ADVOCACY OF THE MODIFIED ROOSEBROECK-SHOCKLEY RELATION FOR
BANDGAP DETERMINATION USING FOURIER TRANSFORM INFRARED
PHOTOLUMINESCENCE SPECTROSCOPY OF HEAVILY P-DOPED GALLIUM
ARSENIDE

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ABSTRACT

Dr. Bruno Ullrich, Advisor

This work demonstrates the applicability of the modified Roosbroeck-Shockley relation for bandgap determination of heavily p-doped gallium arsenide and addresses in detail the absorption coefficient, the temperature dependence of the bandgap, the carrier temperature under laser excitation, and it emphasizes the importance of phonons resulting from photo-excited carrier-carrier interaction for the band gap energy.
To my wife, Alison, who encouraged me to get back in the game. And to my sons, Spencer and Elias, who encouraged me to keep smiling. And to my mom, who was able to teach me the value of learning and to my dad, who tried for so long to instill in me the value of education.
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As with all laborious processes in my life, success is attributable to a large collection of people. I cannot overstate the importance of Dr. Bruno Ullrich to this work. Without him, I would not have started nor finished this journey. My thanks also go to the many people at the Air Force Research Lab who provided top cover (Laura, Joe), or encouragement (the pit crew), or inspiration (Rand, Col S). Finally, I thank Dr. Lewis Fulcher for his flexibility and dedication to BGSU and his students.
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Fitting Parameters
INTRODUCTION

GENERAL INFORMATION

Modeling and prediction of electronic properties of semiconductor materials is critical to the efficient and creative development of devices in the commercial market, several research fields, and for national defense. The level of detail of a particular model will often correlate directly with its accuracy and with its complexity of employment, but that is not always the case. Simple and accurate models are sought to enable quick and useful information about proposed semiconductor structures and various tailorable parameters.

PROBLEM

The goal of this research was to develop a simple and extremely accurate model of the bandgap and spectral shape of heavily p-doped Gallium Arsenide (GaAs) and verify its accuracy using Fourier transformation infrared (FTIR) spectroscopy. A great deal of theoretical and experimental study has been conducted on GaAs and this work builds upon that foundation. Paramount among that work is the Roosbroeck-Shockley relation (RSR) given by 1:

\[ I_0(h\nu) \propto \frac{[h\nu]^2 \alpha(h\nu)}{\exp[h\nu/kT_c]-1}, \]

Eq 1

where \( I_0(h\nu) \) is the intensity of the radiated photoluminescence for a specific energy \( h\nu \) without the influence of self-absorption, \( \alpha(h\nu) \) is the energy dependent absorption coefficient, and \( kT_c \) is the thermal carrier energy, and \( kT \) is the ambient thermal energy of the lattice. The RSR has been used to predict the energy bandgap of semiconductor materials 2, a property of fundamental importance to device design.
The addition of impurities or dopants to a semiconductor introduces additional allowed energy levels. The validity of the RSR has been questioned for heavily doped semiconductors on the basis that these impurity levels can be used by photo-excited carriers to make small, non-optical transitions and therefore break the balance between absorbed and emitted radiation\(^3\). However, Hwang demonstrated the validity of the RSR for both degenerate and non-degenerate GaAs in 1969\(^4\). Additionally, in 1976, Casey and Stern successfully employed the RSR to predict the bandgap reduction of heavily p-doped GaAs at room temperature\(^5\). This thesis advocates the use of a modified RSR as a simple and extremely accurate predictive model of heavily p-doped GaAs and addresses in detail the absorption coefficient, the temperature dependence of the bandgap, the carrier temperature under laser excitation, and it emphasizes the importance of phonons resulting from photo-excited carrier-carrier interaction for the band gap energy.
SEMICONDUCTOR BASICS

All materials can be divided into one of three categories, insulators, conductors, or semiconductors, based upon the ability of the material to conduct electricity, which is related directly to its availability of charge carriers, such as electrons, that are relatively unbound and free to move. A very important property governing the performance of any semiconductor is its bandgap. In its most elementary sense, the bandgap is a measure of the energy difference between the highest allowed electron energy level in the lower energy valance band and the lowest allowed electron energy level in the higher energy conduction band.

**Figure 1: Definition of bandgap**

For a pure material, the energy difference between its valance and conduction band is called the intrinsic bandgap. Non-intrinsic energy levels can be introduced by adding dopant materials, often called impurities, embedded in the otherwise pure material or from interface interactions between two layers of adjacent materials. It is important to note that the bandgap of a material can be tailored using impurities, interface composition and spacing, temperature variation, and so forth.

In an intrinsic semiconductor, the bandgap can be relatively small, as is the case for indium antimonide whose bandgap is approximately 0.17 electron-volts (eV) at a temperature of 300 K\(^6\). By contrast, it can also be rather large as evidenced by a bandgap
of roughly 2.4 eV at 300 K for cadmium sulfide\textsuperscript{7}. These energies that are required to excite an electron from the valance band to the conduction band are well beyond the energy typically available through thermal excitations, roughly 0.026 eV.

However, when dopants are added, additional energy states, usually within the bandgap, are made available to the material. This effectively reduces the amount of energy required to create an excited electron. For sufficiently highly doped semiconductors, these impurity levels may be very close to or even above the lowest conduction band. The latter case is called degenerate, but in either case thermal excitation of an electron is a real possibility. This is a concern shared by many researchers when applying the RSR, since optical emissions are possible but optical absorption is not required in this case. This concern will be further addressed in detail in the results section.

All semiconductors have either a direct bandgap structure or an indirect bandgap structure. When viewing electron energies in momentum space, a direct bandgap structure will have the lowest energy in the conduction band directly above the highest energy in the valance band.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{direct_bandgap.png}
\caption{Energy vs momentum diagram for direct bandgap}
\end{figure}
In direct bandgap semiconductors, an excited electron in the conduction band can transition directly to an unoccupied electron space, called a hole, in the otherwise full valance band while conserving momentum. In this way an excited electron combines with a hole and produces a photon with energy equivalent to the bandgap. This energy is given off as a photon and the process is called radiative recombination.

The opposite of recombination is absorption, which is a process by which the excited electron can get into the conduction band initially. When optical radiation equal to or greater than the bandgap is incident on a material, that radiation can promote an electron from the valance band to the conduction band. The process of excitation or recombination across a bandgap is called an interband transition. Another type of interband transition is noteworthy. Thermal interband excitation of electrons can occur if the bandgap is particularly small and if the thermal energy available is greater than this small bandgap.

![Interband and Intraband Transitions](image)

**Figure 3: Interband and intraband transitions**

Within the conduction band various energy levels exist that are separated by very small energies. Absorption of a very small increment of energy can promote an electron in the conduction band to another of these closely spaced energy levels. This is called an
intraband transition. Interband transitions will be the majority of transitions of interest in this work, but intraband transitions will be discussed as well.

An indirect bandgap semiconductor has a conduction band minimum and valence band maximum with different momenta. Direct recombination between the electron and hole does not conserve momentum and is forbidden unless a phonon interacts.

![Figure 4](image)

**Figure 4: Energy vs. momentum diagram for indirect bandgap**

Electron transitions in indirect bandgap semiconductors require another, usually vibronic, step. An indirect bandgap semiconductor must simultaneously absorb a phonon to conserve momentum and a photon to conserve energy in order for an electron to traverse the bandgap in one step. The probability of that is very low, especially at low temperatures. This makes indirect bandgap semiconductors not efficient as photonic collectors or emitters.
PROPERTIES OF GALLIUM ARSENIDE

Gallium arsenide, GaAs, is a chemical compound that is a direct bandgap semiconductor. Like all semiconductors, it can have properties that are both insulative and conductive, depending on external and internal parameters. It can be used to make many devices including integrated circuits. Because of its direct bandgap structure, it has a high probability to radiate energy when its electronic state relaxes subsequent to stimuli. Due to this, GaAs is frequently used to make emitters and absorbers, primarily light emitting diodes and detectors, both in the near infrared. Of great benefit to the construction of the many potential applications of GaAs is the ability to predict or model the electronic properties of this semiconductor using as simple a model as possible while delivering accurate predictive results.

GaAs has an intrinsic bandgap given by which

\[ E_g = 1.519 - \left(5.405 \times 10^{-4} T^2\right) / \left(T + 204\right) \text{ eV}, \]

where \( T \) is the temperature in Kelvin. This gives a value of about 1.43 eV at room temperature, which corresponds to 873.13 nanometers (nm), just outside the visible range and into the near infrared.

![Figure 5: Visible spectrum](image)
MODIFIED ROOSBROECK_SHOCKLEY RELATION

Of extreme importance to developing useful applications of semiconductor materials is the ability to alter the bandgap of the material for different purposes. Just as important is being able to determine what factors are instrumental in determining that bandgap, such as doping, pressure, temperature, excitation energies and intensities. A good place to start when considering these factors is the principle that, when in equilibrium, the energy added to a semiconductor will eventually be released by that semiconductor. This basic principle was used as a foundation by W. Van Roosbroeck and W. Shockley in 1954 to describe the relationship between absorption and emission in semiconductors. This relationship, called the Roosbroeck-Shockley relation, or RSR, simply states that the rate at which electron-hole pairs are generated by optical absorption is equal to the rate of radiative recombination, or photoluminescence (PL), of those electron-hole pairs. The RSR links emission with absorption in semiconductors, and modification of this relation has yielded a simplified model with very high accuracy which can be used in the development of tailored bandgap materials for specific applications.

SELF-ABSORPTION

The intrinsic RSR, not including the effect of self-absorption of radiation caused by radiative recombination within the material, is given again for clarity:

\[ I_0(h\nu) \propto \frac{[h\nu] \alpha(h\nu)}{\exp[h\nu/kT_c] - 1}, \]

Eq 1

The relationship between \( kT_c \) and \( kT \) will be examined in further detail.

The development of the modified RSR begins with the application of self absorption considerations to the intrinsic RSR. Since the PL may be generated within the
material, it must successfully travel to the surface before it can be detected. The depth within the material that PL can be generated is given by the active thickness, $d$. This is the distance that incident radiation can be expected to penetrate the material. Since the PL is uniformly generated inside the material to a depth of its active thickness, the intensity of the emitted light that is not self absorbed is given by:

$$I(h\nu) \propto I_0(h\nu) \frac{1 - \exp[-\alpha(h\nu)d]}{\alpha(h\nu)d},$$  \hspace{1cm} \text{Eq 3}

Combining the self-absorption proportionality with the intrinsic RSR, and taking into account that $\exp[h\nu/kT_c] \gg 1$, results in the employed modified RSR that was employed for this work:

$$I(h\nu) \propto I_0(h\nu)[1 - \exp[-\alpha(h\nu)d]] \exp[-h\nu/kT_c]$$  \hspace{1cm} \text{Eq 4}

**ADAPTED URBACH RULE**

The next modification resulted from an examination of the density of states used in the determination of the absorption coefficient. Casey and Stern pointed out that the parabolic-band density of states

$$\alpha(h\nu) = A[h\nu-E_g]^{1/2},$$  \hspace{1cm} \text{Eq 5}

agrees well with $\alpha(h\nu)$ for p-type GaAs if the energies of the PL are clearly above the band gap but does not agree well with the absorption behavior for PL energies at and below the band gap ($\approx 1.45$ eV). In fact, below 1.45 eV, $\alpha(h\nu)$ is much larger than predicted from parabolic-band density of states. To address this modeling error, the Urbach rule,

$$\alpha = K_0 \exp\{(\sigma/kT)(E-E_g)\}$$  \hspace{1cm} \text{Eq 6}
was introduced and the absorption coefficient was written as a function of bandgap energy\textsuperscript{12}. Here, $\sigma$ is a dimensionless phenomenological constant that describes the steepness of the band tail. Matching the amplitudes and derivatives of the two absorption functions, the crossover point between the density of states related absorption and Urbach rule absorption is found to be

$$E_{cr} = E_g + \frac{kT}{2\sigma}.$$  \hspace{1cm} \text{Eq 7}

A continuous function for $\alpha(\hbar \nu)$ is constructed by using the expression for parabolic-band density of states

$$\alpha(\hbar \nu) = A[\hbar \nu - E_g]^{1/2},$$  \hspace{1cm} \text{Eq 8}

for energies $\hbar \nu \geq E_{cr}$ and the adapted Urbach rule

$$\alpha(\hbar \nu) = A \left[ \frac{kT}{2\sigma} \exp \left( \frac{\sigma}{kT} [\hbar \nu - E_{cr}] \right) \right],$$  \hspace{1cm} \text{Eq 9}

for $\hbar \nu \leq E_{cr}$. Here the constant $A \approx 10^4 \text{ cm}^{-1}(\text{eV})^{-1/2}$ is related to the saturation value of $\alpha(\hbar \nu)$.\textsuperscript{13}

Additional information about the adapted Urbach rule is important to note. Although the mathematical expression of Urbach’s rule appears simple, the physics that it represents is rather complicated. Although considerable attempts have been made for more than 30 years\textsuperscript{14}, a generally valid model has not yet been established due in large part to the lack of data on the temperature dependence of the $\sigma$ parameter for GaAs. An extensive search of the literature produced attempts to determine Urbach parameters for GaAs using reflectance and transmission measurements\textsuperscript{15} but none have been attempted using PL analysis. Based upon Einstein’s single oscillator model that was used...
to fit the thermal broadening of the absorption edge in the previous attempts, $\sigma(T)$ is given by:

$$\sigma(T) = kT(S_0 h\nu_p)^{-1} \left( \frac{1 + X}{2} + \frac{1}{\exp(h\nu_p / kT) - 1} \right)^{-1}$$

Eq 10

Here, $S_0$ is a dimensionless coupling constant and the parameter $X$ accounts for structural imperfections of the material investigated. The values determined for $S_0$ and $X$ are discussed further in the results and conclusion section.
PHOTOLUMINESCENCE BASICS

Photoluminescence, or PL, is the photonic emission that results from optical excitation of a material. PL analysis is the study of the resulting emission spectrum and is a very straightforward, non-contact, nondestructive method of material characterization. Each photon within the PL spectrum is created by an excited electron returning to its non-excited state. These transition energies can be used to determine electronic energy levels and so PL analysis can be used to investigate a wide range of material parameters. These include surface roughness, interface quality, alloy composition, impurity energy levels, defect density, and, most commonly, bandgap values for the material under investigation. PL can be studied under a variety of conditions including sample temperatures that typically range from 4K to 300K, variable excitation energies that produce information about the electronic structure of a material, and variable incident intensity that can contribute to optical doping.

THERMAL AND INCIDENT INTENSITY AND ENERGY CONSIDERATIONS

Because PL analysis techniques are fairly simple, do not require exotic equipment, and because they require no electrical contacts to be made, the sample preparation and manipulation efforts are minimal. PL analysis is also non-destructive, allowing a high rate of sample re-use. Contributing to the simplicity is the fact that room temperature PL is suitable and will provide adequate information for many purposes. However, the sample temperature does alter the bandgap appreciably and since low temperatures will minimize thermal broadening of the emitted spectrum, liquid helium temperatures are required for the highest resolution\textsuperscript{16}. As will be discussed in more detail in the results section, sample heating may occur, but effects of this are minimal in
moderate temperature situations and can be reduced even further by using low incident intensity.

In addition to thermal considerations, incident energy and intensity are important parameters when using PL analysis techniques because of the effects upon the bandgap. The intensity of the incident light will correlate directly to the density of excited electrons in the material and that is a dominant factor in the generation of the emitted PL signal.

![Figure 6: Photo-excited carrier generation](image)

It is important to note that the carrier density with the greatest effect on PL emission is the larger of either of the carriers supplied by the doping level or by those supplied by photo-excitation\textsuperscript{17}. The relationship between the density of excited electrons and the thermal excitation on the emitted PL will also be discussed further in the results section. The energy of the incident light needs to be at least equal to the lowest energy gap of the material, so a systematic variation of this incident energy can help determine the bandgap. Similarly, the incident energy determines the depth to which the energy will penetrate a particular material. Typical penetration depths are between 1 and 10 micrometers (\(\mu\)m)\textsuperscript{18}.

The disadvantages of PL analysis are straightforward as well. PL analysis can only be used on materials that can be excited by optical means and whose excited electron relaxation results in radiative recombination. Direct bandgap semiconductors fall within these parameters, but indirect bandgap semiconductors do not because the
nonradiative recombination tends to be the dominant relaxation method which results in a low PL efficiency. Although the relative measurements of the density of impurity and defect states that radiate upon recombination within a sample are easily determined, it can be difficult to determine the absolute densities of these parameters without a wide range of excitation energies available.

Typical PL emissions are weak and require sensitive detectors which can limit the applicability of the technique. Additionally, the minimal amount of complex equipment arises from the need to transmit optical energy in a particular wavelength into a pressure and temperature controlled environment while allowing the transmission of quite often different wavelengths out of that sealed environment.

**INFORMATION IN THE SPECTRUM**

A PL spectrum gives direct insight into the energy levels available within a material. When examining the PL emission spectrum, the line width, peak location, and peak intensity are all important quantities that readily offer information about the material under investigation.

In the PL spectrum, a larger intensity response is indicative of a large number of radiative recombination events at a particular energy. Therefore, the peak position of a PL spectrum is direct evidence of an energy transition that is favored within a particular material at specific parameters such as temperature and incident energy. At moderate and higher sample temperatures, this peak will indicate the smallest energy difference available since thermal energy will enable the excited electrons to rapidly move to the lowest energy level available in the conduction band of the material. The presence of defects and impurities within the material are also easily identifiable in low temperature
PL analysis. Defects and impurities will create discrete energy levels that are usually located within the bandgap. These energy levels will trap charge carriers if the material temperature is low enough to prevent thermal activation of the carriers out of these energy levels. When the trapped carrier recombines, the emitted radiation can be used to determine the energy of the defect or impurity.

The line width, or energy range, of the PL peak can be an indicator of the purity of the sample. A larger line width indicates the presence of many possible energy states that lead to recombination as opposed to relatively few available for a pure material.

The intensity of the PL spectrum at any particular energy indicates the amount of radiative recombination experienced by the sample material at that specific energy level. Absolute quantities of recombination are difficult to determine, but relative quantities are readily determined by examining a single experimental run using the Fourier transform PL method that will be described in detail below.

USES OF PHOTOLUMINESCENCE

As detailed above, PL lends itself readily to determination of allowed energy level differences because the energy of the PL spectrum correlates directly to available radiative transition paths within materials and the intensity of the PL spectrum at a specific energy provides information on the frequency of occurrence of those distinct transitions. The most common use of PL is bandgap, or band-to-band transition, determination. Another prevalent use of PL is impurity level and defect detection. Impurities and defects give rise to additional allowed energy levels, thereby altering the intrinsic PL of a material. Temperature and incident intensity studies can help resolve these impurity and defect levels.
Thermal and optical recombination mechanisms are each dominant under different external conditions for various materials. Knowledge of which mechanism is dominant under specific parameters provides valuable information about semiconductor samples. Therefore, recombination methods are also studied using PL analysis. Temperature and incident intensity studies can also help determine proportionalities of thermal and optical recombination methods, but time resolved PL is the method of choice for this\textsuperscript{19}. Because non-radiative recombination mechanisms are typically a sign of defects in a material that adversely affect the performance of devices constructed from the material, PL studies can also assist in determining material quality.
MEASURING TECHNIQUE

INTERFEROMETRY

The primary piece of experimental apparatus used in this work was the BOMEM DA3 Fourier transform (FT) infrared spectrophotometer. At its core is a Michelson interferometer. The interferometer helps to determine the wavelengths of energy that compose the emitted PL spectrum. The PL is collimated and sent to the beamsplitter in the interferometer where the beam is effectively divided into two beams of interest, each containing the same energy composition. A diagram of the experimental set up that includes the interferometer is shown below. The two beams of interest are labeled as “first split beam”, shown in orange, and “second split beam”, shown in blue.

![Diagram of experimental set up](image)

**Figure 7: Diagram of experimental set up**

The two split beams will return to the beamsplitter where they will then recombine and fall on a detector. The first split beam will travel an optical path denoted by OP1 and the second split beam will travel an optical path denoted by OP2. As the moving mirror in the interferometer scans through its motion, OP2 continually changes while OP1 remains constant. The optical path difference, OPD, between the two beams
is equal to OP2-OP1. As OPD reaches an integer multiple of a wavelength that is contained in the emitted PL spectrum, an intensity maximum will be recorded at the detector. Since an internal helium neon (HeNe) laser is traveling the same path as the PL spectrum, the OPD is determined from the number of HeNe interference fringes. In this way, the composition of the PL is determined. The figure below illustrates the result for a fictitious case of monochromatic PL.

**Figure 8: Monochromatic PL**

Since the OPD is determined by the position of the moving mirror which is determined by the HeNe fringe count, this system is capable of providing extremely high spectral resolution greater than 0.02 cm\(^{-1}\) at 10,000 cm\(^{-1}\).

Interferometry is recognized as having two major benefits, the multiplex advantage and the throughput advantage.

Because the interferometer allows the detector to simultaneously record a signal over a range of frequency elements N, a reduction in signal to noise ratio of \(\sqrt{N}\) is possible as long as the dominant contributor to the system noise is the noise of the detector. This is known as the multiplex advantage.
The throughput of the PL signal varies markedly between an interferometer and a dispersive method primarily due to the different geometries allowed in the optical paths of the two methods. The typical slit size through which the PL spectrum must travel when using a dispersive detection method is about 2 cm by 30 μm. Assuming the entire 2 cm height can be illuminated, this gives a total illumination area of about 0.6 mm² whereas the approximately 1.5 mm diameter of the aperture in a typical interferometer yields about 2.25 mm².

Interferometry is also known to have other benefits over dispersive methods of PL analysis. Because only two parts of the BOMEM machine, the beamsplitter and detector, require reconfiguration to tailor the system for peak performance in either the visible or infrared regions, this system has the ability to capture data over a broad range of frequencies with minimal alteration to the experimental set up. Typical ranges of operation are from 1.1 μm to 6.7 μm or from 0.3 μm to 2.5 μm. Also, unlike the simultaneous recording of the FT spectrometer, dispersive methods like grating spectrometery examine a small, very limited, frequency range with each measurement. The time saved using the simultaneous measurements of the interferometer can be substantial when compared to the many successive measurements required to capture the same range by a dispersive method.

**FOURIER TRANSFORMATION**

Fourier transform, FT, is a major component of the effectiveness of the BOMEM DA3 that, as discussed previously, has at its core a Michelson interferometer. FT spectroscopy has been utilized since the late 1980s and has become known as a very capable technique. A Fourier transform is a mathematical technique that relates
frequency to the spatial domain. In this case, it simply means that the frequency of constructive interference is converted to a distance that corresponds to the wavelength of light that is causing the interference.

**Figure 9: Graph of monochromatic PL after FT**

Figure 10 shows a typical result of a Fourier transform of a well defined PL signal.

**Figure 10: Typical PL spectrum after FT**
EXPERIMENT AND RESULTS

EXPERIMENTAL SET UP

As previously stated, FTIR analysis of PL is fairly straightforward. The primary components required are an excitation source, a cryostat, a detector, and a spectrometer. For the sake of clarity, the system diagram is repeated below.

![System Diagram](image)

**Figure 11:**

The incident energy that was used to excite the sample and produce the PL spectrum is the 514.5 nm line of an argon ion laser. The intensity was kept at a constant value of 5 Watts per cm².

The piece of material used in this investigation was an approximately 1 cm² piece of commercial GaAs that was taken from a 2 inch, 500 μm thick wafer. The wafer had an acceptor concentration of $5.2 \times 10^{18} - 1.4 \times 10^{19}$ cm⁻³. This is a high doping level so energy levels introduced by the impurities were expected to merge with the intrinsic valance band²², causing the material to exhibit the electrical conductivity of a metal.

The sample was attached to a copper cold finger using a small amount of silver paste and placed in a Janis continuous flow cryostat with calcium fluoride windows. A Lakeshore temperature controller was used in combination with adjustments to the flow
of liquid helium to generate temperatures from 5K to 300K and a thermocouple was used to determine the temperature of the sample holder. A standard silicon sample was placed at one of the two other sample holder locations on the cold finger and its PL was used to verify the temperature at 5K.

A liquid nitrogen cooled indium arsenide detector was attached to the BOMEM DA3 spectrometer described above to collect and analyze the PL from the sample.

A calcium flouride beamsplitter was chosen for this work. The spectral transmission range of this device is from 4000 cm\(^{-1}\) to 30,000 cm\(^{-1}\) which corresponds to 2.5 \(\mu\)m to 0.33 \(\mu\)m.

The system that was used for this work is shown in Figure 12.

![Figure 12: PL analysis system](image)

**FITTING**

Figure 13 shows PL spectra and their fits at various temperatures. The fitting has been performed with the same minimization algorithm applied in previous fittings from the literature\(^ {23} \) and the parameters found are summarized in Table 1.
Figure 13: Fitted Curves vs predictions

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$E_g$ (eV)</th>
<th>$\sigma$</th>
<th>$kT$ (meV)</th>
<th>$kT_c$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.393</td>
<td>2.0</td>
<td>25.0</td>
<td>29.0</td>
</tr>
<tr>
<td>280</td>
<td>1.398</td>
<td>2.0</td>
<td>24.0</td>
<td>29.0</td>
</tr>
<tr>
<td>250</td>
<td>1.415</td>
<td>1.8</td>
<td>22.0</td>
<td>26.0</td>
</tr>
<tr>
<td>220</td>
<td>1.427</td>
<td>1.7</td>
<td>19.0</td>
<td>26.0</td>
</tr>
<tr>
<td>200</td>
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<td>1.456</td>
<td>1.4</td>
<td>13.0</td>
<td>20.0</td>
</tr>
<tr>
<td>100</td>
<td>1.470</td>
<td>1.2</td>
<td>8.6</td>
<td>16.0</td>
</tr>
<tr>
<td>80</td>
<td>1.475</td>
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<td>6.9</td>
<td>14.0</td>
</tr>
<tr>
<td>50</td>
<td>1.478</td>
<td>0.9</td>
<td>4.3</td>
<td>12.0</td>
</tr>
<tr>
<td>30</td>
<td>1.479</td>
<td>0.65</td>
<td>2.6</td>
<td>10.0</td>
</tr>
<tr>
<td>5</td>
<td>1.479</td>
<td>0.12</td>
<td>0.43</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Table 1: Fitting Parameters
The calculation of the spectral PL intensity distribution was done with the modified RSR including self-absorption of the excited specimen given previously as equation 4. The measurements are shown as solid lines due to the high data density and the broken lines exhibit the theoretical fits. Excellent agreement has been achieved and the only deviation between the fit and the experimental data was found at extremely low temperatures in the vicinity of the boiling point of helium. This warrants additional study and is addressed in the Thermal Equilibrium subsection below.

**PENETRATION DEPTH**

The penetration depth, \( d \), is not a fitting parameter in the common sense because it does not influence the shape of the spectrum but sensitively moves its maximum on the energy scale. At 300 K, perfect agreement between theory and experiment was found for \( d=5.0 \, \mu m \). For the sake of simplicity, the value of \( d \) was kept constant for the remaining temperatures. It has been shown through PL investigations of thin-film CdS that the penetration depth is considerably thinner than the actual sample thickness due to highly absorbed single-photon absorption within the material\(^{24}\). For thin-film CdS with a thickness of 1.58 \( \mu m \), a penetration depth of \( d=0.73 \, \mu m \) was found. This is a much shorter active width than that of GaAs and is caused by the larger (>\(10^5 \, \text{cm}^{-1}\)) saturation absorption coefficient in CdS.

**BANDGAP ALTERATION DUE TO DOPING**

The energy gap values in Table 1 are clearly lower than those of intrinsic GaAs because the sample examined was so heavily doped. At room temperature, the fitting results should match to the well-known gap shrinkage expression of Casey and Stern\(^{25}\)

\[
E_g(eV)=E_{g,i}(eV)-B\times10^{-8}[\rho^{1/3}(\text{cm}^{-3})],
\]

Eq 11
where $E_{g,i}$ is the intrinsic band gap (1.424 eV at 300 K and 1.519 eV at 5 K), the constant $B=1.60$, and $p$ is the acceptor concentration. For the sample investigated, $p$ had a range of $5.2 \times 10^{18} - 1.4 \times 10^{19}$ cm$^{-3}$ which corresponds to 1.396 eV-1.385 eV at 300 K. The values from Table 1 fall within this calculated range. At cryogenic temperatures, 4.2 K – 77 K, $B=2.75^{26 (15)}$ and the energy span 1.462 eV – 1.478 eV is found. The $E_g$ values from Table 1 are in close agreement for this lower temperature range. Theoretical calculations using zero-temperature Green’s function formalism within the random-phase approximation of Sernelius and Persson et al.$^{27}$ resulted in a band gap shrinkage of 0.046 eV and 0.043 eV, respectively, which is up to 15% higher than the value of 0.040 eV found from Table I at 5 K. The difference shows that, according to the nomenclature of Sernelius$^{28}$, the low-temperature band gap shrinkage $\Delta E_g$ refers rather to an “apparent” value than to the “real” band gap decrease. In spite of the fact that the $\Delta E_g$ values at cryogenic temperatures are too small, Table I clearly reflects the tendency that the actual band gap is located in the low-energy part of the emission peak. On the other hand, at higher temperatures, and specifically at room temperature, the values in Table I approach the de facto band gap values, which are closer to the maximum of the PL peak due to the thermal broadening of the transition energies.

**THERMALLY INDUCED BANDGAP VARIATION**

Figure 14 shows the thermally induced energy variation of the band gap.
The squares correspond to the PL maxima in figure 12 and the dots mark the $E_g$ values from Table 1. As pointed out by Olego and Cardona\textsuperscript{29}, the actual GaAs band gap lies below the peak energy of the PL spectra. The fitted solid line was calculated with the relation\textsuperscript{30}

$$E_g(T) = E_g(0) - S[h\nu_p](\coth{h\nu_p/2kT} - 1),$$  
Eq 12

where $E_g(0)$ is the band gap at 0 K (chosen to be 1.480 eV), $S$ is a dimensionless coupling constant (=3.00), and $h\nu_p$ is an average phonon energy (=26.7 meV).

THERMAL EQUILIBRIUM

Another subject of significance is the thermal equilibrium of the sample. It is known that laser excitation causes carrier temperatures to rise above the ambient lattice temperature\textsuperscript{31}. However, the subject has never been thoroughly discussed in the literature. Figure 15 shows $\Delta(kT) = kT_c - kT$ versus $T$. The squares represent the data.
extracted from table I and the solid lines represent linear fits to the data points in the temperature ranges of 5 K-200 K and 200 K-300 K. For temperatures below approximately 200 K, $\Delta(kT)$ remains fairly constant but drops at higher temperatures. This is interpreted as a crossover between carrier temperature dominated and more phonon related PL spectra. In other words, at temperatures approaching room temperature, carrier-phonon interaction is a viable relaxation mechanism but at lower temperatures, the carrier-carrier interaction is the dominant relaxation method despite the larger difference between $kT_c$ and $kT$.

![Figure 15: Delta kT vs temperature](image)

Figure 16 shows the ratio $T_c/T$ versus $T$, which is close to unity in the temperature range 150 K - 300 K.
Figures 15 and 16 each show that at higher ambient temperatures thermal equilibrium is fairly well established, but that at lower temperatures, below 150K, photonic excitation causes a deviation from localized equilibrium. However, the results in Figure 13 demonstrate that the RSR accurately fits the spectra down to temperatures of about 30 K. This observation indicates that the main radiative transition channels in p-type GaAs are reflected by absorption conversion and the detailed balance principle is much less disturbed by thermal non-equilibrium than was expected. Consequently, indirect transitions and doping dependent carrier velocity distributions do not appreciably alter the recombination mechanism of the material. Approaching helium temperatures, however, the principle of detailed balance does not hold for the high-energy part of the emission peak since radiative recombinations without absorptive counterparts take place into the bottom of the zinc impurity band$^{32}$. 

**Figure 16: $T_c/T$ vs $T$**
ABSORPTION COEFFICIENT

It is clearly of importance to compare $\alpha(h\nu)$ from the fit with experimental data for Zn doped GaAs. For this purpose, results were extracted from the paper by Casey Jr. et al.\textsuperscript{33} and their comparison with the fit result is depicted in figure 17.

![Figure 17: Absorption coefficient vs energy](image)

The dashed and dotted lines are the measured $\alpha(h\nu)$ for free hole concentrations of $2.4 \times 10^{18}$ cm\(^{-3}\) and $1.6 \times 10^{19}$ cm\(^{-3}\), which encompasses the doping concentration of the wafer investigated. The solid line shows $\alpha(h\nu)$ calculated with equations 8 and 9 with $A=2.5 \times 10^4$ cm\(^{-1}\)(eV\(^{-1/2}\)) resulting in an effective thickness $d=10$ µm, which is close to the maximum electron diffusion length in GaAs\textsuperscript{34}. Despite the straightforwardness of the model used, the shape of the absorption edge is quite well described.
CONCLUSIONS

This work has shown how the modified RSR reproduces the spectral PL distribution of heavily doped p-type GaAs over a temperature span of 5 K-300 K. Accurate fits have been established by straightforwardly modeling the absorption with density of states and the Urbach rule. Comparisons with the literature values reveal that the modified RSR delivers accurate data of band gap shrinkage due to doping and temperature dependence of the absorption. The work further stresses the capability of the modified RSR to establish the temperature profile of the carrier energy of laser-excited semiconductors. Finally, this work shows that the fundamental principle of detailed balance, upon which the RSR is built, governs the overall spectral emission behavior of p-type GaAs although the theoretical applicability demand, i.e., intrinsic material in the thermal equilibrium, is not established.


