial gyration tensor (g) while stress (X) and strain (x) by second rank symmetric polar tensors. The effect of stress or strain on the optical rotatory power would therefore be represented, in a first-order theory, by fourth rank axial tensors; (R) being the stress-rotatory tensor and (S) the strain-rotatory tensor. The number of independent non-vanishing coefficients and the nature of the piezo-rotatory matrix for the various point groups have also been worked out by the present authors (Ranganath and Ramaseshan, 1969 *a*).

This paper mainly concerns itself with the methods of recovering the piezo-rotatory coefficients for some of the point groups. The problem in this case is different from that in other stress-optic phenomena where the directions of stress and light propagation may be chosen arbitrarily. In the case of piezo-rotatory effects it is very difficult to measure the rotatory power or its change along directions other than that of the optic axis. This constraint limits the number of coefficients that may be recovered and also demands special strategy for making the measurements.

2. THE GYRATION, PIEZO-ROTATORY AND PIEZO-OPTIC TENSORS

In a crystal if ρ is the optical rotatory power along any direction (s_1, s_2, s_3)

$$\rho = g_{ij}s_i s_j$$

i.e.,

$$\rho = g_{11}s_1^2 + g_{22}s_2^2 + g_{33}s_3^2 + 2g_{12}s_1s_2 + 2g_{23}s_2s_3 + 2g_{31}s_3s_1$$

and when referred to the principal axes the optical rotation and the tensor surface are given by

$$\rho = g_{11}s_1^2 + g_{22}s_2^2 + g_{33}s_3^2$$

and

$$g_{11}x^2 + g_{22}y^2 + g_{33}z^2 = 1$$

where there is no *a priori* restriction on the signs of g_{ij}. The matrices representing the gyration tensor for the various non-centrosymmetric point groups are given in Table I. It may be noted that of the 21 non-centrosymmetric point groups only 15 are optically active (Tables I and II) and 6 are optically inactive (Table III). Further just as a liquid may show optical activity an isotropic solid may also exhibit optical activity. These are usually glasses or stereo-specific plastics.

In the first-order phenomenological theory of piezo-rotation, changes in g_{ij}, *i.e.*, $\triangle g_{ij}$ are assumed to be linear functions of stress X_{kl} or strain x_{kl}

i.e.,

$$\triangle g_{ij} = -R_{ijkl}X_{kl}$$

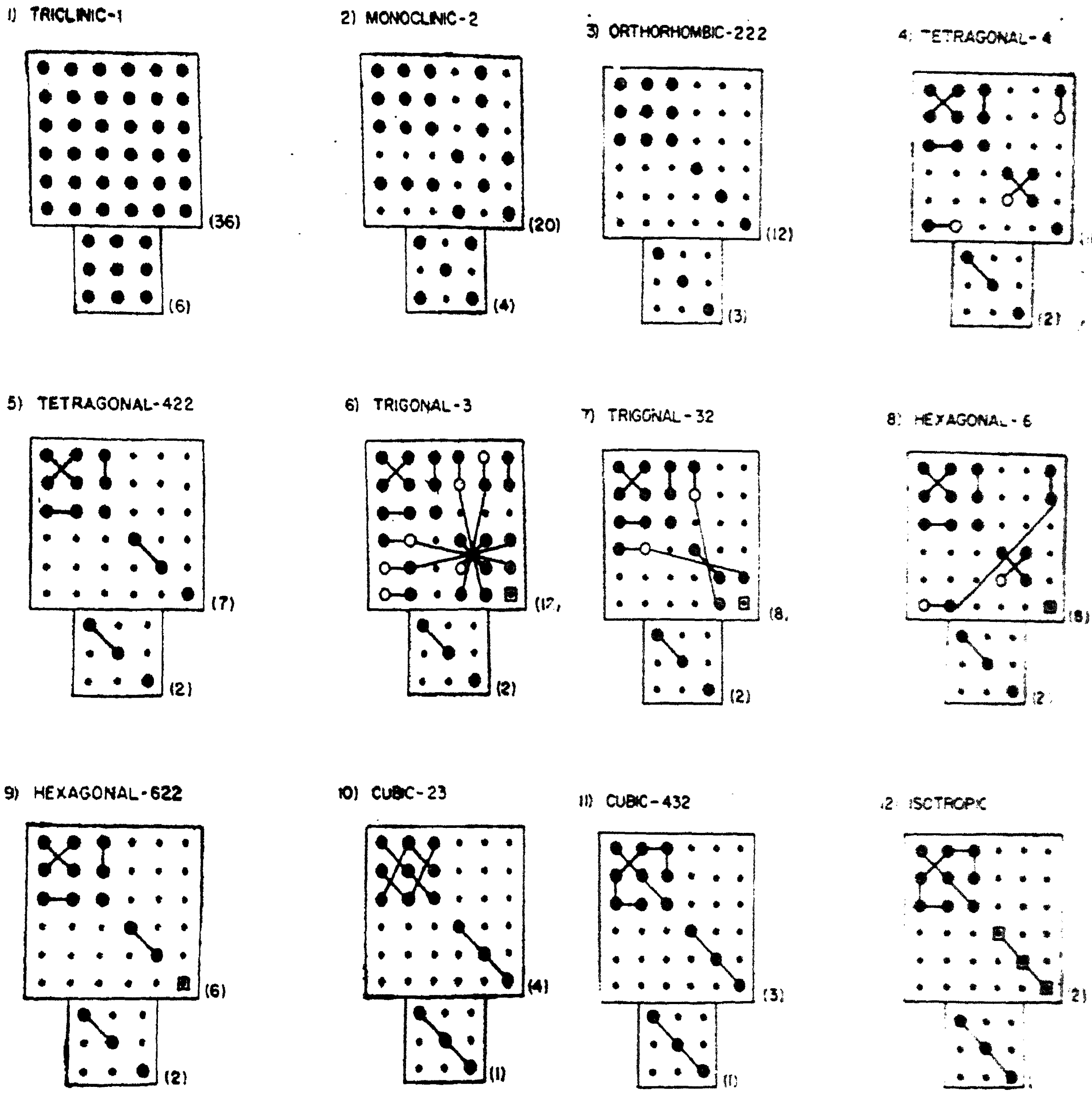
or

$$\triangle g_{ij} = S_{ijkl}x_{kl}.$$

When the non-vanishing coefficients are evaluated (Ramaseshan and Ranganath, 1969) one finds that

TABLE I

The form of the piezo-rotatory (R) and piezo-optic (q) matrices. and the gyration matrix (g) in the enantiomorphic optically active point groups. (R) and (q) have the same form



KEY TO TABLES I, II AND III

⊙—Zero component.

●—Non-zero component.

●—● Equal components of same sign

O—● Equal components of opposite sign

In (R) or (q) matrices

⊙—A component equal to +2 times that to which it is joined

⊙—A component equal to −2 times that to which it is joined.

⊡ $= (R_{11} - R_{12})$ or $(q_{11} - q_{12})$.

In (S) or (p) matrices

⊙—A component equal to that to which it is joined.

⊙—A component equal to the minus of that to which it is joined.

⊡ $= 1/2\,(S_{11} - S_{12})$ or $1/2\,(p_{11} - p_{12})$.

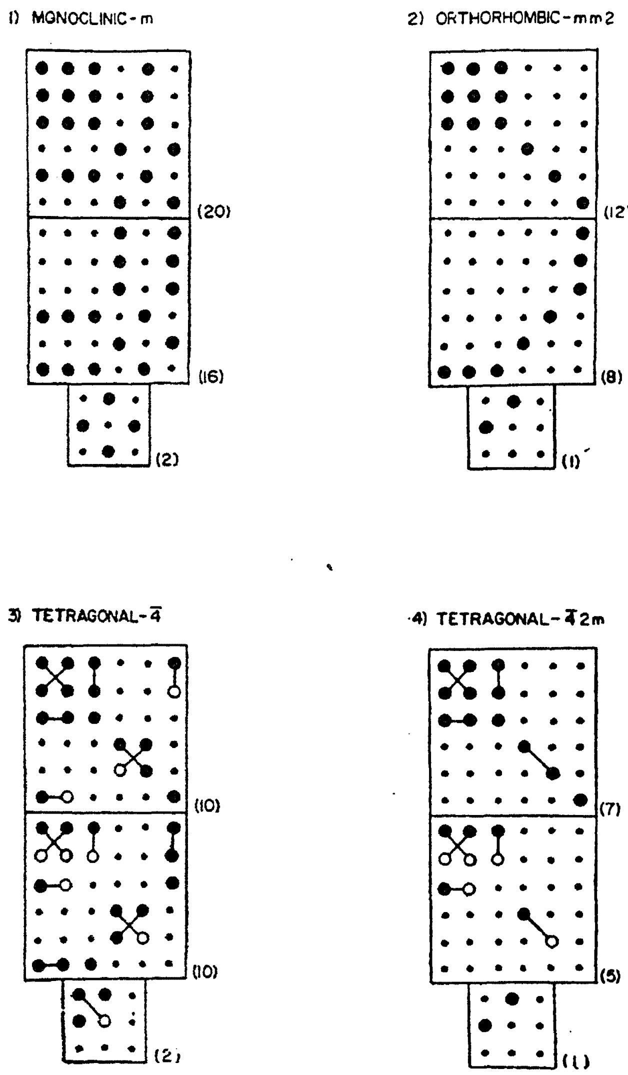
(*a*) piezo-rotatory coefficients exist only for the 21 non-centrosymmetric point groups;

(*b*) in the 11 enantiomorphic optically active point groups the piezo-rotatory and piezo-optic matrices have the same form (Table I);

(*c*) in the 4 non-enantiomorphic optically active point groups the photo-elastic and piezo-rotatory matrices are of different forms (Table II);

TABLE II

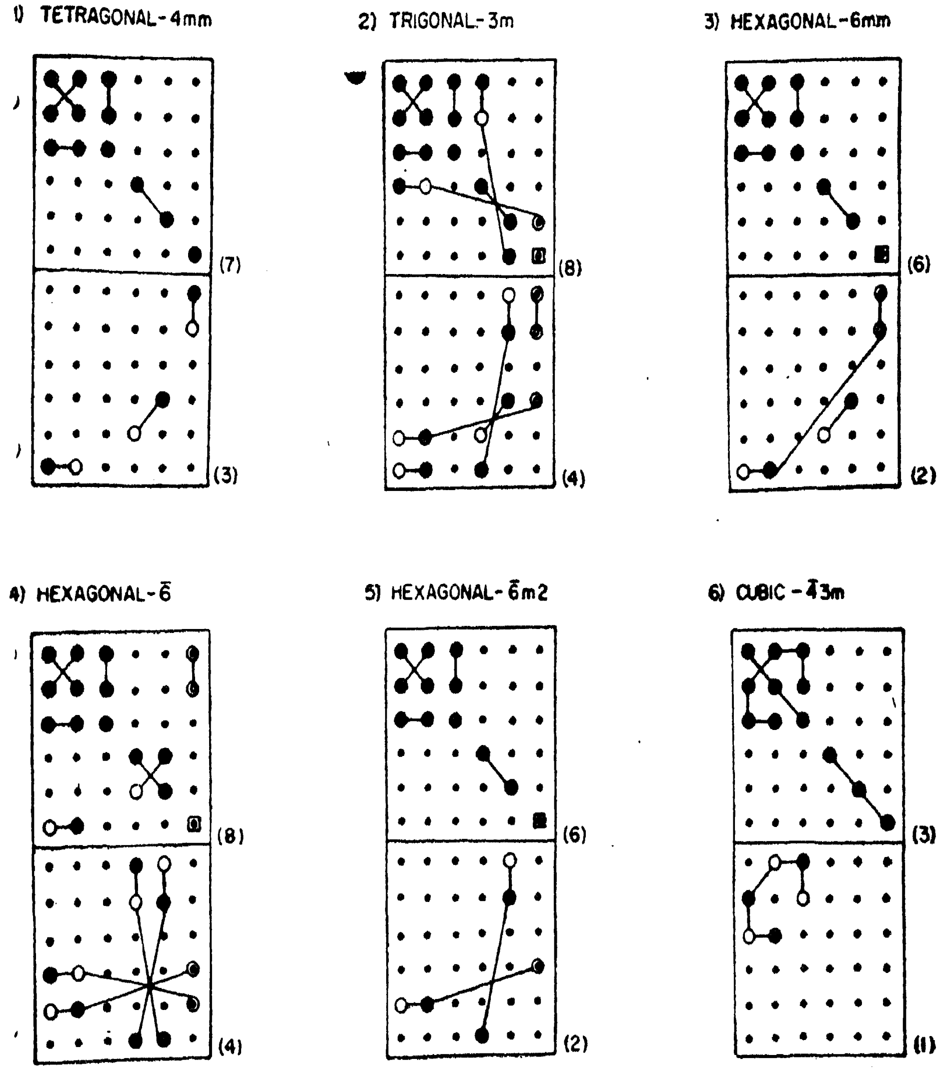
The piezo-optic (q), *piezo-rotatory* (R) *and the gyration matrix* (g) *of the non-enantiomorphic optically active point groups*



(*d*) in the remaining 6 non-enantiomorphic, optically inactive classes the piezo-rotatory coefficients do not vanish, *i.e.*, stress actually induces optical activity in these crystals. The piezo-rotatory and piezo-optic matrices are given in Table III.

TABLE III

The piezo-optic (q) *and the piezo-rotatory* (R) *matrices of the non-enantiomorphic non-optically active point groups* (i.e., $g_{ij} = 0$)



It has been mentioned that optical activity may be most conveniently measured along the optic axes. In the uniaxial crystals of trigonal, tetragonal and haxagonal classes the optic axis coincides with the 3-fold, 4-fold and 6-fold axes respectively. In biaxial crystals the optic axial angle is given by

$$\sin^2 V = \frac{a_2 - a_1}{a_3 - a_1} \qquad a_1 > a_2 > a_3$$

where

$$a_1 = \frac{1}{n_1^2}, \quad a_2 = \frac{1}{n_2^2}, \quad a_3 = \frac{1}{n_3^2};$$

n_1, n_2, n_3 being the principal refractive indices. The optic axes lie in the plane containing n_1 and n_3.

We shall now summarise the effect of stress on the optical ellipsoid (Ramaseshan and Vedam, 1958; Ramachandran and Ramaseshan, 1961).

When a crystal is uniaxially stressed along a 3-fold, 4-fold or 6-fold axis of symmetry, the crystal becomes or remains uniaxial with the optic axis along the stress direction. But if the same uniaxial stress acts along a 2-fold, or a 1-fold axis, the crystal becomes biaxial even if it be a cubic crystal. However, in the latter case the optic axial angle is dependent only on the stress direction and is independent of the magnitude of the stress. In the case of uniaxial and biaxial crystals it also depends on the magnitude of stress.

When a crystal is hydrostatically stressed the symmetry does not alter. An isotropic crystal remains isotropic, a uniaxial crystal remains uniaxial. In the case of biaxial crystals, however, although the symmetry remains the same, there may be a change in the position of the optic axes as the changes in the refractive indices for the 3 principal axes may be different.

3. ISOTROPIC SUBSTANCES

The photoelastic and the peizo-rotatory matrices (which have the same form) are given in Table I (No. 12). There are only two independent peizo-rotatory coefficients namely R_{11} and R_{12}. For a unidirectional stress X, the deformations of the index ellipsoid are given by

$$\triangle a_{11} = -q_{11}X, \quad \triangle a_{22} = \triangle a_{33} = -q_{12}X, \quad \underset{i \neq j}{\triangle a_{ij}} = 0.$$

The solid therefore becomes uniaxial with its optic axis coinciding with the stress direction. Rotatory power along this direction could be measured if suitable holes are provided in the stress apparatus for sending the light along the direction of stress. The deformations in the gyration surface are given by

$$\triangle g_{11} = -R_{11}X, \quad \triangle g_{22} = \triangle g_{33} = -R_{12}X, \quad \underset{i \neq j}{\triangle g_{ij}} = 0.$$

Hence, if $\triangle \rho$ is the change in the optical rotation along the stress direction

$$\triangle \rho = -R_{11}X \quad \text{or} \quad R_{11} = -\frac{\triangle \rho}{X}. \tag{1}$$

For an hydrostatic stress X_h

$$\Delta a_{11} = \Delta a_{22} = \Delta a_{33} = -(q_{11} + 2q_{12}) X_h, \quad \underset{i \neq j}{\Delta a_{ij}} = 0$$

and therefore the substance remains optically isotropic. The changes in the gyration tensor may be described by

$$\Delta g_{11} = \Delta g_{22} = \Delta g_{33} = -(R_{11} + 2R_{12}) X_h, \quad \underset{i \neq j}{\Delta g_{ij}} = 0.$$

Therefore, if we measure the change $\Delta \rho_h$ in rotatory power along any direction

$$\Delta \rho_h = -(R_{11} + 2R_{12}) X_h. \tag{2}$$

From (1) and (2)

$$R_{12} = \frac{1}{2}\left(\frac{\Delta \rho}{X} - \frac{\Delta \rho_h}{X_h}\right).$$

Thus all the components of the piezo-rotation tensor may be determined by measuring changes in the rotatory power for a uniaxial stress along the stress direction and for an hydrostatic stress in any direction.

4. Optically Active Cubic Crystals

(*a*) 432 *Class:*

This is the simplest of the cubic classes wherein all the piezo-rotatory coefficients can be recovered. Unfortunately no crystal belonging to this class has been reported in the literature. The piezo-rotatory and the photoelastic tensors have the same form (Table I, No. 11). There are 3 independent piezo-rotatory coefficients R_{11}, R_{12} and R_{44}.

Application of a stress X_{100} along the cube axis (100) deforms the index ellipsoid and the gyration surface in the following manner:

$$\Delta a_{11} = -q_{11}X_{100}, \quad \Delta a_{22} = \Delta a_{33} = -q_{12}X_{100}, \quad \underset{i \neq j}{\Delta a_{ij}} = 0$$

and

$$\Delta g_{11} = -R_{11}X_{100}, \quad \Delta g_{22} = \Delta g_{33} = -R_{12}X_{100}, \quad \underset{i \neq j}{\Delta g_{ij}} = 0.$$

The crystal becomes uniaxial with the optic axis along the stress direction (100). If $\triangle \rho_{100}$ is the change in rotation along the (100) direction, then

$$\triangle \rho_{100} = - R_{11} X_{100} \quad \text{or} \quad R_{11} = - \frac{\triangle \rho_{100}}{X_{100}}. \tag{3}$$

For an hydrostatic stress X_h, deformations in the index ellipsoid are given by

$$\triangle a_{11} = \triangle a_{22} = \triangle a_{33} = - (q_{11} + 2q_{12}) X_h, \ \underset{i \neq j}{\triangle a_{ij}} = 0.$$

Hence, the crystal remains isotropic, but the radius of the gyration sphere changes and it is given by

$$\triangle g_{11} = \triangle g_{22} = \triangle g_{33} = - (R_{11} + 2R_{12}) X_h, \ \underset{i \neq j}{\triangle g_{ij}} = 0.$$

If $\triangle \rho_h$ is the change in the optical rotatory power in any direction under the hydrostatic stress X_h

$$\triangle \rho_h = - (R_{11} + 2R_{12}) X_h. \tag{4}$$

From (3) and (4)

$$R_{12} = \frac{1}{2} \left(\frac{\triangle \rho_{100}}{X_{100}} - \frac{\triangle \rho_h}{X_h} \right).$$

Changes in the index and gyration tensors under a uniaxial stress X_{111} along the cube diagonal (111) are given by

$$\triangle a_{11} = \triangle a_{22} = \triangle a_{33} = - \tfrac{1}{3} (q_{11} + 2q_{12}) X_{111},$$

$$\triangle a_{12} = \triangle a_{23} = \triangle a_{31} = - \frac{q_{44}}{3} X_{111}$$

and

$$\triangle g_{11} = \triangle g_{22} = \triangle g_{33} = - \frac{R_{11} + 2R_{12}}{3} X_{111},$$

$$\triangle g_{12} = \triangle g_{23} = \triangle g_{31} = - \frac{R_{44}}{3} X_{111}.$$

The first set of equations establish that the crystal becomes uniaxial with the optic axis along the cube diagonal (*i.e.*, stress direction). If $\rho^0{}_{111}$ and ρ_{111}

are the rotatory powers along this direction before and after stress, then one can easily verify that

$$\rho_{111} = \frac{g_{11} + g_{22} + g_{33} + 2g_{12} + 2g_{23} + 2g_{31}}{3}$$

and

$$\rho^{\circ}_{111} = \frac{g^0_{11} + g^0_{22} + g^0_{33} + 2g^0_{12} + 2g^0_{23} + 2g^0_{31}}{3}$$

or

$$\triangle \rho_{111} = \frac{\triangle g_{11} + \triangle g_{22} + \triangle g_{33} + 2 \triangle g_{12} + 2 \triangle g_{23} + 2 \triangle g_{31}}{3}$$

i.e.,

$$\triangle \rho_{111} = -\frac{R_{11} + 2R_{12} + 2R_{44}}{3} X_{111}$$

giving

$$R_{44} = \frac{1}{2}\left(\frac{\triangle \rho_h}{X_h} - \frac{3 \triangle \rho_{111}}{X_{111}}\right).$$

Thus all the 3 constants can be determined from 3 independent measurements.

(*b*) 23 *Class :*

The important optically active crystals $NaClO_3$ and $NaBrO_3$ belong to this class. Photoelastic and piezo-rotatory tensors have the same form as given in Table I (No. 10). There are 4 constants R_{11}, R_{12}, R_{13} and R_{44} to be determined.

(i) If $\triangle \rho_h$ is the change in the optical rotatory power under an hydrostatic stress X_h, then

$$\triangle \rho_h = -(R_{11} + R_{12} + R_{13}) X_h. \tag{5}$$

(ii) If $\triangle \rho_{111}$ is the change in the optical rotatory power along the cube diagonal for a stress X_{111} acting along it, then

$$\triangle \rho_{111} = -\frac{R_{11} + R_{12} + R_{13} + 2R_{44}}{3} X_{111}. \tag{6}$$

(iii) For a stress X_{100} along the cube axis (100) the deformations in the index and the gyration surfaces are given by

$$\triangle a_{11} = - q_{11}X_{100}, \ \triangle a_{22} = - q_{13}X_{100}, \ \triangle a_{33} = - q_{12}X_{100},$$

$$\underset{i \neq j}{\triangle} a_{ij} = 0$$

and

$$\triangle g_{11} = - R_{11}X_{100}, \ \triangle g_{22} = - R_{13}X_{100}, \ \triangle g_{33} = - R_{12}X_{100},$$

$$\underset{i \neq j}{\triangle} g_{ij} = 0.$$

The first set of equations shows that the crystal becomes biaxal. Generally, $q_{11} < q_{13} < q_{12}$ and hence the plane containing the two optic axes is the ZX plane. The angle V that one of the optic axes makes with the stress direction, *i.e.*, X-axis is given by

$$\sin^2 V = \frac{a_{22} - a_{11}}{a_{33} - a_{11}} = \frac{q_{13} - q_{11}}{q_{12} - q_{11}}.$$

If $\triangle \rho_1$ is the change in rotation along this optic axis, then

$$\triangle \rho_1 = - (R_{11} \cos^2 V + R_{12} \sin^2 V) X_{100} \tag{7}$$

determination of $\triangle \rho_1$ should not be difficult because the optic axial angle and the optical axial plane can be completely worked out from a knowledge of photoelastic constants. The optic axial angle is independent of the stress magnitude. Hence, the crystal can be so cut that the optic axes in the stressed crystal are in proper positions to make the measurements.

(iv) When the crystal is subjected to a uniaxial stress X_{110} acting along the (110) direction, the index and the gyration surfaces deform according to the following set of equations:

$$\triangle a_{11} = - (q_{11} + q_{12}) \frac{X_{110}}{2}, \ \triangle a_{22} = - (q_{11} + q_{13}) \frac{X_{110}}{2},$$

$$\triangle a_{33} = - (q_{12} + q_{13}) \frac{X_{110}}{2}, \ \triangle a_{12} = - q_{44} \frac{X_{110}}{2},$$

$$\triangle a_{23} = \triangle a_{31} = 0$$

and

$$\Delta g_{11} = -(R_{11}+R_{12})\frac{X_{110}}{2}, \quad \Delta g_{22} = -(R_{11}+R_{13})\frac{X_{110}}{2},$$

$$\Delta g_{33} = -(R_{12}+R_{13})\frac{X_{110}}{2}, \quad \Delta g_{12} = -R_{44}\frac{X_{110}}{2},$$

$$\Delta g_{23} = \Delta g_{31} = 0.$$

The first set of equations shows that (1) the index ellipsoid undergoes a rotation about the XY plane; (2) the crystal becomes biaxial with YZ as the optic axial plane. If one of the optic axes of the stressed crystal makes an angle V′ with the Z-axis, then

$$\sin^2 V' = \frac{a'_{22} - a'_{33}}{a'_{11} - a'_{33}} = \frac{A}{B}$$

where

$$A = (q_{12}+q_{13}) - \left\{\frac{q_{12}+q_{13}+2q_{11}-\sqrt{(q_{12}-q_{13})^2+4q^2_{44}}}{2}\right.$$

$$B = (q_{12}+q_{13}) - \left\{\frac{q_{12}+q_{13}+2q_{11}+\sqrt{(q_{12}-q_{13})^2+4q^2_{44}}}{2}\right.$$

and the angular displacement θ from the stress direction is given by

$$\tan 2\theta = \frac{q_{12}-q_{13}}{q_{44}}.$$

From a knowledge of V′ and θ one can work out direction cosines l, m, n of the optic axis with reference to the unstressed state. Then the change $\Delta \rho_2$ in that direction for a stress X_{110} is given by

$$\Delta \rho_2 = -\left[(R_{11}+R_{12})l^2 + (R_{11}+R_{13})m^2 + (R_{12}+R_{13})n^2 + R_{44}\, lm\right]\frac{X_{110}}{2}. \tag{8}$$

From the 4 equations (5), (6), (7) and (8) all the piezo-rotatory constants can be worked out. R_{44} is the easiest of all the coefficients to find.

$$R_{44} = \frac{1}{2}\left(\frac{\Delta \rho_h}{X_h} - \frac{\Delta \rho_{111}}{X_{111}}\right).$$

5. Stress-Induced Optical Actvity in Cubic Crystals

(a) $\bar{4}3m$ *Class:*

In this interesting point group, to which ZnS belongs, stress actually should induce optical activity. The photoelastic and the piezo-rotatory tensors are of different forms (Table III, No. 6). From the nature of the two matrices it can be easily concluded that although a uniaxial stress along the 4-fold or 3-fold axis makes the crystal uniaxial with the optic axis along the stress direction, yet the rotation along the optic axis is zero. Even for stress along the 2-fold axis the rotation along the optic axes is zero. For hydrostatic stress also induced optical activity is zero. Hence, to detect this induced rotation and to extract the piezo-rotatory coefficient R_{12} one should stress the crystal in a general direction (l, m, n) which is only a 1-fold symmetry axis. Let X be the uniaxial stress acting along (l, m, n). The deformations in the index and gyration surfaces are given by

$$\triangle a_{11} = - [q_{11}l^2 + q_{12}(m^2 + n^2)] X$$

$$\triangle a_{22} = - [q_{11}m^2 + q_{12}(l^2 + n^2)] X$$

$$\triangle a_{33} = - [q_{11}n^2 + q_{12}(l^2 + m^2)] X$$

$$\triangle a_{23} = - q_{44}\, mn\, X$$

$$\triangle a_{31} = - q_{44}\, ln\, X$$

$$\triangle a_{12} = - q_{44}\, lm\, X$$

and

$$\triangle g_{11} = - R_{12}(m^2 - n^2) X$$

$$\triangle g_{22} = - R_{12}(n^2 - l^2) X \quad \underset{i \neq j}{\triangle g_{ij}} = 0$$

$$\triangle g_{33} = - R_{12}(l^2 - m^2) X.$$

Hence, in general the crystal becomes biaxial. Index and the gyration surfaces in the stressed crystal are

$$a_{11}x^2 + a_{22}y^2 + R_{33}z^2 + 2a_{12}xy + 2\, a_{23}yz + 2\, a_{31}zx = 1$$

and

$$g_{11}x^2 + g_{22}y^2 + g_{33}z^2 = 1.$$

If X, Y, Z be the principal axes of the index ellipsoid, then the index ellipsoid and the Gyration surface are given by

$$A_{11}X^2 + A_{22}Y^2 + A_{33}Z^2 = 1$$

$$G_{11}X^2 + G_{22}Y^2 + G_{33}Z^2 + 2\,G_{12}XY + 2\,G_{23}YZ + 2\,G_{31}ZX = 1$$

A_{ij}'s and G_{ij}'s can be obtained from a knowledge of the refractive index of the unstressed crystal and its photoelastic constants. In the most general case A_{11}, A_{22} and A_{33} will be different.

If $A_{11} < A_{22} < A_{33}$, then the biaxial plane is XZ and if V is the angle that one of the optic axes makes with X-axis. Then rotation along that axis is

$$\rho = G_{11}\cos^2 V + 2\,G_{13}\cos V \sin V + G_{33}\sin^2 V$$

along the other optic axis also we get the same rotation. If this rotation is measured, we can easily find the only existing piezo-rotatory coefficient R_1

$$\rho = -\,R_{12}\,(\cos^2 V + f_{13}\cos V \sin V + f_3 \sin^2 V)\ X$$

i.e.,

$$R_{12} = -\frac{\rho/X}{f_1\cos^2 V + f_{13}\cos V \sin V + f_3 \sin^2 V}$$

where

$$f_1 = \left\{(l^2 - m^2) + \left(\frac{q_{44}}{q_{11} - q_{12}}\right)^2 \left[\frac{n^2 - l^2}{(l^2 - m^2)^2}\, l^2m^2 + \frac{l^2 - m^2}{(n^2 - l^2)^2}\, n^2l^2\right]\right\}$$

$$f_{13} = 2\left\{(l^2 - n^2 - 2m^2)\left(\frac{q_{44}}{q_{11} - q_{12}}\right) - (n^2 - l^2)\left(\frac{q_{44}}{q_{11} - q_{12}}\right)^2\left[\frac{lnm^2}{(l^2 - m^2)(m^2 - n^2)}\right]\right\}$$

$$f_3 = \left\{(l^2 - m^2) + \left(\frac{q_{44}}{q_{11} - q_{12}}\right)^2\left[\frac{m^2 - n^2}{(n^2 - l^2)^2}\, l^2n^2 + \frac{n^2 - l^2}{(m^2 - n^2)^2}\, m^2n^2\right]\right\}$$

and

$$\sin^2 V = \frac{A_{22} - A_{11}}{A_{33} - A_{11}}.$$

6. ENANTIOMORPHIC OPTICALLY ACTIVE UNIAXIAL CRYSTALS

The photoelastic and the piezo-rotatory matrices are of the same form in all these crystals and they are shown in Table I (Nos. 4, 5, 6, 7, 8 and 9). The crystal remains uniaxial under an hydrostatic stress X_h as well as a stress X_0 along the optic axis. In both the cases the optic axis in the stressed crystal is in the same direction as that of the unstressed crystal. If $\triangle \rho_h$ and $\triangle \rho_0$ are the changes in the optical rotatory power along the optic axis for these two stresses, then

$$R_{33} = -\frac{\triangle \rho_0}{X_0}$$

and

$$2R_{31} + R_{33} = -\frac{\triangle \rho h}{X_h}$$

i.e.,

$$R_{31} = \frac{1}{2}\left(\frac{\triangle \rho_0}{X_0} - \frac{\triangle \rho h}{X_h}\right).$$

Hence, the two constants R_{31} and R_{33} can be easily found out. Determination of other constants involve many experimental complications. The actual values of these constants for α-quartz have been computed by the authors (Ranganath and Ramaseshan 1969 *b*).

7. NON-ENANTIOMORPHIC OPTICALLY ACTIVE UNIAXIAL CRYSTALS

Crystals belong to $\bar{4}$ and $\bar{4}2m$ point groups come under this heading. In these the photoelastic and the piezo-rotatory tensors are of different forms as Table II shows. It is clear from the nature of the gyration tensor (Table II, Nos. 3 and 4) that the unstressed crystal has no optical rotation along the optic axis. Again no rotation can be induced by an hydrostatic stress or a uniaxial stress along the optic axis. If we subject the crystal to a stress X acting perpendicular to optic axis, then the changes in the index and gyration tensors are given by

$$\triangle a_{11} = -q_{11}X, \ \triangle a_{22} = -q_{12}X, \ \triangle a_{33} = -q_{31}X, \ \underset{i \neq j}{\triangle a_{ij}} = 0$$

and

$$\triangle g_{11} = -R_{11}X,\ \triangle g_{22} = -R_{12}X,\ \triangle g_{33} = -R_{31}X,\ \underset{i\neq j}{\triangle g_{ij}} = 0.$$

Hence, the crystal becomes biaxial. Normally $q_{31} > q_{11} > q_{12}$, and hence the optic axial plane is YZ plane. The angle V that one of the optic axes makes with Z axis is given by

$$\sin^2 V = \frac{a_{11} - a_{33}}{a_{22} - a_{33}} = \frac{a_{33} - a_{11}}{a_{33} - a_{22}}$$

$$= \frac{-(q_{31} - q_{11})X + (a^\circ_\epsilon - a^\circ_\omega)}{-(q_{31} - q_{12})X + (a^\circ_\epsilon - a^\circ_\omega)}.$$

For most of the crystals this tilt will be very small for normal stresses. In ADP this is 1° per K bar. The optical rotation along the optic axis is given by

$$\rho = g_{33}\cos^2 V + g_{22}\sin^2 V$$

$$= -(R_{31}\cos^2 V - R_{12}\sin^2 V)X$$

As V is very small,

$$\rho \approx -R_{31}X$$

$$R_{31} \approx \frac{-\rho}{X}.$$

Hence, one of the constants can be evaluated.

8. Non-Enantiomorphic Optically Inactive Uniaxial Crystals

Crystals belonging to this class are not optically active in the unstressed state, but they become optically active under stress. The photoelastic and the piezo-rotatory matrices have different forms and they are shown in Table III (Nos. 1, 2, 3, 4 and 5). In none of the classes a stress along the optic axis induces any rotation along the stress direction. Stresses acting perpendicular to the optic axis even though they induce rotation, their maximum effect is felt along directions along which birefringence is also present. Thus experimentally it is difficult to extract any of the piezo-rotation coefficients.

9. Optical Activity in Non-Enantiomorphic Crystals

As has been mentioned earlier it is difficult to make measurements of the optical activity in directions other than that of the optic axis. The only crystal in which accurate measurements of the optical activity have been made perpendicular to the optic axis is α-quartz (Bruhat and Grivet, 1935; Munster and Szivessy, 1935). A method of measuring optical activity perpendicular to the optic axis in the case of the uniaxial crystal benzil was suggested (*see* Ramachandran and Ramaseshan, 1961, p. 166) some years ago. In this positive uniaxial crystal the birefringence progressively decreases as one goes from red to blue so that at $\lambda = 4900$ Å the crystal shows no birefringence. It was suggested that the rotation could be measured at this wavelength in any direction with ease. It is interesting that this method of measuring the rotation when a birefringent crystal becomes isotropic has been used with success by Hobden (1969) in $AgGeS_2$. By this experiment the long-standing problem of the measurement of optical activity in non-enantiomorphic crystals which do not exhibit optical activity along the optic axis has been solved.

At these wavelengths crystals like $AgGeS_2$ and benzil become isotropic and so it must also be possible to obtain the different piezo-rotatory coefficients.

The method of obtaining the piezo-rotatory coefficient given in Section 5 for the point group $\bar{4}3m$ suggests a method by which optical activity could be measured in different directions in these non-enantiomorphic classes. In theory by stressing the crystal in a particular direction it is possible to get the optic axis in a direction that is different from that in the unstressed crystal. It would then be possible to measure the optical activity along the new optic axis. Again, in theory, it should be possible, by choosing different directions and magnitudes of stress, to map out the gyration surface. Here one assumes that the change in the optical activity due to stress is so small that the measured value may be taken to correspond to the optical activity of the unstressed crystal in that direction.

Unfortunately, these speculations prove to be of no use in the cases of ADP and KDP which belong to the non-enantiomorphic group $\bar{4}2m$. The maximum tilt of the optic axis that one could obtain experimentally is much lower than a degree. However, in the case of less birefringent crystals this possibility must be kept in mind.

References

1. Bruhat, G. and Grivet, R. .. *J. Phys. Radium*, 1935, **6**, 12.
2. Hobden, M. V. .. *Acta Cryst.*, 1968, **24 A**, 676.
3. Munster, C. L. and Szivessy, G. *Z. Physik.*, 1935, **36**, 101.
4. Ramachandran, G. N. and Ramaseshan, S. *Crystal Optics—Handbuch der Physic*, Springer Verlag, Berlin, 1961.
5. Ramaseshan, S. and Ranganath, G. S. *Piezo-optic Phenomena—Physics of the Solid State*, Bhagavantam, Festschrift, Academic Press, London, New York, 1969.
6. ——— and Vedam, K. *Photoelastic Effect—Progress in Crystal Physics*, Edited by R. S. Krishnan-Viswanathan, Madras, 1958.
7. Ranganath, G. S. and Ramaseshan, S. *J. Opt. Soc. Amer.*, 1969 *a*, **59**, 1229.
8. ——— .. *Curr. Sci.* 1969 *b*, **38**, 303.