THE THEORY OF OPTICAL ACTIVITY OF CRYSTALS

III. Calculation of the Rotatory Power of β-Quartz

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1. Introduction

In Parts I and II (author, 1951 *a, b*), the general principles of the theory were discussed and they were applied to the cases of $NaClO_3$ and $NaBrO_3$ to calculate the rotatory power. These two crystals belong to the cubic system and their optical activity could be defined by one parameter. A hypothetical uniaxial crystal having a spiral structure (point-group D_4) was also considered in Part I, for which it was shown that the optical activity both along and at right angles to the optic axis could be calculated, provided the optical anisotropies of the individual atoms were known. The results obtained in this case were promising, since the rotation at right angles to the axis was found to be of opposite sense to that along the axis, a fact observed for α-quartz (Bruhat and Grivet, 1935). In this paper, therefore, we consider the case of β-quartz.

The rotatory power along the optic axis has been measured for both α- and β-quartz at various temperatures (Sosman, 1927) while that at right angles to the optic axis has only been measured for α-quartz at room temperature (Bruhat and Grivet, *loc. cit.*). However, the structures of the two modifications are very similar, there being only a slight alteration in the positions of the oxygen atoms at the transition temperature, which changes the point-group symmetry from D_3 of α-quartz to D_6 of β-quartz. Also the optical properties exhibit only small changes of the order of 5% at the transition temperature. Therefore, the values for the rotatory power are not likely to differ appreciably between α- and β-quartz. However, it is more convenient to make calculations for β-quartz, as it belongs to the higher hexagonal point-group, there being thus less independent parameters to consider. Consequently, the calculations have only been made for the hexagonal modification.

The structure of β-quartz has been determined by Bragg and Gibbs (1925). It belongs to the space-group $D_6^4 - C6_2 2$ and the enantiomorphous

space-group $D_6{}^5-$ C6$_4$2 and the co-ordinates of the Si and O atoms are given below, there being 3 SiO$_2$ atoms per unit cell.

Si	$\frac{1}{2}, 0, 0$	$-\frac{1}{2}, -\frac{1}{2}, \frac{1}{3}$	$0, \frac{1}{2}, \frac{2}{3}$
O	$u, \bar{u}, -\frac{1}{6}$	$\bar{u}, 2\bar{u}, \frac{1}{2}$	$2u, \bar{u}, \frac{1}{6}$
	$\bar{u}, u, -\frac{1}{6}$	$u, 2u, \frac{1}{2}$	$2\bar{u}, u, \frac{1}{6}.$

with $u = 0.21$. The unit cell dimensions are $a = 5.01$ A, $c = 5.47$ A, $c/a = 1.09$. A projection of the structure on the basal c plane is shown in Fig. 1, in which the numbers denote the heights of the atoms above the plane through the origin, in units of $c/6$. The arrows indicate how the atoms are linked up; they form left-handed spirals progressing upwards in the direction of the arrows. We denote by OA, OB, OC the hexagonal axes. However, for making calculations, it is preferable to choose the orthogonal set of axes Ox, Oy, Oz shown in Fig. 1. If x', y', z' are the co-ordinates of an
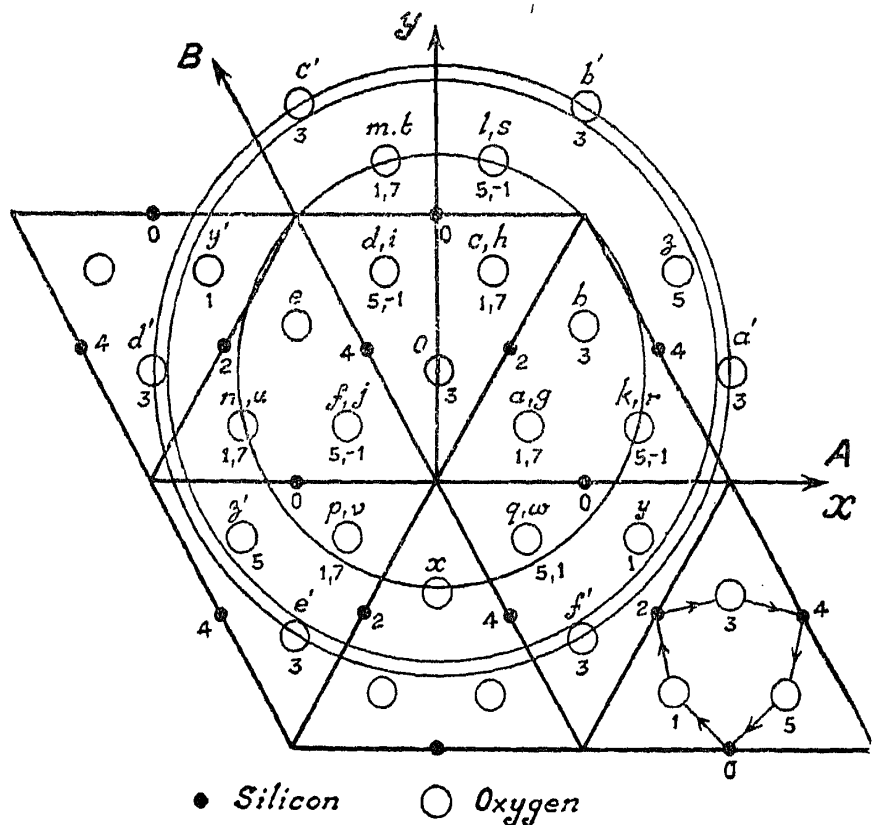

• *Silicon*   ○ *Oxygen*

FIG. 1. Atomic structure of β–quartz

atom in the hexagonal system of axes, then the co-ordinates x, y, z with respect to the rectangular system are given by

$$x = x' - y'/2, \quad y = \sqrt{3}\, y'/2, \quad z = z'.$$

2. Polarisabilities of Silicon and Oxygen Atoms

We may take for the molar refractions the values $R_O = 3.56$ and $R_{Si} = 0.1$ given by Fajans and Joos (1924). The molar refraction of oxygen is thus of the same order as the value in $NaClO_3$ or calcite. As in Part II, we shall make the simplification of neglecting the polarisability of silicon and assume that the optical properties of quartz are solely determined by the oxygen atoms. This is justified since, according to the above values, silicon contributes only about 1% to the molar refraction of SiO_2.

It is now necessary to estimate the anisotropy of an oxygen atom in the structure. In quartz, each oxygen atom is linked to two silicon atoms, the two bonds being nearly at the tetrahedral angle, as is found in oxygen compounds such as water. The following indirect method may therefore be employed for estimating the anisotropy of oxygen. If one examines a table of depolarisation values ($\triangle$) in light-scattering (*e.g.*, Bhagavantam, 1940, p. 54), it is found that $\triangle$ is generally in the neighbourhood of 1·5% for oxygen components such as water, alcohols, ethers, etc. From this, we can estimate the anisotropy β, which may be defined by

$$\beta^2 = [(a_1 - a_2)^2 + (a_2 - a_3)^2 + (a_3 - a_1)^2]/2a^2, \tag{1}$$

where a_1, a_2, a_3 are the principal polarisabilities and $a = (a_1 + a_2 + a_3)/3$ is the mean polarisability. β is related to $\triangle$ by the formula

$$\beta^2 = 45 \triangle/(6 - 7 \triangle) \tag{2}$$

(Bhagavantam, 1940), so that, if $\triangle = 0.015$, $\beta^2 = 0.115$. This value alone is insufficient to fix uniquely $a_1 : a_2 : a_3$. If we assume, in addition, that the molecule has an axis of symmetry, and say $a_2 = a_3$, then a_1/a_2 can be uniquely estimated. Obviously, no such symmetry axis exists for an oxygen atom linked to two groups at 109° 28'. But, we can still estimate a_1, a_2, a_3 by the following method.

It is clear that the effect of a covalent bond would be to pull out the electron distribution of the oxygen atom towards the group to which it is bound. As an idealised case, imagine the bonded oxygen atom to consist of an isotropically polarisable core (O) with polarisability γ and two electron
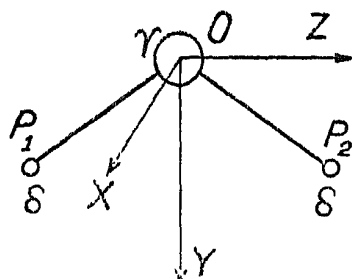

Fig. 2. Axes of polarisability ellipsoid of an oxygen atom

concentrations at P_1 and P_2 with polarisability δ each, the angle P_1OP_2 being $109° 28'$ (Fig. 2). Obviously, the principal axes of the polarisability ellipsoid of the whole group would be along OX, OY, OZ. By working out the values of the principal polarisabilities α_1, α_2, α_3 it can be shown that

$$\alpha_1 < \alpha_3 < \alpha_2 \tag{3}$$

The exact values of the ratios $\alpha_1 : \alpha_2 : \alpha_3$ is immaterial, as it would depend very much on the electron distribution, but the above inequalities would be maintained. In the absence of any further data except the value of β and the relation (4), we may assume that

$$\alpha_1 : \alpha_2 : \alpha_3 = 1 : 1 \cdot 5 : 1 \cdot 25 \tag{5}$$

This makes $\beta = 0 \cdot 12$, which is sufficiently close to the value $0 \cdot 115$ calculated from the depolarisation.

Assuming Fajans and Joos' value given earlier for the mean atomic refraction of oxygen, the values of the principal polarisabilities are found to be

$$\alpha_1 = 1 \cdot 419, \quad \alpha_2 = 2 \cdot 129, \quad \alpha_3 = 1 \cdot 774 \times 10^{-23}. \tag{6}$$
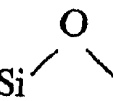
3. Calculation of the Refractive Indices

The general theory of Part I contains, in essence, the formalism required for calculating both the refractive index and the rotatory power and it can be used to calculate the two refractive indices of quartz. However, unlike sodium chlorate, in which the distances between the oxygen atoms in an O_3 group is small compared with the distance between neighbouring groups, the atoms in quartz form an extended structure. The influence of the near neighbours on the refraction of an oxygen atom is therefore appreciable and a larger number of neighbours have to be taken into account for obtaining an accurate result. We shall include all the oxygen atoms occurring within 5 Å of any particular atom in our calculations. There are 33 such and they are indicated by letters $a, b, \ldots \ldots e', f'$ in Fig. 1. The three circles indicate the areas within which the projections of the neighbours should lie if they are in levels 3; (1, 5); (−1, 7) respectively, for them to be within 5 Å from atom O. The distances (R) of the various neighbours and also the values the quantities $p = (3x^2 - R^2)/R^5$, $q = (3y^2 - R^2)/R^5$, $r = (3z^2 - R^2)/R^5$, $s = 3xy/R^5$, $t = 3yz/R^5$, $u = 3zx/R^5$ are shown in Table I. The entries under column 2 will be clear a little later.

The components of the polarisability ellipsoid of the oxygen atom O (with respect to the rectangular system of axes $Oxyz$ of Fig. 1) can be obtained from the values of α_1, α_2, α_3 given above and the configuration of the

TABLE I

Atom	Type	R	p	q	r	s	t	u
b	A_2	2·598	+·101900	−·044920	−·057010	+·043740	..	..
c	A_2	2·598	+·101900	−·044920	−·057010	+·043740	..	..
x	A_2	3·647	−·001030	+·002060	−·001030	..	..	..
a'	A_1	5·010	+·015903	−·007952	−·007952	..	..	..
d'	A_1	5·010	+·015903	−·007952	−·007952	..	..	..
b'	A_1	5·010	−·019900	+·009941	−·007952	+·001032	..	..
c'	A_1	5·010	−·019900	+·009941	−·007952	−·001032	..	..
e'	A_1	5·010	−·019900	+·009941	−·007952	+·001032	..	..
f'	A_1	5·010	−·019900	+·009941	−·007952	−·001032	..	..
a	C_1	2·578	+·007250	−·036450	+·029190	−·037920	+·043800	−·075810
f	B_1	2·578	+·007250	−·036450	+·029190	+·037920	−·043800	−·075810
c	C_2	2·598	−·035240	+·008090	+·027160	+·036620	−·074010	−·0428.0
d	B_2	2·598	−·035240	+·008090	+·027160	−·036620	+·074010	−·042810
g	C_1	4·076	−·008121	−·012535	+·020656	−·003830	−·008853	+·015317
i	B_1	4·076	−·008121	−·012535	+·020656	+·003830	+·008853	+·015317
h	C_2	4·091	−·012467	−·007946	+·020413	+·003927	+·015448	+·008936
i	B_2	4·091	−·012467	−·007946	+·020413	−·003927	−·015448	+·008936
k	B_1	3·990	+·019240	−·013330	−·005913	−·009322	−·004953	+·018539
n	C_1	3·990	+·019240	−·013330	−·005913	+·009322	+·004953	+·018539
l	B_1	3·991	−·013270	+·019198	−·005935	+·009471	+·018623	+·005038
m	C_1	3·991	−·013270	+·019198	−·005935	−·009471	−·018623	+·005038
p	C_2	3·645	−·009054	+·014213	−·005159	+·020094	+·023245	+·013395
q	B_2	3·645	−·009054	+·014213	−·005159	−·020094	−·023245	+·013395
r	B_1	5·089	+·002757	−·006856	+·004102	−·002751	+·002951	−·010996
u	C_1	5·089	+·002757	−·006856	+·004102	+·002751	−·002951	−·010996
s	B_1	5·090	−·006826	+·002733	+·004093	+·002789	−·010964	−·002967
t	C_1	5·090	−·006826	+·002733	+·004093	−·002789	+·010964	−·002967
v	C_2	4·824	−·006052	−·000318	+·006366	+·004953	−·011453	−·006603
w	B_2	4·824	−·006052	−·000318	+·006366	−·004953	+·011453	−·006603
y	C_2	4·750	+·005262	−·000054	−·005208	−·011630	+·006178	−·007752
z'	B_2	4·750	+·005262	−·000054	−·005208	+·011630	−·006178	−·007752
y'	C_2	4·749	+·011348	−·006139	−·005209	−·008115	−·003624	+·009231
z	B_2	4·749	+·011348	−·006139	−·005209	+·008115	+·003624	−·009231

O
Si⟍ ⟋Si bonds in the structure. They are calculated to be

$$a_{11}^{0} = 1 \cdot 539 \times 10^{-23}$$
$$a_{22}^{0} = 2 \cdot 129 \times 10^{-23}$$
$$a_{33}^{0} = 1 \cdot 654 \times 10^{-23}$$
$$a_{23}^{0} = 0$$
$$a_{31}^{0} = -0 \cdot 170 \times 10^{-23}$$
$$a_{12}^{0} = 0$$

$$(7)$$

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The components of the polarisability ellipsoid of the five other oxygen atoms in the unit cell can be readily obtained from these by the application of suitable symmetry operations. Calling atom O to be of type A_1 and the others respectively of types A_2, B_1, B_2, C_1, C_2 the various components are given in Table II. In this table of transformations, the most general case is considered of a tensor L, which is not necessarily symmetric. Owing to the fact that a two-fold axis along Oy passes through atom O, there can only be 5 non-vanishing components for this atom, viz.,

$$L_{11} = a, \quad L_{22} = b, \quad L_{33} = c, \quad L_{13} = d, \quad L_{31} = e.$$

Table II contains all the components of the other atoms in terms of these. Column 2 of Table I gives the type of each atom.

TABLE II

Component	A_1	A_2	B_1	B_2	C_1	C_2
L_{11}	a	a	$\frac{1}{4}a+\frac{3}{4}b$	$\frac{1}{4}a+\frac{3}{4}b$	$\frac{1}{4}a+\frac{3}{4}b$	$\frac{1}{4}a+\frac{3}{4}b$
L_{22}	b	b	$\frac{3}{4}a+\frac{1}{4}b$	$\frac{3}{4}a+\frac{1}{4}b$	$\frac{3}{4}a+\frac{1}{4}b$	$\frac{3}{4}a+\frac{1}{4}b$
L_{33}	c	c	c	c	c	c
L_{23}	0	0	$\frac{\sqrt{3}}{2}d$	$-\frac{\sqrt{3}}{2}d$	$-\frac{\sqrt{3}}{2}d$	$\frac{\sqrt{3}}{2}d$
L_{32}	0	0	$\frac{\sqrt{3}}{2}e$	$-\frac{\sqrt{3}}{2}e$	$-\frac{\sqrt{3}}{2}e$	$\frac{\sqrt{3}}{2}e$
L_{31}	e	$-e$	$\frac{1}{2}e$	$-\frac{1}{2}e$	$\frac{1}{2}e$	$-\frac{1}{2}e$
L_{13}	d	$-d$	$\frac{1}{2}d$	$-\frac{1}{2}d$	$\frac{1}{2}d$	$-\frac{1}{2}d$
L_{12}	0	0	$\frac{\sqrt{3}}{4}(a-b)$	$\frac{\sqrt{3}}{4}(a-b)$	$-\frac{\sqrt{3}}{4}(a-b)$	$-\frac{\sqrt{3}}{4}(a-b)$
L_{21}	0	0	$\frac{\sqrt{3}}{4}(a-b)$	$\frac{\sqrt{3}}{4}(a-b)$	$-\frac{\sqrt{3}}{4}(a-b)$	$-\frac{\sqrt{3}}{4}(a-b)$

From (9) and (11) of Part I, we have the following equations for the atom O, when the electric vector is E_x, if we neglect the phase changes. (As was mentioned in the earlier parts, it is necessary to take the phase changes into account only for calculating the rotation, but not for calculating the refractive index. This is so because $\cos 2\pi R_i/\lambda_0 \simeq 1$ for all the neighbours that are considered, the error introduced by putting it equal to unity being only of the order of in 10^{-6}.)

$$\mu_{x0} = a_{11}^0 \left(E_x + \frac{P_x}{3} + F_{x0} \right) + a_{12}^0 F_{y0} + a_{13}^0 F_{z0}, \text{ etc.} \tag{9}$$

where

$$F_{x0} = \frac{1}{4\pi} \Sigma_j (\mu_{xj} p_j + \mu_{yj} s_j + \mu_{zj} u_j), \text{ etc.} \tag{10}$$

Suppose we write

$$\mu_0(\mu_{x0}, \mu_{y0}, \mu_{z0}) = L_0 (E + P/3), \tag{11}$$

where the tensor L has five non-vanishing components, say a, b, c, d, e as in (8). Then substituting the numerical values of $\alpha_{11}^0, \dots$ from (7) and $p_j, \dots$ from Table II one obtains the following simultaneous equations:

$$
\left.
\begin{aligned}
0 \cdot 75310\, a - 0 \cdot 10728\, b + 0 \cdot 04128\, d &= \ \ 1 \cdot 539 \times 10^{-23} \\
0 \cdot 06014\, a + 0 \cdot 15807\, b + 0 \cdot 89630\, d &= -\, 0 \cdot 170 \quad \text{,,} \\
0 \cdot 10728\, a + 1 \cdot 13096\, b + 0 \cdot 21566\, d &= \ \ 2 \cdot 129 \quad \text{,,} \\
0 \cdot 97235\, c + 0 \cdot 20372\, e &= \ \ 1 \cdot 654 \quad \text{,,} \\
0 \cdot 18810\, c + 0 \cdot 95320\, e &= -\, 0 \cdot 170 \quad \text{,,}
\end{aligned}
\right\} \tag{12}
$$

which, on solving, give

$$a = 2 \cdot 251,\ b = 1 \cdot 239,\ c = 1 \cdot 813,\ d = -\,0 \cdot 559,\ e = -0 \cdot 536 \times 10^{-23}. \tag{13}$$

Adding up the components for the six atoms in the unit cell (of volume V) in the particular cases when the incident electric vector is E_x and E_z, we have

$$
\left.
\begin{aligned}
P_x &= \frac{\Sigma \mu_x}{V} = \frac{3\,(a + b)}{V} \left(E_x + \frac{P_x}{3} \right) \\
P_z &= \frac{\Sigma \mu_z}{V} = \frac{6c}{V} \left(E_z + \frac{P_z}{3} \right)
\end{aligned}
\right\} \tag{14}
$$

Since

$$P_x/E_x = n_\omega^2 - 1 \text{ and } P_z/E_z = n_\epsilon^2 - 1,$$

$$n_\omega = 1 \cdot 500, \quad n_\epsilon = 1 \cdot 522 \tag{15}$$

The experimental values are $1 \cdot 533$ and $1 \cdot 541$ respectively. It is seen that $n_\epsilon > n_\omega$ as found from experiment. The absolute values are, however, smaller by about 1 to 2%, which is of the order of error to be expected due to the omission of the effects of silicon atoms in the calculations. The calculated birefringence is much larger than is observed, $0 \cdot 02$ as against $0 \cdot 008$, but this agreement itself must be considered excellent, as it is much better than the agreement obtained by Bragg (1924) in calcite and aragonite.

4. Calculation of the Rotatory Power

We now consider the phase differences of the incident wave for various atoms in the structure and thus proceed to evaluate the rotatory power,

(a) *Propagation along the optic axis Oz.*—It is necessary to calculate the total moment induced in the six atoms in the unit cell along the y-axis when the electric vector is along Ox. Because of the 6-fold axis of symmetry, it can be shown that the mean induced moment along Oy of all the atoms in the unit cell, when the incident electric vector is along Ox, is the same as the mean of the perpendicularly induced moments of any particular atom (say O of Fig. 3) when the incident electric vector is along Ox and Oy. Consequently, we only make the latter calculation. For an electric vector E_x,

$$\mu_{y0} = \left(E_x + \frac{P_x}{3}\right) \sum_j \exp\left(-2\pi i z_j/\lambda\right)[L_{11}' \,(p_j \alpha_{12} + u_j \alpha_{22} + t_j \alpha_{23})$$

$$+ L_{12}' \,(u_j \alpha_{12} + q_j \alpha_{22} + s_j \alpha_{23}) + L_{13}' \,(t_j \alpha_{12} + s_j \alpha_{22} + r_j \alpha_{23})]$$

$$= i K_1 \,(E_x + P_x/3) \qquad \text{(say)} \qquad (13)$$

Similarly, for incident E_y,

$$\mu_{x0} = i K_2 \,(E_y + P_y/3) \qquad \text{(say)} \qquad (14)$$

Actual calculations give $K_1 = -3 \cdot 639 \times 10^{-4} n_\omega$, $K_2 + 1 \cdot 480 \times 10^{-4} n_\omega$, so that $(K_1 + K_2)/2 = -1 \cdot 080 \times 10^{-4} n_\omega$.

From these,

$$\frac{P_y}{P_x} = \frac{i g_{33}}{n_\omega{}^2 - 1} = -i \times (1 \cdot 080 \times 10^{-4}/1 \cdot 745)\, n_\omega$$

and $g_{33}/n_\omega = -7 \cdot 72 \times 10^{-5}$. Therefore, the rotatory power along the optic axis is

$$\rho_{\shortparallel} = \frac{\pi}{\lambda}\frac{g_{33}}{n_\omega} = -236^\circ. \qquad (16\ a)$$

(b) *Propagation at right angles to the optic axis.*—Just as in case (a), it can be readily shown that the mean value of the perpendicularly induced moment for all the atoms in the unit cell is the mean of the values for any one atom (say 0) for direction of propagation along Ox and Oy. Writing $\mu_\perp = -i K_3 \,(E_z + P_z/3)$ for the former and $i K_4 \,(E_z + P_z/3)$ for the latter, we get

$$K_3 = + 4 \cdot 196 \times 10^{-4}\, \bar{n}, \quad K_4 = -3 \cdot 142 \times 10^{-4}\, \bar{n}$$

so that $(K_3 + K_4)/2 = 0 \cdot 527 \times 10^{-4}\, \bar{n}$, where $\bar{n} = (n_\omega + n_\epsilon)/2$.

From these, $g_{11}/\bar{n} = + 3 \cdot 76 \times 10^{-5}$ and

$$\rho_\perp = \frac{\pi}{\lambda}\frac{g_{11}}{\bar{n}} = + 115^\circ \qquad (16\ b)$$

Thus

$$\rho_\perp/\rho_\| = -0\cdot487. \tag{17}$$

5. Discussion

The above results may be compared with experiment. As mentioned earlier, data are available only for $\rho_\|$ which is $252°/\text{cm}$. This agrees well with the calculated value of $236°$. For α-quartz, $\rho_\perp/\rho_\| = -0\cdot50$, which is very nearly the same as the value obtained above.

It is interesting to note that the sense of optical rotation is the same as the sense of the spiral in the structure. We have considered in this paper a left-handed spiral, *i.e.*, the spiral progresses towards the observer when turned clockwise. $\rho_\|$ in this case is negative, *i.e.*, the rotation is clockwise as the light beam advances towards the observer. However, as was mentioned in connection with the hypothetical crystal in Part I, the sense of rotation would also depend on the nature of the anisotropy of oxygen in the structure.

Summary

Using the general theory of Part I, the rotatory power of β-quartz along and perpendicular to the axis are calculated to be $236°$ and $115°$. These agree well with the value $252°$ observed for the former and the value $0\cdot50$ observed for the ratio of the two in α-quartz.

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