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LETTER TO THE EDITOR

Nonconventional calculation of the second order susceptibility in polar semiconductors

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Abstract

We propose a model for the calculation of the second order susceptibilities of groups II–VI and III–V compound semiconductors. The model is based on the assumption that the dominant effect that contributes to the second harmonic generation is the variation of the polar charge of the bond under the action of the laser radiation field. We show that a simple relation for the second order susceptibility in terms of the basic parameters of the bond follows from the dielectric theory of Phillips. This relation is checked for many experimental values for nonlinear susceptibilities of polar semiconductor compounds taken from the literature.

1. Introduction

There have been many theories attempting to compute the nonlinear optical susceptibility in semiconductors. Among these a class of models generally named *polarizable bond models* connect the nonlinear behaviour of the compound semiconductors with the properties of the polar charge of the bond. In this respect we recall the polarizable bond models of Tang and Flytzanis [1, 2], Levine [3], Mochan and Barrera [4], Wijers *et al* [5], and Patterson and Herrendorfer [6, 7]. We present a new model in the same vein.

The model proposed in this letter for computing the second order susceptibility in polar semiconductors strikes a very good balance between accuracy and simplicity. The starting point is the dielectric theory of Phillips [8–10], which could be considered nonconventional in the sense that: ‘stress is laid throughout on methods for incorporating quantum-mechanical effects into properties of chemical bonds through algebraic relations rather than through variational solutions of the wave equation’ (see the abstract of [10]). Such methods, which avoid direct calculation of the wavefunction, may become important in the future. This point of view is supported by our previous work [11], in which it is shown that such methods provide good results in modelling atomic and molecular systems. The present letter presents new arguments along this line.

Resulting from the Phillips theory, the linear susceptibility in polar semiconductors is a function of the supplementary energy of the bond, due to the existence of the polar charge. In addition, the electric dipole moment of the bond is a function of the bond polarity. Using the tensorial expressions for the first and second order susceptibilities, together with Phillips's relations, we obtain a simple relation for the second order susceptibility. This relation leads to values for the nonlinear susceptibilities of semiconductor compounds that agree well with the experimental values taken from the literature.

The analysis is performed in the CGS electrostatic system.

2. Basic tensorial relations

The unit cell in the II–VI and III–V semiconductor compounds is a cube which contains four tetrahedral bonds. Due to the existence of a polar charge, the bond has a permanent electric dipole, denoted by $\bar{\mu}$. We denote the electric dipole moment induced by an external applied field by $\Delta\bar{\mu}$. It is given by the following relation:

$$\Delta\bar{\mu} = \tilde{\alpha} \cdot \bar{E} \quad (1)$$

where $\tilde{\alpha}$ is the bond polarizability and \bar{E} is the intensity of a variable external electric field. Since the bond polarizability is a function of \bar{E} , relation (1) can be written as

$$\Delta\bar{\mu} = \tilde{\alpha}_0 \cdot \bar{E} + \tilde{\beta} : \bar{E} \cdot \bar{E} + \dots \quad (2)$$

where $\tilde{\alpha}_0$ and $\tilde{\beta}$ are, respectively, the field independent linear and nonlinear bond polarizabilities.

The Cartesian coordinate axes, $O_\kappa xyz$, are fixed for the bond labelled κ , where $\kappa = 1, 2, 3, 4$, corresponding to the four bonds in the unit cell. The origin O_κ of the axes is at the centre of the bond, and the $O_\kappa z$ axis is longitudinal—that is, it is situated along the bond.

Since $\tilde{\alpha}$, $\tilde{\alpha}_0$, and $\tilde{\beta}$ are tensors, equations (1) and (2) can be written as

$$\Delta\mu_i = \sum_j \alpha_{ij} E_j \quad (3)$$

$$\Delta\mu_i = \sum_j \alpha_{0ij} E_j + \sum_{j,k} \beta_{ijk} E_j E_k + \dots \quad (4)$$

where the indices i , j , and k run through the set $\{x, y, z\}$.

The function $\tilde{\alpha}$ can be expanded in powers of the components of the electric field:

$$\alpha_{ij} = \alpha_{ij}|_{\bar{E}=0} + \sum_k \frac{\partial \alpha_{ij}}{\partial E_k} E_k + \dots \quad (5)$$

Introducing (5) in (3), one obtains

$$\Delta\mu_i = \sum_j \alpha_{ij}|_{\bar{E}=0} E_j + \sum_{j,k} \frac{\partial \alpha_{ij}}{\partial E_k} E_j E_k + \dots \quad (6)$$

By identification, from (4) and (6), one obtains

$$\alpha_{0ij} = \alpha_{ij}|_{\bar{E}=0} \quad (7)$$

$$\beta_{ijk} = \frac{\partial \alpha_{ij}}{\partial E_k} \quad (8)$$

Since the bond possess axial symmetry, the following relations hold [12]:

$$\alpha_{zz} = \alpha_{\parallel} \quad (9)$$

$$\beta_{zzz} = \beta_{\parallel} \quad (10)$$

$$\alpha_{xx} = \alpha_{yy} = \alpha_{\perp} \quad (11)$$

$$\beta_{xzx} = \beta_{yzy} = \beta_{\perp} \quad (12)$$

$$E_z = E_{\parallel} \quad (13)$$

where α_{\parallel} and β_{\parallel} are the longitudinal bond polarizabilities, α_{\perp} and β_{\perp} are the transverse bond polarizabilities, and E_{\parallel} is the longitudinal component of the intensity of the variable electric field.

Taking into account the relations (8)–(13), and using the fact that permuting the indices of α_{ij} and β_{ijk} does not change the values of these terms, one obtains

$$\frac{\partial \alpha_{\parallel}}{\partial E_{\parallel}} = \frac{\partial \alpha_{zz}}{\partial E_z} = \beta_{zzz} = \beta_{\parallel} \quad (14)$$

$$\frac{\partial \alpha_{\perp}}{\partial E_{\parallel}} = \frac{\partial \alpha_{xx}}{\partial E_z} = \beta_{xzx} = \beta_{\perp}. \quad (15)$$

We denote by $\chi^{(1)}$ and $\chi_{14}^{(2)}$, respectively, the linear susceptibility and the only nonvanishing term of the second order susceptibility tensor, in Voigt's notation. The following relations between $\chi^{(1)}$ and $\chi_{14}^{(2)}$ and the transverse and longitudinal bond polarizabilities are valid [12]:

$$\chi^{(1)} = \frac{16f}{3a^3}(\alpha_{\parallel} + 2\alpha_{\perp}) \quad (16)$$

$$\chi_{14}^{(2)} = \frac{32f^3}{3\sqrt{3}a^3}(\beta_{\parallel} - 2\beta_{\perp}) \quad (17)$$

where a is the lattice constant and f is a correction factor introduced by Lorentz which accounts for the fact that the electrons do not respond to the externally applied electric field, but rather to an effective field.

3. Initial assumptions

The assumptions that underlie our method are as follows.

- (1) The dominant effect that contributes to the second harmonic generation is the variation of the polar charge of the bond under the action of the laser radiation field [3, 12]. This leads to a supplementary component of the energy of the bond.
- (2) The linear susceptibility is a function of the supplementary energy of the bond due to the existence of the polar charge. Also, the permanent electric dipole moment is a function of the bond polarity. We recall below these relations, which result from the dielectric theory of Phillips [8–10].

The dielectric constant in Phillips's theory [8] is

$$\varepsilon = 1 + \frac{(\hbar\omega_p)^2}{E_{g0}^2 + C_{\alpha\beta}^2} A \quad (18)$$

where \hbar is the normalized Planck constant, E_{g0} is the energy gap of the Jones zone faces, $C_{\alpha\beta}$ is the charge transfer energy of the bond due to the existence of polar charge, and A is a constant approximately equal to unity. The transfer energy $C_{\alpha\beta}$ is a supplementary energy of the bond, due to the asymmetry of the valence charge along the bond, in the absence of any applied electric field. This energy is semiclassical in nature [8] and it leads to an increase of the energy gap of the crystal.

The quantity ω_p is the plasma frequency corresponding to the density of the valence electrons:

$$\omega_p = \sqrt{\frac{4\pi N_b e^2}{m}} \quad (19)$$

where e is the absolute value of the electron charge, m is the electron mass, and N_b is the density of the valence electrons. Taking into account that there are four tetrahedral bonds and eight electrons per unit cell, we have

$$N_b = \frac{8}{a^3} = \frac{3\sqrt{3}}{d^3} \quad (20)$$

where d is the length of the bond.

The relation between the dielectric constant and the linear susceptibility is given by

$$\varepsilon = 1 + 4\pi \chi^{(1)}. \quad (21)$$

From (18) and (21) one can obtain the following expression for the linear susceptibility:

$$\chi^{(1)} = \frac{1}{4\pi} \frac{(\hbar\omega_p)^2}{E_{g0}^2 + C_{\alpha\beta}^2} A. \quad (22)$$

The permanent electric dipole moment is

$$\bar{\mu} = -e\alpha_p \bar{d} \quad (23)$$

where α_p is the bond polarity.

The supplementary energy of the bond due to the existence of polar charge, $C_{\alpha\beta}$, changes with the external applied field. This happens because an infinitesimal variation of the electric field, $d\bar{E}$, leads to the following variation of the interaction energy between the permanent electric dipole and the electric field:

$$dC_{\alpha\beta} = \bar{\mu} d\bar{E} = -e\alpha_p \bar{d} d\bar{E} = -e d\alpha_p dE_{\parallel} \quad (24)$$

(3) The following inequality is strongly fulfilled [12, 13]:

$$\beta_{\parallel} \gg \beta_{\perp}. \quad (25)$$

(4) The bonds possess axial symmetry. This assumption has been used for the deduction of relations (16) and (17).

4. An expression for the second order susceptibility

From (16) and (22) it follows that

$$\alpha_{\parallel} + 2\alpha_{\perp} = \frac{3}{64\pi} \frac{a^3}{f} \frac{(\hbar\omega_p)^2}{E_{g0}^2 + C_{\alpha\beta}^2}, \quad (26)$$

using the fact that $A \cong 1$.

The relation (26) will be differentiated with respect to E_{\parallel} . Using (14), (15), and (22), one obtains

$$\begin{aligned} \beta_{\parallel} + 2\beta_{\perp} &= -\frac{3}{32\pi} \frac{a^3}{f} \frac{(\hbar\omega_p)^2}{(E_{g0}^2 + C_{\alpha\beta}^2)^2} C_{\alpha\beta} \frac{dC_{\alpha\beta}}{dE_{\parallel}} \\ &= -\frac{3\pi}{2} \frac{a^3}{f} \frac{C_{\alpha\beta}}{(\hbar\omega_p)^2} \chi^{(1)2} \frac{dC_{\alpha\beta}}{dE_{\parallel}}. \end{aligned} \quad (27)$$

Table 1. Theoretical and experimental values for $\chi_{14}^{(2)}$ and the bond parameters.

Crystal	f [12]	$C_{\alpha\beta}$ (eV) [8]	d (Å) [13]	α_p [13]	$\chi^{(1)}$ [13]	$\chi_{14}^{(2)}$, theory (10^{-7} esu)	$\chi_{14}^{(2)}$, experiment (10^{-7} esu)		
							[12]	[13]	[2]
GaP	1.25	3.6	2.36	0.52	0.65	4.66	5	5.2	5.2
GaAs	1.525	3.0	2.44	0.50	0.79	9.37	18 ± 8	6.4	9
GaSb	1.93	1.9	2.65	0.44	1.07	21.35	18	20.0	30
InP	1.215	3.5	2.54	0.58	0.68	7.00		8.0	
InAs	1.41	3.2	2.61	0.53	0.90	15.39	20 ± 8	17.4	20
InSb	1.95	2.2	2.80	0.51	1.17	43.59	30 ± 15	24.8	33

Since $\beta_{\parallel} \gg \beta_{\perp}$ (the assumption (3)), from (17) and (27) it follows that

$$\beta_{\parallel} = \frac{3\sqrt{3} a^3}{32 f^3} \chi_{14}^{(2)} = -\frac{3\pi a^3}{2 f} \frac{C_{\alpha\beta}}{(\hbar\omega_p)^2} \chi^{(1)2} \frac{dC_{\alpha\beta}}{dE_{\parallel}}. \quad (28)$$

Finally, from (19), (20), (24), and (28), one obtains

$$\chi_{14}^{(2)} = \frac{4 m}{9 e \hbar^2} f^2 \alpha_p C_{\alpha\beta} d^4 \chi^{(1)2}. \quad (29)$$

This relation is written in the CGS electrostatic system. Introducing the values of the constants it can be written in a simpler form:

$$\chi_{14}^{(2)} = 1.2143 \times 10^{-8} f^2 \alpha_p C_{\alpha\beta} d^4 \chi^{(1)2} \quad (30)$$

where $C_{\alpha\beta}$ is given in electronvolts, d in ångströms, the other quantities are without dimensions, and $\chi_{14}^{(2)}$ is in esu. The values of the correction factor f are taken from table 3 of [12]. Since the values for f are calculated in two ways, we have used the average of the two values. The theoretical values of $\chi_{14}^{(2)}$, computed using relation (30), together with the experimental values, and the values for f , $C_{\alpha\beta}$, d , α_p , and $\chi^{(1)}$, are given in table 1. We also give the references from which the values in the corresponding columns are taken. For a given crystal, the experimental values of $\chi_{14}^{(2)}$ are taken from a few papers, as indicated in table 1.

5. Conclusions

An analysis of table 1 shows that the difference between the theoretical and the experimental values of $\chi_{14}^{(2)}$ is of the same order of magnitude as the difference between the experimental values of $\chi_{14}^{(2)}$ taken from different papers for the same crystal.

The relatively good agreement between the theoretical results and the experimental values taken from the literature suggests that the second order nonlinear effects resulting from the interaction between the laser field and polar semiconductors are generated by the variation of the polarization charge along the bond. This agreement confirms implicitly the accuracy of Phillips's relation for the linear susceptibility (28), and it justifies the physical interpretation of the energy $C_{\alpha\beta}$.

References

- [1] Tang C L and Flytzanis C 1971 *Phys. Rev. B* **4** 2520
- [2] Tang C L 1973 *IEEE J. Quantum Electron.* **9** 755

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- [3] Levine B F 1973 *Phys. Rev. B* **7** 2600
 - [4] Mochan W L and Barrera R G 1986 *Phys. Rev. Lett.* **56** 2221
 - [5] Wijers C M J, de Boeij P L, van Hasselt C W and Rasing Th 1995 *Solid State Commun.* **93** 17
 - [6] Patterson C H and Herrendorfer D 1997 *J. Vac. Sci. Technol. A* **15** 3036
 - [7] Herrendorfer D and Patterson C H 1997 *Surf. Sci.* **375** 210
 - [8] Phillips J C 1968 *Phys. Rev. Lett.* **20** 550
 - [9] Phillips J C 1969 *Covalent Bonding in Crystals, Molecules and Polymers* (Chicago, IL: The University of Chicago Press)
 - [10] Phillips J C 1970 *Rev. Mod. Phys.* **42** 317
 - [11] Popa A 2000 *Multiphoton and Light Driven Multielectron Processes in Organics: Materials, Phenomena, Applications* ed F Kajzar and M V Agranovich (Dordrecht: Kluwer–Academic) p 526
 - [12] Flytzanis C and Ducuing J 1969 *Phys. Rev.* **178** 1218
 - [13] Choy M M, Ciraci S and Byer R L 1975 *IEEE J. Quantum Electron.* **11** 40