Angular Properties of Second-Harmonic Polarization Due to High-Order Nonlinearities: Application to GaSe and InSe

A. Bourdon, E. Bringuier, M. T. Portella,[a] and M. Vivières
Laboratoire d'Optique de la Matière Condensée, Université Pierre et Marie Curie, Tour 13, 4 place Jussieu, 75252 Paris CEDEX 05, France

N. Piccioli
Laboratoire de Physique des Milieux Condensés, Université Pierre et Marie Curie, Tour 13, 4 place Jussieu, 75252 Paris CEDEX 05, France
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An important anomalous behavior is evidenced in the angular response of the polarization vector of second-harmonic radiation generated in layered rhombohedral III-VI semiconductors. We propose a general analysis which may be applied to other nonlinear systems of arbitrarily high order of interaction. The method gives evidence of, at least, a sixth-order effect in our experiments.

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Excited materials have responses that are consistent with their symmetries. However, accidental extra symmetries may be observed when the response is mathematically simple, linear, or quadratic. For instance, cubic materials often exhibit isotropic properties. Isotropy disappears when sufficiently high-order components are taken into account in nonlinear responses; those components need strong excitation to be observed.

In this Letter, we show for the first time that second-harmonic (SH) generation in rhombohedral crystals becomes anisotropic at a high excitation level. We demonstrate that the anisotropy is related to a sixth-order contribution in the nonlinear response of the material. The mathematical analysis developed for that purpose may be easily applied to other nonlinear systems of arbitrarily high order of interaction. The microscopic origin of high-order contributions will not be tackled here.

The layered-structured III-VI semiconductors GaSe and InSe have been chosen because of their good nonlinear optical properties.[1-10] They have been used to generate green ($\lambda = 0.53$ μm) from infrared (IR) light ($\lambda = 1.06$ μm). At those wavelengths no phase matching[1,5,8,11] is possible between the fundamental and second-harmonic radiation but the thickness of our samples (about 6 μm) was not far from the coherence lengths[11] [respectively, 2 and 1.3 μm (Refs. 12 and 13)]. The created green light is partially absorbed inside the materials because the photon energy (2.3 eV) is larger than the band gaps (2 and 1.3 eV, respectively).

A Q-switched mode-locked Nd-doped yttrium aluminum garnet laser provides a series of about 40 IR pulses delayed by 6 ns. Each pulse is about 15 ps broad and its peak power is about 10^6 W. To get a constant vertical polarization with a continuously tunable incident IR power, we use a rotating half-wave plate between two polarizing prisms. A selective filter removes possible visible light coming from the laser or generated inside the plate (Fig. 1).

Samples are mounted on a rotating base; its axis is parallel both to the direction **k** of the incident IR beam and to the **c** axis of the material. This setup ensures constancy of the IR excitation characteristics when the sample is rotated. The generated SH beam also propagates along **k**. Let φ be the angle between the IR polarization direction and a fixed axis of the crystal which is parallel to the layers; similarly, let α be the angle defining the

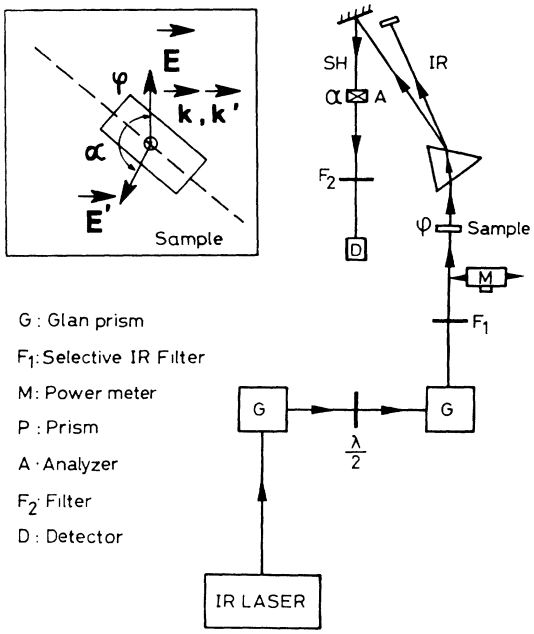

FIG. 1. Schematic view of the experimental setup. Inset: The definition of the angles φ and α of, respectively, the IR and SH polarization vectors **E** and **E'** relative to a fixed axis of the sample; input IR and output SH wave vectors **k** and **k'** are perpendicular to the plane of the figure.

SH polarization direction (Fig. 1). Before detection, a prism followed by another filter eliminates the remaining infrared light.

In both materials, we have three kinds of results; the first ones are observations at fixed angle φ and the last two are angular responses under the maximum available IR excitation: (i) The output SH intensity (Fig. 2) is quadratic versus input power at low excitation but becomes subquadratic for higher input values; (ii) α is linearly connected to φ (Fig. 3, curve c), $\alpha+2\varphi=$const; and (iii) the output SH intensity, versus φ, is the superposition of a constant signal and of an oscillation of periodicity $2\pi/6$ (Fig. 3, curves a and b). The first two results agree with previously known second-order calculations[2,5,11,14] with the exception of the tendency to saturation at a high-excitation level. The third one is new but consistent with the expected symmetry of the intensity response. In fact, its invariance group must have two subgroups: C_{3v} to take crystal symmetry into account (point groups are respectively D_{3h} and C_{3v}) and C_2 for the alternate electromagnetic field invariance, which yields the observed C_{6v} symmetry response. Actually, the laser-beam impact point changes when the sample is rotated, which brings a slow variation to the "constant" signal (Fig. 3, curves a and b). It is not possible to account for the $2\pi/6$ oscillation by an angle between **k** and the **c** axis,[1,5] as it would require an unrealistic value for this angle.

The experiments described above are concerned with two physical quantities, viz., the input polarization **E** of the infrared light and the output polarization **E′** of the green light generated by the medium. The formalism exposed hereafter is intended to connect them. Generally speaking, the mathematical relation between **E′** and **E** may be expressed by a Taylor expansion:

$$E'^{i}=\sum_{j_1}\sum_{j_2}(S_{(2)})^{i}_{j_1 j_2}E^{j_1}E^{j_2}+\cdots+\sum_{j_1}\cdots\sum_{j_N}(S_{(N)})^{i}_{j_1\cdots j_N}E^{j_1}\cdots E^{j_N}. \quad (1)$$

E'^{i} and E^{j} stand for the components of the vectors **E′** and **E**; $(S_{(N)})^{i}_{j_1\cdots j_N}$ are the components of a tensor of order $N+1$. We notice that the (even) Nth-order term is present *only if* the material exhibits a Nth-order nonlinear response. The detailed relationship between the tensors $S_{(2n)}$ $(2\le 2n\le N)$ and the nonlinear susceptibility tensors is not needed in this Letter.

The Nth-order term exhibits specific angular properties, according to the value of N; they may be used to determine N. It is to the mathematical analysis of those properties that we now turn.

For an input field **E** linearly polarized at an angle φ relative to a definite axis of the crystal surface, we have

$$E_x=E_0\cos\varphi,\quad E_y=E_0\sin\varphi. \quad (2)$$

Here a basis of two linear polarizations $\mathbf{e}_x$ and $\mathbf{e}_y$ is used. Introducing the basis of left-handed and right-handed circular polarizations

$$\mathbf{e}_{-1}=(\mathbf{e}_x+i\mathbf{e}_y)/\sqrt{2},\quad \mathbf{e}_1=(\mathbf{e}_x-i\mathbf{e}_y)/\sqrt{2}, \quad (3)$$

yields a new set of components for **E**:

$$\mathbf{E}=E^{-1}\mathbf{e}_{-1}+E^{1}\mathbf{e}_1,\quad E^{m}=(E_0/\sqrt{2})e^{im\varphi}, \quad (4)$$

$$m=-1,1,$$

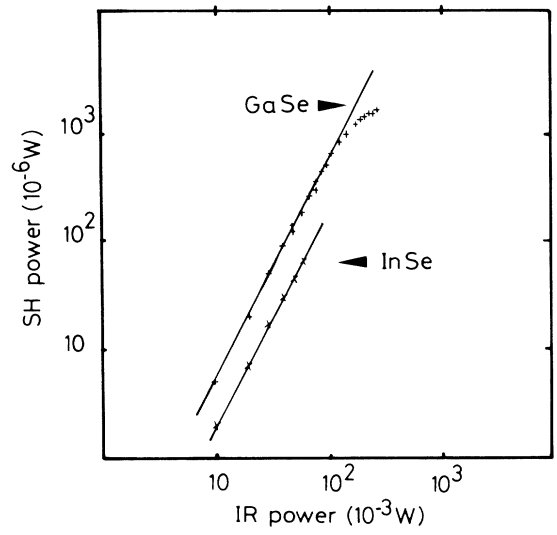

FIG. 2. Measured averaged output SH power vs input IR power at a fixed angle, on logarithmic scales. Incoming peak power is given by a 2×10^6 factor. Impact area is approximately 0.1 mm^2. The solid line has a slope 2. Power measurements have been led to a higher input level on GaSe (+) than on InSe (×).

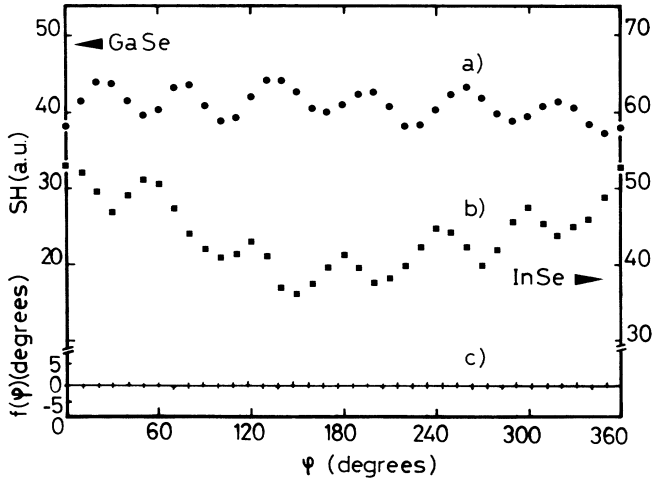

FIG. 3. Curves a and b show the output SH averaged power vs incident IR polarization direction φ for, respectively, GaSe (●) and InSe (■). Curve c is a diagram of $f(\varphi)=\alpha+2\varphi$ for GaSe. No noticeable deviation from a constant law can be observed for either material. Experiments are made at the maximum available IR excitation.

and similarly for $\mathbf{E}'$. Rewriting the term of order $2n$ ($2 \le 2n \le N$) in (1) with these new components yields

$$(E'_{(2n)})^m = (E_0/\sqrt{2})^{2n} \sum_{m_1} \cdots \sum_{m_{2n}} (S_{(2n)})^m_{m_1 \cdots m_{2n}} \exp\left[i \left(\sum_{k=1}^{2n} m_k \right) \varphi \right], \tag{5}$$

where m and the summation indices m_k ($1 \le k \le 2n$) take the values ± 1.

Summing up those terms and letting $M = \sum_{k=1}^{2n} m_k$ gives the complex amplitude

$$E'^m = \sum_{M=-N}^{N} W^m_M e^{iM\varphi}, \tag{6}$$

where N denotes the highest order of the expansion (1) and $\mathbf{W}_M$ is a complex vector (W^{-1}_M, W^1_M) defined by

$$W^m_M = \sum_{n=1}^{N/2} (E_0/\sqrt{2})^{2n} \sum_{m_1} \cdots \sum_{m_{2n}} (S_{(2n)})^m_{m_1 \cdots m_{2n}} \delta \left(\sum_{k=1}^{2n} m_k, M \right), \tag{7}$$

where δ means the Kronecker symbol. [In the writing of W_M, the (even) order N is omitted.]

The intensity of the second harmonic is proportional to

$$||E'||^2 = \sum_{M=-2N}^{2N} e^{iM\varphi} F_M, \tag{8}$$

which exhibits angular oscillations of periodicity $2\pi/M$ for $0 \le M \le 2N$. The Fourier coefficient F_M for $M \ge 0$ is given by

$$F_M = \sum_{k=-N}^{N-M} \langle \mathbf{W}_{k+M}, \mathbf{W}_k \rangle, \tag{9}$$

where $\langle , \rangle$ denotes the usual Hermitian product. Since $F_{-M} = F^*_M$, we need only consider $M \ge 0$; moreover from (7) W_M and, as a result, F_M vanish for odd M. In our system two nonvanishing coefficients are observed, F_0 and F_6 (Fig. 3). From (8) $N \ge 4$ is required. Note that F_2, F_4, and F_8 are forbidden by C_{6v} symmetry.

The orientation α of the output SH polarization is introduced by

$$E'^{-1} = E'^1 e^{-2i\alpha}. \tag{10}$$

If a relation of the kind

$$\alpha = -L\varphi \tag{11}$$

is observed with a suitable origin of angles ($L = 2$ in our rhombohedral crystals), (6) implies the following:

$$W^{-1}_k = 0 \quad \text{if} \quad -N \le k \le -N+2L-1, \tag{12a}$$

$$W^{-1}_k = W^1_{k-2L} \quad \text{if} \quad -N+2L \le k \le N, \tag{12b}$$

$$W^1_k = 0 \quad \text{if} \quad N-2L+1 \le k \le N. \tag{12c}$$

(12a) and (12c) show, respectively, that for $-N \le k \le -N+2L-1$, $\mathbf{W}_k$ is oriented along $\mathbf{e}_1$ and for $N-2L+1 \le k \le N$, $\mathbf{W}_k$ stands along $\mathbf{e}_{-1}$.

If $N-M \le -N+2L-1$, each $\mathbf{W}_k$ appearing in the sum (9) is parallel to $\mathbf{e}_1$, whereas, under the same conditions, every $\mathbf{W}_{k+M}$ is parallel to $\mathbf{e}_{-1}$. Hence the expression (9) for F_M vanishes for $2N-2L+1 \le M \le 2N$. If the nonvanishing Fourier coefficient of highest index is called $F_{\underline{M}}$, we have

$$2N \ge \underline{M} + 2L. \tag{13}$$

If $L = 2$, we conclude that N must be at least 6 for F_6 to be present. So our result provides evidence of at least a sixth-order effect in GaSe and InSe. [In the standard case[14] ($N = 2$), no anisotropy is allowed.]

Now, taking that minimum value of N, and if F_0 and $F_{\underline{M}}$ do exist, we must ensure that all other Fourier coefficients vanish. According to (12), among the numbers W^m_k, only $2N-2L+1$ are linearly independent and $N-L$ of them vanish for odd k. F_M may be expressed as

$$F_M = 2 \sum_{k=-N}^{N-2L-M} (W^1_{k+M})^* W^1_k, \quad 0 \le M \le 2N-2L. \tag{14}$$

Taking our experimental result as an illustrative example, with $N = 6$ and $L = 2$, and relabeling W^1_{-L+2i} by x_i, $|i| \le (N-L)/2$, the $N-L+1 = 5$ remaining expressions (14) of the F_M are rewritten as

$$\begin{aligned}
&M = 8: \; x_{-2} x^*_2 = 0, \\
&M = 6: \; x_{-2} x^*_1 + x_{-1} x^*_2 = F_{\underline{M}}/2, \\
&M = 4: \; x_{-2} x^*_0 + x_{-1} x^*_1 + x_0 x^*_2 = 0, \\
&M = 2: \; x_{-2} x^*_{-1} + x_{-1} x^*_0 + x_0 x^*_1 + x_1 x^*_2 = 0, \\
&M = 0: \; x_{-2} x^*_{-2} + x_{-1} x^*_{-1} + x_0 x^*_0 + x_1 x^*_1 + x_2 x^*_2 = F_0/2.
\end{aligned} \tag{15}$$

The first line ($M = 8$) imposes $x_{-2} = 0$ or $x_2 = 0$. In any case, we are left with $N-L$ variables subject to $N-L$ analogous conditions. The recurrent process stops at $F_{\underline{M}}$; then *one* of the $N-L+1-\underline{M}/2$ products $x_i x^*_{i+\underline{M}/2}$ must not vanish. The set (15) of equations always has a solution.[15]

Returning to the results displayed in Fig. 2, we attribute the subquadratic dependence of SH versus IR power to fourth-order terms and above in (1), whereas the anisotropy F_6 in the nonlinear response (Fig. 3) is to be ascribed to, at least, a sixth-order effect. Because, by (14), to lowest order,[15] $F_6/F_0 \sim E^6_0$, the anisotropy could

be detected only at the maximum available power. However, a detailed study of the function giving the output SH intensity versus incident power is beyond the aim of this Letter.

By a new angular analysis, we have proved that the output field expansion has to be taken up to, at least, sixth order to get a qualitative agreement with experimental SH generation behavior in GaSe or InSe. *A contrario,* second- and fourth-order components may appear without giving rise to any $2\pi/6$ modulation.

Finally, our line of reasoning is clearly not linked to the specific values of N, L, and $\underline{M}$. The relation between α and φ could differ from (11) in materials having other symmetries, which would imply adaptation of our calculations. In any case, an angular analysis is able to detect unambiguously high-order contributions in nonlinear responses which cannot be ascertained by an intensity analysis.

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[a]Present address: Lawrence Berkeley Laboratory, 1 Cyclotron Road, MS 70-110A, University of California, Berkeley, CA 94720.

[1]G. B. Abdullaev, L. A. Kulevskii, A. M. Prokhorov, A. D. Sovel'ev, E. Yu. Solaev, and V. V. Smirnov, Pis'ma Zh. Eksp. Teor. Fiz. **16**, 130 (1972) [JETP Lett. **16**, 90 (1972)].

[2]G. A. Akhundov, A. A. Agaeva, V. M. Salmanov, Yu. P. Sharonov, and I. D. Yaroshetskii, Fiz. Tekh. Poluprovodn. **7**, 1229 (1973) [Sov. Phys. Semicond. **7**, 826 (1973)].

[3]P. Kupecek, E. Batifol, and A. Kuhn, Opt. Commun. **11**, 291 (1974).

[4]J. L. Oudar, Ph. J. Kupecek and D. S. Chemla, Opt. Commun. **29**, 119 (1979).

[5]I. M. Catalano, A. Cingolani, A. Minafra, and C. Paorici, Opt. Commun. **24**, 105 (1978).

[6]I. M. Catalano, A. Cingolani, C. Cali, S. Riva-Sanseverino, Solid State Commun. **30**, 585 (1979).

[7]Yu. F. Solomonov and V. K. Subashiev, Phys. Status Solidi (a) **74**, 75 (1982).

[8]C. Hirlimann, J. F. Morhange, and A. Chevy, Solid State Commun. **69**, 1019 (1989).

[9]C. Hirlimann, J. F. Morhange, M. A. Kanehisa, A. Chevy, and C. H. Brito Cruz, Appl. Phys. Lett. **55**, 2307 (1989).

[10]G. B. Abdullaev *et al.*, Kvantovaya Elektron. **16**, 757 (1989) [Sov. J. Quantum Electron. **19**, 494 (1989)].

[11]Yo Ro Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984), p. 86.

[12]R. Le Toullec, N. Piccioli, M. Mejatty, and M. Balkanski, Nuovo Cimento **38B**, 159 (1977).

[13]N. Piccioli, R. Le Toullec, F. Bertrand, and J. C. Chervin, J. Phys. **42**, 1129 (1981).

[14]J. F. Nye, *Physical Properties of Crystals* (Clarendon Press, Oxford, 1957).

[15]In our problem (Fig. 2), there is an obvious strong second-order term x_0 (note that to lowest order $x_i \sim E_0^{2+2|i|}$). So four terms of five in (15) do not vanish; their determination is easy though lengthy.