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Isotropic and Anisotropic Parts for the Susceptibility Tensor Calculated Using Simplified Bond-Hyperpolarizability Model

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Abstract. In this paper we discuss the importance of separating the susceptibility tensor in the isotropic and anisotropic parts, we show how to do that and what is the contribution from each part to the nonlinear polarizability. Specific examples are given for second harmonic generation in the surface of Si(001) and for third harmonic generation in bulk silicon along (001) direction. Our calculations are performed using simplified bond-hyperpolarizability model.

1. Introduction
Nonlinear optics is a favorite method in the investigation of surface properties of semiconductor materials due to the possibility to probe materials at room temperature, is relatively nondestructive, can be performed in non vacuum condition, but mainly because it is surface sensitive. One of the interesting issues in probing surfaces of semiconductors using nonlinear optics (e.g. higher harmonics) is to identify and separate the nonlinear sources that are generated from the surface and the bulk of the material. In doing so analysis of the nonlinear susceptibility tensor becomes an important part because it is directly related to the symmetry of the material that produces the nonlinear sources.

In a classic paper by Sipe and coworkers [1], they split the tensor describing the nonlocal response for the nonlinear polarization in the isotropic and the anisotropic parts. In general a tensor can be separated in the symmetric and the antisymmetric part or in the isotropic and the anisotropic part [2]. The latter procedure is our interest here, because for second harmonic generation (SHG) on crystals for the surface or the bulk, a common technique is to rotate the crystal around the normal (usually labeled z-axis). This technique is known as Rotational Anisotropy of the SHG (RA-SHG) and the experimental results can be well described using Simplified Bond-Hyperpolarizability Model [3]. Then the intensity
of the SH (second harmonic) signal is a function of the azimuthal angle and change sinusoidally with an integer number of periods for a complete revolution of the crystal.

Describing harmonic generation with SBHM, generates a susceptibility tensor. This is, the polarization is given by [4]

\[ P = \frac{1}{V} \sum_{j} \alpha_{1j} \left[ \hat{b}_j \otimes \hat{b}_j \right] \cdot \vec{E} + \frac{1}{V} \sum_{j} \alpha_{2j} \left[ \hat{b}_j \otimes \hat{b}_j \otimes \hat{b}_j \right] \cdot \vec{E} \otimes \vec{E} \]

\[ + \frac{1}{V} \sum_{j} \alpha_{3j} \left[ \hat{b}_j \otimes \hat{b}_j \otimes \hat{b}_j \right] \cdot \vec{E} \otimes \vec{E} \otimes \vec{E} + \ldots \]

\[ = \chi^{(1)} \vec{E} + \chi^{(2)} \vec{E} \vec{E} + \chi^{(3)} \vec{E} \vec{E} \vec{E} + \ldots \tag{1} \]

where \( V \) is the volume, \( \alpha_{1j} \) are the linear polarizabilities, \( \alpha_{2j} \) and \( \alpha_{3j} \) are the first and second order hyperpolarizabilities and \( \hat{b}_j \) are the unit vectors in the direction of the atomic bonds; whereas \( \vec{E}(\omega) \) is the electric field. Incident polarization can be defined for the electric field (typically \( s\)- or \( p\)-polarization) and even a DC field can be modeled for example for describing electric field induced second harmonic (EFISH) generation [4]. However, we are going to center our discussion about the tensorial nature of the susceptibility.

For a second-order nonlinear phenomena, there is a third-rank tensor which corresponds with the susceptibility represented by \( \chi^{(2)} \). This tensor, in general has 27 elements and can be represented by [6]

\[
\chi^{(2)} = \begin{pmatrix}
X_{111} & X_{112} & X_{113} \\
X_{121} & X_{122} & X_{123} \\
X_{131} & X_{132} & X_{133}
\end{pmatrix}
\]

\[
\chi^{(2)} = \begin{pmatrix}
X_{211} & X_{212} & X_{213} \\
X_{221} & X_{222} & X_{223} \\
X_{231} & X_{232} & X_{233}
\end{pmatrix}
\]

\[
\chi^{(2)} = \begin{pmatrix}
X_{311} & X_{312} & X_{313} \\
X_{321} & X_{322} & X_{323} \\
X_{331} & X_{332} & X_{333}
\end{pmatrix}
\]

where in the component representation of the tensor \( \chi^{(2)} \), the first index "\( i\)" corresponds to the rows in the main external matrix, whereas the column has no index associated. Thus, all the elements in the first row of the inner \( 3 \times 3 \) matrix have \( X_{1jk} \) indices, whereas for the second row it will be \( X_{2jk} \) and so on. The second and third indices "\( j\)" and "\( k\)" will correspond to the usual way of labeling a \( 3 \times 3 \) matrix, they are the rows and columns, respectively, in the inner \( 3 \times 3 \) matrix.

On the other hand, a third-order nonlinear phenomena will be described by a fourth-rank susceptibility tensor. A general fourth-rank tensor, can be represented as a \( 3 \times 3 \) matrix which also has a \( 3 \times 3 \) matrices as elements, this is [6]
There are 81 elements, which are labeled as follows. The first index “i” in $\chi^{(3)}_{ijkl}$ corresponds to the rows and the second index “j” to the columns in the main matrix (the external one). In the same way, the indices “k” and “l” will correspond to the usual way of labeling a $3 \times 3$ matrix, namely, the rows and columns in the inner $3 \times 3$ matrix, respectively.

Fortunately, as is well-known, many of the tensorial elements in equations (2) and (3) are zero for crystals with high symmetry. This is because the susceptibility tensor of the crystal should be the same tensor after a transformation due to some intrinsic symmetry in the crystal and this is the way in which non-zero elements in the tensor are calculated [6]; in Physics this is known as Neumann’s principle [7]. Mathematically, a transformation by a rotation or by another symmetry operation applied to the susceptibility $n$th-rank tensor is calculated by

$$
\chi'_{x'y'z'...x'_n} = R_{x'y} R_{x_2'y_2} R_{x_3'y_3}...R_{x_n'y_n} \chi_{x'y_2'y_3...y_n},
$$

where, as it is mentioned before, the $R_{xy}$ is a matrix defining a symmetry operation or could be a general rotation for an arbitrary angle $\theta$, around z-axis. Note that basically there is a matrix contracting each index in the tensor. For a general rotation $\chi'_{x'y_2'y_3...y_n} = \chi'_{x'y_2'y_3...y_n} (\theta)$, and then it can be separated in isotropic and anisotropic part. Isotropic part is invariant under rotations and the anisotropic part should have all the information about the azimuthal dependence. Thus something is isotropic when it does not change in function of the direction.

A third-rank tensor is isotropic under rotations when it has the form

$$
\mathcal{E} = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & -1 \\
0 & 1 & 0
\end{pmatrix}
$$

which is nothing else than the Levi-Civita tensor $\varepsilon_{ijk}$ [9]. This can be verified by the procedure followed in Reference [7] applied to the tensor given in equation (2), where for anticlockwise rotations around all
the Cartesian axes $x$, $y$ and $z$ the result is $\chi_{ij}\varepsilon_{ikl}$ and in the case of clockwise rotation there is only a minus one multiplying the last result.

In the same way, it is possible to find a fourth-rank tensor which is invariant under rotations in any Cartesian axis. The fourth-rank isotropic tensor has the general form [2, 9]:

$$
\tilde{I} = \begin{pmatrix}
\alpha + \beta + \gamma & 0 & 0 \\
0 & \alpha & 0 \\
0 & 0 & \alpha
\end{pmatrix}
\begin{pmatrix}
0 & \beta & 0 \\
\gamma & 0 & 0 \\
0 & 0 & \gamma
\end{pmatrix}
\begin{pmatrix}
0 & 0 & \beta \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}.
$$

(6)

where $\alpha$, $\beta$, and $\gamma$ are arbitrary constants (scalars). This can be checked using equation (4) for a rotation matrix defined for any Cartesian axis, after transforming the tensor the result is going to be the same tensor given in equation (6). As can be seen, isotropic tensors are more complicated when the rank is higher.

In the next sections, specific examples of the isotropic and the anisotropic parts of the susceptibility tensor will be given for third- and fourth-rank tensors generated through SBHM. Finally, the conclusions and remarks of this work are given.

2. SBHM second-order nonlinear phenomena

First, we are going to discuss SHG in the surface on silicon with the facet (001). The bond vectors in this case are

$$
\vec{b}_i = -\frac{1}{\sqrt{2}} \begin{pmatrix}
\sin \frac{\beta}{2} \\
\sin \frac{\beta}{2} \\
\sqrt{2} \cos \frac{\beta}{2}
\end{pmatrix},
\vec{b}_j = \frac{1}{\sqrt{2}} \begin{pmatrix}
\sin \frac{\beta}{2} \\
\sin \frac{\beta}{2} \\
-\sqrt{2} \cos \frac{\beta}{2}
\end{pmatrix},
\vec{b}_k = \frac{1}{\sqrt{2}} \begin{pmatrix}
-\sin \frac{\beta}{2} \\
\sin \frac{\beta}{2} \\
\sqrt{2} \cos \frac{\beta}{2}
\end{pmatrix},
\vec{b}_l = \frac{1}{\sqrt{2}} \begin{pmatrix}
\sin \frac{\beta}{2} \\
-\sin \frac{\beta}{2} \\
\sqrt{2} \cos \frac{\beta}{2}
\end{pmatrix},
$$

(7)

which are plotted schematically in figure 1 (a). Therefore, the susceptibility tensor is calculated using the second term in equation (1).
where $\alpha_{\beta_j}$ has two different values in this case, depending if the bond vector point “up” or “down” and they are labeled $\alpha_u$ and $\alpha_d$. Also, $\mathbf{R}^{(l)}(\phi)$ is the rotation matrix around z-axis and it is just for the case that the $\hat{b}_j$'s are chosen in a different system of reference with only the z-axis conserved, otherwise it is only needed to take $\phi = 0$. Thus, equation (8) yields

$$\chi^{(2)}(001) = \sum_{j=1}^{V} \alpha_{\beta_j} \begin{pmatrix}
0 & 0 & 2S[\alpha_u \cos^2 \phi + \alpha_d \sin^2 \phi] \\
0 & 0 & (\alpha_u - \alpha_d) S \sin 2\phi \\
2S[\alpha_u \cos^2 \phi + \alpha_d \sin^2 \phi] & (\alpha_u - \alpha_d) S \sin 2\phi & 0 \\
(\alpha_u - \alpha_d) S \sin 2\phi & 2S[\alpha_u \sin^2 \phi + \alpha_d \cos^2 \phi] & 0 \\
(\alpha_u - \alpha_d) S \sin 2\phi & 2S[\alpha_u \sin^2 \phi + \alpha_d \cos^2 \phi] & 0 \\
0 & 0 & 2(\alpha_u + \alpha_d) \cos^2 (\beta / 2) 
\end{pmatrix}, \quad (9)$$

where (001) in $\chi^{(2)}$ is just to remember in which direction is this tensor defined, $S = \sin \beta \sin (\beta / 2) / 2$ and in particular for silicon $\beta = 2 \arccos (1 / \sqrt{3}) \approx 109.47^\circ$. Now by direct comparison between this tensor equation (9) and the isotropic one given in equation (5) it is possible to separate the isotropic and the anisotropic parts:

$$\chi^{(2)}_{\text{iso}}(001) = \chi^{(2)}_{\text{iso}} + \chi^{(2)}_{\text{ani}} \quad (10)$$

whereas the isotropic part is explicitly

$$\chi^{(2)}_{\text{iso}} = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & -1 \\
0 & 1 & 0 
\end{pmatrix}$$

$$\chi^{(2)}_{\text{ani}} = (\alpha_u - \alpha_d) S \sin 2\phi \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
-1 & 0 & 0 \\
0 & -1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 0 
\end{pmatrix}, \quad (11)$$

and the anisotropic part is
It is clear from equation (11) that for some elections of the system of reference for the bond vectors there is not an isotropic part of the SBHM susceptibility tensor for facet (001). Please, note that the angle $\phi$, is for choosing some system of reference for the atomic bonds and if we apply a rotation by and angle $\theta$ to the tensor in equation (12) it will be invariant under this general rotation, i.e. the rotation will give the same tensor after this operation and will not have any dependence with the angle $\theta$. However, if a general rotation is applied to the tensor given by equation (12), it will change and will have and explicit dependence in the angle $\theta$.

In order to compare both results, we are going to find the second harmonic resulting polarization for the particular case of $s$-polarization as the fundamental excitation. Thus the electric field only will have components in the $y$ direction, and after contracting with the full tensor in equation (9):

$$P_s(2\omega) = 2SE^2_s(0, 0, \alpha_s \cos^2 \phi + \alpha_a \sin^2 \phi).$$

Now, for the case in which the tensor was split in the isotropic and anisotropic parts:

$$P_s(2\omega) = \tilde{\chi}_{s0}^{(2)} \cdot \tilde{E} = 2SE^2_s(0, 0, \alpha_s \cos^2 \phi + \alpha_a \sin^2 \phi),$$

as should be, isotropic part is just a constant contribution to the total intensity of the SHG and in this particular case it is zero; whereas the anisotropic part has all the information about the azimuthal dependence of the intensity. The same is true for the $p$-polarization, but we do not show it explicitly here.

In the case of the facet Si(111), the isotropic and anisotropic parts of the susceptibility tensor can be obtained from the correspondent ones for the Si(001) facet. It is only needed to rotate the anisotropic part of the tensor in equation (12) and then add the result with the tensor in equation (11), because the isotropic part is by definition invariant under rotations. As the orientation is different we need to rotate the crystal to a system of reference with the $z$-axis perpendicular to the plane (111). For doing this, two rotations must be performed [10], the first one is around the $z$-axis by an angle of $\pi/4$ (clockwise); then in the new system of reference the second rotation will be around $x$-axis, by $\beta/2$ (counterclockwise), where $\beta$ is the angle between the bonds and it is equal to 109.47° for silicon. The final configuration is shown in figure 1 (b). This procedure of rotating the previous result, can be applied too to facet Si(011), shown in figure 1 (c), but the angles and axis are different that in the previous case [10]. Other procedure...
is to calculate the susceptibility tensor with SBHM [5, 10, 11] starting with the bonds vectors in the adequate direction and then to separate by inspection the isotropic and anisotropic parts.

3. SBHM third-order nonlinear phenomena

For third-order nonlinear phenomena we are going to do the same separation of the isotropic and anisotropic parts of the susceptibility fourth-rank tensor but only for a particular nonlinear effect. In this case, we are going to discuss third harmonic generation for Si(001) only. The SBHM equation describing it, is the last summand in equation (1). Then, the susceptibility tensor is

\[
\chi^{(3)}_{\text{SBHM}} = n_i \begin{pmatrix}
(3 + \cos(4\phi))\sin^4\left(\frac{\beta}{2}\right) & \sin(4\phi)\sin^4\left(\frac{\beta}{2}\right) & 0 & 0 & 0 \\
\sin(4\phi)\sin^4\left(\frac{\beta}{2}\right) & 2\sin^2(2\phi)\sin^4\left(\frac{\beta}{2}\right) & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
\sin^2\beta & 0 & 0 & 0 & 0
\end{pmatrix}
\]

(15)

There is only one hyperpolarizability because this is a bulk effect [10]. In this case, it is also possible to separate in general the isotropic and anisotropic parts of the tensor, but an easy example is going to be shown. For instance, if the azimuthal angle \(\phi = \pi/4\), the general tensor given by equation (15) yields

\[
\chi^{(3)}_{\text{SBHM}}(\phi = \pi/4) = n_i \begin{pmatrix}
2\sin^4\left(\frac{\beta}{2}\right) & 0 & 0 & 0 & 0 \\
0 & 2\sin^4\left(\frac{\beta}{2}\right) & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]

(16)

which we can compare with the general form of the fourth-rank isotropic tensor in equation (6) and after some algebraic and trigonometric manipulation it is easy to separate the isotropic part as
In contrast with the previous case, the contribution of the isotropic part of the tensor equation (17), after contracting with the electric fields describing $s$- and $p$- polarization, is not zero but a constant vector, here we only give explicitly the result for $s$-polarization

$$\vec{P}_{s,\text{ISO}}(3\omega) = \mathcal{X}^{[2]}_{s,\text{ISO}} \cdot \vec{E} \otimes \vec{E} \otimes \vec{E} = 3E^3_y\alpha \sin^2 \beta (0,1,0). \quad (19)$$

Here this contribution of the isotropic part is not only an addition to the intensity of the total polarization because the part of the polarization coming from the anisotropic part of the tensor equation (18) also has component in $y$ direction, this is

$$\vec{P}_{s,\text{ANI}}(3\omega) = \mathcal{X}^{[2]}_{s,\text{ANI}} \cdot \vec{E} \otimes \vec{E} \otimes \vec{E} = -E^3_y\alpha (5 + 7\cos \beta) \sin^2 \left(\frac{\beta}{2}\right) (0,1,0) \quad (20)$$

which generates cross terms when the intensity is calculated. Moreover, the same happens with the $p$-polarization.
4. Conclusions
We have shown that it is always possible to separate the susceptibility tensor, into its isotropic and anisotropic parts. For the case of second harmonic generation tested with \( s \) and \( p \)-polarizations, which is performed by calculating the tensor using SBHM. The separation of isotropic and anisotropic parts, does not offer new insight for the nonlinear polarization, because the contribution of the isotropic part to the nonlinear polarization is zero. This is different for third harmonic generation where the isotropic part has a contribution to the polarization that is not only the addition of a constant to the total intensity but it has a contribution to the angular dependence due to the presence of cross terms in the intensity.

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