Nondegenerate Optical Kerr Effect in Semiconductors

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***Abstract*— We calculate the nondegenerate bound electronic nonlinear refractive index $n_2(\omega_1;\omega_2)$ (i.e., an index change at frequency ω_1 due to the presence of a beam at frequency ω_2) in semiconductors. We calculate this nonlinearity and its dispersion using a Kramers–Kronig transformation on the calculated nondegenerate nonlinear absorption spectrum due to two-photon absorption, electronic Raman and optical Stark effects. The calculated n_2 values and their dispersion are compared to new experimental values for ZnSe and ZnS obtained using a 2-color Z-scan.**

I. Introduction

LIGHT-INDUCED changes in the optical properties of semiconductors have several applications including all optical switching [1]. The ultrafast optical Kerr effect (bound-electronic nonlinear refraction), leading to self-phase modulation and self-lensing of laser beams in solids, has been studied extensively [2]–[4]. Recently, we presented a simple yet comprehensive theory for this nonlinear refractive index n_2 in semiconductors [5], [6]. The theory used a Kramers–Kronig (KK) transformation to derive n_2 from our calculated nonlinear absorption spectrum. The key features of this theory were the band-gap scaling and the dispersion of n_2 which showed excellent agreement with a large number of experimental data for the degenerate case. Here, we derive a more general expression that gives the nondegenerate optical Kerr effect, namely, the change of refractive index at a frequency ω_1 due to the presence of a strong excitation beam at frequency ω_2. We define the nondegenerate coefficient n_2 as well as the nondegenerate nonlinear absorption coefficient α_2 by

$$\Delta n(\omega_1;\omega_2) = 2n_2(\omega_1;\omega_2)I_{\omega_2} \tag{1a}$$

and

$$\Delta \alpha(\omega_1;\omega_2) = 2\alpha_2(\omega_1;\omega_2)I_{\omega_2} \tag{1b}$$

where Δn and $\Delta\alpha$ are the changes in refractive index and absorption coefficient respectively, and I_{ω_2} is the irradiance of the excitation beam at frequency ω_2. The factor of two in these expressions arises from the interference between the pump and the probe beams. In a self-modulation (single-beam) process this factor is unity [7]. The nondegenerate nonlinear coefficients n_2 and α_2 are related to the real and imaginary components of the third order optical succeptibility $\chi^{(3)}(\omega_1,\omega_2,-\omega_2)$, respectively. We showed that the physical mechanisms responsible for the induced change of absorption ($\Delta\alpha$) originated from three processes: two-photon absorption (2PA), electronic Raman, and optical Stark effect [5]. In the following section, we briefly review the formalism leading to an expression for the degenerate n_2 and then present the extension of this theory to the nondegenerate case. In Section III, we present experimental results for ZnSe and ZnS obtained using a 2-color Z-scan [7]. In Section IV, possible effects of the electron–hole Coulomb interaction are considered using a simple Elliott-type envelope function. This simple approximation can qualitatively explain the two-photon and one-photon resonant enhancement of n_2 observed in semiconductors.

II. Theory

The nonlinear Kramers–Kronig relations relate n_2 and α_2 through the dispersion integral [4], [5], [8]

$$n_2(\omega_1;\omega_2) = \frac{2}{\pi}\int_0^\infty \frac{\alpha_2(\omega';\omega_2)}{\omega'^2-\omega_1^2}d\omega'. \tag{2}$$

In [5], $\Delta\alpha(\omega';\omega_2)$ was calculated using a two-parabolic band (TPB) model. In this model a "dressed state" approach is adopted where the wave functions for the initial (valence) and the final (conduction) bands are given as follows:

$$\Psi_j(\boldsymbol{k},\boldsymbol{r},t) = u_j(\boldsymbol{k},\boldsymbol{r})\exp\left[i\boldsymbol{k}\cdot\boldsymbol{r} - \frac{i}{\hbar}\int_0^t E_{\mathrm{j}}(\tau)\,d\tau\right] \tag{3}$$

where j refers to either conduction (c) or valence (v) band and $\boldsymbol{k}$ is the lattice wavevector. The functions u_{j} are the usual (unperturbed) Bloch wavefunctions that have the same periodicity as the lattice. The effects of the optical fields are to alter the energy of the electrons and holes in the final and initial states, respectively. This is written as

$$E_{\mathrm{v}}(\tau) = E_{\mathrm{v0}} + \Delta E_{\mathrm{vv}}(\tau) + \Delta E_{\mathrm{vc}} \tag{4a}$$

$$E_{\mathrm{c}}(\tau) = E_{\mathrm{c0}} + \Delta E_{\mathrm{cc}}(\tau) + \Delta E_{\mathrm{cv}} \tag{4b}$$

where E_{j0} is the unperturbed band energy. $\Delta E_{\mathrm{jj}}(\tau)$ and ΔE_{cv} are the linear (LSE) and quadratic (QSE) optical Stark shifts of the energy bands due to the interaction Hamiltonian as follows:

$$H_{\mathrm{int}} = \frac{e}{m_0c}\boldsymbol{p}\cdot[\boldsymbol{A}_{01}\cos(\omega_1 t) + \boldsymbol{A}_{02}\cos(\omega_2 t)] \tag{5}$$

where $\boldsymbol{p}$ is the momentum operator. $\boldsymbol{A}_{01}$ and $\boldsymbol{A}_{02}$ are the vector potentials of the interacting optical fields. The resultant

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TABLE I
THE VARIOUS CONTRIBUTIONS TO THE NONLINEAR ABSORPTION SPECTRAL FUNCTION $F_2(x_1; x_2)$

Contribution	$F_2(x_1; x_2)$
2-Photon Absorption	$\frac{(x_1+x_2-1)^{3/2}}{2^7 x_1 x_2^2}\left(\frac{1}{x_1}+\frac{1}{x_2}\right)^2$ for $x_1 + x_2 > 1$
Raman	$\frac{(x_1-x_2-1)^{3/2}}{2^7 x_1 x_2^2}\left(\frac{1}{x_1}-\frac{1}{x_2}\right)^2$ for $x_1 - x_2 > 1$
Linear Stark	$-\frac{(x_1-1)^{3/2}}{2^6 x_1 x_2^2}\frac{1}{x_2^2}$ for $x_1 > 1$
Quadratic Stark	$-\frac{1}{2^{10} x_1 x_2^2 (x_1-1)^{1/2}}\left(\frac{1}{x_1-x_2}+\frac{1}{x_1+x_2}-\frac{2(x_1-1)}{(x_1-x_2)^2}-\frac{2(x_1-1)}{(x_1+x_2)^2}\right)$ for $x_1 > 1$

interband absorption change, as calculated using first-order perturbation theory, is given by [5]:

$$\alpha_2(\omega_1;\omega_2) = K\frac{\sqrt{E_{\rm p}}}{n_{01}n_{02}E_{\rm g}^3}F_2(x_1;x_2) \tag{6}$$

where K is a constant, $E_{\rm g}(eV)$ is the band-gap energy, and $x_1 = \hbar\omega_1/E_g, x_2 = \hbar\omega_2/E_{\rm g}$ and $n_{0{\rm j}}\,(j = 1, 2)$ are the linear refractive indices at ω_1 and ω_2, respectively. The dimensionless spectral function F_2, is defined in Table I. The Kane energy $E_{\rm p}\,(\simeq 21\,eV)$ is related to the Kane momentum parameter P by $E_{\rm p} = 2P^2/m\hbar^2$, and is nearly material independent for most semiconductors [9]. In the TPB approximation, this parameter is related to the electron (or hole) effective mass $m_{\rm c}\,(= m_{\rm v})$ through

$$m_{\rm c}/m_0 \simeq E_{\rm g}/E_{\rm p}. \tag{7}$$

The constant K was determined from the average degenerate 2PA coefficient of several semiconductors to be $\simeq 3100\,cmGW^{-1}eV^{5/2}$, but varied by up to $\simeq 30\%$ from one material to the next [9]. A value for K of $\simeq 4000$ gives a better value for ZnSe and ZnS as compared to the calculated value of $1940\,cmGW^{-1}eV^{5/2}$ from the TPB model [5]. This factor of $\simeq 2$ in underestimating the absolute value of β may be simply understood by realizing that the transition can initiate from two valence bands (heavy- and light-hole bands) rather than one as modeled here. More rigorously, a Kane 4-band model has been shown to give a closer absolute agreement for several zinc-blend semiconductors [10].

The dimensionless spectral function F_2, shown in Table I, contains contributions from 2PA when $\hbar\omega_1 + \hbar\omega_2 > E_{\rm g}$, the stimulated Raman effect when $\hbar\omega_1 - \hbar\omega_2 > E_{\rm g}$ and optical Stark effect when $\hbar\omega_1 > E_{\rm g}$ [5]. The nondegenerate 2PA coefficient $\beta(\omega_1;\omega_2)$ is defined as equal to α_2 when $\hbar\omega_1 + \hbar\omega_2 > E_{\rm g}$ (i.e., contains only the 2PA portion of F_2). Note also that there are four terms associated with the quadratic optical Stark effect in Table I. The first two terms represent the repulsion of the bands which reduces the density of states in the vicinity of $\boldsymbol{k} = 0$. The last two terms, on the other hand, arise from the conservation of total number of states and would lead to an increase in density of states at $\boldsymbol{k} > 0$ (i.e., removing states near $\boldsymbol{k} = 0$ adds states at larger $\boldsymbol{k}$). These terms, which contribute less than 10% to the degenerate $n_2(\omega)$ for $\hbar\omega_1/E_{\rm g} < 0.95$, were ignored in [5] but are included here for the nondegenerate $n_2(\omega_1;\omega_2)$. As $\hbar\omega/E_{\rm g} \rightarrow 1$, the contribution to n_2 from the QSE is reduced significantly if these two terms are included.

It must be emphasized that we consider here only below resonance excitation ($\hbar\omega_2 < E_{\rm g}$). For $\hbar\omega_2 > E_{\rm g}$, in addition to the expressions given in Table I, a term accounting for the stimulated Raman gain of the probe beam when $\hbar\omega_2 - \hbar\omega_1 > E_{\rm g}$ must be included. In practice, however, above band-gap resonance excitation leads to well known carrier effects (e.g., band-filling) that mask the bound electronic contributions. Above band-gap ultrafast bound-electronic nonlinearities have, nevertheless, been observed in semiconductor laser amplifiers when operating near the transparency point where changes in carrier populations are negligible [11]. Theoretical analysis of active semiconductors has been presented elsewhere [12].

In calculating $\Delta\alpha(\omega_1;\omega_2)$, it has been assumed that the two interacting beams have the same linear polarization. In general, one may assume that the two optical fields have arbitrary polarizations. For instance, consider two linearly polarized light beams with a fixed relative angle ϕ between their polarizations. If we assume that the valence band couples isotropically to all the $\boldsymbol{k}$ states in the conduction band, we obtain a polarization dependent prefactor

$$K(\phi) = K(1 - \tfrac{2}{3}\sin^2\phi). \tag{8}$$

The primary assumption leading to this symmetry property is that the electron quasimomentum $\hbar\boldsymbol{k}$ is parallel in $\boldsymbol{k}$ space to the interband momentum matrix element $\boldsymbol{p_{cv}}$ [5]. From Kane's $\boldsymbol{k}\cdot\boldsymbol{p}$ theory, this is characteristic of the transitions that initiate from the light-hole valence band [13]. The $\boldsymbol{p_{cv}}$ associated with the heavy-hole to conduction band transition, on the other hand, is effectively perpendicular to $\boldsymbol{k}$, leading to a more complex polarization dependence that varies with wavelength and is different for each mechanism [14]. In this paper, however, we focus our attention on the dispersion of the nondegenerate n_2, and the details of the symmetry properties

TABLE II

THE NONDEGENERATE DISPERSION FUNCTION $G_2(x_1;x_2)$ OF (10) FOR THE ELECTRONIC KERR COEFFICIENT n_2, CALCULATED BY A KK TRANSFORMATION OF F_2 (TABLE I). THE IR DIVEGENT TERMS ASSOCIATED WITH EACH CONTRIBUTION HAVE BEEN REMOVED . NOTE THAT THE TERMS INVOLVING $(\cdots)^{3/2}$ ARE ZERO WHEN THE ARGUMENT $(\cdots)$ IS NEGATIVE. THE LAST TERM DUE TO THE DEGENERATE QSE IS THE LIMIT OF THE NONDEGENERATE $G_2^{\mathrm{QSE}}(x_1;x_2)$ AS $x_1 \to x_2$.

Contribution	$G_2(x_1;x_2)$
2-Photon Absorption	$H(x_1,x_2)+H(-x_1,x_2)$
Raman	$H(x_1,-x_2)+H(-x_1,-x_2)$ where $H(x_1,x_2)=\frac{1}{2^6x_2^4x_1^4}\Big[\frac{5}{16}x_2^3x_1^2+\frac{9}{8}x_1^2x_2^2-\frac{9}{4}x_1^2x_2-\frac{3}{4}x_2^3$ $+\frac{1}{2}(x_1^2+x_1^2)[1-(1-x_2)^{3/2}]+\frac{1}{2}(x_1+x_2)^2[(1-x_1-x_2)^{3/2}-(1-x_1)^{3/2}]$ $-\frac{3}{16}x_1^2x_2^2[(1-x_1)^{-1/2}+(1-x_2)^{-1/2}]+\frac{3}{2}x_1^2x_2(1-x_2)^{1/2}$ $+\frac{3}{4}x_2(x_1+x_2)^2(1-x_1)^{1/2}-\frac{3}{8}x_2^3x_1(1-x_1)^{-1/2}-\frac{1}{32}x_1^2x_2^3(1-x_1)^{-3/2}\Big]$
Quadratic Stark $x_1 \neq x_2$	$\frac{1}{2^9x_1^2x_2^2}\Big[-\frac{1}{2}-\frac{4}{x_1^2}+\frac{4}{x_2^2}-\frac{x_2^2}{x_1}\frac{[(1-x_1)^{-1/2}-(1+x_1)^{-1/2}]}{x_1^2-x_2^2}$ $+\frac{2x_1^2(3x_2^2-x_1^2)}{x_2^2(x_1^2-x_2^2)^2}[(1-x_2)^{1/2}+(1+x_2)^{1/2}]$ $-\frac{2x_2^2(3x_1^2-x_2^2)}{x_1^2(x_1^2-x_2^2)^2}[(1-x_1)^{1/2}+(1+x_1)^{1/2}]\Big]$
$x_1 = x_2$	$\frac{1}{2^9x_1^4}\left[\frac{3}{4}\frac{(1-x_1)^{-1/2}-(1+x_1)^{-1/2}}{x_1}-\frac{(1-x_1)^{-3/2}+(1+x_1)^{-3/2}}{8}-\frac{1}{2}\right]$

associated with a more general two-valence band system will be discussed in future

With $\alpha_2(\omega_1;\omega_2)$ known, we can obtain the refractive contribution $n_2(\omega_1;\omega_2)$ by applying the KK transformation ((2)). This yields

$$n_2(\omega_1;\omega_2)=\frac{\hbar cK}{2}\frac{\sqrt{E_{\mathrm{p}}}}{E_{\mathrm{g}}^4 n_{01}n_{02}}G_2(x_1;x_2). \tag{9}$$

In [5], the interference factor of two, as appears in (1a), was ignored in calculating the n_2 coefficient. In correction, the value of $K \simeq 6000$ gives a better fit to the degenerate n_2 data for semiconductors, although variations of a factor of $\simeq 2$ from one material to another occur. This difference of K values may be attributed to too simplistic a band structure employed in our model and/or electron–hole Coulomb interactions (excitons). The possible effects of excitons are discussed in Section IV.

Equation (9) is indentical to the expression obtained for the degenerate n_2 [5] except the dispersion function G_2 now has a general nondegenerate form determined by the KK integral

$$G_2(x_1;x_2)=\frac{2}{\pi}\int_0^\infty \frac{F_2(\xi;x_2)}{\xi^2-x_1^2}d\xi. \tag{10}$$

It was noted in [5] that as a result of using $\boldsymbol{A}\cdot\boldsymbol{p}$ perturbation theory, the calculated dispersion function G_2 diverges as $x_2 \to 0\,(\omega_2 \to 0)$. Using a power series expansion we identify the divergent terms of each individual contribution and find that the QSE term diverges as x_2^{-2} while the remaining contributions have divergent terms that vary as $x_2^{-1}, x_2^{-2}, x_2^{-3}$, and x_2^{-4}. Upon summing these contributions, however, all divergences cancel except for the x_2^{-2} term. In fact, the contribution of the linear Stark effect (third term in Table I) is only to cancel the x_2^{-4} divergent terms of the 2PA and Raman contributions. Due to their unphysical consequences, it has been a common practice to subtract the remaining divergent terms [15]. This process of divergence removal can be considered as effectively enforcing a sum rule for the two-band system. We obtain an analytical expression for G_2 by evaluating the KK integral of (10). The individual long wavelength divergent terms for each contribution are removed separately and the final result is given in Table II. In summing the 2PA and Raman contributions, all the odd terms in x_2, arising from the individual divergences, cancel. In this paper, we refer to G_2 as the sum of the three divergence-free functions given in Table II ($G_2 = G_2^{\mathrm{2PA}} + G_2^{\mathrm{RAM}} + G_2^{\mathrm{QSE}}$). Knowledge of the individual contribution from each one of the three mechanisms becomes important when considering the polarization dependence of n_2 or in polarization dependent four wave mixing [14].

Fig. 1 depicts the dispersion function G_2 as a function of $x_1 = \hbar\omega_1/E_{\mathrm{g}}$ for various excitation photon energies $x_2 = \hbar\omega_2/E_{\mathrm{g}}$. By examining the terms in Table II, we can determine their relative contributions to n_2 in different spectral

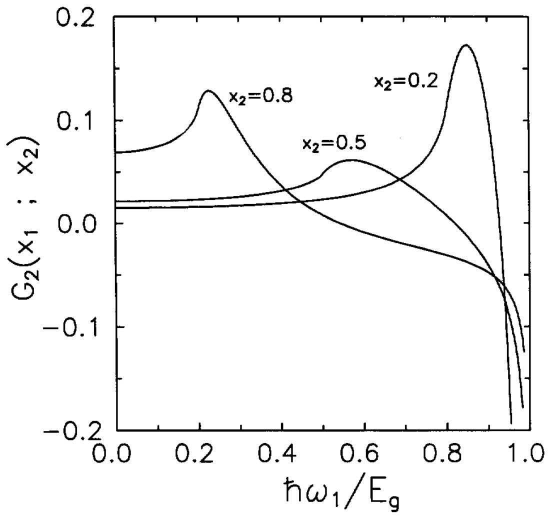

Fig. 1. The nondegenerate dispersion function $G_2(x_1 : x_2)$ as a function of probe photon energy (x_1), calculated for various pump photon energies (x_2).

regimes. A general trend is evident in all the curves: n_2 is nondispersive in the infrared regime ($\hbar\omega_1 \ll E_g - \hbar\omega_2$) where 2PA and Raman terms contribute equally, it reaches a two-photon resonance at $\hbar\omega_1 + \hbar\omega_2 \simeq E_g$ where it has its peak positive value, and above this two-photon resonance n_2 becomes anamolously dispersive and ultimately turns negative due mainly to 2PA and the optical Stark effect as $\hbar\omega_1$ approaches E_g.

III. Experiments

We use the 2-color Z-scan [7], [16] to measure the nondegenerate n_2 in ZnSe and ZnS. A Q-switched and modelocked Nd:YAG laser is used to generate single $t_p \simeq 83$ ps (FWHM) pulses at $\lambda = 1.06\,\mu$m as the excitation beam. Simultaneously, the second-harmonic of the same laser at $\lambda = 532$ nm serves as the weak probe ($t_p \simeq 58$ ps). Using this arrangment, we measure $n_2(2\omega;\omega)$ and $\beta(2\omega;\omega)$. At these wavelengths, the choice of the above materials is appropriate for examining the various dispersion regimes of n_2 as predicted by the theory. An important parameter in the experiment is the sum of the photon energies: $\hbar\omega_1 + \hbar\omega_2 \simeq 3.5$ eV. Since ZnSe has $E_g \simeq 2.6$ eV [17], it is a nondegenerate two-photon absorber at these wavelengths. ZnS, on the other hand, with $E_g \simeq 3.6$ eV [17] exhibits no nondegenerate 2PA. According to this theory however, it should exhibit a two-photon resonance enhanced positive n_2. The degenerate n_2 and 2PA coefficient (β) of ZnSe and ZnS have been studied in the past [5], [9], [16]. The measurements show good agreement with the degenerate limit of the TPB theory [5]. Table III summarizes the earlier results along with the new nondegenerate measurements.

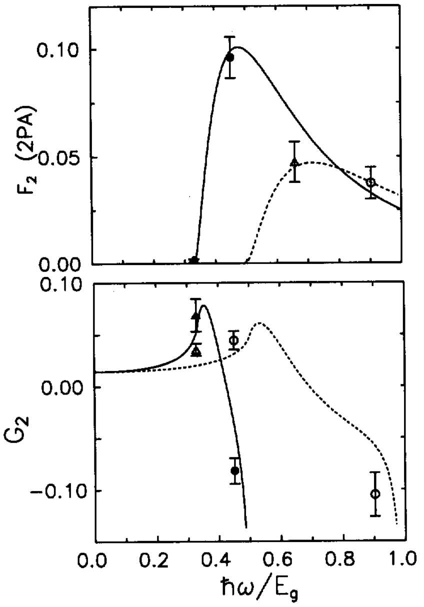

Fig. 2. (a) The measured degenerate $\beta(2\omega;2\omega)$ (open symbols) and nondegenerate $\beta(2\omega;\omega)$ (solid symbols) for ZnSe (circles) and ZnS (triangles) using laser pulses at frequency ω ($\lambda = 1064$ nm) and 2ω ($\lambda = 532$ nm). The data are scaled according to (6) to compare with the calculated $F_2(2x;x)$ (solid line) and $F_2(x;x)$ (dashed line) functions. (b) The corresponding measured n_2 values, scaled according to (9), to compare with the calculated $G_2(2x;x)$ (solid line) and $G_2(x;x)$ (dashed line) functions.

TABLE III
THE MEASURED 2PA COEFFICIENTS $\beta(2\omega;\omega), \beta(2\omega;\omega)$ AND OPTICAL KERR COEFFICIENTS $n_2(2\omega;\omega), n_2(2\omega;2\omega)$ FOR POLYCRYSTALLINE ZnSe AND ZnS SAMPLES USING A TWO-COLOR Z -SCAN TECHNIQUE. HERE, ω CORRESPONDS TO A WAVELENGTH OF 1.064 μm. THE UNITS FOR n_2 AND β ARE [10^{-14} cm^2/W] AND [10^{-9} cm/w], RESPECTIVELY. THE DEGENERATE DATA FOR ZnSe ARE FROM [16].

	Linear Index	Energy Gap	Degenerate				Nondegenerate	
			0.532 μm		1.06 μm		(0.532 μm, 1.06 μm)	
	n_0	E_g (eV)	n_2	β	n_2	β	n_2	β
ZnSe	2.7 (0.532 μm) 2.5 (1.06 μm)	2.6	−6.8	5.8	2.9	0	−5.1	15.3
ZnS	2.4 (0.532 μm) 2.3 (1.06 μm)	3.6	N.A.	3.4	0.76	0	1.5	<0.073

To illustrate the dispersive behavior of the measured n_2 and compare it with this theory, we consider the functions $G_2(2x;x)$ and $F_2^{2PA}(2x;x)$ (2PA contribution in Table I) where $x = \hbar\omega/E_g$ and ω corresponds to the fundamental of the Nd:YAG laser frequency. Figure 2 depicts these functions along with the degenerate versions $G_2(x;x)$ and $F_2^{2PA}(x;x)$. The measured data are scaled by the predicted band-gap dependence of E_g^{-3} for β and E_g^{-4} for n_2, where $K = 4000$ was used. The enhancement of the nondegenerate β in ZnSe is seen to agree with the TPB model. Though good qualitative agreement between experiment and theory is seen, the theory underestimates n_2 by a factor of $\simeq$1.5 when β is quantitatively correct. In other words, as mentioned earlier, degenerate and nondegenerate n_2 values can be fairly predicted by the theory provided that we use $K \simeq 6000$ in (9) for n_2. A discrepancy of $\simeq$1.5 is not surprising for such a simple theory, and it may be attributed to a more complex band structure than considered here and/or the neglect of the electron–hole Coulomb interaction. A simple treatment of the latter interaction based on the Elliott-Loudon approach, given in Section IV, can partially resolve this discrepancy.

For ZnSe, with ω corresponding to the fundamental wavelength of the Nd:YAG laser, $n_2(2\omega;\omega)$ is negative and resonantly enhanced due primarily to the effects of 2PA. As seen in Fig. 2(b), the degenerate n_2 of ZnSe at 532 nm is also negative while at 1.06 μm the dominant contribution of the 2PA resonance results in a positive n_2 [5], [17]. ZnS, on the other hand, has a positive and 2PA resonantly enhanced nondegenerate n_2 at these wavelengths as predicted by the theory.

IV. THE EFFECT OF EXCITONS

It might be expected that the electron–hole Coulomb interaction could lead to an enhancement of the 2PA coefficient near the $\hbar\omega_1+\hbar\omega_2 = E_g$ resonance. The TPB theory (without including this interaction) appears to underestimate the experimental degenerate 2PA coefficients when $2\hbar\omega/E_g$ is above but very near unity [9]. Analogous to the case of single photon (linear) absorption, 2PA excitonic enhancement should reflect the increase in the density of states near the band-edge ($\boldsymbol{k} \simeq 0$ region) where $\hbar\omega_1 + \hbar\omega_2 = E_g$. Additionally, this increased density of states will enhance the Raman and particularly the optical Start contributions near the fundamental absorption edge. Various approches have been taken previously to include this interaction in the perturbation theory of 2PA [18]. While a rigorous treatment can result in cumbersome calculations, approximate enhancement functions have been suggested as an alternative [19], [20]. In particular, Loudon [20] used an envelope function approach similar to that given by Elliott [21] for the interband one-photon absorption. For the continuum of excitons, this envelope function is given by the following [21]:

$$|U(\eta)|^2 = \frac{\pi\eta\exp(\pi\eta)}{\sinh(\pi\eta)} \tag{11}$$

where $\eta^2 = E_b/(\hbar\omega - E_g)$ with E_b denoting the excitonic binding energy. In Loudon's approach the energy denominator of η is replaced by the two-photon energy term $\hbar\omega_1+\hbar\omega_2-E_g$ in the nondegenerate case. In the "dressed state" framework, this can be interpreted as neglecting the excitonic effect on the energy shifts (4) but accounting for it in the transition rate between the "dressed states." Therefore, in generalizing this approximation, we multiply the function $F_2(x_1;x_2)$, in Table I, by the continuum exciton envelope function $|U(\eta)|^2$ where η is now given by

$$\eta^2 = \frac{E}{x_1 \pm x_2 - 1}. \tag{12}$$

Here $E_r = E_b/E_g$, and the $\pm$ sign in the denominator corresponds to 2PA(+) and Raman ($-$), while for the optical Stark effect the denominator in (12) becomes only $x_1 - 1$ (i.e., $x_2 = 0$). Thus, $|U(\eta)|$ directly gives the enhancement of α_2 which has maxima when the denominator of (12) becomes small (i.e., where $x_2 + x_1 = 1$ at the 2PA edge, and when x_1 approaches 1 for the optical Stark effect).

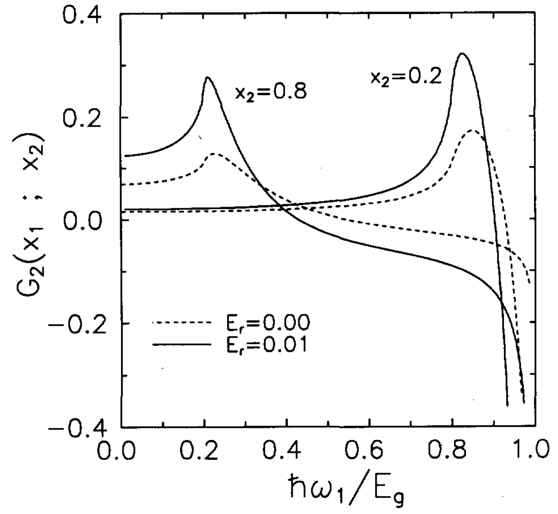

Fig. 3. The excitonic enhanced nondegenerate G_2 function (solid lines) compared to that of Fig. 1 (dashed lines). A typical value of $E_r = 0.01$ was used in the calculation.

In the TPB model and within the effective mass approximation as indicated by (7), $E_r = R/2E_p\epsilon_s^2$ where ϵ_s is the static dielectric constant and $R = 13.6$ eV is the Rydberg energy. Using $E_p \simeq 21$ eV, this gives $E_r \simeq 0.33/\epsilon_s^2$. For most semiconductors ϵ_s ranges from 5 to 10 leading to $E_r \simeq 0.013$ to 0.003. ZnSe and ZnS, for instance, have an E_r of 0.008 and 0.010, respectively [9].

Once the exciton-enhanced nonlinear absorption α_2 is determined, the refractive component can be obtained using the KK integral. This integral and its infrared divergent term can be numerically evaluated. In Fig. 3, the calculated result for the nondegenerate $n_2(\omega_1;\omega_2)$ using a typical value of $E_r \simeq 0.01$ is compared to the case $E_r = 0$ (i.e., no exciton enhancement). As expected, the enhancement is most visible near the one and two-photon transition resonances. The most drastic change is seen near the band-edge ($\hbar\omega_1 \simeq E_g$) where the contribution of the QSE becomes large. This is more clearly examined in Fig. 4 where the effects of excitons on each of the three contributions are plotted individually.[1] It is seen that the QSE contribution has the largest enhancement near the band-edge resonance.

Using $E_r = 0.008$, as shown in Figs. 5(a) and 5(b), we compare the excitonic enhanced F_2 and G_2 functions with the data of Fig. 2. Now using $K = 2600$ for both β and n_2, excellent agreement between theory and experiment is achieved. Additionally, this value for K is closer to the calculated value of $\simeq$1940 [5]. Moreover, the predicted band-edge resonant ($\hbar\omega_1/E_g \simeq 1$) enhancement is now in agreement with experiments, as the theory, without the excitonic effect, underestimated n_2 for AlGaAs [22] and CdS [5] at wavelengths near the band.

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[1] The nonenhanced G_2 in our Fig. 4 (dotted line) is the corrected version of Fig. 4 in [5], in which the long-wavelength divergences of the individual contributions were removed incorrectly, thus suppressing the bandgap resonance of the electronic Raman effect.

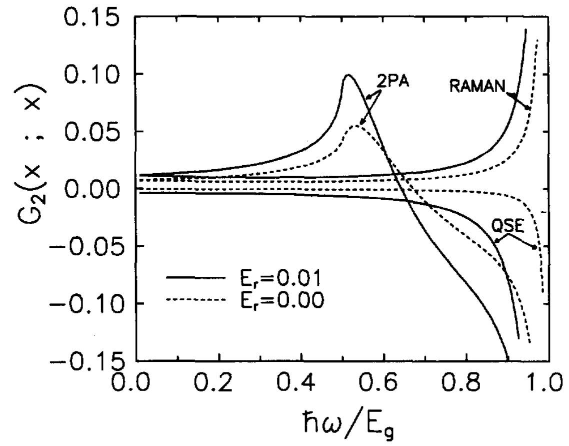

Fig. 4. The effect of excitonic enhancement on the various contributing mechanisms to the degenerate $G_2(x_1;x_1)$ compared to the nonenhanced G_2 as given by Table II.

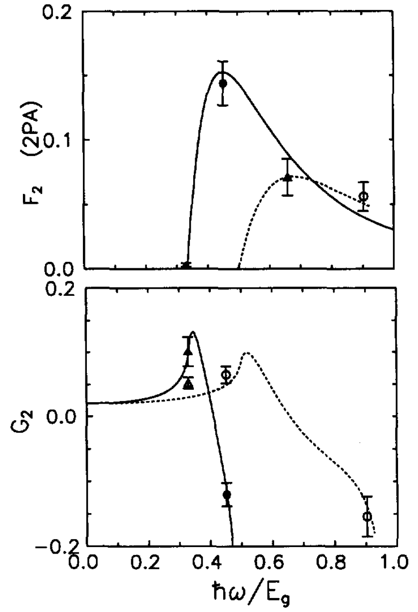

Fig. 5. Data for both (a) and (b) are the same as in Fig. 2 but scaled with $K = 2600$. The lines in (a) and (b) are the F_2 and G_2 functions calculated using the excitonic enhancement with $E_r = 0.008$.

V. CONCLUSION

The nondegenerate 2PA coefficient $\beta(\omega_1;\omega_2)$ and optical Kerr index $n_2(\omega_1;\omega_2)$ were calculated using a *dressed-state* two-parabolic band model. Closed-form analytical expressions were derived giving the variation of these coefficients with bandgap energy, linear index, and photon energy. The experimental results for ZnSe and ZnS show good agreement with this theory for ω_2 and ω_1, the fundamental and second harmonic of the Nd:YAG laser, respectively. Finally, the possible effect of electron–hole Coulomb interaction is considered using an Elliott-type envelope function. This approximation leads to an enhancement of n_2, which is largest near the two-photon and one-photon resonances.

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J. Wang, photograph and biography not available at the time of publication.

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