Dispersion of Bound Electronic Nonlinear Refraction in Solids

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Abstract—A two-band model is used to calculate the scaling and spectrum of the nondegenerate nonlinear absorption $\Delta \alpha(\omega_1; \omega_2)$. From this, the bound electronic nonlinear refractive index $n_2$ is obtained using a Kramers–Krönig transformation. We include the effects of two-photon and Raman transitions and the ac Stark shift (virtual band blocking). The theoretical calculation for $n_2$ shows excellent agreement with measured values for a five order of magnitude variation in the modulus of $n_2$ in semiconductors and wide-gap optical solids. We also present new measurements of $n_2$ in semiconductors using the Z-scan method. The observed change of sign of $n_2$ midway between the two-photon absorption edge and the fundamental absorption edge is also predicted. Thus, we now have a comprehensive theory that allows a determination of $n_2$ at wavelengths beneath the band edge, given only the bandgap energy and the linear index of refraction. Such information is useful for a variety of applications including optical limiting, laser-induced damage, and all-optical switching. Some consequences for all-optical switching are discussed, and a wavelength criterion for the observation of switching is derived.

I. INTRODUCTION

RECENTLY we reported measurements of the nonlinear refractive index $n_2$ of a variety of solids using beam distortion methods (Z-scan technique) [1], [2] and four-wave mixing [3]. These data show a strong systematic dispersion of the bound electronic nonlinearity (electronic Kerr effect $n_2$) near the two-photon absorption (2PA) edge. This eventually turns from positive to negative at higher frequencies. We found that by using a Kramers–Krönig (KK) integral based on the degenerate 2PA spectrum as predicted by a two-parabolic band model, we could predict the observed universal dispersion, scaling, and values of $n_2$ that range over four orders of magnitude and change sign [2]. This KK analysis relates the real and imaginary parts of the third-order susceptibility. The resulting scaling rule correctly predicted the value of $n_2$ for the 26 different materials we had examined at that time, except very near the gap where there was a systematic departure of the data from the theory towards larger negative $n_2$ values. More recent data taken at wavelengths closer to the gap show an even larger departure from the predictions of the 2PA model. We had speculated in [2] that the bandgap resonant ac Stark effect might make $|n_2|$ larger near the gap. Here, we present a model that includes the ac Stark effect and the electronic Raman effect, as well as 2PA. Indeed, the inclusion of these new effects does explain the large negative increase in $n_2$ near the gap.

There are two distinct frequency regimes for nonlinear optics in semiconductors which correspond to real and virtual excitation. Most studies have primarily concentrated on bandgap resonant effects which result in real excitation [4], [5]. The very large nonlinear effects observed are the saturation of interband and excitonic absorption due to photoexcited free carriers and excitons. Real excitations usually result in a reduction of the refractive index at frequencies of interest. In contrast, by exciting optical solids at frequencies much less than the gap, a considerably smaller, but faster, positive nonlinear refractive index $n_2$ due to bound electronic effects is observed [6]. This $n_2$ arises from the real part of the third-order susceptibility $\chi^{(3)}$, and is defined through the refractive index change $\Delta n$ where

$$\Delta n(\omega) = \gamma(\omega) I_0 = n_2(\omega) \frac{|E_0|^2}{2}$$

with $I_0$ and $E_0$ being the irradiance and electric field at frequency $\omega$, respectively, and $n_2 = \text{Re} \chi^{(3)}/n_0$. The linear refractive index is $n_0$, and $\gamma$ and $n_2$ are related by $n_2$ (esu) = $n_0 \gamma / 40\pi$ (SI) where $c$ is the speed of light. The magnitude and dispersion of $n_2$ is of interest because of its importance in applications such as nonlinear propagation in fibers, fast optical switching, self-focusing and damage in optical materials, and optical limiting in semiconductors [7]–[9].

Measurements of wide bandgap dielectrics show that $n_2 > 0$, which explains catastrophic self-focusing damage in such materials as NaCl and SiO$_2$ [8]. Our measurements in semiconductors below or near the 2PA edge ($\omega = E_0/2$) also show positive $n_2$. However, we found recently that for wavelengths substantially above the 2PA edge, $n_2$ is negative [1]. We performed measurements on

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a large number of other materials, including semiconductors and dielectrics, above and below the 2PA edge. As a result, we have been able to clearly demonstrate the dispersion of $n_2$.

Our measurements utilized a newly developed sensitive technique ($Z$ scan) [1], [10] that accurately determines the magnitude and sign of $n_2$, even in the presence of 2PA where it also gives the 2PA coefficient $\beta$. For example we found a negative $n_2$ in materials such as ZnSe at 0.523 $\mu$m where 2PA is present, and a positive $n_2$ at 1.064 $\mu$m where 2PA is absent. The values obtained for $\beta$ were in excellent agreement with our earlier measurements using standard transmission experiments [11]. We also performed picosecond degenerate four-wave mixing (DFWM) measurements which showed this third-order response to be fast (time resolution limited by the 30 ps pulsewidth). At wavelengths where 2PA was present, this fast third-order nonlinearity was dominant at low irradiance (e.g., up to 0.5 GW/cm$^2$ in ZnSe at 532 nm), while at higher irradiance, the slowly decaying 2PA-generated free-carrier refraction (self-defocusing) became important [3]. DFWM studies in other semiconductors and other wavelengths showed this to be a universal phenomenon [12].

It has previously been predicted that $\chi^{(3)}$ should vary as $E_g^4$ [13]. Using this scaling and the relation between $n_2$ and $\chi^{(3)}$ that includes the linear index $n_0$, we can remove the $E_g$ and $n_0$ dependencies from the experimental values of $n_2$ by multiplying them by $n_0 E_g^2$. In Fig. 1, a plot of our experimentally determined scaled values of $n_2$ as a function of $\hbar \omega / E_g$ is shown. We also divide the data by a constant $K'$ which we explain in what follows. We show, on the same plot, several data for large-gap optical crystals obtained from recent measurements by Adair et al. using a "nearly degenerate three-wave mixing" scheme [6]. Our own measurements of several of the same materials studied in [6] show excellent agreement. Assuming that there are no other relevant parameters unique to each material other than bandgap and index, this plot should be general to all optical solids. Upon examination of Fig. 1, we immediately see a trend giving small positive values for low ratios of photon energy to bandgap energy which slowly rises to a broad resonance peak at the 2PA edge and then decreases, eventually turning negative between the two-photon and single-photon absorption edges. We should note that the scaling with $E_g$ hides a variation in magnitude of $n_0$ of four orders of magnitude so that the observation of a universal dispersion curve as in Fig. 1 is quite remarkable. This dispersion curve is qualitatively similar to the dispersion of the linear index around the single-photon absorption edge [14]. As these linear quantities are related by causality via a KK relation, it seems logical to investigate whether the observed dispersion of $n_2$ can be calculated using a nonlinear KK relation between the real and imaginary parts of $\chi^{(3)}$. Indeed, as we showed in [2], making some reasonable assumptions, the observed tendencies as well as the absolute magnitudes of this dispersion are well predicted by such a calculation. The solid line in Fig. 1 as reproduced from [2] is the direct result of such a calculation, including only the degenerate 2PA contribution to the imaginary part of $\chi^{(3)}$. It should be noted that since the 2PA spectrum was previously determined [11], [13], [15], no additional fitting parameter was used in this calculation.

II. KRAMERS–KRONIG (KK) RELATION

Most theoretical calculations of $n_2$ have been confined to the zero-frequency limit [16]–[20]. Of these, semi-empirical formulations have been the most successful in predicting the magnitude of $n_2$ [19], [20]. For example, the formula obtained by Bolling, Glass, and Owyoung (BGO) in relating $n_2$ to the linear index ($n_0$) and the dispersion of $n_0$ in terms of the Abbe number has been successfully applied to a large class of transparent materials [6], [20]. Their theory predicts the low-frequency magnitude of $n_2$, but does not give the dispersion. The KK method predicts the dispersion as well as the magnitude of $n_2$. While the calculation presented in [2] only included 2PA in the imaginary part of $\chi^{(3)}$, the present calculation includes all other relevant contributions, that is, from electronic Raman and the ac Stark effect ("virtual band blocking"). We, however, do not include possible effects from excitonic enhancement [21].

Based on the principle of causality, KK relates the refractive index and the absorption coefficient for any linear material [22]:

$$n(\omega) - 1 = \frac{c}{\pi} \int_0^\infty \frac{\alpha(\omega')}{\omega'^2 - \omega^2} d\omega'.$$  \hspace{1cm} (2)

We now introduce some perturbation $\xi$ into the system, and consider the change in the refractive index resulting from the effect of $\xi$. The KK transformation states that a
change in the refractive index ($\Delta n$) at $\omega$ is associated with changes in the absorption coefficient ($\Delta \alpha$) throughout the spectrum ($\omega'$) and vice versa. We write this as

$$\Delta n(\omega; \xi) = \frac{c}{\pi} \int_{0}^{\infty} \Delta \alpha(\omega'; \xi) \frac{d\omega'}{\omega'^{2} - \omega^{2}}$$

where $\xi$ is a parameter (or parameters) denoting the "cause" of change in the absorption.

The cause need not be of optical origin, but of any external perturbation. For example, this method has been used to calculate the refractive index change resulting from an excited electron–hole plasma [23] and a thermal shift of the band edge [24]. For cases where an electron–hole plasma is injected, the consequent change of absorption gives the plasma contribution to the refractive index. In this case, the $\xi$ parameter is taken as the change in plasma density ($\Delta N$) regardless of the mechanism of generation of the plasma or the pump frequency. In the case of 2PA, the change is due to the presence of a pump field of frequency $\Omega$ (i.e., $\xi = \Omega$). The corresponding nonlinear refraction is $\Delta n(\omega; \Omega)$, which gives the index change at $\omega'$ due to the presence of light at $\Omega$. Although the calculation as illustrated above gives the nondegenerate nonlinear refraction, in most cases we would set $\Omega = \omega$ and consider self-refraction. This gives what is commonly referred to as $n_2$. Van Vechten and Aspnes [18] obtained the low-frequency limit of $n_2$ from a similar KK transformation of the Franz–Keldysh electroabsorption effect where, in this case, $\xi$ is the dc field. It is important to note that we must set $\Omega = \omega$ and not $\Omega = \omega'$, otherwise nonlinear KK relations do not apply as shown, for example, for the two-level atom [25]. The bound electronic contribution to $\chi^{(3)}$ can originate from various absorptive counterparts that are quadratic functions of the pump field. Effects of this order are 2PA, the electronic Raman effect, and the optical Stark effect.

An alternative way of considering the nonlinear Kramers–Krönig calculation is to examine the causality of the system. By treating the system as consisting of the material plus light, causality relations between the nonlinear polarization and additional light field give rise to relations between the real and imaginary parts of $\chi^{(3)}$ [26], [27] in an analogous way to the usual "linear" Kramers–Krönig relations. These resulting relations can be reexpressed in the form given above. One can therefore think of the nonlinear KK relations as being not on a bare material, but on a system consisting of the material and an optical pump.

In order to perform the KK calculation, it is necessary to know the nondegenerate absorption $\Delta \alpha(\omega, \Omega)$, which is the absorption of light at frequency $\omega$ when a light field of frequency $\Omega$ is applied to the material. This is necessary even if only self-refraction is desired. In what follows, we calculate the nondegenerate absorption originating from $\chi^{(3)}$, including the 2PA, ac Stark, and Raman contributions. The degenerate 2PA result, found by setting $\omega = \Omega$, will serve as a check against previous theoretical and experimental results.

Although nondegenerate nonlinear absorption is required for the correct calculation of $n_2$, an estimate can be obtained by substituting the degenerate 2PA at the mean frequency for the nondegenerate absorption:

$$\Delta \alpha(\omega; \omega') \rightarrow \beta \left( \frac{\omega + \omega'}{2} \right) I_{\omega}.$$  

This calculation was presented in [2]. We note that (4) provides a good estimate of $n_2$, except close to the band edge where the ac Stark contribution becomes large. This agreement reflects the fact that the denominator in the KK integrand (3) has the effect of strongly weighting frequencies close to $\omega'$, so for self-refraction, $\Delta \alpha(\omega; \omega')$ needs to be known accurately only for $\omega$ in the vicinity of $\omega'$. This approximation breaks down, however, when it is necessary to include divergent terms such as the ac Stark effect.

### III. Nonlinear Absorption Calculation

Two-photon absorption processes require that perturbation theory be taken to second order. A variation of this is to use first-order perturbation theory on "dressed" states for the conduction and valence bands where the effect of the accelerator (tunneling) of the electrons due to the oscillating electric field is already taken into account [28], [29]. In all of the following, we shall use the dipole approximation for the radiation interaction Hamiltonian:

$$\mathcal{H}_{int} = -\frac{e}{m_0 c} A \cdot p$$  

where $A$ is the magnetic vector potential, $p$ is the electron momentum operator, $-e$ is the electron charge, and $m_0$ is the free electron mass. We assume a two-beam interaction with both beams linearly polarized in the same direction, giving

$$A = \hat{a} [A_{01} \cos (\omega_1 t) + A_{02} \cos (\omega_2 t + \phi)]$$  

where $\hat{a}$ is the unit vector in the direction of the optical polarization. Following Keldysh [28], in the same manner as [29], [30], such a dressed state can be approximated by a Volkov-type wavefunction [31]:

$$\psi(k, r, t) = u_4(k, r) \exp \left[ \frac{i}{\hbar} \int_{0}^{t} E(\tau) \, d\tau \right]$$

where $i$ refers to either the conduction or valence band. $u_4(k, r)$ are the usual Bloch wavefunctions which have the same periodicity as the lattice. The effect of the optical field is to alter the energy of the electrons and holes in the final and initial states, respectively. Only the first- and second-order ac Stark shifting of the bands give rise to a $\chi^{(3)}$ effect:

$$E_c(\tau) = E_{c0} + \Delta E_{c}(\tau) + \Delta E_{cv}$$

$$E_v(\tau) = E_{v0} + \Delta E_{cv}(\tau) + \Delta E_{vc}$$
where, within the effective mass approximation,

\[ E_{c0} = E_g + \frac{\hbar^2 k^2}{2m_e c} \]  \quad (10)  

\[ E_{v0} = \frac{\hbar^2 k^2}{2m_v c} \]  \quad (11)  

\[ \Delta E_{ei}(r) = -\frac{e\hbar}{m_e c} k \cdot A(r) \]  \quad (12)  

where we have defined the hole mass \( m_v \), as being negative. \( \Delta E_{ei} \) and \( \Delta E_{ev} \) are the time-independent quadratic ac Stark shifts of the bands, which are proportional to \( |A_0|^2 \) and will be discussed in Section III-C. The transition rates will be calculated using an \( S \)-matrix formalism [32], with

\[ S = -\frac{i}{\hbar} \int_{-\infty}^{\infty} dt \int d^3r \psi^*_v(k', r, t) 3C_{vc} \psi_v(k, r, t). \]  \quad (13)  

The resulting \( S \)-matrix for these processes is

\[ S = \frac{e e \hat{a} \cdot \hat{p}_{vc}}{m_0 c} \delta_{kk'} \int_{-\infty}^{\infty} dt \]

\[ \cdot \exp \left[ i\omega_1 (\omega_1 t) + i\omega_2 (\omega_2 t + \phi) \right] \]

\[ \cdot \exp \left[ i\eta_1 \sin (\omega_1 t) + i\eta_2 \sin (\omega_2 t + \phi) \right] \]  \quad (14)  

where \( \hat{p}_{vc} \) is the interband momentum matrix element given by

\[ \hat{p}_{vc} = \frac{i}{\hbar} \int d^3r \hat{u}_v^*(k, r) \nabla \hat{u}_v(k, r). \]  \quad (15)  

We define

\[ \hbar \omega_{vc} = E_g - \Delta E_{vc} + \Delta E_{ev} + \frac{\hbar^2 k^2}{2m_v} \]  \quad (16)  

the reduced mass, by

\[ \frac{1}{m_{vc}} = \frac{1}{m_e} - \frac{1}{m_v} \]  \quad (17)  

and

\[ \eta_j = \frac{eA_0 k \cdot \hat{a}}{m_{vc} c \omega_j}. \]  \quad (18)  

In order to perform the time integral, we make use of the identity

\[ \exp \left[ i\eta \sin (\omega t) \right] = \sum_{n = -\infty}^{\infty} J_n(\eta) e^{i\omega nt}. \]  \quad (19)  

On substitution and performing the time integral, the \( S \) matrix becomes

\[ S = \frac{i \pi e \hat{a} \cdot \hat{p}_{vc}}{\hbar} \sum_{n = -\infty}^{\infty} J_n(\eta_1) J_n(\eta_2) \]

\[ \cdot \left\{ A_{01} \delta((m + 1) \omega_1 + n\omega_2 + \omega_{vc}) \right. \]

\[ + \delta((m - 1) \omega_1 + n\omega_2 + \omega_{vc}) \]

\[ + A_{02} \delta((m\omega_1 + (n + 1)\omega_2 + \omega_{vc}) \]

\[ + \delta((m\omega_1 + (n - 1)\omega_2 + \omega_{vc})). \]  \quad (20)  

A. Degenerate 2PA Calculation

The delta function terms in the above expression indicate various combinations of multiphoton absorption processes. From the \( S \)-matrix description, transition rates can be determined [32] which lead to absorption coefficients. We first consider 2PA at frequency \( \omega_1 \) in order to determine the scaling. Therefore, consider the terms arising from \( A_{02} = 0 \), \( m = -1 \), \( n = 0 \). Using the lowest order MacLaurin expansion term for the Bessel function \( J_n(x) = x^n/2^n n! \), and ignoring the quadratic Stark shift terms for now, the resulting change in the transition rate due to 2PA is

\[ \Delta W = \sum_{\text{spin}} \left[ \frac{\alpha^2}{(2\pi)^3} \frac{\pi e^2 A_{01}^2}{2m_v m_{vc} c^2 \omega_1} \right]^2 \left| \hat{a} \cdot \hat{p}_{vc} \right|^2 \]

\[ \cdot \left| k \cdot \hat{a} \right|^2 \frac{1}{2\pi} \delta \left( E_g + \frac{\hbar^2 k^2}{2m_{vc}} - 2\hbar \omega_1 \right). \]  \quad (21)  

A two-band model will be used in this paper for the calculation of transition rates, consisting of a conduction band and a valence band of opposite curvature (\( m_v = -m_e \)), each of which is doubly degenerate in spin. We will consider parabolic bands only. There is an angular dependence in \( k \) space for the \( | \hat{a} \cdot \hat{p}_{vc} |^2 \) and \( | k \cdot \hat{a} |^2 \) terms, which results in a factor of 1/5 when the angular integral is performed, assuming that \( p_{vc} \) is parallel to \( k \). For other cases, the resulting transition rate will have the same functional form and only differ by a numeric factor. For instance, in the Kane four-band model for the heavy-hole band, \( p_{vc} \) is perpendicular to \( k \) [33] and the numeric factor is 2/15.

Using the fact that \( A_{01} = 8\pi e I_J / n_2 \omega_J \) where \( I_J \) is the irradiance (cgs) and \( n_2 \) is the linear index, the result for the change in transition rate is

\[ \Delta W = \frac{2\pi}{S} \frac{e^4}{n_2^2 c^2} \frac{m_v^2}{m_0} \frac{P_{vc}^2}{\hbar} \frac{I_J^2}{(h\omega_1)^5} (2h\omega_1 - E_g)^{3/2} \]  \quad (22)  

from which the two-photon absorption rate can be determined; \( \beta(\omega) = 2h\omega \Delta W / \Omega^2 \). In order to obtain a universal scaling law, we make use of the identity

\[ \frac{P_{vc}^2}{m_0^2} = \frac{E_g}{2m_e}, \]  \quad (23)  

which is obtained using $k \cdot p$ theory [33]. The resulting expression for the 2PA has exactly the same scaling and frequency dependence as that calculated in [13], [15] using the second-order perturbation approach, namely,

$$\beta(\omega) = K \frac{\sqrt{E_p}}{n_0^2 E_s} F_2 \left( \frac{\hbar \omega}{E_s} \right)$$

(24)

where $E_p = 2 |p_{ic}|^2 / m_0$ and

$$F_2(x) = \frac{(2x - 1)^{3/2}}{(2x)^2}.$$  

(25)

Note that $\beta \propto \omega \text{Im} \chi^{(3)}/n_0$. The function $F_2$ is only a function of the ratio of the photon energy $\hbar \omega$ to $E_s$ (i.e., denoting the optically coupled states). The functional form of $F_2$ reflects the assumed band structure and the intermediate states considered in calculating the 2PA transition rate. $E_s$ is nearly material independent and possesses a value $E_s = 21$ eV for most direct gap semiconductors, and $K$ is a material-independent constant:

$$K = \frac{2^2 \pi^4 \varepsilon^4}{5 \sqrt{m_0 c^2}}$$

(26)

which has a value of $K = 1940$ in units such that $\beta$ is in cm/GW and $E_s$ and $E_p$ are in eV. A wealth of experimental and theoretical work regarding 2PA in semiconductors and crystalline materials exists. The best fit to the data of [11] using (24) and (25) gave $K = 3100$ in the same units as above, while Weiler's second-order perturbation calculation for a four-band model gave $K = 5200$ for parabolic bands neglecting any coulomb interaction [15]. When nonparabolicity was included, the predicted values of $\beta$ were on average only 26% higher than experiment; however, the frequency dependence of $\beta$ changed very little. Interestingly, (24) and (25) also give a fair estimate of $\beta$ for a number of transparent materials measured using the third and fourth harmonics of picosecond Nd:YAG laser pulses [34], [9]. In Fig. 2, $\beta$ scaled by $n_0^2/(K \sqrt{E_p} E_s)$ versus $E_s$ on a log–log plot is shown. The slope of the straight line is ~3, and it shows good agreement with the data for semiconductors and is within a factor of ~5, even for wide-gap dielectrics [9].

B. Nondegenerate 2PA and Raman Transitions

We now consider the case where one photon from each of $(\omega_1, \omega_2)$ is absorbed, i.e., terms which contain $\delta(\omega_{ic} - \omega_1 - \omega_2)$, $\delta(\omega_{ic} - \omega_1 + \omega_2)$, and $\delta(\omega_{ic} + \omega_1 - \omega_2)$ in (20). The first term corresponds to nondegenerate 2PA, whereas the second and third terms correspond to Raman transitions. On performing the integral over $k$ space, it can be shown that for 2PA, the change in the transition rate is given as

$$\Delta W = \sum_{\text{spin}} \left[ \frac{d^2 k}{(2\pi)^3} \right] \frac{\varepsilon^2}{2m_0 m_{ic} c^2} |\mathbf{p}_{ic}|^2 \left| k \cdot \mathbf{a} \right|^2$$

$$\cdot \left( \frac{1}{\omega_1} + \frac{1}{\omega_2} \right) \frac{1}{2\pi \hbar} \delta \left( E_s + \hbar^2 k^2 / 2m_{ic} - \hbar \omega_1 - \hbar \omega_2 \right)$$

$$= \frac{2^4 \pi \varepsilon^4}{5} \frac{m_{ic}^{1/2} |\mathbf{p}_{ic}|^2}{m_0^2} \frac{I_1 I_2}{(\hbar \omega_1^2 + \hbar \omega_2^2)}$$

$$\cdot \left( \frac{1}{\hbar \omega_1} + \frac{1}{\hbar \omega_2} \right)^2 (\hbar \omega_1 + \hbar \omega_2 - E_s)^{3/2}.$$  

(27)

Using this expression for the transition rate, a change in absorption of the $\omega_1$ beam due to the presence of $\omega_2$ is calculated to have the general form

$$\Delta \alpha(\omega_1; \omega_2) \rightarrow 2K \frac{\sqrt{E_p}}{n_1 n_2 E_s^2} F_2 \left( \frac{\hbar \omega_1}{E_s} ; \frac{\hbar \omega_2}{E_s} \right) I_2$$

(28)

where for nondegenerate 2PA, the $F_2$ function as obtained from (27) is given by

$$F_2^{2PA}(x_1; x_2) = \frac{(x_1 + x_2 - 1)^{3/2}}{2^7 x_1 x_2^2} \left( \frac{1}{x_1} + \frac{1}{x_2} \right)^2.$$  

(29)

Needless to say, $F_2^{2PA}$, and hence 2PA, is zero when $(x_1 + x_2 - 1) < 0$. 
In a similar manner, the Raman terms can be calculated to give a change in absorption as in (28) with

\[ F_2^{\text{RAM}}(x_1, x_2) = \frac{(x_1 - x_2 - 1)^{3/2} - (-x_1 + x_2 - 1)^{3/2}}{2^2x_1^2x_2^2} \cdot \left( \frac{1}{x_1} - \frac{1}{x_2} \right). \] (30)

The above expression contains the Raman transitions in which an electron is excited from the valence band into the conduction band via absorption of a photon at \( \hbar \omega_1 \) and emission of a photon at \( \hbar \omega_2 \) and vice versa. Therefore, the energy conservation terms corresponding to these transitions denoted by the \(( \cdots )^{3/2}\) terms in (30) are zero when their argument is negative.

The total \( \Delta \alpha(\omega_1; \omega_2) \) from these multiphoton processes is the sum of the 2PA and Raman terms. Note that 2PA turns on when the sum of the frequencies is equal to the bandgap, but the Raman term turns on when the difference of the frequencies is equal to the bandgap so that one frequency must exceed the bandgap.

C. Linear and Quadratic Stark Effects

In addition to multiphoton absorption processes which involve the absorption or emission of a photon from both light fields, there can be a change in the absorption coefficient due to a shift in bandgap as a result of the ac Stark effect. For example, a change in the linear absorption of \( \omega_1 \) occurs when the bands are shifted due to the ac Stark effect caused by \( \omega_2 \). Two terms arise out of this as the \( \lambda \cdot p \) radiation perturbation term couples 1) the conduction (or valence) band to itself, which we will term the linear Stark effect (LSE), and 2) the conduction band to the valence band, which we will term the quadratic Stark effect (QSE). In a physical sense, the effect of the LSE on the linear absorption is essentially a reduction of the oscillator strength by renormalizing the interband coupling due to the acceleration of the electrons (or holes) in their final dressed state. The QSE, on the other hand, alters the linear absorption through blue shifting the bandgap.

The linear Stark shift (self-coupling) can be obtained from the previous calculation by expanding the zero-order Bessel function to the next higher order term in (20), \( J_0(x) = 1 - x^2/4 \). This results in a modification to the S-matrix term which describes the one-photon absorption. The transition rate for the single-photon absorption of \( \omega_1 \) is then modified as

\[ W = \sum_{\text{spins}} \int \frac{d^3k}{(2\pi)^3} \left[ \frac{\epsilon \omega_1}{m_0 c} \right]^2 \left| \vec{a} \cdot \vec{p}_{\text{rec}} \right|^2 \left[ 1 - \left( \frac{\epsilon \omega_1}{2m_0 c\omega_2} \right)^2 \left| k \cdot \vec{a} \right|^2 \right] \frac{1}{2\pi\hbar} \delta \left( E_g + \frac{\hbar^2 k^2}{2m_{\text{rec}}} - \hbar \omega_1 \right). \] (31)

On performing this integral over \( k \) space and considering the term proportional to \( I_1I_2 \), the following is obtained for the change in the transition rate:

\[ \Delta W = -\frac{e^4}{5} \frac{m_{\text{rec}}^{3/2} |p_{\text{rec}}|^4}{n_1 n_2 c^2 m_0^2 (\hbar \omega_1)^3 (\hbar \omega_2)^3} \cdot (\hbar \omega_1 - E_g)^{3/2}. \] (32)

The resultant change of absorption \( \Delta \alpha \) can be given in terms of (28) with \( F_2^{\text{LSE}} \) given by

\[ F_2^{\text{LSE}}(x_1, x_2) = \frac{(x_1 - 1)^{3/2}}{2^2x_1^2x_2^2} \] (33)

where the scaling is the same as in (28).

The quadratic Stark shift resulting from the coupling between the conduction and valence bands due to \( \omega_2 \) is given by

\[ \Delta E_{\text{cv}} = -\Delta E_{\text{rec}} \]

\[ = \left( \frac{e \omega_2}{2m_0 c} \right)^2 \left( \left| \vec{a} \cdot \vec{p}_{\text{rec}} \right|^2 \left[ \left( E_g + \frac{\hbar^2 k^2}{2m_{\text{rec}}} - \hbar \omega_2 \right)^{-1} \right] + \left( E_g + \frac{\hbar^2 k^2}{2m_{\text{rec}}} + \hbar \omega_2 \right)^{-1} \right). \] (34)

It should be expected that in the low-frequency limit \( \hbar \omega_2 \ll E_g \), the energy shift due to the QSE as given by the above equations would approach the classical ponderomotive energy of the electron/hole in an oscillating electromagnetic field. This equivalence can indeed be simply verified by substituting \( |p_{\text{rec}}| \) from (23) into (34), which would yield

\[ \Delta E_{\text{e}} = -\Delta E_{\text{h}} = \frac{e^2 A_0^2}{4m_0 c^2}. \] (35)

This classical energy shift, which is also referred to as the "mass energy shift,"' has been used in previous "dressed state" (tunneling) calculations of the interband transition rate [28, 30].

Returning to the QSE energy shift, we note that this energy term is time independent (i.e., nonoscillating). Therefore, it only appears in the \( \delta \)-function energy conservation terms. Thus, the one-photon transition rate is modified to give

\[ W = \sum_{\text{spins}} \int \frac{d^3k}{(2\pi)^3} \left[ \frac{\epsilon \omega_1}{m_0 c} \right]^2 \left| \vec{a} \cdot \vec{p}_{\text{rec}} \right|^2 \left[ 1 - \left( \frac{\epsilon \omega_1}{2m_0 c\omega_2} \right)^2 \left| k \cdot \vec{a} \right|^2 \right] \frac{1}{2\pi\hbar} \delta \left( E_g + \frac{\hbar^2 k^2}{2m_{\text{rec}}} + \Delta E_{\text{cv}} - \hbar \omega_1 \right). \] (36)

On performing the integration and expanding to obtain the term proportional to \( I_1I_2 \), the change in the transition rate is given as

\[ \Delta W = -\frac{4\pi}{5} \frac{e^4}{n_1 n_2 c^2 m_0^2 (\hbar \omega_1)^3 (\hbar \omega_2)^3} \cdot (\hbar \omega_1 - E_g)^{-1/2} \frac{1}{(\hbar \omega_1 - \hbar \omega_2)} + \frac{1}{(\hbar \omega_1 + \hbar \omega_2)}. \] (37)
TABLE I

<table>
<thead>
<tr>
<th>Contribution</th>
<th>$F_2(x_1; x_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-Photon Absorption</td>
<td>$(x_1 + x_2 - 1)^{1/2} \left( \frac{1}{x_1} + \frac{1}{x_2} \right)$</td>
</tr>
<tr>
<td>Raman</td>
<td>$(x_1 - x_2 - 1)^{1/2} \left( \frac{1}{x_1} - \frac{1}{x_2} \right)$</td>
</tr>
<tr>
<td>Linear Stark</td>
<td>$-\frac{1}{2[x_1x_2^2(x_1 - x_2)]^{1/2}} \left[ \frac{1}{x_1 - x_2} + \frac{1}{x_1 + x_2} \right]$</td>
</tr>
<tr>
<td>Quadratic Stark</td>
<td>$-\frac{1}{2[x_1x_2^2(x_1 - x_2)]^{1/2}} \left[ \frac{1}{x_1 - x_2} + \frac{1}{x_1 + x_2} \right]$</td>
</tr>
</tbody>
</table>

RF excitation) and the resonant ac Stark effect is neglected.

IV. NONLINEAR REFRACTION

In general, we can evaluate the nondegenerate refractive index change $\Delta n(\omega; \Omega)$ as given by the Kramers-Kröning dispersion relation:

$$\Delta n(\omega; \Omega) = \frac{c}{\pi} \int_0^\infty \frac{\Delta \alpha(\omega'; \Omega)}{\omega'^2 - \omega^2} d\omega'. \quad (39)$$

However, there are few experiments which measure this quantity other than at $\Omega = \omega$. We therefore present in this paper only the calculated results for the degenerate $\Delta n(\omega; \omega)$ which, in turn, will lead to the Kerr coefficients $n_2$ or $\gamma$ as defined by (1):

$$\gamma = K \frac{hc}{n_2^2 E_x^4} G_2 \left(\frac{\hbar \omega}{E_x}\right) \quad (40)$$

where the dispersion function $G_2$ is given by

$$G_2(x_2) = 2 \int_0^\infty F_2(x_1; x_2) \frac{dx_1}{x_1^2 - x_2^2}. \quad (41)$$

We have neglected any dispersion in the linear refractive index $n_0$ in the integral. The magnitude of the dispersion is typically only 10% of the background refractive index around the band edge of semiconductors, so we do not anticipate any significant error. All that remains is for the above integral to be evaluated for the various contributions to the nondegenerate absorption $F_2(x_1; x_2)$. All of the integrals are performed in a similar manner and make use of the identity

$$\int_0^\infty \frac{x^{-\mu-1} dx}{(a + x^n)} = a^{\mu-n} \frac{\Gamma(\mu) \Gamma(n - \mu)}{\Gamma(n)} \quad (42)$$

for $n > \mu$. The individual contributions are given in Table II.

On examining the low-frequency limit, it is found that these terms diverge as $\omega \to 0$. In order to investigate such unphysical "infrared" divergences, we go one step back and examine the nondegenerate case as given by (39). This equation indicates that, in general, $\Delta n(\omega; \Omega)$ is not divergent in $\omega$, and therefore any zero-frequency divergence must be in the pump frequency $\Omega$ as it appears in $\Delta \alpha$. To
TABLE II
Dispersion of the Nonlinear Refraction $G_2(h\nu/E_0)$ for Frequencies Below the Band Edge as Defined in (44). $\Theta(x)$ is the Heaviside or Step Function.

<table>
<thead>
<tr>
<th>Contribution</th>
<th>$G_2(x)$</th>
</tr>
</thead>
</table>
| Two-Photon Absorption | $\frac{1}{(2x)^2} \left[ -\frac{3}{8} x^2 (1 - x)^{-1/2} + 3x(1 - x)^{1/2} 
                        \right.$
   | $\left. - 2(1 - x)^{-1/2} + 2\Theta(1 - 2x)(1 - 2x)^{3/2} \right]$     |
| Raman              | $\frac{1}{(2x)^2} \left[ - \frac{3}{8} x^2 (1 + x)^{-1/2} - 3x(1 + x)^{1/2} 
                        - 2(1 + x)^{-1/2} + 2(1 + 2x)^{3/2} \right]$ |
| Linear Stark       | $\frac{1}{2x^2} [4 - (1 - x)^{3/2} - (1 + x)^{3/2}]$                     |
| Quadratic Stark    | $\frac{1}{2x^2} \left[ (1 - x)^{-1/2} - (1 + x)^{-1/2} \right.$
   | $\left. - \frac{x}{2} (1 - x)^{-3/2} - \frac{x}{2} (1 + x)^{-3/2} \right]$ |
| Divergent Term     | $\frac{1}{(2x)^2} \left[ -2 - \frac{35x^2}{8} + \frac{x}{8} (3x - 1)(1 - x)^{-1/2} 
                        - 3x(1 - x)^{1/2} + (1 - x)^{3/2} + \frac{x}{8} (3x + 1)(1 + x)^{-1/2} 
                        + 3x(1 + x)^{1/2} + (1 + x)^{3/2} \right]$ |

Further identify these divergences, $\Delta n(\omega; \Omega)$ can be expanded as a Laurent series around $\Omega = 0$. We find that there exist terms which diverge as $\Omega^{-4}$, $\Omega^{-3}$, $\Omega^{-2}$, and $\Omega^{-1}$. On summing these terms, however, all the divergences vanish apart from a term proportional to $\Omega^{-2}$, leaving the divergent term as

$$G_2^{\text{div}} = \frac{\mathcal{G}(\omega)}{\Omega^2} \quad (43)$$

where $g(\omega)$ has no divergence at $\omega = 0$. Now, by setting $\Omega = \omega$, one arrives at the degenerate divergence function as shown in Table II. This diverging term is expected as $A \cdot p$ perturbation theory has been used in the transition rate calculations, and it is well known that divergences of this order can be introduced [37], whereas the comparable $E \cdot r$ perturbation theory avoids such divergences. The latter perturbation technique, however, is not suitable for solids with extended wavefunctions, and simple scaling rules cannot be easily derived. In a similar manner to Moss et al. [38], we treat such a divergence as unphysical and subtract it from the result for the nonlinear refraction.

The individual contributions to the nonlinear refractive index are shown in Fig. 4 as a function of frequency. The divergence in each physically identifiable process has been subtracted for clarity. It can be seen that the most significant contribution to the spectral dependence of $G_2$ arises from the 2PA term, except close to the band edge where the quadratic Stark term becomes dominant. The linear Stark term arising from the self-coupling of the bands is insignificant compared to the quadratic term. In terms of second-order perturbation theory, this is a result of the momentum matrix element being much larger when taken between conduction and valence bands than between the same bands [13]. The only significance of the linear Stark term in the present calculation is that it cancels terms which diverge as $\omega^{-4}$ arising from the 2PA and Raman contributions.

The general scaled form for $n_2$ is given by

$$n_2 \text{ (esu)} = K' \frac{\sqrt{E_g}}{n_0 E_g} G_2(h\nu/E_g) \quad (44)$$
where, using the value of $K$ obtained from the fit to 2PA in semiconductors (3100), the constant $K' = 1.50 \times 10^{-8}$ when $E_g$ and $E_f$ are defined in eV. Using the value of $K$ predicted by theory (no fitting) gives $K' = 0.94 \times 10^{-8}$. We note the $E_g^{-4}$ dependence for the magnitude of $n_2$, corresponding to the scaling predicted by Wherrett [13].

A graphical comparison of the dispersion function $G_2(\hbar \omega/E_g)$ with measured values of $n_2$ is shown in Fig. 5(a). The values for semiconductors (squares) were obtained from Z-scan measurements at 1.06 and 0.53 $\mu$m [1], [10] (as previously plotted in Fig. 1). Included in these data are some new measurements. We also show "nearly degenerate three-wave mixing" $n_2$ measurements of large-gap optical materials [6] (solid circles) and a measurement of $n_2$ in silica at 249 nm [39] (diamond).

Fig. 5(b) shows the extension to Fig. 5(a) for frequencies close to the band edge where the bound electronic refractive nonlinearity shows a resonance due to the quadratic ac Stark effect. This graph also includes recent measurements of $n_2$ in AlGaAs by LaGasse et al. [40] using femtosecond time-division interferometry techniques (solid triangles). Table III shows the measured values for $n_2$ for the various semiconductors and wide-gap optical solids which are plotted in Fig. 5. The data for the semiconductor bandgaps and linear refractive index were obtained from [41], [42]. From the theory presented here, we also give the predicted values for $n_2$. For the semiconductor measurements at 1.06 and 0.53 $\mu$m (excluding CdSe at 1.06 $\mu$m whose $n_2$ could not be measured with any degree of accuracy because of the 2PA-induced band-filling refractive nonlinearity), we find an average difference of less than 30% between the measured and predicted values. Including the measurements for dielectrics, the average difference was less than a factor of 2. We note, however, that the measured $n_2$ for these wide-gap solids are consistently smaller than the predicted values.

One possible reason for this is that the absorption edge has been used to determine the bandgap. The band structure for these materials is not well known, and the direct gap may well be larger than this. We find, however, for these wide-gap materials, that a good fit to the $n_2$ data can be obtained by using a smaller value for the constant $K' = 0.86 \times 10^{-8}$, as shown by the dashed line in Fig. 5(a).

For frequencies close to the band edge, the Stark effect results in a divergence in the nonlinear refractive index of $(\hbar \omega/E_f)^{-3/2}$. This region can be examined in more detail by reploting data and theory in a log-log plot as shown in Fig. 6. Note the straight line dependence for small detunings, with a slope of $-3/2$ corresponding to the above asymptotic relationship. From Figs. 5(b) and 6, one notices an increasing deviation of the AlGaAs data from the theory as the photon energy is approaching the energy gap. One possible cause for this deviation is the excitonic enhancement which becomes significant near the band edge.

The Stark effect can also be described as virtual band blocking since a blue shift of the band edge is equivalent to a reduction of optically coupled states at photon energies corresponding to the bottom of the band (in a similar manner to the dynamic Burstein-Moss shift [43]). Indeed, the direct saturation model [44] predicts exactly the same frequency and material dependence of the nonlinear refractive index just beneath the band edge. This allows a conceptual link between below-gap (virtual carriers) and bandgap resonant (real carriers) nonlinear optical effects [45].

Hidden in Figs. 5 and 6 is the $E_g^{-4}$ scaling of $n_2$ that gives a variation of $n_2$ from $2.5 \times 10^{-14}$ esu for a material
### TABLE III

List of $n_2$ Data Showing Parameters Used in the Calculation (from [41], [42]) Along with the Experimentally Measured and Theoretically Predicted Values of $n_2$. These $n_2$ data include measurements in [6], [39], [40]. † Indicates where we have used the direct gap rather than the fundamental absorption edge. The column indicated by * Uses a Fit to the Constant $K^*$ for Wide-Gap Materials Rather than the Fit to $2\alpha$ in Semiconductors [See Fig. 5(a)].

<table>
<thead>
<tr>
<th>Material</th>
<th>Wavelength ($\mu$m)</th>
<th>Bandgap (eV)</th>
<th>Refr. Index</th>
<th>$n_2$ (Exp.) $\times 10^{-17}$ (esu)</th>
<th>$n_2$ (Pred.) $\times 10^{-13}$ (esu)</th>
<th>$n_2$ (Pred.)* $\times 10^{-13}$ (esu)</th>
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such as MgF$_2$ at 1.06 $\mu$m to $-2.6 \times 10^{-7}$ esu for AlGaAs at 810 nm [40] and $2.7 \times 10^{-10}$ esu for Ge at 10.6 $\mu$m, which we measured with a picosecond CO$_2$ laser. This five orders of magnitude variation of $n_2$ is better displayed by plotting $n_2$ scaled by $n_0$ and $G_0$ as a function of $E_x$ on a log-log plot, as shown in Fig. 7. In spite of this very large variation in the magnitude of $n_2$ (and the change in sign), this extremely simple model gives good agreement with the data for materials including both semiconductors and insulators. It is found that the $E_x^{-4}$ scaling law holds true over the five orders of magnitude variation in the modulus of $n_2$ for the data presented here. Additionally note that although the measured values of $n_2$ for ZnSe at 1.06 and 0.53 $\mu$m have different signs, both measurements are consistent with the scaling law.

V. IMPLICATIONS FOR ALL-OPTICAL SWITCHING

One of the applications of the nonlinear refractive index $n_2$ is in the role of all-optical switching. Some examples are a nonlinear Fabry–Perot filter for image processing, or parallel optical computing [46], [47], or coupled waveguides for communication switching networks [48], [7]. When it comes to optimizing devices for optical switching, it is important that optical losses in the system are not too large. For instance, if optical absorption is too large, then the change in refractive index will fall off rapidly as the optical beam propagates.

It can be shown that for any optical switching system, one must achieve a refractive index change $\Delta n$ such that

$$|\Delta n| > c_{sw} \alpha \lambda$$  (45)
where $c_{sw}$ is a numeric constant of the order of unity whose precise value depends on the exact switching scheme. For example, using a Fabry–Perot filter, $c_{sw} = (2\sqrt{3\pi})^{-1}$ [49], whereas a nonlinear coupled waveguide gives $c_{sw} = 2$ [50], [51].

Below the band edge, the principal contribution to the absorption at irradiance levels of interest is two-photon absorption, $\alpha = \beta I$. In addition, the electronic Kerr effect gives the change in refractive index $\Delta n = \gamma I$. Hence, in this regime, the requirement for all-optical switching is

$$\frac{\gamma}{\beta \lambda} > c_{sw}. \quad (46)$$

The theory presented in this paper gives the scaling and dispersion for both $\beta$ and $\gamma$, which are related through nonlinear Kramers–König relations. Inserting the functional forms of $\beta$ and $\gamma$ given here gives the frequency dependence for the all-optical switching requirement:

$$\frac{\hbar \omega}{G_2(\hbar \omega/E_g)} > 2\pi c_{sw}. \quad (47)$$

Note that (47) has no explicit material dependence since it is only a function of the ratio $\hbar \omega/E_g$. Thus, although $n_2$ can be enhanced by using smaller gap materials, this does not necessarily improve the conditions for switching. The left-hand side of (47) is plotted in Fig. 8. In the same figure, we also show the experimentally measured values for this parameter $|2\pi\gamma/\beta \lambda|$, for some semiconductors using the $n_2$ values measured here and our 2PA coefficients from [11]. We note that there is a range of optical frequencies where this quantity becomes too small for optical switching, which is given approximately by $0.6 < \hbar \omega/E_g < 0.9$. This region is centered around the point where there is a change of sign in $n_2$, covering most of the range of frequencies where 2PA is observed. Therefore, given a certain wavelength of operation, this immediately excludes certain materials from consideration for all-optical switching. This was first noted by Stegeman et al. [50]. DeLong and Stegeman [52] recently used the results of [2], which only included the 2PA contribution to $\gamma$, to give a similar requirement for all-optical
switching. Our result ignores free-carrier absorption and refraction, exciton effects, and linear absorption which may further restrict or enhance the choice of material.

This result can also be extended to other applications for nonlinear optics. For instance, 2PA has been a problem in the observation of spatial optical solitons based on the electronic Kerr effect [53]. We can use the above result as a rule of thumb in determining for what material/frequency combination 2PA would cause problems for nonlinear refractive applications.

VI. CONCLUSIONS

We have presented a simple two-band model calculation that gives a universal bandgap scaling and dispersion of the electronic Kerr effect in solids. This simple model, for the first time, draws a direct relationship between the nonlinear refractive index \( n_2 \) and its nonlinear absorptive counterparts, namely, two-photon absorption, Raman transitions, and the ac Stark effect. We have also presented measurements of the bound electronic nonlinear refractive index for various materials beneath the band edge. Several new data, along with previously published data, are compared to this theory, and remarkable agreement is observed.

A wide range of theoretical papers exists where nonlinear absorption is calculated by means of transition rates. We used a nonlinear Kramers–Kröning transformation approach to obtain the nonlinear refraction in terms of this electronic nonlinear absorption because this method circumvents a direct calculation of the complex nonlinear susceptibility. However, it is necessary to know the nondegenerate absorption in order to perform the calculation (or refraction in the equivalent converse expression). That is, we need expressions for the nonlinear absorption at all frequencies \( \omega \) when an optical field \( \omega_2 \) is applied. This can be thought of as a pump–probe spectrum where, in the present convention, \( \omega_2 \) would be the pump frequency and \( \omega_1 \) the variable probe frequency. We calculated this nondegenerate nonlinear absorption using a simple two-band model for a direct gap semiconductor. The next stage of complexity would be to do the same calculation for the Kane four-band model of a semiconductor. It was necessary to include transitions over all frequencies so that the Raman and Stark shift terms are included, as well as two-photon absorption.

We performed the Kramers–Kröning integral on the nondegenerate nonlinear absorption to obtain analytic expressions for the nonlinear self-refraction. In this calculation, we set the two frequencies in the nonlinear refraction equal to determine self-refraction, but in general the nondegenerate refraction can also be obtained, i.e., the change in refractive index seen by the light of frequency \( \omega \) when the light of frequency \( \Omega \) is present.

Comparing the experimentally measured values of \( n_2 \) to the theoretical dispersion presented here, we find that good agreement is obtained over a wide range of frequencies and materials, with only one fitting parameter \( K' \) obtained from 2PA measurements in semiconductors. We note, however, that the theoretical value for this parameter is only about 40% smaller than this fitted value for \( K' \). This is quite remarkable, and to some extent surprising as a simple two-band model has been used to calculate the nonlinear refraction with no account for the full-band structure or excitonic effects. However, as has been shown by earlier calculations of the 2PA coefficients in semiconductors [15], the effect of nonparabolicity of the bands becomes important only for small-gap semiconductors such as InSb. Also ignored in this model is the contribution of higher bands (conduction or split-off valence bands), and hence the effect of their specific structure. This can be justified by noticing the strong inverse photon energy dependence of the nonlinear transition rate as shown in Table I. This is better illustrated in Fig. 3 where the change in absorption becomes progressively smaller at higher frequencies \( \hbar \omega / E_g > 1.5 \), and hence the near-gap transitions will dominate. Including the effect of higher bands in calculating the transition rate will contain terms involving high-energy photons, and therefore, it should have a negligible effect.

The other important simplification in our model has been the exclusion of the Coulomb interaction or excitonic enhancement. Earlier calculations of the excitonic effects on two-photon transition rates had indicated a significant enhancement near the two-photon resonance \( \hbar \omega = E_g / 2 \) [15], [21]. For example, the underestimation of both \( n_2 \) and the 2PA coefficient \( B \) of ZnTe at \( \lambda = 1.06 \mu m \) may well be due to this two-photon exciton resonance [11]. Similarly, for photon energies approaching the energy gap, an excitonic enhancement of the quadratic Stark effect is expected. For example, nonlinear refraction can occur due to the ac Stark shift of an exciton resonance [54]. We also expect the contribution from the quadratic Stark effect to be relatively larger when a four-band model for a semiconductor is used since the density of the valence band states is larger, which also may lead to a better fit. Therefore, the deviation of the measured \( n_2 \) data on CdS (at 532 nm) and AlGaAs (at ~ 800 nm) from the predicted values may be due to these other near-bandgap effects.

It is also remarkable that the theory gives a reasonable fit to the data for large-gap optical materials, as well as conventional semiconductors. However, it can be seen that the predicted value for \( n_2 \) is consistently on the large side for these materials. This may be due to the fact that the absorption edge has been used to determine the direct bandgap. We find that for Ge, as expected, it is necessary to use the direct bandgap rather than the smaller indirect gap in order to obtain a satisfactory fit, and the same should be true for wide-gap solids. This is because the transitions involving the lower indirect gaps require phonon scattering, and thus they should have a smaller oscillator strength than direct interband transitions. Unfortunately, the band structure of these materials is not well known. We have also used the mean value of \( E_g \) for
semiconductors in order to predict $n_2$, and this parameter may also be quite different in other materials. We find that for the wide-gap solid data presented here, a better estimate for $n_2$ is obtained by replacing the $K'$ from the fit to the semiconductor 2PA data with a smaller value, which may be more appropriate for these wide-gap materials, as indicated in Fig. 5(a) and Table III.

The change in sign of $n_2$ at about $\hbar\omega/E_g \approx 0.7$ is predicted and observed. It is also demonstrated that the expected $E_g^{-4}$ bandgap dependence holds true for a five order of magnitude variation in the modulus of $n_2$.

It is noted that the main contribution to the dispersion of $n_2$ below the bandgap arises from the two-photon transition term, with the Stark shift term becoming dominant close to the band edge. This partly explains the good fit obtained by using the quasi-nondegenerate two-photon absorption alone, as shown in a previous letter by the authors [2].

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