14.1. Introduction:

It is well known [14.1] that the inter-band optical absorption in semiconductors is accompanied by the transition of an electron from the top of the valence band (VB) to the unoccupied states near the bottom of the conduction band (CB). For such a situation, the optical activation energy (bare after referred to as OAE) corresponds to the band-gap of the semiconductor. Tanenbaum and Briggs [14.2] first observed experimentally that for a degenerate n-type semiconductor, the OAE is greater than the band-gap. The idea of the Burstein and Moss with respect of enhancement of OAE in degenerate n-type semiconductors is known in the literature as the Burstein-Moss shift (BMS). On the basis of BMS, the OAE \( E_A^n \) was obtained as [14.3,14.4-14.9].

\[
E_A^n = E_x + \left[ 1 + \left( \frac{m_e}{m_v} \right) \right] E_f
\]

where \( E_x \) is the intrinsic band-gap of the semiconductor, \( m_e \) is the effective electron mass at the edge of the CB, \( m_v \) is the effective hole mass at the edge of the VB and \( E_f \) is the Fermi energy as measured from the edge of the CB in the vertically upward direction. The deviation of Eq.(14.1) is based on the two assumptions, namely: (a) the band-structure of the degenerate semiconductor is independent of the formulation of band-tails and (b) the optical matrix element (OME) is constant with respect to the wave vector (k). We shall observed that OME, which characterizes the inter-band transition probability of an electron from VB to CB, is not constant with \( k \) for substantial range of it. Besides, the formation of band-tails in degenerate semiconductors for the determination of Fermi energy is an experimental fact [10,11] in the study of BMS. In view of the said two factors, the well known formula for \( E_A^n \), as given by
Eq.(14.1) for degenerate n-type semiconductors will change. We feel that a meaningful theory of optical absorption as well as OAE in such a case should properly take into account of the k-dependence of OME and the effect of band-tailing in the calculation of Fermi energy respectively. In what follows, we present our analysis of the OAE and related issues, such as the optical absorption co-efficient incorporating the wave vector dependence of the OME. We shall provide a brief account of band-tailing effect in the determination of Fermi energy on the basis of a newly formulated electron dispersion law. Finally, we discuss our results on the context of relevant experimental findings.

14.2. Theoretical Analysis

14.2.1. Analysis of Optical Absorption by Semiconductors and other issues

Using the fact that the Fermi-energy \( E_f \) for a degenerate n-type semiconductor lies above the minimum of CB, the matrix element \( W_{\omega} \) characterizing the probability rate of inter-band transition between the VB and CV for such a case can be written [1,9] as

\[
W_{\omega} = \left( \frac{2\pi}{\hbar} \right) \left[ \frac{eA_0}{m} \right]^2 \int \left( \frac{2d^3k}{(2\pi)^3} \right) \epsilon M_{\omega}(k) \left[ 1 - f(E_c - E_f) \right] \delta[E_c(k) - E_v(k) - \hbar \omega]
\]  

(14.2)

where, \( \epsilon \) is the direction of polarization of the light wave vector, \( A_0 \) is the amplitude of the light wave, \( m \) is the free electron mass, \( \hbar \omega \) is the photon energy, \( E_v(k) \) and \( E_c(k) \) are the energies of the electron in VB and CB respectively, \( f(E_c,E_v) \) is the Fermi-Dirac distribution function and \( \epsilon M_{\omega}(k) \) is the optical matrix element (OME) which, can, in turn be expressed as

\[
\epsilon M_{\omega}(k) = \int u_v^*(k,r)(\epsilon,p)u_v(k,r)d^3r
\]

(14.3)
where, $u_c$ and $u_v$ are the wave functions in the CB and VB respectively. In the conventional treatment of optical absorption, $M_{\sigma}(k)$ is approximated by $M_{\sigma}(0)$ which is independent of $k$, for direct band transition. The eigen function $u_c(k,r)$ and $u_v(k,r)$ can be expressed as:

$$u_c(k,r) = \frac{1}{\sqrt{2\eta}}\left\{ (\eta + E_g)u_c(0,r) + \sqrt{\eta - E_g}u_v(0,r) \right\}$$  \hspace{1cm} (14.4)

$$u_v(k,r) = \frac{1}{\sqrt{2\eta}}\left\{ (\eta - E_g)u_c(0,r) - \sqrt{\eta - E_g}u_v(0,r) \right\}$$  \hspace{1cm} (14.5)

where \( \eta = E_c(k) - E_v(k) = \sqrt{E_g^2 + \left( \frac{E_g \hbar^2 K^2}{m_r} \right)} \)  \hspace{1cm} (14.6)

in which $m_r$ is the reduced effective mass and can be written as

$$\frac{1}{m_e} = \frac{1}{m_c} = \frac{1}{m_v}$$  \hspace{1cm} (14.7)

Thus combining Eqs. (14.3) -- (14.5) we can write,

$$M_{\sigma}(k) = \left( \frac{E_g}{\eta} \right) M_{\sigma}(0)$$  \hspace{1cm} (14.8)

where, $M_{\sigma}(0) = \left( \frac{m}{2} \right)^{\frac{3}{2}} \sqrt{\frac{E_g}{m_r}}$  \hspace{1cm} (14.9)

It is worth noting from Eqs.(14.6) and (14.8) that OME is k dependent.

The use of Eqs. (14.2), (14.6) and (14.8) leads to the expression of $W_{\sigma\sigma}$ as

$$W_{\sigma\sigma} = \left( \frac{2}{\pi \hbar} \right)^2 \left\{ \frac{\epsilon e^2}{m} \right\} \left\{ \frac{\epsilon M_{\sigma}(0)^2}{\hbar^2} \right\} \left\{ \frac{m \frac{3}{2} E_g \frac{1}{2} \left( \hbar \omega \right)^2 - E_g \frac{1}{2}}{\hbar \omega} \right\} \left[ 1 + \exp(\gamma) \right]^{-1}$$  \hspace{1cm} (14.10)
where \( \gamma = E_f - \left[ \frac{m_r}{2m_e} \right] [(h\omega)^2 - E_g] \) \hspace{2cm} (14.11)

The optical absorption co-efficient (\( \alpha \)) can, in general, be written [14.12] as

\[
\alpha = \left[ \frac{2h\omega}{e\varepsilon_0CA_0^2} \right]
\]

(14.12)

where, \( n \) is the refractive index of the semiconductor, \( \varepsilon_0 \) is the permittivity of vacuum, and \( C \) is the velocity of light in free space.

Using Eqs. (14.10)-(14.12) we can write

\[
\alpha = \frac{\alpha_0}{1 + \exp(\gamma)}
\]

(14.13)

where, \( \alpha_0 = K \left[ \frac{(2m_r)^{3/2}}{(h\omega)^2} \right] \left[ \frac{E_g^{1/2}}{\sqrt{2}} \right] \sqrt{(h\omega) - E_g^2} \)

(14.14)

in which, \( K = \frac{e^2E_g}{2\pi e_0 \hbar^2 m_r} \)

Physically, \( \alpha_0 \) represents the optical absorption co-efficient for pure semiconductor (i.e., independent of \( E_f \)) taking into account the \( k \)-dependence of the OME. For comparison, we also note here the following form of optical absorption co-efficient (\( \alpha_{op} \)) in the present case considering wave-vector independent OME as

\[
\alpha_0 = K \left[ \frac{(2m_r)^{3/2}}{(h\omega)} \right] \sqrt{(h\omega) - E_g}
\]

(14.15)
For the inter-band transition to occur in a degenerate n-type semiconductor, the above Fermi level in the CB, we find [14.9] from Eq.(14.2) that

$$\hbar \omega_i = E_e(k_f) - E_e(k_r)$$

(14.16)

which corresponds to the case [14.9], at $\hbar \omega = \hbar \omega_\alpha$ from Eqs.(14.11) and (14.13)

$$\frac{1}{1 + \exp(y)} = \frac{1}{2}$$

(14.17)

generating

$$\hbar \omega_i = \sqrt{E_g^2 + 2 \left(1 + \left(\frac{m_e}{m_s}\right)\right) E_g E_f}$$

(14.18)

where, $\hbar \omega_\alpha$ is the OAE and $k_f$ is the momentum vector at the Fermi-surface. For a parabolic band, we have,

$$E_f = \frac{\hbar^2 k_f^2}{2m_e}$$

(14.19)

The Eq.(14.18) expresses the OAE for parabolic band with the inclusion of the k-dependence of OME. For comparison, we note the following form [14.3] of OAE (i.e., $(\hbar \omega_\alpha)$) for a degenerate semiconductor in the absence of band-tailing together with k-independency of OME as:

$$\hbar \omega_\alpha = E_g + \left[1 + \left(\frac{m_e}{m_s}\right)\right] E_f$$

(14.20)

In the limiting case for large $E_g$, Eq.(14.18) may be approximated by Eq.(14.20).
The optical absorption edge for a pure semiconductor is $E_g$, while the optical absorption edges of a n-type semiconductor are $(\hbar \omega_c)$ and $(\hbar \omega_a)$, corresponding to the constancy of OME with $k$ and dependence of OME on $k$ respectively. The shift of the absorption edge, $\Delta_\varepsilon$ and $\Delta_c$, for these two cases are given by

$$
\Delta_\varepsilon = \hbar \omega_\varepsilon - E_g \quad (14.21)
$$

$$
\Delta_c = \hbar \omega_\varepsilon - E_g \quad (14.22)
$$

14.2.2. Calculation of Fermi-energy in Degenerate n-type Semiconductors forming Band Tails

In order to derive the E-K dispersion relation in the present case, the space dependent ($r$) kinetic energy of an electron can be expressed as

$$
E - V = \frac{\hbar^2 k^2}{2m_e} \quad (14.23)
$$

where, $V(r)$ is the impurity potential at a local point $V(r)$. The potential energy can be written as [14.11]

$$
F(V) = \frac{1}{\sqrt{\pi \eta_\varepsilon^*}} \exp \left( - \frac{V^2}{\eta_\varepsilon^*} \right) \quad (14.24)
$$

In which $\eta_\varepsilon = \sqrt{\left( \frac{e^2}{\varepsilon_d} \frac{4\pi N_EL_{pe}}{e_d} \right)}$. 

where \( \varepsilon_d \) is the material dielectric constant, \( N_i \) is the carrier concentration and \( L_s \) is the screening length.

The average of kinetic energy of the whole system is obtained by averaging the local kinetic energy fluctuation as represented by:

\[
\frac{\hbar^2 k^2}{2m_e} \int_{-\infty}^{\infty} F(V) dV = \left( \frac{\hbar^2 k^2}{2m_e} \right) \int_{-\infty}^{\infty} F(V) dV
\]  \hspace{1cm} (14.25)

As the function \( F(V) \) is the Gaussian distribution with the limits of \( V \) extending from \(-\infty\) to \(+\infty\), so in the right hand side of Eq.(14.25), we can extend the limits of \( V \rightarrow E \) to \( V \rightarrow \infty \).

Thus from Eq.(14.25) we can write

\[
\left( \frac{\hbar^2 k^2}{2m_e} \right) = \gamma_0(E, \eta_s)
\]  \hspace{1cm} (14.26)

where \( \gamma_0(E, \eta_s) = \left( \frac{\eta_s}{2\sqrt{\pi}} \right) \exp\left( -\frac{E^2}{\eta_s^2} \right) + \left[ \frac{1}{2E} \left[ 1 + \text{Erf}\left( \frac{E}{\eta_s} \right) \right] \right] \) and \( \text{Erf}(n) \) is the error function.

It may be noted from Eq.(14.26) that when the semiconductor is heavily doped (i.e., \( \eta_s \neq 0 \)), the E-K dispersion relation is no longer related to the exponential and error functions. For \( E < 0 \), \( \eta(E, \eta_s) \) shows a positive value. This indicates that the energy band is tailed into the forbidden region due to the heavy doping. For \( E > 0 \), the parabolic nature of the band is not being exhibited. Besides, for \( E \rightarrow \infty \), i.e., in the deep region of CB, \( \eta(E, \eta_s) \) approaches to the parabolic one. Use of Eq.(14.26) leads to the expression of the density-of-states function as

\[
\rho(E, \eta_s) = 4\pi \sqrt{\frac{2m_e}{\hbar^2}} \sqrt{\gamma_0(E, \eta_s)} \left[ 1 + \text{Erf}\left( \frac{E}{\eta_s} \right) \right]
\]  \hspace{1cm} (14.27)
From Eq.(14.27), the expression of the carrier statistics in the region of very low temperatures can be written as

\[
N_i = \left( \frac{1}{3 \pi^2} \right)^{\frac{3}{2}} \left( \frac{2 m_e \gamma(E_{f*}, \eta_*)}{\hbar^2} \right)^{\frac{3}{2}}
\]

(14.28)

In which \( E_{f*} \) is the Fermi-energy corresponding to the carrier concentration \( N_i \) in the band tailing states.

Conventionally, the Fermi-energy \( (E_f) \) in degenerate semiconductors having parabolic energy bands is given [14.18] by

\[
E_f = \left( \frac{\hbar^2}{2m_e} \right) \left( \frac{3 \pi^2 N_i}{\hbar^2} \right)^\frac{2}{3}
\]

(14.29)

We wish to note that Eq.(14.29) can be obtained from our generalized Eq.(14.28) in the absence of band tailing effects.

14.3. Results and Discussions:

Taking \( n-InSb \) as an example for numerical computations together with the parameters [14.17] \( E_g = 0.235 \text{ev}, m_e = 0.1359 m, m_\nu = 0.45 m, n = 5.13 \) and \( T = 4.2 \text{K} \), in Fig.1 we have plotted the normalized OME (i.e., \( | \epsilon \cdot M_{\omega}(k) | / | \epsilon \cdot M_{\omega}(0) | \) ) with the momentum vector \( k \). It appears from Fig.1 that the normalized OME \( M_{\omega}(k) \) shows large variation with \( k \) near the band edge, where the value of \( k \) is small. As we move away from the band edge (i.e., deep into the CB), the normalized approaches almost a constant value. This indicates that the effect of \( k \)-dependence of OME of various entities, related to optical absorption etc., is expected to be significant near the band edge.
Figure 14.1 Variation of a normalized optical matrix element (i.e., $|\delta M_\nu(K)|/|\delta M_\nu(0)|$) with $k$ for n-InSb at 4.2K.
Figure 14.2 Variations of Fermi energies $E_{\bar{\mu}}$, $E_f$ (in eV) with and without band-tailing effects, respectively, against carrier concentration $N_t$ (in $\text{cm}^{-3}$) for InSb at 300K.
Figure 14.3 Variations of optical activation energies ($\omega_{1}$), ($\omega_{nc}$) and experimental (in eV) with carrier concentration $N_{i}$ (in cm$^{3}$) for n-type InSb at 300K
Figure 14.4 Shifts of the optical absorption edges ($\Delta$ and $c_0$ (in eV)) with respect to carrier concentration $N_i$ (in cm$^{-3}$) for n-type InSb at 300K.
The results relevant to the Fermi-energies \( E_f \) and \( E_{fe} \) (in ev) are presented in Fig. 14.2 for various values of carrier concentration, \( N_t \) (in cm\(^3\)) for InSb. It is apparent from Fig. 14.2 that as the carrier concentration increases, Fermi-energies also increase and \( E_{fe} \) approaches to \( E_f \) at very large of \( N_t \). The value of \( E_{fe} \) is always less than \( E_f \). This Fermi-energies (i.e., \( E_{fe} \) and \( E_f \)) are used to estimate \( (\hbar \omega_r) \) and \( (\hbar \omega_{te}) \) respectively and are plotted in Fig. 14.3.

The graphs in Fig. 14.3 exhibit the variations of the optical activation energies \( (\hbar \omega_r) \), \( (\hbar \omega_{te}) \) and experimental results [14.18] against carrier concentration, \( N_t \) for InSb. It is clear from Fig. 14.3 that \( (\hbar \omega_r) \), in accordance with the present theory, agrees better with the experimental findings than \( (\hbar \omega_{te}) \) which is, in turn, represents the conventional approach.

Fig. 14.4 shows the variations of the shifts of optical absorption edges \( (\Delta \text{ and } \Delta_c \text{ in ev}) \) with carrier concentration \( N_t \) (in cm\(^3\)) for \( n-InSb \). The graphs in this figure indicates that \( \Delta \) is less than \( \Delta_c \).

On the basis of various features as shown in Figs. 14.1-14.4, we can state that for the realistic interpretation of the optical activation energy along with other relevant issues in degenerate n-type semiconductors, it is important to make use of the wave vector dependence of OME together with the influence of band-tails at such higher values of carrier concentrations of which, the present analysis is based. The dispersion relation for heavily doped semiconductors so obtained in a simplified way, is vital in view of the fact that the physical entities like the Einstein relation, thermoelectric power, effective electron mass, specific heat etc. for heavily doped semiconductors can be obtained by using our dispersion law in a simple way. Finally it may be noted that the electron energy spectrum is formulated in this paper represents a simple method of analysis of devices made of heavily doped semiconductors together with the fact that various transport co-efficient of such materials through the respective solutions of the Boltzmann transport equation, which, in turn is controlled by E-K relation as formulated in this paper can also be investigated.