Three-photon absorption spectra of zinc blende semiconductors: theory and experiment

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We calculate the spectrum of three-photon absorption (3PA) in zinc blende semiconductors using Kane's four-band model. We apply this to ZnSe and measure the 3PA spectrum using femtosecond pulses, obtaining excellent agreement. The spectrum shows the apparent onset of 3PA from the split-off band and also shows quantum interference between the several possible evolution pathways when exciting carriers from valence to conduction band. © 2008 Optical Society of America

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Although the field of multiphoton processes in semiconductors is an area of considerable interest, two-photon absorption (2PA) has been the subject of the most intense investigation, while higher-order multiphoton processes such as three-photon absorption (3PA) have received relatively little attention, most likely owing to the considerable difficulty of accurately measuring the response. The 2PA coefficients for a variety of semiconductors have been experimentally measured [1–3] and theoretically calculated using models ranging from simple two-parabolic band models [4–6] to more realistic four-band models accounting for band nonparabolicity [7]. However, regardless of the degree of simplicity, good agreement was shown between the experimental results and all of the models proposed [7,8]. Data on 3PA in semiconductors is scarce, and most experiments have been performed over narrower spectral ranges [9–12]. The disagreement between the theoretical results generated by different models, primarily in the spectral behavior, instills uncertainty about the appropriate methodologies for calculations [12].

One of the methods employed for theoretical calculations is to use time-dependent perturbation theory to calculate transition rates from the valence band to the conduction band resulting from n-photon absorption, taking into account all possible transition routes. This perturbation approach was used by Wherrett [5] for calculating 2PA spectra and generalized for higher-order nonlinearities as well using a two-parabolic band model. Another procedure was originally proposed by Keldysh [13] and uses first-order perturbation theory with "dressed" states, later approximated by Volkov-type electronic wave functions to account for the acceleration of the electrons by the incident ac field [4,6,8].

In principle, the perturbation method can be used for any higher-order nonlinear process. The difficulty arises mostly from how well the band structure is described and whether only some or all transitions are taken into account. However, for higher-order processes, calculations become complicated. To simplify the problem previous attempts have restricted the types of transitions considered (keeping the dominant ones, i.e., larger momentum matrix elements among the various bands and smaller detuning energies) [5].

The tunneling approach is even more difficult to use when dealing with higher-order nonlinearities, since it cannot account for intervalence band transitions when using more than one valence band [6]. It therefore ignores some potentially large contributing transition routes, thus significantly affecting the predicted magnitude of the nonlinear absorption coefficient.

Recent data published by He *et al.* [12] raise further questions on the validity of the two theories, since the trends observed do not match either of the predicted spectra. This disagreement is mostly due to inaccuracies in the modeling of the spectral behavior and indicates that a more refined approach is necessary.

The band-structure model used in our theoretical calculations was developed by Kane [14]. The electron Hamiltonian for a cell-periodic structure is written as

$$H = (\mathbf{p}^2/2m) + \frac{\hbar^2 k^2}{2m} + V + (\hbar/m)\mathbf{k}\cdot\mathbf{p} + (\hbar/4m^2c^2)(\nabla V \times \mathbf{p})\cdot\boldsymbol{\sigma}, \quad (1)$$

where $\mathbf{p}$ and $\boldsymbol{\sigma}$ are the momentum and spin operators, respectively; $\hbar$ is the reduced Planck constant; m is the electron mass; c is the speed of light; V is the potential, and $\mathbf{k}$ is the wave vector. This model takes into account both the interaction of the valence bands and the conduction band via the $\mathbf{k}\cdot\mathbf{p}$ interaction (the fourth term) and the $\mathbf{k}$ independent spin–orbit interaction (the fifth term) for a band structure consisting of one conduction band and three valence bands.

The characteristic equation yields four double roots corresponding to four doubly spin-degenerate energy bands (three valence bands and one conduction band). Kane's model [14] allows for a complete representation of the band structure and band symmetry, quantifying the nonparabolicity of the bands and the amount of band mixing present at each point in k

space. Using this description, we then write the electron–radiation interaction (perturbation) Hamiltonian [15] in SI units as $H_{\text{int}}=(e/i\omega m_0)\times(I/2\varepsilon_0 n_0 c)^{1/2}(\hat{\mathbf{a}}\cdot\hat{\mathbf{p}})$, where I is the irradiance of the incident beam, n_0 is the material's index of refraction, and $\hat{\mathbf{a}}$ is a unit vector parallel to the direction of the incident electric field. By making use of third-order perturbation theory we can express the 3PA rate as

$$W_3=\frac{2\pi}{\hbar}\sum_{v,c}\left|\sum_{i,j}\frac{\langle\Psi_c|H_{\text{int}}|\Psi_j\rangle\langle\Psi_j|H_{\text{int}}|\Psi_i\rangle\langle\Psi_i|H_{\text{int}}|\Psi_v\rangle}{(E_{jv}(k)-2\hbar\omega)(E_{iv}(k)-\hbar\omega)}\right|^2\times\delta(E_{cv}(k)-3\hbar\omega). \quad (2)$$

The index ν corresponds to a valence band (initial state), c corresponds to the conduction band (final state) including spin, while i and j are intermediate states and can be any of the four bands considered, and the Ψs are the respective Bloch wave functions. The summation is performed over all valence-to-conduction band routes considering all possible intermediate states (same as the four bands in our model). We performed our calculations over the entire wavelength range given by $E_g/3\leq hc/\lambda\leq E_g/2$. The 3PA coefficient $\alpha_{(3)}$ is then obtained using the relation $\alpha_{(3)}(\omega)=3\hbar\omega W_3 I^{-3}$ [5]. This way, contributions from each of the three valence bands can be independently analyzed as well as their total additive effect.

The results obtained with this model using the parameters of room temperature ZnSe ($E_g=2.7$ eV, $\Delta=0.42$ eV, $E_p=24.2$ eV, and $n_0=2.49$) [16] are shown in Fig. 1(a) separating contributions from each valence band. The most interesting feature common to all calculated spectra is the peak in 3PA at photon energies just above the onset of 3PA, along with a dip at higher energies. The features seen are evidence of quantum interference. For each pair of initial and final electronic states separated by 3 $\hbar\omega$, there are several paths of evolution for the system. All of these contributions add with appropriate signs, while the magnitude of the 3PA coefficient is proportional to the absolute value of the sum squared. The influence of band mixing on 3PA is apparent in the calculated contribution from each of the valence bands containing the initial state, as shown in Fig. 1(a). Clearly, the 3PA originating in the transitions occurring from the heavy-hole band shows strong spectral modulation caused by quantum interference. The 3PA coefficient at each wavelength can then be greatly affected by this interference. As our calculations show, and as confirmed by our experimental data, choosing particular transitions to be dominant is not as accurate when calculating these spectra since many terms have significant contributions in the summation. Previous theories [5,6] using two-parabolic band models have predicted smooth, single peaked spectra as shown in Fig. 1(b), since these theories take into consideration only particular transition paths. Simply adding the rates obtained by these previous calculations would ignore the significant quantum interference effects.

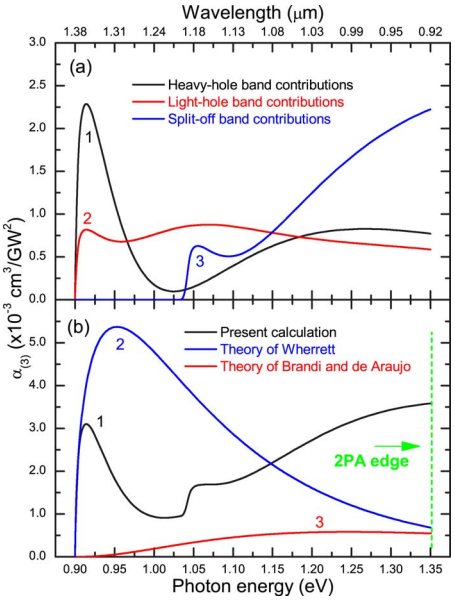

Fig. 1. (Color online) (a) Contributions to the degenerate 3PA coefficient due to transitions from the (1) heavy-hole, (2) light-hole, and (3) split-off bands as a function of photon energy. (b) (1) Calculated degenerate 3PA spectrum compared to previous theories of (2) Wherrett and (3) Brandi and de Araujo.

To verify the calculated results experimentally we used a setup that consists of a Ti:sapphire (Clark-MXR, Model 2010) laser with a pulse width of 140 fs (FWHM), 2 mJ pulse energy, and a repetition rate of 1 KHz. This laser pumps an optical parametric generator–amplifier OPG–OPA (Light Conversion, Model TOPAS), which produces pulses of ~140 fs in the wavelength range of 1.1 to 2.7 μm, providing the tunability required for our experiments. We carefully spatially filter the beam to obtain near-Gaussian spatial profiles. At each wavelength we perform a detailed calibration to accurately determine the energy, the spot size, and the pulse width for the beam used. For each wavelength, we perform Z scans [17] at several energies on a 0.5-mm-thick sample of polycrystalline ZnSe purchased from Meller Optics for the 3PA study. The inset in Fig. 2 shows typical Z-scan traces for ZnSe along with theoretical fittings considering only 3PA at the wavelength of 1.2 μm. Each Z-scan curve is independently fit and the average

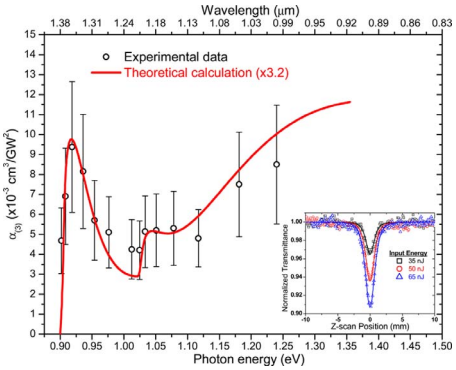

Fig. 2. (Color online) Experimentally obtained spectrum of 3PA coefficient compared to our calculation scaled by a factor of 3.2. Inset shows typical experimental Z scans performed at $\lambda=1200$ nm.

3PA coefficient calculated. The values obtained from fitting individual sets of data are within ±10% of the average, suggesting that only 3PA is present, with negligible contribution from free-carrier absorption or other effects. Also, even though the absolute errors in our measurements are estimated to be about ±35%, the relative errors are smaller, increasing our degree of confidence in the relative magnitude of the features for the measured spectrum.

A plot of our measured values for $\alpha_{(3)}$ is shown in Fig. 2 along with our theoretical calculations. The best match to our experimental data is obtained when using in our calculations 2.71 and 0.37 eV for the bandgap and split-off energies, respectively. These energies are within the range of previously published values [16]. Also, there is an overall discrepancy in absolute magnitude of $\alpha_{(3)}$ by a factor of ~3.2. In the plot, our calculated values are multiplied by this factor to allow for easier comparison. As can be seen, there is strong agreement between the experimental data and our theoretical calculations. Moreover, the theoretically predicted dip in the center of the spectrum and contribution from transitions due to the split-off band are apparent in the experimental data. Another important aspect is the trend in the 3PA values as the wavelength gets closer to the 2PA edge. Our calculations and experimental data show that close to the 2PA edge, the 3PA magnitude is in fact larger by almost 1 order of magnitude than was previously estimated [5,6] and also has the opposite (increasing) trend.

Our results agree with Wherrett's calculations [5] close to the 3PA band edge since the *allowed–allowed–allowed* transitions dominate in this region and the band mixing effects are minimal. The rather remarkable fit of the spectral shape coupled with the relative closeness of the overall magnitude (within a factor of 3.2) shows that the essential physics of the interaction is well accounted for. However, the reasons for the discrepancy in absolute magnitude probably still arise primarily from the limitations of the theoretical model. The original model assumed a temperature of 0 K, and even though we use the room temperature values for the material parameters, we consider an empty conduction band with full valence bands. Also, away from the zone center, there should be less accuracy when predicting the band shapes using Kane's [14] model, since the calculated band structure deviates from measurements. In particular, for ZnSe, this happens at ~1 eV above the band edge, corresponding to energies ~330 meV above the 3PA edge [16]. A more elaborate model, as the one used in [18], needs to be used to obtain a better shape for the conduction band and the heavy-hole band (parabolic here with an effective mass equal to the electron rest mass). Other factors possibly affecting measurements of 3PA are impurities, defects, and excitonic effects for wavelengths close to bandgap resonances [19]. However, we believe that these would produce only small changes to the overall relative shape of the calculated spectrum.

In conclusion, we have calculated the degenerate 3PA spectrum of ZnSe using third-order perturbation theory based on a Kane [14] band structure consisting of three valence bands and a conduction band. This model is realistic for zinc blende structures, since it accounts for the nonparabolicity of the bands and non-zone-center wave functions. Our experimental results match the measured spectral shape recovering all the theoretically predicted features, although the predicted absolute magnitude is a factor of ~3.2 smaller than the experimental data. The predicted dip in the 3PA spectrum due to the quantum interference effects and the onset of the contributions from the split-off band occur in a range close to the zone center, where our theoretical description is fairly accurate. Simpler models cannot produce similar results since band mixing, and all possible evolution paths are not properly taken into consideration.

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References

1. E. W. Van Stryland, M. A. Woodall, H. Vanherzeele, and M. J. Soileau, Opt. Lett. **10**, 490 (1985).
2. A. A. Said, M. Sheik-Bahae, D. J. Hagan, T. H. Wei, J. Wang, J. Young, and E. W. Van Stryland, J. Opt. Soc. Am. B **9**, 405 (1992).
3. M. Balu, L. A. Padilha, D. J. Hagan, E. W. Van Stryland, S. Yao, K. Belfield, S. Zheng, S. Barlow, and S. Marder, J. Opt. Soc. Am. B **25**, 159 (2008).
4. H. D. Jones and H. R. Reiss, Phys. Rev. B **16**, 2466 (1977).
5. B. S. Wherrett, J. Opt. Soc. Am. B **1**, 67 (1984).
6. H. S. Brandi and C. B. de Araujo, J. Phys. C **16**, 5929 (1983).
7. D. C. Hutchings and E. W. Van Stryland, J. Opt. Soc. Am. B **9**, 2065 (1992).
8. M. Sheik-Bahae, D. C. Hutchings, D. J. Hagan, and E. W. Van Stryland, IEEE J. Quantum Electron. **27**, 1296 (1991).
9. I. M. Catalano, A. Cingolani, and A. Minafra, Opt. Commun. **7**, 270 (1973).
10. M. Lepore, R. Tommasi, and I. M. Catalano, Solid State Commun. **84**, 463 (1992).
11. J. U. Kang, A. Villeneuve, M. Sheik-Bahae, G. I. Stegeman, K. Al-hemyari, J. S. Aitchison, and C. N. Ironside, Appl. Phys. Lett. **65**, 147 (1994).
12. J. He, Y. Qu, H. Li, J. Mi, and W. Ji, Opt. Express **13**, 9235 (2005).
13. L. V. Keldysh, Sov. Phys. JETP **20**, 1307 (1965).
14. E. O. Kane, J. Phys. Chem. Solids **1**, 249 (1957).
15. M. Dinu, IEEE J. Quantum Electron. **39**, 1498 (2003).
16. K. H. Hellwege, ed., *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology* (Springer-Verlag, 1982), 17a, 17b, Group III.
17. M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland, IEEE J. Quantum Electron. **26**, 760 (1990).
18. D. C. Hutchings and B. S. Wherrett, Phys. Rev. B **49**, 2418 (1994).
19. M. Weiler, Solid State Commun. **39**, 937 (1981).