Two-photon absorption in direct-gap crystals—an addendum

A. Vaidyanathan and A. H. Guenther
Air Force Weapons Laboratory, Kirtland Air Force Base, New Mexico 87117

S. S. Mitra
Department of Electrical Engineering, University of Rhode Island, Kingston, Rhode Island 02881

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An error made in an earlier paper by the authors regarding the appropriate effective masses to be used in calculations employing the Basov formulation is corrected. The new results for two-photon absorption coefficient obtained from the Basov formula now agree quite well with those computed using Keldysh's treatment. Furthermore, it is shown that improved agreement between theoretical and experimental two-photon absorption coefficients is obtained by including nonparabolicity and degeneracy of the energy bands in the calculations.

I. INTRODUCTION

In an earlier paper[1] (referred to as I hereafter), the Keldysh,[2] Braunstein,[3] and Basov[4] formulas for two-photon absorption (TPA) in direct-gap crystals were critically compared with each other and with the experimental data. It was shown that the Keldysh and Braunstein formulas which describe allowed transitions yielded much better results than the Basov formula which describes forbidden transitions. That result was evidently the outcome of inadvertently using the free-electron mass instead of the band effective mass in the expressions for the intraband-momentum matrix elements.[5] In this note we report the results of new calculations for the TPA coefficients of several zinc-blende-structure semiconductors using the correct mass in the Basov formula. These calculations have been further improved by including the effects of nonparabolicity and degeneracy of the energy bands as described by the Kane model.[6]

II. THEORY

A. Basov formula

When, appropriately, the band effective masses are used in the expressions for the intraband-momentum matrix elements, instead of the free-electron mass,[5] the Basov formula[1,4] takes the following form [compare with Eq. (27) of I]:

$$\beta_B(\omega)=\frac{2^{7/2}\pi e^4 E_g(2\hbar\omega-E_g)^{3/2}}{3\epsilon_\infty C^2(\hbar\omega)^5(m_{cv}^*)^{1/2}}. \tag{1}$$

Equation (1) is derived assuming all the energy bands are quadratic functions of the wave vector $\vec{k}$. When one uses a more accurate nonparabolic expression for the interband energy difference E_{vc}, of the form[6]

$$E_{vc}(\vec{k})=E_g\left(1+\frac{\hbar^2k^2}{m_{vc}^*E_g}\right)^{1/2}, \tag{2}$$

Basov's formula becomes

$$\beta_B^{np}(\omega)=\frac{2^3\pi e^4}{3\epsilon_\infty C^2}\frac{E_g^{3/2}}{(m_{cv}^*)^{1/2}}\frac{1}{(\hbar\omega)^4}\left[\left(\frac{2\hbar\omega}{E_g}\right)^2-1\right]^{3/2}. \tag{3}$$

Equation (3) reduces to Eq. (1) at the absorption edge, where $2\hbar\omega\simeq E_g$, as one would normally expect.

For the zinc-blende-type crystals studied in I, the highest valence band is triply degenerate,[6] at the Brillouin-zone center in the absence of spin-orbit splitting. When the spin-orbit interaction is included and $\vec{k}\cdot\vec{p}$ perturbation applied,[6] there results a heavy-hole band, a light-hole band, and a split-off band as shown in Fig. 1. For the laser wavelengths studied in I, the transitions from all three of these bands are energetically possible in the case of GaAs, InP, and ZnSe, while for InSb and CdTe only transitions from the heavy- and light-hole bands are energetically possible.

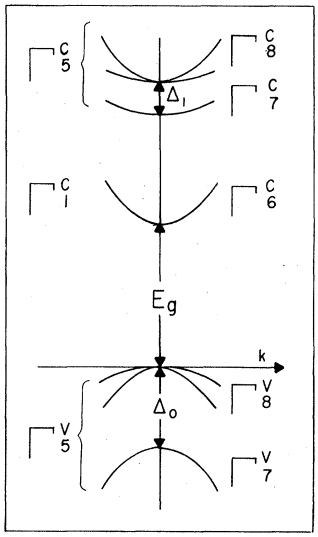

FIG. 1. Schematic of the band structure of a typical zinc-blende-type semiconductor near the center of the Brillouin zone. E_g is the fundamental energy gap, while Δ_0 and Δ_1 are the spin-orbit splittings of the valence and conduction bands, respectively. Each of the bands is doubly degenerate due to spin.

TABLE I. Values of band-structure parameters (Refs. 7–9).

Crystal	Effective mass (units of free-electron mass) Electron	Heavy hole	Light hole	Split-off hole	Valence-conduction band energy gap at 300 K (eV)	Spin-orbit splitting of valence bands (eV)	High-frequency dielectric constant
CdTe	0.09	5	0.13	0.37	1.50	0.927	7.21
GaAs	0.0667	0.68	0.12	0.2	1.435	0.341	10.9
InP	0.0803	0.4	0.086	0.18	1.28	0.11	9.56
InSb	0.0139	0.25	0.012	0.12	0.18	0.81	15.68
ZnSe	0.17	0.6	0.25	0.67	2.58	0.45	5.9

Using the band parameters listed in Table I we carried out Basov-type calculations with aid of Eq. (3) by including all possible two-photon transitions in CdTe, GaAs, InP, InSb, and ZnSe. The resulting TPA coefficients are reported in Table II along with selected experimental data to which the theoretical estimates can be compared. Such calculations cannot be performed for the alkali halides due to the lack of reliable information regarding the relevant band-structure parameters.

B. Keldysh formula

In the past, objections have been raised to the Keldysh formula based on parity considerations.[15] It has been stated that the Keldysh formula always predicts a frequency dependence of the form $(2\hbar\omega - E_g)^{1/2}$, which disagrees with the functional form $(2\hbar\omega - E_g)^{3/2}$ predicted by the second-order perturbation formulas for allowed-forbidden transitions. We note that if one expands the Dawson integral encountered in the Keldysh formula[2] in a series, the first term does yield the one-half power dependence corresponding to allowed-allowed transitions; however, the second and third terms yield three-and five-halves power dependences, respectively, corresponding to allowed-forbidden and forbidden-forbidden transitions. In fact, we can show that the second term of the series expansion of the Keldysh formula closely resembles the Basov formula at the TPA edge.

The second term of the series expansion of the exponential in the Dawson integral expressed by Eq. (15) of I is

$$\frac{1}{3}\left(2\left\langle\frac{E_g}{\hbar\omega}+1\right\rangle-\frac{2E_g}{\hbar\omega}\right)^{3/2}, \tag{4}$$

where the notation $\langle\cdots\rangle$ means the integer part of the argument. Thus, the second term of the series expansion of the Keldysh formula, close to the TPA edge is [see Eqs. (11)–(19) of I]

$$\beta_K^{\text{2nd term}}(2\hbar\omega \simeq E_g)=\frac{2^{5/2}\pi e^4 \exp(4)(2\hbar\omega - E_g)^{3/2}}{27\epsilon_\infty C^2(\hbar\omega)^2 E_g^2 (m_{vc}^*)^{1/2}}. \tag{5}$$

From Eqs. (5) and (1) [or (3)], for $2\hbar\omega \simeq E_g$, we obtain

$$\frac{\beta_K^{\text{2nd term}}}{\beta_B}(2\hbar\omega \simeq E_g)\simeq\frac{\exp(4)}{144}=0.379. \tag{6}$$

TABLE II. Comparison of experimental and theoretical two-photon absorption coefficients that include the effects of band degeneracies (in units of cm/MW).

Crystal	Wavelength (μm)	Theoretical (300 K) Basov (parabolic)	Basov (nonparabolic)	Keldysh (nonparabolic)	Experimental results with nanosecond pulses at room temperature
CdTe	1.064	0.037	0.083	0.051	0.13 ± 0.04[a]
					0.2 – 0.3[a]
GaAs	1.064	0.039	0.088	0.057	0.02 – 5.6[b]
InP	1.064	0.056	0.161	0.080	0.23 – 0.3[c]
					0.26 ± 0.13[c]
InSb	10.64	8.97	14.38	15.21	0.2 – 16[d]
ZnSe	0.694	0.011	0.019	0.018	0.04[e]

[a] Reference 10.
[b] Reference 11.
[c] Reference 12.
[d] Reference 13.
[e] Reference 14.

Thus, close to the TPA edge the second term of the Keldysh formula agrees with the Basov formula, not only in functional form, but also in absolute value to within a factor of three. This agreement must be considered good in view of the vast differences between the two theoretical approaches and the many approximations involved in them. The values of the TPA coefficients away from the absorption edge, obtained from the Keldysh formula by keeping all the terms in it, are in even closer agreement with the Basov results. This can be seen in Table II where the results of the Keldysh formula including the effects of band degeneracies are compared with similar results obtained from the Basov formula. The Keldysh results are found to fall in between the Basov results with parabolic and nonparabolic energy bands, in all the crystals studied here except InSb. In InSb, the Keldysh results are somewhat larger than that of the Basov formula even in the nonparabolic model.

C. Braunstein formula

The Braunstein[3] formula considers the next higher conduction band for the intermediate state. In zinc-blende-type crystals this band also consists of a heavy-mass band, a light-mass band, and a spin-orbit–split-off band.[8] When the degeneracies of the initial and intermediate states are taken into account, the Braunstein results obtained in I are increased by a factor between six and nine. However, the Braunstein formula suffers from the following drawback. It requires knowledge of the band parameters of the higher conduction bands, which in general are not accurately known either from theoretical calculations or experimental data. Thus, the Braunstein formula is generally not suitable for quantitatively reliable calculations and further discussion is omitted here.

III. DISCUSSION

Before making any comparison between the theoretical and experimental results, it is instructive to point out the following: The experimental results are known to be seriously influenced by many factors; laser pulse duration, free-carrier absorption, sample purity (type and concentration of impurities), spatial and temporal fluctuations of the laser pulse, sample temperature and thickness, etc. For example, picosecond pulses are known to afford much smaller TPA coefficients than nanosecond pulses, due to coherence effects such as self-induced transparency, etc.[16] These considerations explain, in part, the large variations in the reported experimental data. The theoretical calculations discussed herein are for intrinsic two-photon absorption in pure crystals at room temperature. Hence, in comparing the theoretical predictions with experimental results we restrict ourselves to experimental data obtained with nanosecond pulses at room temperature, when coherence effects, etc., are usually absent or are of reduced influence. From Table II it can be seen that the theoretical values somewhat underestimate the TPA coefficients. This is not surprising in view of the numerous approximations made in the theoretical calculations regarding the energy bands, oscillator strengths, intermediate states, etc., which may not be accurate, especially away from the band edge. Also, as pointed out earlier the experimental data are affected by many factors resulting in large spreads in the measured TPA coefficients.

These observations point out the need for more experiments using well-characterized lasers and crystals. On the theoretical side, more rigorous calculations that use reliable band structures and momentum matrix elements throughout the Brillouin zone and also include many intermediate states are highly desirable.

IV. CONCLUSION

The effects of degeneracies and nonparabolicity of the energy bands on the two-photon absorption coefficients in direct-gap crystals are studied. The Basov results are found to be increased by as much as a factor of three due to the nonparabolicity of the energy bands. The Keldysh results for degenerate bands are shown to fall in between the corresponding Basov results with parabolic and nonparabolic energy bands, respectively. It is also noted that the theoretical values generally underestimate the experimental two-photon absorption coefficients. In order to achieve closer agreement between theoretical predictions and experimental data, one needs more experimental data obtained with well-characterized lasers and crystals, as well as theoretical values of the two-photon absorption coefficients obtained from rigorous band-structure calculations.

Note added in proof. The authors have recently carried out band-structure calculations of the two-photon absorption coefficients of GaAs, ZnP, CdTe, and ZnSe, using the empirical pseudopotential method. Good agreement is noted between these results[17] and the experimental data.

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