

***Ab initio* calculation of many-body effects on the second-harmonic generation spectra of hexagonal SiC polytypes**

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We investigate the influence of crystal local fields and excitonic effects on the spectrum of the second harmonic generation of three polytypes of silicon carbide by using time-dependent density-functional theory including many-body effects, namely, quasiparticle corrections through the scissors operator, crystal local field effects, and excitonic interaction. The relation between the scalar density response and the components of the rank 3 tensor $d^{(2)}$ is established by calculating the response along different polarization directions. We find that local-field effects, although necessary for a rigorous description in the theory, yield only small contributions to the spectra, whereas excitonic effects have a strong influence on the second harmonic generation. We compare static values of the second harmonic coefficients to recent measurements and obtain very good agreement.

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I. INTRODUCTION

The *ab initio* calculation of second-harmonic generation (SHG) in solids is still a great challenge, both for theoretical developments and computational resources. The problem has been revisited several times, as computational schemes and hardware have improved. In recent work^{1,2} we presented a formalism to calculate the frequency-dependent macroscopic second-harmonic susceptibility within the time-dependent density-functional theory (TDDFT) framework, thus taking advantage of recent developments in this field concerning the inclusion of many-body effects. Doing so, we are able to include crystal local-field and excitonic effects in a straightforward way and have shown that both effects are crucial to obtain quantitative agreement with experiment. In this paper we elaborate on the importance of the two effects by studying them for hexagonal SiC polytypes. The polymorphism is realized by different stacking orders of Si-C bilayers of either cubic (*c*) or hexagonal (*h*) types in the *z* direction.³ One can define the hexagonality *H* of the polytype by the ratio $H = h/(h + c)$, where *h* and *c* are the numbers of hexagonal and cubic layers, respectively. The polymorphism preserves the point group of the crystal symmetry, thus allowing direct comparison of the components of the susceptibility. This provides a way of studying the influence of different electronic structures on the local-field and excitonic effects.

SiC polytypes have been studied extensively in the context of *ab initio* calculations of SHG. Chen *et al.*⁴ use a scheme to calculate the static second-harmonic coefficients in the independent particle approximation of various SiC polytypes. In a later work⁵ the same authors use a refined scheme to describe nonlinear local-field effects for the static susceptibility and find a dependence of local-field corrections on the hexagonality. They report a decrease in most coefficients when local fields are accounted for. Rashkeev *et al.*,⁶ using a computational scheme similar to that of Chen *et al.*,⁴ while neglecting local-field and many-body effects, are able to calculate the imaginary part of the frequency-dependent SHG susceptibility, from which, through a Kramers-Kronig relation, they infer the real part, which then enables them to construct the modulo of the susceptibility. Performing a transition-by-transition analysis

of the spectra, they can assign single spectral features to single band transitions, thereby suggesting nonlinear spectroscopy as a probe for the electronic structure. All these works assume that the quasiparticle effects^{7,8} can be reproduced by a scissors operator.^{9,10} This assumption has been investigated in detail by Adolph and Bechstedt.¹¹ They compared the optical matrix elements calculated with a scissor operator with those obtained by a GW calculation. They found that the scissors operator approach describes the quasiparticle results remarkably well¹¹ for all the SiC polytypes considered in this paper.

Thus most of the previous works^{4-6,11} have mainly focused on the applicability of the theoretical approach used to calculate the nonlinear optical properties and, as far as SiC polytypes are concerned, on the dependence of the static susceptibility on the hexagonality of these systems. Furthermore, Kleinmann permutation relations have been tested on the full spectra and found to be applicable only in the low-frequency range.¹² Thus only few works have been concerned with the full spectrum or its dependence on local-field and excitonic effects.

In this paper, we follow our previous approach^{1,2} but advance two important steps farther in order to obtain the second-harmonic susceptibility for any symmetry of the system considered. First, we employ a systematic way of including crystal local-field corrections in the optical limit, thus being able to show the dependence of the second-harmonic susceptibility on the microscopic electric field; and second, we include many-body effects such as excitons by using TDDFT. The paper is organized as follows. In Sec. II we present the formalism used to obtain the second-harmonic susceptibility from TDDFT, taking great care to obtain the correct elements of the second-harmonic tensor. In Sec. III we proceed to show how the inhomogeneity of the material affects the SHG due to crystal local-fields effects and then, in Sec. IV, show the dependence of excitonic effects on the hexagonality. Finally, in Sec. V we compare our results with previous calculations and experimental data in the static limit.

II. METHOD

We use TDDFT generalized to second-order responses to calculate the second-harmonic susceptibility as outlined

previously.^{2,13} We formulate the macroscopic second-order polarizability in terms of the total electric fields E as

$$P_M(\mathbf{q}_1 + \mathbf{q}_2, \omega) = d^{(2)}(\mathbf{q}_1 + \mathbf{q}_2, \mathbf{q}_1, \mathbf{q}_2, 2\omega, \omega) \mathbf{E}(\mathbf{q}_1) \mathbf{E}(\mathbf{q}_2). \quad (1)$$

In this theoretical section we use $d^{(2)}$ instead of the more widely used $\chi^{(2)}$, because it allows us to keep track of the symmetry properties. We recall that if the last two indices of the tensors are the same, we have $d_{ijj}^{(2)} = \chi_{ijj}^{(2)}$, and if they are different, we have the relation $2d_{ijk} = \chi_{ijk}$.¹⁴ Later, when discussing results, we show $\chi^{(2)}$ quantities, since they are more commonly used.

The macroscopic second-harmonic susceptibility $d^{(2)}$ is expressed in terms of the averaged microscopic second-order current density response as

$$d^{(2)} = \frac{i\pi}{\omega^3} \mathbf{M}(\mathbf{q}) \chi_{\mathbf{j}\mathbf{j}}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) \mathbf{N}(\mathbf{q}_1) \mathbf{N}(\mathbf{q}_2). \quad (2)$$

The terms $\mathbf{M}(\mathbf{q})$ and $\mathbf{N}(\mathbf{q})$ come from averaging the microscopic total fields² and are thus first-order quantities,

$$\mathbf{M}(\mathbf{q}) = \left[1 + 4\pi \tilde{\alpha}(\mathbf{q}, \mathbf{q}) \frac{1}{\omega^2} \frac{\mathbf{q} \mathbf{q}}{q} \right]^{-1}, \quad (3)$$

$$\mathbf{N}(\mathbf{q}) = \left[1 + 4\pi \frac{1}{\omega^2} \frac{\mathbf{q} \mathbf{q}}{q} \tilde{\alpha}(\mathbf{q}, \mathbf{q}) \right]^{-1}, \quad (4)$$

which depend on the linear current density response $\chi_{\mathbf{j}\mathbf{j}}$ via the definition of the quasisusceptibility $\tilde{\alpha}$:

$$\tilde{\alpha}(\mathbf{q}_1, \mathbf{q}_2, \omega) = -\frac{1}{\omega^2} [\chi_{\mathbf{j}\mathbf{j}}(\mathbf{q}_1, \mathbf{q}_2, \omega) - \rho(\mathbf{q}_1) \delta_{\mathbf{q}_1 - \mathbf{q}_2}]. \quad (5)$$

In the optical limit, that is, $\mathbf{q} \rightarrow 0$, we note that transverse and longitudinal responses coincide for uniform electric fields,¹⁵ and thus we can express Eq. (2) solely in terms of its longitudinal projections:

$$\begin{aligned} (\mathbf{q}_1 + \mathbf{q}_2) d^{(2)} \mathbf{q}_1 \mathbf{q}_2 \\ = -i \varepsilon_M(\mathbf{q}_1 + \mathbf{q}_2, 2\omega) \chi_{\rho\rho\rho}(\mathbf{q}_1 + \mathbf{q}_2, \mathbf{q}_1, \mathbf{q}_2, 2\omega, \omega) \varepsilon_M \\ \times (\mathbf{q}_1, \omega) \varepsilon_M(\mathbf{q}_2, \omega), \end{aligned} \quad (6)$$

where $\mathbf{q}$ are polarization directions that coincide, in this limit, with the propagation directions, because for a longitudinal field, polarization and propagation are parallel. We also note that in this limit the linear prefactor, Eqs. (3) and (4), are both identical to the macroscopic dielectric functions ε_M .¹⁶

The microscopic second-order density response $\chi_{\rho\rho\rho}$ is obtained via the second-order TDDFT Dyson equation,

$$\begin{aligned} \chi_{\rho\rho\rho}(1, 2, 3) \\ = \chi_{\rho\rho\rho}^{(0)}(1, 2, 3) + \int d4 d5 \chi_{\rho\rho\rho}^{(0)}(1, 4, 3) f_{uxc}(4, 5) \chi_{\rho\rho}(5, 2) \\ + \int d4 d5 \chi_{\rho\rho\rho}^{(0)}(1, 2, 4) f_{uxc}(4, 5) \chi_{\rho\rho}(5, 3) + \int d4 d5 d6 d7 \\ \times \chi_{\rho\rho\rho}^{(0)}(1, 5, 4) f_{uxc}(5, 6) \chi_{\rho\rho}(6, 2) f_{uxc}(4, 7) \chi_{\rho\rho}(7, 3) \\ + \int d4 d5 d6 \chi_{\rho\rho}^{(0)}(1, 4) g_{xc}(4, 5, 6) \chi_{\rho\rho}(6, 3) \chi_{\rho\rho}(5, 2) \\ + \int d4 d5 \chi_{\rho\rho}^{(0)}(1, 4) f_{uxc}(4, 5) \chi_{\rho\rho\rho}(5, 2, 3), \end{aligned} \quad (7)$$

where we used the shorthand $1 = \mathbf{r}_1, t_1$, etc., $\chi_{\rho\rho}$ is the linear density response, and $\chi_{\rho\rho}^{(0)}$ and $\chi_{\rho\rho\rho}^{(0)}$ are the independent particle (Kohn-Sham) responses.

The linear kernels

$$f_{vxc}(1, 2) = u(1, 2) + f_{xc}(1, 2), \quad (8)$$

which are the sum of the Coulomb potential $u(1, 2) = u(1) \delta(1, 2)$ and the exchange correlation kernel, allow the inclusion of many-body effects. The difference between the microscopic and the macroscopic response is due to the local fields that stem from the spatial inhomogeneity of the crystal. The second-order kernel $g_{xc}(1, 2, 3) = \delta f_{xc}(1, 2) / \delta \rho(3)$ is set to 0 throughout the following, since it is assumed to yield only negligible contributions.

The density response function $\chi_{\rho\rho\rho}$ is the response of a scalar quantity to a scalar field and is hence a scalar; in contrast, we aim to calculate the third rank tensor $d^{(2)}$, which, in general, has 27 components. This relation between the tensor components of $d^{(2)}$ and the scalar longitudinal density response is given by Eq. (6). Writing it with the vector components of $\mathbf{q}$, we have

$$\begin{aligned} \sum_{ijk} (q_{1i} + q_{2i}) d_{ijk}^{(2)} q_{1j} q_{1k} \\ = -i \varepsilon_M(\mathbf{q}_1 + \mathbf{q}_2, 2\omega) \chi_{\rho\rho\rho}(\mathbf{q}_1 + \mathbf{q}_2, \mathbf{q}_1, \mathbf{q}_2, 2\omega, \omega) \\ \times \varepsilon_M(\mathbf{q}_1, \omega) \varepsilon_M(\mathbf{q}_2, \omega). \end{aligned} \quad (9)$$

This means that to obtain single tensor components we have to perform TDDFT calculations along different polarization directions.

There are four different kinds of tensor components, according to their index structure: the diagonals $d_{iii}^{(2)}$, two different block diagonals $d_{ijj}^{(2)}$ and $d_{ijj}^{(2)}$, and the off-diagonals $d_{ijk}^{(2)}$. We also note that for SHG the last two indices are interchangeable, that is, $d_{ijk}^{(2)} = d_{ikj}^{(2)}$. Depending on the symmetry, some components can be 0, which facilitates the solution of Eq. (9) for some symmetry groups. This also means that for the same tensor component, it might be necessary to do a calculation with different polarizations, depending on the symmetry group of the crystal.

a. Components $d_{iii}^{(2)}$: For components of this form it is sufficient to perform a calculation with the polarizations in $\mathbf{q}_1 = \mathbf{q}_2 = \mathbf{e}_i$, where $\mathbf{e}_i$ is the unit vector in the Cartesian direction $i \in \{x, y, z\}$. Equation (9) thus reads

$$d_{iii}^{(2)} = -i \varepsilon_M(\mathbf{e}_i, 2\omega) \chi_{\rho\rho\rho}(2\mathbf{e}_i, \mathbf{e}_i, \mathbf{e}_i) \varepsilon_M(\mathbf{e}_i, \omega) \varepsilon_M(\mathbf{e}_i, \omega). \quad (10)$$

This is obviously true for any symmetry.

b. Components $d_{ijj}^{(2)}$ and $d_{ijj}^{(2)}$: In most crystal symmetries the components $d_{ijj}^{(2)}$ and $d_{ijj}^{(2)}$ are not simultaneously nonzero. The exceptions are groups C_1 and C_{6v} , which we have to consider separately. In the general case it is sufficient to make a calculation with the polarizations $\mathbf{q}_1 = \mathbf{e}_i$ and $\mathbf{q}_2 = \mathbf{e}_j$. With this choice of polarization directions, Eq. (9) reads

$$\begin{aligned} 2d_{ijj} + d_{ijj} = -i \varepsilon_M(\mathbf{e}_i + \mathbf{e}_j, 2\omega) \chi_{\rho\rho\rho} \\ \times (\mathbf{e}_i + \mathbf{e}_j, \mathbf{e}_i, \mathbf{e}_j) \varepsilon_M(\mathbf{e}_i, \omega) \varepsilon_M(\mathbf{e}_j, \omega). \end{aligned} \quad (11)$$

So since one of the two components on the left-hand side is 0, this equation yields the non-zero component.

For the symmetry groups C_1 and C_{6v} the two components are not independent. Therefore we have to perform an additional TDDFT calculation, with the polarizations $\mathbf{q}_1 = \mathbf{e}_i$ and $\mathbf{q}_2 = -\mathbf{e}_j$ yielding Eq. (9) as

$$2d_{ij}^{(2)} - d_{ijj}^{(2)} = -i\varepsilon_M(\mathbf{e}_i - \mathbf{e}_j, 2\omega)\chi_{\rho\rho\rho} \times (\mathbf{e}_i - \mathbf{e}_j, \mathbf{e}_i, -\mathbf{e}_j)\varepsilon_M(\mathbf{e}_j, \omega)\varepsilon_M(-\mathbf{e}_j, \omega). \quad (12)$$

Adding or subtracting this from Eq. (11) yields the single component.

c. Components $d_{ijk}^{(2)}$: For the symmetry groups (T_d , T , D_6 , and D_4) the off-diagonal elements are the only nonzero components. Then it is sufficient to do a single calculation with $\mathbf{q}_1 = \mathbf{q}_2 = \mathbf{e}_i + \mathbf{e}_j + \mathbf{e}_k$, yielding the component directly; for example, for the cubic T_d . Note that the factor in front of $d_{ijk}^{(2)}$ in this expression can change depending on how many of these components are nonzero in a specific symmetry group.

$$3d_{ijk}^{(2)} = -i\varepsilon_M[(\mathbf{e}_i + \mathbf{e}_j + \mathbf{e}_k), 2\omega]\chi_{\rho\rho\rho} \times [2(\mathbf{e}_i + \mathbf{e}_j + \mathbf{e}_k), \mathbf{e}_i + \mathbf{e}_j + \mathbf{e}_k, \mathbf{e}_i + \mathbf{e}_j + \mathbf{e}_k] \times \varepsilon_M\mathbf{e}_i + \mathbf{e}_j + \mathbf{e}_k, \omega)\varepsilon_M(\mathbf{e}_i + \mathbf{e}_j + \mathbf{e}_k, \omega). \quad (13)$$

In the case of the symmetry groups C_1 , C_2 , D_3 , C_3 , D_{2d} , S_4 , D_2 , and C_6 , there is no generally applicable combination. Instead, one has to decide for each symmetry which is the best way to obtain the component.

A. Computational details

For the TDDFT calculation with our implementation,²⁷ we use density-functional theory (DFT) ground states obtained with the ABINIT package,¹⁷ which gives the Kohn-Sham

energies and wave functions in terms of a basis of plane waves. The local density approximation for the exchange and correlation potential is used and the atomic core electrons are approximated by norm-conserving pseudopotentials of the Troullier-Martins form.¹⁸ The primitive unit cells of the three polytypes have 4, 8, and 12 atoms, respectively, and we used a cutoff of 50 Ha for the basis of all polytypes. The experimental cell parameters are $a = 5.8$ Bohr for all compounds and $c = 9.37$, 18.99, and 28.55 for 2h, 4h, and 6h, respectively.

Calculations of the second-harmonic spectra are done with a random sampling of the Brillouin zone for hexagonal polytypes. Convergence was reached with 1600 $\mathbf{k}$ points for 2h $d_{zzz}^{(2)}$, 2400 for 2h $d_{xxz}^{(2)}$, and 800 for all 4h and 6h components. Convergence of the local-field effects with respect to the number of included $\mathbf{G}$ vectors was reached at 23 for 2h $d_{xxz}^{(2)}$, 59 for 2h $d_{zzz}^{(2)}$, 39 for 4h $d_{xxz}^{(2)}$, and $d_{zzz}^{(2)}$ and 43 for all 6h components. The number of conduction bands necessary for convergence in the considered energy range was 12, 24, and 36 for the 2h, 4h, and 6h components, respectively. The basis size for the DFT wave functions when used in the TDDFT calculation was sufficiently converged with 300 plane waves for all polytypes.

Quasiparticle effects are accounted for by shifting the conduction states by a constant (scissors) shift of $\Delta = 0.8$ eV, which has been demonstrated to yield results in excellent agreement with GW calculations.¹¹

III. LOCAL-FIELD EFFECTS

When calculating $d_{ijk}^{(2)}$ according to Eq. (6), crystal local-field effects are included in $\chi_{\rho\rho\rho}$ and in the ε_M . The noninteracting (Kohn-Sham) response function $\chi_{\rho\rho\rho}^{(0)}$ in momentum space is represented as a rank 3 tensor in terms of reciprocal lattice vectors $\mathbf{G}$:

$$\begin{aligned} \chi_0^{(2)}(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G}, \mathbf{q}_1 + \mathbf{G}_1, \mathbf{q}_2 + \mathbf{G}_2, 2\omega, \omega) \\ = \frac{2}{V} \sum_{nn'n''\mathbf{k}} \frac{\langle n_{\mathbf{k}} | e^{-i(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{G})\mathbf{r}} | n'_{\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2} \rangle}{(E_{n\mathbf{k}} - E_{n'\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2} + 2\omega + 2i\eta)} \left[(f_{n\mathbf{k}} - f_{n''\mathbf{k} + \mathbf{q}_2}) \frac{\langle n'_{\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2} | e^{i(\mathbf{q}_1 + \mathbf{G}_1)\mathbf{r}} | n''_{\mathbf{k} + \mathbf{q}_2} \rangle \langle n''_{\mathbf{k} + \mathbf{q}_2} | e^{i(\mathbf{q}_2 + \mathbf{G}_2)\mathbf{r}} | n_{\mathbf{k}} \rangle}{(E_{n\mathbf{k}} - E_{n''\mathbf{k} + \mathbf{q}_2} + \omega + i\eta)} \right. \\ + (f_{n\mathbf{k}} - f_{n''\mathbf{k} + \mathbf{q}_1}) \frac{\langle n'_{\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2} | e^{i(\mathbf{q}_2 + \mathbf{G}_2)\mathbf{r}} | n''_{\mathbf{k} + \mathbf{q}_1} \rangle \langle n''_{\mathbf{k} + \mathbf{q}_1} | e^{i(\mathbf{q}_1 + \mathbf{G}_1)\mathbf{r}} | n_{\mathbf{k}} \rangle}{(E_{n\mathbf{k}} - E_{n''\mathbf{k} + \mathbf{q}_1} + \omega + i\eta)} \\ + (f_{n'\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2} - f_{n''\mathbf{k} + \mathbf{q}_1}) \frac{\langle n'_{\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2} | e^{i(\mathbf{q}_2 + \mathbf{G}_2)\mathbf{r}} | n''_{\mathbf{k} + \mathbf{q}_1} \rangle \langle n''_{\mathbf{k} + \mathbf{q}_1} | e^{i(\mathbf{q}_1 + \mathbf{G}_1)\mathbf{r}} | n_{\mathbf{k}} \rangle}{(E_{n'\mathbf{k} + \mathbf{q}_1} - E_{n''\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2} + \omega + i\eta)} \\ \left. + (f_{n'\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2} - f_{n''\mathbf{k} + \mathbf{q}_2}) \frac{\langle n'_{\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2} | e^{i(\mathbf{q}_1 + \mathbf{G}_1)\mathbf{r}} | n''_{\mathbf{k} + \mathbf{q}_2} \rangle \langle n''_{\mathbf{k} + \mathbf{q}_2} | e^{i(\mathbf{q}_2 + \mathbf{G}_2)\mathbf{r}} | n_{\mathbf{k}} \rangle}{(E_{n'\mathbf{k} + \mathbf{q}_2} - E_{n''\mathbf{k} + \mathbf{q}_1 + \mathbf{q}_2} + \omega + i\eta)} \right]. \quad (14) \end{aligned}$$

This enters in the TDDFT Dyson equation, (7), where the Coulomb potential in momentum space $u(\mathbf{q} + \mathbf{G}) = \frac{4\pi}{|\mathbf{q} + \mathbf{G}|^2}$ connects it with the full $\chi_{\rho\rho\rho}$. The second place in which local-field effects enter is in the macroscopic dielectric functions ε_M , which relate the microscopic response to the macroscopic susceptibility. These quantities also contain local-field effects

and are calculated according to the Adler-Wiser relation,¹⁹⁻²¹

$$\varepsilon_M(\omega) = \lim_{\mathbf{q} \rightarrow 0} \frac{1}{\varepsilon_{\mathbf{G}=0, \mathbf{G}=0}^{-1}(\mathbf{q}, \omega)}, \quad (15)$$

where, again, a careful consideration of the $\mathbf{G}$ dependence is crucial.

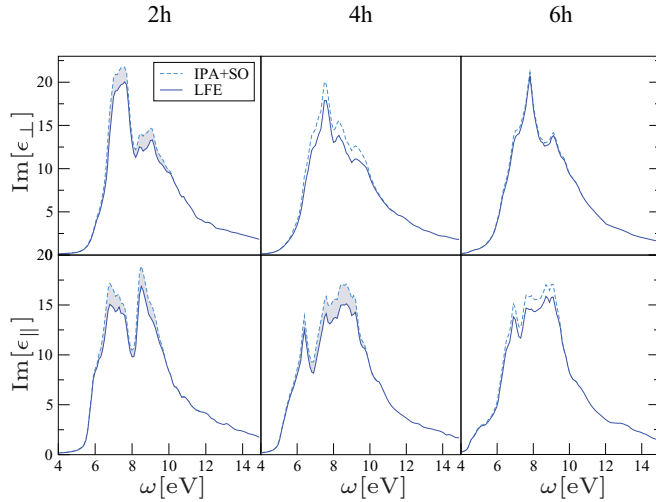


FIG. 1. (Color online) Influence of local fields on the imaginary part of the components of the linear dielectric tensor for the SiC polytypes 2h, 4h, and 6h, where calculations accounting for local fields are denoted LFE and those where they are neglected as IPA + SO. Both calculations include quasiparticle effects via the scissors operator (SO). For the perpendicular component $\varepsilon_{\perp}$, local-field effects decrease with decreasing hexagonality and vanish for 6h, while the local-field effect for the $\varepsilon_{\parallel}$ component is independent of the hexagonality.

Therefore we have to analyze local-field effects in the linear dielectric tensor as well. Due to the crystal symmetry the hexagonal polytypes have an optical anisotropy with two independent components of the dielectric tensor, which are commonly denoted $\varepsilon_{\parallel} = \varepsilon_{zz}$ and $\varepsilon_{\perp} = \frac{1}{2}(\varepsilon_{xx} + \varepsilon_{yy})$. In Fig. 1 we show the local-field effect contribution in these two components for the three polytypes. Note that here and in the following local field, calculations are always performed including quasiparticle effects via the scissors operator. We can see a clear trend for the $\varepsilon_{\perp}$ component, where the effect decreases with decreasing hexagonality and almost vanishes for the 6h polytype. The effect for the $\varepsilon_{\parallel}$ component, however, seems to be independent of the hexagonality, being of the same magnitude for all three polytypes. We also note that the relative local-field effect in the $\varepsilon_{\parallel}$ component is of the same size as for the $\varepsilon_{\perp}$ in 2h.

Since local-field effects stem from the microscopic fields that are due to the inhomogeneity of the crystal, we would like to link this dependence of the local-field effect to the electronic densities of the different polytypes and thus explain the different behavior in terms of the different electronic densities. Inhomogeneity of a density can be considered as the variation from a mean value. To quantify inhomogeneity in this sense, we consider the Fourier transform of the density, which decomposes the density into its constituent frequencies. The reasoning here is that for a homogeneous density, only one Fourier component will be present, while inhomogeneous densities have a more complex decomposition.

We perform a discrete Fourier transform on the real-space DFT densities for the different polytypes and consider the $(b_1, 0, 0)$ and $(0, b_2, 0) = (0, 0, b_3)$ directions, which correspond to the $\parallel$ and $\perp$ directions, respectively. Inspection of the three-dimensional Fourier-transformed density shows that,

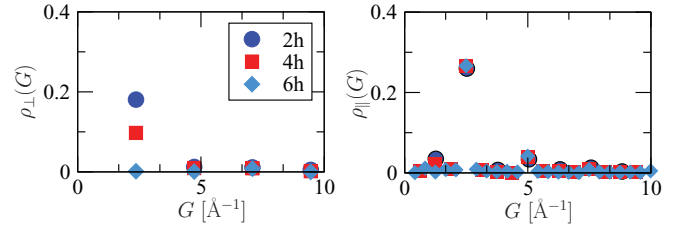


FIG. 2. (Color online) Fourier decomposition of the electronic densities of the three polytypes 2h, 4h, and 6h along the directions $\mathbf{b}_1$ and $\mathbf{b}_2 = \mathbf{b}_3$, which correspond to the $\parallel$ and $\perp$ directions, respectively. Values are normalized to the maximum of each transform, which occurs at $G = 0$ and is not shown here. The different number of points in the b_1 direction for the different polytypes is due to the different size of the unit cell in that direction.

indeed, these directions yield the only significant contribution. In Fig. 2 we compare the result for the three polytypes. First, we note the strong dependence on hexagonality of the density in the $\perp$ direction, where the values at the first $\mathbf{G}$ decrease with decreasing hexagonality. Indeed, the 6h polytype exhibits no significant deviation from the maximum at $G = 0$ (not shown in Fig. 2) and can thus be interpreted as being almost completely homogeneous. This behavior is consistent with the absence of local-field effects for this component of 6h. We find the same consistency for the z direction, where all densities show the same dispersion and no polytype-related dependence is discernible in the spectra. Furthermore, we note that the value of the peak at $G = 2.5 \text{ \AA}^{-1}$ is the same as for the peak for the 2h in the $\perp$ direction at the same G values, indicating the same importance of local-field effects for the $\varepsilon_{\perp}$ of 2h and the $\varepsilon_{\parallel}$ for all polytypes. Also, this corresponds to the observations we made for Fig. 1.

The analysis of the electronic density is thus consistent with the influence of local-field effects on the linear dielectric tensor. As far as the second-harmonic susceptibility is concerned, however, it is not enough to consider only the linear ε_M that enter in Eq. (9), but also the contribution of the second-order TDDFT Dyson equation, (7) where local fields are accounted for as well, must be considered. Figure 3 shows the zzz and xzx component of the macroscopic second-order susceptibility for the same polytypes as in Fig. 1. While the influence of the local field on the xzx component can be seen to be roughly the same as for $\varepsilon_{\perp}$, the overall trend is not as clear as in the linear case. This is partly due to the fact that xzx accounts for effects in two crystallographic directions, but also due to the more complex mixing of effects in the Dyson equation. For the zzz component the comparison with the linear case is more complicated to interpret, since the only discernible local-field effects in $\chi^{(2)}$ occur in the 2h component, while in $\varepsilon_{\parallel}$ it is roughly the same for all polytypes.

To better understand how the crystal local fields enter into the macroscopic second-order susceptibility, we note that in the limiting case $\mathbf{G} = 0$ and $f_{xc} = 0$, that is, no local-field effects and no exchange and correlation (here referred to as the independent particle approximation; IPA), the ε_M prefactors of the $\chi_{\rho\rho\rho}$ cancel with the linear terms of the TDDFT Dyson equation:

$$(\mathbf{q}_1 + \mathbf{q}_2)d_{\text{IPA}}^{(2)}\mathbf{q}_1\mathbf{q}_2 = -i\chi_{\rho\rho\rho}^{(0)}(\mathbf{q}_1 + \mathbf{q}_2, \mathbf{q}_1, \mathbf{q}_2, 2\omega, \omega). \quad (16)$$

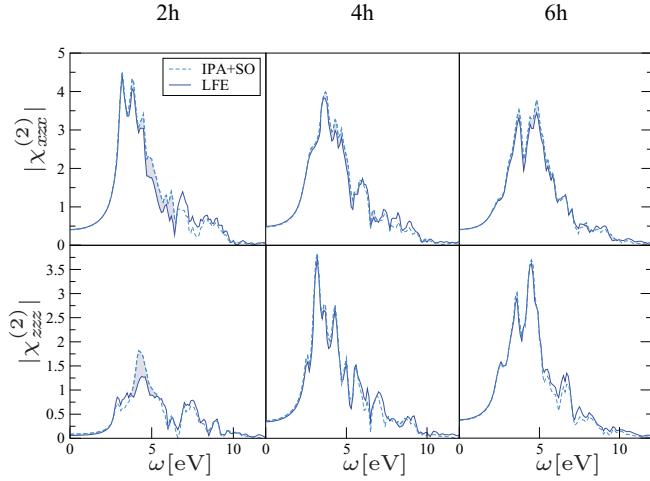


FIG. 3. (Color online) Local-field effects (LFEs) for the xzx (upper panels) and zzz (lower panels) components of $\chi^{(2)}$ (in a.u.) for the three SiC polytypes compared with an independent particle calculation (IPA + SO) where no local-field effects are accounted for. Both calculations include quasiparticle effects via the scissors operator (SO).

This exact cancellation in the absence of local fields means that in the presence of local fields there is still some considerable cancellation, since the local-field effects in the ε_M are not very strong.

IV. EXCITONIC EFFECTS

As for the local-field effects, excitonic effects are included in two places in Eq. (9), the ε_M and the $\chi_{\rho\rho\rho}$ via the second-order TDDFT Dyson equation, (7). However, while in the local-field case the two contributions have the tendency to cancel each other, the situation is different for the excitonic effects. In the calculation of ε_M as well as in the TDDFT Dyson equation, we use the model kernel

$$f_{xc} = -\frac{\alpha}{|\mathbf{q} + \mathbf{G}|^2}, \quad (17)$$

which corrects the absence of a long-range interaction for the optical limit and has been shown to yield excellent results for the linear response compared to the solution of the Bethe-Salpeter equation.^{22,23} The value of α is thus an effective parameter that reproduces the Bethe-Salpeter result. The simplicity of this kernel has the drawback that it is a static approximation to what is generally a dynamic problem. Therefore, the value used for α should change slightly with the energy range one is considering. This means, especially, that for the static limit of $\chi^{(2)}(\omega)$, one has to use a different value of α .

We show the influence of this kernel on the linear macroscopic dielectric function in Fig. 4. In Fig. 5 we show the effect the long-range kernel has on the macroscopic second-order susceptibility for the different polytypes by comparing it to the results where only local fields are accounted for. We note that there is no apparent dependence of the excitonic effects on the hexagonality, but both components and all polytypes show a dramatic increase in the intensity of $\chi^{(2)}$.

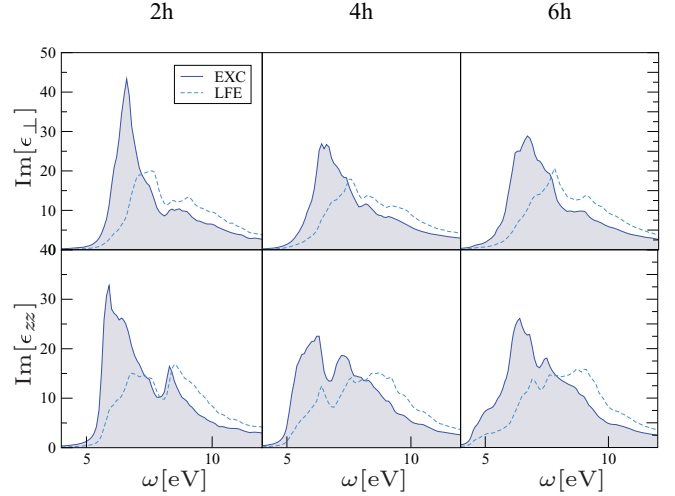


FIG. 4. (Color online) Influence of the long-range kernel, Eq. (17), on the macroscopic dielectric function with $\alpha = 0.5$.

While the microscopic $\chi_{\rho\rho\rho}$ (not shown here) differs by orders of magnitude, depending on whether or not local fields are included, the effect of the long-range kernel in the second-order TDDFT Dyson equation turns out to be negligible; that is, its inclusion does not affect the resulting $\chi_{\rho\rho\rho}$. Therefore, in this scheme, almost all excitonic effects of the second-order susceptibility stem from the ε_M and how they are incorporated into the equation. Considering, however, the influence of the long-range kernel on the ε_M as shown in Fig. 4, we note that it is weaker than in the nonlinear case, and above all it only increases the peaks at the onset of absorption.

The overall increase in $\chi^{(2)}$ can be understood by considering again the limiting case of $\mathbf{G} = 0$, but this time keeping the f_{uxc} according to Eq. (17). In this case it is possible to solve the TDDFT Dyson equation, (7), analytically and thus obtain

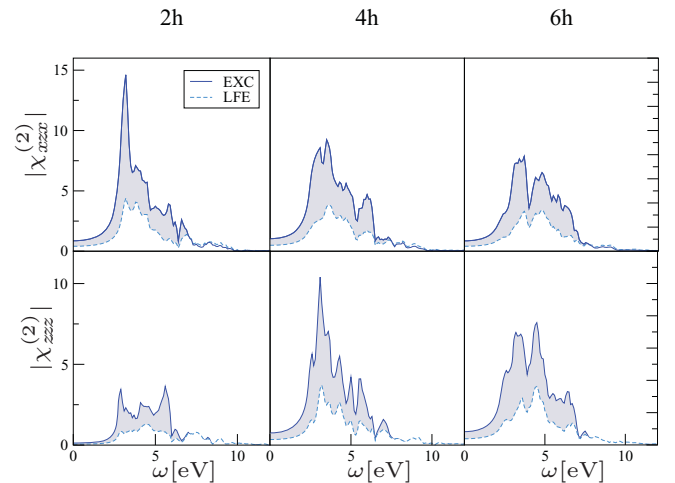


FIG. 5. (Color online) Excitonic effects (EXC) for the xzx (upper panels) and zzz (lower panels) components of $\chi^{(2)}$ (in a.u.) for the three SiC polytypes compared with a calculation where only local fields are accounted for, i.e., Fig. 3. The value of α is 0.5²³ and both calculations include quasiparticle effects via the scissors operator.

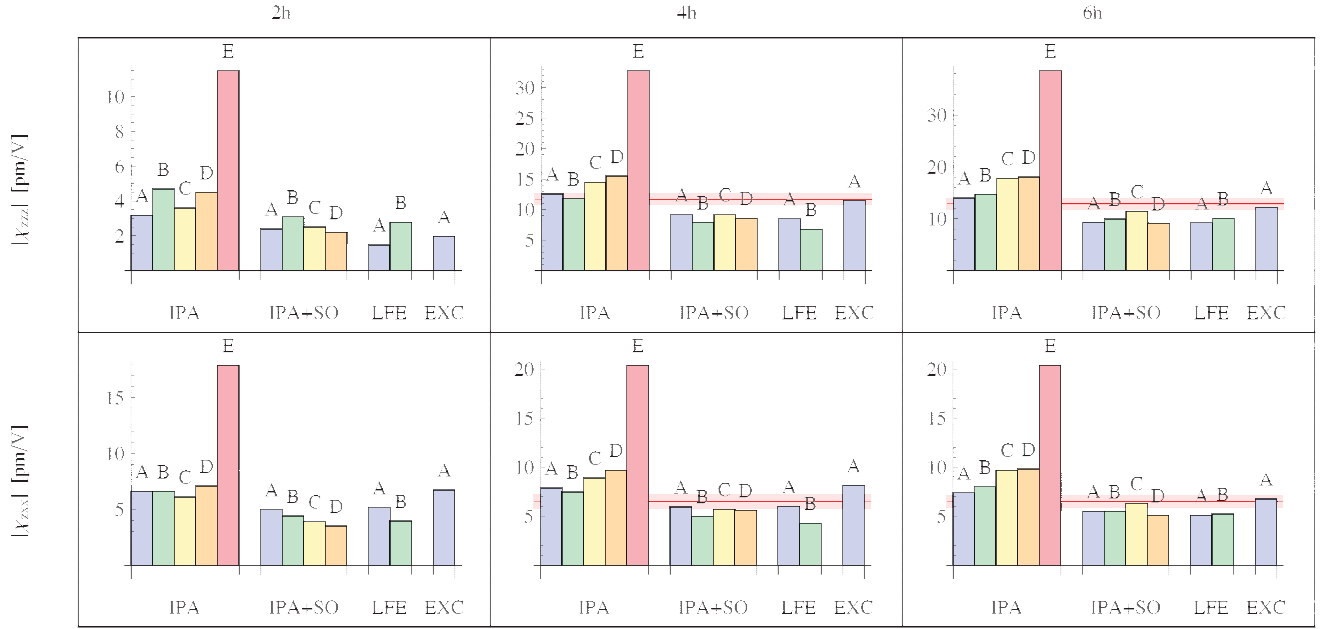


FIG. 6. (Color online) Static second-harmonic coefficients for the SiC polytypes considered. Values from (A) the present work, (B) Chen *et al.*,⁵ (C) Rashkeev *et al.*,⁶ (D) Adolph and Bechstedt,¹¹ and (E) Wu and Guo.²⁴ Experimental values, where available, are taken from Sato *et al.*²⁶ and are shown as horizontal lines, with the margin of error as a shadow. The value of α for the EXC calculation is 0.2 taken from Botti *et al.*²⁵

an expression for the effect of the kernel on the susceptibility. We find (here, explicitly for the zzz component)

$$\frac{d_{zzz}^{(2)}(\omega)}{\chi^{(0)}(2\mathbf{e}_z, \mathbf{e}_z, \mathbf{e}_z, 2\omega, \omega)} = A(\mathbf{e}_z, 2\omega)A(\mathbf{e}_z, \omega)A(\mathbf{e}_z, \omega), \quad (18)$$

where

$$A(\mathbf{q}, \omega) = 1 - \frac{\alpha}{4\pi} [\varepsilon_M(\mathbf{q}, \omega) - 1]. \quad (19)$$

This means that when ε_M is smooth, the change of $d_{zzz}^{(2)}$ with the long-range kernel is directly proportional to α . In contrast, when ε_M is changing significantly, the change directly affects the spectrum of $\chi^{(2)}$. This explains why in all spectra in Fig. 5 the low-energy peaks are most prominently increased, because it is this feature in the ε_M that changes most. For the high-energy range, when the ε_M are close to 1, we do not see considerable change. This is consistent with the behavior of Eq. (19), which is close to 1 when ε_M is close to 1.

V. STATIC COEFFICIENTS

Since experimental data are only available for static values of the considered polytypes, in Fig. 6 we report our results for $\chi^{(2)}(0)$ for the different components and polytypes. In this limit we have $\chi_{zxx}^{(2)} = \frac{1}{2}\chi_{xzx}^{(2)}$ because of Kleinmann symmetry.¹⁴ Also shown are results of previous theoretical studies that report the coefficients in the different approximations, independent particles (IPA), IPA with quasiparticle shift accounted for by the scissors operator (IPA + SO), local-field effects (LFE), and excitonic effects (EXC). We note an overall agreement between the reported results, with the exception of the results of Wu and Guo,²⁴ which seem to use a definition of $\chi^{(2)}$ that is twice as large as ours. The general trend observed

in all polytypes and components is that the values decrease when the quasiparticle shift is included and decrease even further when local fields are accounted for. We also report our results including excitonic effects, here using a different value of α , taken from Botti *et al.*,²⁵ where it is shown to give the correct static dielectric constant. The need for a different value of this parameter for the static limit comes from the fact that f_{xc} is generally not static and the α value used for the spectral results above is designed to reproduce the dynamic features of the spectrum, whereas here we are in the static limit. We note from Fig. 6 that when we account for excitonic effects in this way, we obtain a very good agreement with the experimental values. The effect of the excitonic kernel is again an increase, as observed in the spectra. Here we see, however, that this increase largely just compensates the combined decrease in the quasiparticle shift and local-field effects, so that the excitonic results are very close to the IPA results. This means that early calculations of the second-harmonic coefficients that yielded satisfactory results largely profited from a cancellation of effects. It also means, of course, that for the static coefficients, one can consider the IPA a sufficient approximation.

VI. CONCLUSION

In this paper we have investigated the influence of crystal local fields and excitonic effects on the SHG spectra of silicon carbide polytypes. The scalar density response function is related to the macroscopic tensor components by the polarization directions of its matrix elements, which has to be carefully analyzed to yield the desired components. We find that most influences of the local fields and excitonic effects can be traced back to the behavior of the linear dielectric function, which

features in the equation for the macroscopically averaged second-harmonic susceptibility. Local-field effects, although essential in the formulation of the theory, turn out to be only of minor influence on the spectra, but yield a slight overall decrease in the components. Excitonic effects, in contrast, are shown to influence the spectra dramatically, leading to an increase in the calculated second-harmonic spectra of up to 100%.

The accuracy of our method can only be assessed in the static limit, due to the lack of experimental data for a higher frequency range. We show not only that our calculations are in agreement with previous ones when lower levels of approximations are used, but also that the combination of local-field and excitonic effects as described by our

method yields excellent agreement with recent experimental measurements.

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