Symmetry and Piezoelectricity: Evaluation of α-Quartz coefficients

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Piezoelectric coefficients of α-Quartz are derived from symmetry arguments based on Neumann's Principle with three different methods: Fumi, Landau-Lifshitz and Royer-Dieulesaint. While Fumi method is tedious and Landau-Lifshitz requires additional physical principles to evaluate the piezoelectric coefficients, Royer-Dieulesaint is the most elegant and most efficient of the three techniques.

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I. INTRODUCTION AND MOTIVATION

Physics students are exposed to various types of symmetry [1] and conservation laws in Graduate/Undergraduate Mechanics and Electromagnetism with Lorentz transformation and Gauge symmetries, in Graduate/Undergraduate Quantum Mechanics during the study of Atoms and Molecules. In undergraduate courses such as Special Relativity, Lorentz Transformation is used to unify symmetries between Mechanics and Electromagnetism.

In Graduate High Energy Physics, the CPT theorem where C denotes charge conjugation ($Q \to -Q$), P is parity ($\boldsymbol{r} \to -\boldsymbol{r}$) and T is time reversal ($t \to -t$) as well as Gauge symmetry ($A_i \to A_i + \partial_i \chi$) provide an important insight into the role of symmetry in the building blocks of matter and unification of fundamental forces and interaction between particles.

Graduate/undergraduate Solid State Physics provide 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 Kramers 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 existence of different phases while possessing different symmetries are each characterized by an order parameter that controls the behaviour of the corresponding free energy.

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

This work about the role of crystalline symmetries and their role in the determination of piezoelectric coefficients d of α-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 Solid State Physics, Statistical Physics or Materials Science course.

It is organized as follows. After reviewing α-Quartz properties and symmetries, we tackle the evaluation of d coefficients with symmetry on the basis of Fumi method. In section 3 we treat the same problem by Landau-Lifshitz method that contains a more physical approach than Fumi and finally in Section 4 we tackle it with a special method, the Dieulesaint-Royer procedure that combines both previous approaches. The appendix contains detailed information about Point Groups and Symmetry operations.

II. α-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, computers, resonators, cameras, ovens...). Quartz is the second most important material after Silicon. Its formula is silicon dioxide SiO_2 and its solid state unit cell is shown in fig.1.

α-Quartz has a trigonal structure (rhombohedral [2]) belonging to $\boldsymbol{D}_3$ point symmetry group (Schoenflies classification) or 32 (Hermann-Mauguin or International classification).

Quartz exists in two varieties: left-handed and right-handed that are mirror images of each other as displayed in fig.2. Handedness or Chirality implies that the two varieties have the same lattice energy (crystal energy of formation) and lack of center symmetry within each variety indicates that they belong to non-centro-symmetric groups as explained in the appendix.

The technological importance of Quartz originates from the values of its quality factor Q that indicates the sharpness of resonance and electro-mechanical coupling coefficient K that determines the conversion efficiency of mechanical

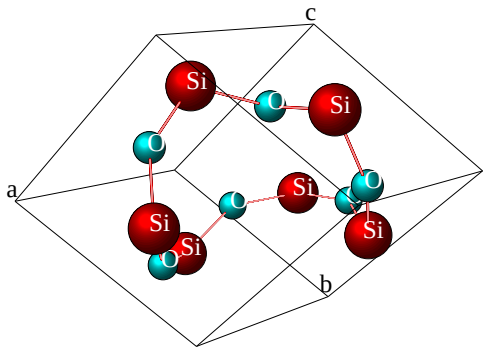

FIG. 1: Solid state unit cell of α-quartz SiO_2. a= 4.9134 Å, b= 4.9134 Å, c= 5.4053 Å, angles $(\boldsymbol{a}, \boldsymbol{b})$= 120°, $(\boldsymbol{a}, \boldsymbol{c})$= 90 °, $(\boldsymbol{b}, \boldsymbol{c})$ = 90 °. Figure drawn with Steffen Weber JSV software.

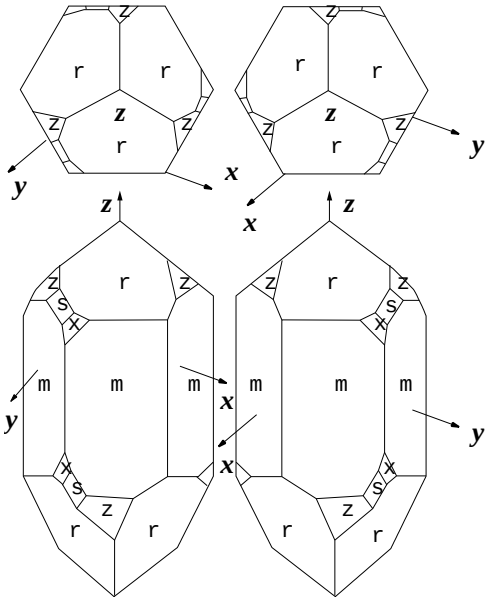

FIG. 2: Left-handed and right-handed types of Quartz with x,r,s,z and m faces. In the left-hand case, an x- or s-face is present on the left side of a top r-face. The right-hand type is when an x- or s-face is present on the right side of a top r-face.

into electrical energy and vice versa as compared with other materials as seen in fig.3.

Piezoelectricity is a fundamental property of Quartz and is found in non-centrosymmetric crystals that occur in two types of point symmetry groups (PSG) (see fig. 5). There are ten PSG called polar groups (possessing a special direction) associated with pyroelectric and piezoelectric materials (possessing spontaneous polarization along the special direction) and ten other PSG that are piezoelectric only (their polarization being induced by mechanical deformation).

These PSG are classified as polar and non polar:

- Pyroelectric and piezoelectric (Polar groups displaying spontaneous polarization along a special direction):
  - Triclinic system $\boldsymbol{C}_1$
  - Monoclinic system $\boldsymbol{C}_s$, $\boldsymbol{C}_2$
  - Orthorhombic system $\boldsymbol{C}_{2v}$
  - Tetragonal system $\boldsymbol{C}_4$, $\boldsymbol{C}_{4v}$
  - Trigonal (Rhombohedric) system $\boldsymbol{C}_3$, $\boldsymbol{C}_{3v}$
  - Hexagonal system $\boldsymbol{C}_6$, $\boldsymbol{C}_{6v}$
- Piezoelectric only (Non polar groups characterized by a polarization induced by mechanical deformation):

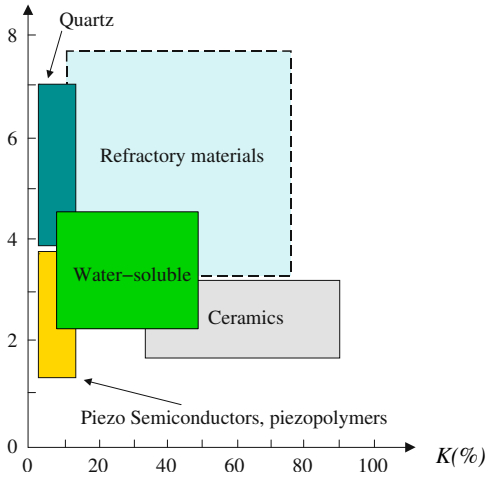

FIG. 3: Logarithm of the quality factor $\log_{10} Q$ and electro-mechanical coupling coefficient K of Quartz and other materials indicating the importance of Quartz as originating from its high Q value. Adapted from Ballato [4].

- Orthorhombic system $\boldsymbol{D}_2$
- Tetragonal system $\boldsymbol{D}_4$, $\boldsymbol{D}_{2d}$, $\boldsymbol{S}_4$
- Trigonal (Rhombohedric) system $\boldsymbol{D}_3$
- Hexagonal system $\boldsymbol{D}_6$, $\boldsymbol{C}_{3h}$, $\boldsymbol{D}_{3h}$
- Cubic system $\boldsymbol{T}$, $\boldsymbol{T}_d$

Quartz belongs to $\boldsymbol{D}_3$ group that possesses an order 3 rotation symmetry axis ($2\pi/3$ angle) that we might take along $\boldsymbol{z}$ axis. This axis has the $\mathcal{R}(\boldsymbol{z}, 2\pi/3)$ rotation symmetry operation as well as three order 2 axes (π rotation symmetry) in the xy plane. The coordinate system we use is cartesian with basis vectors $\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3$ such that $\boldsymbol{e}_i \cdot \boldsymbol{e}_j = \delta_{ij}$ and any vector is expressed in this basis as: $\boldsymbol{r} = x\boldsymbol{e}_1 + y\boldsymbol{e}_2 + z\boldsymbol{e}_3$.
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 ϕ about the $\boldsymbol{z}$ axis denoted by $\mathcal{R}(\boldsymbol{z}, \phi)$ and represented by:

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

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

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{2}$$

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

III. EVALUATION OF PIEZOELECTRIC COEFFICIENTS BY FUMI METHOD

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

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

The j, k symmetry is exploited with Voigt notation that amounts to replace two indices by a single one according to the recipe: 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 $d_{i,jk}$ coefficients is 18 since $i = 1, 2, 3$ and Voigt index has six possibilities.
As a result, the Voigt piezoelectric matrix is 6×3 with the explicit entries:

$$\begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \tag{3}$$

where elements whose Voigt index is 4,5,6 are given by: $d_{i4} = d_{i23} + d_{i32}$, $d_{i5} = d_{i31} + d_{i13}$, $d_{i6} = d_{i12} + d_{i21}$ for $i = 1, 2, 3$ as a result of symmetry. 与课件定义不同，课件定义为di4=di23=di32。多出来的系数体现在电场的表达式上。
Appendix B lists symmetry operations proper to each symmetry group. Quartz D_3 trigonal group has the symmetry operations: E, $2C_3$, $3C_2$. The 3-fold rotation by $2\pi/3$ about $\boldsymbol{z}$ axis is denoted $\mathcal{R}(\boldsymbol{z}, 2\pi/3)$ and the 2-fold rotation by π about the $\boldsymbol{x}$ axis is denoted $\mathcal{R}(\boldsymbol{x}, \pi)$.

In order to perform symmetry transformations on the $d_{i,jk}$ coefficients, we apply the Italian physicist Fausto G. Fumi [3] rule that states they transform as $x_i, x_j x_k$ written symbolically as $d_{i,jk} \sim x_i, x_j x_k$ with the condition of respecting the order of the corresponding factors.

We start by considering rotational symmetry of order 2 about x or $\mathcal{R}(\boldsymbol{x}, \pi)$ operations:

The relationship between the rotated axes and the original axes in the 2-fold rotation about $\boldsymbol{x}$ is given as:

$$x' = x, y' = -y, z' = -z \tag{4}$$

Let us consider the implications of this mapping on some tensor elements.
d_{111} transforms as:

$$x'x'x' = xxx \tag{5}$$

Thus $d'_{111} = d_{111}$ by Neumann's Principle, implying $d_{11} \neq 0$.
Coefficient d_{211} transforms as:

$$y'x'x' = (-y)xx \tag{6}$$

Thus $d'_{211} = -d_{211} = d_{211}$ by Neumann's Principle, implying $d_{211} = 0$ or $d_{21} = 0$.
From this result, we infer that tensor elements with odd number of indices 2 and 3 are 0 by the 2-fold rotation (because of the transformation $y, z \rightarrow -y, -z$).
Hence, fourteen coefficients d_{113}, d_{131}, d_{112}, d_{121}, d_{211}, d_{222}, d_{233}, d_{223}, d_{232}, d_{311}, d_{322}, d_{333}, d_{323}, d_{332} 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:

$$\begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & d_{26} \\ 0 & 0 & 0 & 0 & d_{35} & d_{36} \end{pmatrix} \tag{7}$$

From the initial 18 coefficients only 8 coefficients $d_{11}, d_{12}, d_{13}, d_{14}, d_{25}, d_{26}, d_{35}, d_{36}$ survive after the $\mathcal{R}(\boldsymbol{x}, \pi)$ symmetry.

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

For the 3-fold rotation about z, we use eq. 1 with $\phi = \frac{2\pi}{3}$ to express the relationship between the rotated coordinates and the original ones:

$$x' = -\frac{1}{2}x - \frac{\sqrt{3}}{2}y, y' = \frac{\sqrt{3}}{2}x - \frac{1}{2}y, z' = z \tag{8}$$

- Coefficient d_{11}, or d_{111} transforms as:

$$\begin{aligned} x'x'x' &= (-\frac{1}{2}x - \frac{\sqrt{3}}{2}y)(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y)(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y) \\ &= -\frac{1}{8}xxx - \frac{\sqrt{3}}{8}xxy - \frac{\sqrt{3}}{8}xyx - \frac{3}{8}xyy \\ &\quad -\frac{\sqrt{3}}{8}yxx - \frac{3}{8}yxy - \frac{3}{8}yyx - \frac{3\sqrt{3}}{8}yyy \end{aligned} \tag{9}$$

This implies: $d'_{111} = -\frac{1}{8}d_{111} - \frac{3}{8}d_{122} - \frac{3}{8}d_{212} - \frac{3}{8}d_{221}$.
Moving on to Voigt notation and using Neumann's Principle, we have:

$$d'_{11} = -\frac{1}{8}d_{11} - \frac{3}{8}d_{12} - \frac{3}{8}d_{26} \equiv d_{11} \tag{10}$$

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

- Coefficient d_{12} or d_{122} transforms as:

$$\begin{aligned} x'y'y' &= (-\frac{1}{2}x - \frac{\sqrt{3}}{2}y)(\frac{\sqrt{3}}{2}x - \frac{1}{2}y)(\frac{\sqrt{3}}{2}x - \frac{1}{2}y) \\ &= -\frac{3}{8}xxx - \frac{\sqrt{3}}{8}xxy + \frac{\sqrt{3}}{8}xyx - \frac{1}{8}xyy \\ &\quad -\frac{3\sqrt{3}}{8}yxx + \frac{3}{8}yxy + \frac{3}{8}yyx - \frac{\sqrt{3}}{8}yyy \end{aligned} \tag{11}$$

yielding: $d'_{122} = -\frac{3}{8}d_{111} - \frac{1}{8}d_{122} + \frac{3}{8}d_{212} + \frac{3}{8}d_{221}$.
Using Voigt notation and Neumann's Principle, we get:

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

implying: $d_{11} + 3d_{12} - d_{26} = 0$.

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:

$$\begin{aligned} x'z'z' &= (-\frac{1}{2}x - \frac{\sqrt{3}}{2}y)zz \\ &= -\frac{1}{2}xzz - \frac{\sqrt{3}}{2}yzz \end{aligned} \tag{13}$$

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 $d_{25} = d_{213} + d_{231}$ transforms as:

$$\begin{aligned} y'x'z' &= (\frac{\sqrt{3}}{2}x - \frac{1}{2}y)(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y)z \\ &= -\frac{\sqrt{3}}{4}xxz - \frac{3}{4}xyz + \frac{1}{4}yxz + \frac{\sqrt{3}}{4}yyz \end{aligned} \tag{14}$$

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

This leads to $d_{213} = -d_{123}$ implying $d_{25} = -d_{14}$.

- Coefficient d_{313} being a part of d_{35} i.e. $d_{313}+d_{331}$ transforms as:

$$\begin{aligned} z'x'z' &= z(-\frac{1}{2}x-\frac{\sqrt{3}}{2}y)z \\ &= -\frac{1}{2}zxz-\frac{\sqrt{3}}{2}zyz \end{aligned} \tag{15}$$

This gives $d'_{313}=-\frac{1}{2}d_{313}-\frac{\sqrt{3}}{2}d_{323}$ resulting in $d'_{313}=-\frac{1}{2}d_{313}$ since d_{323} =0. Therefore we get with Neumann's Principle $d_{313}=0$ and $d_{331}=0$ implying $d_{35}=0$.

- Coefficient d_{312} being a part of d_{36} or $d_{312}+d_{321}$ transforms as:

$$\begin{aligned} z'x'y' &= z(-\frac{1}{2}x-\frac{\sqrt{3}}{2}y)(\frac{\sqrt{3}}{2}x-\frac{1}{2}y) \\ &= -\frac{\sqrt{3}}{4}zxx+\frac{1}{4}zxy-\frac{3}{4}zyx+\frac{\sqrt{3}}{4}zyy \end{aligned} \tag{16}$$

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:

$$d'_{312}=\frac{1}{4}d_{312}-\frac{3}{4}d_{321}\equiv d_{312} \tag{17}$$

that is: $d_{312}=-d_{321}$ implying $d_{36}=d_{312}+d_{321}=0$.

Collecting all coefficients the piezoelectric matrix becomes:

$$\begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{18}$$

IV. EVALUATION OF PIEZOELECTRIC COEFFICIENTS BY LANDAU-LIFSHITZ METHOD

Instead of working with matrices while applying Fumi [3] recipe to the transformation of coefficients $d_{i,jk}\sim x_i; x_jx_k$, we recall that performing rotation operations in a plane orthogonal to z may be described by complex variables as done in Landau-Lifshitz book [2]:
$\xi\rightarrow\xi e^{\frac{2i\pi}{3}}$ $\eta\rightarrow\eta e^{-\frac{2i\pi}{3}}$, $z\rightarrow z$.

We can use new complex variables ξ,η in the xy plane through the variable change: $\xi=x+iy$, $\eta=\xi^*=x-iy$. Note that the variable sets ξ,η as well as xy are linearly independent (possessing a non-zero Wronskian) [2].

1. Rotational symmetry of order 3 about $\boldsymbol{z}$ axis or $\mathcal{R}(\boldsymbol{z},2\pi/3)$ operations:
Index separation i,jk yields by Fumi [3] rule, terms such as $(z,\xi\eta),(\eta,z\xi),(\xi,z\eta)$. The transformation applies in the same manner to complex phases:
$x_i\rightarrow x_ie^{i\phi_i}, x_j\rightarrow x_je^{i\phi_j}, x_k\rightarrow x_ke^{i\phi_k}$ obtaining $(x_i,x_jx_k)\rightarrow(x_i,x_jx_k)e^{i(\phi_i+\phi_j+\phi_k)}$ where (x_i,x_jx_k) coordinates represent $(z,\xi\eta)$.

The transformation $d_{z,z\xi}\rightarrow d_{z,z\xi}e^{\frac{2i\pi}{3}}$ along with $\boldsymbol{D}_3$ symmetry (invariance with respect to rotation $\mathcal{R}(\boldsymbol{z},2\pi/3)$ implies: $d_{z,z\xi}=d_{z,z\xi}e^{\frac{2i\pi}{3}}$ which results in: $d_{z,z\xi}(1-e^{\frac{2i\pi}{3}})=0$, thus $d_{z,z\xi}=0$. Similarly $d_{\xi,zz}$, $d_{\eta,zz}$ are zero since total phase would be $\pm\frac{2\pi}{3}$, same for $d_{z,\xi\xi}$, $d_{z;\eta\eta}$ for which the phase is $\pm\frac{4\pi}{3}$.

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

Finally the 6 non-zero terms correspond to the combination: $d_{z,\xi\eta}, d_{\eta,z\xi}, d_{\xi,z\eta}, d_{\xi,\xi\xi}, d_{\eta,\eta\eta}, d_{z,zz}$. Note the existence of $d_{z,\xi\eta}, d_{\eta,z\xi}, d_{\xi,z\eta}$ terms with z appearing only once [3].

2. Rotational symmetry of order 2 about x or $\mathcal{R}(\boldsymbol{x}, \pi)$ operations:

This symmetry is carried out through the following transformations:
$x \to x, y \to -y, z \to -z$ i.e. $\xi \to \eta, \eta \to \xi, z \to -z$.
This eliminates all terms containing an odd number of z such as $d_{z,\xi\eta}, d_{z,zz}$.

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

Finally only 2 terms $d_{\eta,z\xi}$ and $d_{\xi,\xi\xi}$ remain since we have: $d_{\eta,z\xi} = -d_{\xi,z\eta}$ and $d_{\xi,\xi\xi} = d_{\eta,\eta\eta}$.

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

The energy of the system is given by (z,ξ,η) par $-\boldsymbol{E.P} = -E_i P_i = -E_i d_{i,jk}\sigma_{jk}$, obtaining:
$-\boldsymbol{E.P} = -2d_{\eta,z\xi}(E_\eta\sigma_{z\xi} - E_\xi\sigma_{z\eta}) - d_{\xi,\xi\xi}(E_\xi\sigma_{\xi\xi} + E_\eta\sigma_{\eta\eta})$.

We apply Fumi [3] 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 σ components as $\sigma_{\xi\xi} = \sigma_{xx} - \sigma_{yy} + 2i\sigma_{xy}$ whereas $\xi\eta = xx + yy$ should yield: $\sigma_{\xi\eta} = \sigma_{xx} + \sigma_{yy}$ and so forth.

The energy writes: $2a(E_y\sigma_{zx} - E_x\sigma_{zy}) + b[2E_y\sigma_{xy} - E_x(\sigma_{xx} - \sigma_{yy})]$, with real constants a, b defined by $a = 2id_{\eta,z\xi}$, and $b = 2d_{\xi,\xi\xi}$. As a result, we have the remaining components $d_{x,yz} = -d_{y,zx} = a$ and $d_{y,xy} = -d_{x,xx} = d_{x,yy} = -b$.

Collecting all terms, the matrix becomes:

$$\begin{pmatrix} b & -b & 0 & a & 0 & 0 \\ 0 & 0 & 0 & 0 & -a & -b \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

Moving on to Voigt representation, we transform:
$d_{i,jk} \to d_{i,jj}, j = 1,2,3$ when $j = k$ whereas $d_{i,jk} \to 2d_{i,jk}$ for terms $j \neq k$, since we have to account for coefficients symmetry: $yz \leftrightarrow zy, xz \leftrightarrow zx, xy \leftrightarrow yx$.
Thus we obtain:

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

that might be written in the form shown in eq. 18 which is exactly the result obtained previously by Fumi method.

V. EVALUATION OF PIEZOELECTRIC COEFFICIENTS BY ROYER-DIEULESAINT METHOD

Royer-Dieulesaint [7] 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 2-fold rotation about x axis, we infer as before that tensor elements with odd number of indices 2 and 3 are 0 from the transformation $y, z \to -y, -z$).

As a result, the piezoelectric matrix is written as in eq. 7.

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

The eigenvalues of this matrix are: $\lambda_1=e^{i\phi},\lambda_2=e^{-i\phi},\lambda_3=1$ and the corresponding eigenvectors are given by: $\boldsymbol{\xi}_1=\left(\frac{1}{\sqrt{2}},\frac{i}{\sqrt{2}},0\right),\boldsymbol{\xi}_2=\left(\frac{i}{\sqrt{2}},\frac{1}{\sqrt{2}},0\right),\boldsymbol{\xi}_3=(0,0,1)$.

From the eigenvectors we derive the transformation matrix that takes us from the $(\boldsymbol{\xi}_1,\boldsymbol{\xi}_2,\boldsymbol{\xi}_3)$ to the initial orthonormal basis $\boldsymbol{e}_1,\boldsymbol{e}_2,\boldsymbol{e}_3$ such as:

$$A=\begin{pmatrix}\frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} & 0\\ \frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0\\ 0 & 0 & 1\end{pmatrix} \tag{19}$$

In the $(\boldsymbol{\xi}_1,\boldsymbol{\xi}_2,\boldsymbol{\xi}_3)$ basis, the piezoelectric coefficient tensor is written as η_{ijk} and the transformation from d_{ijk} to η_{ijk} is given by $d_{ijk}=A_{il}A_{jm}A_{kn}\eta_{lmn}$.

A symmetry transformation combined with Neumann's Principle yields:

$$\eta_{ijk}=\lambda_i\lambda_j\lambda_k\eta_{ijk} \tag{20}$$

If we call ν_1 the number of indices equal to 1 and ν_2 the number of indices equal to 2, $\lambda_i\lambda_j\lambda_k=\exp[i(\nu_1-\nu_2)\frac{2\pi}{n}]$ for a symmetry axis of order n. In the $\mathcal{R}(\boldsymbol{z},2\pi/3)$ symmetry $n=3$ and η_{ijk} components are not zero whenever $\nu_1-\nu_2$ is a multiple of n. This implies that η_{123}, η_{213}, η_{312} and η_{333} are not zero since $\nu_1-\nu_2=0$ as well as components η_{111} and η_{222} since $\nu_1-\nu_2=\pm3$.

Let us consider first d_{ijk} case with $i,j,k\neq3$ such that coefficients are expressed in terms of η_{111} and η_{222} only.

Thus $d_{ijk}=A_{i1}A_{j1}A_{k1}\eta_{111}+A_{i2}A_{j2}A_{k2}\eta_{222}$ for $i,j,k\neq3$.

For instance, if we want to evaluate d_{11} i.e. d_{111}, we write: $d_{111}=A_{11}A_{11}A_{11}\eta_{111}+A_{12}A_{12}A_{12}\eta_{222}=0$. Using matrix A elements given in eq. 19 we get: $d_{111}=\frac{1}{2\sqrt{2}}\eta_{111}-\frac{i}{2\sqrt{2}}\eta_{222}$.

Moving on to d_{12} i.e. d_{122}, we obtain in the same way: $d_{122}=-\frac{1}{2\sqrt{2}}\eta_{111}+\frac{i}{2\sqrt{2}}\eta_{222}$ 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 $d_{212}=-\frac{1}{2\sqrt{2}}\eta_{111}+\frac{i}{2\sqrt{2}}\eta_{222}$ which implies that $d_{26}=-2d_{11}$ (factor 2 originates from the fact d_{26} is equivalent to d_{212} or d_{221} as previously done 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 $d_{133}=A_{1l}A_{3m}A_{3n}\eta_{lmn}$, we use $A_{13}=A_{23}=A_{31}=A_{32}=0$, obtaining: $d_{133}=A_{11}A_{33}A_{33}\eta_{133}+A_{12}A_{33}A_{33}\eta_{233}=0$ since both η_{133} and η_{233} are zero.

In the d_{35} case, one has to evaluate d_{313} and d_{331}. Evaluating $d_{313}=A_{3l}A_{1m}A_{3n}\eta_{lmn}$ yields $d_{313}=A_{33}A_{11}A_{33}\eta_{313}+A_{33}A_{12}A_{33}\eta_{323}$ which is zero since both $\eta_{313}$and η_{323} 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 Fumi and Landau-Lifshitz previous result given in eq. 18.

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

$$\begin{pmatrix}-2.3 & 2.3 & 0 & -0.67 & 0 & 0\\ 0 & 0 & 0 & 0 & 0.67 & 4.6\\ 0 & 0 & 0 & 0 & 0 & 0\end{pmatrix} \tag{21}$$

VI. CONCLUSION

Symmetry is illustrated in the the evaluation of piezoelectric coefficients of α-Quartz by three distinct methods: Fumi, Landau-Lifshitz ans Royer-Dieulesaint. Fumi method is general, straightforward and tedious, Landau-

Lifshitz method requires many physical concepts that must be adapted to every encountered situation whereas Royer-Dieulesaint is the most elegant while general and not requiring any additional concepts as with Landau-Lifshitz. Advanced methods to deal with symmetry are based on Group theoretical description of Tensors and Tensor fields such as described in ref. [9], however they require deep knowledge of Group Theory [10].

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[3] Fumi rule is based on the fact, components of an arbitrary tensor A transform as product of the corresponding indices, i.e. $A_{ijkl...} \sim x_i x_j x_k x_l ...$ Consequently $d_{i,jk} \sim x_i, x_j x_k$; see F.G. Fumi Nuovo Cimento Vol. IX, 739 (1952).

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[9] M. El-Batanouny and F. Wooten, *Symmetry and Condensed Matter Physics, A Computational Approach*, Cambridge University Press, New-York (2008).

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Appendix A: Point symmetry groups and symmetry operations

We first present 3D Point Symmetry Groups in fig. 4. The classification into centro, non centrosymmetric groups as well as polar and non-polar groups is given in fig. 5. Finally symmetry operations pertaining to each group is presented in Table I.

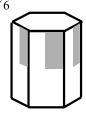
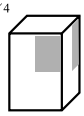
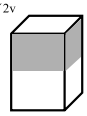
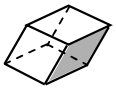
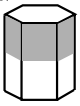
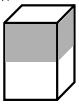
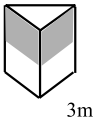
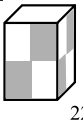
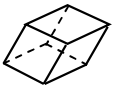
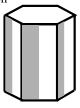
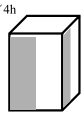
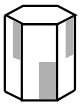
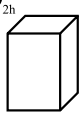
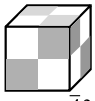
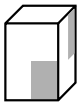
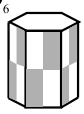
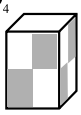
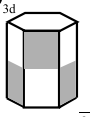
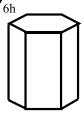
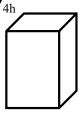
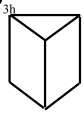
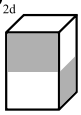
CUBIC	HEXAGONAL	TETRAGONAL	TRIGONAL	ORTHO-RHOMBIC	MONOCLINIC	TRICLINIC
O_h  m3m	C_6  6	C_4  4	C_3  3	C_{2v}  2mm	C_2  2	C_1  1
O  432	C_{6v}  6mm	C_{4v}  4mm	C_{3v}  3m	D_2  222	C_{2h}  2/m	S_2  $\bar{1}$
T_h  m3	C_{6h}  6/m	C_{4h}  4/m	S_6  $\bar{3}$	D_{2h}  2/mmm	C_{1h}  m	
T_d  $\bar{4}$3m	C_{3h}  $\bar{6}$	S_4  $\bar{4}$	D_3  32			
T  23	D_6  622	D_4  422	D_{3d}  $\bar{3}$m			
	D_{6h}  6/mmm	D_{4h}  4/mmm				
	D_{3h}  $\bar{6}$2m	D_{2d}  $\bar{4}$2m				

FIG. 4: Crystallographic point symmetry groups in 3D. Adapted from Ashcroft and Mermin [5].

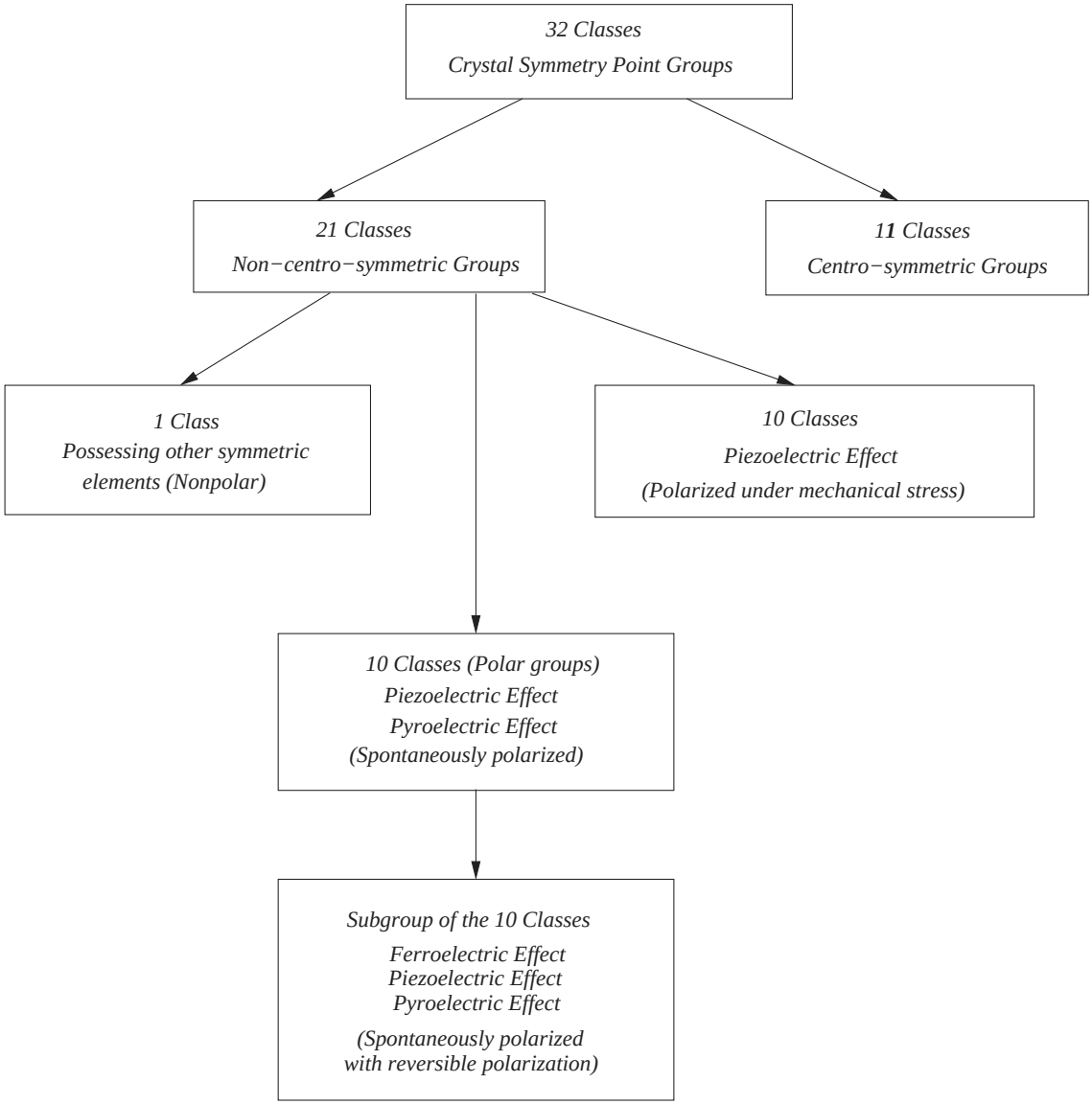


FIG. 5: Point symmetry groups in which pyroelectric and piezoelectric effects are expected by lack of center symmetry. We have 10 groups in each case. Polar groups allow spontaneous polarization whereas in non-polar groups polarization appears after application of stress. Adapted from Kao [6].

(S)	(H-M)	Symmetry operation	N
		Cubic systems	
T	23	E, $4C_3$, $4C_3^2$, $3C_2$	12
T_h	m3	E, $8C_3$, $3C_2$, $3\sigma_v$, i, $8S_6$	24
O	432	E, $6C_4$, $8C_3$, $3C_2$, $6C_2^{'}$	24
T_d	43m	E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$	24
O_h	m3m	E, $8C_3$, $6C_2$, $6C_4$, $3C_2^{'}$, i, $6S_4$, $8S_6$, $3\sigma_h$, $6\sigma_d$	48
		Tetragonal systems	
C_4	4	E, C_4, C_2, C_4^3	4
S_4	4	E, S_4, C_2, S_4^3	4
C_{4h}	4/m	E, C_4, C_2, C_4^3, i, S_4^3, σ_h, S_4	8
D_4	422	E, $2C_4$, $2C_2$, $2C_2^{'}$, $2C_2^{''}$	8
C_{4v}	4mm	E, $2S_4$, C_2, $2C_2^{'}$, $2\sigma_d$	8
D_{2d}	42m	E, $2S_4$, C_2, $2C_2^{'}$, $2\sigma_d$	8
D_{4h}	4/mmm	E, $2C_4$, C_2, $2C_2^{'}$, $2C_2^{''}$, i, $2S_4$, σ_h, $2\sigma_v$, $2\sigma_d$	16
		Orthorhombic systems	
D_2	222	E, C_2, $C_2^{'}$, $C_2^{''}$	4
C_{2v}	mm2	E, C_2, σ_v, $\sigma_v^{'}$	4
D_{2h}	mmm	E, C_2, $C_2^{'}$, $C_2^{''}$, i, σ, σ', σ''	8
		Monoclinic systems	
C_2	2	E, C_2	2
C_3	m or 2	E, σ_h	2
C_{2h}	2/m	E, C_2, i, σ_h	4
		Triclinic systems	
C_1	1	E	1
C_i	1	E, i	2
		Trigonal systems	
C_3	3	E, C_3, C_3^2	3
S_6	3	E, C_3, C_3^2, i, S_6^5, S_6	6
D_3	32	E, $2C_3$, $3C_2$	6
C_{3v}	3m	E, $2C_3$, $3\sigma_v$	6
D_{3d}	3m	E, $2C_3$, $3C_2$, i, $2S_5$, $3\sigma_d$	12
		Hexagonal systems	
C_6	6	E, C_6, C_3, C_2, C_3^2, C_6^5	6
C_{3h} (S_3)	6 or 3/m	E, C_3, C_3^2, σ_h, S_3, S_3^5	6
C_{6h}	6/m	E, C_6, C_3, C_2, C_3^2, C_6^5, i, S_3^5, S_6^5, σ_h, S_6, S_3	12
D_6	622	E, $2C_6$, $2C_3$, C_2, $3C_2^{'}$, $3C_2^{''}$	12
C_{6v}	6mm	E, $2C_6$, $2C_3$, C_2, $3\sigma_v$, $3\sigma_d$	12
D_{3h}	6m2	E, $2C_3$, $3C_2$, σ_h, $2S_3$, $3\sigma_v$	12
D_{6h}	6/mmm	E, $2C_6$, $2C_5$, C_2, $3C_2^{'}$, $3C_2^{''}$, i, $2S_3$, $2S_6$, σ_h, $3\sigma_d$, $3\sigma_v$	24

TABLE I: Point symmetry groups in the Schoenflies (S) and Hermann-Mauguin (H-M) nomenclature with corresponding symmetry operations and order N. The primed and double primed operations such as $C_3^{'}$ and $C_3^{''}$ correspond to 3-fold rotation by $2\pi/3$ with respect to axes other than the standard axis (usually z). σ_v is a reflection operation with respect to a vertical plane (containing the z axis) whereas σ_h is reflection with respect to a horizontal plane and σ_d is reflection with respect to a diagonal plane. The primed and double primed operations such as σ' and σ'' correspond to reflection operations with respect to planes other than the standard plane.