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TEMPERATURE DEPENDENCE OF ABSORPTION SPECTRA OF *p*-TYPE GaP

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The theoretical analysis of the optical absorption due to band-impurity (impurity-band) electron transitions involving deep impurity levels in semiconductors is considered. Also absorption spectra of GaP was observed at room temperature and the results were found to be in agreement with the theoretical results if the electron -phonon interaction is taken into consideration.

1. Introduction

Although the extrinsic absorption edge and extrinsic infrared free carrier absorption of *n*- and *p*-type GaP have been extensively studied[1-2], the absorption spectrum below the indirect band edge in the range $1.0\ \text{eV} < h\nu < 2.3\ \text{eV}$ has received little attention. IR absorption gives valuable information on the energy band structure, lattice vibrations and scattering mechanisms in semiconductors. In *p*-type materials the free holes can give rise to direct intervalence-band absorption and phonon assisted interband absorption[3]. The effect of lattice vibrations on optical transitions between discrete levels have been discussed in many publications[4].

The aim of this work is to perform a theoretical analysis of the optical absorption due to band-impurity (impurity-band) electron transitions involving deep impurity levels in semiconductors, then to apply the results to the interpretation of the observed spectra of GaP which we have obtained.

2. *General theory of absorption line shapes*

The usual formula for the absorption cross section can be written in the form:

$$\sigma(\nu) = \left[\frac{n}{\varepsilon}\left(\frac{E_e}{E}\right)^2\right] \frac{8\pi^3 \nu}{3c} I_{ab}(h\nu). \tag{1}$$

Following Lax[5] in the adiabatic and Condon approximations we can write the normalized line shape function for transitions from state a to state b as:

$$I_{ab}(h\nu) = A v_m \sum_n \left| \int X_{bn} P_{ba}(x) X_{am}(x)\, \mathrm{d}x \right|^2 \delta(E_{bn} - E_{am} - h\nu). \tag{2}$$

We regard state a as the lower electronic state and b as higher electronic state. Let (x) denote a set of nuclear coordinates, $P_{ba}(x)$ is the transition electric dipole matrix element between the initial and final electronic states, X_{am} is the vibrational state which is associated with electronic state a and satisfies the following equation:

$$[T_N + E_l(x_l)]\, \Phi_{la}(x_l) = E_{la}\, \Phi_{la}(x_l), \tag{3}$$

where T_N is the operator representing the kinetic energy of the nuclei, and $E_l(x_l)$ is the adiabatic potential. If broadening is unimportant, I_{ba} is simply a delta function, and the integrated cross section $\int \sigma(\nu)\, \mathrm{d}(h\nu)$, reduces to usual atomic absorption formula[6]. In the harmonic approximation using the normal coordinates a_l, the adiabatic potential for the ground state becomes:

$$E_a(Q_l) = \frac{1}{2} \sum_i \Omega_{la}\, Q_l^2, \tag{4}$$

where

$$\Omega_{la}^2 = M_l\, \omega_{la}^2.$$

Q_l, M_l and ω_{la} are the normal coordinate, mass and frequency of the ith normal mode, respectively.

Using:

$$T_N = -\sum \frac{\hbar^2}{2M_l} (\partial^2/\partial Q_l^2) \tag{5}$$

Eq. (3) for the ground state may be written in the form:

$$\sum \left[\frac{-\hbar^2}{2M_l}\left(\frac{\partial^2}{\partial Q_l^2}\right) + \frac{1}{2}\Omega_{la}^2\, Q_{la}^2\right] \Phi_{am}(Q_l) = E_{am}\, \Phi_{am}(Q_l). \tag{6}$$

Φ_{am} is a harmonic oscillator wave function. The solutions to Eqs. (6) are:

$$\Phi_{am}(x_l) = \prod \varphi_{am}(Q_l). \tag{7}$$

We are interested in the transition from the ground state a to some excited state b. In order to evaluate Eq. (2) and to avoid any complications, we expand the adiabatic potential for the excited state b in the normal coordinates for the ground state

$$E_b(x_i) = E_{ab} + \sum_i A_i Q_i + \frac{1}{2} \sum_i M_i \omega_{ib}^2 Q_i^2 + \sum_{i \neq j} B_{ij} Q_i Q_j. \tag{8}$$

The cross term $Q_i Q_j$ causes severe problems. We assume that it is small and can be neglected.

The solutions of Eq. (3) with the adiabatic potential of Eq. (8) are:

$$\Phi_{bn}(x_i) = \prod_i \varphi_{bni}(Q_i).$$

Using the variational principle[7], we find that the one coordinate function φ_{bni} satisfies:

$$\left\{\frac{-\hbar^2}{2M_i}\frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\Omega_{ib}^2 Q_i^2 + Q_i\left[A_i + \sum_{j \neq i} B_{ij} \int \varphi_{bnj}(Q_i)\, Q_j\, \varphi_{bnj}(Q_j)\, \mathrm{d}Q_i\right]\right\} \varphi_{bni}(Q_i)$$

$$= E_{bni}\, \varphi_{bni}(Q_i). \tag{10}$$

Eq. (10) has the form of harmonic oscillator equation. It will be convenient to express Eq. (2) as an invariant expression, P_{ba} is considered as an arbitrary operator. Introducing the integral representation:

$$\delta(E_{bn} - E_{am} - h\nu) = h^{-1} \int_{-\infty}^{\infty} \exp\left[\mathrm{i}(E_{bn} - E_{am} - h\nu)\, t/\hbar\right] \mathrm{d}t \tag{11}$$

the line shape function of Eq. (2) may be written in the from:

$$I_{ba}(h\nu) = h^{-1} \int_{-\infty}^{\infty} \mathrm{d}t \exp\left[-\mathrm{i}t/\hbar\,(E_{bn} - E_{am})\right] \prod_i g_i(t), \tag{12}$$

where:

$$g_i(t) = A \sum |X_{bn}\, P_{ba}(x)\, X_{am}|^2 \cdot \exp\left[-\mathrm{i}t/\hbar\,(E_{ami} - E_{bni})\right]. \tag{13}$$

The Fourier transform of the line shape function is a product of functions $g_i(t)$, which involve only the ith normal coordinate. $g_i(t)$ is the Fourier transform of the line shape function for the case in which only the ith mode is present.

The convolution theorem could be used to write Eq. (12) as an N fold convolution:

$$I_{ab}(h\nu) = \int \ldots \int I_{ab}^{(1)} I_{ab}^{(2)}(E_2 - E_1) \ldots \cdot I_{ab}^{N}(E - E_{N-1})\, \mathrm{d}E_1\, \mathrm{d}E_{N-1} \tag{14}$$

where N is the total number of modes and $I^i_{ab}(h\nu)$ is the line shape function for mode i.

The line shape due to linear modes is considered in the semiclassical approximation[5]. In order to compute the function defined by Eq. (12) we evaluate the overlap integral:

$$S_{ab} = \int \varphi_{am}(q)\, \varphi_{bn}(q)\, \mathrm{d}q. \tag{15}$$

It is easy to show that this integral is given by[8]:

$$S_{mn} = \exp\left[-a^{3/4}\right] (m!/n!)^{1/2} (-a/\sqrt{2})^{n-m} L_m^{n-m}(a^2/2). \tag{16}$$

$L_B^\gamma(\varepsilon)$'s are Laguerre polynomials[9]. For $T = 0$ only $m = 0$, ground vibrational state is occupied and line shape function is easily evaluated.

Let $L_0^\gamma(\varepsilon) = 1$, $P = n - m$ we find:

$$I_{ab}(h\nu) = \sum_{P=0}^{\infty} \exp(-a^2/2)\, (1/2\, a^2)^P/P!. \tag{17}$$

The linear mode line shape for any temperature may also be evaluated. The ground and excited state frequencies are the same, the energy vibration of transition depends on the difference between excited and ground state vibrational quantum numbers. The semiclassical line shape[5] for a linear mode is given by:

$$I_{ab}(h\nu) = \left[\frac{\tanh(\hbar\Omega/2K\,T)}{\pi\,(a\,\hbar\,\Omega)^2}\right]^{1/2} \cdot \exp\left[-(\hbar\,\omega - E_{ab})^2\, \frac{\tanh(\hbar\,\Omega/2K\,T)}{(a\,\hbar\,\Omega)^2}\right]. \tag{18}$$

For high temperatures Eq. (18) is completely adequate to simplify the calculations. The photon absorption cross section is[10]:

$$\sigma(\hbar\,\omega) = \sigma_0 \int_{E_I}^{\infty} E_f^2\, \frac{I_{ab}(\hbar\,\omega)\, [(E/E_I - 1)]^{1/2}}{\hbar\,\omega\, [E/E_I]^2}\, \frac{\mathrm{d}E}{E_I} \tag{19}$$

where σ_0 is slightly dependent on temperature. The absorption cross section can be written as a function of two dimensionless variables; the relative photon energy $\hbar\,\omega/E$ and the temperature dependent parameter Θ which may be written in the form[5]

$$\Theta = (a\,\hbar\,\Omega/E_I)^2\, \mathrm{cth}\,(\hbar\,\Omega/2K\,T). \tag{20}$$

$\hbar\,\Omega$ is the energy of lattice vibration, a — the dimensionless constant for the interactions of the bound electron with the localized vibration, $\hbar\,\omega$ the energy of the absorbed photons, and E_I the minimum energy gap between the impurity level and the band linked to the level.

3. *Results and discussion*

Fig. 1 shows the theoretical dependence of the absorption cross section on temperature using Eqs. (19) and (20). The absorption spectrum is wide and its width increases with temperature, while the magnitude of the absorption cross section at the peak σ (0) decreases. The theoretical positions of the peak of the absorption cross section as a function of temperature parameter (Θ) is shown in Fig. 2. There is no shift in the position of the peak at temperature parameter ≥ 0.08.

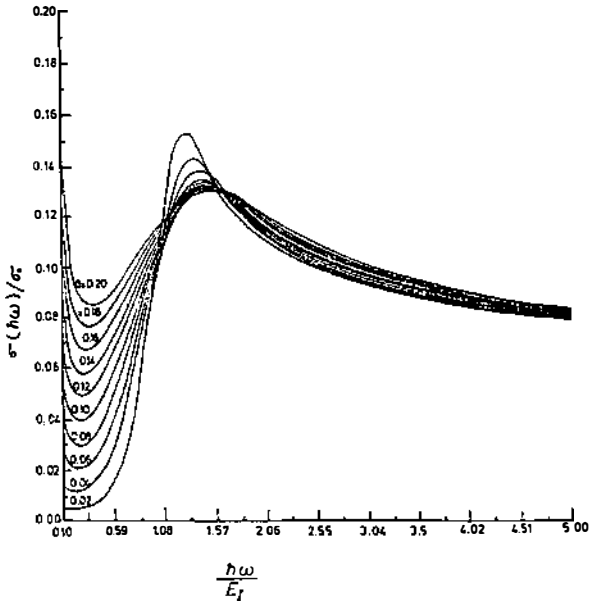

Fig. 1. Dependence of theoretical absorption cross section σ/σ_0 on GaP-Zn on $(\hbar\omega/E_i)$ at different temperature $\Theta = 0$, 0.02, 0.04, 0.06, 0.08, 0.10, 0.14, 0.16.

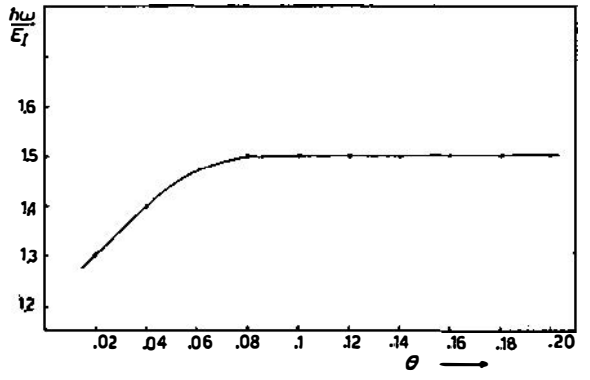

Fig. 2. Theoretical positions of the absorption cross section peak as a function of temperature.

It can be shown that the line spectrum from semiclassical theory (Eq. (19)) is a good approximation to the quantum line shape in two cases: first if the frequency of the oscillator $\hbar\omega$ is small compared to the temperature KT, and second if the coupling constant α is large.

Fig. 3 shows the decrease of the magnitude of the absorption peak with increasing temperature parameter till $\Theta \approx 0.16$, and becomes unchanged at $\Theta \approx \approx (0.16—0.2)$. This is attributed to the photoionization of holes from Zn acceptors to the valence bands. The photoionization absorption is directly proportional to the density of the neutral acceptors and hence increases as the temperature decreases. We find that the widths of absorption bands vary with Θ, as predicted by

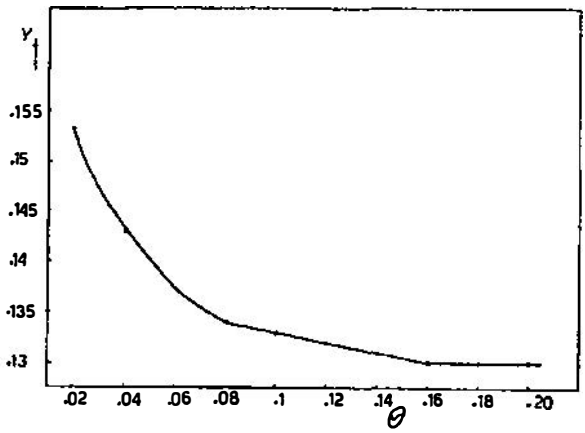

Fig. 3. Intensity of absorption cross section at the peak as a function of temperature.

the semiclassical model. It is difficult to estimate the magnitude of interband matrix element for GaP. To check the experimental results with theory the material must have a broad energy gap and must be neutral to avoid the free carrier absorption. The material must have a certain degree of ionicity for the electron — hole interaction to take place.

The experimental absorption spectra were recorded on an IKS-21 monochromator. The thickness of the GaP-Zn samples was 300 μm. The concentration of Zn in GaP was $10^{18}\,cm^{-3}$.

Fig. 4 shows the absorption spectra of the sample GaP-Zn at 300K. Thus the experimental results (4a), confirm the theoretical data (4b). Fig. 4 shows a wide band spectrum, no sharp lines and the band width is strongly dependent on temperature. Changing the temperature of the sample causes a great perturbation in the localized mode associated with longitudinal optical phonon LO vibrations, whose energy in GaP is 0.05 eV.

If the electron phonon interaction term $\alpha = 0$, Eq. (20) converts into the familiar Luckovsky equation and there is a disagreement between the absorption spectrum and the results calculated from Eq. (20). The integral in Eq. (20) was carried out numerically using the Gauss quadrature by means of (Gould SEL) computer in the International Centre for Theoretical Physics in Trieste, Italy.

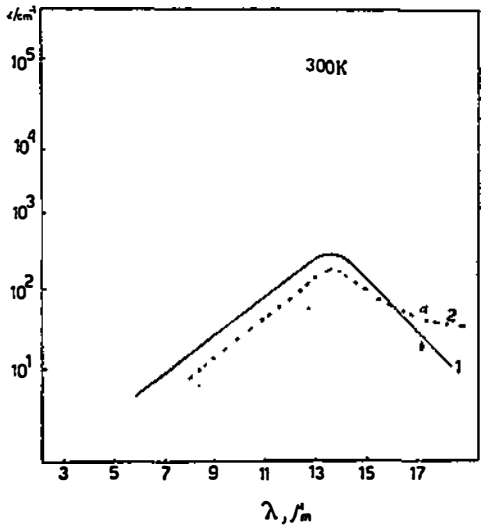

Fig. 4. The absorption spectrum of GaP-Zn at 300 K.

The values used are $\alpha = 3.7$ for the constant of electron hole interaction, $E = 0.062$ eV. The effect of concentration of Zn in GaP on the shift of the absorption peak was not taken into consideration in Eq. (20). It is our intention to pursue the study of this effect in the future.

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TEMPERATURNA ZAVISNOST APSORPCIONOG SPEKTRA *p*-TIPA GaP

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Načinjena je teorijska analiza optičke apsorpcije koja je posljedica vrpca-nečistoća (nečistoća-vrpca) elektronskih prijelaza u kojima učestvuju duboki nivoi nečistoća u poluvodičima. Također je mjeren apsorpcioni spektar GaP na sobnoj temperaturi i nađeno je slaganje s teorijom ako se uzme u obzir i elektron — fonon međudjelovanje.