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Correlating the Optical Rotation of α-Quartz with a Skew Matrix of a Dielectric Tensor

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Abstract

A beam of polarized light propagating along the helical axis of α-quartz interacts with $SiO_{4/2}$ groups consecutively. When a skew matrix of a resultant dielectric tensor is compared to a skew matrix of a rotation matrix, the polarizability components of an $SiO_{4/2}$ group, with two sets of results, may be derived since the specific rotation along the helical axis is known for 5892.9 Å light at 293 K. Both sets have the same mean value for the components. The mean is close to an empirical result based on the bond refractivity of Si-O. In comparison with the optical rotation sign (+ or −) along the optic axis, an opposite rotation sign is derived along the directions perpendicular to both the optic axis and any diad axis. In α-quartz, the inactive directions 33.83° from its optic axis are interpreted. The diad-axis directions are predicted to be inactive directions. Bunn's empirical formula is interpreted.

Introduction

Barron (1975) suggested that optical-rotation components can be isolated in the study of crystals. α-quartz was chosen for a theoretical study of the relationship between its helical structure and its rotatory properties. Because of the birefringence, it is difficult to determine experimentally the rotatory power of α-quartz in sections parallel to its optic axis (Wahlstrom, 1979). Since the specific rotation along the optical axis of α-quartz was known, the polarizability components of an $SiO_{4/2}$ group in a left-handed quartz with + optical rotation can be derived with the assumption that there is a relationship between the skew matrix of a resultant dielectric tensor and the skew matrix of a rotation matrix. Some inactive directions in α-quartz can be interpreted or predicted based on its structure and this assumption. Wahlstrom (1979) predicted that 'light traveling at right angles to the optic axis is rotated but in an opposite sense to that propagated along the optic axis'. The same proposal for helix optical activity was also mentioned by Barron (1982, p. 285). Based on the structure of α-quartz, the rotation sign changes as predicted.

The specific rotations along the two directions perpendicular to the optic axis were calculated. Note that the proportionality between the rotation angle and the thickness along the helical axis can also be interpreted through the multiplication of rotation matrices. Bunn's empirical formula (Bunn, 1961), used to calculate the directional polarizabilities of a molecule in order to optimize the molecular orienta-

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tion in a crystal cell (Chen, Schug & Viers, 1986), is briefly interpreted in this paper.

Theoretically, optical rotation is interpreted as the phase difference in Fresnel's equation. Circular differential refraction refers to the method where both refractive indices of left and right circular polarized light waves are expanded with multipole tensors (see Barron, 1982, p. 242). A more basic method is the refringent-scattering approach (see Barron, 1982). However, both methods are complicated and approximate since only part of the multiple tensors are used. Empirically, there are chirality functions to calculate the optical rotation (see Mason, 1982; Barron, 1982, p. 220).

The space group of (−)-α-quartz is $P3_121$ and that of (+)-α-quartz is $P3_221$. A screw triad axis in the crystal is an optic axis **Z**. Rotation diad axes are perpendicular to the optic axis (see Fig. 1). The crystal parameters in a hexagonal coordinate system are $a = 4.914$ and $c = 5.409$ Å (Boisen & Gibbs, 1985). In a unit cell, there are three $SiO_{4/2}$ groups connected by a screw triad axis.

Theory

For a beam of incident plane-polarized light, assume that an optical rotation angle is a dihedral angle along its traveling direction from an electric field strength **E** to a displacement **D**. Assume that the dihedral angle can be represented by the angle between **D** and **E**. A rotation matrix may be considered as a possible transformation matrix between the two vectors.

A resultant dielectric tensor is also the coefficient of the linear relationship between **D** and **E** if the intensity of the light is weak. The resultant dielectric tensor is a product of group dielectric tensors. Each of the group tensors consists of a polarizability tensor of an $SiO_{4/2}$ group in a unit cell. The resultant dielectric tensor is composed of a symmetric matrix and a skew matrix. Through the comparison between the skew part of the resultant dielectric tensor and the skew part of the rotation matrix of **E**, the relationship between the polarizability components of $SiO_{4/2}$ and the rotation angle may be obtained. The group-polarizability components are thus derived, since the rotation angle along the helical axis is known and the polarizability components of the crystal are obtained from the refractive indices of the crystal through the Lorenz-Lorentz equation.

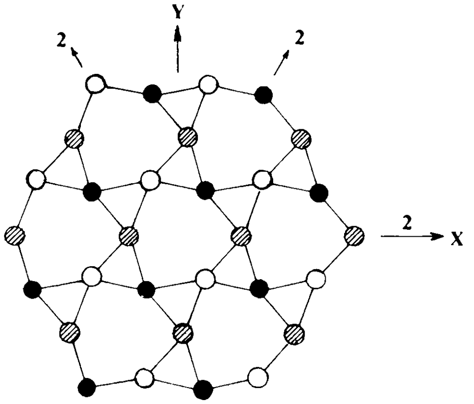

Fig. 1. Projection of three layers of Si atoms along the optic axis **Z**. Heights indicated by shading. (**X**, **Y**, **Z**) in a right-handed system (Gibbs, 1926).

I. *Polarizability tensors of* $SiO_{4/2}$ *groups*

The Cartesian coordinate system as shown by Kleinman & Spitzer (1962) in Fig. 1 of their paper is chosen for a crystal cell of (+)-α-quartz with a left-handed structure such that **Z** is the optic axis (the screw triad axis); **X** is a diad (twofold) axis of the crystal. **X**, **Y** and **Z** are in a right-handed system.

Each $SiO_{4/2}$ group is in a tetrahedral configuration with an O atom at each of the four vertices and an Si atom at the center. Three quarter-turn inversion axes of an $SiO_{4/2}$ tetrahedron were chosen as a right-handed Cartesian basis (**i**, **j**, **k**) with Si at the origin. **i** is a unit vector along a diad axis in an outward direction from a screw triad axis. **k** deviates from **Z** by 16.31° clockwise as viewed along (−**i**). The value 16.31° was calculated based on the coordinates of the O and the Si atoms (Julian & Lane, 1968). Suppose that α_{ii} ($i = 1, 2, 3$) are the polarizability components of each $SiO_{4/2}$ group with respect to its own basis (**i**, **j**, **k**), (**i**′, **j**′, **k**′) or (**i**″, **j**″, **k**″). The polarizability matrices of the three $SiO_{4/2}$ groups with respect to their own coordinate systems are in the same form,

$$\alpha_{ii} = \begin{bmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{22} & 0 \\ 0 & 0 & \alpha_{33} \end{bmatrix}$$

$$[i = 1, 2, 3; \text{ basis } (\mathbf{i}, \mathbf{j}, \mathbf{k}), (\mathbf{i}', \mathbf{j}', \mathbf{k}') \text{ or } (\mathbf{i}'', \mathbf{j}'', \mathbf{k}'')].$$

Through the orthogonal transformations, those bases are turned 16.31° counterclockwise as viewed along (−**i**), (−**i**′) or (−**i**″). The bases of these three groups are respectively changed to the right-handed Cartesian basis (**x**, **y**, **z**), (**x**′, **y**′, **z**′) or (**x**″, **y**″, **z**″), where **x** is **i**, **x**′ is **i**′, and **x**″ is **i**″. All the axes **z**, **z**′ and **z**″ are parallel to the axis **Z**. Among the three new bases, the basis (**x**, **y**, **z**) is parallel to the basis of the unit cell (**X**, **Y**, **Z**) such that **x**, **y** and **z** are parallel to **X**, **Y** and **Z**, respectively.

$$A_{ij} = \begin{bmatrix} \alpha_{11} & 0 & 0 \\ 0 & A_{22} & B \\ 0 & B & A_{33} \end{bmatrix}$$

$$[i, j = 1, 2, 3; \text{ basis } (\mathbf{x}, \mathbf{y}, \mathbf{z}), (\mathbf{x}', \mathbf{y}', \mathbf{z}') \text{ or } (\mathbf{x}'', \mathbf{y}'', \mathbf{z}'')],$$

where

$$A_{22} = \alpha_{22}\cos^2 16.31° + \alpha_{33}\sin^2 16.31°;$$

$$A_{33} = \alpha_{22}\sin^2 16.31° + \alpha_{33}\cos^2 16.31°;$$

$$B = -\alpha_{22}\cos 16.31° \sin 16.31° + \alpha_{33}\cos 16.31° \sin 16.31°.$$

Each of the bases (**x**, **y**, **z**), (**x**′, **y**′, **z**′) and (**x**″, **y**″, **z**″) was further converted to the basis of the crystal cell (**X**, **Y**, **Z**) by means of a new orthogonal transformation. A_{ij}, A'_{ij} and A''_{ij} are the three polarizability tensors of the three groups with respect to the basis of the unit cell (**X**, **Y**, **Z**). Since only the directions are important (**x**, **y**, **z**) and (**X**, **Y**, **Z**) can be treated as the same basis despite the displacement between their origins,

$$A'_{ij} = \begin{bmatrix} (\alpha_{11}+3A_{22})/4 & -3^{1/2}(\alpha_{11}-A_{22})/4 & -3^{1/2}B/2 \\ -3^{1/2}(\alpha_{11}-A_{22})/4 & (3\alpha_{11}+A_{22})/4 & -B/2 \\ -3^{1/2}B/2 & -B/2 & A_{33} \end{bmatrix}$$

[basis (**X**, **Y**, **Z**)];

$$A''_{ij} = \begin{bmatrix} (\alpha_{11}+3A_{22})/4 & 3^{1/2}(\alpha_{11}-A_{22})/4 & 3^{1/2}B/2 \\ 3^{1/2}(\alpha_{11}-A_{22})/4 & (3\alpha_{11}+A_{22})/4 & -B/2 \\ 3^{1/2}B/2 & -B/2 & A_{33} \end{bmatrix}$$

[basis (**X**, **Y**, **Z**)].

The tensor A'_{ij} in the basis (**X**, **Y**, **Z**) is the result of an orthogonal transformation of a tensor A_{ij} in the basis (**x**′, **y**′, **z**′) with a planar rotation angle $m = -120°$ through the basis turning clockwise around an unaltered axis **Z** as viewed along −**Z**. A''_{ij} in the basis (**X**, **Y**, **Z**) is the result of a transformation from A_{ij} in the basis (**x**″, **y**″, **z**″) with $m = 120°$,

$$\begin{bmatrix} \cos m & \sin m & 0 \\ -\sin m & \cos m & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \alpha_{11} & 0 & 0 \\ 0 & A_{22} & B \\ 0 & B & A_{33} \end{bmatrix} \begin{bmatrix} \cos m & -\sin m & 0 \\ \sin m & \cos m & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \left[\begin{matrix} \alpha_{11}\cos^2 m + A_{22}\sin^2 m \\ -\alpha_{11}\cos m \sin m + A_{22}\cos m \sin m \\ B\sin m \end{matrix}\right.$$

$$\left.\begin{matrix} -a_{11}\cos m \sin m + A_{22}\cos m \sin m & B\sin m \\ \alpha_{11}\sin^2 m + A_{22}\cos^2 m & B\cos m \\ B\cos m & A_{33} \end{matrix}\right]$$

$$= \begin{bmatrix} (\alpha_{11}+3A_{22})/4 & 3^{1/2}(\alpha_{11}-A_{22})/4 & 3^{1/2}B/2 \\ 3^{1/2}(\alpha_{11}-A_{22})/4 & (3\alpha_{11}+A_{22})/4 & -B/2 \\ 3^{1/2}B/2 & -B/2 & A_{33} \end{bmatrix} = A''_{ij}.$$

II. *A dielectric tensor and a rotation tensor*

The linear relationship between a displacement **D** and a field strength **E** is $D_i = \sum_j \varepsilon_{ij} E_j$ $(i, j = 1, 2, 3)$. The dielectric tensor ε_{ij} is $\delta_{ij} + 4\pi Nd\ A_{ij}$, $\delta_{ij} + 4\pi Nd\ A'_{ij}$ or $\delta_{ij} + 4\pi Nd\ A''_{ij}$ depending on which of the three $SiO_{4/2}$ groups in a unit cell is referred to. δ_{ij} is the Kronecker delta, N is Avogadro's constant, d is the density of α-quartz in mol ml^{-1}, A_{ij}, A'_{ij} and A''_{ij} are in ml group^{-1}.

While an incident beam of light travels along +**Z**, it passes through the three $SiO_{4/2}$ groups in a left-handed structure consecutively. It passes through the first group with dielectric tensor $\varepsilon_{lj}(1)$ and polarizability tensor A'_{lj} $(l, j = 1, 2, 3)$ and then passes through the second group with $\varepsilon_{kl}(2)$ and A_{kl} $(k, l = 1, 2, 3)$. The beam then meets the third group with $\varepsilon_{ik}(3)$ and A''_{ik} $(i, k = 1, 2, 3)$. The linear relationships are:

$$D_i = \sum_k \varepsilon_{ik}(3) D_k; \qquad D_k = \sum_l \varepsilon_{kl}(2) D_l;$$

$$D_l = \sum_j \varepsilon_{lj}(1) E_j.$$

Thus

$$\begin{aligned} D_i = \sum_j \varepsilon_{ij} E_j &= \sum_{k,l,j} \varepsilon_{ik}(3)\varepsilon_{kl}(2)\varepsilon_{lj}(1) E_j \\ &= \sum_{k,l,j} (\delta_{ik} + 4\pi Nd A''_{ik})(\delta_{kl} + 4\pi Nd A_{kl}) \\ &\quad \times (\delta_{lj} + 4\pi Nd A'_{lj}) E_j \\ &= \sum_j [s(\mathbf{Z})_{ij,\mathrm{sym}} + t(\mathbf{Z})_{ij,\mathrm{skew}}]\ E_j, \end{aligned} \tag{1}$$

where i, j, k, $l = 1$, 2, 3. ε_{ij} is a resultant dielectric tensor. $s(\mathbf{Z})_{ij,\mathrm{sym}}$ and $t(\mathbf{Z})_{ij,\mathrm{skew}}$ are respectively a symmetric matrix and a skew matrix of the dielectric tensor for a beam of light traveling along the +**Z** axis. The entries of an unsymmetrical dielectric tensor ε_{ij} are:

$$\begin{aligned} \varepsilon_{11} = {} & (1 + 4\pi Nd\alpha_{11})[1 + \pi Nd(\alpha_{11} + 3A_{22})]^2 \\ & - 3(\pi Nd)^2(\alpha_{11} - A_{22})^2(1 + 4\pi NdA_{22}) \\ & - 48(\pi Nd)^3 B^2(\alpha_{11} - A_{22}) \\ & - 12(\pi Nd)^2 B^2(1 + 4\pi NdA_{33}); \end{aligned}$$

$$\begin{aligned} \varepsilon_{22} = {} & (1 + 4\pi NdA_{22})[1 + \pi Nd(3\alpha_{11} + A_{22})]^2 \\ & - 3(\pi Nd)^2(\alpha_{11} - A_{22})^2(1 + 4\pi Nd\alpha_{11}) \\ & - 8(\pi NdB)^2[1 + \pi Nd(3\alpha_{11} + A_{22})] - 4(\pi NdB)^2 \\ & \times \{2[1 + \pi Nd(3\alpha_{11} + A_{22})] - (1 + 4\pi NdA_{33})\}; \end{aligned}$$

$$\begin{aligned} \varepsilon_{33} = {} & (1 + 4\pi Nd\alpha_{33})^3 - 16(\pi NdB)^2(1 + 4\pi NdA_{33}) \\ & + 4(\pi NdB)^2(1 + 4\pi NdA_{22}) \\ & - 12(\pi NdB)^2(1 + 4\pi Nd\alpha_{11}); \end{aligned}$$

$$\begin{aligned} \varepsilon_{21} = -\varepsilon_{12} = {} & 2 \times 3^{1/2}(\pi Nd)^2(\alpha_{11} - A_{22})^2 \\ & \times [1 + 2\pi Nd(\alpha_{11} + A_{22})] \\ & + 4 \times 3^{1/2}(\pi Nd)^2 B^2 \\ & \times [4\pi Nd(A_{33} - A_{22} - \alpha_{11}) - 1]; \end{aligned}$$

$$\begin{aligned} \varepsilon_{31} = -\varepsilon_{13} = {} & 8 \times 3^{1/2}(\pi Nd)^2 B[\alpha_{11} + A_{22} - 2A_{33} \\ & + \pi Nd(\alpha_{11}^2 - A_{22}^2 - 4A_{33}^2 + 4\alpha_{11}A_{22} \\ & - \alpha_{11}A_{33} + A_{22}A_{33} + 2B^2)]; \end{aligned}$$

$$\varepsilon_{32}=\varepsilon_{23}=-8(\pi Nd)^3B(3\alpha_{11}^2+A_{22}^2+4A_{33}^2\\ -6\alpha_{11}A_{33}-2A_{22}A_{33}-2B^2).$$

The entries of $t(\mathbf{Z})_{ij,\mathrm{skew}}$ are

$$t(\mathbf{Z})_{ij,\mathrm{skew}}=\begin{bmatrix}0 & -t_{21} & -t_{31}\\ t_{21} & 0 & 0\\ t_{31} & 0 & 0\end{bmatrix},$$

where $t_{21}=\varepsilon_{21}$; $t_{31}=\varepsilon_{31}$. The entries of the symmetric part $s(\mathbf{Z})_{ij,\mathrm{sym}}$ are

$$s(\mathbf{Z})_{ij,\mathrm{sym}}=\begin{bmatrix}\varepsilon_{11} & 0 & 0\\ 0 & \varepsilon_{22} & \varepsilon_{32}\\ 0 & \varepsilon_{32} & \varepsilon_{33}\end{bmatrix}.$$

It may be assumed that the direction change from **E** to **D** is mainly due to the skew matrix, $t(\mathbf{Z})_{ij,\mathrm{skew}}$. Therefore, we compare only the skew part of the dielectric tensor with the skew matrix of a + rotatory matrix,

$$\begin{bmatrix}0 & \sin\Phi & 0\\ -\sin\Phi & 0 & 0\\ 0 & 0 & 0\end{bmatrix} \quad\text{and}\quad \begin{bmatrix}\cos\Phi & \sin\Phi & 0\\ -\sin\Phi & \cos\Phi & 0\\ 0 & 0 & 1\end{bmatrix}.$$

and neglect the contribution due to the symmetric part. The positivity of the angle Φ means dextrorotatory when viewed along $-\mathbf{Z}$. If the absolute value of t_{21} is not larger than 1, let us assume that

$$t_{21}=-\sin\Phi, \tag{2}$$

where

$$\Phi=21.724^\circ\,\mathrm{mm}^{-1}\times5.409\times10^{-7}\,\mathrm{mm}=1.175\times10^{-5\circ}$$

is a dextrorotatory angle. The value $21.724^\circ\,\mathrm{mm}^{-1}$ along the optic axis for the plane-polarized light with the wavelength 5892.9 Å at 293 K was obtained from the *International Critical Tables of Numerical Data, Physics, Chemistry and Technology* (1929). The density of α-quartz, $d=0.04404\,\mathrm{mol\,ml}^{-1}$, was calculated from the parameters of the unit cell, the number of groups in the unit cell and the atomic weights of silicon and oxygen. Equation (2) is the relationship between an off-diagonal entry in a rotation matrix and the corresponding entry in a skew part of a dielectric tensor.

III. *The polarizability components of a group*

The average $\langle A_{ij}\rangle$ of A_{ij}, A'_{ij} and A''_{ij} as shown below is a tensor with three principal polarizabilities of α-quartz.

$$\langle A_{ij}\rangle=N\begin{bmatrix}(\alpha_{11}+A_{22})/2 & 0 & 0\\ 0 & (\alpha_{11}+A_{22})/2 & 0\\ 0 & 0 & A_{33}\end{bmatrix}. \tag{3}$$

The refractive indices of α-quartz are 1.544246 (ordinary index) and 1.553355 (extraordinary index) at 291 K for light with wavelength 5892.9 Å (*International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, p. 341). The principal molar polarizabilities of α-quartz, derived from these refractive indices through the Lorenz-Lorenz formula, are 1.7119 and $1.7356\,\mathrm{ml\,mol}^{-1}$. They are respectively equal to the entries of the molar polarizabilities in (3),

$$N(\alpha_{11}+A_{22})/2=1.7119\,\mathrm{ml\,mol}^{-1}, \tag{4}$$

$$NA_{33}=1.7356\,\mathrm{ml\,mol}^{-1}. \tag{5}$$

From (2), (4) and (5), two sets of solutions were obtained from a quadratic equation. The first set is $\alpha_{11}=2.829\times10^{-30}$, $\alpha_{22}=2.854\times10^{-30}$, $\alpha_{33}=2.884\times10^{-30}$, while the second set is $\alpha_{11}=2.886\times10^{-30}$, $\alpha_{22}=2.792\times10^{-30}$, $\alpha_{33}=2.890\times10^{-30}\,\mathrm{m}^3\,\mathrm{group}^{-1}$. Both sets have the mean value $\langle\alpha_{ii}\rangle=2.856\times10^{-30}\,\mathrm{m}^3\,\mathrm{group}^{-1}$. The mean value is close to an empirical result based on bond refractivity of Si-O, 1.80 (Xu, 1978). The refractivity of an $\mathrm{SiO}_{4/2}$ group is $R=1.80\times4=7.20\,\mathrm{ml\,mol}^{-1}$. Since $R=4\pi N\alpha/3$, the empirical polarizability α is $2.85\times10^{-30}\,\mathrm{m}^3\,\mathrm{group}^{-1}$. The mean value $\langle\alpha_{ii}\rangle$ of α_{11}, α_{22} and α_{33} is close to the empirical result.

IV. *The rotation diad axes are the inactive directions*

Direction **X** is a diad axis. When a beam of light travels along $+\mathbf{X}$, it meets two groups with polarizability tensors A'_{kl} and A''_{ik} simultaneously. Then, the light passes a group with polarizability tensor A_{lj}. Since the resultant tensor of A'_{kl} and A''_{ik} is a diagonal matrix and A_{lj} is also a diagonal matrix, the product of the two diagonal matrices is a diagonal matrix. The off-diagonal entries are zeros. Since $\sin\Phi=0$ (main value: $\Phi=0$), direction **X** is an inactive direction. The three diad axes connected by a screw triad axis are the inactive directions.

V. *Interpretation of inactive directions* 33.83° *from* **Z**

The Cartesian coordinates of the three Si atoms and the O atoms in a unit cell of (+)-α-quartz with a left-handed helical structure are given by Julian & Lane (1968) and Kleinman & Spitzer (1962). The coordinates in a hexagonal coordinate system are given by Boisen & Gibbs (1985). When an incident beam of light travels along the normal direction of the coplane of the three Si atoms, the wave front of the plane-polarized light meets the three $\mathrm{SiO}_{4/2}$ groups simultaneously and the resultant molar polarizability tensor will be the average $\langle A_{ij}\rangle$ of the three tensors A_{ij}, A'_{ij} and A''_{ij}, as given in (3).

The resultant matrix is diagonal. The corresponding dielectric tensor $\varepsilon_{ij}=\delta_{ij}+4\pi Nd\ \langle A_{ij}\rangle$ is also diagonal. All the entries of its skew matrix are zeros. If the zero entry of the skew matrix is compared to the entry of a rotation matrix, then $\sin\Phi=0$ (main value: $\Phi=0$). Therefore, the normal direction $\mathbf{n}_1$

shown in Fig. 2 is an optically inactive direction. It is 42.0° from **Z**. The inactive direction was reported by Wahlstrom (1979) as 33.83° between **Z** and the normal direction $\mathbf{n}_2$ of a crystal cut sheet. The difference is less than 10°.

To obtain the value 42.0°, the Cartesian coordinates of the three Si atoms, $x_1 = 2.308$, $y_1 = 0.000$, $z_1 = 0.000$, $x_2 = -1.154$, $y_2 = 1.999$, $z_2 = -1.802$, and $x_3 = -1.154$, $y_3 = -1.999$, $z_3 = 1.802$ (Julian & Lane, 1968) are substituted in the coplane equation

$$\begin{vmatrix} X - x_1 & Y - y_1 & Z - z_1 \\ x_2 - x_1 & y_2 - y_1 & z_2 - z_1 \\ x_3 - x_1 & y_3 - y_1 & z_3 - z_1 \end{vmatrix} = 0.$$

Thus

$$(z_3 x_1 - z_3 x_3)\,Y + (x_1 y_2 - x_3 y_2) Z = 0$$

or

$$6.245\,Y + 6.926 Z = 0.$$

The above equation refers to a plane containing the origin and the **X** axis. The angle between **Y** and the coplane of the three Si atoms is $\tan^{-1}(-6.245/6.926) = -42.03°$. Therefore, the angle between **Z** and the normal direction of the coplane (the inactive direction) is 42.0° (absolute value, see Fig. 2).

Other inactive directions can also be predicted based on the assumption that the resultant dielectric tensors are symmetric.

VI. *Rotation angle and thickness*

The method meets the proportional requirement between the rotation angle and the thickness of a cut sheet. Assume that the beam of plane-polarized light is rotated by Φ (°) as it travels through a unit-cell length. If the path length of the light in the medium is n times the unit-cell length and the rotation angle is $n\Phi$ then the rotation angle is proportional to the thickness of the cut sheet. Thus, the following relation should hold:

$$\begin{bmatrix} \cos\Phi & \sin\Phi & 0 \\ -\sin\Phi & \cos\Phi & 0 \\ 0 & 0 & 1 \end{bmatrix}^n = \begin{bmatrix} \cos n\Phi & \sin n\Phi & 0 \\ -\sin n\Phi & \cos n\Phi & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

The proof follows by induction. The relation is valid for $n = 1$. Assume it is valid for n. If it is valid for $n+1$ it must be valid for any natural number. Since

$$\begin{bmatrix} \cos\Phi & \sin\Phi & 0 \\ -\sin\Phi & \cos\Phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \cos n\Phi & \sin n\Phi & 0 \\ -\sin n\Phi & \cos n\Phi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} \cos n\Phi \cos\Phi - \sin n\Phi \sin\Phi & \cos n\Phi \sin\Phi + \sin n\Phi \cos\Phi & 0 \\ -\sin n\Phi \cos\Phi - \cos n\Phi \sin\Phi & -\sin n\Phi \sin\Phi + \cos n\Phi \cos\Phi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} \cos(n+1)\Phi & \sin(n+1)\Phi & 0 \\ -\sin(n+1)\Phi & \cos(n+1)\Phi & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

the relation is valid for $n+1$. Hence the rotation angle is proportional to the number of unit cells of α-quartz. That is, the rotation angle is proportional to the thickness of a cut sheet.

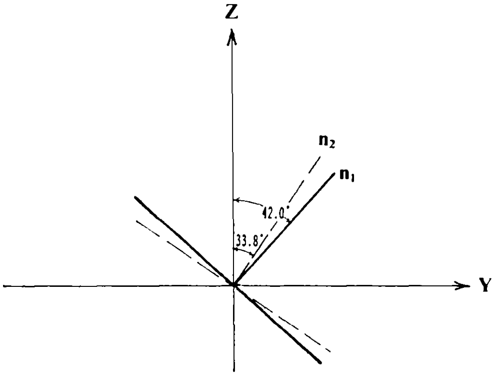

Fig. 2. The normal direction $\mathbf{n}_1$ of a coplane of three Si atoms in a unit cell deviates by 42.0° from **Z**, while the normal direction $\mathbf{n}_2$ of a cut sheet (an inactive direction) deviates by 33.8° from **Z**.

VII. *Interpretation of Bunn's empirical formula*

In Bunn's empirical formula (Bunn, 1961), the polarizability of a molecule along a direction **i** is

$$P_i = \sum (P_l \cos^2 \Phi + P_t \sin^2 \Phi).$$

The summation is over all the bonds in a molecule or group. For each bond, P_l is a longitudinal bond polarizability along the bond orientation **l**; P_t is a transverse bond polarizability along any direction **t** perpendicular to the bond. Φ is the angle between the bond direction **l** and the direction **i**. Assume **v** is perpendicular to both **i** and **l**. Then, **t** is perpendicular to both **l** and **v** (Fig. 3) such that **l**, **t** and **v** are in a right-handed system. **j** is perpendicular to both **i** and **v** such that (**i**, **j**, **v**) is in a right-handed system (Fig. 3). If rotated around **v** through an angle Φ, the bond polarizability tensor changes its coordinate system

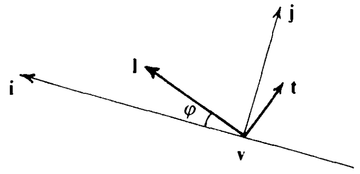

Fig. 3. The right-handed systems (**l**, **t**, **v**) and (**i**, **j**, **v**).

from (**l**, **t**, **v**) to (**i**, **j**, **v**) through the orthogonal transformation

$$\begin{bmatrix} \cos\Phi & \sin\Phi & 0 \\ -\sin\Phi & \cos\Phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} P_l & 0 & 0 \\ 0 & P_t & 0 \\ 0 & 0 & P_v \end{bmatrix} \times \begin{bmatrix} \cos\Phi & -\sin\Phi & 0 \\ \sin\Phi & \cos\Phi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} P_l\cos^2\Phi + P_t\sin^2\Phi & -(P_l - P_t)\cos\Phi\sin\Phi & 0 \\ -(P_l - P_t)\cos\Phi\sin\Phi & P_t\cos^2\Phi + P_l\sin^2\Phi & 0 \\ 0 & 0 & P_v \end{bmatrix},$$

where $P_v = P_t$. Bunn's empirical formula is simply the summation of the entry $P_l\cos^2\Phi + P_t\sin^2\Phi$ over all the bonds in a molecule or group.

Discussion

(1) If a beam of light propagates along the positive direction of **Y**, the wave front consecutively meets the groups Si(1) (open circles in Fig. 1), Si (2) (shaded circles) and Si(3) (filled circles) owing to the crystal structure $P3_221$. Because of the crystal structure, the relationship between **D** and **E** along **Y** and the skew matrix along **Y**,

$$t(\mathbf{Y})_{ij,\mathrm{skew}} = \begin{bmatrix} 0 & -t_{21} & -t_{31} \\ t_{21} & 0 & 0 \\ t_{31} & 0 & 0 \end{bmatrix},$$

are the same as those along **Z**.

While the crystal is viewed along the (−**Y**) direction, the skew part of a clockwise-rotation matrix around **Y** (roll) is

$$\begin{bmatrix} 0 & 0 & -\sin\Phi \\ 0 & 0 & 0 \\ \sin\Phi & 0 & 0 \end{bmatrix},$$

from

$$\begin{bmatrix} \cos\Phi & 0 & -\sin\Phi \\ 0 & 1 & 0 \\ \sin\Phi & 0 & \cos\Phi \end{bmatrix}.$$

Assume that $t_{31} = \sin\Phi(\mathbf{Y})$ if the absolute value of t_{31} is not larger than one. For the first set of polarizability components, the rotation angle $\Phi(\mathbf{Y})$ is −0.00732° for a length of 4.256 Å, since $a\cos 30° =$ 4.914 Å $\cos 30° =$ 4.256 Å. The calculated specific rotation for the set is −17 200° mm^{-1} (equivalent to +80° mm^{-1}) along **Y**. As for the second set of polarizability components, $\Phi(\mathbf{Y}) = -0.0195°$ for a length of 4.256 Å. The calculated specific rotation of the second set is −45 794° mm^{-1} (equivalent to −74° mm^{-1}) along **Y**.

(2) Wahlstrom (1979) predicted the +/− sign change between the direction along the optic axis and the direction perpendicular to the optic axis. For (+)-α-quartz, the results were + along **Z** and − along **Y**. The sign change matches the predictions of both Wahlstrom (1979) and Barron (1982, p. 285).

(3) When a beam of light travels along a negative direction of **Z**, the rotation angle changes from clockwise to counterclockwise or *vice versa*. Since the direction of view is also changed, the rotation remains as + or − with respect to the observer.

(4) Barron (1975) mentioned that, for a sufficiently long helix, isotropy is expected in a basal plane XY. It is isotropic for the refractive indices of α-quartz in the basal plane XY because the refractive indices refer to the average of group polarizability tensors of a unit cell. For optical rotations along directions **X** and **Y**, however, the rotation angles are anisotropic in the basal plane XY depending on this interpretation.

(5) Barron (1982) mentioned that electric-dipole-electric-quadrupole optical activity was of equal importance and that use of the electric-dipole-magnetic-dipole contribution alone leads to erroneous results. Since the electric quadrupole and the magnetic dipole were not considered together, the polarizability in a skew part of a dielectric tensor, which was fitted to a rotation matrix, might include the factors of those higher-order multipoles. The calculated average polarizability of an $SiO_{4/2}$ group was so close to an empirical result that the empirical result might also include the factors of the higher-order multipoles.

Concluding remarks

Two sets of the principal polarizabilities of an $SiO_{4/2}$ group in α-quartz were derived. Both sets have the same mean value of the polarizability components. The mean value is close to an empirical result.

The inactive directions 33.83° from the optic axis were interpreted as corresponding to directions 42.0° from the axis. The diad axes were predicted to be inactive directions.

The optical-rotation sign along the directions perpendicular to both the optic axis and a diad axis is opposite to the rotation sign along the optic axis.

The interpretation meets the requirement that the rotation angle is proportional to the thickness of α-quartz. Bunn's empirical formula was also interpreted.

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Le Coloriage des Familles de Positions Equivalentes Générales et Spéciales dans les Groupes d'Espace Bidimensionnels Quadricolorés*

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Abstract

The properties of the colouring of the general and special sets of equivalent points are studied for the 184 classes of equivalent four-coloured space groups connected with the 17 two-dimensional space groups. Every general set of equivalent points is divided into four equal subsets of points bearing one of the colours C_1, C_2, C_3, C_4. The same situation occurs in some cases for special sets of equivalent points. In particular cases, a special set of two-coloured equivalent points may be divided into two equal subsets (*e.g.* one subset of positions bearing the colours C_1C_2, the other one bearing the colours C_3C_4) or into four equal subsets (*e.g.* C_1C_2, C_1C_3, C_2C_4, C_3C_4) or into six equal subsets (C_1C_2, C_1C_3, C_1C_4, C_2C_3, C_2C_4, C_3C_4). There exist special sets bearing three colours; they divide into four equal subsets ($C_1C_2C_3$, $C_1C_2C_4$, $C_1C_3C_4$, $C_2C_3C_4$). There are also special sets of equivalent points bearing the four colours. The study is illustrated by several examples.

Introduction

Dans un mémoire précédent (Rekik & Billiet, 1991), nous avons donné la liste des 281 sous-groupes d'indice 4 des 17 groupes d'espace bidimensionnels; ils se répartissent en 184 classes de sous-groupes conjugués.

Un groupe d'espace quadricoloré est un couple 'groupe d'espace G - sous-groupe g d'indice 4' [pour la définition et les propriétés fondamentales des groupes colorés voir, par exemple, Jarratt & Schwarzenberger (1980), Schwarzenberger (1980, 1984) et Senechal (1975, 1979, 1988)]; chaque complexe a_ig de la partition de G relative à g correspond à une couleur C_i (quatre couleurs en tout: C_1, C_2, C_3, C_4):

$$G = a_1g + a_2g + a_3g + a_4g$$

$$\text{avec } a_1 \in g, \quad a_j \notin a_ig, \quad j > i.$$

Si le sous-groupe g' est conjugué de g, le couple G–g' définit par convention un groupe d'espace quadricoloré équivalent à celui défini par G–g; il existe donc 184 classes de groupes quadricolorés équivalents correspondant aux 17 groupes d'espace bidimensionnels.

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* An unrefereed English translation may be obtained from the authors upon request.

† Auteur responsable à qui doit être envoyée toute correspondance.

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