THEORETICAL INTERPRETATION OF THE OPTICAL ACTIVITY OF QUARTZ

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1. INTRODUCTION

a-QUARTZ belongs to the trigonal enantiomorphous hemihedral class of symmetry, the space-group being represented by D_3^4 (or the enantiomorphous D_3^6). The structure accordingly has a threefold screw axis. The unit cell consists of three SiO_2 triplets spaced at equal intervals along the vertical axis, each turned through 120° with respect to its predecessor. It can scarcely be doubted that this screw structure is responsible for the optical rotatory power of quartz. Theories which seek to correlate the optical activity with the ultimate structure of the substance exhibiting it have been put forward by various authors in the past (*vide* the reviews by Condon, 1937; Kauzmann *et al.*, 1940). Applications of these theories to evaluate the results in particular crystals have been comparatively few. For the case of quartz, there have been three attempts to calculate the rotatory power theoretically. The first is by Hylleraas (1927), who has applied Born's general theory of coupled oscillators (1915). Hylleraas has deduced from the known data for the double refraction and the rotatory power, the values of two lattice constants, which agree well with the X-ray data. The second attempt is by de Mallemann (1930) who has estimated the rotatory power in terms of the refractivities of the atoms constituting the crystal. More recently, Ramachandran (1951) has made detailed calculations of the first order terms of the polarisability theory and obtains good values for the rotatory power for the propagation of light both along and at right angles to the optic axis. Though all these authors get a fairly good agreement with the observed values, none of them has derived an explicit law of rotatory dispersion for quartz, which is certainly a characteristic and noteworthy feature of the phenomenon.

The rotatory power of quartz has been the subject of extensive experimental study. Accurate data is available over a wide range of wavelengths. Numerous attempts have been made to represent these data by means of rotatory dispersion formulæ (*vide* Servant 1939, 1941). Most of these formulæ,

468

h ich generally involve a large number of terms, fail in the remote ultra-violet and besides, they are open to objection from the theoretical stand-point. For, as has been pointed out in an earlier paper (author, 1952 *b*), the negative terms appearing in these formulæ have been assigned arbitrary strengths and do not conform to the summation rule of Kuhn (1927). It has also been shown by the present author (1952 *a*) that the entire data from the visible to the extreme ultraviolet is accurately represented by the formula

$$\rho = \frac{k\lambda^2}{(\lambda^2 - \lambda_0^2)^2}, \tag{1}$$

where $k = 7\cdot186$ and $\lambda_0 = 0\cdot0926283\,\mu$. The rotatory dispersion at right angles to the optic axis has been measured by Bruhat and Weil (1936), who have summarised their results as follows. The ratio of the rotatory powers normal to and along the optic axis of quartz is independent of the wave-length between the range 5780 A.U. to 2540 A.U., the ratio being $-0\cdot54$, to within an accuracy of $0\cdot5$ per cent. It is obvious, therefore, that the rotatory dispersion formula normal to the optic axis would also be of the same type as (1) with the value of λ_0 unaltered, the constant k being re-duced in the ratio of $-0\cdot54$.

In the present paper, a theoretical interpretation of the optical activity of quartz, based on coupled oscillators, has been put forward, in which the approach to the problem is quite different from the three previous attempts to evaluate the rotatory power of this crystal. Briefly, the basis of the theory is as follows. While the screw structure of quartz is responsible for its optical activity, one may remark that it would not by itself suffice. For, if we assume that each SiO_2 unit constituting such a structure is an optically independent entity, it can readily be shown that the rotatory power would vanish. It is necessary therefore, to consider the SiO_2 groups as forming a connected system, if the observed optical behaviour of the crystal is to be understood. The basic idea of this paper is that the screw-like structure of the crystal influences the spectroscopic behaviour of the constituent units and it is this which ultimately gives rise to its rotatory power. It is shown, from simple considerations of symmetry, that the characteristic frequency of the individual units is split into two components which differ from each other, as a result of the coupling between the neighbouring entities in the crystal. It is further shown that this splitting affords a ready explanation of the rotatory power of quartz both along and normal to the optic axis. The principal merit of this treatment is that it leads directly to an expression for the rotatory power of the same form as (1), which, as has already been pointed out, agrees very well with the actual observed data for quartz.

2. The Quartz Model

Let us construct a simple model based on the screw structure of quartz. We shall replace each SiO_2 triplet by a linear resonator located at its centre of gravity and lying approximately along the line joining the oxygens. Let the natural frequency of vibration of the charged particle in each resonator when uncoupled be ω_0. Let us assume that there is a feeble coupling between the neighbouring resonators. Since the successive resonators are exactly identical, there would be a resonance interaction and the frequencies would be affected. Thus, the question that comes up for consideration is that of finding how the presence of a threefold axis in the structure influences the modes and frequencies of vibration of these constituent units. We shall proceed to examine this point. The characteristic feature of this model is that by a translation of c/3 and a rotation of 120° about the c-axis, the entire system is brought into coincidence with itself. We may, therefore, assume that such an operation, which is a purely geometrical procedure, would not alter the physical state and accordingly the modes and frequencies of vibration of the system. This indicates that the effect of the symmetry operation on a normal co-ordinate would be either to leave it unchanged or transform it into its negative. Fixing our attention on any particular normal mode, we notice that for this to be the case, the particles in the successive resonators should vibrate with equal amplitude and in directions differing by 120° as measured about the optic axis, and their phases should satisfy one or other of the following conditions; (a) the phases identical in the successive resonators or (b) the phases opposite in the successive resonators.* It is evident that the frequency of vibration would be different in the two cases, the magnitude of the difference being dependent on the strength of the interaction between the neighbours. In other words, the natural frequency ω_0 of the individual units is split into two frequencies, ω_1 and ω_2, as a result of the coupling between the successive resonators. This *simplified* picture is, of course, a purely *classical* one. We shall now see how the optical activity of quartz could be accounted for, on the basis of these remarks.

3. The Theory

It can easily be seen in the simplified model presented above, that the dynamic or vibrational pattern of the entire crystal (including both modes of vibration) can be completely reproduced by a unit consisting of a pair of adjacent resonators. Let us call this unit the compound resonator. We

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* It will be noticed that a similar result has been arrived at with regard to the atomic vibrations in the successive cells of a crystal lattice by Sir C. V. Raman in his treatment of crystal dynamics (1943).

shall base our calculations on such a compound resonator and then extend them to the whole crystal, remembering of course, that the successive compound resonators are situated about a threefold screw axis.

Let the charge and mass of the particle in each resonator be q and M respectively. Let us, for convenience, put $q = fe$ and $M = fm$, where e and m are respectively the charge and mass of the electron, and f is the oscillator strength according to the usual definition. Let us choose a rectangular set of axes, the Z axis being parallel to the optic axis.

Propagation along the Optic Axis.—When plane polarised light is incident along the optic axis of quartz, it is split into two circular vibrations of opposite senses, which travel with different velocities in the medium. Since these two vibrations are coherent, they combine at every point to form a plane polarised vibration which is rotated with respect to the plane of polarisation of the incident light, the rotation increasing directly as the thickness traversed. If n_l and n_r be the refractive indices for left-handed and right-handed circular light, then the rotation per unit length is given by

$$\rho = \frac{\pi}{\lambda} (n_l - n_r). \tag{2}$$

We shall now proceed to calculate n_l and n_r.

Let right-circularly polarised light represented by

$$\left. \begin{array}{l} x = E_0 \cos \omega t \\ y = - E_0 \sin \omega t \end{array} \right\} \tag{3}$$

be incident along OZ. The force exerted by the light wave on the charged particle of any resonator whose direction cosines are α, β, γ, is

$$F_1 = feE_0 \left[\alpha \cos \omega t - \beta \sin \omega t \right]. \tag{4}$$

The force on the particle on the successive resonator which is rotated through $\theta \, (= 120°)$ about the Z axis would be

$$F_2 = (\alpha \cos \theta - \beta \sin \theta) feE_0 \cos (\omega t - \phi)$$
$$- (\alpha \sin \theta + \beta \cos \theta) feE_0 \sin (\omega t - \phi) \tag{5}$$

where $\phi = \dfrac{2\pi \bar{n} d}{\lambda}$, $\bar{n}$ being the mean refractive index and d is the distance between the two resonators as measured along the optic axis. Since ϕ is small, we may put $\cos \phi = 1$ and $\sin \phi = \phi$ in (5) and we get

$$F_2 = feE_0 \left[\{ \alpha (\cos \theta + \phi \sin \theta) - \beta (\sin \theta - \phi \cos \theta) \} \cos \omega t \right.$$
$$\left. + \{ \alpha (\phi \cos \theta - \sin \theta) - \beta (\cos \theta + \phi \sin \theta) \} \sin \omega t \right]. \tag{6}$$

Let us confine our attention to the compound unit formed by these two adjacent resonators. We have just seen that the compound resonator has two normal modes of vibration, one in which the two particles vibrate with equal amplitude and in the same phase and the other in which the two particles vibrate with equal amplitude but opposite in phase. Hence the force exerted on these particles expressed in the two normal co-ordinates are respectively

$$R_{\xi_1} = \frac{1}{\sqrt{2}} (F_1 + F_2) \tag{7}$$

$$R_{\xi} = \frac{1}{\sqrt{2}} (F_1 - F_2). \tag{8}$$

Substituting for F_1 and F_2, we get

$$R_{\xi_1} = \frac{feE_0}{\sqrt{2}} [\{a (1 + \cos \theta + \phi \sin \theta) - \beta (\sin \theta - \phi \cos \theta)\} \cos \omega t$$

$$+ \{a (\phi \cos \theta - \sin \theta) - \beta (1 + \cos \theta + \phi \sin \theta)\} \sin \omega t] \tag{9}$$

$$= (a_{\xi_1}') feE_0 \cos (\omega t + \sigma) \tag{10}$$

where

$$(a_{\xi_1}')^2 = (a^2 + \beta^2) (1 + \cos \theta + \phi \sin \theta),$$

neglecting higher powers of ϕ. Therefore, the equation of motion of the particles would be of the form

$$\ddot{\xi}_1 + \omega_1^2 \xi_1 = (a_{\xi_1}') \frac{feE_0}{M} \cos (\omega t + \sigma) \tag{11}$$

$$\therefore \qquad \xi_1 = (a_{\xi_1}') \frac{feE_0 \cos (\omega t + \sigma)}{M (\omega_1^2 - \omega^2)}. \tag{12}$$

Hence, the dipole moment induced

$$= \{(a_{\xi_1}') fe\}^2 \frac{E_0}{M (\omega_1^2 - \omega^2)}$$

$$= (a_{\xi_1}')^2 f \frac{e^2}{m} \frac{E_0}{(\omega_1^2 - \omega^2)} \tag{13}$$

putting $M = fm$. The dipole moment could be expressed as two components at right angles to each other, say m_g and m_k,

where

$$m_g = a^2 (1 + \cos \theta + \phi \sin \theta) f \frac{e^2}{m} \frac{E_0}{(\omega_1^2 - \omega^2)}$$

and

$$m_k = \beta^2 \left(1 + \cos\theta + \phi\sin\theta\right) f \frac{e^2}{m} \frac{E_0}{(\omega_1{}^2 - \omega^2)}.$$

These results are for a single compound resonator. Since the successive compound resonators are situated about a threefold axis of symmetry, it can easily be shown that the mean polarisability per unit volume for right circular vibration

$$= \frac{N'\left(m_g + m_k\right)}{2E_0},$$

where N' is the number of compound resonators per unit volume and is equal to $N/2$, where N is the number of resonators per unit volume.

$$\therefore \quad (n_r{}^2 - 1)_{\xi_1} = 4\pi \, N' \frac{(m_g + m_k)}{2E_0}$$

$$= \pi N \, (a_{\xi_1}')^2 \frac{e^2}{m} \frac{f}{(\omega_1{}^2 - \omega^2)}, \tag{16}$$

In a similar manner we get for the other mode of vibration

$$(n_r{}^2 - 1)_{\xi_2} = \pi N \, (a_{\xi_2}')^2 \frac{e^2}{m} \frac{f}{(\omega_2{}^2 - \omega^2)}, \tag{17}$$

where

$$(a_{\xi_2}')^2 = (\alpha^2 + \beta^2)\, (1 - \cos\theta - \phi\sin\theta).$$

Let us write

$$(n_r{}^2 - 1) = (n_r{}^2 - 1)_{\xi_1} + (n_r{}^2 - 1)_{\xi_2}. \tag{18}$$

For left-circular light given by

$$\left.\begin{array}{l} x = E_0 \cos\omega t \\ y = E_0 \sin\omega t \end{array}\right\} \tag{19}$$

we have similarly,

$$(n_l{}^2 - 1)_{\xi_1} = \pi N \, (a_{\xi_1}')^2 \frac{e^2}{m} \frac{f}{(\omega_1{}^2 - \omega^2)} \tag{20}$$

and

$$(n_l{}^2 - 1)_{\xi_2} = \pi N \, (a_{\xi_2}')^2 \frac{e^2}{m} \frac{f}{(\omega_2{}^2 - \omega^2)}, \tag{21}$$

where

$$(a_{\xi_1}')^2 = (\alpha^2 + \beta^2)\, (1 + \cos\theta - \phi\sin\theta)$$

$$(a_{\xi_2}')^2 = (\alpha^2 + \beta^2)\, (1 - \cos\theta + \phi\sin\theta)$$

and

$$(n_l{}^2 - 1) = (n_l{}^2 - 1)_{\xi_1} + (n_l{}^2 - 1)_{\xi_2} \tag{22}$$

$$\therefore \quad (n_l{}^2 - n_r{}^2) = \pi N \frac{e^2}{m} f$$

$$\left[\frac{(a_{\xi_1}{}')^2 - (a_{\xi_1}{}'')^2}{\omega_1{}^2 - \omega^2} + \frac{(a_{\xi_2}{}')^2 - (a_{\xi_2}{}'')^2}{\omega_2{}^2 - \omega^2} \right] \tag{23}$$

where

$$(a_{\xi_1}{}')^2 - (a_{\xi_1}{}'')^2 = -2(a^2 + \beta^2)\,\phi \sin \theta$$

$$(a_{\xi_2}{}')^2 - (a_{\xi_2}{}'')^2 = 2(a^2 + \beta^2)\,\phi \sin \theta.$$

It will be noticed that the numerators of the two terms of (23) are equal in magnitude but opposite in sign, and this is in conformity with the summation rule of Kuhn's which states that the sum of the numerators determining the contributions of the different absorption frequencies to the rotatory power should vanish. Putting $(n_l + n_r) = 2\bar{n}$ in (23), we get

$$2\bar{n}(n_l - n_r) = 2\pi N \frac{e^2}{m} f (a^2 + \beta^2)\,\phi \sin \theta \left[\frac{1}{\omega_2{}^2 - \omega^2} - \frac{1}{\omega_1{}^2 - \omega^2} \right]. \tag{26}$$

Let

$$\left. \begin{array}{l} \omega_1{}^2 = \omega_0{}^2 + 2\pi^2 \epsilon \\[4pt] \omega_2{}^2 = \omega_0{}^2 - 2\pi^2 \epsilon \end{array} \right\}. \tag{27}$$

We shall assume that the resonators are feebly coupled, so that ϵ is a small quantity. Substituting $\phi = 2\pi\bar{n}d/\lambda$ and expressing in ν's $(= \omega/2\pi)$, we find that

$$(n_l - n_r) = \frac{Ne^2 d \sin \theta}{m\lambda} \left(\frac{a^2 + \beta^2}{2} \right) \frac{f\epsilon}{(\nu_0{}^2 - \nu^2)^2} \tag{29}$$

neglecting $\epsilon^2/4$ in the denominator.

Hence, the rotation per unit length

$$\rho = \frac{\pi}{\lambda}(n_l - n_r) = \frac{\pi N e^2 d \sin \theta}{m\lambda^2} \left(\frac{a^2 + \beta^2}{2} \right) \frac{f\epsilon}{(\nu_0{}^2 - \nu^2)^2} \tag{30}$$

$$= \frac{A_0 \lambda^2}{(\lambda^2 - \lambda_0{}^2)^2}, \tag{31}$$

where

$$A_0 = \frac{\pi N e^2 d \sin \theta \, \lambda_0{}^4}{mc^4} \left(\frac{a^2 + \beta^2}{2} \right) f\epsilon.$$

If, more generally, we assign several resonators having different frequencies of vibration to each SiO_2 unit, then, assuming that the resonance interaction

between identical resonators in the successive units predominates, it can easily be shown that

$$\rho = \sum_k \frac{A_k \lambda^2}{(\lambda^2 - \lambda_k^2)^2} \tag{32}$$

The ordinary refractive index along the optic axis is given by the relation

$$(n_\omega^2 - 1) = \tfrac{1}{2}\left[(n_l^2 - 1) + (n_r^2 - 1)\right]$$

$$= \pi N \frac{e^2}{m} (\alpha^2 + \beta^2) f \left[\frac{1 + \cos\theta}{(\omega_1^2 - \omega^2)} + \frac{1 - \cos\theta}{(\omega_2^2 - \omega^2)}\right]$$

$$= 4\pi N \frac{e^2}{m} \frac{f\left(\dfrac{\alpha^2 + \beta^2}{2}\right)}{(\omega_0^2 - \omega^2)} \tag{33}$$

approximately, assuming that $\omega_1 \approx \omega_2$. Thus, we notice that if the coupling between the neighbours is feeble, the splitting of the frequency manifests itself only in a second order effect like optical activity and not in a grosser effect like refraction.

Propagation Normal to the Optic Axis.—The theory of propagation of light in an optically active birefringent medium for directions inclined to the optic axis has been dealt with by various workers (*vide* Pockels, 1906). Along such directions, two similar elliptically polarised waves with opposite senses of rotation and lying crossed to each other (*i.e.*, the major axis of one falling on the minor axis of the other) travel unchanged. The axes of the ellipses coincide with the principal planes. If ρ is the rotatory power along any direction and δ the phase difference due to birefringence alone (if $\rho = 0$), then the actual phase difference per unit length between the two elliptic waves is given by

$$\Delta = [\delta^2 + (2\rho)^2]^{\frac{1}{2}} \tag{34}$$

and the ratio of the axes

$$\chi = \left(\frac{2\rho}{\delta}\right). \tag{35}$$

Proceeding in the same manner as before, approximate expressions for the refractive indices of the two ellipses may be derived. We shall base our arguments on the same compound resonator which was considered previously.

Let a right-rotating ellipse given by

$$x = E_0 \cos \omega t$$
$$z = -\left(\frac{2\rho}{\delta}\right) E_0 \sin \omega t \qquad \Bigg\}$$

(36)

be incident along the Y axis.

$$\therefore F_1 = feE_0 \left[a \cos \omega t - \left(\frac{2\rho}{\delta}\right) \gamma \sin \omega t \right]$$

(37)

and

$$F_2 = feE_0 \left[(a \cos \theta - \beta \sin \theta) \cos (\omega t - \psi_y) - \left(\frac{2\rho}{\delta}\right) \gamma \right.$$
$$\left. \sin (\omega t - \psi_y) \right]$$

(38)

where $\psi_y = \frac{2\pi \bar{n} p_y}{\lambda}$, where $\bar{n}$ is the mean refractive index and p_y the distance between the resonators as measured along the Y axis.

$$\therefore R_{\xi_1} = \frac{feE_0}{\sqrt{2}} \left[\left\{ a (1 + \cos \theta) - \beta \sin\theta + \psi_y \gamma \left(\frac{2\rho}{\delta}\right) \right\} \cos \omega t \right.$$
$$\left. + \left\{ \psi_y a \cos \theta - \psi_y \beta \sin \theta - 2\gamma \left(\frac{2\rho}{\delta}\right) \right\} \sin \omega t \right].$$

(39)

Therefore the moment induced m_y

$$= \tfrac{1}{2} \left[a^2 (1 + \cos \theta)^2 + \beta^2 \sin^2 \theta - 2a\beta \sin \theta (1 + \cos \theta) \right.$$
$$\left. + 2\psi_y \left(\frac{2\rho}{\delta}\right) a\gamma (1 - \cos\theta) + 2\psi_y \left(\frac{2\rho}{\delta}\right) \beta\gamma \sin\theta \right]$$
$$f \frac{e^2}{m} \frac{E_0}{(\omega_1{}^2 - \omega^2)}$$

(40)

neglecting higher powers of ψ_y and $\left(\frac{2\rho}{\delta}\right)$. If, on the other hand, we consider a similar ellipse given by

$$y = E_0 \cos \omega t$$
$$z = -\left(\frac{2\rho}{\delta}\right) E_0 \sin \omega t \qquad \Bigg\}$$

(41)

propagated along the X direction, the moment

$$m_x = \tfrac{1}{2} \left[a^2 \sin^2 \theta + \beta^2 (1 + \cos \theta)^2 + 2a\beta \sin \theta (1 + \cos \theta) \right.$$
$$\left. - 2\psi_x \left(\frac{2\rho}{\delta}\right) a\gamma \sin\theta + 2\psi_x \left(\frac{2\rho}{\delta}\right) \beta\gamma (1 - \cos\theta) \right] f \frac{e^2}{m}$$
$$\frac{E_0}{\omega_1{}^2 - \omega^2}$$

(42)

where $\psi_x = \dfrac{2\pi \bar{n} p_x}{\lambda}$, where p_x is the distance between the resonators as measured along the X axis. Without any loss of generality, we may choose the axes suitably so that $\psi_x = \psi_y = \psi$. Since the successive compound resonators are situated about a threefold axis of symmetry, the mean polarisability per unit volume is

$$\frac{N'(m_x + m_y)}{2E_0} = \frac{N(m_x + m_y)}{4E_0},$$

where N and N′ have the same significance as before.

$$\therefore \quad (n_r^2 - 1)_{\xi_1} = 4\pi N' \frac{(m_x + m_y)}{2E_0} \tag{43}$$

$$= \pi N (a_{\xi_1}{}')^2 \frac{e^2}{m} \frac{f}{(\omega_1^2 - \omega^2)}, \tag{44}$$

where

$$(a_{\xi_1}{}')^2 = \left[(\alpha^2 + \beta^2)(1 + \cos\theta) + \psi \left(\frac{2\rho}{\delta}\right) \Gamma\right],$$

where

$$\Gamma = \alpha\gamma(1 - \cos\theta - \sin\theta) + \beta\gamma(1 - \cos\theta + \sin\theta).$$

In a similar manner,

$$(n_r^2 - 1)_{\xi_2} = \pi N (a_{\xi_2}{}')^2 \frac{e^2}{m} \frac{f}{(\omega_2^2 - \omega^2)}, \tag{45}$$

where

$$(a_{\xi_2}{}')^2 = \left[(\alpha^2 + \beta^2)(1 - \cos\theta) - \psi \left(\frac{2\rho}{\delta}\right) \Gamma\right].$$

For the crossed left-rotating ellipse given by

$$\left. \begin{array}{rl} x \ (\text{or } y) &= \left(\dfrac{2\rho}{\delta}\right) E_0 \cos\omega t \\[2mm] z \quad\ \ &= E_0 \sin\omega t \end{array} \right\} \tag{46}$$

we have

$$(n_l^2 - 1)_{\xi_1} = \pi N (a_{\xi_1}{}')^2 \frac{e^2}{m} \frac{f}{(\omega_1^2 - \omega^2)} \tag{47}$$

and

$$(n_l^2 - 1)_{\xi_2} = \pi N (a_{\xi_2}{}')^2 \frac{e^2}{m} \frac{f}{(\omega_2^2 - \omega^2)}, \tag{48}$$

where

$$(a_{\xi_1}{}')^2 = \left[4\gamma^2 - \psi \left(\frac{2\rho}{\delta}\right) \Gamma\right]$$

A10

and

$$(a_{\xi_2}')^2 = \left[\psi\left(\frac{2\rho}{\delta}\right)\Gamma\right]$$

$$\therefore \quad (n_l^2 - n_r^2) = (n_l^2 - n_r^2)_{\xi_1} + (n_l^2 - n_r^2)_{\xi_2} \tag{49}$$

$$= \pi N \frac{e^2}{m} f \left[\frac{(a_{\xi_1}')^2 - (a_{\xi_1}')^2}{\omega_1^2 - \omega^2} + \frac{(a_{\xi_2}')^2 - (a_{\xi_2}')^2}{\omega_2^2 - \omega^2}\right], \tag{50}$$

where

$$(a_{\xi_1}')^2 - (a_{\xi_1}')^2 = \left[4\gamma^2 - (\alpha^2 + \beta^2)(1 + \cos\theta) - 2\psi\left(\frac{2\rho}{\delta}\right)\Gamma\right]$$

and

$$(a_{\xi_2}')^2 - (a_{\xi_2}')^2 = \left[-(\alpha^2 + \beta^2)(1 - \cos\theta) + 2\psi\left(\frac{2\rho}{\delta}\right)\Gamma\right].$$

Now,

$$\frac{2\pi}{\lambda}(n_l^2 - n_r^2) = 2\bar{n}\,\Delta = 2\bar{n}\,[\delta^2 + (2\rho)^2]^{\frac{1}{2}} \qquad \text{from (34)}$$

$$= 2\bar{n}\left[\delta + \frac{2\rho^2}{\delta}\right] \quad \text{approximately.} \tag{51}$$

From (50), $\frac{2\pi}{\lambda}(n_l^2 - n_r^2)$ may be written as two parts, say P and Q, where

$$P = \frac{2\pi}{\lambda}\pi N \frac{e^2}{m} f \left[\frac{4\gamma^2 - (\alpha^2 + \beta^2)(1 + \cos\theta)}{\omega_1^2 - \omega^2}\right.$$

$$\left. - \frac{(\alpha^2 + \beta^2)(1 - \cos\theta)}{\omega_2^2 - \omega^2}\right] \tag{52}$$

and

$$Q = \frac{2\pi}{\lambda} \cdot \pi N \frac{e^2}{m} f \left[2\psi\left(\frac{2\rho}{\delta}\right)\Gamma\right] \left[\frac{1}{(\omega_2^2 - \omega^2)} - \frac{1}{(\omega_1^2 - \omega^2)}\right]. \tag{53}$$

P could be approximately written as

$$\frac{2\pi}{\lambda}\pi N \frac{e^2}{m} f \left[\frac{4\gamma^2 - 2(\alpha^2 + \beta^2)}{\omega_0^2 - \omega^2}\right] \tag{54}$$

assuming that $\omega_1 \approx \omega_2$.

Now, in the above model, it can easily be seen that the expression for the extraordinary refractive index is

$$n_\epsilon^2 - 1 = 4\pi N \frac{e^2}{m} \frac{f\gamma^2}{(\omega_0^2 - \omega^2)} \tag{55}$$

while that for the ordinary index is (33).

Hence

$$P = \frac{2\pi}{\lambda}(n_\epsilon^2 - n_\omega^2) = 2\bar{n}\,\delta. \tag{56}$$

Thus from (51) and (56), we find that we may equate

$$Q = 2\bar{n}\left(\frac{2\rho^2}{\delta}\right).\tag{57}$$

Comparing the values of Q from (53) and (57) and substituing for ψ, we get,

$$\rho = \frac{4\pi^3\,Ne^2p\,\Gamma f}{m\lambda^2}\left[\frac{1}{\omega_2{}^2 - \omega^2} - \frac{1}{\omega_1{}^2 - \omega^2}\right].\tag{58}$$

Here again we notice that Kuhn's summation rule is fulfilled. Substituting $(\omega_1{}^2 - \omega_2{}^2) = 4\pi^2\epsilon$, and expressing in terms of ν's, we get

$$\rho = \frac{\pi Ne^2\,p\,\Gamma f\epsilon}{m\lambda^2\,(\nu_0{}^2 - \nu^2)^2} = \frac{B_0\,\lambda^2}{(\lambda^2 - \lambda_0{}^2)^2},\tag{59}$$

where

$$B_0 = \frac{\pi Ne^2p\lambda_0{}^4\Gamma\,f\epsilon}{mc^4}.$$

We thus arrive at the interesting result that the rotatory dispersion formulæ normal to and along the optic axis are identical in form. This is in conformity with the observations of Bruhat and Weil.

4. Evaluation of the Magnitude of the Splitting of the Characteristic Frequency

It will be noticed that, throughout, in the derivation of the formulæ for the rotatory power, the assumption has been made that the resonators are feebly coupled, so that ϵ is taken to be a small quantity. It would, therefore, be of great interest to make an actual estimation of the extent of the splitting of the characteristic frequency of each resonator. In fact, from the known data for the refraction and the rotation, such an estimation is possible.

It has been shown in an earlier paper by the present author, that the ordinary dispersion of quartz along the optic axis can be fitted up fairly well by a one-term formula of the Sellemeyer-Drude type involving the characteristic wavelength appearing in (1). The formula is

$$n_\omega{}^2 - 1 = \frac{1\cdot35\lambda^2}{\lambda^2 - (0\cdot0926283)^2}.\tag{60}$$

Now, in the model which we have just considered, the expressions for the rotatory power and the refraction are respectively:

$$\rho = \frac{\pi Ne^2d\sin\theta\,\lambda_0{}^4\,F\epsilon}{mc^4}\cdot\frac{\lambda^2}{(\lambda^2 - \lambda_0{}^2)^2}\tag{31 \textit{a}}$$

where $F = \frac{1}{2}(\alpha^2 + \beta^2)f$, ρ is expressed in radians per cm. and λ in cm.,

and $n_\omega^2 - 1 = \dfrac{Ne^2 \lambda_0^2 F}{m\pi c^2} \dfrac{\lambda^2}{(\lambda^2 - \lambda_0^2)}.$　　　　　　　　(33 a)

It should be pointed out here that the constant occurring in the numerator of formula (60) is independent of the units in which λ is expressed. On the other hand, that appearing in the rotatory dispersion formula (1) is only valid when λ is expressed in microns.

If we assume that the characteristic wavelength λ_0 of each resonator has the same value as that used in (1), then from (60) and (33 a) we obtain the relation

$$\frac{Ne^2 \lambda_0^2 F}{m\pi c^2} = 1 \cdot 35. \qquad (61)$$

For α-quartz, the average volume occupied by a single SiO_2 triplet has been calculated to be $37 \cdot 4 \times 10^{-24}$ c.c. (Sosman, 1927).

$$\therefore N = 2 \cdot 68 \times 10^{22} \text{ resonators per c.c.}$$

We also have $e = 4 \cdot 8 \times 10^{-10}$ e.s.u.

$$\frac{e}{m} = 5 \cdot 3 \times 10^{17} \text{ e.s.u.}$$

$$\lambda_0 = 0 \cdot 926283 \times 10^{-5}$$

$$c = 3 \times 10^{10} \text{ cm./sec.}$$

and hence from (61), we find that

$$F = 6 \cdot 5 \qquad (62)$$

From the X-ray data, the parameter c of the unit cell of α-quartz is found to be $5 \cdot 393$ A.U. Therefore,

$$d = c/3 = 1.8 \times 10^{-8} \text{ cm.}$$

Also,

$$\sin \theta = \sin 120° = \sqrt{3}/2$$

$$\lambda_0^4 = 0 \cdot 736 \times 10^{-20}$$

$$\frac{\lambda^2}{(\lambda^2 - \lambda_0^2)^2} = 3 \cdot 027 \times 10^8, \text{ for } \lambda = 5893 \times 10^{-8} \text{ cm.}$$

For $\lambda = 5893 \times 10^{-8}$ cm. $\rho = 217°$ per cm. $= 217/57 \cdot 3$ radians per cm. Hence, from (31 a),

$$\epsilon = 6 \cdot 36 \times 10^{29}$$

$$= \nu_1{}^2 - \nu_2{}^2 = 2\nu_0 \, \delta\nu_0$$

$$= \frac{2c^2}{\lambda_0{}^3} \, \delta\lambda_0 \text{ (numerically)}$$

$$\therefore \ \delta\lambda_0 = 28 \text{ A.U.}$$

We thus see that the characteristic wavelength λ_0 of each resonator is split into a close doublet, λ_1 and λ_2, which differ by 28 A.U. as a result of the coupling between the neighbouring resonators. It is gratifying to find that the assumption that the coupling constant is small is supported by the above calculation.

5. THE RATIO $\rho_\perp/\rho_{||}$

We shall now proceed to evaluate the birefringence and the ratio of the rotatory powers normal to and along the optic axis. The expressions for the two refractive indices are given by (33) and (55) respectively, while

$$\frac{\rho_\perp}{\rho_{||}} = \frac{B_0}{A_0} = \frac{p\,[\alpha\gamma\,(1 - \cos\theta - \sin\theta) + \beta\gamma\,(1 - \cos\theta + \sin\theta)]}{d \cdot \frac{1}{2}\,(\alpha^2 + \beta^2)\sin\theta}.$$

$$(62)$$

The value of the various constants occurring in these formulæ may be obtained from the X-ray data for quartz.

Assuming that the resonators be exactly along the line joining the oxygens in each SiO_2 triplet, it is readily shown that they are inclined at an angle of about 64° 46′ to the vertical Z-axis. Fig. 1 (b) shows the projection of a compound resonator formed by the two SiO_2 units A and B, on the X-Y plane. The axes of X and Y have been chosen to be equally inclined to AB, since in such a case, ψ_x and ψ_y occurring in (40) and (42) would be equal. As has already been pointed out, the successive compound resonators are situated about a threefold axis of symmetry and hence it is enough if we just consider the unit AB for our calculations. The direction cosines of the resonator A are found to be $\alpha = -0 \cdot 8738$, $\beta = 0 \cdot 2342$ and $\gamma = 0 \cdot 4263$. When these values are substituted in the expressions for the refractive indices, it is found that the birefringence is not exactly accounted for. Hence the values have been altered to $-0 \cdot 8$, $0 \cdot 1523$ and $0 \cdot 5812$ respectively, in which case the calculated birefringence agrees exactly with the experimental value.

Silicons at levels
0, 3c/9, 6c/9

Oxygens at levels
c/9, 2c/9, 4c/9, 5c/9, 7c/9, 8c/9

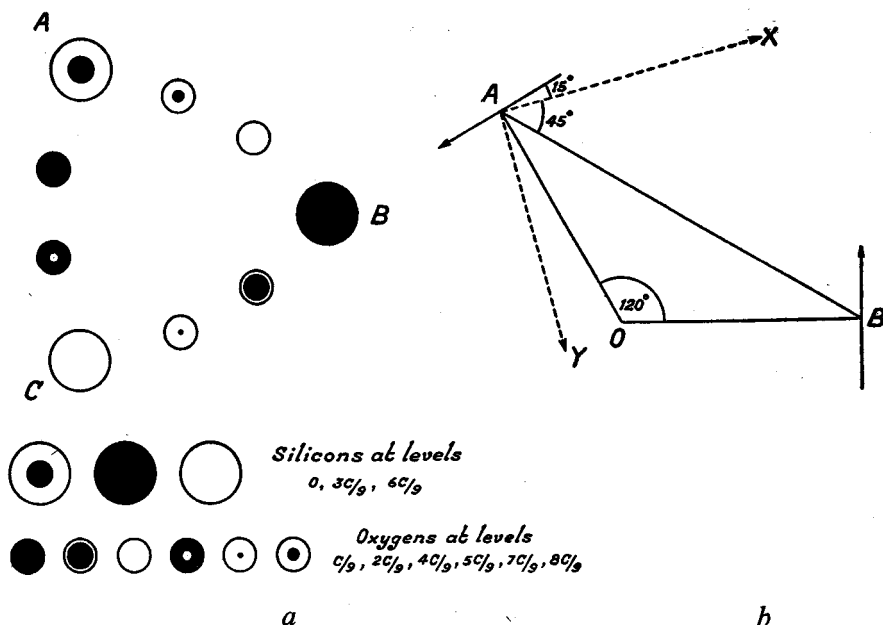*a*   *b*

Fig. 1. Projection of unit cell on basal plane

From the X-ray data, it is readily shown that p $(= \text{AB}/\sqrt{2})$ and d are $2 \cdot 8$ A.U. and $1 \cdot 8$ A.U. respectively. We then obtain the result

$$\frac{\rho_{\perp}}{\rho_{\parallel}} = -0 \cdot 5,$$

which differs but slightly from the observations of Bruhat and Weil.

6. Discussion of Results

We have seen how, by means of an elementary model, the rotatory dispersion of quartz, both along and transverse to the optic axis, can be explained in a simple manner. The model also accounts for the refractive dispersion of quartz quite satisfactorily. For, quartz is a unique substance in which the dispersion of $\rho_{\parallel}$, $\rho_{\perp}$*, n_{ω} and n_{ϵ} are all represented fairly well by means of a single absorption wavelength at about 926 A.U. (Chandrasekhar, 1952 a; Ramdas, 1952). Thus, the approximation involved in replacing each SiO_2 triplet by a single resonator is to a large extent justified.

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    * In an earlier paper, the present author (1952 b) had fitted a formula for $\rho_{\perp}$. This formula is incorrect as it is based on the preliminary observations of Bruhat and Grivet, the later and more accurate measurements of Bruhat and Weil having been inadvertently overlooked. The data of the latter authors establish clearly the fact that λ_0 is the same for $\rho_{\perp}$ and $\rho_{\parallel}$.

These are also certain general features about optical activity which emerge from this theory. First of all, we notice from (31) that ρ is proportional to $\sin \theta$. Hence, it follows that the sense of the rotation depends on the sign of θ. This leads to the result that the two enantiomorphous forms have opposite rotation. The refractive index, on the other hand, is independent of θ, and therefore, is the same for right and left-rotating quartz. Secondly we find that ρ is proportional to ϵ, the coupling constant. Thus, if the coupling vanishes, the rotation would be zero. This is in conformity with the well-known result of the coupled oscillator theory, that only coupled electrons contribute to the rotatory power. Thirdly, the rotation is proportional to the phase of the incident light wave. If the wavelength of the incident radiation is made very large compared to the interatomic dimensions, then the rotatory power would vanish. This also follows indirectly from the rotatory dispersion formula itself. In refraction, however, the phase does not come into consideration.

In view of the remarkable agreement of the formula (1) with the observed data for quartz, it appears that the idea that its optical activity arises as a result of the splitting of the characteristic frequency in the crystal structure is certainly justified. This is further supported by the fact that the magnitude of the splitting, as estimated from the known data for refraction and rotation, is very small, which is actually the assumption underlying the theory. In fact, such a model may be used, more generally, to give a simple explanation of the optical activity of crystals which are not active in the state of solution.

In conclusion, I record my sincere thanks to Prof. Sir C. V. Raman for the discussions I had with him during the course of this work.

7. SUMMARY

As a result of the interaction between the successive entities constituting the crystal, the spectroscopic behaviour of the individual units would be altered and it is found that this affords a ready explanation of the optical activity of quartz. Replacing each SiO_2 unit by a linear resonator of natural frequency ω_0, it is shown from simple considerations of symmetry, that ω_0 is split into two frequencies ω_1 and ω_2. By a classical discussion, it is demonstrated that this splitting gives rise to optical activity both along and transverse to the optic axis. The expression for the rotatory power is found to be of the form

$$\rho = k\lambda^2/(\lambda^2 - \lambda_0^2)^2$$

which fits remarkably well with the observed data for quartz. From the known values of refraction and rotation, the magnitude of the splitting has

been estimated to be 28 A.U., which supports the assumption underlying the theory that the resonators are feebly coupled. By assuming that the resonators lie approximately, though not exactly, along the line joining the oxygens in each SiO_2 triplet, it has been possible to quantitatively account for the birefringence and the negative rotation transverse to the optic axis.

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