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Band-structure calculations of the two-photon absorption coefficients of GaAs, InP, CdTe, and ZnSe

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The two-photon absorption coefficients of crystalline GaAs, InP, CdTe, and ZnSe at 1.064 and 0.694 μm are calculated by means of a new model which combines the elements of second-order perturbation theory and band-structure calculations. A sufficient number of intermediate states are included to ensure adequate convergence. This calculational procedure is shown to represent a significant improvement over currently available theoretical models, and the results are in good agreement with available experimental data.

In the last two decades there have been numerous theoretical and experimental studies of the two-photon absorption (TPA) coefficients of crystalline solids.[1-19] In spite of these extensive investigations, a generally accepted quantitative description of two-photon absorption has not been achieved even for the simplest of semiconductors, as is evidenced by the unacceptably large disparity between theoretical estimates and the available experimental measurements. These differences stem largely from the simplifying models employed to describe the electronic band structure, the approximate manner in which the oscillator strengths are estimated, and incorrectly truncating the summation over the intermediate states [see Eq. (1) below]. In an attempt to improve this situation we have calculated the two-photon absorption coefficients of several direct-gap zinc-blende-type, crystalline semiconductors by first computing their electronic band structures and oscillator strengths throughout the first Brillouin zone by means of the empirical pseudopotential method, followed by a numerical evaluation of the two-photon transition probabilities employing second-order perturbation theory.

Within the context of second-order perturbation theory, the transition-probability rate of an electron in a crystalline solid (with direct energy gap E_g) going from an initial valence-band state $|v\vec{k}\rangle$ to a final conduction-band state $|c\vec{k}\rangle$ by the simultaneous absorption of two photons is given by

$$W=\frac{2\pi}{\hbar}\int\frac{d\vec{k}}{(2\pi)^3}\left|\sum_n\frac{H_{vn}H_{nc}}{E_{vn}(\vec{k})-\hbar\omega}\right|^2\delta(E_{vc}(\vec{k})-2\hbar\omega), \tag{1}$$

where the photon energies are such that $2\hbar\omega \geq E_g > \hbar\omega$. In Eq. (1) E_{ij}'s are the energy separation between states i and j at wave vector $\vec{k}$, the summation is over all intermediate states n, and the $\vec{k}$ integral extends over the entire first Brillouin zone. The interaction Hamiltonian H is of the form $H=(e/mc)$, $\vec{A}\cdot\vec{P}$, where $\vec{A}$ is the vector potential of the radiation and $\vec{P}$ is the momentum operator. The two-photon absorption coefficient β is related to the two-photon transition-probability rate W by the equation

$$\beta=4\hbar\omega W/I^2, \tag{2}$$

where I is the intensity of the incident radiation. It is obvious from Eq. (1) that to evaluate the two-photon transition probability, knowledge of the electronic energies and wave functions throughout the first Brillouin zone is needed. We obtain these at room temperature by performing empirical psuedopotential calculation (EPM), using the available psuedopotential form factors.[20] We used up to 35 plane waves at each $\vec{k}$ point and obtained the Bloch functions and eigenenergies of the highest four valence bands and the lowest 31 conduction bands to an accuracy of approximately 0.1 eV near the Fermi level and to within 0.5 eV away from the Fermi level. (Each of these bands is doubly degenerate due to spin.) The reliability of the higher-energy bands obtained in this calculation was checked by computing the conduction-electron effective masses, which also involve sums over all the energy bands of the crystal. The results agreed with the experimentally known effective masses to within 10%. In order to numerically integrate Eq. (1) we convert the delta function in energy to a delta function in wave vector by use of the following relation:

$$\delta(E_{vc}(\vec{k})-2\hbar\omega)=\sum_l\frac{\delta(\vec{k}-\vec{k}_l)}{|\vec{\nabla}_{\vec{k}}E_{vc}(\vec{k})|}\ , \tag{3}$$

TABLE I. Comparison of theoretical and experimental two-photon absorption coefficients (in units of cm/MW) at room temperature.

Crystal	Wavelength (μm)	Theoretical				Experimental results obtained with nanosecond pulse
		Braunstein[a]	Basov[b]	Lee and Fan[c]	Present	
CdTe	1.064	0.007	0.037		0.201	0.13 ± 0.04[d] 0.2 – 0.3[d]
ZnSe	0.694	0.002	0.011		0.081	0.04[e]
InP	1.064	0.008	0.056	0.096	0.351	0.26 ± 0.13[f] 0.23 – 0.3[f]
GaAs	1.064	0.007	0.039	0.058	2.179	0.02 – 5.6[g]

[a] References 1 and 5.
[b] References 3 and 5.
[c] Reference 4.
[d] References 7 and 17.
[e] Reference 8.
[f] Reference 4.
[g] References 4, 8, 10, 11, and 17–19.

where $\vec{k}_t$ represents all values of $\vec{k}$ for which $E_{vc}(\vec{k}) = 2\hbar\omega$. The momentum matrix elements are calculated throughout the Brillouin zone by means of the relation

$$|P_{ij}|^2 = |\langle j\vec{k}\,|\hbar\vec{\nabla}_{\vec{r}}|\,i\vec{k}\rangle|^2, \tag{4}$$

where $|i\vec{k}\rangle$ and $|j\vec{k}\rangle$ are the Bloch functions obtained using the empirical pseudopotential method. In calculating W from Eq. (1) we considered the transitions originating from the highest three valence bands, and included the intermediate states in all the 35 energy bands obtained in this calculation. The resulting two-photon absorption coefficient had a convergency of 0.0001 cm/MW.

The converged two-photon absorption coefficients of GaAs, InP, CdTe, and ZnSe at 1.064 and 0.694 μm at room temperature, obtained in this calculation, are reported in Table I along with the results of other theoretical calculations based on second-order perturbation theory and selected experimental data to which the theories apply. Results using the models of Braunstein[1] and Basov[3] are seen to be 1 or 2 orders of magnitude smaller than our results. The biggest deficiency of the former two models, apart from the simplified band-structure schemes employed and the approximate manner in which the oscillator strengths are estimated, is the inaccurate manner in which the summation over the intermediate states in Eq. (1) is truncated. Specifically, Braunstein considered only one higher conduction band for the intermediate state, while Basov considered only the intermediate states in the initial and final bands.

This calculation includes both of these intermediate states, and in addition, those in all other valence and conduction bands. Furthermore, unlike the models of Braunstein and Basov, the present calculation reported herein fully takes into account the degeneracies of all the energy bands involved. Finally, while Braunstein considered only the highest single valence band for the initial electronic state, and Basov included the highest two valence bands, we have considered the highest three valence bands for the initial state whenever the transitions from these bands to the lowest conduction band are energetically possible. The model of Lee and Fan[4] takes into account the valence band degeneracies, and also considers excitonic effects. As a result, the TPA coefficients predicted by their model are significantly larger than those of Braunstein and Basov. However, in the present calculation we do not include excitonic effects, since these are known[2,4] to be small when the two-photon energy is quite a bit larger than the energy gap, such as in the cases studied here. In spite of this, our results are considerably larger than those of Lee and Fan. This apparently arises from our use of more accurate energy bands and momentum matrix elements, which are obtained from detailed band-structure calculations. In fact, Pidgeon *et al.*[6] have recently shown that the nonparabolicity of the energy bands alone can dramatically increase the calculated TPA coefficients in semiconductors, especially away from the band edge.

Before making any comparison between the theoretical and experimental results, it is instructive to point out the following. The experimental results are known to be drastically affected by many factors: laser pulse duration, free-carrier absorption, impurity type and concentration, spatial and temporal fluctuations of the laser pulse, sample temperature and thickness, experimental technique employed, etc. It is known[9,12] that in going from nanosecond pulses to picosecond pulses the TPA coefficient decreases by as much as three orders of magnitude, due to coherence effects such as self-induced transparency, etc. Whether the free-carrier absorption is included or not in the analysis of a given set of nonlinear transmittance data has a serious influence on the values of the TPA coefficients deduced from the same data.[14] Large impurity concentrations can drastically reduce the TPA due to saturation effects.[13] At high laser intensities the TPA coefficients could considerably decrease due to the increase in the "effective energy gap" of the crystal.[15,16] These considerations explain, in part, the large variations in the reported experimental data.

We will, therefore, take the following approach in comparing theories with experiments. We will restrict ourselves to the experimental data relating to nanosecond pulses, at room temperature, where coherence effects are usually absent. First, we will apply the various theoretical models to those crystals where the experimental data are unambiguous. Based on the success or failure of the different theories for reliable predictions of the nonlinear absorption coefficients in these crystals, we will be able to propose definite values for the TPA coefficients in crystals where there is a large disparity between the experimental data. Following this approach, we find that in the case of CdTe the result of the present calculation agrees well with the results of the two experiments[7,17] which report the pulse duration to be in the nanosecond regime. (The experimental data of Ref. 7 should be quite accurate since they were obtained using a laser calorimetric method, which had much greater sensitivity than nonlinear transmittance measurements.) By contrast, the results of Braunstein and Basov formulas are orders of magnitude smaller. The same trend is noted in ZnSe also. In InP our result is larger than the experimental data by a factor whose value is less than 1.5, while that of Lee and Fan model is smaller than the experimental results by a factor between 2.5 and 3.

Based on these observations we make the following conclusions: The models of Braunstein and Basov grossly underestimate the TPA coefficients, for reasons explained earlier. The model of Lee and Fan also underestimates them, albeit to a lesser degree, especially when the two-photon energy is significantly larger than the band gap. This obviously arises from their use of approximate expressions for the electronic energies and oscillator strengths, which may not be accurate away from the band edge. The present calculation overestimates the TPA coefficients, by a factor of approximately 2. This probably arises due to our approximating the true electronic wave functions by the pseudowave functions obtained with the EPM. Band-structure calculations employing other methods, such as orthogonalized plane wave, augmented plane wave, Green's function, etc., should shed more light on this situation. However, we conclude the results of the present calculation are significantly more reliable than those of earlier models, because of the use of more realistic energy bands and oscillator strengths and the inclusion of many intermediate states, resulting in good convergency. Finally, based on the above observations, we favor a value of the order of unity for the TPA coefficient of pure GaAs at 1.06 μm, when free-carrier absorption, coherence effects, etc. are absent, in close agreement with the experimental result of Arsenev *et al.*[8]

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