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Theory for two-beam two-photon photoconductivity in solids and its application to ZnS crystals*

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A theory for two-beam two-photon photoconductivity is presented that explains most of the features of the two-beam two-photon conductivity measurements recently reported by Koren and Yacoby in ZnS.

The advent of the high-power laser has stimulated considerable work on multiple-photon photoconductivity in both semiconductors and insulators.[1-5] In the work discussed here, a study was made of changes in conductivity as a function of intensity and pulse width.[4] The change in conductivity as a function of intensity can be used to determine A_n, the basic parameter of multiple-photon absorption, which is related to the absorption coefficient $\alpha = n\hbar\omega A_n I^{n-1}$. The experiments just cited were performed with one laser beam. More recently, two-photon photoconductivity using two laser beams was reported by Koren and Yacoby.[6] They were not only able to measure the change in conductivity as a function of intensity, but also the change in conductivity as a function of one of the laser lights. In the present paper we present a theory for two-beam two-photon photoconductivity and use this theory to explain the experimental results of Koren and Yacoby (KY).

When the excitation of a laser beam is not too high, say below 20 MW/cm^2, the experimental evidence shows that the recently developed theory[5,7] explains two-photon photoconductivity quite well.[3,7] According to this theory, the change in conductance for any type of excitation can be written

$$\Delta G \cong \left(\frac{a}{c}\right)(\mu_e + \mu_p) e\tau \int_0^L F(x)\, dx, \tag{1}$$

where μ_e and μ_p are the mobility of the electrons and holes, respectively, and τ is the lifetime of the free carriers. Other variables occurring in Eq. (1) are defined in Fig. 1, while F is any type of generation rate. In the two-beam two-photon case, the generation rate can be written in the form[7]

$$W = F = \alpha_{11}[I_1(x)]^2 + \alpha_{22}[I_2(x)]^2 + \alpha_{12} I_1(x) I_2(x), \tag{2}$$

where I_1 and I_2 are the intensities of the two laser beams in the solid and where they satisfy the following differential equations:

$$\frac{dI_1}{dx} = -(2\alpha_{11} I_1^2 + \alpha_{12} I_1 I_2)\hbar\omega_1, \tag{3}$$

$$\frac{dI_2}{dx} = -(\alpha_{21} I_1 I_2 + 2\alpha_{22} I_2^2)\hbar\omega_2, \tag{4}$$

$$\alpha_{21} = \alpha_{12}.$$

Equations (3) and (4) are nonlinear differential equations, and they are very difficult to solve. But in the case where $2\hbar\omega_2 < E_g$ and $I_2 \gg I_1$, we may ignore both the first term in Eq. (3) and the second term in Eq. (4), giving

$$\frac{dI_1}{dx} \cong -\alpha_{12} I_1 I_2 \hbar\omega_1, \tag{5}$$

$$\frac{dI_2}{dx} \cong -\alpha_{21} I_1 I_2 \hbar\omega_2. \tag{6}$$

Coefficient α_{12} is related to the transition probability by the expression

$$\begin{aligned} W &= \alpha_{12} I_1 I_2 \\ &= \sum_{E_f} \sum_{E_i} \left| \sum \frac{\langle f|\vec{A}_1\cdot\vec{p}|m\rangle\langle m|\vec{A}_2\cdot\vec{p}|i\rangle}{E_m - E_i - \hbar\omega_2} + \sum_m \frac{\langle f|\vec{A}_2\cdot\vec{p}|m\rangle\langle m|\vec{A}_1\cdot\vec{p}|i\rangle^2}{E_m - E_i - \hbar\omega_1} \right|^2 \\ &\quad \times \delta(E_f - E_i - \hbar\omega_1 - \hbar\omega_2). \end{aligned} \tag{7}$$

Equations (5) and (6) can readily be solved as

$$I_1(x) = \frac{I_1^0(1-R)e^{\hbar\omega_2 C_1 \alpha_{12} x}}{1 + [I_1^0(1-R)/C_1][e^{\hbar\omega_2 C_1 \alpha_{12} x} - 1]} \tag{8}$$

and

$$I_2(x) = \frac{I_2^0(1-R)e^{-\hbar\omega_2 C_1 \alpha_{12} x}}{1 - [I_2^0(1-R)/C_1'][e^{-\hbar\omega_2 C_1 \alpha_{12} x} - 1]} \tag{9}$$

where

$$C_1 = (1-R)[I_1^0 - (\hbar\omega_1/\hbar\omega_2) I_2^0]$$

and

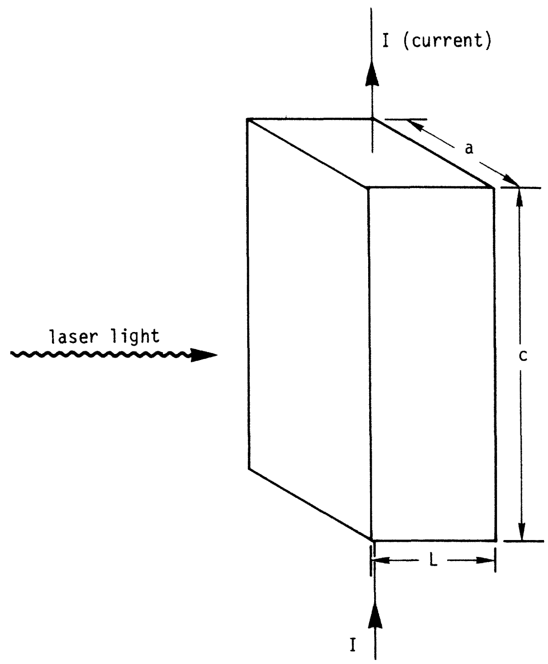

FIG. 1. Crystal geometry used in the derivation of Eq. (1).

$$C_1' = (\hbar\omega_2/\hbar\omega_1)C_1 .$$

After substituting the intensities given in Eqs. (8) and (9) into (1), we obtain

$$\Delta G = \frac{\tau(a/c)e(\mu_e+\mu_p)I_1^0 I_2^0(1-R)(e^{\hbar\omega_2 C_1\alpha_{12}L}-1)}{\hbar\omega_2 I_1^0 \exp(\hbar\omega_2 C_1\alpha_{12}L) - \hbar\omega_1 I_2^0} \qquad (10)$$

In the case in which $1 > \hbar\omega_2 C_1\alpha_{12}L$, Eq. (10) becomes

$$\Delta G \cong \alpha_{12}\tau(a/c)e(\mu_e+\mu_p)I_1^0 I_2^0(1-R)^2 \times [L - \tfrac{1}{2}L^2(1-R)\alpha_{12}(\hbar\omega_2 I_1^0 + \hbar\omega_1 I_2^0)] \qquad (11)$$

For a general band structure, α_{12} is very difficult to evaluate. We shall therefore limit our work to cubic crystals, whose wave functions for conduction and valence bands can be approximated by Kane's wave functions[8] at $k=0$:

conduction band:

$$\psi_{c_1} = |iS^1\uparrow\rangle', \quad \psi_{c_2} = |iS^1\downarrow\rangle';$$

valence band V_1:

$$\psi_{v_1} = [(X-iY)\downarrow]'/\sqrt{2}, \quad \psi_{v_2} = [(X+iY)\uparrow]'/\sqrt{2},$$

valence band V_2:

$$\begin{aligned}
\psi_{v_2^1} &= (\tfrac{1}{3})^{1/2}[(X-iY)\uparrow]'/\sqrt{2} + (\tfrac{2}{3})^{1/2}(Z^1\downarrow)', \\
\psi_{v_2^2} &= (\tfrac{1}{3})^{1/2}[-(X+iY)\downarrow]'/\sqrt{2} + (\tfrac{2}{3})^{1/2}(Z^1\uparrow)', \\
\psi_{v_3^1} &= (\tfrac{2}{3})^{1/2}[(X-iY)\uparrow]'/\sqrt{2} - (\tfrac{1}{3})^{1/2}(Z^1\downarrow)', \\
\psi_{v_3^2} &= (\tfrac{2}{3})^{1/2}[-(X+iY)\downarrow]'/\sqrt{2} - (\tfrac{1}{3})^{1/2}(Z^1\uparrow)';
\end{aligned} \qquad (12)$$

and

$$\begin{bmatrix} \uparrow' \\ \downarrow' \end{bmatrix} = \begin{bmatrix} e^{-i\phi'/2}\cos\frac{1}{2}\theta' & e^{i\phi'/2}\sin\frac{1}{2}\theta' \\ -e^{-i\phi'/2}\sin\frac{1}{2}\theta' & e^{i\phi'/2}\cos\frac{1}{2}\theta' \end{bmatrix} \begin{bmatrix} \uparrow \\ \downarrow \end{bmatrix},$$

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta'\cos\phi' & \cos\theta'\sin\phi' & -\sin\theta' \\ -\sin\phi' & \cos\phi' & 0 \\ \sin\theta'\cos\phi' & \sin\theta'\sin\phi' & \cos\theta' \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}, \quad S' = S.$$

The angles θ', ϕ' are the usual polar angles of the k vector referred to the crystal symmetry axes x, y, and z with θ' measured from z and ϕ' measured from x.

Substituting the wave functions given in Eq. (12) into (7), we obtain the following results for the coefficient α_{12}:

$$\begin{aligned}
\alpha_{12}(\hbar\omega_1\hbar\omega_2) = {} & \left(\frac{2^{9/2}\pi}{15}\right)\left(\frac{e^4}{m^2}\right)\left(\frac{\hbar^2}{c^2}\right)\left(\frac{1}{\epsilon_1\epsilon_2}\right)^{1/2}\left(\frac{1}{\hbar\omega_1}\right)^2\left(\frac{1}{\hbar\omega_2}\right)^2 \left|\langle s|\frac{\partial}{\partial x}|x\rangle\right|^2 \\
& \times\Bigg\{(m_{cv_1})^{1/2}(\hbar\omega_1+\hbar\omega_2-E_{g_1})^{3/2}\left[(2-\cos^2\theta)\left(\frac{1}{(\hbar\omega_1)^2}+\frac{1}{(\hbar\omega_2)^2}\right)+\left(\frac{1}{\hbar\omega_1}\right)\left(\frac{1}{\hbar\omega_2}\right)(3\cos^2\theta-1)\right] \\
& + (m_{cv_2})^{1/2}(\hbar\omega_1+\hbar\omega_2-E_{g_2})^{3/2}\left[\frac{2}{3}\left(\frac{1}{(\hbar\omega_1)^2}+\frac{1}{(\hbar\omega_2)^2}\right)(2+\tfrac{3}{2}\cos^2\theta)+\frac{1}{3}\left(\frac{1}{\hbar\omega_2}\right)\left(\frac{1}{\hbar\omega_1}\right)(11\cos^2\theta+3)\right] \\
& + \tfrac{5}{3}(m_{cv_3})^{1/2}(\hbar\omega_1+\hbar\omega_2-E_{g_3})^{3/2}\left[\left(\frac{1}{\hbar\omega_1}\right)^2+\left(\frac{1}{\hbar\omega_2}\right)^2+\frac{2\cos^2\theta}{\hbar\omega_1\hbar\omega_2}\right]\Bigg\},
\end{aligned} \qquad (13)$$

where c is the velocity of the light, m is the mass of a free electron, ϵ_1, ϵ_2 are dielectric constants of the medium, and

$$1/m_{cv_i} = 1/m_c + 1/m_{v_i} \quad (i = 1, 2, 3),$$

where m_{v_1}, m_{v_2}, and m_{v_3} are the effective masses of the holes in the valence bands V_1, V_2, and V_3, respectively. The θ in Eq. (13) is the angle between the two polarization vectors of the two linearly polarized beams.

Equation (13) is for the case where one linearly polarized light beam interacts with another linearly polarized light beam of a different frequency. For the case where one or both of the light beams is randomly polarized, one must average α_{12} over the angles of the random polarized beams to obtain a correct α_{12}, which we call $(\alpha_{12})_A$. After a few simple calculations it can be shown that in both of these cases $(\alpha_{12})_A$ can be obtained from Eq. (13) by simply replacing $\cos^2\theta$ by $\frac{1}{3}$.

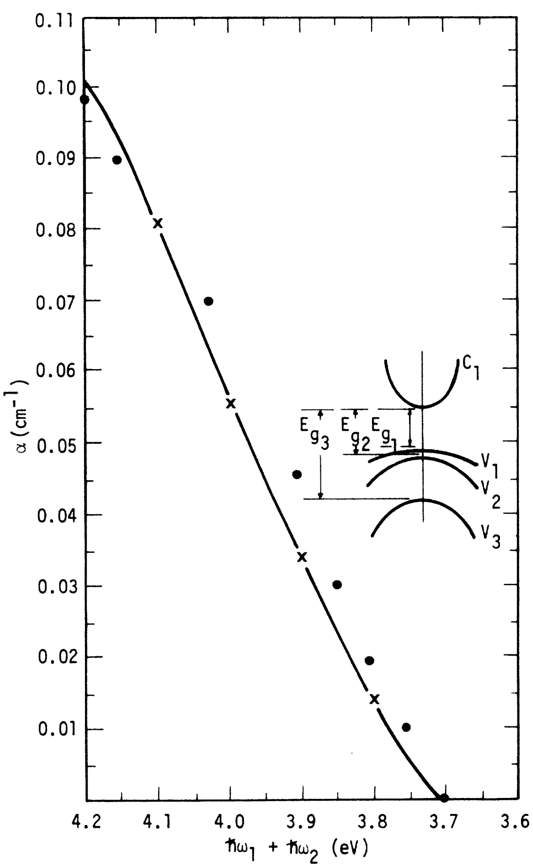

FIG. 2. Comparison between the two-photon absorption coefficient α as a function of $\hbar\omega_1 + \hbar\omega_2$, obtained from the experimental results (points) of Ref. 9, and the theoretical results (line and crosses) of $\alpha = \hbar\omega_1(\alpha_{12})_A I_2^0 \times (1-R)$, for $\hbar\omega_1 = 1.17$ eV, and for $m_{cv_i} = 0.34m$ $(i = 1, 2, 3)$.

Both of the light beams are randomly polarized, in the experiment of KY. Hence, we have to use $(\alpha_{12})_A$ in Eq. (10) for the photoconductivity

$$\Delta G = KeI_2^0(1-R)^2(\eta_1\hbar\omega_1 c)(\alpha_{12})_A \times [1 - \tfrac{1}{2}L(1-R)(\alpha_{12})_A(\hbar\omega_1 I_2^0 + \hbar\omega_2 I_1^0)], \quad (14)$$

where

$$K = \tau(\mu_e + \mu_p)La/c,$$

and η_1 is the number of photons per cm^3 with energy $\hbar\omega_1$.

The matrix elements

$$\left|\langle s|\hbar\frac{\partial}{\partial x}|x\rangle\right|^2$$

can be obtained from the experimental absorption curve of Panizza[9] by assuming that at $\hbar\omega_1 + \hbar\omega_2 = 4.2$ eV and at $I_2^0 = 15$ MW/cm^2, the measured absorption coefficient is equal to that obtained from the equation $\alpha = \hbar\omega_1(\alpha_{12})_A I_2^0(1-R)$, i.e.,

$$\left|\langle s|\hbar\frac{\partial}{\partial x}|x\rangle\right|^2 = 1.2 \times 10^{-39}. \quad (15)$$

Using the matrix elements in Eq. (15), the theoretical plot of α as a function of $\hbar\omega_1 + \hbar\omega_2$ is shown in Fig. 2, together with the measured absorption curve.

Since the mobility and the lifetime of the carriers were not given in the work of KY, we have lumped the lifetime-mobility product together and determined it from the photoconductivity curve of KY at $\hbar\omega_1 + \hbar\omega_2 = 4.6$ eV,

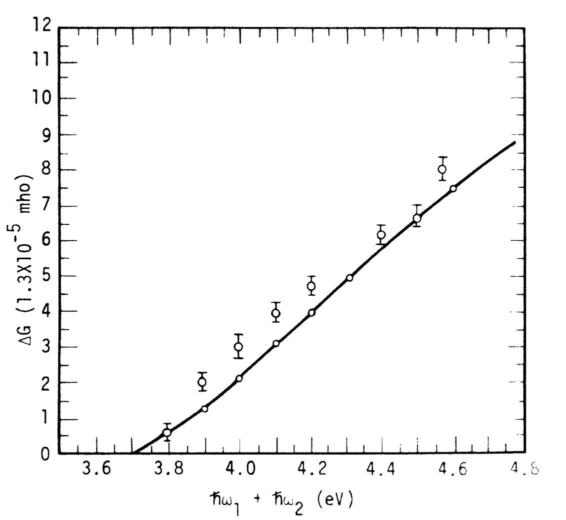

FIG. 3. Comparison between the two-photon photocunductivity ΔG as a function of $\hbar\omega_1 + \hbar\omega_2$, obtained from the experimental results (Φ) of Ref. 6, and the theoretical results (circles) of Eq. (14), for $I_2^0 = 16$ MW/cm^2, $\eta = 10^{23}$, and $m_{cv_i} = 0.34\,m\,(i = 1, 2, 3)$.

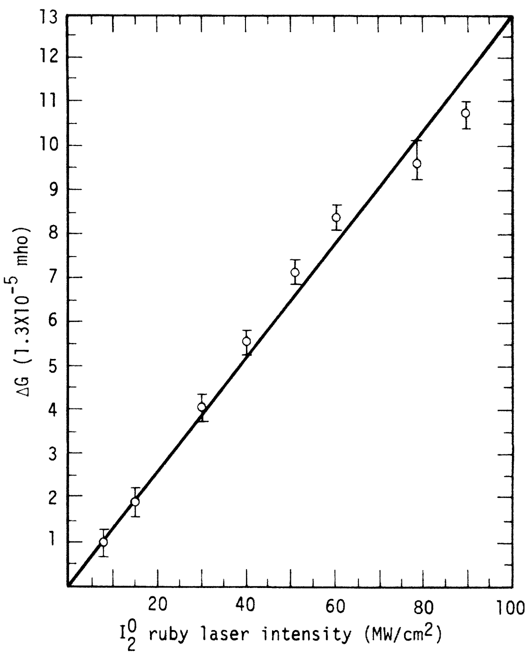

FIG. 4. Comparison between the two-photon photoconductivity ΔG as a function of the ruby laser intensity, obtained from the experimental results (circles) of Ref. 6, and the theoretical results (solid line) of Eq. (14). $\eta_1 = 10^{23}$ photons $cm^{-2} sec^{-1}$, $\hbar\omega_1 = 1.17$ eV, $\hbar\omega_2 = 2.6$ eV (dye laser).

$$K \cong 10^{-6}\ cm^2/V. \quad (16)$$

In the experiments of KY, the dimensions of a, c, and L are, 0.4, 0.1, and 30×10^{-4} cm. Therefore, $(aL/c) = 1.2\times10^{-2}$ cm. Using Eq. (15) together with K in Eq. (16), we have plotted ΔG as a function of the sum of the wavelength of the two laser beams, as a function of ruby light intensity, and as a function of the dye laser intensity. (See

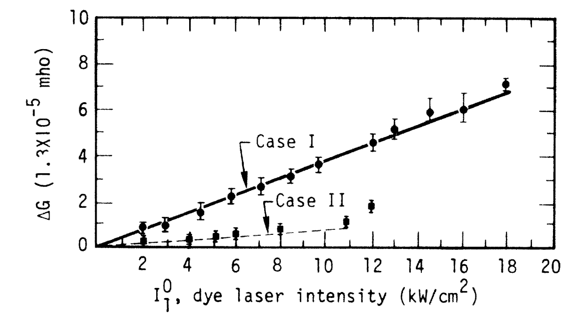

FIG. 5. Comparison between the two-photon photocunductivity ΔG as a function of the dye laser intensity at two different wavelengths, obtained from the experimental results of Ref. 6, and the theoretical results of Eq. (14), given $I_2^0 = 16$ MW/cm^2, $\hbar\omega_2 = 1.78$ eV. Case I experimental (circles) and theoretical (solid line) for $\hbar\omega_1 = 2.7$ eV; and case II experimental (squares) and theoretical (solid line) for $\hbar\omega_1 = 2.15$ eV.

Figs. 3, 4, and 5, respectively.)

Based upon the comparison between the theoretical results and those from measured values for ΔG and α, the theory presented in the present paper predicted the two-beam two-photon absorption and photoconductivity quite well for choosing the constant K. The biggest error that occurs in the present theory is a consequence of the simple model used in evaluating the coefficient α_{12}. Other errors arise from the fact that the crystal used in this experiment is not really a cubic crystal but a composite of both hexagonal and cubic structures. Hence, the present theoretical work may be too idealized for such a crystal structure.

Because of the simple band model used to calculate α_{12}, the present theory cannot explain the change in conductivity for $\hbar\omega_1 + \hbar\omega_2 > 4.6$ eV.

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