Second-Harmonic Generation in GaAs: Experiment versus Theoretical Predictions of $\chi^{(2)}_{xyz}$

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For GaAs we have determined $|\chi^{(2)}_{xyz}(-2\omega; \omega, \omega)|$ in second-harmonic generation experiments using two-photon energies between 2 and 5 eV. In addition to the E_1, $E_1 + \Delta_1$, E'_0, and E_2 critical-point bulk transitions of GaAs, a surprisingly strong surface transition at 3.35 eV was observed for natively oxidized GaAs(001) samples. A detailed comparison with theoretical predictions reveals that calculations that include many-particle effects at the level of the "scissors" approximation can describe the overall frequency dependence of the second-harmonic susceptibility reasonably well.

The determination of nonlinear optical susceptibilities, and, in particular, of the second-harmonic susceptibility tensor $\chi^{(2)}_{\alpha\beta\gamma}(-2\omega; \omega, \omega)$ of noncentrosymmetric materials has been a subject of primary concern and continuing interest in nonlinear optics since the early years of this field [1,2]. The knowledge of magnitude and frequency dependence of nonlinear optical susceptibilities is not only important for a basic understanding of nonlinear optical processes but also indispensable for the development of novel nonlinear optical materials [3].

Among other crystals that can be used to generate the second-harmonic of laser light, GaAs stands out as an archetypical and frequently studied material [1,4–12]. As with all III-V semiconductors of the zinc blende type, GaAs has $\overline{4}3m$ symmetry, the highest point symmetry possible for a noncentrosymmetric crystal. Because of this symmetry, only six elements of the second-harmonic susceptibility tensor are nonzero, and these six elements are equal: $\chi^{(2)}_{xyz} = \chi^{(2)}_{yzx} = \chi^{(2)}_{zxy} = \chi^{(2)}_{xzy} = \chi^{(2)}_{zyx} = \chi^{(2)}_{yxz}$ [2].

Over the last three decades, a number of experimental and theoretical studies on second-harmonic generation (SHG) in GaAs have been performed. Nevertheless, experimental work has been limited to relatively narrow spectral regions, mainly to second-harmonic photon energies in the region of the E_1 transition of GaAs [1,4,5,7]. Moreover, experimental data published for the same spectral region by different groups differ substantially [1,4,7]. On the theory side, calculations have been performed for various III-V semiconductors on much larger frequency scales [10–12]. However, a consistent picture of $\chi^{(2)}_{xyz}$ did not emerge from these calculations either, as even recent theoretical studies employing state-of-the-art techniques revealed considerable differences on a qualitative level [11,12]. With these limitations, a comparison of available experimental and theoretical data is not conclusive, and the question as to what level of theory is really needed to adequately describe nonlinear optical susceptibilities of III-V semiconductors is left unanswered.

In this Letter, we report experimental data for $|\chi^{(2)}_{xyz}|$ of GaAs for a large range of second-harmonic photon energies from 2 to 5 eV. Our study reveals how the various critical-point interband transitions in GaAs, and a surprisingly strong surface resonance, contribute to the frequency dependence of $|\chi^{(2)}_{xyz}|$. This work presents the first conclusive comparison of experimental data with theoretical predictions for the second-harmonic susceptibility of a noncentrosymmetric semiconductor.

We used (001)-oriented GaAs, and the second-harmonic susceptibility $\chi^{(2)}_{xyz} = 2d_{14}$ of GaAs was determined by measurement of the reflected s-polarized second-harmonic light generated with p-polarized laser radiation [9]. The SHG signal obtained with these polarizations is anisotropic with respect to a rotation of the sample around the [001] surface normal [Eq. (1)]. The inevitable presence of the surface leads to additional contributions to $\chi^{(2)}_{xyz}$ that may complicate the analysis of bulk SHG spectra and have to be considered.

One contribution, which affects only few atomic layers at the surface, arises from the structural discontinuity of the surface and from physical or chemical changes in the atomic surface layers. This effect, well known and systematically exploited in second-harmonic generation studies of surface properties of centrosymmetric materials [13], can be described by a surface susceptibility tensor $\chi^{(2)}_{s,\alpha\beta\gamma}$. We note that for GaAs(001) the surface region contributes through the tensor elements $\chi^{(2)}_{s,xyz} = \chi^{(2)}_{s,xzy} = \chi^{(2)}_{s,yxz} = \chi^{(2)}_{s,yzx}$ to SHG in the p-in/s-out configuration, and that this surface contribution cannot be separated from that of $\chi^{(2)}_{xyz}$ of bulk GaAs by a different choice of polarizations [9]. Below we show that a surface contribution is not only detectable but even can give rise to a prominent feature in the bulk SHG spectrum of GaAs.

A second complication originates from the electrostatic field E_{depl} of a depletion layer near the GaAs surface which gives rise to electric-field-induced SHG [8,9]. To reduce this effect to a negligible extent, we used semi-insulating GaAs(100) wafers ($\rho > 10^7 \ \Omega \, cm^{-1}$).

SHG spectra were obtained with tunable intense 14 ps light pulses from a parametric generator/amplifier system pumped by the third harmonic of a Nd:YAG laser. The experimental setup is similar to that described in Ref. [14]. The plane of incidence was parallel to the

crystallographic [100] direction of GaAs, and the angle of incidence was 65°. To obtain absolute values of $|\chi^{(2)}_{xyz}|$, the strength of the SHG signal from the GaAs sample was compared to that of α-quartz. For this purpose, the GaAs sample was replaced with a crystalline quartz plate, and the wavelength-dependent intensity oscillations of the second-harmonic light generated in the quartz plate were measured in transmission geometry for second-harmonic energies around 3.0 and 5.0 eV [15]. Our determination of absolute values of $|\chi^{(2)}_{xyz}|$ for GaAs is based on $\chi^{(2)}_{xxx}(\alpha\text{-quartz}) = (0.59 \pm 0.03)$ pm/V for an excitation wavelength of 1.064 μm [16,17]. The frequency dependence of $\chi^{(2)}_{xxx}$ (α-quartz) was assumed to follow Miller's rule which holds reasonably well for α-quartz [17]. Details of our experimental procedures will be published in a forthcoming paper [15].

In Fig. 1 we show the SHG spectrum of semi-insulating GaAs for second-harmonic photon energies between 2 and 5 eV, measured with p and s polarizations of the fundamental and second-harmonic light, respectively. The spectrum is presented in units of the nonlinear intensity reflection coefficient, $R_{ps} = I^{2\omega}_s/(I^\omega_p)^2$. R_{ps} is related to $\chi^{(2)}_{xyz}$ through

$$R_{ps} = |\chi^{(2)}_{xyz}|^2|r_{ps}|^2 = |\chi^{(2)}_{xyz}|^2 \frac{32(2\omega)^4}{\epsilon_0 c^5}\cos^2(2\phi)$$
$$\times \left| \frac{k_{1z}k_{2z}\sin\theta\cos\theta}{(K_{1z}+K_{2z})(K_{2z}+2k_{2z})[(k_{2z}+\epsilon(\omega)k_{1z})]^2} \right|^2.$$
$$(1)$$

r_{ps} includes the Fresnel coefficients for transmission of the fundamental and second-harmonic fields from vacuum to GaAs and vice versa, respectively. With the z direction defined along the surface normal, k_{1z} and K_{1z} are the perpendicular components of the fundamental and the second-harmonic wave vector, respectively, in vac-

uum and k_{2z} and K_{2z} are the perpendicular components in the bulk of GaAs. $\epsilon(\omega)$ is the dielectric function of GaAs, θ the angle of incidence, and ϕ the azimuthal angle between the plane of incidence and the [100] direction of the sample.
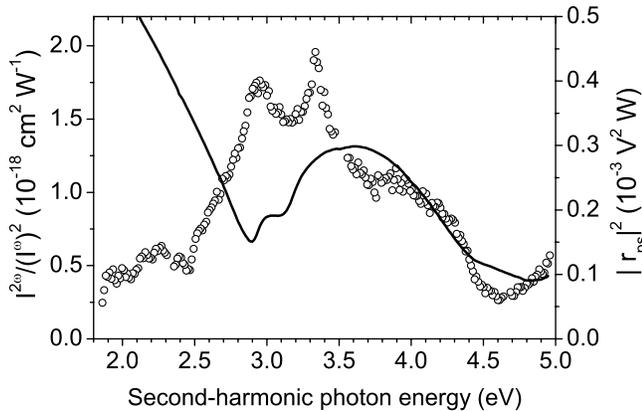
The spectrum in Fig. 1 exhibits two prominent features at 2.9 and 3.35 eV. The feature at 2.9 eV is identified as the two-photon resonance of the E_1 interband transition at 2.91 eV, which is responsible for the first strong maximum of the linear dielectric function $\epsilon(\omega)$ of GaAs [18] shown in Fig. 2. The energies of all critical-point transitions of GaAs up to 6 eV, as reported by Lautenschlager et al. [19], are also indicated in Fig. 2.

The marked SHG resonance at 3.35 eV in Fig. 1 is not related to a transition in the bulk of GaAs. There is no critical point in the joint density of states for the bulk band structure of GaAs in this energy range [19]. Linear-optical spectra of GaAs [19] and the dielectric function of bulk GaAs [18] (Fig. 2) do not exhibit a spectral feature at this energy. Moreover, this SHG resonance was also observed with similar energy and intensity in n-doped GaAs(001) with a dopant concentration of 2×10^{18} cm^{-3} [15]. We thus can safely rule out that a bulk transition in GaAs is responsible for this resonance. Schmitz et al. [20] have grown thin β-Ga$_2$O$_3$ films on a CoGa(001) substrate and observed with electron energy loss spectroscopy a resonance at 3.3 eV which they assigned to a gap state in the gallium oxide. Our GaAs(001) samples, which we used as received from the manufacturer without further surface treatment, were also covered with a gallium surface oxide. We therefore assign the 3.35 eV SHG resonance to a two-photon transition in the gallium surface oxide. Our assignment to a transition specific of the oxidized GaAs(001) surface is supported

FIG. 1. Symbols: SHG spectrum of semi-insulating GaAs(001) obtained with p-polarized fundamental and s-polarized second-harmonic light. Line: spectral dependence of $|r_{ps}|^2$ [see Eq. (1)] for GaAs(001) and for $\theta = 65°$, $\phi = 0°$.
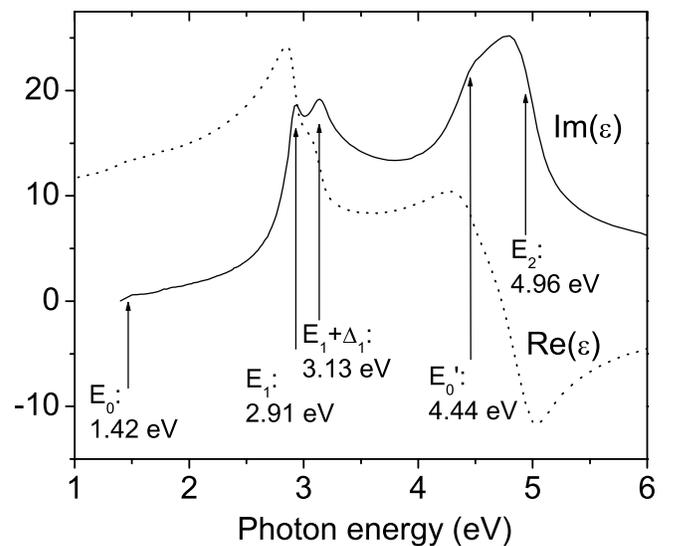
FIG. 2. Dielectric function ϵ and energies of critical-point bulk interband transitions of GaAs at room temperature.

by the SHG study of Lotem *et al.* [5]: their spectrum of $|\chi^{(2)}_{xyz}|$ obtained from (111)-oriented GaAs with an etched surface did not show a resonance around 3.35 eV, but was similar to ours in Fig. 3 with regard to the bulk transitions between 2.9 and 3.6 eV. Although SHG experiments with appropriate modifications of the GaAs(001) surface are needed to obtain more information on this surface transition, our present work demonstrates that even in the presence of a strong bulk signal SHG can provide useful information about surface properties of noncentrosymmetric semiconductors.

We point out that the reproducibility of our SHG spectra of semi-insulating GaAs(001) was very good for second-harmonic photon energies above 2.7 eV. For lower energies we observed deviations from a smooth frequency dependence, and unexpected spectral features in this range such as the minimum near 2.5 eV in Fig. 1 were not consistently reproduced in different experimental runs. In future SHG experiments we will investigate whether resonant excitation of the EL2 deep donor defects in GaAs [21] by the fundamental photons affects the frequency dependence of $|\chi^{(2)}_{xyz}|$ of semi-insulating GaAs for two-photon energies between 2.0 and 2.6 eV.

To evaluate $|\chi^{(2)}_{xyz}|$ from the SHG spectrum, we have calculated the factor $|r_{ps}|^2$ in Eq. (1) using the data in Ref. [18] for the dielectric function of GaAs. $|r_{ps}|^2$ is shown in Fig. 1 and exhibits a strong frequency dependence with minima at the E_1 and $E_1 + \Delta_1$ energies and a broader structure caused by the E_0' and E_2 transitions. The resulting spectrum of $|\chi^{(2)}_{xyz}|$ is shown in Fig. 3. For the energy of the E_1 transition we find $|\chi^{(2)}_{xyz}| = 750 \pm$
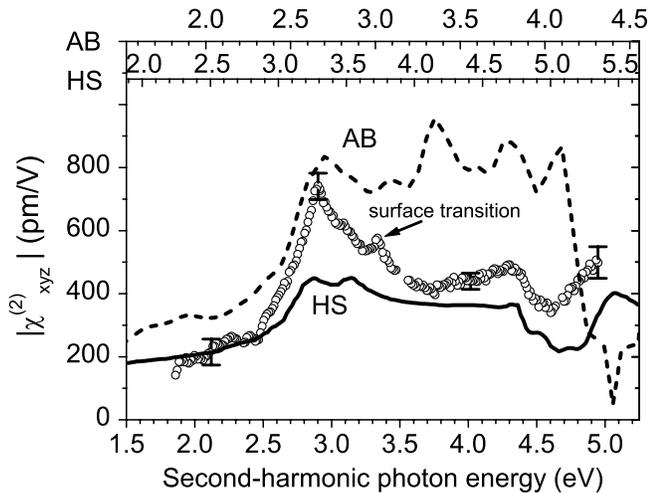
FIG. 3. Spectral dependence of $|\chi^{(2)}_{xyz}|$ of GaAs. Symbols: experimental results. Dashed line: calculation by Adolph and Bechstedt (AB). Solid line: calculation by Hughes and Sipe (HS). For a better comparison of theory and experiment the energy scales of the calculated spectra have been modified as described in the text. The original energy scales of the theoretical spectra are reproduced at the top of the figure.

40 pm/V. This value is in excellent agreement with the result of Yeganeh *et al.* [7]. The spin-split transition $E_1 + \Delta_1$ is clearly observable in $|\chi^{(2)}_{xyz}|$ as a shoulder at 3.1 eV [22], although it is much weaker than the E_1 transition. The broad minimum in $|\chi^{(2)}_{xyz}|$ around 4.6 eV is related to the E_0' and E_2 transitions and will be discussed in detail below. A one-photon contribution of the E_0 direct bandgap transition at 1.42 eV is not discernable in our spectrum of $|\chi^{(2)}_{xyz}|$, consistent with the comparatively small strength of this transition in linear-optical spectra (Fig. 2) [23].

In Fig. 3 we compare our experimental data of $|\chi^{(2)}_{xyz}|$ with the results of recent state-of-the-art calculations by Hughes and Sipe (HS) [11] and by Adolph and Bechstedt (AB) [12]. These authors also reported theoretical results for the dielectric function of GaAs. The results of HS were based on full-band-structure, self-consistent calculations within the local density approximation (LDA) utilizing the full-potential linearized augmented plane-wave (FLAPW) method. Self-energy corrections were included at the level of the scissors approximation [11]. AB performed electronic-structure calculations at the LDA level based on the plane-wave pseudopotential method. These authors included many-body quasiparticle effects beyond the scissors approximation [12].

In both theoretical studies [11,12] the energies of the critical-point interband transitions in GaAs deviate considerably from the experimental values [19]. Notice that these deviations cannot be explained by the much smaller effect of the temperature dependence of the transitions. Rather they originate from the approximations used to describe the excited states in the calculations. For a closer comparison between theory and experiment the transition energies of the calculated spectra have to be corrected accordingly. For this purpose we modified the energy scales for the theoretical data in Fig. 3 as follows: from the calculated imaginary part of $\epsilon(\omega)$ in Refs. [11,12] the theoretical energies of the E_1 and E_2 transitions of GaAs were obtained. We then modified the energy scales of the theoretical data by linear rescaling $E_{mod} = a + bE_{orig}$. The parameters a and b were determined by matching the E_1 and E_2 peaks of $\text{Im}[\epsilon(\omega)]$ to the experimental room-temperature values. The bottom scale in Fig. 3 represents the two-photon energies of our experimental data and also E_{mod} for the theoretical results for $|\chi^{(2)}_{xyz}|$, while the two top scales are the original energies E_{orig} of Refs. [11,12], respectively.

For the largest part of the spectrum our experimental data of $|\chi^{(2)}_{xyz}|$ are between the theoretical predictions of AB and HS. For the energy of the E_1 transition we find almost quantitative agreement between our experimental data and the data by AB (dashed line in Fig. 3). The spin-split transition $E_1 + \Delta_1$ which is resolved in our spectrum and also in the previous work of Lotem *et al.* [5] is, however, not reproduced in their calculation. The agreement between theory and experiment worsens

dramatically for higher energies, particularly between 3.5 and 5 eV, despite of the advanced treatment of many-particle effects. Between 4.6 and 5 eV our data exhibit an increase of $|\chi^{(2)}_{xyz}|$ while the calculated spectrum shows a decrease. The origin for this disagreement is discussed below.

The values of $|\chi^{(2)}_{xyz}|$ calculated by HS (solid line in Fig. 3) are consistently lower than our data for energies above 2.5 eV, particularly for the E_1 energy. For energies above 3.3 eV, however, the spectrum of HS is much closer to our experimental data than that of AB. In addition, the overall spectral dependence of the results of HS between 3 and 5 eV agrees surprisingly well with ours, considering their treatment of excited states within the semipheno-menological scissors approximation. The weak dispersion of $|\chi^{(2)}_{xyz}|$ between 3.5 and 4.3 eV, and the valley structure in the range of the E'_0 and E_2 transitions between 4.3 and 5.0 eV, are well reproduced in their calculations. The valley structure is related to the different signs of the E'_0 and E_2 resonances in the imaginary part of $\chi^{(2)}_{xyz}$: the negative contribution of the E'_0 transition at 4.44 eV interferes with the positive contribution of the E_2 transition at 4.96 eV [11], giving rise to the minimum of $|\chi^{(2)}_{xyz}|$ at 4.6 eV in our spectrum and at a (modified) energy of 4.7 eV in the spectrum of HS. Contrary to HS, AB found a negative sign for the E_2 transition which is responsible for the strong decrease of $|\chi^{(2)}_{xyz}|$ at a (modified) energy of 5 eV in their spectrum. This spectral dependence is not consistent with our experimental data. We note that the negative sign of the E'_0 contribution causes a strong violation of Miller's rule [2] between 4 and 5 eV [15], while the rule approximately holds in the energy region of the E_1 and $E_1 + \Delta_1$ transitions [5,15].

In conclusion, we have reported the experimental spectrum of $|\chi^{(2)}_{xyz}(\omega, \omega)|$ of GaAs from 2 to 5 eV, and revealed how the interband transitions at the various critical points of GaAs, and a surface resonance at 3.35 eV, determine the frequency dependence of the second-harmonic susceptibility. Our data allowed for the first time a conclusive comparison with theoretical predictions of $\chi^{(2)}_{xyz}$, showing that calculations at the level of the scissors approximation can reproduce the overall frequency dependence of the second-harmonic susceptibility of GaAs in this energy range reasonably well.

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[1] R. K. Chang, J. Ducuing, and N. Bloembergen, Phys. Rev. Lett. **15**, 415 (1965).

[2] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).

[3] E. Ghahramani, D. J. Moss, and J. E. Sipe, Phys. Rev. Lett. **64**, 2815 (1990).

[4] F. G. Parsons and R. K. Chang, Opt. Commun. **3**, 173 (1971).

[5] H. Lotem, G. Koren, and Y. Yacoby, Phys. Rev. B **9**, 3532 (1974).

[6] D. Bethune, A. J. Schmidt, and Y. R. Shen, Phys. Rev. B **11**, 3867 (1975).

[7] M. S. Yeganeh, J. Qi, J. P. Culver, A. G. Yodh, and M. C. Tamargo, Phys. Rev. B **46**, 1603 (1992).

[8] J. Qi, M. S. Yeganeh, I. Koltover, A. G. Yodh, and W. M. Theis, Phys. Rev. Lett. **71**, 633 (1993).

[9] T. A. Germer, K. W. Kolasinski, J. C. Stephenson, and L. J. Richter, Phys. Rev. B **55**, 10 694 (1997).

[10] M.-Z. Huang and W. Y. Ching, Phys. Rev. B **47**, 9464 (1993).

[11] J. L. P. Hughes and J. E. Sipe, Phys. Rev. B **53**, 10 751 (1996).

[12] B. Adolph and F. Bechstedt, Phys. Rev. B **57**, 6519 (1998).

[13] G. Lüpke, Surf. Sci. Rep. **35**, 75 (1999).

[14] G. Erley, R. Butz, and W. Daum, Phys. Rev. B **59**, 2915 (1999).

[15] St. Bergfeld and W. Daum (to be published).

[16] J. Jerphagnon and S. K. Kurtz, Phys. Rev. B **1**, 1739 (1970).

[17] K. Hagimoto and A. Mito, Appl. Opt. **34**, 8276 (1995).

[18] E. D. Palik in *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic Press, New York, 1997), Vol. I, p. 429.

[19] P. Lautenschlager, M. Garriga, S. Logothetidis, and M. Cardona, Phys. Rev. B **35**, 9174 (1987).

[20] G. Schmitz, P. Gassmann, and R. Franchy, J. Appl. Phys. **83**, 2533 (1998).

[21] G. M. Martin, Appl. Phys. Lett. **39**, 747 (1981).

[22] The SHG spectrum in Fig. 1 lacks structure at the $E_1 + \Delta_1$ energy because the spin-split feature in $|\chi^{(2)}_{xyz}|^2$ is largely compensated by that of $|r_{ps}|^2$.

[23] A resonance due to one-photon excitation of the E_0 transition was reported in a previous SHG study of GaAs [7]. Our spectra for both *p*-in/*s*-out and *p*-in/*p*-out polarizations (with a good signal-to-noise ratio in this spectral range) do not show any indication of such a resonance.