Kramers-Kronig relation between n_2 and two-photon absorption

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ABSTRACT

Nonlinear refractive index and two-photon absorption measurements on semiconductors show that the bound electronic nonlinearity can be calculated from two-photon absorption dispersion via a simple Kramers-Kronig analysis. This analysis shows n_2 changing from positive to negative as the photon energy approaches the band-gap energy, consistent with observations. Additionally, this simple calculation, which assumes two parabolic bands, gives good agreement with measured values of n_2 in wide-gap dielectrics that are 2 to 3 orders of magnitude smaller than in semiconductors.

2. INTRODUCTION

The study of nonlinear optics in semiconductors has concentrated on bandgap-resonant effects. The very large nonlinear effects observed in this case are the saturation of interband and excitonic absorption due to photoexcited free carriers and excitons, and the associated negative change in the refractive index. In contrast, by exciting optical solids at frequencies much less than the gap, a considerably smaller, and faster, positive nonlinear refractive index (n_2) due to bound electronic effects is observed. However, recently we found that measurements in semiconductors substantially above the two-photon-absorption (2PA) edge yield negative values for n_2.[1] This dramatic dispersion of n_2 can be partially explained using a nonlinear Kramers-Kronig (KK) relation between n_2 and the 2PA coefficient β, or between the real and imaginary parts of the third order nonlinear susceptibility $\chi^{(3)}$. The magnitude and dispersion of n_2 is of interest because of its importance in nonlinear propagation in fibers, fast optical switching, self-focusing and damage in optical materials, and optical limiting in semiconductors. In this letter, we describe our calculation of the bound electronic Kerr effect, n_2, and compare our results with data for a large number of materials, including semiconductors and dielectrics.

This n_2 arises from the real part of $\chi^{(3)}$, and is defined through the refractive index change Δn, where

$$\Delta n(\omega) = \gamma(\omega)\, I_\omega = \frac{n_2(\omega)}{2} |E_\omega|^2 , \qquad (1)$$

with I_ω and E_ω being the irradiance and electric field at frequency ω respectively and $n_2 = (2\pi/n_0)\mathrm{Re}\{\chi^{(3)}\}$. The linear refractive index is n_0, and γ and n_2 are related by $n_2(\mathrm{esu}) = (cn_0\gamma/40\pi)(\mathrm{MKS})$ with c the speed of light.

Most theoretical calculations of n_2 have been confined to the zero frequency limit.[2-6] Semi-empirical formulations have been most successful in predicting the magnitude of n_2.[5,6] For example, the formula obtained by Boling, 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.[6,7] Their theory predicts the low frequency magnitude of n_2. We describe a KK method of calculation of n_2 that predicts the dispersion as well as the magnitude of n_2. This calculation assumes that 2PA gives the dominant contribution to n_2 and that other contributions from Raman and the AC Stark effect or virtual band-blocking are ignored. We will return to this assumption later.

3. CAUSALITY AND KRAMERS-KRONIG TRANSFORMATION

Based on the principle of causality, the KK transformation states that a change in the refractive index (Δn) at ω is associated with changes in the absorption coefficient ($\Delta\alpha$) throughout the spectrum (ω') and vice versa. We write this as:

$$\Delta n(\omega;\xi) = \frac{c}{\pi} \int_0^\infty \frac{\Delta\alpha(\omega';\xi)}{\omega^2-\omega'^2} \, d\omega', \qquad (2)$$

where c is the velocity of light in vacuum and ξ 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 such as thermal excitation, etc. For cases where an electron-hole plasma is injected, the consequent change of absorption has been used to obtain the plasma contribution to the refractive index. In this case, the ξ parameter is taken as the change in plasma density (ΔN) regardlesss of the mechanism of generation of the plasma or the pump frequency.[8] In the case of 2PA the change is due to the presence of a pump field at Ω (ie. $\xi=\Omega$). The corresponding nonlinear refraction is $\Delta n(\omega,\Omega)$, which gives the dispersion of the index change with ω. For the case of self-refraction, $\omega=\Omega$, and this gives what is commonly referred to as n_2. Van Vechten and Aspnes [4] obtained the low frequency limit of n_2 from a similar KK transformation of the Franz-Keldysh electro-absorption effect where, in this case, ξ is the DC field. 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 may include 2PA, the electronic Raman effect, and the optical Stark effect. Here we consider only 2PA.

A wealth of experimental and theoretical work regarding 2PA in semiconductors and crystalline materials exists. In accordance with the predictions derived from either second order perturbation theory [9,10] or a Keldysh-type formalism [11], the 2PA coefficients of the semiconductors studied in Ref. [12] were found to be in good agreement with the theoretical expression given as:

$$\beta(2\omega') = K \frac{\sqrt{E_p}}{n_0^2 E_g^3} F_2(2\hbar\omega'/E_g) , \qquad (3)$$

where K is a material independent constant and E_p (related to the Kane momentum parameter, a momentum matrix element) is nearly material independent and posseses a value of $\simeq21$ ev for most direct gap semiconductors. Note $\beta=(4\pi\omega/n_0)\text{Im}\{\chi^{(3)}\}$. The function F_2 is only a function of the ratio of the photon energy $\hbar\omega'$ to E_g (ie. 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. The simplest model assumes a pair of isotropic and parabolic bands and intermediate states that are degenerate to initial (valence) or final (conduction) states. Neglecting the Coulomb interaction, this simple formalism yields:[10]

$$F_2(2x) = \frac{(2x-1)^{3/2}}{(2x)^5} \quad \text{for } 2x>1 . \qquad (4)$$

The best fit to the data of Ref. 12 using Eqs. 3 and 4 gave K=3.1x10³ in units such that E_p and E_g were in eV and β was in cm/GW, while theory gave 5.2x10³.[9] When nonparabolicity was included the average β was 26% lower than theory; however, the frequency dependence of β changed very little. Interestingly, Eqs. 3 and 4 also give a fair estimate of β for a number of transparent materials measured using the 3rd and 4th harmonics of picosecond Nd:YAG laser pulses.[13,14]

Equations 3 and 4 pertain to a degenerate case where the two photons involved are of the same frequency and

source. For a KK transformation the nondegenerate 2PA coefficient for two distinct frequencies is needed (ie. Ω the "cause" and ω' the integration variable in Eq. 2). Extending the same simple model to obtain the non-degenerate 2PA coefficient has led to dispersion functions that are afflicted with "infrared divergences".[15,16] This has been a common problem originating from the use of the A·p perturbation to calculate the bound electronic nonlinear susceptibilities in solids.[15] Although special cases have been considered [17], a general theory that would rigorously address the proper scaling and dispersion of the non-degenerate 2PA is yet to be developed. For this reason we assume that the dispersion function F_2 for the nondegenerate 2PA coefficient, $\beta(\omega',\Omega)$, can be given by Eqn. 4 modified with the substitution of $2\hbar\omega'$ by $\hbar\omega'+\hbar\Omega$; thus, $F_2(2x)$ is replaced by $F_2(x'+X)$, where $x'=\hbar\omega'/E_g$ and $X=\hbar\Omega/E_g$, and $x'+X>1$. This substitution is strictly valid only for $x'=X$, however, the predictions resulting from this substitution show remarkable agreement with the data, as will be shown.

The change of the absorption spectrum (at ω') induced by the presence of a strong pump at Ω can be written for 2PA as $\Delta\alpha(\omega';\Omega) = \beta(\omega';\Omega)I_\Omega$, where I_Ω denotes the irradiance of the pump field. Similarly the change in refractive index at ω induced by the presence of a strong pump at Ω can be written as $\Delta n(\omega;\Omega) = \gamma(\omega;\Omega)I_\Omega$. Applying the KK transformation Eq. 2 at this point yields a relation between $\gamma(\omega;\Omega)$ and $\beta(\omega',\Omega)$. Using Eq. 3 with $F_2(x'+X)$ in Eq.2 we obtain for the degenerate case ($\omega=\Omega$):

$$\gamma = K \frac{\hbar c\sqrt{E_p}}{2n_0{}^2E_g^4} G_2(\hbar\omega/E_g) ,$$ (5)

where the dispersion function $G_2(x)$ is given by,

$$G_2(x) = \frac{-2+6x-3x^2-x^3-3/4x^4-3/4x^5+2(1-2x)^{3/2}\Theta(1-2x)}{64x^6} ,$$ (6)

with $\Theta(x)$ being the unit step function.

Using the value of K obtained from the 2PA measurements, $E_p=21$ eV, and converting from γ to n_2, we obtain the final expression for n_2 as:

$$n_2(esu) = K' \frac{G_2(\hbar\omega/E_g)}{n_0E_g^4} ,$$ (7)

where $K'=3.4\times10^{-8}$ and E_g is in ev. Equation 7 explicitly shows an E_g^{-4} band-gap dependence for the magnitude of n_2, and the sign and the frequency dispersion of this quantity are given by the simple closed form function G_2. We can now readily compare the predictions of this theory with experiment.

4. COMPARISON WITH EXPERIMENTAL RESULTS

Utilizing a newly developed technique (Z-scan) for n_2 measurements [1,18] that can determine its magnitude and sign, we have measured n_2 for several materials at 1.06 and 0.53 μm. This simple technique has been shown to be an accurate and sensitive tool for measuring n_2 even in the presence of nonlinear absorption. We find, for example, in materials such as ZnSe at 0.53 μm, where 2PA is present, n_2 is negative, but that the sign changes at 1.06 μm. Picosecond degenerate-four-wave-mixing measurements show this third order response (time resolution limited by the 30 ps pulsewidth), while at higher irradiances the slowly decaying 2PA generated free-carrier refraction is seen.[19] We have also measured n_2 in a number of wide-gap dielectrics using the Z-scan method.

A graphical comparison of the data is given in Fig. 1 which shows the band-gap scaling law and in Fig. 2

where the dispersion and sign of n_2 are explicitly compared to the G_2 of Eq. 7. Many of the experimental values for large gap optical crystals are obtained from recent measurements by Adair et.al. using a "nearly degenerate-three-wave-mixing" scheme.[7]
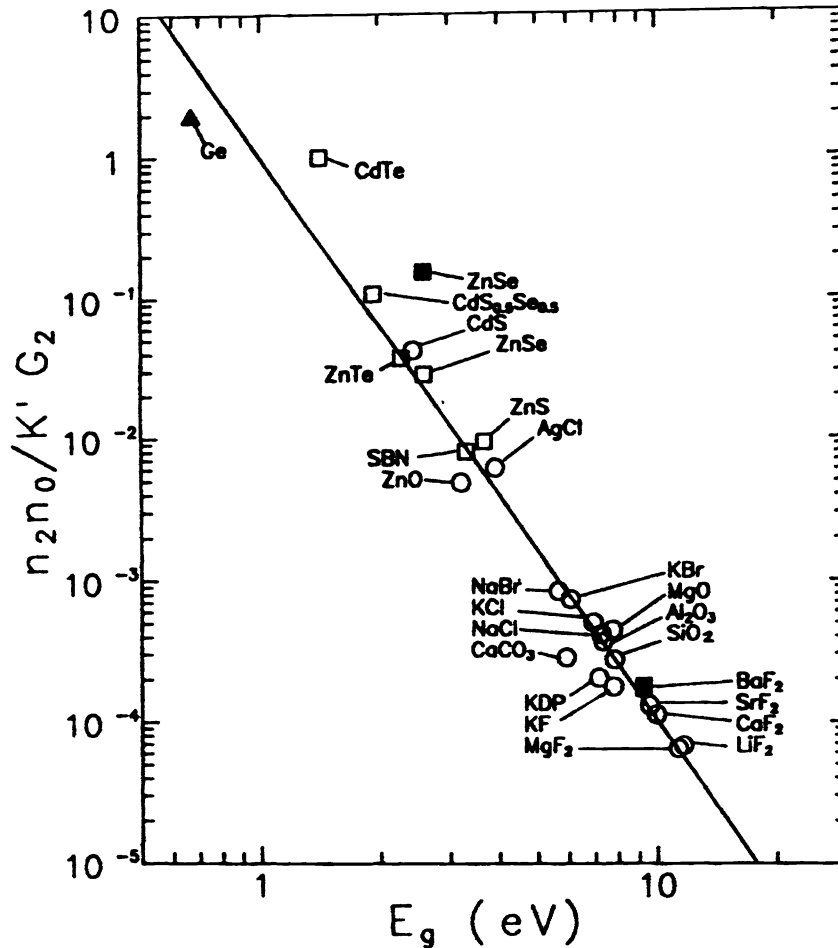

Fig. 1   A log-log plot of the scaled n_2 versus energy gap (E_g) for a large class of optical materials. The solid line represents the theoretical result as obtained from Eq.(7) with no adjustable parameters and has a slope of -4. The open circles represent the data from ref.[7] all obtained at λ=1.06 μm. The remaining data are our measurements using the Z-scan technique taken at λ=1.06 μm (open squares), at λ=.532 μm (solid squares) and at λ=10.6 μm (solid triangle).

The dispersive behavior of n_2 in Fig. 2 is seen to be most significant within the range $E_g/2<\hbar\omega<E_g$ where 2PA is present and relatively small in the low frequency limit $\hbar\omega<<E_g$. A noticeable difference between the magnitude of the measured and calculated values is seen near the one photon absorption edge. Considering the simplicity of the model in deriving Eq. 7, such deviations are not unexpected. The measured large negative values of n_2 as compared to the calculated values near the fundamental absorption edge may be attributed to the refraction due to the "optical Stark effect" which is also referred to as "virtual band-blocking" and has been ignored in our calculations. The contribution of this mechanism to the electronic nonlinear susceptibility has been shown to have a strong band-gap resonance and follows the same scaling as given in Eq. 7.[20] This effect, which is negative for all frequencies below the band-gap, vanishes quickly for longer wavelengths ($\hbar\omega<E_g/2$) and has negligible contribution in the transparency region of the material. The E_g^{-4} dependence of n_2 gives a variation of n_2 from n_2=7x10^{-14} esu for a material such as BaF_2 to

$n_2 = 1.5 \times 10^{-11}$ esu for ZnSe at 1.06 μm which turns negative at 0.53 μm to $n_2 = -4 \times 10^{-11}$ esu. In spite of this very large variation in magnitude of n_2 (and change in sign), this extremely simple model gives good agreement with the data for materials including both semiconductors and insulators, except very near the absorption edge. However, we must emphasize that the justification for splitting 2ω into $\omega' + \Omega$ in Eq. 4 is empirical.
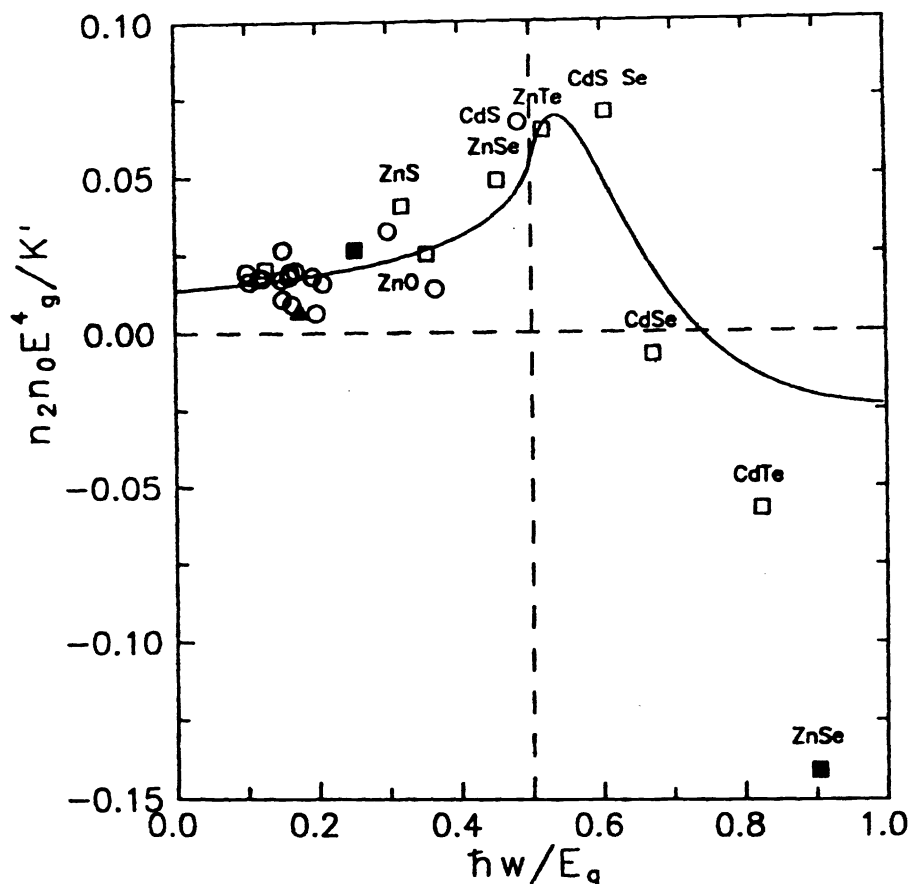

Fig. 2   The calculated dispersion function G_2 versus $\hbar\omega/E_g$. The same n_2 data as in Fig. 1, here scaled as $n_2 n_0 E_g^4/K'$, are compared with the theory. Only the semiconductor data within the highly dispersive region are labeled for comparison.

5. CONCLUSION

We conclude from the excellent overall agreement with the predicted magnitude and dispersion of n_2 to the large number of experimental data, that the KK model presented gives a significant if not dominant contribution to n_2. This in turn implies that the bound electronic nonlinear refractive index is predominantly a causal consequence of two-photon absorption just as the linear index is a causal consequence of linear absorption.

6. AKNOWLEDGEMENT

7. REFERENCES

1. M. Sheik-bahae, A.A. Said, T.H. Wei, D.J. Hagan, and E.W. Van Stryland, "Sensitive Measurements of Optical Nonlinearities Using a Single Beam," to be published in IEEE J. Quantum Electron.

2. S.S. Jha and N. Bloembergen, "Nonlinear Optical Susceptibility in Group-IV and III-V Semiconductors," Phys. Rev. 171, 891-898(1968).

3. C. Flytzanis, "Third Order Optical Susceptibilities in IV-IV and III-V Semiconductors," Phys. Lett. 31A, 273-274(1970).

4. J.A. Van Vechten and D.E. Aspnes, "Franz-Keldysh contributions to Third-Order Optical Susceptibilities," Phys. Lett. 30A, 346-347(1969).

5. C.C. Wang, "Empirical Relation between the Linear and the Third-Order Nonlinear Optical Susceptibilities," Phys. Rev. B, 2, 2045-2048(1970).

6. N.L. Boling, A.J. Glass, and A. Owyoung, "Empirical Relationships for Predicting Nonlinear Refractive Index Changes in Optical Solids," IEEE J. Quantum Electron. QE-14, 601-608(1978).

7. R. Adair, L.L. Chase, and S.A. Payne, "Nonlinear Refractive Index of Optical Crystals," Phys. Rev. B 39, 3337-3349(1989).

8. D.A.B. Miller, C.T. Seaton, M.E. Prise, and S.D. Smith, "Band-gap Resonant Nonlinear Refraction in III-V Semiconductors," Phys. Rev. Lett. 47, 197-200(1981).

9. M.H. Weiler, "Nonparabolicity and Exciton Effects in Two-Photon Absorption in Zincblende Semiconductors," Solid State Commun. 39, 937-940(1981).

10. B.S. Wherrett, "Scaling Rules for Multiphoton Interband Absorption in Semiconductors," J. Opt. Soc. Am. B 1, 67-72(1984).

11. H.S. Brandi and C.B. de Araujo, "Multiphoton Absorption Coefficients in Solids: a Universal Curve," J. Phys. C 16, 5929-5936(1983).

12. E.W. Van Stryland, M.A. Woodall, H. Vanherzeele, and M.J. Soileau, "Energy Band-gap Dependence of Two-Photon Absorption," Opt. Lett. 10, 490-492(1985).

13. P. Liu, W.L. Smith, H. Lotem, J.H. Bechtel, N. Bloembergen, and R.S. Adhav, "Absolute Two-Photon Absorption Coefficients at 355 and 266 nm," Phys. Rev. B 17, 4620-4632(1978).

14. E.W. Van Stryland, Y.Y. Wu, D.J. Hagan, M.J. Soileau, and K. Mansour, "Optical Limiting with Semiconductors," J. Opt. Soc. Am. B, 5, 1980-1989(1988).

15. J.M. Worlock, "Two-Photon Spectroscopy", in Laser Handbook, F.T. Arecchi and E.O. Schulz-DuBois, eds. (North-Holland Publ. Co.,1972) pp.1323-1369.

16. G.D. Mahan, "Theory of Two-Photon Spectroscopy in Solids," Phys. Rev. 170, 825-838(1968).

17. F.V. Bunkin, "Two Quantum Transitions in Optics," Sov. Phys. JETP, 23, 1121-1123(1966).

18. M. Sheik-bahae, A.A. Said, and E.W. Van Stryland, "High Sensitivity, Single Beam n_2 Measurements," Opt. Lett. 14, 955-957(1989).

19. D.J. Hagan, E. Canto, E. Miesak, M.J. Soileau, and E.W. Van Stryland, "Picosecond Degenerate Four Wave Mixing Studies in ZnSe," paper, TUX, pp.160, Technical Digest of the Conference on Lasers and Electro-Optics, Anaheim, CA, OSA Technical Digest Series, No. 7, 1988.

20. B.S. Wherrett, A.C. Walker, and F.A.P. Tooley, "Nonlinear Refraction for CW Optical Bistability," in Optical Nonlinearities and Instabilities in Semiconductors, H. Haug, eds. (Academic Press, Inc. 1988.) pp.239-272.