

Free Carrier Absorption Due to Polar Modes in the III-V Compound Semiconductors

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The longitudinal polar modes of vibration in the III-V compound semiconductors play an important part in determining their transport properties, such as mobility. One would therefore expect them to be important for free carrier absorption, as well, in these semiconductors. A quantum mechanical calculation of the free carrier absorption arising from these modes has been made and gives an absorption varying as $\lambda^{2.5}$, and such behavior has been reported experimentally in InP and GaP. The calculated value of the absorption coefficient in InP is in good agreement with experiment.

I. INTRODUCTION

THE absorption produced by the free carriers in a semiconductor may be observed in the infrared beyond the edge of the intrinsic absorption. The absorption arises through the interaction of the electrons with the lattice perturbed by vibrations or imperfections. The absorption process can be considered quantum mechanically¹ as a two-step process in which the electron absorbs a photon and is excited to an intermediate state, where it interacts with lattice vibrations or impurities and reaches a final state, the net result being the absorption of the photon. The theory of the free carrier absorption arising from the acoustic modes of lattice vibrations was first worked out by Frohlich² and later in great detail by various authors³ who have shown them to be important in determining the free carrier absorption in germanium. Ehrenreich⁴ has shown that the optic polar modes of vibration of the lattice determine the transport properties of the III-V compound semiconductors; and as the same scattering mechanisms are operative in the transport and the free carrier absorption processes, we should expect the optic polar modes to be effective for the free carrier absorption in these compound semiconductors. We shall indeed find this to be the case for these compound semiconductors.

II. QUANTUM THEORY OF THE FREE CARRIER ABSORPTION DUE TO POLAR MODES

The free carrier absorption takes place as a two-step process, the two parts of the process being: (1) an absorption by the electron of the light quantum (energy $\hbar\omega$) and (2) an interaction with the longitudinal polar modes (phonons of energy $\hbar\omega_l$). We have to consider all possible processes in which a light quantum is absorbed, i.e., we cannot limit ourselves to those in which the first stage is this absorption and the second

the interaction with the phonons, but must also take account of the processes in which a phonon interacts with an electron first and then the photon is absorbed. There are thus four distinct sequences that must be considered. The total transition probability for a two-step process is given by⁵

$$\frac{P}{N} = \sum_f \frac{2\pi}{\hbar} \sum_i \left| \frac{(0|H_1|i)(i|H_2|f)}{E_i - E_0} \right|^2 \rho(E_f), \quad (1)$$

where N is the number of electrons in the volume; the subscripts 0, i , and f refer to the initial, intermediate, and final states, respectively; $(0|H_1|i)$ and $(i|H_2|f)$ are the matrix elements of interaction with the radiation field and the interaction with the phonons; the E 's are energies and $\rho(E_f)$ is the density of final states. As we are interested in the total absorption, the summation is over all final states. Since the electrons interact only with the longitudinal polar modes, we do not consider the interaction with the transverse modes of the optic branch.

For the two processes with photon absorbed first, the conservation conditions for the wave vector and the energies are

$$\mathbf{k}_i = \mathbf{k}_0, \quad \mathbf{k}_f = \mathbf{k}_0 \mp \mathbf{q}; \quad E_i - E_0 = -\hbar\omega.$$

For phonon interaction preceding, the conditions are

$$\mathbf{k}_i = \mathbf{k}_0 \mp \mathbf{q}, \quad \mathbf{k}_f = \mathbf{k}_i; \quad E_i - E_0 = \hbar\omega.$$

The conservation of energy for the whole process is given by

$$E_f = \frac{\hbar^2}{2m^*} (\mathbf{k}_0 \pm \mathbf{q})^2 \mp \hbar\omega_l = E_0 = \frac{\hbar^2}{2m^*} \mathbf{k}_0^2 + \hbar\omega, \quad (2)$$

where the electron energy surfaces are assumed to be spherical.

The upper sign in the above equations corresponds to phonon emission while the lower sign corresponds to phonon absorption; \mathbf{q} is the wave number vector of the phonon. The matrix element for the perturbation

⁵ W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, New York, 1944).

¹ H. Y. Fan, *Reports on Progress in Physics* (The Physical Society, London, 1956), Vol. 14, p. 119.

² H. Frohlich, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 325.

³ H. J. Meyer, *Phys. Rev.* **112**, 298 (1958); R. Rosenberg and M. Lax, **112**, 843 (1958).

⁴ H. Ehrenreich, *J. Phys. Chem. Solids* **2**, 131 (1957).

due to the radiation field is, for the first two processes,²

$$(0|H_1|i) = -\frac{e}{(\epsilon V)^{1/2}} \frac{\hbar^2}{m^*} \left(\frac{2\pi}{\hbar\omega}\right)^{1/2} k_0 \cos\eta, \quad (3)$$

where V is the volume, ϵ is the dielectric constant at frequency ω , and η is the angle between the polarization direction of the radiation field and \mathbf{k} ; the radiation field is normalized for one photon in the volume V of the crystal. For the process in which the phonon interaction precedes k_0 in (3) is replaced by $|\mathbf{k}_0 \pm \mathbf{q}|$, i.e., $[k_0^2 + (2m^*/\hbar)(\omega \mp \omega_l)]^{1/2}$ obtained from Eq. (2).

The matrix element for the perturbation by the lattice vibrations is given by²

$$(i|H_2|f) = \pm \left(\frac{\hbar}{2\gamma\omega_l}\right)^{1/2} \frac{4\pi i e V^{-1/2}}{q} \begin{cases} (n_q)^{1/2} \\ (n_q+1)^{1/2} \end{cases}, \quad (4)$$

where the upper sign and $n_q^{1/2}$ apply to phonon absorption, while the lower sign and $(n_q+1)^{1/2}$ apply to phonon emission; n_q , the quantum number of the lattice vibrational mode, is given by

$$n_q = (e^z - 1)^{-1}, \quad z = \hbar\omega_l/kT, \quad (5)$$

and ω_l is assumed to be constant for the optic branch. The factor γ in (4) is defined by

$$4\pi/\gamma\omega_l^2 = \epsilon_\infty^{-1} - \epsilon_0^{-1}, \quad (6)$$

where ϵ_∞ is the high-frequency dielectric constant and ϵ_0 is the static dielectric constant.

An assumption implicit in our perturbation treatment and particularly in writing down (4) is that the phonon field and the electron field interact only weakly. This is expressed quantitatively by means of the coupling constant²:

$$\alpha = (e^2/\hbar)(m_0/2\hbar\omega_l)^{1/2}(\epsilon_\infty^{-1} - \epsilon_0^{-1})(m^*/m_0)^{1/2}$$

(m_0 is the free electron mass), the electron being strongly or weakly coupled to the phonon field depending on whether α is, respectively, greater or less than unity. Ehrenreich estimates a value of 0.014 for α in InSb. The estimated values of α for GaAs, InP, and GaP, from the data in Table I, are 0.054, 0.031, 0.092, respectively. Therefore, it is permissible to regard the phonon field as a weak perturbation.

The number of \mathbf{q} values in a volume $d\Omega_q$ in q space is $Vd\Omega_q/(2\pi)^3$, therefore the density of final states per unit energy range is given by

$$\rho(E_f) = \frac{V}{(2\pi)^3} \frac{d\Omega_q}{dE_f} = \frac{V}{(2\pi)^2} \frac{m^* q dq}{\hbar^2 k_0}. \quad (7)$$

By substituting the various expressions in (1) and integrating over q , remembering that the limits of the q integration (obtained from the conservation of energy

TABLE I. Calculation of the absorption coefficient of the III-V compound semiconductors.

Compound	Effective mass of electron (m^*/m_0)	Dielectric constants ϵ_0	Dielectric constants ϵ_∞	Refractive index n	Phonon energy in eV	Absorp. coef. μ (in cm^{-1})	
InP	0.07	15	10.6	3.1	0.043	4.7	5
GaAs	0.072	12.51	11.1	3.4	0.035	1.1	...

equation) are

$$\begin{aligned} q_{\max} &= \left[k_0^2 + \frac{2m^*}{\hbar}(\omega - \omega_l) \right]^{1/2} + k_0 \\ q_{\min} &= \left[k_0^2 + \frac{2m^*}{\hbar}(\omega - \omega_l) \right]^{1/2} - k_0 \end{aligned} \quad \left. \begin{array}{l} \text{for processes} \\ (1) \text{ and } (3); \end{array} \right\} \quad (8)$$

$$\begin{aligned} q_{\max} &= \left[k_0^2 + \frac{2m^*}{\hbar}(\omega + \omega_l) \right]^{1/2} + k_0 \\ q_{\min} &= \left[k_0^2 + \frac{2m^*}{\hbar}(\omega - \omega_l) \right]^{1/2} - k_0 \end{aligned} \quad \left. \begin{array}{l} \text{for processes} \\ (2) \text{ and } (4); \end{array} \right\}$$

we obtain

$$\frac{P}{N} = \frac{2\pi e^4 \omega_l \cos^2 \eta}{\epsilon V m^* \hbar \omega^3} (\epsilon_\infty^{-1} - \epsilon_0^{-1}) \langle F \rangle, \quad (9)$$

where $\langle F \rangle$, the average over the Maxwellian distribution for the electrons, is given by

$$\begin{aligned} \langle F \rangle &= \left(\frac{2m^* kT}{\pi \hbar^2} \right)^{1/2} \left\{ 2(n_q + 1) \int_0^\infty dx x e^{-x} \right. \\ &\quad \times \left[2 + \frac{a}{x} - 2 \left(1 + \frac{a}{x} \right)^{1/2} \right] \sinh^{-1} \left(\frac{x}{a} \right)^{1/2} \\ &\quad \left. + 2n_q \int_0^\infty dx x e^{-x} \left[2 + \frac{b}{x} - 2 \left(1 + \frac{b}{x} \right)^{1/2} \right] \right. \\ &\quad \left. \times \sinh^{-1} \left(\frac{x}{b} \right)^{1/2} \right\}, \quad (10) \end{aligned}$$

where $a = \hbar(\omega - \omega_l)/kT$, $b = \hbar(\omega + \omega_l)/kT$, $x = E/kT$. Now noting that $(\cos^2 \eta)_{\text{av}} = \frac{1}{3}$ and $\sigma_Q(\omega) = (\epsilon V/4\pi)P$, we have

$$\sigma_Q(\omega) = \frac{N e^4 \omega_l}{6 m^* \hbar \omega^3} (\epsilon_\infty^{-1} - \epsilon_0^{-1}) (1 - e^{-\xi}) \langle F \rangle; \quad (11)$$

$\xi = \hbar\omega/kT$, and the factor $(1 - e^{-\xi})$ takes into account induced emission.

Let us examine the following cases of interest:

Case 1. $a \gg 1$, $b \gg 1$.—We have

$$\begin{aligned} \sigma_Q(\omega) &= \frac{N e^4 \omega_l}{3 m^* \hbar \omega^3} \left(\frac{2m^* kT}{\pi \hbar^2} \right)^{1/2} (1 - e^{-\xi}) \\ &\quad \times [2(n_q + 1)G(a) + 2n_q G(b)], \quad (12) \end{aligned}$$

where

$$G(x) = e^{x/2} K_0\left(\frac{x}{2}\right) + \frac{x}{2} e^{x/2} K_1\left(\frac{x}{2}\right) - 2 - \frac{2}{x},$$

$$\delta = \epsilon_\infty^{-1} - \epsilon_0^{-1},$$

$K_0(x)$ and $K_1(x)$ being the modified Bessel functions. (See Appendix for evaluation of the integrals.)

$$\sigma_Q(\omega) \simeq \frac{\sqrt{2} N e^4 \delta}{3 m^*} \frac{\hbar \omega_l}{(\hbar \omega)^3} (\hbar \omega)^{\frac{1}{2}} \left(\frac{e^z + 1}{e^z - 1} \right) \times \left[1 + \frac{11}{4\xi} - \frac{4}{(\pi\xi)^{\frac{1}{2}}} \dots \right], \text{ for } \hbar \omega / kT \gg 1. \quad (13)$$

Here, we note that $\sigma_Q(\omega)$ varies as $\lambda^{2.5}$ which is the behavior experimentally observed by Newman⁶ in InP.

Case 2. $a \ll 1$, $b \geq 1$.—We have

$$\sigma_Q(\omega) = -\frac{2 N e^4 \omega_l \delta}{3 m^* \hbar \omega^3} \left(\frac{2 m^* kT}{\pi \hbar^2} \right)^{\frac{1}{2}} \frac{(1 - e^{-\xi})}{(e^z + 1)} G(b)$$

$$\simeq -\frac{2 N e^4 \omega_l \delta}{3 m^* \omega^2} \left(\frac{2 m^*}{\pi \hbar^2 kT} \right)^{\frac{1}{2}} \frac{e^{z/2}}{(e^z - 1)} \times \left\{ K_0(b/2) + \frac{b}{2} K_1(b/2) - (2 + 2/b) e^{-b/2} \right\}$$

for $\xi \leq 1$, (14)

yielding the result $\sigma_Q(\omega) \propto \omega^{-2}$, the semiclassical behavior one should expect.

III. COMPARISON WITH SEMICLASSICAL THEORY

In order to compare $\sigma_Q(\omega)$ with the classical expression $\sigma_c(\omega) = \sigma_{dc} / \omega^2 \tau^2$, we eliminate δ from the expression for $\sigma_Q(\omega)$ by using the expression for mobility (due to scattering by polar modes only) obtained by Howarth and Sondheimer,⁷ giving

$$\tau = \frac{8\delta}{3\pi^{\frac{1}{2}} \omega_l e^2} \left(\frac{kT \hbar^2}{2m^*} \right)^{\frac{1}{2}} \chi(z) (e^z - 1), \quad (15)$$

where $\chi(z) \sim 1$, for $z \leq 1$, $\chi(z) = \frac{3}{8}(\pi z)^{\frac{1}{2}}$, $z \gg 1$. Therefore using (15), we obtain, for Case 1,

$$\sigma_Q(\omega) \simeq \sigma_c(\omega) \frac{8}{9\sqrt{\pi}} \chi(z) (e^z + 1)^{\frac{1}{2}} \xi^{\frac{1}{2}} \left(1 + \frac{11}{4\xi} \dots \right); \quad (16)$$

i.e., we find $\sigma_Q(\omega) > \sigma_c(\omega)$, and $\sigma_Q(\omega) \propto \omega^{-2.5}$.

⁶ R. Newman, Phys. Rev. **111**, 1518 (1958).

⁷ D. Howarth and E. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).

For case 2,

$$\sigma_Q(\omega) = \sigma_c(\omega) \frac{16}{9\pi} \chi(z) e^{z/2} \times \left\{ K_0(b/2) + \frac{b}{2} K_1(b/2) - \left(2 + \frac{2}{b} \right) e^{-b/2} \right\}, \quad (17)$$

$$\sigma_Q(\omega) \simeq \sigma_c(\omega).$$

The calculated values of the absorption coefficient μ given by $\mu = (4\pi / nc) \sigma_Q(\omega)$, obtained from Eq. (13), are given in Table I⁸. The absorption coefficient has been calculated for the case $\hbar \omega = 0.1$ eV, $N = 4 \times 10^{16} \text{ cm}^{-3}$. n is the refractive index of the medium.

DISCUSSION

The above theory should be applicable to the compound semiconductors InP, GaP, and GaAs; we also see from the above table that there is good agreement between theory and experiment in the case of InP, explaining the $\lambda^{2.5}$ dependence as well. In the case of GaP, preliminary data by Spitzer⁹ seemed to indicate the same sort of behavior. In the case of GaAs,¹⁰ the absorption has been observed on highly doped material; the impurity absorption predominates and gives a λ^3 behavior of the absorption coefficient. It would be interesting to apply these results to the lead compound semiconductors, where polar modes have been invoked to explain the temperature variation of the mobility in these compound semiconductors. Thus in these III-V compound semiconductors, the polar modes play an important part in determining the mobility as well as optical absorption in the infrared.

APPENDIX

The integrals appearing in (10) can be evaluated by using the following integrals in reference 7:

$$J^n(x) = \int_0^\infty y^n \sinh^{-1} \left(\frac{y}{2x} \right)^{\frac{1}{2}} e^{-y} dy$$

$$= n J^{n-1}(x) + \frac{1}{2} I_0^n(x), \quad n \geq 1$$

$$= \frac{1}{2} e^x K_0(x), \quad n = 0.$$

⁸ The experimental values for m^* , ϵ_0 , ϵ_∞ have been taken from the following: reference 6; T. S. Moss and A. K. Walton, Proc. Phys. Soc. (London) **74**, 131 (1959); G. Picus, E. Burstein, B. W. Hennis, and M. Hass, J. Phys. Chem. Solids **8**, 282 (1959).

⁹ W. G. Spitzer (private communication).

¹⁰ W. G. Spitzer and J. M. Whelan, Phys. Rev. **114**, 59 (1959).