Two-Photon Absorption in Zinc-Blende Semiconductors

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It is shown that a three-band, nonparabolic, model for zinc-blende semiconductors provides a universal curve for the frequency dependence of the two-photon coefficient, whose magnitude differs between semiconductors by the factor $(E_g{}^3 n_p{}^2)^{-1}$. Good agreement is obtained with reported coefficients at 300°K for InSb, $Hg_{1-x}Cd_xTe$, GaAs, and CdTe.

Two-photon absorption can become the dominant loss mechanism for semiconductors subjected to sufficiently intense laser light in the frequency range $\hbar\omega_p < E_g < 2\hbar\omega_p$, where ω_p is the laser frequency and E_g is the energy gap. The proper understanding of this effect can yield information not accessible to one-photon transitions, and is important for the operation of a number of devices such as "inducible absorbers," two-photon–pumped and spin-flip Raman lasers, and infrared detectors. There has been a long-standing discrepancy, in some cases of more than an order of magnitude, between reports of the measured frequency dependence of the two-photon absorption coefficient and the theoretically predicted values, in particular for two-photon energies much greater than E_g (see, for example, Basov *et al.*,[1] Lee and Fan,[2] and Doviak *et al.*[3])

We show in the present work that a simple three-band model calculation provides a single comprehensive description of both the magnitude and the frequency dependence of the two-photon absorption coefficient for a wide range of III-V and II-VI zinc-blende semiconductors. For a given photon energy the magnitude of the coefficient differs between semiconductors by the factor $(E_g{}^3 n_p{}^2)^{-1}$; n_p is the refractive index at the radiation frequency.

The variation of laser intensity, I, with distance, z, through the crystal is given by

$$-dI/dz = K_1 I + K_2 I^2 + \Delta n(\sigma_n + \sigma_p) I, \tag{1}$$

where K_1 and K_2 are the one- and two-photon absorption coefficients respectively, σ_n and σ_p are the electron and hole absorption cross sections, and Δn is the number of generated free carriers. If a pulsed laser is the radiation source, Δn will be a function of time given by

$$\frac{d(\Delta n)}{dt} = \frac{K_2 I^2}{2\hbar\omega_p} - r\Delta n, \tag{2}$$

where r is the recombination coefficient, which itself may depend on Δn. In general, the absorption due to photocreated holes makes a significant contribution, in which case K_2 has to be extracted numerically from the raw transmission data in terms of Eqs. (1) and (2).[4,5]

Following second-order perturbation theory, the electron transition rate due to two-photon absorption is given by[2]

$$M = \frac{2\pi}{\hbar}\left(\frac{4\pi^2 e^4 I^2}{n_p{}^2 c^2 m^4 \omega_p{}^4}\right)\sum_f \int \left| \sum_t \frac{\langle f|\vec{\epsilon}\circ\vec{p}|t\rangle\langle t|\vec{\epsilon}\cdot\vec{p}|i\rangle}{E_t - E_i - \hbar\omega_p} \right|^2 \delta(E_f - E_i - 2\hbar\omega_p)\frac{dk}{(2\pi)^3}, \tag{3}$$

where $\vec{p}$ is the electron momentum operator and $\vec{\epsilon}$ the polarization of the radiation. The matrix elements are taken between states of the entire many-electron system. The two-photon absorption coefficient is

$$K_2 = (2\hbar\omega_p/I^2)M. \tag{4}$$

We take the three-band model[6] for the conduction and valence bands of zinc-blende semiconductors. This introduces the important result that, even for large-gap semiconductors, certain of the bands become very highly nonparabolic at wave vectors that are relevant for two-photon absorption, particularly when $2\hbar\omega_p$ is significantly larger than E_g. This nonparabolicity is well established from, for example, interband magneto-optical studies at high energies,[7] but has hitherto been neglected in the analysis of two-photon absorption.[1,2] Under the assumption of spherical bands, two-photon absorption excites electrons across the band gap at a wave vector whose magnitude is given by

$$E_f(k) - E_i(k) = 2\hbar\omega_p. \tag{5}$$

We shall consider the three-band model in the

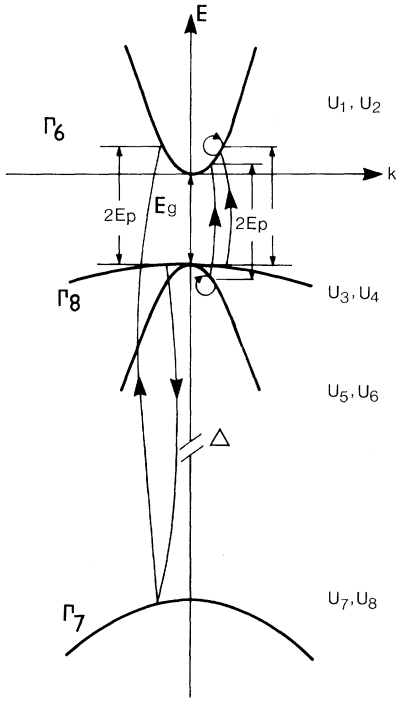

FIG. 1. Conduction and valence bands of InSb-type materials near $\vec{k}=0$. Typical two-photon absorption transitions are shown.

extreme cases: (i) for small-gap semiconductors in which the spin-orbit splitting, Δ, is large compared to the band gap, and (ii) in the opposite extreme, where Δ is taken to be zero. In either case the k value satisfying Eq. (5) is larger in the nonparabolic model, by a factor of as much as $\sqrt{2}$ as $\hbar\omega_p$ tends to E_g. K_2 is basically proportional to the cube of the k value through the joint density of states, which is essentially proportional to k (exactly proportional in the parabolic approximation), and the dipole moment matrix elements.[2] As a result the nonparabolic model is immediately expected to produce results of order 3 times the parabolic approximation. In practice we shall show that an increase by a factor of 7 occurs for $\hbar\omega_p \sim E_g$.

Figure 1 shows the energy bands appropriate for large spin-orbit splitting. There are two types of process to be considered for transitions originating from the Γ_8 or Γ_7 valence band and terminating in the Γ_6 conduction band. These are evaluated using the set of band-edge basis functions U_1 to U_8, which diagonalize the spin-orbit interaction in the (J, M_J) representation.[2,6,8]

There are in total twelve final states in the summation $\sum_f$, each involving sums over intermediate transition schemes of the two types shown. We first take the limit where we neglect the split-off band (we show below that this makes very little difference, even in large-gap materials). We may neglect free mass terms by comparison to the conduction and light-hole effective mass $[m_{c0} \simeq -m_{lh0} = \frac{4}{3}(P^2/E_g)m/\hbar^2]$. The intermediate-state summation for the transition scheme whereby an electron initially in U_3 is excited to U_1 reduces to

$$\sum_t = i\left(\frac{m}{\hbar}\right)^2 \frac{kP^3}{E_g}\left[\frac{4}{3}\cdot\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{3}}\cdot\frac{2}{\sqrt{6}}\right]\cos\theta \sin\theta e^{-i\varphi}, \tag{6}$$

where[6] $P = (-i\hbar/m)\langle S|p_z|Z\rangle$; θ and φ describe the orientation of the radiation polarization with respect to the chosen $\vec{k}$ direction. The first term in square brackets corresponds, in the single-particle transition scheme, to $U_3 \rightarrow U_1, U_1 \rightarrow U_1$ and the second to $U_6 \rightarrow U_1, U_3 \rightarrow U_6$ transitions. The other two contributions are neglected under the above approximations. In the summation there are further transitions involving excitation from the light-hole states U_5, U_6 to U_1 and from the heavy-hole states U_4 to U_1; the latter specifically requires an intervalence step. Also there are five equivalent transitions from the valence states to the spin-down conduction state U_2.

Carrying out the summation and performing the integration over the angles φ, θ give

$$M = \left(\frac{e^4 I^2}{c^2 m^4 n_p^2 \hbar\omega_p^4}\right)\left(\frac{m^2 p^3}{\hbar^2 E_g}\right)2\pi \int k^4 dk \left\{\frac{16}{135}\left(\left[\frac{2}{E_{gh}(k)-\hbar\omega_p} - \frac{1}{E_{gl}(k)-\hbar\omega_p}\right]^2 + \left[\frac{1}{E_{gl}(k)-\hbar\omega_p}\right]^2\right)\right.$$
$$\left. \times \delta(E_{gh}(k) - 2\hbar\omega_p) + \frac{16}{45}\left[\frac{1}{E_{gh}(k)-\hbar\omega_p}\right]^2 \delta(E_{gl}(k) - 2\hbar\omega_p)\right\}, \tag{7}$$

where $E_{gh}(k)$ and $E_{gl}(k)$ are the heavy-hole and light-hole to conduction-band energy gaps at finite k.

It is in the evaluation of the k integration that it is essential to account properly for the dependence of $E_{gh}(k)$ and $E_{gl}(k)$ on k. The correct energy gaps are

$$E_{gh}(k) = \frac{E_g}{2}\left[1 + \left(1 + \frac{8}{3}\frac{k^2P^2}{E_g^2}\right)^{1/2}\right], \quad E_{gl}(k) = E_g\left(1 + \frac{8}{3}\frac{k^2P^2}{E_g^2}\right)^{1/2}. \tag{8}$$

Carrying out the δ-function integration results in

$$K_2 = 4\pi(e^4/\hbar c^2)(P/n_p^2 E_g^3) f(\hbar\omega_p/E_g), \tag{9}$$

where

$$f(\alpha) = \frac{(2\alpha-1)^{3/2}}{\alpha^3}\left\{\frac{4}{45}\,3^{3/2}\left[\left(\frac{2}{\alpha}-\frac{1}{3\alpha-1}\right)^2+\frac{1}{(3\alpha-1)^2}\right](4\alpha-1)\alpha^{3/2}+\frac{2}{15}\left(\frac{3}{2}\right)^{3/2}\alpha(2\alpha+1)^{3/2}\right\}. \tag{10}$$

Thus we have a universal curve for the frequency dependence of K_2, within the stated approximations. The curve is scaled only by the factor $Pn_p^{-2}E_g^{-3}$. It may be noted, furthermore, that P is constant for zinc-blende semiconductors to within about 6%. In plotting results we take values for the room-temperature dielectric constant from the literature.[9]

K_2 is plotted in Fig. 2; the dramatic divergence from the parabolic approximation, for which

$$f(\alpha) = \tfrac{16}{45}\,3^{3/2}[(2\alpha-1)^{3/2}/\alpha^{7/2}](4\alpha-1), \tag{11}$$

is noted.

Also shown is the calculation for the other limiting extreme in which the spin-orbit splitting Δ is taken as zero. As there is then no spin mixing in the valence band one can consider as eigenstates along the k_z axis $(S - iPkZ/E_g)$, X, Y, and $(Z - iPkS/E_g)$, spin up or spin down. There are then six terms in $\sum_f$ each containing at least two contributions in $\sum_t$. The resulting two-photon absorption coefficient is, however, very similar to the large-Δ limit, Eq. (9), with

$$f(\alpha) = \frac{(2\alpha-1)^{3/2}}{\alpha^3}\,\frac{2}{15}\left[\left(\frac{2}{\alpha}-\frac{1}{3\alpha-1}\right)^2(4\alpha-1)(2\alpha)^{3/2}+2(2\alpha+1)^{3/2}\right]. \tag{12}$$

Points on the figure refer to experimental determination of K_2 by Miller *et al.*[10] and Bechtel and Smith.[11] These show better agreement with the present nonparabloic-model than with the parabolic-model calculations.

There are various other reports of experimental evaluations in the literature. Firstly, we note that Bechtel and Smith obtain for ZnTe a value of 0.008 cm MW^{-1}, which scales to 14 cm MW^{-1} in Fig. 2. However, this result was obtained at a two-photon energy only marginally above the ZnTe band gap. As Lee and Fan[2] have shown, exciton effects play an important role in ZnTe at the band gap. Secondly, we are in accord with Ref. 11 that the apparent two-photon coefficient is strongly affected by experimental technique. If the laser pulses are not reproduced accurately; then somewhat larger coefficients may be inferred than the true values; indeed several larger values have been reported.[2,12] In contrast an anomalously low value of K_2 for InSb reported previously by one group[4] appears to be associated with the fact that material of conduction-electron concentration $>10^{17}$ cm^{-3} was used; this produces significant band filling for small-gap materials, hence reducing K_2, and gives rise to strong nonlinear refractive effects that were not accounted for in the experiment.

In conclusion we have demonstrated a basic frequency dependence of K_2. Agreement with experimental results is obtained for compounds whose energy gaps vary from 0.18 eV (InSb) to 1.5 eV (CdTe). At two-photon energies significantly greater than E_g the parabolic-band model has been shown to be seriously in error.

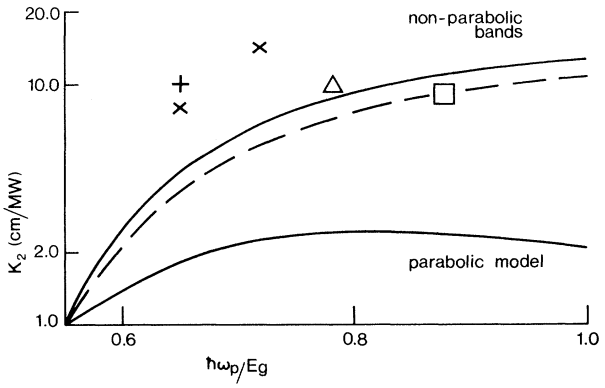

FIG. 2. The two-photon absorption coefficient, K_2, of InSb at room temperature calculated for nonparabolic bands, emphasizing the increase at high photon energies with respect to the parabolic model. Full lines are for the situation $\Delta \gg E_g$, while the dashed line is the result for the opposite extreme, $\Delta = 0$. Symbols indicate experimental results scaled by the factor $(n_p^2 E_g^3)/(n_p^2 E_g^3)_{InSb}$. The symbols crosses and plus refer to results obtained by us for InSb and $Hg_{0.78}Cd_{0.20}Te$ (Ref. 10), with the same room-temperature band gap ($E_g = 0.18$ eV). Square and triangle are for GaAs ($E_g = 1.35$ eV) and CdTe ($E_g = 1.5$ eV) (Ref. 11) scaled by factors 350 and 394, respectively.

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Angular Momentum of the Cosmic Background Radiation

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The effect of a nontrivial conserved isotropic total angular momentum $M^2 = m_x^2 + m_y^2 + m_z^2$ on the equilibrium distribution of energy in a photon gas is examined. It is shown that the correspondingly modified Planck law takes the form

$$F(\nu) = \text{const}\,\nu\gamma^{-1}\ln[(1-e^{-\beta\nu-\gamma\nu^2})/(1-e^{-\beta\nu})],$$

where β and γ are parameters determined by the energy and angular momentum. This law provides a good fit to the spectrum of the cosmic background radiation observed by Woody and Richards.

Woody and Richards[1] have reported new measurements of the cosmic background radiation (CBR) out to 40 cm^{-1}, and noted deviations from a simple blackbody law which are significant at the 5σ level. The possibility of deviations arising from a nontrivial isotropic angular momentum for the CBR had been noted earlier in the chronometric cosmology (for which see Segal[2]), and it is natural, therefore, to explore this possibility and to compare its implications with the recent observations.

More specifically, in the chronometric cosmology, the CBR prediction arises from the temporal homogeneity of the theory, which implies energy conservation, together with the maximization of randomness as measured by the entropy. In accordance with general statistical mechanics, this yields the Planck law (cf. Mayer[3]), but the possibility remains open *a priori* that other conserved quantities may exist, and modify the result correspondingly, which would then not appear as a simple blackbody law. Thus, if in addition to the energy H, the quantities $K_1, K_2, \ldots$ are conserved, then maximization of entropy with these constraints leads to the density matrix $D = C \times \exp[-(\beta H + \gamma_1 K_1 + \gamma_2 K_2 + \ldots)]$, where C is a nor-

