Universal constraints for the third-harmonic generation susceptibility

N P Rapapa† and S Scandolo†‡

† International Centre for Theoretical Physics (ICTP), I-34014 Trieste, Italy
‡ International School for Advanced Studies, Via Beirut 4, I-34014 Trieste, Italy

Abstract. From the analytical properties of the third-harmonic generation susceptibility and from its asymptotic behaviour in the frequency variable, a set of eight Kramers–Kronig relations and nine sum rules are obtained. These universal constraints are used to generate a simplified model for the static limit of $\chi^{(3)}$ in insulating systems with inversion symmetry. The static limits of $\chi^{(3)}$ calculated within this model for silicon and germanium are shown to be in qualitative agreement with the experimental data.

1. Introduction

Although the search for efficient nonlinear optical materials would greatly benefit from a reliable theoretical estimate of the nonlinear susceptibilities of these systems, any 'first-principles' method is commonly known to be inapplicable for systems exceeding the unit-cell size of a few atoms. The fundamental reason for this failure is the presence, in the theoretical expression for the nonlinear susceptibilities, of summations over the (infinite) set of excited states, for which both their dipole matrix elements and their energies must be known. The search for simplified methods for the calculation of the nonlinear susceptibilities has therefore been an active field of research starting from the late 1960s, when the first nonlinear optical experiments were performed. It has recently been shown that the nonlinear susceptibilities must satisfy a set of stringent and general constraints, namely sum rules, which depend on the specific nonlinear phenomena considered [1]. Apart from the intrinsic relevance of these relations, the existence of universal constraints can be of great help in approximate calculations of the nonlinear susceptibilities. For example, a set of sum rules found [2] for the second-harmonic generation (SHG) susceptibility $\chi^{(2)}(\omega, \omega)$ have been used [3] to determine the parameters of a very simplified model for the static limit of $\chi^{(2)}$. Once this model susceptibility had been forced to verify the sum rules, excellent agreement with the experimental results was found for a large number of III–V and II–VI semiconductors. In addition, the model susceptibility was shown to satisfy Miller's well known phenomenological rule [4].

Recent experimental work has demonstrated that the real and the imaginary parts of the nonlinear susceptibility $\chi^{(3)}(\omega, \omega, \omega)$, responsible for third-harmonic generation (THG), can be separately measured in a wide frequency range [5]. This opened up the possibility of verifying the Kramers–Kronig relations for $\chi^{(3)}$ [6], in agreement with earlier theoretical findings [7]. Using a theory recently developed to uncover the consequences of causality on the frequency-dependent nonlinear susceptibilities [1], this paper aims at presenting the

full set of Kramers–Kronig relations and sum rules that the real and the imaginary parts of $\chi^{(3)}(\omega, \omega, \omega)$ must verify. The extreme usefulness of Kramers–Kronig relations and sum rules for the *linear* response, documented by a huge literature in the past decades, suggests a variety of similar applications in the *nonlinear* case. Insofar as $\chi^{(3)}$ is concerned, these relations could be used, for example, to extract the phase of $\chi^{(3)}$ from its modulus, they could provide strict constraints on the behaviour of $\chi^{(3)}$ outside the frequency range of measurement, and they could be of help in the normalization of measured spectra (absolute measurements are particularly difficult in nonlinear optics).

In section 2 we give the basic definitions and we find the asymptotic limit of $\chi^{(3)}(\omega, \omega, \omega)$ in the frequency variable. In section 3 we obtain the set of eight Kramers–Kronig relations and nine sum rules. Finally, on the basis of these sum rules, a simplified model for $\chi^{(3)}$ in systems with inversion symmetry is proposed in section 4. In section 5 we test this model in the case of silicon and germanium, and good agreement is found with the experimental data.

2. Definitions and asymptotic behaviour

The third-order contribution to the nonlinear polarizability $P(t)$ in terms of the electric field $E(t)$ is

$$P_i^{(3)}(t) = \int dt_1 \int dt_2 \int dt_3 G_{ijkl}^{(3)}(t_1, t_2, t_3) E_j(t - t_1) E_k(t - t_2) E_l(t - t_3) \quad (1)$$

where the Kubo response function [8] in third order, with Cartesian indices i, j, k and l is

$$G_{ijkl}^{(3)}(t_1, t_2, t_3) = -\frac{e^4}{6i\Omega\hbar^3} \sum_P \theta(t_1)\theta(t_2 - t_1)\theta(t_3 - t_2)$$
$$\times \mathrm{Tr}\left\{\left[x_l(-t_3), [x_k(-t_2), [x_j(-t_1), x_i]]\right]\rho_0\right\} \quad (2)$$

Ω being the total volume, P any permutation of the pairs (t_1, j), (t_2, k) and (t_3, l), θ the Heaviside step function, x denoting the total position operator $\sum_\alpha x^{(\alpha)}$ ($\alpha = 1, ..., N$ is the number of electrons), ρ_0 a stationary density matrix (such that $[\rho_0, H_0] = 0$). The total position operator evolves, in the Heisenberg picture, according to the unperturbed Hamiltonian $H_0 = \sum_\alpha \left[p_\alpha^2/(2m) + V(r_\alpha)\right] + V_{ee}$, where the total potential energy is split into an external contribution V (which includes ion–electron interactions), plus the electron–electron interaction V_{ee}.

The phenomenon of third-harmonic generation can be obtained considering a monochromatic electric field of frequency ω, performing the integrals in (1) and selecting the contribution to the polarizability at frequency 3ω. We obtain

$$P_i^{(3)}(t)_{3\omega} = \chi_{ijkl}^{(3)}(\omega, \omega, \omega) E_j(t)_\omega E_k(t)_\omega E_l(t)_\omega \quad (3)$$

where $\chi^{(3)}(\omega, \omega, \omega)$ is the Fourier transform of $G^{(3)}(t_1, t_2, t_3)$ with $\omega_1 = \omega_2 = \omega_3$. Defining $\tau^+ = t_1 + t_2 + t_3$, $\tau_1 = t_1 - t_2$ and $\tau_2 = t_2 - t_3$ we have

$$\chi_{ijkl}^{(3)}(\omega, \omega, \omega) = \int d\tau^+ e^{i\omega\tau^+} \int d\tau_1 \int d\tau_2 G_{ijkl}^{(3)}(t_1, t_2, t_3). \quad (4)$$

The asymptotic behaviour of equation (4) as $\omega \to \infty$ can be obtained by integrating by parts on τ^+ and assuming that $G^{(3)}$ and all its derivatives vanish at infinite times. We obtain

$$\chi^{(3)}(\omega, \omega, \omega) = -\sum_m \frac{\left[\int d\tau_1 d\tau_2 \frac{\partial^m}{\partial\tau^{+m}} G^{(3)}(t_1, t_2, t_3)\right]_{\tau^+ \to 0^+}}{(-i\omega)^{m+1}}. \quad (5)$$

The evaluation of (5) is performed using (2) and calculating out analytically the derivatives. Following closely the derivation presented in [2] we obtain, after some lengthy but straightforward algebra, the asymptotic behaviour

$$\chi_{ijkl}^{(3)}(\omega, \omega, \omega) = \frac{\frac{Ne^4}{27m^4}\left\langle \frac{\partial^4 V}{\partial x_i \partial x_j \partial x_k \partial x_l}\right\rangle_0}{\omega^8} + o(\omega^{-8}) \tag{6}$$

where N is the electron density, the average is performed in the ground state of the system and $o(\omega^{-8})$ stands for a term that decays *strictly faster* than ω^{-8}.

3. Kramers–Kronig relations and sum rules

Since the analytical properties of $\chi^{(3)}(\omega, \omega, \omega)$ as a function of ω, have already been assessed [7, 1], we can consider all types of analytical functions $\omega^n \chi^{(3)}$ that vanish sufficiently quickly at infinity to be square integrable. This occurs up to $n = 6$. Then, by Titchmarsh's theorem [9] and using the fact that $\chi^{(3)}(-\omega, -\omega, -\omega) = \chi^{(3)\star}(\omega, \omega, \omega)$, we obtain the following set of eight Kramers–Kronig relations, where the tensorial indices have been dropped for convenience:

$$\mathrm{Re}\chi^{(3)}(\omega, \omega, \omega) = \frac{2}{\pi\omega^m}\int_0^\infty \frac{\omega'^{m+1}\mathrm{Im}\chi^{(3)}(\omega', \omega', \omega')}{\omega'^2 - \omega^2}\,\mathrm{d}\omega' \tag{7}$$

$$\mathrm{Im}\chi^{(3)}(\omega, \omega, \omega) = -\frac{2}{\pi\omega^{m-1}}\int_0^\infty \frac{\omega'^m\mathrm{Re}\chi^{(3)}(\omega', \omega', \omega')}{\omega'^2 - \omega^2}\,\mathrm{d}\omega' \tag{8}$$

with $m = 0, 2, 4$ and 6.

Although the above Kramers–Kronig relations for $m = 0$ closely resemble those found in the linear case, and have indeed previously been established by Ridener and Good [7] and experimentally verified by Kishida *et al* [6], the additional relations with $m = 2, 4$ and 6 are peculiar to the THG susceptibility and may also find direct application in the analysis of experimental data.

From the above Kramers–Kronig relations, a preliminary set of seven sum rules can be easily obtained by considering $\omega = 0$ in (7) and (8). When $m = 0$ in (7) we have

$$\chi^{(3)}(0, 0, 0) = \frac{2}{\pi}\int_0^\infty \frac{\mathrm{Im}\chi^{(3)}(\omega', \omega', \omega')}{\omega'}\,\mathrm{d}\omega'. \tag{9}$$

We also obtain, from (8),

$$\int_0^\infty \omega^n \mathrm{Re}\chi^{(3)}(\omega, \omega, \omega)\mathrm{d}\omega = 0 \tag{10}$$

with $n = 0, 2$ and 4. From (8) we have

$$\int_0^\infty \omega^n \mathrm{Im}\chi^{(3)}(\omega, \omega, \omega)\mathrm{d}\omega = 0 \tag{11}$$

with $n = 1, 3$ and 5.

Finally, using the superconvergence theorem [10] on the Kramers–Kronig relations (7) and (8), when $m = 6$, and comparing the asymptotic behaviour thus obtained with the asymptotic behaviour independently derived in expression (6), we obtain the two additional sum rules

$$\int_0^\infty \omega^6 \mathrm{Re}\chi^{(3)}(\omega, \omega, \omega)\mathrm{d}\omega = 0 \tag{12}$$

and

$$\int_0^\infty \omega^7 \mathrm{Im}\chi_{ijkl}^{(3)}(\omega, \omega, \omega)\mathrm{d}\omega = -\frac{\pi}{54}\frac{Ne^4}{m^4}\left\langle\frac{\partial^4 V}{\partial x_i \partial x_j \partial x_k \partial x_l}\right\rangle_0. \tag{13}$$

The tensorial indices have been explicitly reported only in (13), since only in this case does the value of the constant on the right-hand side (RHS) depend on them. Although the additional sum rule (12) can be formally re-cast into expression (10) by extending the validity of the latter up to $n = 6$, sum rule (13) is peculiar to THG, and can be formally considered as the analogue of the well-known absorption sum rule of linear optics, although $\mathrm{Im}\chi^{(3)}$ is by no means related to absorption processes, but simply to the phase of the third-order polarizability. Moreover, being the only non-vanishing sum rule, equation (13) can be assumed a measure of the overall strength of THG in a given system.

We conclude this section by stressing that no approximations have been introduced in order to derive the above Kramers–Kronig relations and sum rules. Their validity is therefore general, the only system-dependent quantity being the average on the RHS of sum rule (13). In spite of the extreme sensitivity of $\chi^{(3)}(\omega, \omega, \omega)$ to the energies and dipole matrix elements of the excited states, its frequency moments (10)–(12) vanish, or, as in (13), they are simply related to ground-state properties such as the ground state wavefunction and the external potential.

4. A simplified model for the static limit of $\chi^{(3)}$

Although widely documented and characterized experimentally, the phenomenon of THG in solids and in particular in semiconductors, lacks a firm theoretical understanding. Many different approaches have been devised to handle the formidable task of summing three times over the complete set of excited states, as required by perturbation theory to third order. Apart from the early empirical attempts by Jha and Bloembergen [13], Levine [14] and Flytzanis [15], the more recent calculations [16–18], based on first-principles methods, are still to be considered unsatisfactory, since only an order-of-magnitude agreement with experiments is typically claimed.

Any model, particularly those based on first principles, must satisfy the above Kramers–Kronig relations and sum rules, and we believe this is the case for all approaches proposed so far. In the following sections, however, we propose a different approach for the evaluation of the THG susceptibility, namely we force a *very* simplified model for $\chi^{(3)}$ to satisfy the sum rule constraints. The qualitative agreement of this oversimplified theory with experiments is taken as an indication of the extreme usefulness of sum rules in the theory of THG.

The model we propose, analogously to that which has already been done for SHG [3], is based on a single resonant frequency ω_0 and follows from the exact expression of the THG susceptibility [12]

$$\chi_{ijkl}^{(3)}(\omega, \omega, \omega) = \frac{e^4}{\Omega\hbar^3}\sum_{m,n,p}\left(\frac{\langle\Psi_g|x_i|\Psi_p\rangle\langle\Psi_p|x_j|\Psi_m\rangle\langle\Psi_m|x_k|\Psi_n\rangle\langle\Psi_n|x_l|\Psi_g\rangle}{(\omega_{pg} - 3\omega - i\gamma)(\omega_{mg} - 2\omega - i\gamma)(\omega_{ng} - \omega - i\gamma)}\right.$$

$$+\frac{\langle\Psi_g|x_j|\Psi_p\rangle\langle\Psi_p|x_i|\Psi_m\rangle\langle\Psi_m|x_k|\Psi_n\rangle\langle\Psi_n|x_l|\Psi_g\rangle}{(\omega_{pg} + 3\omega - i\gamma)(\omega_{mg} - 2\omega - i\gamma)(\omega_{ng} - \omega - i\gamma)}$$

$$+\frac{\langle\Psi_g|x_j|\Psi_p\rangle\langle\Psi_p|x_k|\Psi_m\rangle\langle\Psi_m|x_i|\Psi_n\rangle\langle\Psi_n|x_l|\Psi_g\rangle}{(\omega_{pg} + 3\omega - i\gamma)(\omega_{mg} + 2\omega - i\gamma)(\omega_{ng} - \omega - i\gamma)}$$

$$\left.+\frac{\langle\Psi_g|x_j|\Psi_p\rangle\langle\Psi_p|x_k|\Psi_m\rangle\langle\Psi_m|x_l|\Psi_n\rangle\langle\Psi_n|x_i|\Psi_g\rangle}{(\omega_{pg} + 3\omega - i\gamma)(\omega_{mg} + 2\omega - i\gamma)(\omega_{ng} + \omega - i\gamma)}\right) \tag{14}$$

by re-writing it in the algebraically equivalent expression (tensorial indices $ijkl$ on the α coefficients have been omitted for the sake of clarity)

$$\chi_{ijkl}^{(3)}(\omega, \omega, \omega) = \sum_n \frac{\alpha_1^n}{(\omega_n - \omega_g - \omega - i\gamma)}$$
$$+ \frac{\alpha_2^n}{(\omega_n - \omega_g - 2\omega - i\gamma)} + \frac{\alpha_3^n}{(\omega_n - \omega_g - 3\omega - i\gamma)}$$
$$+ \sum_{n'} \frac{\alpha_4^{n'}}{(\omega_{n'} - \omega_g - \omega - i\gamma)^2} + \sum_{n''} \frac{\alpha_5^n}{(\omega_{n''} - \omega_g - \omega - i\gamma)^3}$$
$$+ \sum_{n'''} \frac{\alpha_6^{n'''}}{(\omega_{n'''} - \omega_g - 2\omega - i\gamma)^2} + (\omega \to -\omega)^* \tag{15}$$

where n' labels doubly resonant states, namely states for which another state q exists such that $\omega_{qn'} = \omega_{n'g}$ or $2\omega_{qn'} = \omega_{n'g}$, n'' labels triply resonant states, namely states for which another two states q and q' exist such that $\omega_{qq'} = \omega_{q'n''} = \omega_{n''g}$; and finally n''' labels states for which another state q exists such that $2\omega_{qn'''} = 3\omega_{n'''g}$. In systems with inversion symmetry, it can easily be seen from (14) that some of the above summations are restricted to states with the same parity as the ground state g (even states). This occurs for the summation over n in the second term on the RHS of (15) and for the summation over n''' in the last term. On the other hand, the remaining summations are restricted to states with opposite parity with respect to g (odd states). In our simplified single-frequency model we assume that the excitation energy of the odd states is $\hbar\omega_0$, whereas even states lie yet higher in energy by $\hbar\omega_0$. The extreme crudeness of the single-frequency model is such that it is clearly not deemed reliable in the frequency range in which the excitations take place, in which many resonances and a complicated dispersion are expected. However, once the sum rules have been imposed, we expect this model to be sufficiently accurate *outside* this frequency range, namely at high frequencies (in which it is actually asymptotically exact) and in the low-frequency limit, at which it will be compared with the experimental data.

Given the above assumption concerning the excitation frequencies, expression (15) reduces to

$$\chi_{ijkl}^{(3)}(\omega, \omega) = \frac{\alpha_1}{(\omega_\circ - \omega - i\gamma)} + \frac{\alpha_3}{(\omega_\circ - 3\omega - i\gamma)}$$
$$+ \frac{\alpha_4}{(\omega_\circ - \omega - i\gamma)^2} + \frac{\alpha_5}{(\omega_\circ - \omega - i\gamma)^3} + (\omega \to -\omega)^*. \tag{16}$$

Imposing the sum rules (11) and (13) upon the above expression for the THG susceptibility completely determines the value of the parameters α as a function of the constant c on the RHS of sum rule (13) and of the frequency ω_0, as follows:

$$\alpha_1 = -\frac{1269}{512} \frac{c}{\omega_0^7} \qquad \alpha_3 = \frac{6561}{512} \frac{c}{\omega_0^7}$$
$$\alpha_4 = -\frac{135}{128} \frac{c}{\omega_0^6} \qquad \alpha_5 = -\frac{9}{128} \frac{c}{\omega_0^5}. \tag{17}$$

Substituting these values into (16), in the limit $\gamma \to 0$, we obtain

$$\chi_{ijkl}^{(3)}(\omega, \omega, \omega) = \frac{Ne^4}{3m^4} \left\langle \frac{\partial^4 V}{\partial x_i \partial x_j \partial x_k \partial x_l} \right\rangle_0 \frac{1}{(9\omega^2 - \omega_0^2)(\omega^2 - \omega_0^2)^3}. \tag{18}$$

where no implicit summation on the repeated indices is assumed. Since the linear susceptibility is given, in the single-frequency approximation, by

$$\chi_{ii}^{(1)}(\omega) = \frac{Ne^2}{m} \frac{1}{(\omega_\circ^2 - \omega^2)} \tag{19}$$

the THG susceptibility can finally be written as

$$\chi_{ijkl}^{(3)}(\omega, \omega, \omega) = \Delta_{ijkl} \chi_{ii}^{(1)}(3\omega) \chi_{jj}^{(1)}(\omega) \chi_{kk}^{(1)}(\omega) \chi_{ll}^{(1)}(\omega). \tag{20}$$

with Δ_{ijkl} being given by

$$\Delta_{ijkl} = -\frac{\left\langle \frac{\partial^4 V}{\partial x_i \partial x_j \partial x_k \partial x_l} \Big|_0 \right\rangle}{3N^3 e^4}. \tag{21}$$

Due to the close resemblance of expression (20) to the phenomenological rule proposed by Miller [4] for SHG, it has been suggested that equation (20) might hold also in the case of THG [13, 26]. Our simple model not only reproduces this phenomenological rule, but also provides an expression for the Δ_{ijkl} coefficient. Again, equation (20) is thought to be valid only in the high-frequency and the low-frequency regions of the optical spectrum. Since the high-frequency asymptotic behaviour of (20) has already been shown to be exact, we will compare, in the following section, the static limit of (20) with experimental data for Si and Ge.

5. The static limit

The static limit of (20) in a cubic system simply gives

$$\chi_{ijkl}^{(3)}(0, 0, 0) = -\frac{\left\langle \frac{\partial^4 V}{\partial x_i \partial x_j \partial x_k \partial x_l} \Big|_0 \right\rangle}{3N^3 e^4} \chi^{(1)}(0)^4 . \tag{22}$$

Moreover, the diamond crystal symmetries impose that the only non-vanishing components of $\chi^{(3)}$ are $\chi_{1111}^{(3)}$ and $\chi_{1212}^{(3)}$. Since the static limit of the linear susceptibility is known, we are left with evaluating the expectation value of the fourth derivative of the potential. In particular, since only negligible effects are expected on the static limit of $\chi^{(3)}$ from the electronic core levels, we get rid of these levels by taking the fourth derivative of the pseudo-potential V_p and performing the average on the valence electrons only. This can be performed in reciprocal space as

$$\left\langle \frac{\partial^4 V}{\partial x_i \partial x_j \partial x_k \partial x_l} \right\rangle_0 = \Omega_c \sum_{G} G_i G_j G_k G_l n^\star(G) V_p(G) \tag{23}$$

where Ω_c is the unit-cell volume, G a reciprocal lattice vector, and $n(G)$ and $V_p(G)$ the Fourier transforms of the valence electron density and pseudo-potential, respectively. We observe, however, that, in the definition of the pseudo-potentials the screening due to the interaction between valence electrons is often taken into account, even though the bare ionic potential should be used, as shown in section 2. If this is the case, we must subtract, as a first approximation, the Hartree contribution due to the electron density, so that, in reciprocal space, we have

$$V_p(G) = V_p^{(s)}(G) - \frac{4\pi}{G^2} n(G) \tag{24}$$

where $V_p^{(s)}$ is the screened pseudo-potential. In the specific cases of Si and Ge, we use the valence charge density computed by Chelikowsky and Cohen [23], and the screened

pseudo-potential form factors of Cohen and Bergstresser [24]. The resulting values of $\chi^{(3)}$ are listed in table 1 together with the experimental data available in the literature. Also reported in table 1 are the results of other recent calculations of the static limit of $\chi^{(3)}$. The results of table 1 indicate that our estimates for silicon agree well with experiments within the experimental accuracy, whereas for germanium they disagree by at most a factor of eight. The overall agreement of our calculations is, however, comparable to that obtained with first-principle or other extensive techniques. A possible source of discrepancy with experiments, in the case of Ge compared with Si, is the single-frequency approximation adopted. This approximation is in fact more reliable in systems with larger energy gaps and smaller band widths, for which the static limit of the optical constants is less affected by the finite width of the excitation spectrum.

Table 1. Calculated values of $\chi^{(3)}_{1111}$, $\chi^{(3)}_{1212}$ and $\chi^{(3)}_{1212}/\chi^{(3)}_{1111}$, in units of 10^{-11} esu, compared with experimental data from [26] and with other calculations based on different approaches.

	$\chi^{(3)}_{1111}$			$\chi^{(3)}_{1212}$			$\chi^{(3)}_{1212}/\chi^{(3)}_{1111}$		
	Present calc.	Experiment	Other calcs.	Present calc.	Experiment	Other calc.	Present calc.	Experiment	Other calcs.
Si	2.99	2.4 ± 1.5	3.07[a] 0.8[b] 4.8[c]	0.98	1.15 ± 0.7	1.90[a] 0.5[b] 2.3[c]	0.33	0.48	0.62[a] 0.63[b] 0.48[c]
Ge	8.89	40 ± 20	30.7[a] 6.9[b] 206[c]	2.99	24 ± 12	10.3[a] 6.9[b] 102[c]	0.34	0.60	0.33[a] 1.0[b] 0.5[c]

[a] [18].
[b] [16] using a semi-*ab-initio* method.
[c] [16] using an empirical tight-binding method.

Also reported in table 1 is the ratio $\chi^{(3)}_{1212}/\chi^{(3)}_{1111}$, which is supposed to be affected by a smaller experimental uncertainty than are the single values of $\chi^{(3)}$ [25]. Again, our calculation predicts a value for this ratio in reasonable agreement with experiments for Si, but rather inaccurate for Ge. Notice that the values of the ratio both for Si and for Ge are very close to the value of a third of an isotropic medium [26], the anisotropy parameter $\sigma = (3\chi^{(3)}_{1212} - \chi^{(3)}_{1111})/\chi^{(3)}_{1111}$ being almost vanishing for both semiconductors.

Table 2. Calculated values of Miller's constants Δ_{1111} and Δ_{1212}, in units of 10^{-11} esu, with experimental data taken from [26].

	Δ_{1111}		Δ_{1212}	
	Present calculation	Experiment	Present calculation	Experiment
Si	5.09	4.0 ± 2.4	1.67	2.0 ± 1.2
Ge	4.38	20 ± 10	1.47	12 ± 6

In table 2 we report the calculated values of Miller's delta Δ_{ijkl}, compared with the experimental data. Although the tiny reduction in this constant from Si to Ge could be well interpreted as support for the empirical rule found for SHG, for which in fact the value of Miller's constant varies by only ±20% with respect to the average value in III–V compounds, the experimental data seem to disprove the validity of this rule for THG.

6. Conclusions

Universal constraints for the third-harmonic nonlinear susceptibility, in the form of Kramers–Kronig relations and sum rules, have been presented. Their usefulness in the construction of approximate models for $\chi^{(3)}(\omega, \omega, \omega)$ has been demonstrated in the specific case of a single-frequency model. It has been shown that once sum rules are imposed on this very crude model, reasonable agreement with experiments is found for the static limit of $\chi^{(3)}$ in silicon and germanium.

Acknowledgment

References

[1] Bassani F and Scandolo S 1991 *Phys. Rev.* B **44** 8446
[2] Scandolo S and Bassani F 1995 *Phys. Rev.* B **51** 6925
[3] Scandolo S and Bassani F 1995 *Phys. Rev.* B **51** 6928
[4] Miller R C 1964 *Appl. Phys. Lett.* **5** 17 (1964); see also Shen Y R 1984 *The Principles of Nonlinear Optics* (New York: Wiley) p 37
[5] Hasegawa T, Iwasa Y, Sunamura H, Koda T, Tokura Y, Tachibana H, Matsumoto M and Abe S 1992 *Phys. Rev. Lett.* **69** 668
[6] Kishida H, Hasegawa T, Iwasa Y, Koda T and Tokura Y 1993 *Phys. Rev. Lett.* **70** 3724
[7] Ridener F L Jr and Good R H Jr 1974 *Phys. Rev.* B **10** 4980
[8] Kubo R 1957 *J. Phys. Soc. Japan* **12** 570; see also Butcher P N and Cotter D 1990 *The Elements of Nonlinear Optics* (Cambridge: Cambridge University Press)
[9] Nussenzveig H M 1972 *Causality and Dispersion Relations* (New York: Academic)
[10] Altarelli M, Dexter D L, Nussenzveig H M and Smith D Y 1972 *Phys. Rev.* B **6** 4502
[11] Peiponen K-E 1988 *Phys. Rev.* B **37** 6463
[12] Shen Y R 1984 *The Principles of Nonlinear Optics* (New York: Wiley)
[13] Jha S S and Bloembergen N 1968 *Phys. Rev.* **171** 891
[14] Levine B F 1969 *Phys. Rev. Lett.* **22** 787
[15] Flytzanis C 1970 *Phys. Lett.* A **31** 273
[16] Moss D J, Ghahramani E, Sipe J E and van Driel H M 1990 *Phys. Rev.* B **41** 1542
[17] Nayak S K, Sahu T and Mohanty S P 1993 *Physica* B **191** 334
[18] Ching W J and Huang M-Z 1993 *Phys. Rev.* B **47** 9479
[19] Arya K and Jha S S 1979 *Phys. Rev.* B **20** 1611
[20] Wang C C 1970 *Phys. Rev.* B **2** 2045
[21] Van Vechten J A and Aspnes D E 1969 *Phys. Lett.* A **30** 346
[22] Wynne J J and Boyd G D 1968 *Appl. Phys. Lett.* **11** 228
[23] Chelikowski J R and Cohen M L 1976 *Phys. Rev.* B **14** 556
[24] Cohen M L and Bergstresser T K 1966 *Phys. Rev.* **141** 789
[25] Wynne J J 1969 *Phys. Rev.* **178** 1295
     Burns W K and Bloembergen N 1971 *Phys. Rev.* B **4** 3437
[26] Singh S 1986 *CRC Handbook of Laser Science and Technology III* ed M J Weber (Boca Raton, FL: CRC)