Symmetry and piezoelectricity: evaluation of $\alpha$-quartz coefficients

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Received 1 April 2017, revised 1 July 2017
Accepted for publication 27 July 2017
Published 4 October 2017

Abstract

Piezoelectric coefficients of $\alpha$-quartz are derived from symmetry arguments based on Neumann’s principle using three different methods: Fumi, Landau–Lifshitz and Royer–Dieulesaint. While the Fumi method is tedious and the Landau–Lifshitz method requires additional physical principles to evaluate the piezoelectric coefficients, the Royer–Dieulesaint method is the most elegant and most efficient of the three techniques.

Keywords: piezoelectricity, piezoelectric constants, piezoelectric materials

(Some figures may appear in colour only in the online journal)

1. Introduction and motivation

Physics students are exposed to various types of symmetry [1] and conservation laws in graduate/undergraduate courses on mechanics, and to electromagnetism with Lorentz transformation and gauge symmetries in graduate/undergraduate quantum mechanics, during the study of atoms and molecules. In undergraduate courses such as those on special relativity, Lorentz transformation is used to unify symmetries between mechanics and electromagnetism.

In graduate-level high energy physics, the CPT theorem, where $C$ denotes charge conjugation ($Q \rightarrow -Q$), $P$ is parity ($r \rightarrow -r$) and $T$ is time reversal ($t \rightarrow -t$), as well as gauge symmetry ($A_i \rightarrow A_i + \partial_i \chi$), provides an important insight into the role of symmetry in the building blocks of matter and the unification of fundamental forces and interaction between particles.

Graduate/undergraduate-level solid state physics provides a direct illustration of how crystal symmetry plays a fundamental role in the determination of physical constants and transport coefficients as well as conservation and simplification of physical laws. The relation between symmetry and dispersion relations through Kramer’s theorem (T symmetry) is
another example of the power of symmetry in solid state physics. In graduate/undergraduate
statistical physics students are exposed to the role of symmetry and its breaking in phase
transitions with the existence of different phases; while possessing different symmetries are
each characterized by an order parameter that controls the behavior of the corresponding free
energy.

The emergence of symmetry in physical systems in not obvious; however, a good starting
point to understand this particular point is through the crystal symmetry paradigm, simply
illustrated with ice formation by slowly cooling liquid water.

This work is about the role of crystalline symmetries and their role in the determination
of piezoelectric coefficients $d$ of $\alpha$-quartz on the basis of three different methods. It could be
used to illustrate the role of symmetry and its implications in an undergraduate or graduate
course on solid state physics, statistical physics or materials science.

It is organized as follows. After reviewing the properties and symmetries of $\alpha$-quartz, we
tackle the evaluation of $d$ coefficients with symmetry on the basis of the Fumi method. In
section 3 we treat the same problem using the Landau–Lifshitz method which contains a more
physical approach than Fumi, and finally, in section 4 we tackle it with a special method, the
Dieulesaint–Royer procedure which combines both the previous approaches. The appendix
contains information about point symmetry groups, their characteristics and symmetry
operations, as well as matrices for performing some of these operations.

2. $\alpha$-quartz symmetries

Quartz is a very important material from the technological point of view since it is an essential
component of all oscillators (clocks) used in consumer electronics devices (watches, com-
puters, resonators, cameras, ovens...). Quartz is the second most important material after
silicon. Its formula is silicon dioxide, $\text{SiO}_2$, and its solid state unit cell is shown in figure 1.

$\alpha$-quartz has a trigonal structure (rhombohedral [2]) belonging to the $D_3$ point symmetry
group [3] (Schoenflies classification) or 32 (Hermann–Mauguin or International classification).

Quartz exists in two varieties, left-handed and right-handed, which are mirror images of
each other, as displayed in figure 2. Handedness, or chirality, implies that the two varieties
have the same lattice energy (crystal energy of formation), and a lack of center symmetry within each variety indicates that they belong to non-centro-symmetric groups [4].

The technological importance of piezoelectric materials originates from the values of their mechanical quality factor $Q$, which indicates the sharpness of resonance, and electro-mechanical coupling coefficient $K$, which determines the conversion efficiency of mechanical into electrical energy and vice versa. The large $Q$ value of quartz, indicating that its acoustic loss is low, makes it quite attractive. While the intrinsic $Q$ of quartz is $10^7$ at 1 MHz, quartz resonators may have $Q$ factors ranging from several $10^4$ to several $10^5$, that is several orders of magnitude higher than the best $LC$ circuits.

Piezoelectricity is a fundamental property of quartz and is found in non-centrosymmetric crystals that occur in two types of point symmetry groups [3] (PSG). There are ten PSGs (see appendix) called polar groups (possessing a special direction) associated with pyroelectric and piezoelectric materials (polarization along the special direction) and ten other PSGs that are piezoelectric only (their polarization being induced by mechanical deformation).

These PSGs are classified as polar and non-polar [4] (see appendix):

- Pyroelectric and piezoelectric (polar groups displaying polarization along a special direction):
  - Triclinic system $C_1$
  - Monoclinic system $C_{1}, C_2$
  - Orthorhombic system $C_{2v}$
  - Tetragonal system $C_4, C_{4v}$
  - Trigonal (rhombohedral) system $C_3, C_{3v}$
  - Hexagonal system $C_6, C_{6v}$
• Piezoelectric only (non-polar groups characterized by a polarization induced by mechanical deformation):
  – Orthorhombic system $D_2$
  – Tetragonal system $D_{4h}, D_{2d}, S_4$
  – Trigonal (rhombohedral) system $D_3$
  – Hexagonal system $D_{6h}, C_{3v}, D_{3h}$
  – Cubic system $T, T_d$

Quartz belongs to the $D_{3h}$ group that possesses an order three rotation symmetry axis ($2\pi/3$ angle) that we might take along the $z$ axis. This axis has the $R(\pi, 2\pi/3)$ rotation symmetry operation as well as three order two axes (π rotation symmetry) in the $xy$ plane. The coordinate system we use is Cartesian with basis vectors $e_1, e_2, e_3$ such that $e_i \cdot e_j = \delta_{ij}$ and any vector is expressed on this basis as: $\mathbf{r} = xe_1 + ye_2 + ze_3$.

Neumann’s principle states that ‘symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal’ implying that crystal physical quantities are preserved after performing point group symmetry operations on them.

A symmetry operation such as a rotation by an angle $\phi$ about the $z$ axis denoted by $R(\phi)$ and represented by:

$$
\begin{pmatrix}
 x' \\
 y' \\
 z'
\end{pmatrix} =
\begin{pmatrix}
 \cos \phi & -\sin \phi & 0 \\
 \sin \phi & \cos \phi & 0 \\
 0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
 x \\
 y \\
 z
\end{pmatrix}
$$

(1)

transforms $\mathbf{r} = xe_1 + ye_2 + ze_3$ into $\mathbf{r}' = x'e_1 + y'e_2 + z'e_3$. This is different from the case of rotation with basis change, implying that the transformed vector $\mathbf{r}' = x'e_1 + y'e_2 + z'e_3$ is expressed on the rotated basis ($e'_1, e'_2, e'_3$) such that:

$$
\begin{pmatrix}
 x' \\
 y' \\
 z'
\end{pmatrix} =
\begin{pmatrix}
 \cos \phi & \sin \phi & 0 \\
 -\sin \phi & \cos \phi & 0 \\
 0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
 x \\
 y \\
 z
\end{pmatrix}
$$

(2)

We examine below symmetry operations and the implications of Neumann’s principle in order to simplify the piezoelectric coefficients.

3. Evaluation of piezoelectric coefficients by the Fumi method

Piezoelectric coefficients are represented by $d_{ijk}$, a rank three tensor with indices $i, j, k = 1, 2, 3$ corresponding to $x \rightarrow 1, y \rightarrow 2, z \rightarrow 3$. They originate from the relation $P_i = d_{ijk}\sigma_{jk}$ linking polarization vector $P$ to stress tensor $\sigma$.

In total, we have 27 $d_{ijk}$ coefficients since $i, j, k = 1, 2, 3$, however writing $d_{ijk}$ means index $i$ must be treated separately from indices $j, k$ since $i$ relates to polarization $P$ whereas $j, k$ indices relate to the symmetric stress tensor $\sigma$, i.e. $\sigma_{jk} = \sigma_{kj}$.

The $j, k$ symmetry is exploited with Voigt notation, which amounts to replacing two indices by a single one, according to the formulation: when $j = k$, $(j, k) \rightarrow j$ and when $j \neq k$, $(j, k) \rightarrow 9 - (j + k)$. More specifically, we have six possibilities: $11 \rightarrow 1, 22 \rightarrow 2, 33 \rightarrow 3, 23 \rightarrow 4, 31 \rightarrow 5, 12 \rightarrow 6$.

The total number of $d_{ijk}$ coefficients is 18 since $i = 1, 2, 3$ and the Voigt index has six possibilities.

As a result, the Voigt piezoelectric $3 \times 6$ rectangular matrix is written with the explicit entries:
where elements whose Voigt index is 4, 5, 6 are given by:
\[ d_{i} = d_{i31} + d_{i13} d_{3i}, \]
\[ d_{i} = d_{i32} + d_{i23} d_{3i}, \]
\[ d_{i} = d_{i34} + d_{i43} d_{3i}. \]

The quartz \( D_3 \) trigonal group has the symmetry operations: \( E, 2C_3, 3C_2 \) (see appendix for corresponding matrices and symmetry). The three-fold rotation by \( 2\pi/3 \) about the \( z \) axis is denoted by \( R(z, 2\pi/3) \) and the two-fold rotation by \( \pi \) about the \( x \) axis is denoted by \( R(x, \pi) \).

In order to perform symmetry transformations on the \( d_{ij} \) coefficients, we apply the rule of the Italian physicist Fausto G. Fumi [5], that states they transform as \( x \times x \), written symbolically as \( \sim \), with the condition of respecting the order of the corresponding factors. The Fumi rule is based on the fact that components of an arbitrary tensor \( A \) transform as the product of the corresponding indices, i.e. \( A_{ijkl} \sim x_i x_j x_k x_l \). Consequently \( d_{ij} \sim x_i x_j \).

We start by considering rotational symmetry of order two about \( x \) or \( R(x, \pi) \) operations (see appendix).

The relationship between the rotated axes and the original axes in the two-fold rotation about \( x \) is given as:
\[ x' = x, \quad y' = -y, \quad z' = -z. \]
Let us consider the implications of this mapping on some tensor elements.

\( d_{111} \) transforms as:
\[ d_{111}' = d_{111} \] by Neumann’s principle, implying \( d_{111} = 0 \).

Coefficient \( d_{211} \) transforms as:
\[ d_{211}' = -d_{211} \] by Neumann’s principle, implying \( d_{211} = 0 \) or \( d_{211} = 0 \).

From this result, we infer that tensor elements with an odd number of indices 2 and 3 are 0 by the two-fold rotation (because of the transformation \( y, z \rightarrow -y, -z \)).

Hence, fourteen coefficients \( d_{113}, d_{131}, d_{132}, d_{211}, d_{222}, d_{233}, d_{232}, d_{232}, d_{311}, d_{122}, d_{333}, d_{323}, d_{322} \) are zero along with their ten Voigt equivalents \( d_{15}, d_{16}, d_{21}, d_{22}, d_{23}, d_{24}, d_{31}, d_{32}, d_{33}, d_{34} \).

As a result, the piezoelectric matrix is written as:
\[
\begin{pmatrix}
  d_{11} & d_{12} & d_{13} & d_{14} & 0 & 0 \\
 0 & 0 & 0 & 0 & d_{25} & d_{26} \\
 0 & 0 & 0 & 0 & d_{35} & d_{36}
\end{pmatrix}
\] (7)

From the initial 18 coefficients only eight coefficients, \( d_{11}, d_{12}, d_{13}, d_{14}, d_{25}, d_{26}, d_{35}, d_{36} \), survive after the \( R(x, \pi) \) symmetry.

Let us investigate the impact of rotational symmetry of order three about the \( z \) axis or \( R(z, 2\pi/3) \) on these coefficients.

For the three-fold rotation about \( z \), we use equation (1) with \( \phi = \frac{2\pi}{3} \) to express the relationship between the rotated coordinates and the original ones:
\[ x' = -\frac{1}{2}x - \frac{\sqrt{3}}{2}y, \quad y' = \frac{\sqrt{3}}{2}x - \frac{1}{2}y, \quad z' = z \]
\[ (8) \]
• Coefficient $d_{11}$, or $d_{111}$, transforms as:

$$x'x'x' = \left( -\frac{1}{2}x - \frac{\sqrt{3}}{2}y \right) \left( \frac{1}{2}x - \frac{\sqrt{3}}{2}y \right) \left( \frac{1}{2}x - \frac{\sqrt{3}}{2}y \right)$$

$$= -\frac{1}{8}xxx - \frac{\sqrt{3}}{8}xxy - \frac{\sqrt{3}}{8}yxx - \frac{3}{8}xyy$$

$$- \frac{\sqrt{3}}{8}yxx - \frac{3}{8}yxy - \frac{3}{8}yxx - \frac{3\sqrt{3}}{8}yyy$$

(9)

This implies: $d'_{111} = -\frac{1}{8}d_{11} - \frac{3}{8}d_{12} - \frac{3}{8}d_{26} - \frac{3}{8}d_{221}$.

Moving on to Voigt notation and using Neumann’s principle, we have:

$$d'_{11} = -\frac{1}{8}d_{11} - \frac{3}{8}d_{12} - \frac{3}{8}d_{26} \equiv d_{11}$$

resulting in: $3d_{11} + d_{12} + d_{26} = 0$.

• Coefficient $d_{12}$ or $d_{122}$ transforms as:

$$x'y'y' = \left( -\frac{1}{2}x - \frac{\sqrt{3}}{2}y \right) \left( \frac{\sqrt{3}}{2}x - \frac{1}{2}y \right) \left( \frac{\sqrt{3}}{2}x - \frac{1}{2}y \right)$$

$$= -\frac{3}{8}xxx - \frac{\sqrt{3}}{8}xxy + \frac{\sqrt{3}}{8}yxx - \frac{1}{8}xyy$$

$$- \frac{3\sqrt{3}}{8}yxx + \frac{3}{8}yxy - \frac{3}{8}yxx - \frac{3\sqrt{3}}{8}yyy$$

(11)

yielding: $d'_{122} = -\frac{3}{8}d_{11} - \frac{1}{8}d_{12} + \frac{3}{8}d_{26} + \frac{3}{8}d_{221}$.

Using Voigt notation and Neumann’s principle, we get:

$$d'_{12} = -\frac{3}{8}d_{11} - \frac{1}{8}d_{12} + \frac{3}{8}d_{26} \equiv d_{12}$$

(12)

implying: $d_{12} + 3d_{12} - d_{26} = 0$.

Combining relations $3d_{11} + d_{12} + d_{26} = 0$ and $3d_{11} + d_{12} + d_{26} = 0$, we get: $d_{12} = -d_{11}$ and $d_{26} = -2d_{11}$.

• Coefficient $d_{13}$ or $d_{133}$ transforms as:

$$x'z'z' = \left( -\frac{1}{2}x - \frac{\sqrt{3}}{2}y \right)zz$$

$$= -\frac{1}{2}xzz - \frac{\sqrt{3}}{2}yzz$$

(13)

This yields $d'_{133} = -\frac{1}{2}d_{133} - \frac{\sqrt{3}}{2}d_{233}$ and consequently $d'_{133} = -\frac{1}{2}d_{133}$ since $d_{233} = 0$.

Using Neumann’s principle, $d'_{133} = -\frac{1}{2}d_{133} \equiv d_{133}$ implies $d_{133} = 0$ and consequently $d_{13} = 0$.

• Coefficients $d_{14}$ and $d_{25}$, $d_{213}$ being part of $d_{25} \equiv d_{213} + d_{231}$, transforms as:
\[ y'x'z' = \left( \frac{\sqrt{3}}{2} x - \frac{1}{2} y \right) \left( -\frac{1}{2} x - \frac{\sqrt{3}}{2} y \right) z \]
\[ = \frac{\sqrt{3}}{4} xz - \frac{3}{4} yz + \frac{1}{4} yxz + \frac{\sqrt{3}}{4} yz \]  
(14)

Thus \( d'_{213} = -\frac{\sqrt{3}}{4} d_{113} - \frac{1}{4} d_{123} + \frac{1}{4} d_{213} + \frac{\sqrt{3}}{4} d_{223} \), implying \( d'_{213} = -\frac{3}{4} d_{213} + \frac{3}{4} d_{213} \equiv 0 \).

This leads to \( d_{213} = -d_{132} \) implying \( d_{25} = -d_{14} \).

- Coefficient \( d_{313} \), being a part of \( d_{35} \), i.e. \( d_{313} + d_{331} \), transforms as:

\[ z'x'y' = z \left( -\frac{1}{2} x - \frac{\sqrt{3}}{2} y \right) \]
\[ = \frac{1}{2} xz - \frac{\sqrt{3}}{2} yz \]  
(15)

This gives \( d'_{313} = -\frac{1}{4} d_{313} - \frac{\sqrt{3}}{4} d_{323} \) resulting in \( d'_{313} = -\frac{1}{2} d_{313} \) since \( d_{323} = 0 \). Therefore we get with Neumann’s principle that \( d_{313} = 0 \) and \( d_{331} = 0 \), implying \( d_{15} = 0 \).

- Coefficient \( d_{312} \), being a part of \( d_{36} \) or \( d_{312} + d_{321} \), transforms as:

\[ z'x'y' = z \left( -\frac{1}{2} x - \frac{\sqrt{3}}{2} y \right) \left( \frac{\sqrt{3}}{2} x - \frac{1}{2} y \right) \]
\[ = -\frac{\sqrt{3}}{4} xz - \frac{1}{4} yz + \frac{\sqrt{3}}{4} yz \]  
(16)

thus \( d'_{312} = -\frac{\sqrt{3}}{4} d_{311} + \frac{1}{4} d_{312} - \frac{3}{4} d_{321} + \frac{\sqrt{3}}{4} d_{322} \).

This yields:

\[ d'_{312} = \frac{1}{4} d_{312} + \frac{3}{4} d_{321} \equiv d_{312} \]  
(17)

that is: \( d_{312} = -d_{321} \), implying \( d_{30} = d_{312} + d_{321} = 0 \).

Collecting all coefficients, the piezoelectric matrix becomes:

\[
\begin{pmatrix}
    d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\
    0 & 0 & 0 & -d_{14} & -2d_{11} & 0 \\
    0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]  
(18)

4. Evaluation of piezoelectric coefficients by Landau–Lifshitz method

Instead of working with matrices while applying the Fumi [5] method to the transformation of coefficients \( d_{ik} \sim x_i; x_j, x_k \), we recall that performing rotation operations in a plane orthogonal to \( z \) may be described by complex variables, as done in the book by Landau and Lifshitz [2]:

\[ \xi \rightarrow \xi e^{i\varphi}, \eta \rightarrow \eta e^{i\varphi}, z \rightarrow z. \]

We can use new complex variables \( \xi, \eta \) in the \( xy \) plane through the variable change: \( \xi = x + iy, \eta = \xi^* = x - iy \). Note that the variable sets \( \xi, \eta \) as well as \( xy \) are linearly independent (possessing a non-zero Wronskian) [2].
1. Rotational symmetry of order three about the \( z \) axis or \( R(z, 2\pi/3) \) operations:

Index separation \( i, jk \) yields by Fumi [5] rule, terms such as \((z, \xi\eta), (\eta, \zeta\xi), (\xi, \eta\zeta)\). The
transformation applies in the same manner to complex phases:

\[
x_i \to x_i e^{i\phi_0}, x_j \to x_j e^{i\phi_0}, x_k \to x_k e^{i\phi_0}
\]

obtaining \((x_i, x_j, x_k) \to (x_i, x_j, x_k) e^{i(\phi_0 + \phi + \phi)}\) where
\((x_i, x_j, x_k)\) coordinates represent \((z, \xi\eta)\).

The transformation \( d_{z\xi\zeta} \to d_{z\xi\zeta} e^{i\theta} \) along with \( D_3 \) symmetry (invariance with respect to
rotation \( R(z, 2\pi/3) \) implies: \( d_{z\xi\zeta} = d_{z\xi\zeta} e^{i\theta} \) which results in: \( d_{z\xi\zeta}(1 - e^{i\theta}) = 0 \), thus
\( d_{z\xi\zeta} = 0 \). Similarly \( d_{\xi\zeta\zeta}, d_{h,zz} \) are zero since the total phase would be \( \pm \frac{2\pi}{3} \), and the same
for \( d_{\xi\xi\xi}, d_{\zeta\zeta\zeta} \) for which the phase is \( \pm \frac{2\pi}{3} \).

The non-zero terms invariant with respect to \( R(z, 2\pi/3) \) should contain a combination
of \((z, \xi\eta), (\eta, \zeta\xi), (\xi, \eta\zeta)\) (\(\xi\xi\zeta\), (\(\eta\eta\zeta\), (\(\zeta\zeta\xi\) since the total phase obtained after
\( R(z, 2\pi/3) \) operation is 0 or \( \pm 2\pi \).

Finally the six non-zero terms correspond to the combination \( d_{\xi\xi\eta}, d_{\eta\eta\zeta}, d_{\zeta\zeta\xi} \)
\(d_{\xi\eta\eta}, d_{\zeta\eta\xi}, d_{\xi\zeta\zeta} \). Note the existence of \( d_{\xi\zeta\zeta} + d_{\eta\eta\xi} \) terms with \( z \) appearing only
once [5].

2. Rotational symmetry of order two about \( x \) or \( R(x, \pi) \) operations:

This symmetry is carried out through the following transformations:

\[
x \to x, y \to -y, z \to -z, \quad i.e. \xi \to \eta, \eta \to \xi, \quad z \to -z.
\]

This eliminates all terms containing an odd number of \( z \) such as \( d_{\xi\zeta\zeta}, d_{\zeta\zeta\xi} \).

Applying transformation to \( d_{h,zz} \), we get \( d_{\xi,-\xi\eta} \) or \(-d_{\xi,\eta\xi}\), thus the term \( d_{h,zz} \) is not zero
(resulting from changing index \( \eta \) into \( \xi \)), whereas \( d_{\xi,\xi\eta} \) transforms into \( d_{z,-\zeta\eta} \) or \(-d_{\zeta,\xi\eta}\),
thus this term is zero.

Finally only two terms \( d_{h,zz} \) and \( d_{\xi,\xi\xi} \) remain since we have: \( d_{h,zz} = -d_{\xi,\xi\eta} \)
and \( d_{\xi,\xi\xi} = d_{\eta,\eta\eta} \).

Going back to \( x, y \) variables from \( \xi, \eta \), we use energy conservation in order to avoid
problems stemming from non-orthogonality of the coordinate system \((z, \xi, \eta)\) in contrast with
the \((z, x, y)\) orthogonal system.

The energy of the system is given by \((z, \xi, \eta)\) par

\[-E.P = -E_i P_j = -E_i d_{i,jk} \sigma_{jk}, \]

obtaining:

\[-E.P = -2d_{zz\xi}(E_\xi \sigma_{x\xi} - E_\zeta \sigma_{y\eta}) - d_{\xi\xi\eta}(E_\zeta \sigma_{x\eta} + E_\eta \sigma_{y\xi}). \]

We apply the Fumi [5] rule to transform energy in system \((z, x, y)\) using correspondence
between indices and tensor components as follows: \( E_\xi = E_x + iE_y, E_\eta = E_x - iE_y \). Similarly,
\( \xi \xi = xx - yy + 2ixy \) should yield stress tensor \( \sigma \) components as
\( \sigma_{xx} = \sigma_{yy} + 2ixy \) whereas \( \xi \eta = xx + yy \) should yield: \( \sigma_{xx} = \sigma_{yy} \) and so forth.

The energy is written \( 2a(E_\xi \sigma_{x\xi} - E_\zeta \sigma_{y\eta}) + b(2E_\eta \sigma_{xy} - E_i (\sigma_{xx} - \sigma_{yy})) \), with real
constants \( a, b \) defined by \( a = 2d_{zz\xi}, \) and \( b = 2d_{\xi\xi\eta} \).

As a result, we have the remaining components \( d_{zz,xx} = d_{zz,yy} = -b \).

Collecting all terms, the matrix becomes:

\[
\begin{pmatrix}
b & -b & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -a & -b \\
0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]

Moving on to the Voigt representation, we transform:

\( d_{i,jk} \to d_{ij,k} \) \( j = 1, 2, 3 \) when \( j = k \) whereas \( d_{i,jk} \to 2d_{i,jk} \) for terms \( j \neq k \), since we have
to account for the coefficient symmetry: \( yz \leftrightarrow zy, zx \leftrightarrow zx, xy \leftrightarrow yx \).
Thus we obtain:

\[
\begin{pmatrix}
  b & -b & 0 & 2a & 0 & 0 \\
 0 & 0 & 0 & -2a & -2b & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 \\
\end{pmatrix}
\]

which might be written in the form shown in equation (18), which is exactly the result obtained previously using the Fumi method.

5. Evaluation of piezoelectric coefficients by Royer–Dieulesaint method

The Royer–Dieulesaint [6] method is the most elegant. It is based on dealing with rotation matrices through their eigenvalues, which classifies this method as an intermediate between Fumi and Landau–Lifshitz.

After performing two-fold rotation about the \( x \) axis, we infer as before that tensor elements with an odd number of indices 2 and 3 are 0 (from the transformation \( y, z \rightarrow -y, -z \)).

As a result, the piezoelectric matrix is written as in equation (7).

In order to tackle the \( R(\phi) \) transformation, we start with the corresponding general rotation matrix given in equation (1) with \( \phi = \frac{2\pi}{n} \) and \( n \) an integer.

This matrix has a unity eigenvalue along the rotation axis and two complex conjugate eigenvalues belonging to the plane orthogonal to the rotation axis: \( \lambda_1 = e^{i\theta}, \lambda_2 = e^{-i\theta}, \lambda_3 = 1 \).

The corresponding eigenvectors are: \( \xi_1 = \left( \frac{1}{\sqrt{2}}, \frac{i}{\sqrt{2}}, 0 \right), \xi_2 = \left( \frac{i}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0 \right), \xi_3 = (0, 0, 1) \).

Note that \( \xi_1 \) and \( \xi_2 \) are orthogonal since their inner product is zero given that for two complex vectors \( u, v \) the inner product is not given by \( \sum u_i v_i \) but by \( \sum u_i \overline{v}_i \).

From the eigenvectors we derive the transformation matrix that takes us from the orthonormal \( (\xi_1, \xi_2, \xi_3) \) basis to the initial orthonormal basis \( (e_1, e_2, e_3) \) such as:

\[
A = \begin{pmatrix}
\frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} & 0 \\
\frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

In the \( (\xi_1, \xi_2, \xi_3) \) basis, the piezoelectric coefficient tensor is written as \( \eta_{ijk} \) and the transformation from \( d_{ijk} \) to \( \eta_{ijk} \) is given by \( d_{ijk} = A_{il} A_{jm} A_{kn} \eta_{lmn} \).

A symmetry transformation combined with Neumann’s principle yields:

\[
\eta_{ijk} = \lambda_i \lambda_j \lambda_k \eta_{ijk}
\]

If we call \( \nu_1 \) the number of indices equal to 1 and \( \nu_2 \) the number of indices equal to 2, \( \lambda_i \lambda_j \lambda_k = \exp[i(\nu_1 - \nu_2)\frac{2n\pi}{3}] \) for a symmetry axis of order \( n \). In the \( R(z, 2\pi/3) \) symmetry \( n = 3 \) and \( \eta_{ijk} \) components are not zero whenever \( \nu_1 - \nu_2 \) is a multiple of \( n \). This implies that \( \eta_{111}, \eta_{113}, \eta_{131} \) and \( \eta_{313} \) are not zero since \( \nu_1 - \nu_2 = 0 \) as well as components \( \eta_{111} \) and \( \eta_{222} \) since \( \nu_1 - \nu_2 = \pm 3 \).

Let us consider first the \( d_{ijk} \) case with \( i, j, k = 3 \) such that coefficients are expressed in terms of \( \eta_{111} \) and \( \eta_{222} \) only.

Thus \( d_{ijk} = A_{i1} A_{j1} A_{k1} \eta_{111} + A_{i2} A_{j2} A_{k2} \eta_{222} \) for \( i, j, k = 3 \).
For instance, if we want to evaluate $d_{11}$, i.e. $d_{111}$, we write: $h_{111} = \sum_{i} A_{ii} \eta_{111} + A_{22} A_{12} \eta_{222}$. Using matrix $A$ elements given in equation (19) we get: $d_{111} = \frac{i}{2 \sqrt{2}} \eta_{111} - \frac{i}{2 \sqrt{2}} \eta_{222}$.

Moving on to $d_{12}$, i.e. $d_{122}$, we obtain in the same way: $h_{122} = -\frac{i}{2 \sqrt{2}} \eta_{111} + \frac{i}{2 \sqrt{2}} \eta_{222}$, which implies that $d_{11} = -d_{12}$.

In the same manner we can evaluate $d_{26}$, i.e. $d_{212}$ or $d_{221}$. We obtain $d_{212} = -\frac{i}{2 \sqrt{2}} \eta_{111} + \frac{i}{2 \sqrt{2}} \eta_{222}$ which implies that $d_{26} = -2d_{11}$ (the factor two originates from the fact $d_{26}$ is equivalent to $d_{212}$ or $d_{221}$ as previously seen in the Landau–Lifshitz section).

Elements containing digit 3 are $d_{13}$, $d_{35}$ and $d_{36}$. They are all zero, as we know from Fumi analysis. Let us retrieve this result in the case of $d_{13}$ or $d_{133}$. In order to evaluate $h_{133} = \sum_{i} A_{im} A_{3i} \eta_{lin}$, we use $A_{13} = A_{23} = A_{31} = A_{32} = 0$, obtaining: $d_{133} = A_{1i} A_{3i} A_{3j} \eta_{ij} + A_{2i} A_{3i} A_{3j} \eta_{ij} = 0$ since both $\eta_{133}$ and $\eta_{233}$ are zero.

In the $d_{33}$ case, one has to evaluate $d_{313}$ and $d_{333}$. Evaluating $d_{313} = A_{3i} A_{lm} A_{3n} \eta_{lin}$ yields $d_{313} = A_{3i} A_{3l} A_{3m} \eta_{lm} + A_{3i} A_{3n} A_{3j} \eta_{ij}$, which is zero since both $\eta_{133}$ and $\eta_{233}$ are zero.

The rest of the elements are obtained in the same fashion and the final outcome is exactly what we obtained earlier from Fumi and Landau–Lifshitz, albeit in a faster and more compact form.

The piezoelectric coefficient matrix obtained is the same as for the Fumi and Landau–Lifshitz methods, as given in equation (18).

For right-handed $\alpha$-quartz, the actual numerical \cite{7,8} values are (each should be multiplied by $10^{-12}$ in order to get (Coulomb/Newton) SI units):

\[
\begin{pmatrix}
-2.3 & 2.3 & 0 & -0.67 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 4.6 \\
0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]  

(21)

6. Conclusion

Symmetry is illustrated in the evaluation of piezoelectric coefficients of $\alpha$-quartz by three distinct methods: Fumi, Landau–Lifshitz and Royer–Dieulesaint. The Fumi method is general, straightforward and tedious, and the Landau–Lifshitz method requires many physical concepts that must be adapted to every encountered situation, whereas the Royer–Dieulesaint method is the most elegant while general and does not require any additional concepts as with Landau–Lifshitz. Incidentally, another tedious albeit straightforward method to evaluate the coefficients is published in Newnham’s book \cite{9}. It involves performing symmetry transformations on Voigt rectangular matrices for which the transformation formula is given by $[d’]_{ij} = [a_{kl}] [d_{lm}] [\alpha^{-1}]_{ij}$ (Einstein summation convention). The Voigt $[d]$, $[d’]$ matrices are $3 \times 6$ rectangular, whereas the basis change matrices are $[a] (3 \times 3)$ and $[\alpha^{-1}] (6 \times 6)$. After evaluating the inverse of the $6 \times 6 [\alpha]$ matrix, it is necessary to perform two matrix multiplications for each coefficient $d’_{ij}$ ($i = 1..3, j = 1..6$). Finally, there exist advanced methods to deal with symmetry that are instead based on group theoretical descriptions of tensors and tensor fields, as described in \cite{10}. They require a deep knowledge of group theory \cite{11} that exceeds a customary physics curriculum.
Appendix A. Matrices for some symmetry operations

Identity matrix:

\[ E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]  \hspace{1cm} (A1)

Reflection with respect to \( yz \) plane (considered as vertical, thus \( \sigma_z \equiv \sigma_y \)):

\[ \sigma_x = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]  \hspace{1cm} (A2)

Reflection with respect to \( xz \) plane (considered as vertical, thus \( \sigma_y \equiv \sigma_x' \)):

\[ \sigma_y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]  \hspace{1cm} (A3)

Reflection with respect to \( xy \) plane (considered as horizontal, thus \( \sigma_z \equiv \sigma_y \)):

\[ \sigma_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \]  \hspace{1cm} (A4)

Inversion matrix:

\[ i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \]  \hspace{1cm} (A5)

Rotation by an angle \( \frac{2\pi}{n} \) about the \( x \) axis:

\[ \mathcal{R}(x, \frac{2\pi}{n}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \frac{2\pi}{n} & -\sin \frac{2\pi}{n} \\ 0 & \sin \frac{2\pi}{n} & \cos \frac{2\pi}{n} \end{pmatrix} \]  \hspace{1cm} (A6)

Rotation by an angle \( \frac{2\pi}{n} \) about the \( z \) axis:

\[ \mathcal{R}(z, \frac{2\pi}{n}) = C_n = \begin{pmatrix} \cos \frac{2\pi}{n} & -\sin \frac{2\pi}{n} & 0 \\ \sin \frac{2\pi}{n} & \cos \frac{2\pi}{n} & 0 \\ 0 & 0 & 1 \end{pmatrix} \]  \hspace{1cm} (A7)

Appendix B. Point symmetry groups and symmetry operations

The classification into centro, non-centrosymmetric groups, as well as polar and non-polar groups, is given in figure 3. Symmetry operations pertaining to each group are presented in table 1.
Point symmetry groups in which pyroelectric and piezoelectric effects are expected by lack of centre symmetry. We have ten groups in each case. Polar groups allow spontaneous polarization whereas in non-polar groups polarization appears after application of stress. Polar groups do not require spontaneous polarization for the existence of pyroelectricity. Tourmaline or lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) crystals are pyroelectric without spontaneous polarization. Polarization appears as a result of temperature change in these materials. Ferroelectric point groups are not defined by reversible polarization, while this is a material dependent definition and actually it is not physically realizable in some materials, e.g. because of coercive field higher than breakdown strength etc. In the ‘10 classes (polar groups)’ case, we have variants of spontaneous polarization orientations (more domain states), reflecting symmetry descent at ferroelectric phase transition without being related to any specific material property [12]. Reprinted from Kao [4], Copyright (2004), with permission from Elsevier.

**Table 1.** Point symmetry groups in the Schoenflies (S) short notation and Hermann–Mauguin (H-M) nomenclature with corresponding symmetry operations and order N. The primed and double primed operations such as $C_{3}'$ and $C_{2}''$ correspond to three-fold rotation by $2\pi/3$ with respect to axes other than the standard axis (usually z). $\sigma_v$ is a reflection operation with respect to a vertical plane (containing the z axis) whereas $\sigma_h$ is reflection with respect to a horizontal plane and $\sigma_d$ is reflection with respect to a diagonal plane. The primed and double primed operations such as $\sigma_v'$ and $\sigma_v''$ correspond to reflection operations with respect to planes other than the standard plane. Note that in the triclinic system $S_2$ is sometimes called $C_t$ and in the monoclinic system $C_{1b}$ is sometimes called $C_m$. Adapted from Grundmann [13].

| (S) | (H-M) | Symmetry operation | N  |
|-----|-------|--------------------|----|
| Cubic systems                                                                 |    |
| $T$ | m$^{3}$ | $E$, $4C_{3}$, $4C_{3}^{2}$, $3C_{2}$ | 12 |
| $T_d$ | m$^{3}$ | $E$, $8C_{3}$, $3C_{2}$, $3\sigma_v$, i, $8S_{6}$ | 24 |
| $O$  | 432   | $E$, $6C_{4}$, $8C_{3}$, $3C_{2}$, $6C_{2}'$ | 24 |
### Table 1. (Continued.)

| (S) | (H-M) | Symmetry operation | N |
|-----|-------|--------------------|---|
| $T_d$ | 4/3 m | $E, 8C_3, 3C_2, 6S_d, 6σ_d$ | 24 |
| $O_h$ | m3m | $E, 8C_i, 6C_2, 6C_4, 3C^2, i, 6S_d, 8S_{6h}, 3μ, 6σ_d$ | 48 |

**Hexagonal systems**

| $C_6$ | 6 | $E, C_6, C_3, C_2, C_1^6, C_1^3$ | 6 |
| $C_{3h}$ | 6 | $E, C_3, C_3^3, σ_h, S_3, C_3^3$ | 6 |
| $C_{6h}$ | 6/m | $E, C_6, C_3, C_2, C_1^6, C_1^3, i, S_3^3, S_3^3, σ_h, S_3^3, S_3$ | 12 |
| $D_6$ | 622 | $E, 2C_6, C_3, C_2, 3C^3, 3C^3_2$ | 12 |
| $C_{6v}$ | 6 mm | $E, 2C_6, 2C_3, C_2, 3σ_3, 3σ_d$ | 12 |
| $D_{3h}$ | 62 m | $E, 2C_3, 3C_2, σ_h, 2S_3, 3σ_3$ | 12 |
| $D_{6h}$ | 6/mmm | $E, 2C_{6h}, 2C_6, C_3, C_2, 3C^3, 3C^3_2, i, 2S_{3h}, 2S_{3h}, σ_h, 3σ_d, 3σ_v$ | 24 |

**Tetragonal systems**

| $C_4$ | 4 | $E, C_4, C_2, C_1^4$ | 4 |
| $S_4$ | 4 | $E, S_4, C_2, C_1^4$ | 4 |
| $C_{4v}$ | 4 mm | $E, 2S_4, C_2, 2C_1^4, 2σ_d$ | 8 |
| $C_{4h}$ | 4/m | $E, C_4, C_2, C_1^4, i, S_4^2, σ_h, S_4$ | 8 |
| $D_4$ | 422 | $E, 2C_4, 2C_2, 2C_1^4, 2C_1^2_2, σ_1^2$ | 8 |
| $D_{2d}$ | 42 m | $E, 2S_4, C_2, 2C_1^4, 2σ_d$ | 8 |
| $D_{4h}$ | 4/mmm | $E, 2C_{4h}, C_4, 2C_1^4_2, 2C_1^2_2, i, 2S_{4h}, σ_h, 2σ_v, 2σ_d$ | 16 |

**Trigonal systems**

| $C_3$ | 3 | $E, C_3, C_1^3$ | 3 |
| $C_{3v}$ | 3 m | $E, 2C_3, 3σ_v$ | 6 |
| $S_6$ | 3 | $E, C_3, C_1^3, i, S_6^2, S_6$ | 6 |
| $D_3$ | 32 | $E, 2C_3, 3C_2$ | 6 |
| $D_{3d}$ | 3 m | $E, 2C_3, 3C_1^3, i, 2S_6, 3σ_d$ | 12 |

**Orthorhombic systems**

| $C_{2v}$ | 2 mm | $E, C_2, σ_v, σ''_v$ | 4 |
| $D_2$ | 222 | $E, C_2, C_1^2, C_1^2_2$ | 4 |
| $D_{2h}$ | 2/mmm | $E, C_2, C_1^2, C_1^2_2, i, σ_v, σ''_v, σ''_v$ | 8 |

**Monoclinic systems**

| $C_2$ | 2 | $E, C_2$ | 2 |
| $C_{1h}$ | m | $E, σ_h$ | 2 |
| $C_{2h}$ | 2/m | $E, C_2, i, σ_h$ | 4 |

**Triclinic systems**

| $C_1$ | 1 | $E$ | 1 |
| $S_2$ | 1 | $E, i$ | 2 |
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