Research Article

Bond Model of Second- and Third-Harmonic Generation in Body- and Face-Centered Crystal Structures

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In this work, we describe the third- and fourth-rank tensors of body- and face-centered cubic systems and derive the *s*- and *p*-polarized SHG far field using the simplified bond-hyperpolarizability model. We also briefly discuss bulk nonlinear sources in such structures: quadrupole contribution, spatial dispersion, electric-field second-harmonic generation, and third-harmonic generation, deriving the corresponding fourth rank tensor. We show that all the third- and fourth-rank tensorial elements require only one independent fitting parameter.

1. Introduction

Surface characterization using nonlinear methods offers several advantages due to its nondestructive nature and the ability to investigate many industrial processes in real-time and nonvacuum conditions. In the past, a comprehensive understanding up to the microscopic atomic level of the measured second-harmonic generation (SHG) data—even for low symmetry samples such as diamond lattices—was difficult because surfaces, in their full complexity, are described by a third-rank tensor with up to 27 complex and 81 complex components if using second- and third-harmonic generations, respectively [1, 2]. In a series of papers, Powell et al. [3], Peng et al. [4], and Adles and Aspnes [5] have argued consistently that azimuthal measurements of rotated silicon samples using higher harmonics can be described by the so-called simplified bond-hyperpolarizability model (SBHM). The first major finding was that the then available SHG data for Si(111) in Reference [6] could be well fitted by just using two complex parameters, the “up” hyperpolarizability used for the upward pointing bond and the

“down” hyperpolarizability used for the three downward pointing bonds. Just using these two complex parameters is a major advantage compared to previous phenomenological description for the same case [7–9]. Later on, SBHM was applied to model surface rotational anisotropy (RA) SHG experiment for a nonvicinal Si(111) surface with success [10] although it has recently been shown by using arbitrary input polarization that bulk quadrupolar effects also contribute to SHG [11]. However, SBHM was also criticised and tested against experiment by using Si(111) with different offcut directions and different offcut magnitude [12].

It turned out that the influence of steps due to the miscut is important. In our understanding, this counter argument is not fair because it is well known that steps induce a major effect for the Si(111) case, and therefore, at least a third parameter should be added, only describing the C_2 rotational symmetry of samples with steps as mentioned correctly by McGilp. Indeed when this parameter is inserted, SBHM simulation can be applied to study the variations of the RASHG intensity peak upon changes in the surface vicinity as small as 1° [13]. In a response, Adles and Aspnes

included effects like retardation, spatial dispersion, and magnetic effects, proportional to quadrupole contributions in addition to the anharmonic restoring force acting on the bond charge [5]. This inclusion, however, enhances the number of freely fittable parameters, and its strictness and simplicity is thereby lost.

Another important step towards the understanding of SHG in diamond and zincblende lattices was the investigation of the third-rank susceptibility tensor that was obtained from the simplified bond-hyperpolarizability model (SBHM) and group theory (GT) [14, 15], where it was shown that one can derive from GT the SBHM tensor. The work was later extended to show that the model can fit electric-field-induced second-harmonic (EFISH) experimental results in metal-Oxide semiconductor (MOS) with good accuracy [16]. Further test upon the validity of SBHM to model experimental RASHG data from zincblende samples which are non-centrosymmetric confirmed the existence of bulk dipole radiation as the dominant source of SHG [17].

2. Basic Theory

The simplified bond-hyperpolarizability model (SBHM) is an alternative approach to describe nonlinearity, in particular SHG from materials and interfaces. Even though it is a phenomenological theory requiring the hyperpolarizabilities to be obtained from experimental fitting, it does provide a physical framework in which nonlinear optical (NLO) spectra can be represented and analyzed at the bond level in simple terms. Influenced by the somewhat unfamiliar Ewald-Oseen extinction theorem in linear optics [18–20], where the radiating field from the material is seen as direct superposition from all the dipole fields inside the material, SBHM assumes that a similar approach can be worked out for nonlinear optics. The specific assumptions made in this model are as follows:

- (i) The system consists of (partial) charges localized in bonds, and the applied field E causes a displacement of the charge at each bond site *only* along the bond.
- (ii) Using Newton's equation of motion, the induced dipole oscillates harmonically and anharmonically with time under the action of the applied electric field and appropriate restoring and dissipation forces.
- (iii) The number of bonds is determined by the amount of the next nearest neighbors; thus, there are eight bonds for bcc and twelve bonds for fcc, originating at *each* atom.
- (iv) The nonlinear part of motion is summarized in terms of complex hyperpolarizabilities that can be obtained by solving the equation of motion.
- (v) In classical physics, each accelerated charge radiates, and the far field is calculated as the superposition of the fields radiated by each dipole.
- (vi) An additional consideration which has not been described in Reference [3] is the coherent superposition of all atomic dipoles. These, by the external fundamental field coherently driven dipoles, radiate in phase, the fundamental as well as the

second-harmonic output. Because the distance between the dipoles is much smaller than the wavelength, the coherent superposition leads the angle of incidence (AOI) equal to angle of excidence ($\theta_o = \theta_i$). This can be explained from the Huygens principle: constructive interference or coherent superposition (equal phase plane) from all radiating dipoles in reflection/transmission is always directed at an angle equal to the AOI angle (Figure 1, which also depicts the applied coordinate system in this work) and the field interferes destructively for all other angles. Also in transmission, a coherent superposition occurs, but it should be noted that usually $\theta_i^\omega \neq \theta_i^{2\omega}$, both determined by the dispersion relation, respectively, Snell's law.

If we consider second-harmonic and third-harmonic generation, the motion of the charge q_j can be described by the equation of motion in the following form:

$$m \frac{d^2 \mathbf{x}}{dt^2} = q_j \mathbf{E}_{\text{loc}}(\omega) \cdot \hat{\mathbf{b}}_j e^{-i\omega t} - \kappa_1 (\mathbf{x} - \mathbf{x}_0) - \kappa_2 (\mathbf{x} - \mathbf{x}_0)^2 - \kappa_3 (\mathbf{x} - \mathbf{x}_0)^3 - \gamma \frac{d\mathbf{x}}{dt}, \quad (1)$$

where $\mathbf{x}$ is the position of the charge in a local coordinate system that lies along the $\hat{\mathbf{b}}_j$ direction, $\mathbf{x}_0$ is the equilibrium position, $\mathbf{E}_{\text{loc}}(\omega)$ is the local field at the position of the atom which is related to the macroscopic field through $\mathbf{E}_{\text{loc}}(\omega) = (\epsilon(\omega) + 2/3)\mathbf{E}(\omega)$, κ_1 is the harmonic spring constants, whereas κ_2 and κ_3 are the first- and second-anharmonic spring constants, and γ is a frictional coefficient.

At this point, we would like to address several important limitations of our SBHM because exact expression of the local fields $\mathbf{E}_{\text{loc}}(\omega)$ and hyperpolarizabilities are not actually calculated, and the latter requires ab initio quantum mechanical calculation which lies beyond the scope of our model and is simply treated as a fitting parameter. It has been shown by Mendoza and Mochán that the nonlinear susceptibility can be written in terms of the linear polarizability at the fundamental and second-harmonic frequencies [21, 22]. In addition, they have also shown comprehensively in their study about local fields of SHG spectra in Si surfaces [21] that the local field also depends on surface modification such as surface reconstruction and relaxation which we ignore in our model. Another limitation in our SBHM is that we assume the nonlinear second- and third-order susceptibilities to be off-resonance so that they are independent of the frequency and therefore obey the Kleinman symmetry. This assumption needs to be emphasized because resonant SHG radiation experiments from Si surface shows that the SH intensity peak does not arise from dipolar SH transition but indeed from the large uncompensated local-field gradient at the surface as shown convincingly in Reference [21]. It is remarkable that they also develop an exactly solvable model for surface SHG consisting of a semi-infinite system made up of a continuous distribution of harmonic polarizable entities, each of which responds nonlinearly to the gradient of the local field prior to the development of SBHM [23]. Nevertheless, our results may be useful as a first approximation to the response of fcc and

FIGURE 1: Coordinate system showing the incoming p -polarized field and the outgoing p - and s -polarized fields. It follows from the assumptions of SBHM that the response for the bond, which is almost parallel to the incoming field, is strongest.

bcc crystals, and as will be shown, it requires using only a few number of parameters.

The direction of the j -th bond is defined by the unit vector $\hat{\mathbf{b}}_j$. Assuming that $\mathbf{x}$ can be written as an expansion:

$$\mathbf{x} = \mathbf{x}_0 + \Delta\mathbf{x}_1 e^{-i\omega t} + \Delta\mathbf{x}_2 e^{-i2\omega t} + \Delta\mathbf{x}_3 e^{-i3\omega t} + \dots \quad (2)$$

It follows that to the lowest order, the induced linear $\mathbf{p}_{1j}$, quadratic $\mathbf{p}_{2j}$, and cubic $\mathbf{p}_{3j}$ dipoles of the j -th charge are given by

$$\mathbf{p}_{1j} = q_j \Delta\mathbf{x}_1 \hat{\mathbf{b}}_j = \frac{q_j^2 \mathbf{E}_{\text{loc}}(\omega) \cdot \hat{\mathbf{b}}_j}{\kappa_1 - m\omega^2 - i\gamma\omega} \hat{\mathbf{b}}_j = \alpha_{1j} \hat{\mathbf{b}}_j (\hat{\mathbf{b}}_j \cdot \mathbf{E}_{\text{loc}}(\omega)), \quad (3)$$

$$\mathbf{p}_{2j} = q_j \Delta\mathbf{x}_2 \hat{\mathbf{b}}_j = \frac{q_j^2 \kappa_2 \Delta\mathbf{x}_1^2}{\kappa_1 - 4m\omega^2 - 2i\gamma\omega} \hat{\mathbf{b}}_j = \alpha_{2j} \hat{\mathbf{b}}_j (\hat{\mathbf{b}}_j \cdot \mathbf{E}_{\text{loc}}(\omega))^2, \quad (4)$$

$$\mathbf{p}_{3j} = q_j \Delta\mathbf{x}_3 \hat{\mathbf{b}}_j = \frac{q_j^2 \kappa_3 \Delta\mathbf{x}_2^2}{\kappa_1 - 9m\omega^2 - 3i\gamma\omega} \hat{\mathbf{b}}_j = \alpha_{3j} \hat{\mathbf{b}}_j (\hat{\mathbf{b}}_j \cdot \mathbf{E}_{\text{loc}}(\omega))^3, \quad (5)$$

where α_{1j} , α_{2j} , and α_{3j} are, respectively, the microscopic linear polarizability, first-order nonlinear hyperpolarizability, and second-order nonlinear hyperpolarizability of the j -th bond. Therefore, the total polarization can be written as

$$\begin{aligned} \mathbf{P} &= \frac{N}{V} \sum_j \mathbf{p}_j = \frac{N}{V} \sum_j (\alpha_{1j} \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j) \cdot \mathbf{E}_{\text{loc}}(\omega) \\ &+ \frac{N}{V} \sum_j (\alpha_{2j} \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j) \cdot (\mathbf{E}_{\text{loc}}(\omega) \otimes \mathbf{E}_{\text{loc}}(\omega)) \\ &+ \frac{N}{V} \sum_j (\alpha_{3j} \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j) \cdot (\mathbf{E}_{\text{loc}}(\omega) \otimes \mathbf{E}_{\text{loc}}(\omega) \otimes \mathbf{E}_{\text{loc}}(\omega)). \end{aligned} \quad (6)$$

In macroscopic terms, we can write:

$$\begin{aligned} \mathbf{P} &= \epsilon_0 \overleftrightarrow{\chi}_1 \cdot \mathbf{E}(\omega) + \epsilon_0 \overleftrightarrow{\chi}_2 \cdot \mathbf{E}(\omega) \otimes \mathbf{E}(\omega) \\ &+ \epsilon_0 \overleftrightarrow{\chi}_3 \cdot \mathbf{E}(\omega) \otimes \mathbf{E}(\omega) \otimes \mathbf{E}(\omega), \end{aligned} \quad (7)$$

where V is the volume, N is the number of atomic units, and χ_1 , χ_2 , and χ_3 are the first-, second-, and third-order susceptibility tensors of the system, respectively. In the preceding

equation, the nomenclature highlights already the triadic product of the bond directions, as well as the dyadic product of the electric fields for SHG and the quadratic product of the bond and triadic product of the field for THG. With the assumption that the bond charges radiate as dipoles, the far-field radiation field $\mathbf{E}_{\text{ff}}$ can be written as

$$\mathbf{E}_{\text{ff}} = k^2 \frac{e^{ikr}}{r} \left(\sum_j \mathbf{p}_j - \hat{\mathbf{k}} \left[\hat{\mathbf{k}} \cdot \sum_j \mathbf{p}_j \right] \right) = k^2 \frac{e^{ikr}}{r} (\overleftrightarrow{\mathbf{I}} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \cdot \sum_j \mathbf{p}_j, \quad (8)$$

where $\overleftrightarrow{\mathbf{I}}$ is the unit tensor and $\mathbf{k} = k\hat{\mathbf{k}}$ is the wave vector pointing in the direction of the observer. By combining Equations (6) and (8), the different orders of susceptibilities can be defined in intrinsic terms as sums of dyadic, triadic, etc., products of bonds, with the description of the observed radiation and the action of the applied fields both represented as external operators. Extensions to higher orders are obvious.

Equation (8) describes the radiation of an arbitrary number of dipoles located in the origin. A possible phase difference between radiated fields of different bonds is reasonably neglected because λ is large against the distance between the nucleus and the bond. Within a typical wavelength, however, there are $\sim 10^4$ atoms, which are *coherently* driven by the incoming fundamental field. Their phases, e.g., different due to a nonzero angle of incidence, have to be taken into account and second-harmonic radiation of the dipoles has to be added coherently. Despite a single dipole radiates in all the solid angle $\theta_i \neq \theta_o$ (with the exception of the bond direction), using the Huygens principle however, leads immediately, by considering the phases of the coherently radiating atomic dipoles, to one transmission and reflection direction. The coherent back radiation into air at an AOI $= \theta$ for the harmonic wave is the same as for the fundamental one, and the forward radiation into the substrate is determined by the dispersion relation for $\epsilon(2\omega)$.

Many SHG experiments have been performed at single wavelength by a rotating sample. The azimuthal angle ϕ , which describes a rotation of the system, is allocated to each bond direction by applying the rotation matrix $R_z(\phi)$ where ϕ is measured from the x axis:

$$R_z(\phi) = \begin{pmatrix} \cos \phi & -\sin \phi & 0 \\ \sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (9)$$

The s and p polarizations of the incoming and outgoing beams lead to four combinations labeled p - p , p - s , s - p , and s - s , where the first and second letters refer to the polarizations of the incident and emerging beams, respectively. The incoming s - and p -polarized beams are given by $\mathbf{E}_s = E_s \hat{\mathbf{y}}$ and $\mathbf{E}_p = E_p (-\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta)$.

In our contribution, we critically extend the SBHM to calculate the third- and fourth-rank tensors of body-centered cubic (bcc) and face-centered cubic (fcc) lattices. Furthermore, a single dipole radiates in all the solid angles (with the exception of the bond direction) such that according to Reference [3], the SHG radiation should be measurable in all the upper and lower half spaces. Using the Huygens principle, however, leads immediately, by considering the phases of the radiating atomic dipoles, which are driven coherently by the fundamental field, to the fact that SHG radiation of a stratified layer is only allowed into one transmission and reflection direction.

3. FCC and BCC Surface Response

In this section, we apply SBHM to predict SHG response from the surface of body-centered cubic (bcc) and face-centered cubic (fcc) crystal structures. We are aware that SBHM will be problematic for most metals exhibiting this crystal structure because comparison between SHG intensity from metal surfaces with the SBHM profile will produce different results due to the existence of free electrons in metal therefore exceeding contributions from the bounded dipoles along the bonds. However for nonmetal crystals with fcc and bcc structures such as certain chalcogenide semiconductors, SBHM should produce a good approximation of the SHG far field that is reflected from the surface. The bond orientations for the (001), (110), and (111) surfaces of a bcc crystal is presented in Figure 2.

We first define the corresponding unit bond vectors, the unit vector for incoming and outgoing p -polarized beams, and the unit vector for s -polarized beams. For a bcc (001) crystal orientation, we specify the four up bonds to have the same hyperpolarizability α_u and have the following direction (Figure 2(a)):

$$\hat{\mathbf{b}}_1 = \begin{pmatrix} \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \end{pmatrix},$$

$$\hat{\mathbf{b}}_2 = \begin{pmatrix} -\frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \end{pmatrix},$$

$$\hat{\mathbf{b}}_3 = \begin{pmatrix} \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \end{pmatrix},$$

$$\hat{\mathbf{b}}_4 = \begin{pmatrix} -\frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \end{pmatrix}. \quad (10)$$

However, for the four down bonds, we assign a down hyperpolarizability α_d with the following bond vector orientation:

$$\hat{\mathbf{b}}_5 = \begin{pmatrix} \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{3}} \end{pmatrix},$$

$$\hat{\mathbf{b}}_6 = \begin{pmatrix} -\frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{3}} \end{pmatrix},$$

$$\hat{\mathbf{b}}_7 = \begin{pmatrix} \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{3}} \end{pmatrix},$$

$$\hat{\mathbf{b}}_8 = \begin{pmatrix} -\frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{3}} \end{pmatrix}, \quad (11)$$

FIGURE 2: Bond orientation of bcc crystal structures: (a) (001), (b) (110), and (c) (111).

with the defined p and s incoming and outgoing field orientation given by the following equation (Figure 1):

$$\begin{aligned} \mathbf{E}_{p,\text{in}} &= \begin{pmatrix} -\cos \theta \\ 0 \\ \sin \theta \end{pmatrix}, \\ \mathbf{E}_{p,\text{out}} &= \begin{pmatrix} \cos \theta \\ 0 \\ \sin \theta \end{pmatrix}, \\ \mathbf{E}_s &= \mathbf{E}_{s,\text{in}} = \mathbf{E}_{s,\text{out}} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}. \end{aligned} \quad (12)$$

Let us first consider the third-rank tensor which characterizes the crystal response to the incoming second-harmonic field. It is straightforward to see from Equation (6) that the second-order susceptibility tensor is given by the direct product of each bond:

$$\overleftrightarrow{\chi}_{ijk}^{(2)} = \frac{N}{V} \frac{1}{\epsilon_0} \left(\frac{\epsilon(\omega) + 2}{3} \right)^2 \sum_j (\alpha_{2j} \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j). \quad (13)$$

For the case of bcc (001) surface, we just need to insert Equations (10) and (11) into Equation (13) for arbitrary z -axis rotation ϕ and set $\phi = 0$ at the end. The result is

$$\overleftrightarrow{\chi}_{ijk}^{(2)} = -\frac{4\alpha_{\text{eff}}N}{3\sqrt{3}V} \frac{1}{\epsilon_0} \left(\frac{\epsilon(\omega) + 2}{3} \right)^2 \begin{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{pmatrix}, \quad (14)$$

where $\alpha_{\text{eff}} = \alpha_u - \alpha_d$ is the effective hyperpolarizability. For clarity, we explain the indices in the third-rank tensor as follows. In this case, the third-rank tensor can be understood as a 9×3 matrix divided into three matrices having a dimension 3×3 . For a general third-rank tensor ($i, j, k = 1; 2; 3$), the first index i corresponds to the rows in the main matrix (the external one). Similarly, the indices j and k will correspond to the usual way of labeling a 3×3 matrix, where the indices j and k are, respectively, the rows and columns in the inner 3×3 matrix. Analogously, but using the bond definition for the bcc (110) surface, we obtain

$$\overleftrightarrow{\chi}_{ijk}^{(2)} = -\frac{2\sqrt{2}\alpha_{\text{eff}}N}{3\sqrt{3}V} \frac{1}{\epsilon_0} \left(\frac{\epsilon(\omega) + 2}{3} \right)^2 \begin{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 4 \end{pmatrix} \end{pmatrix}, \quad (15)$$

and for completeness, we also provide the third-rank tensor of a bcc (111) surface:

$$\chi_{ijk}^{(2)} = -\frac{4\alpha_{\text{eff}}N}{9V} \left(\frac{\varepsilon(\omega) + 2}{3\varepsilon_0} \right)^2 \begin{pmatrix} \begin{pmatrix} 1 & -1 & 1 \\ -1 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} -1 & -1 & 0 \\ -1 & 1 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{5}{2} \end{pmatrix} \end{pmatrix}. \quad (16)$$

It can be seen that there is only one independent parameter in the third-rank tensor for all the three bcc crystal orientations, namely, α_{eff} . So, SBHM is indeed very restrictive when fitting low-symmetry crystals. Furthermore, it can also be inferred from the location of the nonzero elements that all the tensors are symmetric. In other words, they obey the Kleinman symmetry [14]:

$$d_{ijk} = d_{jki} = d_{kij} = d_{ikj} = d_{jik} = d_{kji}. \quad (17)$$

Evaluating Equation (8) for the case of second-harmonic generation and the given bond orientations, we can obtain an expression for the 4 polarization far fields. Summing up the anharmonic bond dipole contributions from all the 8 bonds, and for simplicity writing $\gamma = (N/V)(1/\varepsilon_0)((\varepsilon(\omega) + 2)/3)$, we get for a (001) bcc crystal the following formulas:

$$\begin{aligned} \mathbf{E}_{\text{ff},ss} &= 0, \\ \mathbf{E}_{\text{ff},sp} &= \frac{4\gamma^2}{3\sqrt{3}}\alpha_{\text{eff}} \sin \theta [\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta], \\ \mathbf{E}_{\text{ff},ps} &= 0, \\ \mathbf{E}_{\text{ff},pp} &= -\frac{2\gamma^2}{3\sqrt{3}}\alpha_{\text{eff}} (\sin 3\theta - \sin \theta) [\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta], \end{aligned} \quad (18)$$

and for bcc (110), we get

$$\begin{aligned} \mathbf{E}_{\text{ff},ss} &= 0, \\ \mathbf{E}_{\text{ff},sp} &= \frac{2\sqrt{2}\gamma^2}{3\sqrt{3}}\alpha_{\text{eff}} \sin \theta \sin^2 \phi [\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta], \\ \mathbf{E}_{\text{ff},ps} &= -\frac{\sqrt{2}\gamma^2}{3\sqrt{3}}\alpha_{\text{eff}} \sin 2\theta \sin 2\phi \hat{\mathbf{y}}, \\ \mathbf{E}_{\text{ff},pp} &= -\frac{2\sqrt{2}\gamma^2}{3\sqrt{3}}\alpha_{\text{eff}} (\cos^2 \theta \cos^2 \phi \sin \theta - 2 \sin^3 \theta) \\ &\quad \cdot [\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta], \end{aligned} \quad (19)$$

whereas for bcc (111), we obtain:

$$\begin{aligned} \mathbf{E}_{\text{ff},ss} &= \frac{4\gamma^2}{9}\alpha_{\text{eff}} (\cos 3\phi - \sin 3\phi) \hat{\mathbf{y}}, \\ \mathbf{E}_{\text{ff},sp} &= -\frac{4\gamma^2}{9}\alpha_{\text{eff}} (\cos \theta (\cos 3\phi + \sin 3\phi) - \sin \theta) \\ &\quad \cdot [\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta], \\ \mathbf{E}_{\text{ff},ps} &= -\frac{4\gamma^2}{9}\alpha_{\text{eff}} \cos^2 \theta (\cos 3\phi - \sin 3\phi) \hat{\mathbf{y}}, \\ \mathbf{E}_{\text{ff},pp} &= \frac{2\gamma^2}{9}\alpha_{\text{eff}} (2 \cos^3 \theta (\sin 3\phi + \cos 3\phi) \\ &\quad + 5 \sin^3 \theta - 2 \sin \theta \cos^2 \theta) \\ &\quad \cdot [\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta]. \end{aligned} \quad (20)$$

It can be seen from symmetry consideration that if the up and down hyperpolarizabilities are the same, bcc crystals will not produce any SHG far field as can be seen by the formulas above. Thus in the bulk where the hyperpolarizabilities are equal, no SHG signal will appear, and the upper and lower bond dipole radiations cancel each other out.

For an fcc crystal structure, we have instead of 8 bonds for a single atom 12 bonds. The orientations of the bonds for (001), (110), and (111) fcc crystal structures are given in Figure 3. For completeness, we provide the bond vectors for the fcc (001) surface. These are the four up bonds with hyperpolarizability α_u :

$$\begin{aligned} \hat{\mathbf{b}}_1 &= \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \\ \hat{\mathbf{b}}_2 &= \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ 0 \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \\ \hat{\mathbf{b}}_3 &= \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \\ \hat{\mathbf{b}}_4 &= \begin{pmatrix} 0 \\ -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \end{aligned} \quad (21)$$

FIGURE 3: Bond orientation of fcc crystal structures: (a) (001), (b) (110), and (c) (111).

and then, we have the four bonds at the xy plane with the hyperpolarizability α_i :

$$\begin{aligned}
 \hat{\mathbf{b}}_5 &= \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}, \\
 \hat{\mathbf{b}}_6 &= \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}, \\
 \hat{\mathbf{b}}_7 &= \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{pmatrix}, \\
 \hat{\mathbf{b}}_8 &= \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix},
 \end{aligned} \tag{22}$$

and finally, the four down bonds with hyperpolarizability α_d :

$$\begin{aligned}
 \hat{\mathbf{b}}_1 &= \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix}, \\
 \hat{\mathbf{b}}_2 &= \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix}, \\
 \hat{\mathbf{b}}_3 &= \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}, \\
 \hat{\mathbf{b}}_4 &= \begin{pmatrix} 0 \\ -\frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}.
 \end{aligned} \tag{23}$$

The third-rank tensor for the fcc (001) surface orientation is obtained using Equation (13) as in the bcc surface:

$$\chi_{ijk}^{(2)} = -\frac{\alpha_{\text{eff}} N}{\sqrt{2V}} \frac{1}{\epsilon_0} \left(\frac{\epsilon(\omega) + 2}{3} \right)^2 \begin{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \end{pmatrix}, \quad (24)$$

whereas the fcc (110) surface third-rank tensor is

$$\chi_{ijk}^{(2)} = -\frac{\alpha_{\text{eff}} N}{2V} \frac{1}{\epsilon_0} \left(\frac{\epsilon(\omega) + 2}{3} \right)^2 \begin{pmatrix} \begin{pmatrix} 0 & 0 & 2 \\ 0 & 0 & 0 \\ 2 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\ \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 3 \end{pmatrix} \end{pmatrix}, \quad (25)$$

and for the fcc (111) surface third-rank tensor, we have

$$\chi_{ijk}^{(2)} = -\frac{\alpha_{\text{eff}} N}{4\sqrt{6}V} \frac{1}{\epsilon_0} \left(\frac{\epsilon(\omega) + 2}{3} \right)^2 \begin{pmatrix} \begin{pmatrix} 1 & -1 & 4 \\ -1 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} -1 & -1 & 0 \\ -1 & 1 & 4 \\ 0 & 1 & 0 \end{pmatrix} \\ \begin{pmatrix} 4 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 8 \end{pmatrix} \end{pmatrix}. \quad (26)$$

As in the case of the bcc surface, SBHM restricts the fcc surface tensors to have only one independent element which is the effective hyperpolarizability α_{eff} . The interface hyperpolarizability α_{int} cancels each other out and vanishes.

Repeating the procedure by now summing the far-field contribution from the 12 bonds, we obtain for a (001) fcc structure the following 4 polarization fields:

$$\begin{aligned} \mathbf{E}_{\text{ff},ss} &= 0, \\ \mathbf{E}_{\text{ff},sp} &= \frac{\gamma^2}{\sqrt{2}} \alpha_{\text{eff}} \sin \theta [\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta], \\ \mathbf{E}_{\text{ff},ps} &= 0, \\ \mathbf{E}_{\text{ff},pp} &= -\frac{\gamma^2}{4\sqrt{2}} \alpha_{\text{eff}} (3 \sin 3\theta - 5 \sin \theta) [\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta]. \end{aligned} \quad (27)$$

For a (110) fcc crystal, we get

$$\begin{aligned} \mathbf{E}_{\text{ff},ss} &= 0, \\ \mathbf{E}_{\text{ff},sp} &= \frac{2\sqrt{2}\gamma^2}{3\sqrt{3}} \alpha_{\text{eff}} \sin \theta \sin^2 \phi [\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta], \\ \mathbf{E}_{\text{ff},ps} &= -\frac{\sqrt{2}\gamma^2}{3\sqrt{3}} \alpha_{\text{eff}} \sin 2\theta \sin 2\phi \hat{\mathbf{y}}, \\ \mathbf{E}_{\text{ff},pp} &= -\frac{2\gamma^2}{3} \sqrt{\frac{2}{3}} \alpha_{\text{eff}} (\sin(\theta) \cos^2(\theta) \cos^2(\phi) - 2 \sin^3(\theta)) \\ &\quad [\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta], \end{aligned} \quad (28)$$

and finally for a (111) fcc crystal, we obtain

$$\begin{aligned} \mathbf{E}_{\text{ff},ss} &= -\frac{\gamma^2}{4\sqrt{6}} \alpha_{\text{eff}} (\sin 3\phi - \cos 3\phi) \hat{\mathbf{y}}, \\ \mathbf{E}_{\text{ff},sp} &= -\frac{\gamma^2}{4\sqrt{6}} \alpha_{\text{eff}} (\cos \theta (\cos 3\phi + \sin 3\phi) - 4 \sin \theta) \\ &\quad [\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta], \\ \mathbf{E}_{\text{ff},ps} &= -\frac{\gamma^2}{4\sqrt{6}} \alpha_{\text{eff}} \cos^2 \theta_i (\cos 3\phi - \sin 3\phi) \hat{\mathbf{y}}, \\ \mathbf{E}_{\text{ff},pp} &= -\frac{\gamma^2}{4\sqrt{6}} \alpha_{\text{eff}} (5 \sin(2\theta + \theta) - \sin(2\theta - \theta) - 10 \sin \theta) \\ &\quad - \cos^2 \theta_i \cos \theta (\cos 3\phi + \sin 3\phi) [\hat{\mathbf{x}} \cos \theta + \hat{\mathbf{z}} \sin \theta]. \end{aligned} \quad (29)$$

Again, we can easily see from the obtained formulas that if the up and down hyperpolarizabilities are equal, $\alpha_{\text{eff}} = 0$ and a fcc bulk will not produce any dipolar SHG signal, and thus as in the case of bcc, no SHG can arise from the bulk of a fcc crystal.

4. BCC and FCC Bulk Response

Before proceeding to the discussion of third-harmonic generation (THG), it is instructive to understand that,

in principle, the SHG total intensity from measurement such as rotational anisotropy spectroscopy (RAS) from a sample may also contain linear SHG field superposition from within the bulk in a competing magnitude with dipolar SHG contribution from the surface, although it is not of dipolar nature. Indeed Peng et al. mentioned that bulk quadrupolar sources and spatial dispersion may also contribute to the total SHG intensity. It is also possible that electric-field-induced SHG (EFISHG) effects in the interface give additional contribution to the total field. Remarkably such additional sources can also be simulated using SBHM although it will only be discussed briefly here. The bulk quadrupolar contribution can be calculated via

$$\begin{aligned} \mathbf{P}_Q^{(2),\text{bulk}} &= \varepsilon_0 \chi_Q^{(2)} \cdots \mathbf{E}_b(\omega) (-i) \otimes \nabla_b \otimes \mathbf{E}_b(\omega), \\ &= \frac{N}{V} \frac{1}{\varepsilon_0} \left(\frac{\varepsilon(\omega) + 2}{3} \right)^2 \sum_{j=1}^n (\beta_{2j} \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j) \\ &\quad \cdots \mathbf{E}_b(\omega) \otimes (-i) \nabla_b \otimes \mathbf{E}_b(\omega), \end{aligned} \quad (30)$$

where $\chi_D^{(2)}$ and $\chi_Q^{(2)}$ are, respectively, the third- and fourth-rank susceptibility tensors; whereas $\mathbf{E}_b(\omega)$ and ∇_b are the macroscopic field inside the bulk and its gradient, respectively; β_{2j} is the bulk quadrupolar SHG hyperpolarizability; and n is the total number of bonds within the conventional cell. Inside the bulk, it is reasonable to only use one bulk hyperpolarizability for all of the bond orientation. The spatial dispersion can be modelled using SBHM in a similar fashion:

$$\begin{aligned} \mathbf{P}_{\text{SD}}^{(2),\text{bulk}} &= \frac{N}{V} \frac{1}{\varepsilon_0} \left(\frac{\varepsilon(\omega) + 2}{3} \right)^2 \sum_{j=1}^n (\beta_{2j} \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j) \\ &\quad \cdots \mathbf{E}_b(\omega) \otimes (2i) \otimes \mathbf{k}_0 \otimes \mathbf{E}_b(\omega), \end{aligned} \quad (31)$$

but now using the outgoing wave $\mathbf{k}_0$ and a factor $2i$ instead. Finally, laser photo induced or charge separation in the interface may also cause EFISHG effect and can also be modelled using SBHM via a fourth rank tensor:

$$\begin{aligned} \mathbf{P}_{\text{EFISH}}^{(2),\text{bulk}} &= \frac{N}{V} \frac{1}{\varepsilon_0} \left(\frac{\varepsilon(\omega) + 2}{3} \right)^3 \sum_{j=1}^n (\alpha_{2j} \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j) \\ &\quad \cdots \mathbf{E}_{\text{int}}(\omega) \otimes \mathbf{E}_{\text{int}}(\omega) \otimes \mathbf{E}_0, \end{aligned} \quad (32)$$

where α_{2j} is the interface dipolar SHG hyperpolarizability and $\mathbf{E}_{\text{int}}(\omega)$ is the electric field at the interface $\mathbf{E}_0$ is the EFISH DC field.

The fields arising from quadrupole, spatial dispersion, and EFISH are linearly mixed together with the surface dipolar SHG field contribution; hence, they may be hard to distinguish in low symmetry lattices although it is possible in some cases to separate their contributions for certain surface orientation using arbitrary polarization [11]. It is thus reasonable to measure the third-harmonic generated far field when probing the bulk especially in centrosymmetric materials where dipolar SHG contribution is forbidden inside the bulk, but dipolar THG and odd-order nonlinear effects are not. This is due to the fact that the number of layers within the bulk involved in generating THG, and it is far larger than the surface THG. Even though the total element in a fourth-rank tensor is 81, it can in many cases be severely simplified especially for low-symmetric structures such as diamond, bcc, and fcc. It is also straightforward to apply SBHM to calculate the fourth-rank tensor, just adding another direct product of the bonds as given in Equation (13):

$$\chi_{ijkl}^{(3)} = \frac{N}{V} \frac{1}{\varepsilon_0} \left(\frac{\varepsilon(\omega) + 2}{3} \right)^3 \sum_j (\alpha_{3j} \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j \otimes \hat{\mathbf{b}}_j). \quad (33)$$

The hyperpolarizability inside the bulk can be assumed to be the same for all bonds; therefore, $\alpha_{3j} = \alpha_{\text{bulk}}$. Setting $\phi = 0$, we obtain for the case of bcc (100) bulk the following fourth-rank tensor:

$$\begin{aligned} \chi_{ijkl}^{(3)} &= \frac{8\alpha_{\text{bulk}} N}{9V} \frac{1}{\varepsilon_0} \left(\frac{\varepsilon(\omega) + 2}{3} \right)^3 \\ &\quad \cdot \begin{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix} \end{pmatrix}. \end{aligned} \quad (34)$$

As can be seen, the fourth-rank tensor in Equation (34) consists of a 3×3 matrix, where each component of the matrix consists of 3×3 matrix elements. The first index i in the tensor corresponds to the rows and the second index j to the columns in the main matrix (the external one). It follows, then, that all the elements in the first row and first column of the external 3×3 have χ_{11kl} indices, whereas for the second

row and third column of the external matrix, it will be χ_{23kl} and so on. In the same way, the indices k and l will correspond to the usual way of labeling a 3×3 matrix, namely, the rows and columns in the inner 3×3 matrix, respectively. However, for the bcc (110) bulk, we have the following:

$$\chi_{ijkl}^{(3)} = \frac{\alpha_{\text{bulk}} N}{2V} \frac{1}{\epsilon_0} \left(\frac{\epsilon(\omega) + 2}{3} \right)^3 \cdot \begin{pmatrix} \begin{pmatrix} 4 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} 0 & 2 & 0 \\ 2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 2 \\ 0 & 0 & 0 \\ 2 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 2 & 0 \\ 2 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & 2 \\ 0 & 0 & 0 \\ 2 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{pmatrix}, \quad (35)$$

and for the bcc (111), we obtain

$$\chi_{ijkl}^{(3)} = \frac{8\alpha_{\text{bulk}} N}{27V} \frac{1}{\epsilon_0} \left(\frac{\epsilon(\omega) + 2}{3} \right)^3 \cdot \begin{pmatrix} \begin{pmatrix} 6 & 0 & 0 \\ 0 & 2 & -1 \\ 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} 0 & 2 & -1 \\ 2 & 0 & -1 \\ -1 & -1 & 0 \end{pmatrix} \begin{pmatrix} 1 & -1 & 1 \\ -1 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 2 & -1 \\ 2 & 0 & -1 \\ -1 & -1 & 0 \end{pmatrix} \begin{pmatrix} 2 & 0 & -1 \\ 0 & 2 & 1 \\ -1 & 1 & 1 \end{pmatrix} \begin{pmatrix} -1 & -1 & 0 \\ -1 & 1 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\ \begin{pmatrix} 1 & -1 & 1 \\ -1 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} -1 & -1 & 0 \\ -1 & 1 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 7 \end{pmatrix} \end{pmatrix}. \quad (36)$$

Remarkably, SBHM only demands—again—one independent parameter inside the fourth-rank tensor. We note here that the Kleinman symmetry is fulfilled for the three bcc bulk orientation, and this is in agreement with the inherent assumption of SBHM [24].

For the fcc (100) bulk, we obtain

$$\chi_{ijkl}^{(3)} = \frac{\alpha_{\text{bulk}}}{\epsilon_0} \frac{N}{V} \left(\frac{\epsilon(\omega) + 2}{3} \right)^3 \cdot \begin{pmatrix} \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{pmatrix}, \quad (37)$$

and for the fcc (110) bulk,

$$\chi_{ijkl}^{(3)} = \frac{\alpha_{\text{bulk}}}{\epsilon_0} \frac{N}{V} \left(\frac{\epsilon(\omega) + 2}{3} \right)^3 \cdot \begin{pmatrix} \begin{pmatrix} 4 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 2 \\ 0 & 0 & 0 \\ 2 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & 2 \\ 0 & 0 & 0 \\ 2 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{pmatrix}. \quad (38)$$

The fcc (111) bulk fourth rank tensor can be obtained similarly, but it is not depicted here because it is very lengthy. However, it is easy to infer that it also contains only one independent tensor element which is α_{bulk} . It should be noted that the bulk fourth-rank susceptibility tensor to calculate the bulk quadrupole source, spatial dispersion, EFISH, and THG for bcc and fcc crystal structures has the same form because they are defined in Equation (33). However, one should take care of the susceptibility α_{bulk} which is also a function of the frequency as can be seen in Equation (5), so it can be different for different sources and should be fitted experimentally—as is the case of any phenomenology theory.

5. Conclusion

We have calculated the bcc and fcc third-rank surface susceptibility tensors and its corresponding far field. In addition, we also discuss its bulk nonlinear effects and calculate its fourth-rank tensor. It is remarkable to see that

the high-restriction SBHM imposes on both the bcc and fcc surfaces as well as its bulk susceptibility tensors where we have shown that it only requires one independent element to describe SHG and THG radiations in reflection.

Data Availability

The [Mathematica.nb] data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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