Group theory description of third harmonic generation in diamond and zincblende lattice

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Abstract. We provide a description that shows the importance in finding a susceptibility tensor in nonlinear optics and apply group theory to derive a fourth rank tensor of $O_h$ point group related to the bulk symmetry of monoatomic diamond semiconductor such as Silicon. It is well known that the fourth rank tensor is closely related to the third order nonlinear susceptibility tensor in nonlinear optics through Neumann’s principle and is crucial to understand third harmonic generation (THG) and electric field induced second harmonic generation (EFISH). Using a general Rodriguez rotation, we were able to obtain a three-dimensional rotation matrix required to perform the symmetry operations, whereas their reflection matrices are derived using a Householder formula. We also show how a $T_d$ point group corresponding to zincblende can be obtained by breaking the symmetry of the $O_h$ tensor rather than repeating the tedious procedure when obtaining the $O_h$ tensor. Assuming a driven frequency far from the resonance frequency, we can apply Kleinman symmetry and demonstrate that the number of independent components in the $O_h$ and $T_d$ fourth rank tensor is reduced from four to just two.

1. Introduction
We live in a world where the system’s response towards perturbations is often nonlinear. Nonlinearity can be found in many fields of science, such as the generation of higher harmonics radiation. It is produced by a nonlinear polarization source that is generated inside the material and can be treated both classically or quantum mechanically using perturbation theory introduced by Armstrong, Blombergen, Ducuing, and Pershan (ABDP) [1]. Although the quantum mechanical model should be valid for a wider phenomenon, such as nonlinearity due to excitons in semiconductors [2], the physics is difficult to visualize. Thus, classically phenomenological models pioneered by John Sipe [3] through a polarizable charged sheet using Green’s theory are therefore still maintained but can contain up to 10 parameters to interpret the second harmonic generation (SHG) intensity from nonvicinal semiconductors [4]. The understanding that nonlinearity can be highly simplified through a classically phenomenological model came in 2002 through the work of D. E. Aspnes Group who introduced the simplified bond hyperpolarizability model (SBHM) assuming SHG radiation produced by anharmonic charge oscillation along atomic bonds [5]. It was later extended to investigate relative dipole and quadrupole contribution [6] and to cope for third harmonic generation (THG) [7].
It was soon realized that the validity of the higher rank tensor obtained in SBHM by direct product of bond vectors hinges on comparison with the tensor obtained by group theory, since the latter depends only on the symmetry of the material which must be geometrically correct. This link was established through the work of Kurt Hingerl’s group in 2013 where one us (Hardhienata) was involved [8]. It was shown that the tensor obtained in SBHM can be related to group theory (GT) with good agreement, especially if Kleinman Symmetry (KS) is applied [9]. They proved later that KS is indeed an inherent property of SBHM [10]. The model was recently adapted to include THG and EFISH in diamond semiconductors [11], arbitrary input polarization angle to identify bulk quadrupoles [12], SHG from zincblende structures [13], and the ability to determine vicinality and absorption in semiconductors using nonlinear optics particularly SHG [13].

Furthermore, group theory (GT) usually used to simplify the computational effort in band structure calculation with highly computational electronic. Macroscopically the type of linear and nonlinear optical source from within the material depends on the band structure and symmetry of the semiconductor [14], the latter is expressed through the macroscopic nonlinear susceptibility. The mathematical procedure to reduce the tensor components based on symmetry property is group theory and plays a vital role in the investigation of solid state physics both classically and quantum mechanically [15], which is an important discipline that was developed in the 20th century [16].

The optical response of the materials can be described by the relation between polarization and electric field. However, if the electric field used is quite large, as is the case for Femto or Pico second lasers, the polarization response is nonlinear, and the relation between the polarization and electric field comprises of a linear and nonlinear terms:

\[ P_i = \chi^{(1)}_{ij} E_j + \chi^{(2)}_{ijk} E_j E_k + \chi^{(3)}_{ijkl} E_j E_k E_l \ldots \]  

Equation (1) applies for electric dipoles and can be derived from a classical force equation assuming damped charge forced anharmonic oscillation solved using the Rayleigh-Schrödinger perturbation theory [17]. The magnitude of \( \chi^{(1)} \) is in general function of the frequency which is inferable through familiar linear dispersive relations and is a consequence of causality (e.g.) Kramers-Kröning relation. Here, \( \chi^{(2)} \) and \( \chi^{(3)} \) is the second-, third-order susceptibility tensor (also known as the third and fourth rank tensor, respectively). The susceptibility tensor contains many information about the symmetry of nonlinearly optical materials that are crucial in understanding the origin of nonlinear radiation. If the potential is centrosymmetric as is the case for diamond cubic systems such as Silicon, the second order nonlinear susceptibility in equation (1) vanishes (zero) inside the bulk due to parity symmetry. However, the odd order susceptibilities including third order (or fourth rank tensor) are still allowed and will be analyzed using GT.

2. Methodology

2.1. Cartesian coordinate rotation

To obtain the correct tensor that represents a given symmetry, we apply certain matrix transformational operation on the most general tensor with the idea that these operations should leave the geometry of the unchanged symmetry. The amount of allowed symmetry operation depends on how high the symmetry of the crystal is. Generally, if a crystal structure has high symmetry, such as the case of a silicon bulk, then the number of requirely transformational operation becomes higher. Due to symmetry, applying certain rotational and mirror operation should invariably leave the crystal geometry corresponding to certain point group, therefore the tensor before and after the operation should be the same and a mathematical consistency requires some elements to be zero. Generally, the applied transformational operation that is used to obtain the three-dimensional rotation matrix of the materials consists of rotation of the Cartesian coordinates [18].
To find the identity matrix $E$ (derived from the German word *Einheitsmatrix*), we use $360^\circ$ or $2\pi$ for $\theta$. Because interestingly, crystals in nature tend to maintain an efficient periodicity without free or blank spaces in between they retain such symmetry, so that it is invariant through certain rotation only. In other words, because the crystals must completely be filled with the periodic repetition of the basic building block, only two-, three-, four-, and six-fold rotations are possible [8]. These possible rotations are given by the angles of $\pi$, $2\pi$, $\pi/2$, and $\pi/3$. The type of the symmetry axis of the crystals is symbolized by the rules of the Schönflies notation, which for rotation is symbolized by $C_n$, where $C$ is the rotation and $n$ denotes the $n$-fold rotation. For a two-fold rotation, the angle is 180 degrees so that $\frac{2\pi}{n}$ [18].

### 2.2. Rodriguez rotation

Because the bulk symmetry is three dimensional, the rotation of the Cartesian coordinate cannot be used directly, but it must be combined with Rodriguez rotation. It is a formulation that is associated with the parameter and Euler-Rodriguez formula that applies to a general three-dimensional rotation in the bulk [19]. The combination of rotation about the Cartesian coordinates and Rodriguez equation gives the correct representation of the bulk tensor.

The Rodriguez rotation satisfies $v = v_{\parallel} + v_{\perp}$. Here, $v$ is the vector contained in the rotation elements of the group. This indicates that the each vector element within this group contains a parallel and perpendicular vector. Using the identity rule from calculus vectors and allowing rotation $v_{rot} = v_{rot\parallel} + v_{rot\perp}$ and $v_{rot\perp} = (\cos \theta)v_{\perp} + (\sin \theta)(n \times v_{\perp})$ we obtained the equation:

$$
\begin{pmatrix}
(n \times v)_x \\
(n \times v)_y \\
(n \times v)_z
\end{pmatrix} =
\begin{pmatrix}
n_y v_z - n_z v_y \\
n_z v_x - n_x v_z \\
n_x v_y - n_y v_x
\end{pmatrix} = NV
$$

(2)

Because $v_{rot} = vR$, we obtained the following equation:

$$
R = I + \sin \theta(n) + (1 - \cos \theta)n^2
$$

(3)

where, $R$ is the so called Rodriguez rotation matrix, and $I$ is the identity element matrix. Then we can get the new rotation transformation [20]:

$$
R_\theta =
\begin{pmatrix}
n_1^2(1 - \cos \theta) + \cos \theta & n_1n_2(1 - \cos \theta) - n_3 \sin \theta & n_1n_3(1 - \cos \theta) + n_2 \sin \theta \\
n_1n_2(1 - \cos \theta) + n_3 \sin \theta & n_2^2(1 - \cos \theta) + \cos \theta & n_2n_3(1 - \cos \theta) - n_1 \sin \theta \\
n_1n_3(1 - \cos \theta) - n_2 \sin \theta & n_2n_3(1 - \cos \theta) + n_1 \sin \theta & n_3^2(1 - \cos \theta) + \cos \theta
\end{pmatrix}
$$

(4)

where, $n$ is the unit vector and satisfies $n_1^2 + n_2^2 + n_3^2 = 1$.

### 2.3. Reflection operation

We now describe a reflection operation which is as important as the rotational operation discussed beforehand. Generally, the reflection operation can be obtained from the called Householder matrix, the matrix is usually called by the various names: Householder formula, Transformation of Householder, Householder reflection, or elementary reflector. Householder transformation is a reflection through orthogonal plane to a given vector unit, such as vector unit $v$ and expressed in the form of a matrix [21]. This reflection can be expressed as follows:

$$
Hv = v - 2vv_{\parallel}
$$

(5)
Because the preferred \( H \) matrix is a single matrix that can transform to all of the normal vector unit \( v \), then the normal vector \( v \) that is parallel must be projected on the \( x \)-axis, therefore:

\[
v _ {\parallel} = \frac{x}{|x|} |v| \cos \theta
\]  
(6)

By eliminating \( \cos \theta \) in equation (6), we found the new reflection matrix of \( H \). The form of the Householder matrix is:

\[
H = \begin{pmatrix}
1-(n_1)^2 & -2n_1n_2 & -2n_1n_3 \\
-2n_2n_2 & 1-(n_2)^2 & -2n_2n_3 \\
-2n_3n_3 & -2n_2n_3 & 1-(n_3)^2
\end{pmatrix}
\]  
(7)

3. Result

The bulk fourth rank tensor related to the Third Harmonic Generation (THG) from a diamond cubic crystal, such as Silicon, can be produced by applying the following procedure: apply rotation of \( \pi/3 \) about the \( z \)-axis, apply rotation of \( \pi/2 \) about the center side of the cube to another center side of the cube where the axis also passes through the center of cube, then apply the \( \pi/4 \) rotation. Afterwards apply the before mentioned angle of rotation to the combined Cartesian coordinate and Rodriguez rotation, inverse the identity matrix, then apply the reflection to diagonal and horizontal plane. When all the procedures are implemented accordingly, the next step is combining the rotation operation with reflection operation through the equation:

\[
S_4 = \sigma_h C_4
\]  
(8)

When the procedure is completed a total of 16 matrix elements of the \( O_h \) is obtained. It is the point group of Silicon bulk. The most general form of the fourth rank tensor is contain a total of 81 components. To simplify the general tensor from is transformed using the corresponding rotation and reflection operation that we have found previously. The procedure of transforming the tensor is [19]:

\[
d_{ijkl} = \sum_{im} \sum_{jn} \sum_{ko} \sum_{lp} d_{mnop} n_i r_m r_j n_k r_l
\]  
(9)

Equation (9) must satisfy Neumann principle which can be stated as: the component of the symmetry operation of the group in the crystals must be invariant under transformation [9]. Based on this rule, the entire tensor components after the transformation that are equal to the negative of the corresponding elements before the operation is performed must be zero. Then the fourth rank tensor becomes:

\[
\begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
\]  
(10)

The tensor elements in equation (10) show that the maximum independent component of the bulk that can be owned by \( O_h \) point group is four. Assuming that the input frequency is much smaller than natural frequency (e.g. far resonance) of the silicon crystals, then we can use Kleinman symmetry: the
index of the each components can be exchanged freely [9]. Application of Kleinman symmetry immediately reduces the amount of independent component from four to just two. According to the SBHM only one independent component is responsible in the fourth rank tensor to generate THG [13].

Interestingly, when the material is Zincblende, which just diamond cubic, but with two atoms instead such as GaAs, rather than the monoatomic Si the symmetry inside the bulk breaks from \( O_\text{h} \) to a lower symmetry because now the structure has Ga or As centre surrounded by four As or Ga atoms respectively forming an alternating \( Sp^3 \) atomic orbital (tetrahedral). If this is the case, then from the 48 symmetry elements only 24 remain, and this is called \( T_\text{d} \) point group. It is understandable then, that \( T_\text{d} \) is a subgroup of \( O_\text{h} \), because it can be obtained by breaking the \( O_\text{h} \) symmetry. When the symmetry is reduced from 48 to 24 the tensor in equation (10) is the same with the tensor of the \( T_\text{d} \) point group in fourth rank tensor, but in the third rank tensor the tensor form of the \( O_\text{h} \) point group and \( T_\text{d} \) point group is very different. Equation (10) can be formed into reduced tensor, to make it simple, because the reduced tensor has merely 36 component. In the reduced tensor notation, equation (10) becomes:

\[
\begin{pmatrix}
    d_{3333} & d_{3322} & d_{3322} & 0 & 0 & 0 \\
    d_{3322} & d_{3333} & d_{3322} & 0 & 0 & 0 \\
    d_{3322} & d_{3322} & d_{3333} & 0 & 0 & 0 \\
    0 & 0 & 0 & 2d_{3223} + 2d_{3232} & 0 & 0 \\
    0 & 0 & 0 & 0 & 2d_{3223} + 2d_{3232} & 0 \\
    0 & 0 & 0 & 0 & 0 & 2d_{3223} + 2d_{3232}
\end{pmatrix}
\] (11)

Another form of the reduced tensor of a \( T_\text{d} \) and \( O_\text{h} \) point group is by simplifying the indeces of the tensor component with just two indices referring to the convention in [18]. Then equation (11) becomes:

\[
\begin{pmatrix}
    d_{11} & 0 & 0 & 0 & d_{44}/4 & 0 & 0 \\
    0 & d_{12} & 0 & d_{44}/4 & 0 & 0 & 0 \\
    0 & 0 & d_{12} & 0 & d_{44}/4 & 0 & 0 \\
    0 & d_{44}/4 & 0 & 0 & d_{11} & 0 & 0 \\
    d_{44}/4 & 0 & 0 & 0 & 0 & d_{12} & 0 \\
    0 & 0 & d_{44}/4 & 0 & 0 & d_{11} & 0 \\
    d_{44}/4 & 0 & 0 & d_{44}/4 & 0 & 0 & d_{12}
\end{pmatrix}
\] (12)

From equation (12), we can see that the maximum independent tensorial component owned by a \( T_\text{d} \) point group is 2, with the rule that \( d_{44}/4 \) is \( d_{12} \) and \( d_{12} \) is the same with the \( d_{21} \). Further work is required to compare this finding with the SBHM.
4. Conclusion
We have derived the corresponding fourth rank tensor describing THG for a diamond cube
semiconductor point group using group theory (GT) which has the $O_h$ point group. We show that four
independent tensorial components are necessary to describe THG which are immediately reduced to two
if Kleinman symmetry is assumed. We show how the symmetry is broken from $O_h$ to $T_d$ for the case of
zincblende structure which is a subgroup of $O_h$ with only 2 independent component.

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