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Verification of the scaling rule for two-photon absorption in semiconductors

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Abstract. The simple parametric scaling rules for the two-photon absorption coefficients, β_2, predicted by recent theory, have been experimentally confirmed by the measurement of β_2 in ten different semiconductors using carefully characterized picosecond 1 and 0·5 μm pulses. We find

$$\beta_2(\text{cm/GW}) = (3{\cdot}1 \pm 0{\cdot}5) \times 10^3 \sqrt{E_p}\, F_2(2\hbar\omega/E_g) n^{-2} E_g^{-3},$$

where $E_p \simeq 21$ eV for the semiconductors studied, E_g is the energy gap in eV, n the refractive index and $F_2(x) = (x-1)^{3/2}/x^5$. This relation allows the prediction of β_2 in other materials at other wavelengths, which is useful in the design of nonlinear optical elements. The strong self-defocusing observed is consistent with nonlinear refraction by the two-photon-generated free carriers.

The rapidly developing use of semiconductors in nonlinear optical devices demands a careful study of their nonlinear optical properties. A nonlinear optical parameter that has received considerable attention over the past two decades is the two-photon absorption coefficient, β_2 [1]. Knowledge of the scaling laws governing two-photon absorption allows the prediction of nonlinearities useful in the design of nonlinear optical elements and for tailoring of the nonlinearity for a specific need (for example, varying the band-gap energy of mixed ternary compounds). Other nonlinearities may be limited in efficiency by the onset of two-photon absorption, such that it sets design limits for devices based on these nonlinearities. In addition, strong self-refraction effects that accompany two-photon absorption have device applications [2].

Figure 1 shows values of experimentally determined values of β_2 for GaAs and CdSe at a wavelength of 1 μm reported in the literature over the past 19 years. Two things to notice about this graph are the extreme variations in β_2 (this is a semi-logarithmic graph) and that there is a general trend with time toward smaller values. Clearly, comparisons of theory to these experiments are meaningless unless we can understand the reasons for these differences.

The variation in β_2 could be due to extrinsic material variations (impurities, etc.) or due to experimental error in method and/or interpretation. The downward trend in reported values over these years could also be due to the production of better

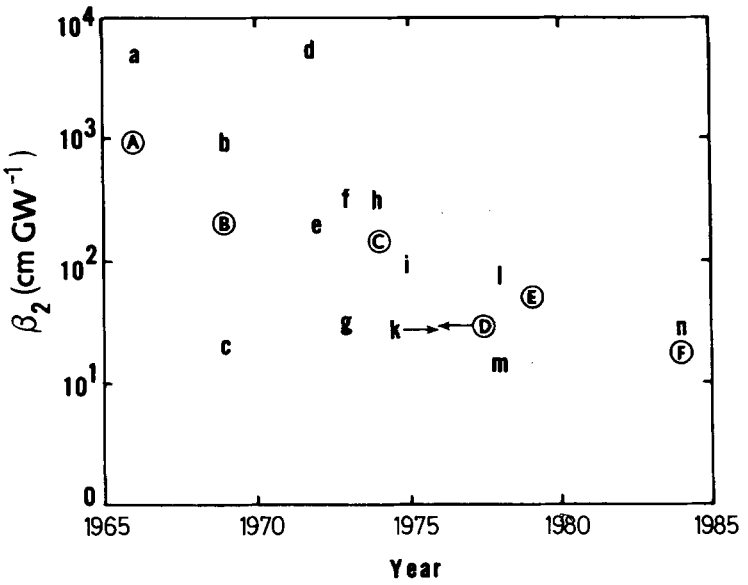

Figure 1. A semi-logarithmic plot of the reported two-photon absorption coefficients of GaAs (lower case letters) and CdSe (upper case letters) against the year of the study: (*a*) [16], (*b*) [17], (*c*) [18], (*d*) [19], (*e*) [20], (*f*) [21], (*g*) [21], (*h*) [9], (*i*) [22], (*k*) [23], (*l*) [24], (*m*) [25], (*n*) this work, (A) [16], (B) [18], (C) [26], (D) [3], (E) [27], (F) this work.

materials or to better experimental techniques and interpretation. Our conclusion from a systematic study of ten different semiconductors is that the extrinsic material properties play a relatively minor role and that near-intrinsic values of β_2 can be determined with the proper experimental technique. The evidence to support these conclusions is contained in the experiments conducted by Bechtel and Smith [3] in 1976 using a similar technique on different samples, which gave values of β_2 in excellent agreement with the values obtained in this work for the four materials common to both studies. Also, both the scaling laws for β_2 and the absolute values of β_2 predicted by theory are confirmed by our experiments [4–6].

We find

$$\beta_2(\text{cm/GW}) = (3{\cdot}1 \pm 0{\cdot}5) \times 10^3 \sqrt{E_p} F_2(2\hbar\omega/E_g) n^{-2} E_g^{-3}, \tag{1}$$

where n is the refractive index, E_g is the band-gap energy and $F_2(x) = (x-1)^{3/2}/x^5$ [7]. E_p is nearly constant (21 eV) for the materials studied and is given by $E_p = 2P^2m/\hbar^2$, where P is the Kane momentum parameter and m is the electron mass [8]. This relation holds for the semiconductors studied except for ZnTe where two photons couple states only 3 per cent above the band edge. Here it is expected that exciton effects might be important and indeed the measured value of β_2 is considerably larger than predicted by equation (1) [6, 9]. Note that ZnTe was also studied by Bechtel and Smith with a similarly large result for β_2 [3]. In addition, as $2\hbar\omega/E_g$ approaches unity, the allowed–forbidden transitions upon which equation (1) is based become small (as evidenced by F_2) and eventually this leads to allowed–allowed transitions becoming dominant [1, 4].

The table shows the materials studied, the measured values of β_2 and the β_2 determined by equation (1) along with E_g, n and E_p. Figure 2 shows the data and

Materials studied, materials parameters and two-photon absorption coefficients.

Material	Form[a]	E_g (eV)	n	E_p (eV)[b]	β_2^{exp} (cm GW^{-1})	β_2^{theor} (cm GW^{-1})
($\lambda = 1{\cdot}06\ \mu$m,	$2\hbar\omega = 2{\cdot}3$ eV)					
GaAs[c]	Z	1·42[i]	3·43[i]	25·7	23	19·7
CdTe[d]	Z	1·44[e]	2·84[e]	20·7	22	25·1
CdTe[d]	Z_p	1·44[e]	2·84[e]	20·7	15	25·1
CdSe[e]	W	1·74[j]	2·56[e]	21	18	18·6
$CdS_{0{\cdot}25}Se_{0{\cdot}75}$[e]	W	1·78[k]	2·51[k]	21	15	17·7
$CdS_{0{\cdot}5}Se_{0{\cdot}5}$[e]	W	1·93[k]	2·45[k]	21	10	12·1
ZnTe[e]	Z	2·26[i]	2·79[e]	19·1	4·5	0·89
($\lambda = 0{\cdot}53\ \mu$m,	$2\hbar\omega = 4{\cdot}68$ eV)					
CdS[e]	W	2·42[e]	2·60[i]	21	5·5	4·87
ZnSe[f]	Z_p	2·67[i]	2·70[i]	24·2	5·5	4·27
ZnO[g]	W	3·2[m]	2·05[i]	21	5·0	4·77
ZnS[h]	Z_p (clear)	3·66[i]	2·40[i]	20·4	2·0	2·10
ZnS[h]	Z_p (yellow)	3·66[i]	2·40[i]	20·4	3·5	2·10

(*a*) Z = zincblende, W = wurtzite, p = polycrystalline; (*b*) values taken from [28] (for values not listed in this reference the value of 21 eV was assumed); (*c*) Morgan Semiconductors, Garland, Texas; (*d*) II–VI Inc., Saxonburg Pennsylvania; (*e*) Cleveland Crystals, Euclid, Ohio; (*f*) Raytheon Co., Bedford, Massachusetts; (*g*) Atomergic Chemetals, Plainview, New York; (*h*) CVD Inc., Woburn, Massachusetts; (*i*) [12]; (*j*) [13]; (*k*) values obtained by extrapolation as a function of composition between the known values for CdSe and CdS, see [14]; (*m*) [15].

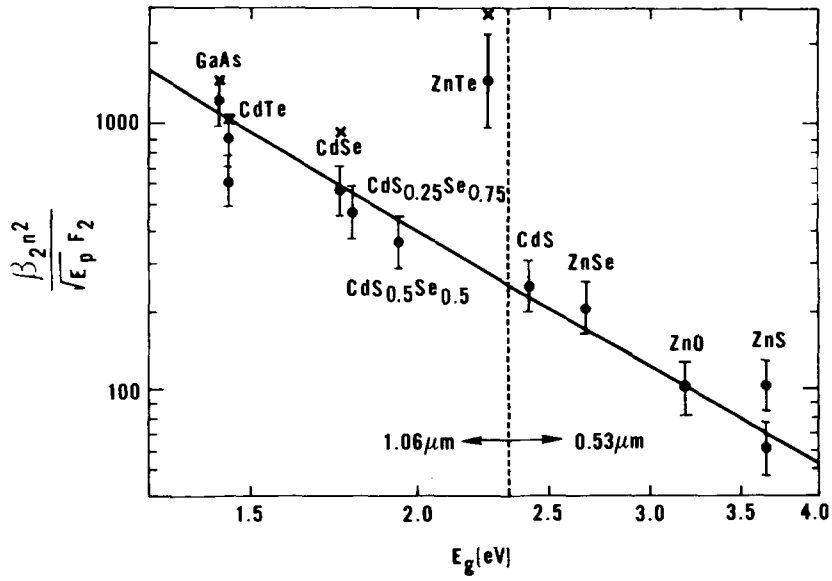

Figure 2. A log–plot of the scaled two-photon absorption coefficient versus bandgap energy. The solid line is given by equation (1) and has slope −3. The × are data from [3].

equation (1) plotted to emphasize the E_g^{-3} dependence of β_2. The value of the constant $3{\cdot}1 \times 10^3$ was determined by performing a least-squares fit of the data, excluding ZnTe, to the parametric dependence of equation (1). This constant is approximately a factor of 1·7 lower than the value predicted from the simple two-band model that led to the parametric dependence of equation (1) [6]. If a more sophisticated band structure, including the split-off bands and band non-parabolicity, is included the absolute values are on average within 26 per cent of the calculated values. The parametric dependencies, however, remain unchanged and F_2 changes only slightly, although the algebraic expression for F_2 becomes quite complicated [6].

The agreement with theory is remarkable in light of previous results, especially when it is noted that the samples are different semiconductors having different structures. It shows that while the true band structure is quite complex, the intermediate states that are most important can be accurately modelled with a simple band structure. In fact the two-band model predictions (see equation (1)) are quite adequate [4]. This is a very fortuitous result since it means that refinements in band structure do not lead to large changes in β_2, nor to changes in scaling. This observation is in marked contrast to the statements of a recent review article on multiphoton absorption (MPA) which concluded that 'the results of simple analytical models are generally inaccurate and unreliable, because of their incompleteness by not fully taking into account all the parameters that influence the MPA coefficients' [1]. It is also interesting to note that the non-perturbative approach to multiphoton absorption gives the same scaling law as equation (1) in the limit of small two-photon absorption [10]. Actually, it has been shown by Wherrett, who uses among other methods a dimensional analysis approach [4], that this must be true for any theory of two-photon absorption.

The reasons for the extreme spread in previous results as exemplified by the data of figure 1 are primarily experimental. The downward trend shows the improvement in experimental method and interpretation. Early work was plagued by the multimode nature of lasers in both space and frequency, which result in large variations in irradiance and which will always yield an underestimate of the irradiance when not resolved. This in turn leads to an overestimate of β_2. An additional problem is that most researchers have used pulses of several nanoseconds duration where the two-photon-generated carrier absorption can actually dominate the overall absorption. This again will result in an overestimate of β_2. The use of much shorter pulses which allows higher irradiance with lower energy, reduces the relative contribution of photo-generated carrier absorption with respect to two-photon absorption to a negligible ratio. One clear conclusion for future experiments is that short pulses are preferable, if not required, to obtain accurate values of β_2; this is the opposite of the conclusion drawn in [1]. Fears of self-induced transparency or other coherent effects expressed by these authors are not founded for picosecond pulses which are much longer than electron transverse relaxation times in these semiconductors [11].

Another possible experimental problem is the large self-defocusing observed in these samples. Even when the absorption of the photo-generated carriers is kept small by using picosecond pulses, the change in refractive index caused by them can be large [12]. Additionally, even if the defocusing within the sample is negligible, free-space propagation to the detector can change the energy distribution on the detector and even result in energy missing the detector [7, 2]. We show in figure 2 the

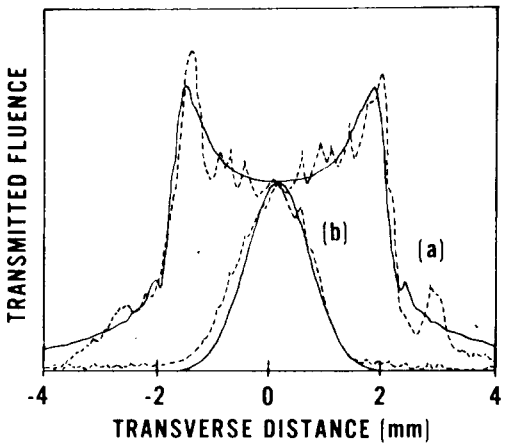

Figure 3. Vidicon scan through the centre of the beam transmitted through the CdSe sample at an irradiance of (*a*) 1 GW cm^{-2}, (*b*) 0·3 GW cm^{-2} at a distance of 0·5 m behind the sample. The pulsewidth used was 92 ps FWHM. The beam profiles are normalized to have the same on-axis fluence. The dashed line is experimental and the solid line the theoretical fit.

transmitted spatial fluence distribution as displayed on a vidicon used in a region of linear response (equivalent to a pinhole scan) for two different input irradiance levels. The theoretical fit (figure 2) assumes that the nonlinearity is completely accounted for by an index change proportional to the carrier density produced by the previously determined value of β_2 [28]. This represents a single parameter fit for the index change per carrier. The result gives an index change of $\sim 3{\cdot}5 \pm 1$ times the Drude contribution, which may be explained by band blocking from interband transitions [29].

Given the above experimental considerations, we used well-characterized collimated TEM_{00}, nearly transform-limited picosecond pulses, thin samples (2–5 mm) and large-area uniform-response detectors. The transmission detector was in turn placed directly behind the sample.

In conclusion, we have verified experimentally the scaling rule predicted by theory for two-photon absorption in semiconductors giving us a predictive capability. For example, if we extend our result to two-photon absorption in InSb at 10·6 μm at 300 K, we obtain a value of $\beta_2 = 6{\cdot}8$ cm MW^{-1}. This value is in excellent agreement with the value of 8 cm MW^{-1} using an analysis in which photo-generated carriers were carefully accounted for [30]. We have also explained the mechanism responsible for the observed self-defocusing, namely the photo-generated carriers. Combinations of two-photon absorption and self-refraction have uses for nonlinear optical elements such as optical power limiters [2].

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