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One-photon Keldysh absorption in direct-gap semiconductors

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We have adapted the Keldysh multiphoton absorption theory to one-photon transitions in semiconductors. We find that the Keldysh theory is in good agreement with both the absolute values and with the frequency dependence of the absorption coefficients of InSb and GaAs. We have also reexamined the often used first-order perturbation approach and derived an expression for the absorption coefficient using the $\vec{k}\cdot\vec{p}$ method. A comparison between theory and experimental data has been carried out without adjustable parameters.

I. INTRODUCTION

The measurement and the interpretation of nonlinear optical absorption coefficients have been the subject of active and often controversial discussions in the past few years.[1] A theoretical approach was proposed by Keldysh[2] to describe nonlinear absorption processes of arbitrary photon multiplicity. His conclusions, however, were criticized by Weiler, who suggested that Keldysh's transition probabilities for multiphoton processes of even multiplicity are in contradiction with the accepted perturbation theory and parity considerations.[3]

In fact, recent experiments[4] involving four-photon transition in ZnS are at variance with Keldysh's prediction, while they are in fair agreement with perturbative semiclassical calculations.[5] Until now it has been argued that, at best, Keldysh's theory should provide acceptable results only for nonlinear processes of fairly high photon multiplicity.

Apparently, instead, the Keldysh absorption theory is fairly successful when applied to single-photon transition processes in direct-gap semiconductors, even for incident-photon energies which are quite a bit larger than the band-gap energy.

The results of our investigation can be summarized as follows:

(i) Keldysh's transition rate is not meant to describe one-photon processes. Still, the theoretical absorption data above the bandgap can be accurately fitted by a power law of the form $(\hbar\omega - E_g)^\beta$, where E_g is the band-gap energy and β is very close to $\frac{1}{2}$. This is the expected behavior of the absorption coefficient for direct allowed-allowed transitions.[6]

(ii) The theoretical absorption data without adjustable parameters are in good agreement both with the absolute value and with the frequency dependence of the absorption coefficients of pure InSb. Good agreement is also found for pure samples of GaAs, in which the exciton contribution to the absorption coefficient appears to be small. Sturge's[7] classic data displaying the exciton structure near the band edge of GaAs and the influence of the continuum exciton states on the absorption process, cannot be represented, not suprisingly, by either Keldysh's theory or the results of the conventional perturbation theory. In Sec. II we review the main results of the Keldysh theory and specialize the conclusions to the case of one-photon transition processes. We also review the conventional first-order perturbation calculation for direct transitions between parabolic bands and argue for the validity of the relation $p_{vc}^2/m^2 = E_g/4m^*$, relating the momentum matrix element p_{vc} between valence and conduction bands with the band-gap energy E_g. The parameters m and m^* are, respectively, the free-electron and the reduced electron-hole effective mass.

In Sec. III we analyze representative absorption data for InSb and GaAs and compare them with the theoretical results of the Keldysh and the first-order perturbation theories.

II. SURVEY OF THE THEORETICAL RESULTS

A. Keldysh theory

Keldysh's model[2] comprises a generalization of the theory of Zener breakdown to include multiphoton ionization of gases and crystalline materials in the presence of strong alternating fields. As in many semiclassical calculations, the electric dipole operator is the transition-inducing perturbation. The initial and final states, however, are assumed perturbed by the field. In the case of a crystalline system, the initial and final states are assumed to have the form

$$\psi_p^{(c,v)}(\vec{r},t)=u_{p(t)}^{(c,v)}(\vec{r})\times\exp\left[\frac{i}{\hbar}\left(\vec{p}(t)\cdot\vec{r}-\int_0^t \epsilon_{(c,v)}(p(\tau))\,d\tau\right)\right], \tag{2.1}$$

where the time-dependent momentum $\vec{p}(t)=\vec{p}+(e\vec{E}_0/\omega)\sin\omega t$ describes the accelerated motion of the charges in both the conduction c and valence v bands under the action of the applied electric field $\vec{E}=\vec{E}_0\cos\omega t$. The Bloch functions $u_{p(t)}^{(c,v)}(\vec{r})$ are the unperturbed crystal functions corresponding to the time-dependent momentum $p(t)$. The energy $\epsilon_{(c,v)}(p(t))$ is the energy of the conduction or valence bands corresponding to the momentum $p(t)$ of the charge.

Keldysh's calculations are carried out in the single-electron approximation under the assumption that the band structure of the semiconductor satisfies the energy-momentum relation

$$E(k)=E_g\left(1+\frac{\hbar^2k^2}{m^*E_g}\right)^{1/2}, \tag{2.2}$$

where $m^{*-1}=m_e^{*-1}+m_h^{*-1}$, and m_e^* and m_h^* are, respectively, the effective masses of the electron and the heavy hole. The general expression for the transition rate per unit volume is quite involved. In the limiting case when the parameter

$$\gamma=(\omega/eE_0)(2m^*E_g)^{1/2} \tag{2.3}$$

is much larger than unity[8] (this condition is well satisfied for most semiconductors of interest), Keldysh's transition rate per unit volume is simplified to

$$W(E_0)=\frac{2\omega}{9\pi}\left(\frac{m^*\omega}{\hbar}\right)^{3/2}\Phi[(2\langle x+1\rangle-2x)^{1/2}]\times\left(\frac{e^2E_0^2}{16m^*\omega^2E_g}\right)^{\langle x+1\rangle}\times\exp\left[2\langle x+1\rangle\left(1-\frac{e^2E_0^2}{4m^*\omega^2E_g}\right)\right]. \tag{2.4}$$

The function $\Phi(z)$ is the Dawson integral

$$\Phi(z)=e^{-z^2}\int_0^z e^{y^2}\,dy, \tag{2.5}$$

the variable x is defined by

$$x=\frac{E_g}{\hbar\omega}\left(1+\frac{e^2E_0^2}{4m^*\omega^2E_g}\right), \tag{2.6}$$

and the brackets $\langle\cdots\rangle$ indicate the integer part of the argument. We notice that $\langle x+1\rangle$ represents the order of photon multiplicity of the transition.

The absorption coefficient α due to the resonant interaction of the incident radiation with the medium is defined, as usual, by the rate equation

$$\frac{dI}{dl}=-\alpha I \tag{2.7}$$

for the light flux I in the material, and is related to the transition rate in Eq. (2.4) by

$$\alpha=2\hbar\omega(2R_0)W(E_0)/\epsilon_\infty^{1/2}E_0^2. \tag{2.8}$$

Equation (2.8) is computed from the rate equation

$$\frac{dN_{\mathrm{ph}}}{dt}=-\frac{\alpha}{\hbar\omega}I=-\frac{dN_e}{dt}=-W(E_0) \tag{2.9}$$

describing the rates of change of the photon number density N_{ph} and of the conduction-electron density N_e due to absorption across the band gap. In Eq. (2.8) (which we have written in mks units), R_0 denotes the vacuum impedance and ϵ_∞ the high-frequency dielectric constant of the medium; the multiplying factor of 2 is introduced to account for the electron-spin degeneracy. At first sight, the absorption coefficient given by Eq. (2.8) appears to be inconsistent with the defining rate equation (2.7) because of its apparent dependence upon E_0. In reality, the numerical values of α calculated using Keldysh's transition rate [Eq. (2.4)] are virtually field independent. Equation (2.8) will be used in Sec. III to compare the predictions of the Keldysh theory with the experimental absorption data.

B. Conventional first-order perturbation theory

In terms of the electronic transition rate per unit volume W, the one-photon absorption coefficient is given by

$$\alpha=2W(\epsilon_\infty)^{1/2}/cN_{\mathrm{ph}}, \tag{2.10}$$

where N_{ph} is the photon density. The factor of 2, as already mentioned, accounts for the electron-spin degeneracy. Various expressions for α appear in the literature,[6] which all have the energy dependence

$$\alpha=K(\hbar\omega-E_g)^{1/2} \tag{2.11}$$

for allowed transitions in a direct-gap semiconductor. The expressions for the coefficient K, which involves characteristic semiconductor properties, vary in detail as reported in the literature. In this section we briefly review the derivation of K and point out the differences from reported expressions.

If $\vec{A}$ is the vector potential associated with the radiation in a medium, the interaction Hamiltonian is given by

$$\mathcal{H} = (e/mc)\vec{A}\cdot\vec{p}\,. \tag{2.12}$$

The probability that an electron in the valence band with a wave vector $\vec{k}$ makes a transition to the conduction band with wave vector $\vec{k}'$ is given by[9,10]

$$w(\omega, t, \vec{k}, \vec{k}') = \frac{e^2}{m^2c^2\hbar^2}\left| \int_0^t dt' \int d^3r\, \psi_c^* \vec{A}\cdot\vec{p}\,\psi_v \right|^2, \tag{2.13}$$

where ψ_c and ψ_v denote the conduction- and valence-band wave functions, respectively. In terms of the Bloch functions u_c and u_v, Eq. (2.13) may be rewritten

$$W = \frac{4\pi e^2}{\hbar m^2 c^2} A_0^2 \int \frac{d^3k}{(2\pi)^3} |p_{vc}|^2\, \delta(E_c - E_v - \hbar\omega)\,, \tag{2.14}$$

where A_0 is the amplitude of the vector potential and

$$p_{vc} \equiv \hbar \int d^3r\, e^{-i(\vec{k}'-\vec{\kappa})\cdot\vec{r}} u_c^* \hat{e}\cdot\vec{\nabla}(e^{i\vec{k}\cdot\vec{r}} u_v)\,; \tag{2.15}$$

$\hat{e}$ is the unit polarization vector and $\vec{\kappa}$ is the wave vector of the incident-light field. Assuming parabolic energy bands with a direct gap, one obtains, after further simplifications, the following expression for the transition rate per unit volume:

$$W = \frac{1}{\pi\hbar}\left(\frac{e}{mc}\right)^2 A_0^2 |p_{vc}|^2 \left(\frac{2m^*}{\hbar^2}\right)^{3/2} (\hbar\omega - E_g)^{1/2}\,. \tag{2.16}$$

The momentum matrix element p_{vc} may be obtained from the $\vec{k}\cdot\vec{p}$ method[11] in terms of the effective mass and band gap. The valence- and conduction-band effective masses m_v^* and m_c^* for small values of $\vec{k}$ and for the two-band model satisfy the following approximate relations:

$$m/m_v^* = 1 - 2p_{vc}^2/mE_g \tag{2.17}$$

and

$$m/m_c^* = 1 + 2p_{vc}^2/mE_g\,. \tag{2.18}$$

Keeping in mind that the opposite signs in front of p_{vc}^2 in Eqs. (2.17) and (2.18) indicate the opposite curvatures of the two bands, one may rewrite these equations as

$$m/|m_v^*| = 2p_{vc}^2/mE_g - 1 \tag{2.17'}$$

and

$$m/|m_c^*| = 2p_{vc}^2/mE_g + 1\,. \tag{2.18'}$$

Combining these last results, one finds

$$p_{vc}^2/m^2 = E_g/4m^*\,, \tag{2.19}$$

where m^* is the electron-hole reduced effective mass defined in Sec. II. Noting that

$$A_0^2 = 2\pi N_{\text{ph}}\hbar c^2/\epsilon_\infty, \quad \text{(cgs)},$$

and using Eq. (2.19), the transition rate per unit volume [Eq. (2.16)] takes the form

$$W = \frac{e^2 N_{\text{ph}} (2m^*)^{1/2}}{\hbar^2 \epsilon_\infty} \frac{E_g}{\hbar\omega} (\hbar\omega - E_g)^{1/2}\,. \tag{2.20}$$

Finally the one-photon absorption coefficient becomes

$$\alpha = \frac{2e^2(2m^*)^{1/2}}{c\hbar^2(\epsilon_\infty)^{1/2}} \frac{E_g}{\hbar\omega} (\hbar\omega - E_g)^{1/2} \quad \text{(cgs)}. \tag{2.21}$$

This expression for α is almost identical to the one given by Elliott[9] except for a factor of 2 and the momentum matrix element. Other expressions for α in the current literature[6] are often reported without the additional $E_g/\hbar\omega$ energy dependence. This has the effect of extending the range of agreement of the perturbation theory with the experimental data beyond the actual limits of the calculation. Also the free-electron mass is not always appropriately replaced by the electron-hole reduced effective mass.

III. COMPARISON WITH EXPERIMENTAL ABSORPTION DATA

A. One-photon absorption in InSb

In our analysis we have adopted the following procedure:

(i) Conventional first-order perturbation theory for isotropic parabolic bands leads to the following dependence of the absorption coefficient α on $\hbar\omega - E_g$:

$$\alpha = \text{const} \times (\hbar\omega - E_g)^{1/2}\,, \tag{3.1}$$

provided $\hbar\omega \sim E_g$. Thus we fit the experimental data in the vicinity of the band gap to Eq. (3.1) and determine the numerical values of the constant and of the band gap E_g.

TABLE I. Empirical relation for the absorption coefficients of InSb reported in Ref. 12. The band-gap energy E_g has been calculated by a least-squares fitting procedure. The reduced effective mass m^* and the high-frequency dielectric constant ϵ_∞ have been obtained from Refs. 13 and 14, respectively.

$\alpha = (2.026 \times 10^4)(\hbar\omega - E_g)^{1/2}$ cm^{-1}

$\hbar\omega, E_g$ in eV

$E_g = 0.2248$ eV

$m^* = 0.0113m$

$\epsilon_\infty = 15.7$

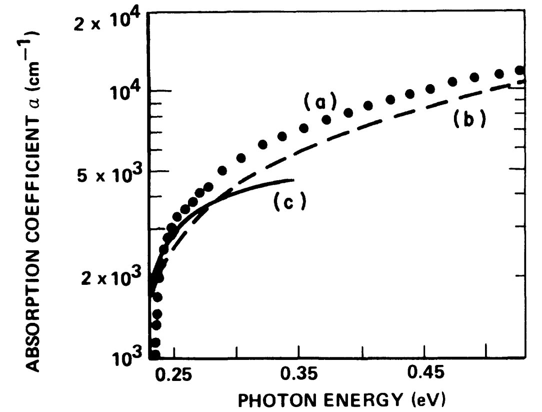

FIG. 1. Comparison between (a) the experimental values of the absorption coefficient of pure InSb taken from Ref. 12, (b) the Keldysh-model calculation, and (c) the conventional perturbation-theory calculation (which is valid only near the band edge).

(ii) We use the calculated value of the band gap in the Keldysh formula and deduce the one-photon absorption coefficient. We note that at this point the comparison between the experimental data and Keldysh's theory does not involve any adjustable parameters since we use experimentally determined values for the high-frequency dielectric constant and the reduced effective mass.

(iii) The one-photon absorption coefficients calculated in (ii) are plotted as a function of $\hbar\omega - E_g$ and the slope of the log-log plot is determined by least-squares fitting procedures in the vicinity of the band gap. The experimental data points have been taken from Fig. 3 of Ref. 12. The empirical equation which fits the data around the band edge is listed in Table I together with the reduced effective mass and the high-frequency dielectric constant which are needed for the theoretical comparison. In Fig. 1 we have plotted the experimental data together with the results of the numerical evaluation of Eqs. (2.8) and (2.21). We note that the quantitative agreement between the Keldysh theory and the measured data is rather good, especially if we consider the large range of incident-photon energies included in the comparison.

TABLE II. List of parameters for GaAs used in the theoretical fit of Figs. 3–6. The values for reduced effective mass m^* and dielectric constant ϵ_∞ have been obtained from Refs. 16 and 14, respectively.

Data source, Ref.	E_g (eV)	m^*	ϵ_∞
15	1.403	0.059	10.9
7 (21° K)	1.521	0.059	10.9
7 (294° K)	1.435	0.059	10.9

In Fig. 2 we have plotted the Keldysh absorption coefficient as a function of the energy difference $\hbar\omega - E_g$ for the set of data of Fig. 1. The least-squares-fit value of the slope of the curve in this region is $\beta = 0.493$, in close agreement with the theoretical value of $\frac{1}{2}$ predicted for direct-allowed transitions.

B. One-photon absorption in GaAs

The experimental absorption data chosen for this analysis were reported by Kudman and Seidel[15]

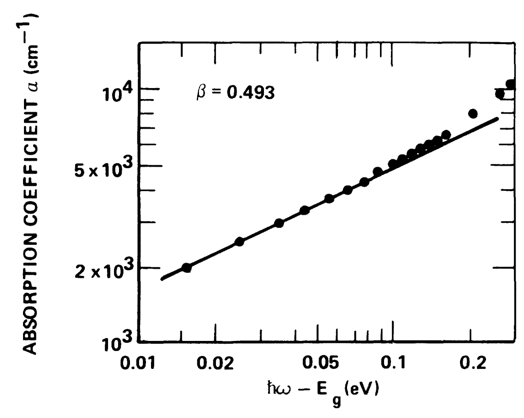

FIG. 2. Keldysh-model absorption coefficient near the band edge of InSb calculated from parameters taken from experimental data of Ref. 12 (dots). The functional dependence in the vicinity of the band gap is well represented by a power law with an exponent $\beta = 0.493$ (solid line).

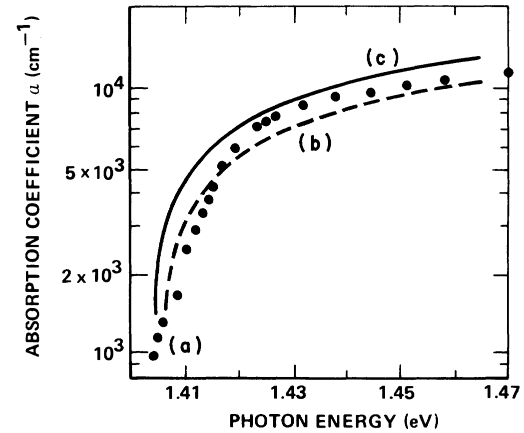

FIG. 3. Comparison between (a) the experimental values of the absorption coefficient of GaAs at room temperature (Ref. 15), (b) the Keldysh-model calculation, and (c) the conventional perturbation-theory calculation.

and by Sturge.[7] (See Table II for a summary of the relevant parameters.) The procedure followed in the analysis of Kudman and Seidel's data was the same as the one used in the case of InSb. The explored range of incident-photon energies is significantly smaller than that in the InSb measurements. The agreement between the theoretical and experimental data is not as satisfactory (Fig. 3). Still it is rather surprising that the theoretical predictions work as well as they do, especially if we consider that no adjustable parameters were used in the fit.

The logarithmic dependence of the absorption coefficient on $\ln(\hbar\omega - E_g)$ for the values of α predicted by the Keldysh theory is shown in Fig. 4. The slope of the straight portion of the absorption curve above the band gap is $\beta = 0.516$, in close agreement with the expected value of $\frac{1}{2}$.

Sturge's low-temperature data[7] were not expected to be approximated as well by both Eqs. (2.8) and (2.21) in view of the exciton contribution at 21 °K (Fig. 5). We expected, instead, to find a closer agreement with the room temperature data, in view of the ionized nature of the excitonic system.

Our expectation did not materialize (Fig. 6). In particular, it is evident from both Figs. 5 and 6 that the theoretical curves do not even reproduce the qualitative shape of the absorption spectrum. In both cases we have tried to improve the agreement between theories and experiments by multiplying the theoretical absorption coefficients by Elliott's[9] exciton correction factor. (This has been justified theoretically for the first-order perturbation calculation, but not in the case of the Keldysh analysis.) The result of this correction produced theoretical values which agreed qualitatively with the energy dependence of the absorption coefficient, but which exceeded the expected absolute values by about a factor of 2. Since in this analysis we have decided not to use adjustable parameters, we have not plotted the corrected values along with the other results in Figs. 5 and 6.

In conclusion, we have shown that in the case of InSb and GaAs a close agreement can be obtained between the results of first-order perturbation theory, modified on the basis of the $\vec{k}\cdot\vec{p}$ method,[11] and the experimental data for photon energies close to the band gap, but the agreement is not so good for photon energies significantly different from the band gap. More suprisingly, we have

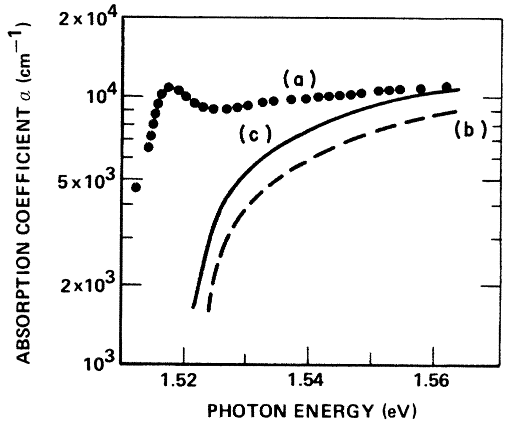

FIG. 5. Comparison between (a) the experimental values of the absorption coefficient of GaAs at 21°K taken from Ref. 7, (b) the Keldysh-model calculation, and (c) the conventional perturbation-theory calculation.

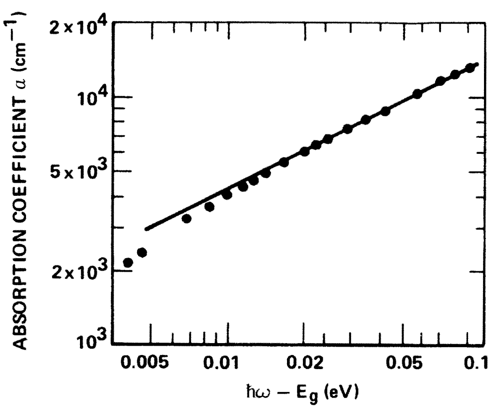

FIG. 4. Keldysh-model absorption coefficient near the band edge of GaAs calculated from parameters taken from experimental data Ref. 15 (dots). The theoretical prediction above the band gap is well represented by a power law with an exponent $\beta = 0.516$ (solid line).

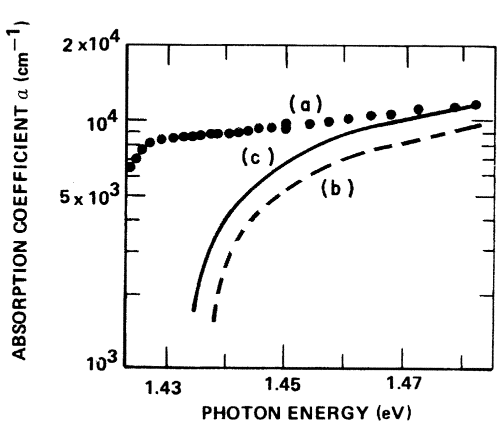

FIG. 6. Comparison between (a) experimental values of the absorption coefficient of GaAs at 294°K taken from Ref. 7, (b) the Keldysh-model calculation, and (c) the conventional perturbation-theory calculation.

also found that Keldysh's absorption coefficient applies well to describe the data selected in our analysis, and that its predicted behavior in the vicinity of the band gap is closely approximated by a power-law relation of the type given by Eq. (3.1). We stress that, for both semiconductors chosen in this analysis, no adjustable parameters were used in the theoretical expressions. The comparison with Sturge's data has revealed that Elliott's exciton correction factor yields values of the predicted absorption coefficients which are typically too high by about a factor 2.

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