Structural Mechanics from Nonlinear Optics – the α to β Phase Transition in Quartz

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Second harmonic generation SHG may be used as an experimental technique in structural crystallography. By applying a bond polarizability model to the nonlinear optical coefficients of quartz, the rotation of the SiO₄ tetrahedron with temperature is observed. Additionally, the oxygen positional parameter x in β quartz is obtained in excellent agreement with previously published X-ray results.

Introduction

The usefulness of a bond additivity model for linear polarizability, \( \chi \), is well established (LeFèvre, 1965). A similar model, (Bergman & Crane, 1974; Crane & Bergman, 1976) applied to the quadratic polarizability, d, while perhaps less widely known, should prove even more useful. This model combined with relatively simple optical measurements (second harmonic generation) can be used to determine crystal structures and to observe microscopic details of crystal phase transitions. The utility of this model resides in part in the fact that while linear polarizabilities, \( \chi \)'s, seldom change by more than a few percent over a (reversible) phase transition, d's on the other hand, may undergo large changes of magnitude, even becoming identically zero in transitions to centrosymmetric symmetry.

This paper describes two particular applications of the above model to the study of high and low quartz. The first case uses measurement of optical second harmonic intensity as a function of crystal temperature to 'observe' the rotation of the SiO₄ tetrahedron. In the second application the ratio of second harmonic intensities in the high and low-temperature phases is used to determine the (nonsymmetry-fixed) oxygen positional parameter in the β phase. Both applications give results which are in excellent agreement with the published X-ray data.

Theory

The macroscopic field-induced polarization \( \mathbf{P} \) is generally given as a power series in electric field \( \mathbf{E} \):

\[
\mathbf{P} = \mathbf{P}_0 + \chi \mathbf{E} + d \mathbf{E}^2 + \ldots
\]

where \( \chi \) is the linear polarizability and \( d \) is the quadratic polarizability ("nonlinear coefficient") which leads to second harmonic generation (SHG). The microscopic polarizabilities corresponding to \( \chi \) and \( d \) are \( \chi \) and \( \beta \). Both \( d_{ijk} \) and \( \beta_{ijk} \) are symmetric with respect to interchange of \( j \) and \( k \) indices.

The bond additivity model for second-order polarizability, \( \beta \), makes the following assumptions (Crane & Bergman, 1976): first, the second-order polarizability of a crystal is the (tensor) sum of polarizabilities of individual bonds (and in some cases unshared electron pairs) in the unit cell: second, each bond may be presumed to have symmetry \( C_\infty \).

The bond polarizability \( \beta \) may then be represented by the \( 3 \times 6 \) matrix

\[
\beta_{ij} = \begin{bmatrix}
\beta_{14} & \beta_{15} & 0 \\
\beta_{15} & -\beta_{14} & 0 \\
\beta_{31} & \beta_{31} & 0 \\
\end{bmatrix}
\]

with the simplifying contraction (Voigt, 1910) \( jk \rightarrow j \) (or \( 11 \rightarrow 1; 22 \rightarrow 2; 33 \rightarrow 3; 23, 32 \rightarrow 4; 31, 13 \rightarrow 5; 12, 21 \rightarrow 6 \)). The requirement that \( \beta_{ijk} \) and \( d_{ijk} \) are fully symmetric in \( i,j,k \) in nondispersive media (Kleinman, 1962) leads us to assume that \( \beta_{15} = \beta_{31} \) and that \( \beta_{14} \leq \beta_{31}, \beta_{13} \).

The macroscopic (crystal) nonlinear coefficient \( d_{ijk} \) then is given by

\[
d_{ijk} = V^{-1} \sum_s \left[ \sum_{p,q,r} a_{ij} a_{pq} a_{rs} \beta_{pqr} \right]_s
\]

where the sum is over bonds, \( s \), \( V \) is the unit-cell volume and \( (a_{ij}) \) is the matrix of the transformation from the bond coordinate system to the crystal coordinate system. The two specific expressions for (2) to be used in this paper are

\[
d_{111} = V^{-1} \sum_s [ l^3 \beta_0 + 3l \beta_{31} ]_s
\]

and

\[
d_{123} = V^{-1} \sum_s [ lmn \beta_0 + (n^2 - m^2) \beta_{14} ]_s
\]

where \( \beta_0 \equiv 3 \beta_{31} \) and \( l, m, n \) are the direction cosines of bond \( s \).

Equations (2) then relate crystal structure and bond polarizability to measurable quantities, namely the nonlinear coefficients \( d_{ijk} \). Previously, this equation has been used to derive bond polarizabilities from measured nonlinear coefficients and known crystal structures (Bergman & Crane, 1974; Crane & Bergman, 1976; Tofield, Crane & Bergman, 1974; Bergman & Crane, 1975). In crystalline quartz however, it is pos-
The structure of quartz consists of corner-linked SiO₄ tetrahedra (Brill, Hermann & Peters, 1942; Young & Post, 1962; Smith & Alexander, 1963) as depicted in Fig. 1. These tetrahedra lie on the crystallographic 〈twofold〉 axis. In the high-temperature phase (T > 573°C) the other twofold axes of the tetrahedron coincide with the y and z crystal axes (Young, 1962). In the low-temperature phase, each tetrahedron has rotated about its z axis with the angle of rotation of φ = 15.9° at T = 23°C.

Low quartz (D₃ symmetry) has two independent nonlinear coefficients, (Nye, 1957) d₁₁(=d₁₁₁) and (Kleinman forbidden) d₁₄(= d₁₂₃). In the high-temperature phase, (symmetry class 0₃) d₁₁ is identically zero.

Before employing the full microscopic model [equations (1)-(3)] to these coefficients, it is instructive to consider a somewhat simpler model. Specifically, the macroscopic (crystal) polarizability 

\[ \delta_{ij} \]

may be considered as the (tensor) sum of the polarizabilities \( \beta_{ijk} \) of the three SiO₄ tetrahedra in the unit cell. If we assume an undistorted tetrahedron, (symmetry T), the assumed axial nature of the Si–O bond imposes severe restrictions upon the symmetry of the SiO₄ unit. Fig. 1 shows the four oxygen atoms in an ideal Tₐ symmetry arrangement about the silicon. The small circular arrows around the Si–O bonds represent their axial nature. Clearly, the mirror planes of ideal Tₐ symmetry do not exist in this system. Hence, the SiO₄ can have, at most, Tₐ symmetry. Perhaps the best description of the SiO₄ is to assign magnetic symmetry Tₐ (The actual distorted SiO₄ in quartz is C₂ in the α phase and D₂ in the β phase.)

The description of the (Kleinman) forbidden coefficient, \( d_{14} \), in terms of \( \alpha \), \( \theta \), and \( \phi \) gives the relation

\[ d_{14} = (18V^{-1}\sin^2(\theta)\cos^2(\alpha)\cos^2(\phi) + \sin^2(\alpha)\sin^2(\phi))\beta_{14}. \]

Equation (6) is the desired odd function of \( \phi \). It is readily shown that for \( \alpha \) near 45° and \( \theta \) near 54° the variation in \( d_{11} \) is second order (i.e. negligible) with respect to \( \alpha \) and \( \theta \).

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which is also derived in Appendix I. Here, for \( \alpha \) near 45° and \( \theta \) near 54°, \( d_{14} \) is insensitive to changes in \( \phi \).

If \( \beta_0 \) (\( = \beta_{33} - 3\beta_{31} \)) is assumed constant over the
range $T = 23$ to $573°C$, and if the tetrahedral distortion remains small, then equation (6) becomes
\[ d_{11} = d_0 \sin (2\varphi) \] (8)
which provides a method for measuring $\varphi(T)$ from a relatively simple second harmonic generation experiment.

\[ \varphi(T) = \frac{1}{2} \sin^{-1} \sin 2\varphi_0 \left( \frac{d_{11}(T)}{d_{11}(23^\circ)} \right) \] (9)

where $\varphi_0 = 159°$ is the room temperature rotation angle.

It is interesting to note here that our model demonstrates the relation between two recent publications. The first of these, Grimm & Dorner (1975), identifies $\varphi$ as an order parameter and gives a Landau theory functional form for $\varphi(T)$. The other paper, Bachheimer & Dolino (1975), asserts, on the basis of group symmetry properties, that $d_{111}$ is itself a representation of the order parameter. Equation (9) with $\varphi \leq 16°$ shows equivalence of the two representations.

The previous discussion tacitly assumed a very small tetrahedral distortion. Measurement of the other coefficient, $d_{14}$, may be used as a test of this assumption. Additionally, the ratio of $d_{14}$ in high quartz to $d_{14}$ in low quartz at $23°C$ can be used to determine the oxygen structure parameter $x$ in high quartz. This is possible through (AI.6) of Appendix I, i.e.

\[ d_{14} = 9V^{-1} (n_1^2 + n_2^2 - \frac{8}{3}) \beta_{14} \] (10)

where $n_1$ and $n_2$ are the two distinct direction cosines (with respect to the $z$ axis) of Si $\rightarrow$ O bonds. In high quartz symmetry requires that $n_1 = n_2 = n$. Therefore if $n_1$ and $n_2$ are known for low quartz, the ratio [via equation (10)] $d_{14}(573°C)/d_{14}(23°C)$ can be solved for $n$ in high quartz. Since $n_1^2 + n_2^2$ is very nearly equal to $\frac{3}{2}$ in both crystal phases, this is a very sensitive measurement of $n$. Further, since $n$ is related to the single atomic positional parameter $x$, via the relation (derived in Appendix II):

\[ 3x^2 - \frac{3}{4}x + \frac{1}{4} + \frac{1}{36} \left( \frac{c_0}{d_0} \right)^2 \left( 1 - \frac{1}{n^2} \right) = 0 \] (11)

one may deduce the structure of $\beta$ quartz from a second harmonic experiment and knowledge of the structure of $\alpha$ quartz.

**Experimental**

A $5°$ wedge of levo quartz was prepared with one face (the incident face) exactly $45°$ to the $y$ and $z$ axes (Crane & Bergman, 1976). This allowed measurement of second harmonic light due to $d_{11}$ and $d_{25} = -d_{14}$ with the same fundamental laser beam. The quartz wedge, mounted in an oven, was placed in one branch of the dual-beam optical system shown in Fig. 3. The second harmonic light from the quartz crystal and from the reference crystal (phase matched LiIO$_3$) were detected by twin boxcar integrators and the ratio of the outputs was recorded as a function of translation of the quartz wedge across the beam. The nonlinear coefficient $d$ is proportional to the square root of the measured second harmonic intensity. [Details of this type of measurement have been described elsewhere. (Crane & Bergman, 1976; Wynne & Bloembergen, 1969; Boyd, Kasper & McFee, 1971).]

The furnace was controlled by a (L & N) Electromax controller (better than 0.1° temperature stability) and the actual temperature was measured (with 1° accuracy) with a Pt/Pt-1000 Rh thermocouple in intimate contact with the steel crystal holder. At each temperature, the system was allowed to equilibrate for 15 min before the second harmonic measurement was begun. The laser used was an acoustically $Q$-switched Nd: YAG laser operating at 1.06μ. The power output was controlled to maintain a constant second harmonic output from the reference crystal throughout.
the entire experimental sequence. At the end of the experimental sequence, the crystal was allowed to cool back to room temperature and the second harmonic signal was found to be the same intensity as at the beginning of the sequence.

The experimental results of measurements of $d_{11}$ are shown in Fig. 4 where the quantity shown is the rotation angle $\varphi(T)$ derived from equation (9). The excellent agreement with conventional X-ray results is shown by inclusion of values of $\varphi$ calculated from the high-temperature X-ray data (Young, 1962). Also shown, for comparison, are points from Grimm & Dorner’s (1975) predicted $\varphi(T)$ and data from Bachheimer & Dolino’s (1975) Maker Experiment measurements of $d_{11}(T)$.

As a final comparison, the SHG-determined rotation angle $\varphi$ has been used with the assumption of a nondeforming tetrahedron to calculate atom positional parameters at a point just below the transition and just above the transition. These are compared in Table 1 with the parameters determined by X-ray diffraction. The other nonlinear coefficient $d_{14}$ was measured at 580°C relative to $d_{11}$ at 23°C. Using the relation (Crane & Bergman, 1976) $d_{14}(23°C)/d_{11}(23°C)=0.009$ then gave the desired ratio $d_{14}(580°C)/d_{14}(23°C)=0.29$.

The decrease in $d_{14}$ at higher temperature justifies the assumption of nondeforming tetrahedra in the preceding analysis. Since the absolute sign of $d_{14}$ in the high-temperature phase is unknown, there are two possible values of $n$ from (10): $n=0.5789$ (for $d_{14}$ positive) and 0.5758 (for $d_{14}$ negative), where $n_1$ and $n_2$ at room temperature were obtained from Young & Post (1962).

The two possible corresponding positional parameters [from equation (11)] are $x=0.213$ (1) and 0.208 (1). The corresponding O-Si-O bond angles are 110.3 and 107.7°. By comparison, the previously published (Young, 1962) positional parameter is 0.209±0.002 giving an O-Si-O angle of 108.3°.

The uncertainty of the sign of the forbidden coefficient, $d_{14}$, in the $\beta$ phase unfortunately leaves some ambiguity in the oxygen positional parameter. Although both structures are nearly the same, it is clear that the structure with $x=0.213$ ($n^2>\frac{1}{2}$) is in close agreement with the X-ray determined structure, while also requiring the smallest deformation of the tetrahedron. This solution is also desirable from the consideration that it does not require $d_{14}$ to change sign over the transition. Actually either parameter is in excellent agreement with the X-ray data.

### Conclusion

Second harmonic generation and the bond additivity model have been demonstrated to provide a relatively simple way of obtaining structural information about crystals. The rotation of the SiO$_4$ tetrahedron as observed via the temperature dependence of $d_{11}$ is in excellent agreement with previously published X-ray data. This also provides direct experimental confirmation of the theoretical $\varphi(T)$ of Grimm & Dorner (1975). Finally, the measurement of $d_{14}$ gives calculated positional parameters in very close agreement with the published (X-ray) structure.

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### APPENDIX I

The derivations of the Si → O bond direction cosines as functions of $\alpha$, $\theta$, and $\varphi$ are most easily accomplished by considering the diagrams of Figs. 1 and 2. By inspection we see that in the $\beta$ phase ($\varphi=0$) the direction cosines of the Si → O$_1$ and Si → O$_{\text{II}}$ bonds are

$$[\cos(\theta), -\sin(\theta) \sin(\alpha), -\sin(\theta) \cos(\alpha)]$$

and

$$[-\cos(\theta), -\sin(\theta) \sin(\alpha), \sin(\theta) \cos(\alpha)]$$

respectively. The full set of direction cosines in the $\alpha$ phase is obtained then by rotating these two vectors by $\varphi$ around the $\xi$ axis and using the twofold rotation symmetry about this axis to generate the remaining two vectors. The full set of direction cosines for this tetrahedron is:

### Table 1. A comparison of positional parameters determined via SHG with conventional X-ray determined positional parameters

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>0.4152 (8)</td>
<td>0.2678 (6)</td>
<td>0.1184 (4)</td>
<td>0.4705 (3)</td>
<td>X-ray (Young &amp; Post, 1962)</td>
<td></td>
</tr>
<tr>
<td>570</td>
<td>0.4170 (24)</td>
<td>0.2401 (25)</td>
<td>0.1455 (27)</td>
<td>0.4865 (10)</td>
<td>X-ray (Young, 1962)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.425</td>
<td>0.244</td>
<td>0.144</td>
<td>0.484</td>
<td>SHG ($d_{11}$)</td>
<td></td>
</tr>
<tr>
<td>580</td>
<td>0.4153 (21)</td>
<td>0.2133 (28)</td>
<td>0.1527 (38)</td>
<td>0.4922 (12)</td>
<td>X-ray (Young, 1962)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.430</td>
<td>0.215</td>
<td>0.170</td>
<td>0.500</td>
<td>SHG ($d_{14}$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>*</td>
<td>0.213</td>
<td></td>
<td></td>
<td>SHG ($d_{14}$)</td>
<td></td>
</tr>
</tbody>
</table>

* These parameters are given in the coordinate systems of Young & Post (1962) and Young (1962). See Wyckoff (1948).

† Symmetry requires that $x=2y$, $z=0.1667$ and $u=0.5000$ in the high-temperature ($T>573°C$) phase.
The direction cosines of the Si \( \rightarrow \) O bonds in the remaining two tetrahedra in the unit cell may be obtained from (AI.1) by rotations of 120° around the \( z \) axis, but this is unnecessary in the present case.

A closed-form expression for equation (2) of the text is,

\[
d_{ijk} = V^{-1} \sum \left( \alpha_i \alpha_j \alpha_k (\beta_{33} - 3 \beta_{31}) \right) + \left( \delta_{ijk} + \delta_{ikj} + \delta_{kji} \right) \beta_{31} + \left( \sigma \sum \delta_i \delta_j \delta_k \right) \beta_{14}, \tag{AI.2}
\]

where \( \alpha_i \) is the \( i \)th direction cosine of bond \( s \), \( \delta_{ijk} \) is the Kronecker delta, \( \epsilon_{ijk} \) is the fully antisymmetric Levi-Civita density (\( \epsilon_{ijk} = +1 \) for even permutations of \( i,j,k, = 1,2,3 \), \( -1 \) for odd permutations and \( 0 \) if any two indices are the same) and \( |\sigma| \) is an operator which changes sign under reflection.

Evaluating this for coefficient \( d_{111} \) gives us equation (3a) of the text, i.e.

\[
d_{111} = V^{-1} \sum \left( \beta_{31} \beta_0 + 3l \beta_{31} \right) \tag{AI.3}
\]

\( (\beta_0 = \beta_{33} - 3 \beta_{31}) \). In quartz, the summation of \( l \) vanishes because of the \( C_3 \) symmetry. Now it is easily shown for a set of vectors related by \( C_3 \) symmetry, one of which has direction cosines \( (l,m,n) \), that

\[
\sum \delta_i \delta_j \delta_k = \frac{1}{2} \left( 4l^2 - 3l + 3ln^2 \right). \tag{AI.4}
\]

Now using relations (AI.1) and summing over the initial tetrahedron we obtain

\[
d_{111} = \frac{2}{3} V^{-1} \cos \theta \sin^2 \theta \tag{AI.5}
\]

which is readily simplified to give equation (6) of the text.

In a similar manner (AI.2) for \( d_{123} \) is

\[
d_{123} = V^{-1} \left[ \sum \left( \beta_{31} \beta_0 + (n^2 - m^2) \beta_{14} \right) \right], \tag{AI.6}
\]

which is of course equation (3b) of the text. Here it is easily shown that in any uniaxial point group the sum of \( lmn \) vanishes. Further, \( m^2 \) in (AI.6) may be replaced by its 'average value' of \( (1 - n^2)/2 \). Again summing over the unit cell, we obtain

\[
d_{123} = 9 V^{-1} \left( \begin{array}{c} n_1^2 + n_2^2 - \frac{3}{2} \end{array} \right) \beta_{14}, \tag{AI.7}
\]

where \( n_1 + n_2 \) are the two unique values of \( n \) in the unit cell. Substituting from equations (AI.1) gives equation (7) of the text.

APPENDIX II

The atom positions in the high-temperature, \( \beta \), phase of quartz (symmetry \( P6_222 \)) (Henry & Lonsdale, 1962) are three Si atoms at \( \left( \frac{1}{2},0,0 \right) \), \( \left( 0,\frac{1}{2},\frac{1}{2} \right) \) and \( \left( \frac{1}{2},\frac{1}{2},0 \right) \). O atoms are located at positions \( \left( x,2x,\frac{1}{4} \right) \), \( \left( x,2x,\frac{1}{4} \right) \), \( \left( x,2x,\frac{1}{4} \right) \), \( \left( 2x,2x,\frac{1}{4} \right) \), and \( \left( 2x,2x,\frac{1}{4} \right) \). Consider the bond from Si\( \left( \frac{1}{2},0,0 \right) \) to \( O(\frac{1}{2},\frac{1}{2},\frac{1}{2}) \). Converting to an orthogonal coordinate system where \( y = 2x \)\( \times \) the O atom is given by coordinates \( O(\frac{1}{2},\frac{1}{2},\frac{1}{2}) \). We readily see that

\[
\delta z(Si \rightarrow O) = \frac{1}{6} \beta_{30} \tag{AI.1}
\]

\[
r^2 = (3x^2 - \frac{3}{2}x + \frac{1}{4}) + \left( \frac{1}{6} \beta_{30} \right)^2 \tag{AI.2}
\]

where \( \delta z \) is the \( z \) component of \( Si \rightarrow O \) and \( r \) is the length of \( Si \rightarrow O \) in units of \( a_0 \) since \( n \) is defined as \( \delta z/r \). One readily obtains from (AI.1) and (2)

\[
3x^2 - \frac{3}{2}x + \frac{1}{4} + \left( \frac{1}{6} \beta_{30} \right)^2 \left( 1 - \frac{1}{n^2} \right) = 0 \tag{AI.3}
\]

which for a given value of \( n \) may be solved for \( x \). (One of the two solutions thus obtained leads to a tetrahedron so badly distorted as to be physically unbelievable.)

References


