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Four-Photon Transitions in Semiconductors

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ABSTRACT. The four-photon interband electronic transitions have been theoretically investigated in semiconductors. Expressions for the absorption of four-photons are calculated using fourth-order perturbation theory through four different band models. The results show that the five-band model gives the dominant contribution to the absorption coefficient. A numerical application for the case of ZnS is in agreement with the available experimental results.

As laser sources of high intensity are now available, multiphoton spectroscopy is becoming very important in studying the electronic structure of solids. A detailed analysis of the two-photon interband transition rate has been performed both theoretically and experimentally (see for instance the review articles of Worlock 1972, Bassani 1972, Denisov and Makarov, 1973).

Three-photon interband transitions in semiconductors were investigated theoretically by Bassani and Hassan (1972) and Yee (1972) on the basis of semiclassical treatment of photons. Adopting a four-band model, the results were found to be analogous to those for one-photon processes with the same parity selection rules. The results of Bassani and Hassan (1972) have been confirmed experimentally in the case of CdS by Asjkinadze (1969) and Catalano *et al.* (1974 a and b).

The purpose of this work was to compute the rate of transition for electronic interband

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transitions by absorbing four photons in semiconductors. Two different types of band models have been adopted. Using first, only the initial valence and the final conduction bands as a two-band model. The four matrix elements, in this case, are all forbidden except one which couples those two bands. On the other hand, by increasing the number of bands, taking other valence or conduction bands as intermediate states, one has, in this case, three-, four-, and five-band models depending on the number of intermediate states included. The number of forbidden matrix elements depends on the number of intermediate states used. Finally, we compare the results obtained with the available experimental data for ZnS crystal. The results show that, the five-band model gives results in good agreement with the experimental observation.

General Formalism

From fourth-order time-dependent perturbation theory, the probability amplitude for an electron to make a transition from state v of the valence band to state c of the conduction band can be written in the form:

$$a_{cv} = (-i/\hbar)^4 \sum_{n_1 n_2 n_3} \int_0^t dt_1 \mathcal{H}'_{cn_1}(t_1) \int_0^{t_1} dt_2 \mathcal{H}'_{n_1 n_2}(t_2)$$

$$\cdot \int_0^{t_2} dt_3 \mathcal{H}'_{n_2 n_3}(t_3) \int_0^{t_3} dt_4 \mathcal{H}'_{n_3 v}(t_4),$$

where $\mathcal{H}'_{cn_1}$, $\mathcal{H}'_{n_1 n_2}$, $\mathcal{H}'_{n_2 n_3}$ and $\mathcal{H}'_{n_3 v}$ are the electron-photon matrix elements between states v and c and the n's intermediate states due to the perturbation Hamiltonian of the photons.

$$\mathcal{H}' = \frac{e}{mc} (\underline{A}_1.\underline{P} + \underline{A}_2.\underline{P} + \underline{A}_3.\underline{P} + \underline{A}_4.\underline{P}),$$

where the vector potentials of the electromagnetic fields are

$$A_j = A_{oj}\, \underline{\epsilon}_j \exp[i(\underline{\eta}_j.\underline{r}.\omega_j t)] + cc,$$

where $j = 1,2,3,4$, $\underline{\eta}_j$ being the wave vectors of the photons, ω_j their angular frequencies and $\underline{\epsilon}_j$ their polarizations. We do not consider the nonlinear effect due to the terms A^2 in first order because it contributes much less at the wavelength of interest here.

We obtain, the following expression for the transition rate taking into account the different permutations of the four photons 1,2,3 and 4.

$$W_{cv} = \frac{d}{dt} |a_{cv}|^2$$

$$= \frac{2\pi}{\hbar} \left(\frac{e}{mc}\right)^8 |A_{o1} A_{o2} A_{o3} A_{o4}|^2 \sum_n$$

$$\left[\frac{(1+P_{23} + P_{23}P_{34} + P_{34} + P_{34}P_{23} + P_{24})\underline{M}_{cv}^{(1)}}{(E_{n_3} - E_v - \hbar\omega_4)(E_{n_2} - E_v - \hbar\omega_3 - \hbar\omega_4)(E_{n_1} - E_v - \hbar\omega_2 - \hbar\omega_3 - \hbar\omega_4)} + \right.$$

$$+\frac{(1+P_{34}+P_{34}P_{41}+P_{41}+P_{41}P_{34}+P_{31})\,\underline{M}_{cv}^{(2)}}{(E_{n_3}-E_v-\hbar\omega_1)(E_{n_2}-E_v-\hbar\omega_4-\hbar\omega_1)(E_{n_1}-E_v-\hbar\omega_3-\hbar\omega_4-\hbar\omega_1)}+$$

$$+\frac{(1+P_{21}+P_{21}P_{14}+P_{14}+P_{14}P_{21}+P_{24})\underline{M}_{cv}^{(3)}}{(E_{n_3}-E_v-\hbar\omega_4)(E_{n_2}-E_v-\hbar\omega_1-\hbar\omega_4)(E_{n_1}-E_v-\hbar\omega_2-\hbar\omega_1-\hbar\omega_4)}+$$

$$+\frac{(1+P_{32}+P_{32}P_{21}+P_{21}+P_{21}P_{32}+P_{31})\underline{M}_{cv}^{(4)}}{(E_{n_3}-E_v-\hbar\omega_1)(E_{n_2}-E_v-\hbar\omega_2-\hbar\omega_1)(E_{n_1}-E_v-\hbar\omega_3-\hbar\omega_2-\hbar\omega_1)}]|^2\times$$

$$\times\ \delta(E_c-E_v-\hbar\omega_1-\hbar\omega_2-\hbar\omega_3-\hbar\omega_4) \tag{1}$$

where $\underline{M}_{cv}$ are the product of four electron-photon matrix elements of different permutations and P_{ij} exchanges photon $\hbar\omega_i$ with photon $\hbar\omega_j$. The other symbols have the usual meaning.

The absorption coefficient of photon $\hbar\omega_1$ becomes

$$\alpha_{cv}(\omega_1)=\frac{2n_1}{N_1 c}\int\frac{d\underline{k}}{(2\pi)^3}\,W_{cv} \tag{2}$$

where n_1 and N_1 are the refractive index and the photon density respectively.

Explicit Expressions and Band Models

We wish to perform the integrals indicated in expression (2) under the assumption of spherical valence and conduction bands, centered at the same point of the Brillouin zone. We expand the energies retaining only quadratic terms and we can write:

$$E_v=-\alpha_v\underline{K}^2,$$
$$E_c=E_g+\alpha_c\underline{K}^2,$$
$$E_{n_s'}=\Delta_{n_s'}-\alpha_{n_s'}\underline{K}^2,$$

where $\alpha_i=\dfrac{\hbar^2}{2\,m_i^*}$ are the inverse effective masses and the energies are referred to the top of the valence band.

a) Five-band Model

In this case, the summation over the intermediate states reduces to three intermediate conduction or valence states (see Fig. 1a). All the electro-photon matrix elements are

allowed and the product matrix $\underline{M}_{cv}$ becomes:

$$|\underline{M}_{cv}^{(1)}| = |\underline{P}_{cn_1}^{(1)} \underline{P}_{n_1n_2}^{(2)} \underline{P}_{n_2n_3}^{(3)} \underline{P}_{n_3v}^{(4)}|$$

where,

$$\underline{P}_{jk}^{(1)} = <j|\underline{\epsilon}_i.\underline{P}|\underline{k}> ,$$

are the dipole matrix elements and $\underline{\epsilon}_j$ are the photon polarizations.

The result of the integration of equation (2) is:

$$\alpha_{cv}(\omega_1) = 3C_1|\Gamma|^2(\hbar\omega_1 + \hbar\omega_2 + \hbar\omega_3 + \hbar\omega_4 - E_g)^{1/2} \tag{3}$$

where,

$$\Gamma = \left| \frac{(1 + P_{23} + P_{23}P_{34} + P_{34} + P_{34}P_{23} + P_{24})\underline{M}_{cv}^{(1)}}{(\triangle_{n_3} + \beta_3\Gamma - \hbar\omega_4)(\triangle_{n_2} + \beta_2\Gamma - \hbar\omega_3 - \hbar\omega_4)(\triangle_{n_1} + \beta_1\Gamma - \hbar\omega_2 - \hbar\omega_3 - \hbar\omega_4)} + \right.$$

$$+ \frac{(1 + P_{34} + P_{34}P_{41} + P_{41} + P_{41}P_{34} + P_{31})\underline{M}_{cv}^{(2)}}{(\triangle_{n_3} + \beta_3\Gamma - \hbar\omega_1)(\triangle_{n_2} + \beta_2\Gamma - \hbar\omega_4 - \hbar\omega_1)(\triangle_{n_1} + \beta_1\Gamma - \hbar\omega_3 - \hbar\omega_4 - \hbar\omega_1)} +$$

$$+ \frac{(1 + P_{21} + P_{21}P_{14} + P_{14} + P_{14}P_{21} + P_{24})\underline{M}_{cv}^{(3)}}{(\triangle_{n_3} + \beta_3\Gamma - \hbar\omega_4)(\triangle_{n_2} + \beta_2\Gamma - \hbar\omega_1 - \hbar\omega_4)(\triangle_{n_1} + \beta\Gamma - \hbar\omega_1 - \hbar\omega_2 - \hbar\omega_4)} +$$

$$\left. + \frac{(1 + P_{32} + P_{32}P_{21} + P_{21} + P_{21}P_{32} + P_{31})\underline{M}_{cv}^{(4)}}{(\triangle_{n_3} + \beta_3\Gamma - \hbar\omega_1)(\triangle_{n_2} + \beta_2\Gamma - \hbar\omega_1 - \hbar\omega_2)(\triangle_{n_1} + \beta_1\Gamma - \hbar\omega_1 - \hbar\omega_2 - \hbar\omega_3)} \right|$$

where,

$$\beta_i = \left(\frac{\alpha_{n_1} + \alpha_v}{(\alpha_c + \alpha_v)} \right) \text{ and}$$

$$C_1 = \frac{16\pi^3\hbar^3e^8\, N_2N_3N_4}{n_1n_2^2n_3^2n_4^2\, m^8c\omega_1\omega_2\omega_3\omega_4\, (\alpha_c + \alpha_v)^{3/2}}$$

the number 3 related to the number of coupling processes.

b) Four-band Model

Here, one of the four photon matrix elements is forbidden. The three allowed matrix

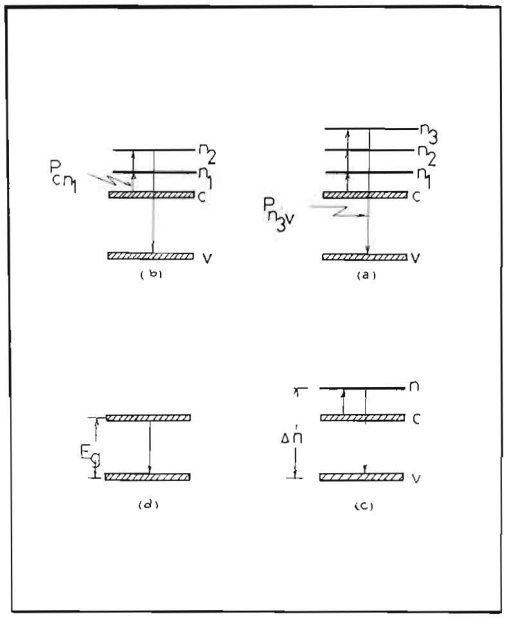

Fig. 1. A schematic diagrams representing the five- (a), four- (b), and three- (c), and two- (d) band models. The arrows indicate the coupling matrix elements.

elements couple the valence and conduction band to two intermediate states (see Fig. 1b), so that:

$$\underline{M}_{cv}^{(1)} = |\underline{P}_{cn_1}^{(1)}\ \underline{P}_{n_1n_2}^{(2)}\ \underline{P}_{n_2v}^{(3)}|$$

and the four-photon absorption coefficient becomes:

$$\alpha_{cv}(\omega_1) = 2C_2|\ \Gamma\ |^2(\hbar\omega_1 + \hbar\omega_2 + \hbar\omega_3 + \hbar\omega_4 - E_g)^{3/2} \tag{4}$$

where

$$C_2 = \frac{16\pi^3\,\hbar^5 e^8\ N_2N_3N_4}{n_1n_2^2n_3^2n_4^2m^8c\omega_1\omega_2\omega_3\omega_4\ (\alpha_c + \alpha_v)^{5/2}}$$

c) Three-band Model

This model contains the valence, conduction and only one intermediate band as indicated in Fig. 1c. The product $\underline{M}_{cv}$ is:

$$\underline{M}_{cv}^{(1)} = |\underline{P}_{cn}^{(1)}\ \underline{P}_{nv}^{(2)}|$$

and by integration we get:

$$\alpha_{cv}(\omega_1) = C_3 |\Gamma|^2 (\hbar\omega_1 + \hbar\omega_2 + \hbar\omega_3 + \hbar\omega_4 - E_g)^{5/2} \tag{5}$$

where

$$C_3 = \frac{16\pi^3 \hbar^7 e^8 N_2 N_3 N_4}{n_1 n_2^2 n_3^2 n_4^2 m^8 c \omega_1 \omega_2 \omega_3 \omega_4 (\alpha_c + \alpha_v)^{7/2}}$$

d) Two-band Model

The summation over the intermediate states, in this case, is cancelled out (see Fig. 1d). We have only the valence and conduction bands. The product matrix $\underline{M}_{cv}$ reduces to $|\underline{M}_{cv}^{(1)}| = |\underline{P}_{cv}^{(1)}|$, *i.e.*, only one-photon matrix element is allowed which couple these two bands. The four-photon absorption coefficient is then,

$$\alpha_{cv}(\omega_1) = C_4 |\Gamma|^2 (\hbar\omega_1 + \hbar\omega_2 + \hbar\omega_3 + \hbar\omega_4 - E_g)^{7/2} \tag{6}$$

where

$$C_4 = \frac{16\pi^3 \hbar^9 e^8 N_2 N_3 N_4}{n_1 n_2^2 n_3^2 n_4^2 m^8 c \omega_1 \omega_2 \omega_3 \omega_4 (\alpha_c + \alpha_v)^{9/2}}$$

Selection Rules

The knowledge of the photon matrix elements is required to obtain numerical values to be compared with experimental results. Some preliminary results, however, can be obtained from the symmetry properties of the crystal without explicit calculation of the crystal wave functions. It is possible to decide if the matrix elements are zero or different from zero and consequently to establish selection rules which exclude some intermediate states. The general rules to be followed are the same as in the first-, second-, and third-order processes and are well discussed in the literature by Tinkham (1964).

In deriving expressions (3) to (6), we have already used the basic selection rule of the dipole approximation $\triangle \underline{k} = 0$ for the matrix elements of the radiation field. In addition, we have other selection rules due to the rotational symmetry of the perturbation operator and of the wave functions. Every matrix elements $< \psi^{\alpha} \; 0^{\gamma} \; \psi^{\beta} >$ is different from zero only when the product of the irreducible representation γ times the irreducible representation ß contains the irreducible representation α of the other function. For instance, in a crystal with inversion symmetry, four-photon transitions are allowed only between states of the same parity, because the operator $\underline{P}$ is odd and it has non-zero matrix elements only between states of different parity.

The selection rules will depend on the polarization of the radiation, and this will produce a dependence of the absorption on the angles $\hbar$ that the polarization vectors make with the optical axis and with each other.

Application to Cubic ZnS and Discussion

An indirect quantitative method (by Catalano *et al.* (1975)) based on nonlinear photoconductivity has been applied to the measurement of the four-photon nonlinear cross-section in ZnS. This is obtained by comparing the photocurrent induced by three- and four-photon absorption using two different wavelengths. From this experiment, one obtains for the four-photon absorption coefficient the value 2×10^{-13} cm^{-1}.

The ZnS crystal does not have inversion symmetry, so that contribution from all the band models are permitted. However, the energy dependence and the numerical values of the matrix elements control which model gives the dominant contribution. It is clear from the above expression that the five-band model provides the largest contribution.

To make a comparison between our theoretical results and the above experimental data, it is convenient to use photons of the same frequency. Therefore, expression (3) becomes:

$$\alpha_{cv} = \frac{C_1'|\underline{M}_{cv}|^2 (4\hbar\omega - E_{\hbar})^{1/2}}{\{[\triangle n_3 + \beta_3(4\hbar\omega - E_g) - \hbar\omega][\triangle_{n_2} + \beta_2(4\hbar\omega - E_g) - 2\hbar\omega][\triangle_{n_1} + \beta_1(4\hbar\omega - E_g) - 3\hbar\omega]\}^2} \tag{7}$$

where

$$C_1' = \frac{1152\pi^3 \hbar^3 e^8 N^3}{cn^7 m^8 \omega^4 (\alpha_c + \alpha_v)^{3/2}}$$

Using the band parameters for ZnS, we obtained for $\alpha_{cv}(\omega)$ the value 1.6×10^{-13} cm^{-1} where an Nd-laser ($h\omega = 1.17$ eV and $N = 3 \times 10^{-15}$ cm^{-1}) has been used with a value of the electron-photon matrix element (see Bassani and Hassan 1972) of 3.56×10^{-38} erg.g. The above theoretical value for the four-photon absorption coefficient is in good agreement with the experimental results by Catalano *et al.* (1975) in ZnS crystal. Figure 2 shows this relation between our theoretical calculations and the experimental data by Catalano *et al.* (1975) adapted to our functions.

Conclusion

To conclude, we wish to emphasize that for obtaining values of the absorption coefficient within the range of the experimental observations, one must apply a perturbative method adopting a five-band model where all the photon-matrix elements are allowed. Other band models by Yee (1971) or quantum treatment by Kovarski and Yu Perlin (1971) give values at least two orders of magnitude smaller than the experimental value by Catalano *et al.* (1975).

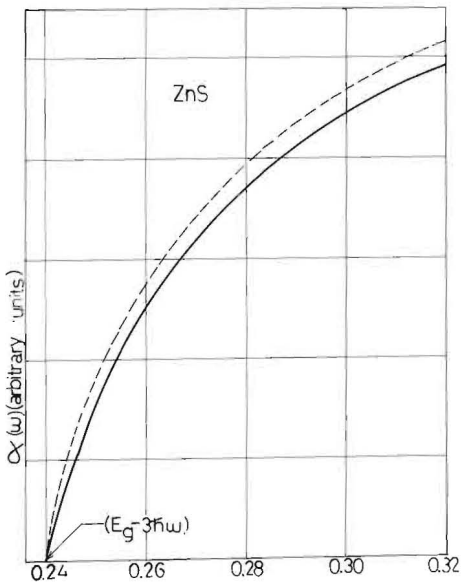

Fig. 2. Behaviour of the four-photon absorption coefficient as a function of the photon energy for the case of ZnS. The solid curve is the theoretical calculation and the dashed curve is the experimental data by Catalano *et al.* (1975).

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الانتقالات الرباعية الفوتونات في أشباه الموصلات

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درست الانتقالات الإلكترونية عبر الطبقات المصحوبة بامتصاص أربعة فوتونات في أشباه الموصلات نظرياً. وقد حسبت معادلات معاملات الامتصاص من خلال أربعة نماذج مختلفة للطبقات. أوضحت النتائج أن النموذج الخماسي الطبقات يعطي القيمة الأعلى لمعامل الامتصاص.

أعطى التطبيق العددي في حالة كبريتيد الزنك نتائج متفقة مع التجارب المعملية المتاحة.

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