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Four-Photon Transition in Semiconductors*

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Based on a simple spherical energy-band model for the conduction and valence bands in cubic crystal, the transition probability for four-photon absorption is calculated theoretically by use of the Hartree-Fock and Hartree approximations for wave functions. These results are compared with those by Keldysh's high-frequency–limit time-dependent tunneling theory in a numerical example by applying the calculations to a ZnS crystal.

INTRODUCTION

Calculation of the multiple-photon transition probability in solids is approached in one of two ways: by perturbation theory[1,2] or by Keldysh's high-frequency–limit time-dependent tunneling theory.[3,4] When a static magnetic field is not influencing the crystals, the magnitude of transition probability and the absorption coefficient calculated by perturbation theory agree very well with the experimental result. This is confirmed by the work of Basov *et al.*[5] with two-photon excitation in GaAs crystals and that of others[6–8] with three-photon excitation in GaP and CdS. In the absence of a static field, Keldysh's theory sometimes gives a smaller value for the transition probability than perturbation theory.[5] However, when a magnetic field is applied to the crystals (as in the recent two-photon magnetoabsorption experiment by Weiler *et al.*[9]), calculations by the Keldysh approach are more accurate than those by the perturbation theory.

The question of why the two approaches differ so in describing different experimental situations is not yet resolved.[4]

To date, no detailed calculation has been made of the four-photon transition probability in semiconductors by the perturbation theory. The purpose of this paper is to present such a calculation, using the Hartree-Fock approximation for the wave functions. We include in our calculation the usually neglected term $(2m)^{-1}(e/c)^2\vec{A}\cdot\vec{A}$. In this paper we also derive the four-photon transition probability by the Hartree approximation (see Appendix), comparing results by our original calculation, the Hartree approximation, and the Keldysh theory in a numerical example. The chosen example is application of the calculations to a ZnS crystal.

When the previously neglected term is included in the perturbed Hamiltonian, the sum of all matrix elements making up the transition probability proportional to the fourth power of the excitation intensity consists of second- and third-order terms, as well as the fourth-order-term matrix element.

CALCULATIONS

The Hamiltonian for the N-particle system, when the particles are interacting with the radiation field of frequency ω, can be written as

$$H=\sum_j^N\left[\frac{-\hbar^2\nabla^2}{2m}+eV(r_j)\right]+\sum_j^N\left[\left(\frac{e}{mc}\right)\vec{A}_j^T\cdot\vec{P}_j+\frac{1}{2m}\left(\frac{e}{c}\right)^2\vec{A}_j^T\cdot\vec{A}_j^T\right],\quad H=H_0+H_1=H_0+(H_1'+H_1'') \tag{1}$$

where

$$H_1'+H_1''=\sum_j^N\left[\left(\frac{e}{mc}\right)\vec{A}_j^T\cdot\vec{P}_j+\frac{1}{2m}\left(\frac{e}{c}\right)^2\vec{A}_j^T\cdot\vec{A}_j^T\right],\quad A_j^T=A_j+A_j^*.$$

According to the time-dependent perturbation theory, the total transition probability for the four-photon absorption between a group of initial and a group of final states can be written as

$$W^4=\frac{2\pi}{\hbar}\sum_{i,k}\sum_n\left|\frac{H_{kn}''H_{ni}''}{E_{ni}-2\hbar\omega}+\sum_{n,n_1}\frac{H_{kn}''H_{nn_1}'H_{n_1i}'}{(E_{n_1i}-\hbar\omega)(E_{ni}-2\hbar\omega)}+\sum_{n,n_1}\frac{H_{kn}'H_{nn_1}''H_{n_1i}'}{(E_{n_1i}-\hbar\omega)(E_{ni}-3\hbar\omega)}+\sum_{n,n_1}\frac{H_{kn}'H_{nn_1}'H_{n_1i}''}{(E_{n_1i}-2\hbar\omega)(E_{ni}-3\hbar\omega)}\right.$$
$$\left.-\sum_{n,n_1,n_2}\frac{H_{kn}'H_{nn_1}'H_{n_1n_2}'H_{n_2i}'}{(E_{n_2i}-\hbar\omega)(E_{n_1i}-2\hbar\omega)(E_{ni}-3\hbar\omega)}\right|^2\delta(E_k-E_i-4\hbar\omega), \tag{2}$$

where

$$H''_{n_s n_t} = \left(\frac{1}{2m}\right)\left(\frac{e}{c}\right)^2 \left\langle n_s \left| \sum_j^N \vec{A}_j \cdot \vec{A}_j \right| n_t \right\rangle \qquad \text{and} \qquad H'_{n_s n_t} = \frac{e}{mc} \left\langle n_s \left| \sum_j^N \vec{A}_j \cdot \vec{P}_j \right| n_t \right\rangle .$$

In semiconductor materials, the ground-state wave function (in the independent-particle approximation) is that when all one-electron states in the valence bands are occupied. This ground-state wave function, in the Hartree-Fock approximation, can be expressed[10] as

$$\bar{\psi}_g = \bar{\psi}_i = (N!)^{-1/2} P \psi_{m_1}(r_1)\psi_{m_2}(r_2)\psi_{m_3}(r_3)\cdots\psi_{m_i}(r_i)\psi_{m_{i+1}}(r_{i+1})\cdots\psi_{m_N}(r_N). \tag{3}$$

The subscript m appearing in the wave function of Eq. (3) designates the quantum states of the electrons in the valence band; e.g., $m_i = (v, k_i) = k_i^v$.

If one of the electrons in the valence band makes a transition to the conduction band under the influence of H_1, the excited state, in the Hartree-Fock approximation,[10] is

$$\bar{\psi}_{n_t} = (N!)^{-1/2} P \psi_{m_1}(r_1)\psi_{m_2}(r_2)\psi_{m_3}(r_3)\cdots\psi_{n_t}(r_i)\psi_{m_{i+1}}(r_{i+1})\cdots\psi_{m_N}(r_N), \tag{4}$$

where n_t designates the quantum states of the electron in the conduction band; e.g., $n_s = (c, k_s) = k_s^c$.

The wave functions ψ_{m_i} and ψ_{n_t} occurring in Eqs. (3) and (4) are the Bloch wave functions for the electrons in the conduction and valence bands, respectively.

The matrix element of H_1' between functions, given in Eqs. (3) and (4), can be written[10] as

$$\int \bar{\psi}_{n_t}\left(\sum_j^N \frac{e}{mc}\vec{A}_j\cdot\vec{P}_j\right)\bar{\psi}_g\, d^N\vec{r} = \int_V \psi^*_{n_t}\left(\frac{eA}{mc}\vec{\alpha}\cdot\vec{P}\right)\psi_{m_i}\, d\vec{r}_i = H'_{n_t m_i} = H'_{k_t^c k_i^v}. \tag{5}$$

Similarly, the matrix element of H_1' between two different excited states[10] is

$$\int \bar{\psi}_{n_t}\left(\sum_j^N \frac{e}{mc}\vec{A}_j\cdot\vec{P}_j\right)\bar{\psi}_{n_s}\, d^N\vec{r} = \int_V \psi^*_{n_t}\left(\frac{eA}{mc}\vec{\alpha}\cdot\vec{P}\right)\psi_{n_s}\, d\vec{r}_i = H'_{k_t^c k_s^c} = H'_{n_t n_s}, \tag{6}$$

where $\vec{\alpha}$ is the polarization vector of the radiation field and V is the volume of the crystal. In terms of the notation for the matrix elements given in Eqs. (5) and (6), (2) takes the form

$$W^4 = \frac{2\pi}{\hbar}\sum_{k_f^c, k_i^v}\left|\sum_{k_1^c}\frac{H''_{k_f^c k_1^c} H''_{k_1^c k_i^v}}{(E_{k_1^c k_i^v} - 2\hbar\omega)} + \sum_{k_2^c, k_1^c}\frac{H''_{k_f^c k_1^c} H'_{k_1^c k_2^c} H'_{k_2^c k_i^v}}{(E_{k_1^c k_i^v} - 2\hbar\omega)(E_{k_2^c k_i^v} - \hbar\omega)} + \sum_{k_2^c, k_1^c}\frac{H'_{k_f^c k_1^c} H''_{k_1^c k_2^c} H'_{k_2^c k_i^v}}{(E_{k_1^c k_i^v} - 3\hbar\omega)(E_{k_2^c k_i^v} - \hbar\omega)}\right.$$

$$\left. + \sum_{k_2^c, k_1^c}\frac{H'_{k_f^c k_1^c} H'_{k_1^c k_2^c} H''_{k_2^c k_i^v}}{(E_{k_1^c k_i^v} - 3\hbar\omega)\,(E_{k_2^c k_i^v} - 2\hbar\omega)} + \sum_{k_1^c, k_2^c, k_3^c}\frac{(-1)H'_{k_f^c k_1^c} H'_{k_1^c k_2^c} H'_{k_2^c k_3^c} H'_{k_3^c k_i^v}}{(E_{k_3^c k_i^v} - \hbar\omega)\,(E_{k_2^c k_i^v} - 2\hbar\omega)\,(E_{k_1^c k_i^v} - 3\hbar\omega)}\right|^2 \delta\left(E_{k_f^c} - E_{k_i^v} - 4\hbar\omega\right) . \tag{7}$$

Based on our assumption for the ground state of the many-body system given in Eq. (1), we obtain $n_t = m_t = (v, k_t)$, when $t \neq i$ implies that two electrons are occupying the same electron state in the valence band. Hence, deducing from the property of the Hartree-Fock wave function, Eq. (4) automatically equals zero. Thus the summation of the intermediate states in Eq. (7) contains only the conduction-band states.

When the wave vector $\vec{k}$ of the electrons takes on discrete values in the Brillioun zone, the matrix elements given in (5) and (6) can be written as[10]

$$H'_{k_s^c k_t^v} = \frac{N_s}{V}\,\delta_{\vec{k}_s+\vec{q},\vec{k}_t}\int_\Omega u^*_{c\vec{k}_s}\left(\frac{eA}{mc}\vec{\alpha}\cdot\vec{p}\right)u_{v(\vec{k}_s+\vec{q})}\, d\vec{r}, \tag{8}$$

$$H'_{k_s^c k_t^c} = \frac{N_s\delta_{\vec{k}_s+\vec{q},\vec{k}_t}}{V}\int_\Omega u^*_{c\vec{k}_s}\left(\frac{eA}{mc}\vec{\alpha}\cdot\vec{p}\right)u_{c(\vec{k}_s+\vec{q})}\, d\vec{r} + \vec{\alpha}\cdot(\vec{k}_s+\vec{q})\frac{\delta_{\vec{k}_s+\vec{q},\vec{k}_t}}{\Omega}\int_\Omega u^*_{c\vec{k}_s}u_{c(\vec{k}_s+\vec{q})}\, d\vec{r}. \tag{9}$$

Similarly, we can write the matrix element $H''_{k_s^c k_t^c}$ as

$$H''_{k_s^c k_t^c} = \frac{1}{2m}\left(\frac{e}{c}\right)^2\vec{A}\cdot\vec{A}\;\frac{\delta_{\vec{k}_s+2\vec{q},\vec{k}_t}}{\Omega}\int_\Omega u^*_{c\vec{k}_s}u_{c(\vec{k}_s+\vec{q})}\, d\vec{r},$$

where N_s is the number of the unit cell in the crystal, Ω is the volume of the unit cell, and $\vec{q}$ is the wave vector of the electromagnetic wave.

In the limit as $q \to 0$, we can write the matrix elements of Eqs. (8)–(10)[11] as

$$H'_{k_s^c k_s^v} \cong \delta_{\vec{k}_s+\vec{q},\vec{k}_t} H'_{k_t^c k_t^v} , \tag{11}$$

$$H'_{k_s^c k_t^c} \cong \delta_{\vec{k}_s+\vec{q},\vec{k}_t} H'_{k_t^c k_t^c} , \tag{12}$$

$$H''_{k_s^c k_t^c} \cong \delta_{\vec{k}_s+\vec{q},\vec{k}_t} \frac{1}{2m}\left(\frac{\epsilon}{c}\right)^2 \vec{A}\cdot\vec{A}, \tag{13}$$

$$H''_{k_s^v k_t^c} = 0 \quad \text{for all } k_s \text{ and } k_t . \tag{14}$$

For continuous values of $\vec{k}$, the matrix elements given in Eq. (12) for $k_s = k_t$ can be written in the spherical energy-band approximation[12] as

$$H'_{k_t^c k_t^c} = \frac{eA}{m_e c} (\vec{\alpha}\cdot \hbar \vec{k}_t). \tag{15}$$

If we substitute the matrix elements given in (8)–(14) into Eq. (7) and then carry out the summations for the initial and intermediate states of the resulting equation, we obtain the following after changing the final summation into an integral:

$$\frac{W^4}{V} = \frac{2\pi}{\hbar}\left(\frac{1}{2\pi}\right)^3 \int d^3k_f \delta(E_{k_f^c} - E_{k_f^v} - 4\hbar\omega) \left| \frac{H'_{k_f^c k_f^c} H''_{k_f^c k_f^c} H'_{k_f^c k_f^v}}{(\hbar^2 k_f^2/2m_{cv} + E_g - \hbar\omega)(\hbar^2 k_f^2/2m_{cv} + E_g - 3\hbar\omega)} \right.$$

$$+ \frac{H''_{k_f^c k_f^c} H'_{k_f^c k_f^c} H'_{k_f^c k_f^v}}{(\hbar^2 k_f^2/2m_{cv} + E_g - 2\hbar\omega)(\hbar^2 k_f^2/2m_{cv} + E_g - \hbar\omega)}$$

$$\left. + \frac{(-1) H'_{k_f^c k_f^c} H'_{k_f^c k_f^c} H'_{k_f^c k_f^c} H'_{k_f^c k_f^v}}{(\hbar^2 k_f^2/2m_{cv} + E_g - \hbar\omega)(\hbar^2 k_f^2/2m_{cv} + E_g - 2\hbar\omega)(\hbar^2 k_f^2/2m_{cv} + E_g - 3\hbar\omega)} \right|^2 , \tag{16}$$

where m_v is the effective mass of the electrons in the valence band and $1/m_{cv} = 1/m_c + 1/m_v$.

Now if we substitute Eq. (12) into (13) and make the approximation that $\langle c, k | H_1' | v, k\rangle \cong \langle c, 0 | H_1' | v, 0\rangle$,[5] we obtain the following final result after carrying out the integrations with respect to the final and initial states:

$$\frac{W^4}{V} = \frac{2^8}{3}\left(\frac{\pi}{\hbar}\right)^3 \left(\frac{1}{\omega^{12}}\right)\left(\frac{e^2}{c}\right)^4 \frac{1}{\epsilon^2} \left(\frac{1}{m^2 m_c}\right)^2 I^4 |\langle \vec{\alpha}\cdot\vec{p}\rangle|^2$$

$$\times \left(\frac{2m_{cv}}{\hbar^2}\right)^{5/2} (4\hbar\omega - E_g)^{3/2} \left[1 - \frac{8}{5}\frac{m_{cv} m}{m_c^2}\frac{(4\hbar\omega - E_g)}{(\hbar\omega)} + \frac{16}{21}\left(\frac{m_{cv} m}{m_c^2}\right)^2 \frac{(4\hbar\omega - E_g)^2}{(\hbar\omega)^2}\right] . \tag{17}$$

Notice that when $(4\hbar\omega - E_g) \to 0$, or when $(m_{cv} m/m_c)(4\hbar\omega - E_g) \to 0$, the most important term in Eq. (17) is the first one. This term comes from the third term of Eq. (2), and this in turn comes from third-order perturbation theory when the term H_1'' is included. On the other hand, when $(m_{cv} m/m_c)(\hbar\omega - E_g) > 1$, the third term is the important one. This term comes from the last term of Eq. (2) and does not contain the matrix element $H''_{n_s n_c}$. Hence, under this condition, we can ignore all except the last term in Eq. (2) when calculating the transition probability.

It is shown in the Appendix that if the transition probability is calculated by the wave functions of the Hartree-Fock approximation, we obtain the following result:

$$\frac{W_h^4}{V} = \left(\frac{2^8}{3}\right)\left(\frac{\pi}{\hbar}\right)^3 \left(\frac{1}{\omega^{12}}\right)\left(\frac{e^2}{c}\right)^4 \frac{1}{\epsilon^2}\left(\frac{1}{m_{cv}^2 m}\right)^2 I^4 |\langle \vec{\alpha}\cdot\vec{p}\rangle|^2 \left(\frac{2m_{cv}}{\hbar^2}\right)^{5/2}\left(\frac{8}{21\hbar^2\omega^2}\right)(4\hbar\omega - E_g)^{3/2}$$

$$\times \left[(4\hbar\omega - E_g)^2 - \frac{28}{15} m_{cv} \frac{|\langle \vec{\alpha}\cdot\vec{p}\rangle|^2}{m^2} (4\hbar\omega - E_g) + \frac{28}{27}(m_{cv})^2 \frac{|\langle \vec{\alpha}\cdot\vec{p}\rangle|^4}{m^4}\right],$$

where

$$|\langle \vec{\alpha}\cdot\vec{p}\rangle|^2 = |\langle c, 0 | \vec{\alpha}\cdot\vec{P} | v, 0\rangle|^2 . \tag{18}$$

Equations (17) and (18) are slightly different. The reason for this difference is that in the Hartree approximation Pauli's exclusion principle was not taken into account. As a result, the summations of the intermediate states over the valence-band states are not zero. As a comparison, we also write Keldysh's formula here[3]:

$$W=\frac{2\omega}{9\pi}\left(\frac{m_{cv}\omega}{\hbar}\right)^{3/2}\Phi[(2\langle\chi+1\rangle-2\chi)^{1/2}]\left(\frac{e^2E^2}{16m_{cv}\omega^2E_g}\right)^{\langle\chi+1\rangle}\exp\left[2\langle\chi+1\rangle\left(1-\frac{e^2E^2}{4m_{cv}\omega^2E_g}\right)\right],$$

$$\Phi(z)=e^{-z^2}\int_0^z e^{y^2}dy,\quad \chi\equiv\frac{E_g}{\hbar\omega}\left(1+\frac{e^2E^2}{4m_{cv}\omega^2E_g}\right), \tag{19}$$

where $\langle\chi\rangle$ means the integer part of χ; here, $\langle\chi+1\rangle=4$.

To apply Eq. (17), we now make an order-of-magnitude calculation for the four-photon transition in a ZnS crystal.

Given the published values $E_g=3.8$ eV, $m_c=0.3m$, $m_{cv}=0.28m$, where m is the mass of the electron, and $\epsilon=4.95$ for the intrinsic parameters of a ZnS crystal[13] and using a neodymium laser (1.17 eV) with an input intensity of 100 MW/cm^2, we obtain the value $W^4=10^{18}$ e/cm^3 sec. Assuming the average life τ of the electrons to be 10^{-9} sec, we obtain $N=W^4_\tau=10^9$ e/cm^3. In a photoconductivity experiment, electron concentration of this magnitude is measurable through the change of conductivity.[14] It is interesting to note that in a four-photon experiment on an alkalide-halide crystal at an input intensity of 100 MW/cm^2, Aseyev *et al.*[14] obtained the same order of magnitude for electrons in the conduction band.

If we substitute the given parameter values for a ZnS crystal into Eqs. (18) and (19), we obtain a transition probability on the order of 10^{19} and 10^{16} e/cm^{3}sec, respectively.

As evident from this example, Keldysh's formula gives a smaller value for the transition probability than does the perturbation calculation. This has been noted also by Basov *et al.*[5] for the two-photon case. By Keldysh's theory, the four-photon absorption should be extremely difficult to observe through a change of photoconductivity when the light intensity is 100 MW/cm^2.

In the above numerical example, we have made the assumption[8] that

$$\frac{|\langle c\cdot 0|\vec{\alpha}\cdot\vec{p}|v\cdot 0\rangle|^2}{m^2}\cong\frac{3}{4}\frac{E_g}{m_{cv}}.$$

CONCLUSIONS

Equation (17) shows that the four-photon transition probability contains three terms. The first and second terms arise from the inclusion of the term $(2m)^{-1}(e/c)^2\,\vec{A}\cdot\vec{A}$ in the calculation. As expected, the transition probability is proportional to the fourth power of the incident intensity. The present result can be generalized easily to more than one valence band by changing $|\langle c,0|H'|v,0\rangle|^2$ to $|\langle c,0|H'|v_i,0\rangle|^2$, changing m_{cv} to m_{cvi}, and summing on the "i."

If the crystal is not pure and the experiment is made at temperatures at which ionization of the crystal's impurities by the phonons is important, the formula in Eq. (18) may be just as good an approximation as that in Eq. (17).

The absorption coefficient for the four-photon transition can be obtained from the formula $K=(4\hbar\omega W^4)/I$.

APPENDIX

In the Hartree approximation, the ground-state wave function for the many-body Hamiltonian given in Eq. (1) is

$$\bar{\psi}_g=\psi_{m_1}(r_1)\,\psi_{m_2}(r_2)\cdots\psi_{m_3}(r_3)\cdots\times\psi_{m_i}(r_i)\,\psi_{m_{i+1}}(r_{i+1})\cdots\psi_{m_N}(r_N) \tag{20}$$

and that for the excited states is

$$\bar{\psi}_{n_t}=\psi_{m_1}(r_1)\,\psi_{m_2}(r_2)\cdots\psi_{n_t}(r_i)\,\psi_{m_{i+1}}(r_{i+1})\cdots\psi_{m_N}(r_N)\,. \tag{21}$$

Since Pauli's principle is not taken into account in the Hartree approximation, the quantum number n_t is not restricted to the quantum states of the electrons in the conduction-band states. This means that n_t can be either (c,k_t) or (v,k_t).

It can be shown that the matrix elements of H_1' and H_2'' between the wave functions in (20) and (21) are the same as those given in (8)–(14) when $n_t=k_t^c$. When $n_t=k_t^v$, the matrix elements of H_1' and H_2'' between the wave functions (20) and (21) are

$$H'_{k_t^v k_s^v}\cong\delta_{\vec{k}_s+\vec{q},\vec{k}_t}\,H'_{k_t^v k_t^v}, \tag{22}$$

$$H'_{k_s^v k_t^v}\cong\delta_{\vec{k}_s+\vec{q},\vec{k}_t}\left(\frac{1}{2m}\right)\left(\frac{e}{c}\right)^2\vec{A}\cdot\vec{A}\,. \tag{23}$$

For continuous values of k, the matrix elements given in Eq. (22) for $k_s=k_t$ can be written in the spherical energy-band approximation[12] as

$$H'_{k_t^v k_t^v}=-\frac{eA}{m_v c}\,(\vec{\alpha}\cdot\hbar\vec{k})\,. \tag{24}$$

Considering that $H''_{k_t^c k_t^v} \cong 0$ for all $\vec{k}_t$ and $\vec{k}_s$ and writing Eq. (2) in terms of the quantum number k_t^c and k_s^v, we obtain the total transition probability in the Hartree approximation as follows:

$$W = \frac{2\pi}{\hbar} \sum_{k_f^c} \sum_{k_i^v} \left| \sum_{i=1}^{14} M_i \right|^2 \delta\left(E_{k_f^c} - E_{k_i^v} - 4\hbar\omega\right) , \tag{25}$$

where

$$M_1 = \sum_{k_1^c, k_2^c, k_3^c} \frac{-H'_{k_f^c k_1^c} H'_{k_1^c k_2^c} H'_{k_2^c k_3^c} H'_{k_3^c k_i^v}}{(E_{k_1^c k_i^v} - 3\hbar\omega)(E_{k_2^c k_i^v} - 2\hbar\omega)(E_{k_3^c k_i^v} - \hbar\omega)} , \tag{26}$$

$$M_2 = \sum_{k_1^c, k_2^v, k_3^c} \frac{-H'_{k_f^c k_1^c} H'_{k_1^c k_2^v} H'_{k_2^v k_3^c} H'_{k_3^c k_i^v}}{(E_{k_1^c k_i^v} - 3\hbar\omega)(E_{k_2^v k_i^v} - 2\hbar\omega)(E_{k_3^c k_i^v} - \hbar\omega)} , \tag{27}$$

$$M_3 = \sum_{k_1^c, k_2^c, k_3^c} \frac{-H'_{k_f^c k_1^v} H'_{k_1^v k_2^c} H'_{k_2^c k_3^c} H'_{k_3^c k_i^v}}{(E_{k_1^v k_i^v} - 3\hbar\omega)(E_{k_2^c k_i^v} - 2\hbar\omega)(E_{k_3^c k_i^v} - \hbar\omega)} , \tag{28}$$

$$M_4 = \sum_{k_1^c, k_2^c, k_3^v} \frac{-H'_{k_f^c k_1^c} H'_{k_1^c k_2^c} H'_{k_2^c k_3^v} H'_{k_3^v k_i^v}}{(E_{k_1^c k_i^v} - 3\hbar\omega)(E_{k_2^c k_i^v} - 2\hbar\omega)(E_{k_3^v k_i^v} - \hbar\omega)} , \tag{29}$$

$$M_5 = \sum_{k_1^v, k_2^c, k_3^v} \frac{-H'_{k_f^c k_1^v} H'_{k_1^v k_2^c} H'_{k_2^c k_3^v} H'_{k_3^v k_i^v}}{(E_{k_1^c k_i^v} - 3\hbar\omega)(E_{k_2^c k_i^v} - 2\hbar\omega)(E_{k_3^v k_i^v} - \hbar\omega)} , \tag{30}$$

$$M_6 = \sum_{k_1^c, k_2^v, k_3^v} \frac{-H'_{k_f^c k_1^c} H'_{k_1^c k_2^v} H'_{k_2^v k_3^v} H'_{k_3^v k_i^v}}{(E_{k_1^v k_i^v} - 3\hbar\omega)(E_{k_2^v k_i^v} - 2\hbar\omega)(E_{k_3^v k_i^v} - \hbar\omega)} , \tag{31}$$

$$M_7 = \sum_{k_1^v, k_2^v, k_3^v} \frac{-H'_{k_f^c k_1^v} H'_{k_1^v k_2^v} H'_{k_2^v k_3^c} H'_{k_3^c k_i^v}}{(E_{k_1^v k_i^v} - 3\hbar\omega)(E_{k_2^v k_i^v} - 2\hbar\omega)(E_{k_3^c k_i^v} - \hbar\omega)} , \tag{32}$$

$$M_8 = \sum_{k_1^v, k_2^v, k_3^v} \frac{-H'_{k_f^c k_1^v} H'_{k_1^v k_2^v} H'_{k_2^v k_3^v} H'_{k_3^v k_i^v}}{(E_{k_1^v k_i^v} - 3\hbar\omega)(E_{k_2^v k_i^v} - 2\hbar\omega)(E_{k_3^v k_i^v} - \hbar\omega)} , \tag{33}$$

$$M_9 = \sum_{k_1^c, k_2^c} \frac{H''_{k_f^c k_1^c} H'_{k_1^c k_2^c} H'_{k_2^c k_i^v}}{(E_{k_1^c k_i^v} - 2\hbar\omega)(E_{k_2^c k_i^v} - \hbar\omega)} , \tag{34}$$

$$M_{10} = \sum_{k_1^c, k_2^v} \frac{H''_{k_f^c k_1^c} H'_{k_1^c k_2^v} H'_{k_2^v k_i^v}}{(E_{k_1^c k_i^v} - 2\hbar\omega)(E_{k_2^v k_i^v} - \hbar\omega)} , \tag{35}$$

$$M_{11} = \sum_{k_1^c, k_2^c} \frac{H'_{k_f^c k_1^c} H''_{k_1^c k_2^c} H'_{k_2^c k_i^v}}{(E_{k_1^c k_i^v} - 3\hbar\omega)(E_{k_2^c k_i^v} - \hbar\omega)} , \tag{36}$$

$$M_{12} = \sum_{k_1^v, k_2^v} \frac{H'_{k_f^c k_1^v} H''_{k_1^v k_2^v} H'_{k_2^v k_i^v}}{(E_{k_1^v k_i^v} - 3\hbar\omega)(E_{k_2^v k_i^v} - \hbar\omega)} , \tag{37}$$

$$M_{13} = \sum_{k_1^c, k_2^v} \frac{H'_{k_f^c k_1^c} H'_{k_1^c k_2^v} H''_{k_2^v k_i^v}}{(E_{k_1^c k_i^v} - 3\hbar\omega)(E_{k_2^v k_i^v} - 2\hbar\omega)} , \tag{38}$$

$$M_{14} = \sum_{k_1^v, k_2^v} \frac{H'_{k_f^c k_1^v} H'_{k_1^v k_2^v} H''_{k_2^v k_i^v}}{(E_{k_1^v k_i^v} - 3\hbar\omega)(E_{k_2^v k_i^v} - 2\hbar\omega)} . \tag{39}$$

If we substitute the matrix elements in (8)–(14) and (22)–(24) into Eq. (25) and then carry out the summations for the intermediate and the initial states, we can simplify the transition probability to the following form:

$$W^4 = (2)\left(\frac{2\pi}{\hbar}\right) \frac{V}{(2\pi)^3} \int d^3k_f \delta(E_{k_f^c k_f^v} - 4\hbar\omega) \left| g_1 \bar{H}'_{k_f^c k_f^v} (\vec{\alpha} \cdot \hbar\vec{k}_f)^3 + (|\bar{H}'_{k_f^c k_f^v}|^2 g_2 + g_3) \bar{H}'_{k_f^c k_f^v} (\vec{\alpha} \cdot \hbar\vec{k}_f) \right|^2 , \tag{40}$$

where

$$\bar{H} = \langle c, k_f | \vec{\alpha} \cdot \vec{p} | v, k_f \rangle \quad ,$$

$$g_1 = \left(\frac{eA}{c}\right)^4 \frac{1}{m} \left[\frac{(m_c)^{-3}}{(E_{k_f^c k_f^v} - 3\hbar\omega)(E_{k_f^c k_f^v} - 2\hbar\omega)(E_{k_f^c k_f^v} - \hbar\omega)} + \frac{(m_c)^{-2}(m_v)^{-1}}{(\hbar\omega)(E_{k_f^c k_f^v} - 2\hbar\omega)(E_{k_f^c k_f^v} - 3\hbar\omega)} \right.$$
$$\left. + \frac{(m_c m_v^2)^{-1}}{2(\hbar\omega)^2 (E_{k_f^c k_f^v} - 3\hbar\omega)} + \frac{(m_v)^{-3}}{6(\hbar\omega)^3} \right] \quad , \tag{41}$$

$$g_2 = -\left(\frac{eA}{c}\right)^4 \frac{1}{m^3} \left[\frac{(m_c)^{-1}}{(2\hbar\omega)(E_{k_f^c k_f^v} - 3\hbar\omega)(E_{k_f^c k_f^v} - \hbar\omega)} + \frac{(m_c)^{-1}}{(3\hbar\omega)(E_{k_f^c k_f^v} - 2\hbar\omega)(E_{k_f^c k_f^v} - \hbar\omega)} + \frac{(m_v)^{-1}}{3(\hbar\omega)^2 (E_{k_f^c k_f^v} - 2\hbar\omega)} \right.$$
$$\left. + \frac{(m_v)^{-1}}{6(\hbar\omega)^2 (E_{k_f^c k_f^v} - \hbar\omega)} \right] , \tag{42}$$

$$g_3 = \frac{1}{2m^2} \left(\frac{eA}{c}\right)^4 \left[\frac{(m_c)^{-1}}{(E_{k_f^c k_f^v} - \hbar\omega)(E_{k_f^c k_f^v} - 2\hbar\omega)} + \frac{(m_c)^{-1}}{(E_{k_f^c k_f^v} - \hbar\omega)(E_{k_f^c k_f^v} - 3\hbar\omega)} + \frac{(m_v)^{-1}}{(\hbar\omega)(E_{k_f^c k_f^v} - 2\hbar\omega)} \right.$$
$$\left. - \frac{(m_c)^{-1}}{(2\hbar\omega)(E_{k_f^c k_f^v} - 3\hbar\omega)} - \frac{(m_v)^{-1}}{(2\hbar\omega)(\hbar\omega)} \right] , \tag{43}$$

where

$$E_{k_f^c k_f^v} = \left(\frac{\hbar^2 k_f^2}{2m_{cv}} + E_g\right).$$

In deriving Eqs. (16) and (36), we have used the property of the Kronecker δ, $(\delta_{ij})^2 = \delta_{ij}$. If we assume that the polarization vector $\vec{\alpha}$ of the electromagnetic wave points in the z axis and make the approximation that the matrix element $H'_{\vec{k}_f^c \vec{k}_f^v}$ is independent of the vector $\vec{k}_f$, we obtain, after carrying out the integration, the result given in Eq. (18).

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Carrier Repopulation from Infrared Faraday Rotation under Hot-Carrier Conditions

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The magnitude of the Faraday rotation in Ge and Si under hot-electron conditions has been estimated for different orientations of the magnetic and the hot-electron dc field. The possibility of the evaluation of carrier repopulation from the analysis of Faraday-rotation data is discussed. The conditions required for a successful experiment for the application of the method are examined. It is found that the experiment is possible at room temperature, but the conditions are more favorable at liquid-nitrogen or lower temperatures.

I. INTRODUCTION

The Faraday rotation of infrared signals is produced in semiconductors mainly by the free carriers if the wavelength of the signal is beyond the absorption edge. The specific angle of rotation is determined by the frequency of the signal, the dielectric constant of the material, the free-carrier concentration, and the effective mass of the carriers. It is independent of the momentum relaxation time of the carriers if the frequency is such that the product of the frequency and relaxation time is much larger than unity. Therefore, one may determine one of the above-mentioned three parameters of the material, i.e., the dielectric constant, the carrier concentration, and the effective mass of carriers, since we know two of them from other experiments. This method has been applied to obtain the effective mass of carriers in III-V compounds and in Ge.[1-3]

The free carriers in a semiconductor, except in a few cases, normally occupy one valley or equivalent valleys in equal numbers in a many-valley semiconductor. The carrier population in the different valleys may be altered when a high electric field is applied to produce hot-electron conditions. Such population transfer affects significantly the conductivity and galvanomagnetic properties of semiconductors under hot-electron conditions and