PHOTOLUMINESCENCE OF III-V SEMICONDUCTORS AND RELATED HETEROSTRUCTURES

UNDER HYDROSTATIC PRESSURE

BY

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For my Mother and late Father

To whom I am eternally indebted
There is an A B C of ignorance which precedes knowledge
and a Doctoral ignorance that comes after it.

Montaigne "Of Vain Subtleties", Essays 1580
A good many times I have been present at gatherings of people, who, by the standards of the traditional culture, are thought highly educated and who have with considerable gusto been expressing their incredulity at the illiteracy of scientists. Once or twice I have been provoked and have asked the company how many of them could describe the Second Law Of Thermodynamics. The response was cold; it was also negative.

C.P. Snow "The Two Cultures" Rede Lecture 1959 Chpt 1
ABSTRACT

This thesis describes an experimental investigation of the photoluminescence emissions from firstly, bulk In$_{0.53}$Ga$_{0.47}$As and secondly, InGaAs\textbackslash InP and AlAs\textbackslash GaAs quantum well structures, as a function of hydrostatic pressure.

Two high pressure systems have been developed and successfully used in the course of this work, an 8kbar piston and cylinder system and a miniature diamond anvil cell.

From the high pressure measurements on the bulk InGaAs, both at room and liquid nitrogen temperatures, it is shown that the pressure dependence of the direct band-edge luminescence is non-linear and independent of temperature. Using an empirical equation of state and making some assumptions as to the value of the bulk modulus, it is found that the band-edge luminescence is linearly dependent upon the lattice constant and may be described by a band-edge deformation potential of $-8.25 \pm 0.1$eV. Theory compares favourably with this value.

From low temperature measurements of both quantum well systems it has been possible to deduce a quantitative description of how the conduction and valence band-edge discontinuities vary as a function of the applied pressure. It is shown that the band-offset ratio changes with pressure. This work constitutes the first observation of this phenomenon which had previously been thought either too small to be of consequence, or simply ignored. It is found that the conduction-band discontinuity in InGaAs\textbackslash InP quantum wells decreases at $-2.3 \pm 0.6$meV/kbar while its valence-band discontinuity remains constant. The valence-band discontinuity in the AlAs\textbackslash GaAs superlattice is directly measured to increase at $+1.1 \pm 0.1$meV/kbar. An analysis of reported data for
Al$_x$Ga$_{1-x}$As/GaAs quantum wells shows that the pressure coefficient of the valence-band discontinuity is linearly dependent upon the alloy composition $x$.

Theories of band-offset ratios and in particular the "model-solid" theory of Van de Walle and Martin (Van de Walle 1987), agree exceedingly well with these experimental findings. It is suggested that such agreement lends weight to the assumption that heterojunction band-edge discontinuities are intrinsic to the bulk properties of the host materials.
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J. D. Lambkin
The following papers, based on the work presented in this thesis, have been published in the scientific literature.


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Glossary Of Symbols and Abbreviations

- $a_0$ Lattice constant
- $a_{\Gamma}$ Conduction-band deformation potential at $\Gamma$
- $a_{x^c}$ Conduction-band deformation potential at $X$
- $a_v$ Valence-band deformation potential
- $a_b$ Bohr radius
- $b$ Shear deformation-potential (tetragonal symmetry)
- $B_0$ Bulk modulus
- $B'_0$ Differential bulk modulus with respect to pressure
- $CB$ Conduction Band
- $C_{ij}$ Elastic constants
- $d$ Shear deformation-potential (rhombahedral symmetry)
- $DAC$ Diamond Anvil Cell
- $E_0$ General CB - VB band-gap
- $E_1$ Linear pressure coefficient (see Equ.2.13)
- $E_2$ Quadratic pressure coefficient (see Equ.2.13)
- $E_{\text{con}}$ Total confinement energy
- $E_{\text{ex}}$ Exciton binding energy
- $E_c$ Energy of conduction band at $\Gamma$
- $E_{\text{PL}}$ Photoluminescence transition energy
- $E_{\text{I}}$ Type-I PL transition energy
- $E_{\text{II}}$ Type-II PL transition energy
- $E_v$ Energy of valence band at $\Gamma$
- $E_{v,av}$ Average energy of the valence band, averaged over the heavy-hole, light-hole and spin split-off bands
- $E_{v,s-o}$ Energy of the spin-orbit split off valence-band
- $E_{\Gamma}$ $\Gamma^c - \Gamma^v$ direct band-gap
\( E^X_\Gamma \) indirect band-gap
\( E^L_\Gamma \) indirect band-gap
\( E_g \) Direct band gap \((\Gamma_6 - \Gamma_4)\)
\( h \) Planck's constant
\( HH \) Heavy Hole
\( j \) Total angular momentum quantum number
\( j_z \) The component of \( j \) in the \( z \) direction
\( k_B \) Boltzmann's constant
\( k \) Wave vector
\( L_z \) Quantum well width
\( LCAO \) Linear Combination of Atomic Orbitals
\( LH \) Light Hole
\( LDS \) Low Dimensional Structures
\( m_e^* \) Electron effective mass
\( m_{LH}^* \) Light-hole effective mass
\( m_{HH}^* \) Heavy-hole effective mass
\( m_{s-o}^* \) Spin-Orbit effective mass
\( m_e^0 \) Electron mass
\( m_r^* \) Reduced effective mass
\( MBE \) Molecular Beam Epitaxy
\( MOCVD \) Metal Organic Chemical Vapour Deposition
\( p \) Pressure
\( p \) The momentum operator \(-ih\mathbf{V}\)
\( P \) Momentum matrix element used in the \( k.p \) formalism
\( PL \) Photoluminescence
\( PLE \) Photoluminescence Excitation spectroscopy
\( q \) Charge of an electron
\( Q_c \) Fractional conduction-band offset (see Equ. 3.16b)
Q_v
Fractional valence-band offset (see Equ.3.16a)

T
Temperature

T_d
Group theory notation for zinc blende semiconductors

VB
Valence Band

α
Temperature coefficient (see appendix C)

β
As above

δE_{001}
LH - HH splitting due to a strain of tetragonal
symmetry (see Equ.s 2.14 and 2.15)

δE_{111}
LH - HH splitting due to a strain of rhombohedral
symmetry (see Equ.s 2.14 and 2.16)

Δ
Dilatation; Fractional change in volume ΔV/V₀

Δa/a₀
Fractional change in lattice constant

ΔE_v
Valence-band discontinuity

ΔE_c
Conduction-band discontinuity

ΔΓ
Electron confinement energy(Γ potential well)

Δ Γ_{1e}
Heavy-hole confinement energy

ΔX_{1e}
Electron confinement energy(X potential well)

Δ₀
Spin-orbit splitting (Γทย - Γось)

ε₀
Permittivity of free space

ε_r
Relative permittivity

ε_{1j}
Strain Tensor

ε_{11}, ε_{22}, ε_{33}
Strain components in the x, y and z directions

ε⊥
Strain perpendicular to an interface

ε∥
Strain parallel to the interface

ν
Frequency

ΔΓ-Γ
Direct band-gap deformation potential(Γᵉ⁻Γᵇ)

ΔX-Γ
Indirect band-gap deformation potential(Xᵉ⁻Γᵇ)
The advent of Molecular Beam Epitaxy (MBE) and Metal Organic Chemical Vapour Deposition (MOCVD) as growth techniques, with their ability to form ultrathin films to within atomic monolayer accuracy, has as a consequence, created a new field of semiconductor physics; the electronic and optical behaviour of Low Dimensional Structures (LDS). The proposal for an "engineered" LDS superlattice was first made by Esaki and Tsu in 1969 (Esaki 1970). It was in 1974 however, that Dingle's optical absorption measurements unequivocally demonstrated the reduced dimensionality through the quantization of energy levels in quantum wells, formed from ultrathin layers (50Å) of GaAs sandwiched between relatively thick layers of AlGaAs (Dingle 1974).

Since the early seventies a considerable research effort has been expended in the field of LDS, both in the fundamental physics and the exploitation of these structures in useful devices. The most significant devices utilising the two dimensional nature of these structures are High Electron Mobility Transistors (HEMTs) and quantum well lasers. An essential requirement in successfully designing such devices is an accurate description of the electronic band-structure of the heterojunction interface, or more prosaically, an accurate knowledge of the band-offset ratios.

The work covered in this thesis is an attempt to obtain further insight into the physics of the band-edge discontinuities by observing the photoluminescence (PL) from LDS under the perturbation of hydrostatic pressure, the variable of fundamental interest being the change in
lattice constant. High pressure PL has already been successfully used in determining the electronic properties of both bulk semiconductors and LDS systems (Gell 1987). In LDS systems, most effort has concentrated on GaAs/AlGaAs quantum wells, where for example, hydrostatic pressure has been used to accurately and unambiguously determine the band-edge discontinuities (Venkateswaran 1986 and Wolford 1986). The LDS systems studied in this work are In$_{0.53}$Ga$_{0.47}$As/InP type-I quantum wells and AlAs/GaAs type-II superlattices.

The thesis is structured in the following manner; chapter 2 describes the behaviour of bulk semiconductors under hydrostatic pressure necessary to understand the pressure behaviour of quantum well systems. The chapter also contains a description of the phenomenon of PL in direct-gap semiconductors and how it relates to the fundamental band-gap. Chapter 3 describes the theory used to model the PL emissions from quantum wells. Van de Walle and Martin's theory (Van de Walle 1987) of band-edge discontinuities is then reviewed, highlighting the fundamental problems facing any theory of band-edge discontinuities. Chapter 4 details the experimental apparatus and procedures used in the course of this work. The pressure dependence of the band-edge PL of InGaAs lattice matched to InP is presented in chapter 5. This measurement is required for the accurate modelling of the high pressure PL data from InGaAs/InP quantum well structures described in chapter 6. Chapter 6 also contains the high pressure PL data from an AlAs/GaAs superlattice. The interpretation of these high pressure data show how the type-I luminescence from the InGaAs/InP quantum well is sensitive to the pressure dependence of the conduction-band discontinuity, while the type-II luminescence from the AlAs/GaAs superlattice is sensitive to the
pressure dependence of the valence-band discontinuity. Some concluding remarks are made in chapter 7 together with several recommendations for future work.
Chapter 2

BEHAVIOUR OF BULK III-V SEMICONDUCTORS UNDER PRESSURE

2.1 Introduction

This chapter gives a brief outline of the theory behind the behaviour of bulk III-V semiconductors under pressure necessary to understand the pressure behaviour of quantum well systems.

A band diagram representative of direct gap III-V semiconductors is presented to establish the notation of the various band edges. To gain some insight into how the electronic structure changes with pressure and because of its use in the calculation of quantum well eigenvalues (chapter 3), a simple account of k.p theory is given. Deformation potentials are then introduced as the fundamental method of describing the pressure behaviour of band edges.

Finally, an introduction to the phenomenon of photoluminescence in bulk material is given, indicating how the recorded spectra relate to the minimum energy gap.

2.2 Band Structure

Fig.2.1 shows a schematic band diagram of GaAs which is presented as representative of a zinc blende semiconductor with $T_d$ group symmetry.
Fig. 2.1 A schematic band diagram of GaAs at 0K. Also shown are the approximate pressure coefficients of the \( \Gamma \), \( L \), and \( X \) gaps with respect to the top of the valence band at the \( \Gamma \) point, which are representative of most III-V semiconductors.
Also shown are the approximate band-gap pressure coefficients associated with each symmetry point. Fig. 2.2 is a schematic band diagram at the \( \Gamma \) point defining the basis states used in the k.p formalism. Parameters relating to the band structure of III-V semiconductors pertinent to this work are presented in Tables A. I and A. II in appendix A.

2.2.1 k.p Theory

The k.p method (Kane 1966) is a particularly useful method for theoretically determining the band structure of a semiconductor and its subsequent behaviour when perturbed. The technique uses a combination of quantum perturbation theory and experimental data to calculate the dispersion relations about any given wave number \( k' \), usually a high symmetry point in the Brillouin zone. The essentials of the k.p method may be shown by considering the Schrödinger equation for an electron in a perfectly periodic lattice (ignoring the spin-orbit interaction) as in Eq. 2.1,

\[
\left( \frac{p^2}{2m} + V(r) \right) \Psi(r) = E\Psi(r) \tag{2.1}
\]

where \( m \) is the mass of the electron, \( E \) the energy eigenvalue and \( p \) the operator \( p = -i\hbar \nabla \). The potential \( V(r) \) is the potential in which the electron moves and has the periodicity of the lattice. According to Bloch’s theorem the wave function \( \Psi(r) \) may be written as a product of a
Fig. 2.2 A schematic band diagram at the $\Gamma$ point of a III-V semiconductor (with $T_d$ group symmetry), indicating the notation used in the text to describe the various bands. Also shown are the total angular momentum quantum numbers associated with the basis states used in the k.p formalism.
plane wave and a function \( U_k(r) \) also required to have the periodicity of
the lattice. The periodicity also demands that the Bloch functions \( U_k(r) \)
also satisfy the following:

\[
\begin{bmatrix}
\frac{1}{2m} (p + \hbar k)^2 + V(r)
\end{bmatrix}
U_k(r) = E(k)U_k(r) \quad [2.2]
\]

which is equivalent to:

\[
\begin{bmatrix}
\frac{p^2}{2m} + \frac{\hbar}{m} k.p + \frac{\hbar^2 k^2}{2m} + V(r)
\end{bmatrix}
U_k(r) = E(r)U_k(r) \quad [2.3]
\]

The \( k.p \) and \( \hbar^2 k^2/2m \) terms of Equ.2.3 are both treated as a perturbation
of the normal crystal Hamiltonian (Equ. 2.1), for which it is assumed
that solutions for the given value of \( k' \) exist. As is shown in Fig.2.2,
it is often the case that the unperturbed solution for the bottom of the
conduction band is considered to be atomic s-orbital like (with total
angular momentum \( j = 1/2 \)) and the top of the valence band to be p-orbital
like (with \( j = 3/2 \)). Using such wavefunctions, or basis states and
ignoring the spin-orbit interaction, perturbation theory provides the
following expressions for the conduction and valence bands expanded about
\( k' = 0 \) for small values of \( k \), (Long 1968);

\[
E_{\text{HH}}(k) = E_V + \frac{\hbar^2 k^2}{2m} \quad [2.4a]
\]
\[
E_{s-o}(k) = E_v + \frac{\hbar^2 k^2}{2m}
\]  \[2.4b\]

\[
E_{LH}(k) = E_v - \frac{k^2 P^2}{E_g} + \frac{\hbar^2 k^2}{2m}
\]  \[2.5a\]

\[
E_{CB}(k) = E_c + \frac{k^2 P^2}{E_g} + \frac{\hbar^2 k^2}{2m}
\]  \[2.5b\]

where the band-gap energy \(E_g\) is given by the difference between the conduction-band and the valence-band energies \(E_c - E_v\). The momentum matrix element \(P\) describes the degree of coupling that occurs between the basis states and \(m\) is the free electron mass. Equ. 2.4a and 2.4b represent two "heavy-hole" bands. In reality this degeneracy is lifted when the spin-orbit interaction is introduced, one band being lowered with respect to the other to become the spin split-off band. This interaction also affects the values of their effective masses. Equ. 2.5a and 2.5b represent the "light-hole" valence and conduction bands respectively.

The reciprocal effective mass is proportional to the second derivative with respect to \(k\) of the above dispersion relations (Kittel 1976). Since the above expressions require \(k \neq 0\), \(\hbar^2 k^2/2m\) is also very small and is considered negligible when compared to \(k^2 P^2/E_g\). The effective masses of conduction and light-hole valence bands are then simply given by,
for \( k \approx 0 \), \( m_e^n \approx m_{\text{LH}} \approx \frac{\hbar^2 E_g}{2p^2} \) \[2.6\]

This relatively simple model reveals that the effective masses of the electrons and light holes depend upon the band gap of the material. It is found empirically that \( P \) has the same magnitude for most III/V semiconductors and hence the effective masses are approximately proportional to the semiconductor's band gap. This behaviour which has been experimentally measured in GaAs, InP and the quaternary GaInAsP (Adams 1986), must be taken into account when modelling the pressure behaviour of luminescence transitions in quantum wells.

The equivalent dispersion relations for Equ.s 2.4 and 2.5 which allow for the spin-orbit interaction are given in Long (1968). The spin-orbit interaction introduces several interesting features. Apart from the inclusion of the spin split-off band with its relatively light effective mass, the spin-orbit interaction also introduces significant non-parabolic terms into the dispersion relations of the conduction and light-hole bands. It is found that the magnitude of these terms are greater when \( E_g \) is small. This non-parabolicity may be equivalently described by an effective mass that is energy dependent, i.e.

\[ E(k) = \frac{\hbar^2 k^2}{2m^*(E)} \] \[2.7\]

where \( m^*(E) \) is the energy dependent effective mass.
Even when the spin-orbit coupling is considered, the heavy-hole dispersion relation remains essentially flat for $k \approx 0$ (i.e. Equ.2.4a remains unchanged) and its effective mass equal to that of the free electron. This is caused by the heavy-hole band deriving its curvature from interactions with higher lying bands that are not included in this four-band model. The inclusion and importance of the effects of higher lying bands have been investigated by Hermann and Weisbuch (Hermann 1977).

2.3 The Effect Of Strain Upon The Band Structure

It is perhaps intuitive that the application of a stress to a crystal lattice that alters its inter-atomic spacing will have a significant effect upon the electronic band-structure. If, for example, a crystal is subjected to a hydrostatic pressure (i.e. a pure dilatational stress) one may then naively consider using a Linear Combination of Atomic Orbitals (LCAO) approach (Harrison 1980), that the increase in the interaction between the bonding and antibonding states will produce an increase in their separation. This is found to be true for the zone center of III-V semiconductors although it is not necessarily the case for other symmetry points in the band structure.

An important feature of applying hydrostatic pressure is that the symmetry of the system and hence the degeneracies within the band structure, are preserved. This allows properties measured under
hydrostatic pressure to be easily related to those of the material at ambient pressure.

2.3.1 Hydrostatic Deformation Potentials

For a cubic crystal subject to a pure dilatation, the energy of any given band with an ambient energy $E$ may be expressed in the form (Bardeen 1950),

$$E(\Delta) = E + a\Delta$$  \[2.8\]

where $\Delta$ is the dilatation given by,

$$\Delta = \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33} = \frac{\Delta V}{V_0}$$  \[2.9\]

which is equivalent to the fractional change in the volume and where $\varepsilon_{ii}$ are the cartesian strain tensors. The coefficient $a$ is defined as the hydrostatic band-edge deformation potential and has units of energy. These deformation potentials are of considerable importance since they represent the interaction between the electrons and holes and the acoustic modes of vibration of the lattice. They therefore play an important role in determining electron and hole mobilities.

Notably, these deformation potentials describe absolute changes of energy with respect to a fixed reference level such as the vacuum level.
It is also possible to define band-gap deformation potentials that describe the relative change in energy between different electronic states as a function of dilatation as shown below,

\[ E^0(\Delta) = E^0_c(\Delta) - E^0_v(\Delta) \]  \[ 2.10 \]

\[ = E^0 + (a^0_c - a^0_v) \frac{\Delta V}{V_0} \]  \[ 2.11 \]

\[ = E^0 + \Xi \frac{\Delta V}{V_0} \]  \[ 2.12 \]

where \( E_c^0 \) and \( E_v^0 \) are the energies of the ambient conduction and valence bands respectively, \( a^0_c \) and \( a^0_v \) are their respective deformation potentials, \( E^0_0 \) is the band gap at ambient pressure and \( \Xi \) the band-gap deformation potential. The band-gap deformation potentials may be measured by techniques such as high pressure photoluminescence (described in chapter 4), however, changes in energy with respect to an absolute reference level are much harder to derive, both experimentally and theoretically. The problem of theoretically deriving these absolute deformation potentials has much in common with the theoretical determination of the band-edge discontinuities in quantum well systems (Martin 1987). This aspect is discussed in more detail in chapter 3. Theoretical and experimental values of the deformation potentials are presented in Table B.1 in appendix B.
As Equ. 2.12 shows, the variable of fundamental interest is the change in volume caused by a given stress. Experimentally, however, the variable parameter is the applied stress, or more specifically the applied hydrostatic pressure. Empirically it is found that the change in the various band gaps may be fitted by a quadratic relationship in pressure \( p \), as in Equ. 2.13,

\[
E_0(p) = E_0 + E_1 p + E_2 p^2
\]  

where \( E_1 \) and \( E_2 \) are the linear and quadratic pressure coefficients respectively. The values of the pressure coefficients for GaAs (Goni 1987) are for example; \( E_1 = 10.8 \text{meV/kbar} \) and \( E_2 = -14.0 \times 10^{-3} \text{meV/kbar}^2 \). Those of other semiconductors of interest are given in Table B.1 in appendix B. In general it is found that the pressure coefficients of most \( T_d \) semiconductors are very similar. The \( \Gamma_6^c \) to \( \Gamma_8^v \) direct gap increases at approximately 10meV/kbar, the \( \Gamma_8^v \) to \( X_6^c \) decreases at some 1.5meV/kbar while the \( \Gamma_8^v \) to \( L_6^c \) increases at 5meV/kbar, as indicated in Fig.2.1. The relationship between the applied stress and resulting change in volume for a given material is governed by its equation of state and is discussed in chapter 5.
2.3.2 Uniaxial Strain Deformation Potentials

The concept of deformation potentials may also be applied to cases of non-hydrostatic pressure, i.e. uniaxial strain. Provided any stress applied to the crystal remains within a linear regime, which is true for the practical purposes covered here, the resulting strain may be considered to be a linear superposition of a pure dilatational strain and a pure deviatoric strain (i.e. a strain that only causes a change in shape but not in volume). From the discussion of the previous section it is clear that the dilatational strain component of the uniaxial strain will alter the position of the band edges according to the values of the hydrostatic deformation potentials.

The effect of the pure deviatoric strain component, however, is to break the cubic symmetry of the crystal and produce a unique symmetry axis. This in turn causes a lifting of the degeneracy in the valence band at the zone centre and introduces anisotropies into the valence-band dispersion relations. Neglecting the spin split-off band, the deviatoric strain separates the heavy-hole and light-hole bands equally about their unstrained position. This implies that their average energy remains constant. The strain splitting is proportional to the magnitude of the strain and may also be described in terms of deformation potentials (Pollak 1968). For strain along the [001] direction the shifts in the light-hole and heavy-hole bands with respect to their unstrained position are described by the following:
\[ \Delta E_{LH} = -\frac{3}{4} \delta E_{001} \]  

\[ \Delta E_{HH} = +\frac{3}{4} \delta E_{001} \]  

where \[ \delta E_{001} = 2b (\epsilon_{33} - \epsilon_{11}) \]  

and \( b \) is the shear deformation potential for a strain of tetragonal symmetry.

For the case of uniaxial strain in the [111] direction the results of Equ. s 2.14 are similar although \( \delta E_{001} \) is now replaced with \( \delta E_{111} \) where,

\[ \delta E_{111} = 2 \sqrt{3} \ d \ \epsilon_{12} \]  

and \( d \) is the deformation potential for a rhombahedral symmetry. Experimental and theoretical values for these deformation potentials are given in Table B.1 in appendix B.

Although the experiments covered in this work are concerned with hydrostatic pressure, the inadvertent presence of uniaxial strain should always be born in mind. Uniaxial stresses may, for example, arise in high pressure systems when the hydrostatic pressure fluid solidifies, either at excessively high pressures or when the system is being cooled to cryogenic temperatures. Alternatively, uniaxial strains may be
intrinsically present within the sample due to lattice mismatch between its constituent materials, an epilayer and its substrate for example. This affect may be further exacerbated by a difference in compressibilities between the two materials, leading to an increase or decrease in uniaxial strain with applied pressure. The effect of any uniaxial strain will be to generate an effective hydrostatic pressure greater than, or less than, the applied pressure and consequently lead to the measured hydrostatic-pressure coefficients being erroneous.

2.4 The Effect Of Temperature Upon The Band Gap

It is found experimentally that the band gap of semiconductors increases with decreasing temperature. There are two main contributions to this observed temperature dependence. Firstly, a dilatational contribution that increases the band gap though the reduction in lattice spacing caused by the thermal contraction of the material. This accounts for less than a third of the observed experimental temperature dependence. The second contribution is caused by the electron-phonon interaction. At temperatures much lower than the Debye temperature the band gap varies proportionately to the square of the temperature, whereas much above the Debye temperature the band gap varies linearly.

The temperature dependence of the band gap may be fitted by the following empirical relation (Varshni 1967),
\[ E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \]  

where \( E_g(0) \) is the band gap of the material at 0K and \( \alpha \) and \( \beta \) are constants. For example, GaAs has the following values; \( E_g(0) = 1.5216 \text{eV}, \) \( \alpha = 8.871 \times 10^{-4} \text{eV/K} \) and \( \beta = 572. \) Values for InAs and InP are given in Table C.1 in appendix C.

2.5 Photoluminescence (PL)

When an electron occupying a high energy state makes a transition to an empty lower energy state, then all, or almost all, of the energy difference between the two states may be emitted as electromagnetic radiation.

An essential requirement for observable light emission is that a sufficient quantity of excited states become occupied through some excitation process. The method of excitation determines the nomenclature of the luminescence. For example, excitation by electric current causes electroluminescence, bombardment with an electron beam-cathodoluminescence and optical excitation-photoluminescence (PL). A schematic representation of PL is shown in Fig.2.3.

The phenomenon of PL is essentially a problem of quantum mechanical radiation theory (Schiff 1968, Haug 1972), although strictly quantum electrodynamics provides the most rigorous treatment. Time dependent perturbation theory, however, shows that the probability of a radiative
Fig. 2.3 A simple representation of the process of photoluminescence. The in-coming photon of energy $E_{ex}$ is absorbed creating in the process an electron/hole pair. The electron/hole pair may subsequently recombine at the conduction and valence band-edges, emitting a photon whose energy is approximately equal to the band gap.

transition is given by the product of the density of states and the square of the optical matrix element $M$. The form of the optical matrix element from an initial state described by $\Psi_{k',r'}$ and a final state $\Psi_{k,r}$ is the same for any absorption and emission processes (spontaneous or stimulated) and is given by the overlap integral,

$$M = \int \Psi_{k',r'}(r) A_o \cdot r \Psi_{k,r}(r) \, dr$$ \hspace{1cm} [2.18]

where $r$ is the co-ordinate operator and $A_o$ the polarization vector of the emitted or absorbed radiation described by the plane wave solution,

$$A = A_o \, e^{i(g \cdot r - \omega t)}$$ \hspace{1cm} [2.19]
where \( g \) is the propagation vector and \( \omega \) the angular frequency of the radiation. In order to obtain a finite value of the overlap integral and hence produce a finite probability of a transition or absorption, two criteria, or selection rules, must be observed:

i) \( h \omega = |E_{k,r} - E_{k',r'}| \)

and,

ii) \( k = k' \)

These two selection rules reiterate the laws of conservation of energy and momentum. The second selection rule in effect demands that radiative and absorptive transitions are always direct, i.e. that they always connect states with the same \( k \) value and hence occur vertically on an \( E-k \) diagram as shown in Fig.2.4.

![Fig.2.4](image)

Fig.2.4 A representation of photoluminescence in \( k \)-space, indicating that photoluminescence transitions must occur vertically.
A comprehensive quantum mechanical approach is highly complex; a meaningful treatment of even band-to-band transitions would have to include phenomena such as non-parabolic anisotropic band-structures and the possibility of phonon mediated transitions. It is possible, however, to gain useful information using a more statistical approach. Van Roosbroeck and Shockley (Van Roosbroeck 1954) use the principle of detailed balance to allow the radiative recombination rate to be related to the observable optical absorption coefficient. The principle of detailed balance may be stated in the form, for a system in thermal equilibrium, the rates of a process and of its inverse are equal and balance in detail. This means that at thermal equilibrium, the rate of optical generation of electron-hole pairs is equal to their rate of radiative recombination. This implies that the radiative recombination rate at a frequency $\nu$ may be given by,

$$ R(\nu) \, d\nu = P(\nu) \, \rho(\nu) \, d\nu $$  \[2.20\]

where $\rho(\nu)$ is the density of photons of frequency $\nu$ in an interval $d\nu$ and $P(\nu)$ is the probability of absorbing a photon of energy $h\nu$. The probability $P(\nu)$ is related to the absorption coefficient through the following,

$$ p(\nu) = \alpha(\nu) \, (c/n) $$  \[2.21\]
where $\alpha(\nu)$ is the absorption coefficient, $c$ the velocity of light and $n$ the material's refractive index. The density of photons may be obtained from Planck's radiation law and when substituted into Equ. 2.20 along with Equ. 2.21 gives the Roosbroek-Shockley relation,

$$R(\nu) d\nu = \frac{\alpha(\nu) 8\pi\nu^2 n^2}{c^2 \left[ \exp(h\nu/kT) - 1 \right]} \, d\nu$$

[2.22]

In principle, therefore, the above relation allows a transformation between the absorption spectrum of a semiconductor and the expected emission spectrum. Again, the above treatment may become relatively complex when factors such as a non-thermal equilibrium distribution of carriers is introduced, i.e. when the carriers have a short lifetime.

Although the quantum mechanical and Roosbroek-Shockley treatments of radiative transitions give some insight into the process of PL, in reality the phenomenon of PL is exceptionally diverse, not lending itself to a comprehensive theoretical treatment and continues to be dominated by experiment. The complexity lies in the large number of competing processes involved in the relaxation of the excited state, both radiatively and non-radiatively. Ultimately luminescence only occurs if the probability of the radiative processes is greater than that of the non-radiative processes. Hence any truly comprehensive treatment of PL also requires the simultaneous treatment of all the other possible relaxation processes.

Some radiative and non-radiative processes that occur in PL may
include the following (schematically shown in Figs.2.5):

a) Excitonic Transitions

A hole and electron as a pair of oppositely charged particles will experience a coulombic attraction. The electron and hole will orbit around one another forming a hydrogen like particle known as an exciton. Using this hydrogenic analogy as a model, the ionization energy or binding energy of the exciton may be expressed as,

\[ E_{\text{EB}}(n) = -\frac{\mu^* q^4}{2(4\pi\epsilon_0 e^2)^2 h^2 n^2} \]  

where \( n \) is an integer greater than or equal to 1, \( \mu^* \) the reduced mass:

\[ \frac{1}{\mu^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \]

\( q \) the charge of an electron and the remaining symbols have their usual meaning. When the exciton collapses the energy of the emitted photon is simply,

\[ h\nu = E_g - E_{\text{EB}}(n) \]  

The exciton may therefore be represented in a band diagram by a state having its own binding energy below the conduction band-edge. It is also possible that the exciton may itself become bound to impurities present within the semiconductor and hence form bound excitonic states even lower in energy. These bound excitons are characterised by line widths less than \( k_B T \) (provided that the impurity concentration is fairly low) and are
Fig. 2.5 Several recombination mechanisms that occur in bulk semiconductors. (a) Transition from an exciton, i.e. a bound electron and hole pair. The energy $E_{EB}$ represents the exciton's binding energy. (b) Band-to-band recombination of free electrons and holes. (c) Donor and acceptor transitions. (d) Indirect transitions that require the mediation of a phonon in order to conserve momentum.
essentially temperature independent when $k_B T$ is less than the binding energy. In GaAs at 1.4K, widths of the order 0.1meV have been found for excitons bound to shallow impurities, while free excitons on the other hand have widths in the order of 1.0meV.

b) Band-To-Band Transitions

Band-to-band transitions constitute the recombination of free carriers from the fundamental conduction and valence bands. The process may be considered as the inverse of the absorption process as previously described. Although excitonic states represent the lowest-energy states for electron-hole recombination, these normally only occur in good quality material and at low temperatures. At temperatures where that $k_B T$ is greater than the binding energy of the exciton, or where impurities cause local distortions in the field, the excitons will tend to ionize into free carriers. The luminescence spectrum is then characterised by a low-energy threshold at $\hbar \nu = E_g$ and a temperature dependent exponential high-energy tail. At low excitation the half-width of the emission peak is approximately equal to $0.7k_B T$.

c) Impurity Related Processes

Radiative transitions may also occur from an electron in the conduction band to an acceptor state, or alternatively from an electron in a donor state to the valence band. It may be shown (Pankove 1975) that when either the conduction band and donor states or when the valence band
and acceptor states are full, then the probability of a band-to-band transition is approximately four times as great as an impurity mediated transition. When the concentration of impurities becomes large the donor or acceptor states may merge to form an impurity band. The luminescence is then dominated by a broad band below the fundamental band-gap of the host semiconductor. Since the electron effective mass is considerably less than the hole mass, the donor ionization energy is less than the acceptor ionization energy. Consequently a donor to valence-band transition will be at a higher energy than the conduction band to acceptor state.

d) Electron Phonon Interactions.

Optical transitions may also occur in indirect-gap semiconductors provided the transitions are mediated by a process that helps satisfy the $k$ selection rule, such as the emission or absorption of phonons. However, direct transitions in direct-gap semiconductors may also be accompanied by the emission of phonons, particularly at low temperature. A narrow emission peak from an exciton may be replicated several times at lower energies given by,

$$h\nu = E_g - E_{EB} - mE_p$$  \[2.25\]

where $m$ is an integer number of phonons emitted of energy $E_p$ and $E_{EB}$ is the exciton binding energy.
A full treatment of the various non-radiative process is at present not completely satisfactory, however, such processes may include the following:
a) Recombination Through Defects,
b) Band-To-Band Non-Radiative Transitions (electron-lattice Interactions),
c) Auger Recombination, (electron-electron interactions).

Of particular significance with regards to PL, is the recombination through defects, either structural or impurity related. The theoretical problem with such processes is that in general they are multi-phonon processes, since the energy to be dissipated is considerably greater than any single phonon energy. A possible description may involve the capture of a carrier into an excited state by a defect, which is then followed by a cascade of one phonon-transitions until the ground state is reached (Lax 1960). The fact that the defect is localised in space allows at least one of the carriers to become strongly coupled to the lattice and in turn enables a multi-phonon process to become more probable. This coupling is not present in band-to-band radiationless recombination and this is therefore considered to be an exceedingly rare event.

Although Auger recombination may be the dominant process in some narrow-gap semiconductors, it is only considered to become significant at high temperature and with a high concentration of neutral donors or acceptors.

In conclusion therefore, the poorer the crystal quality, the weaker
the PL intensity and the broader the emission.
3.1 Introduction

Chapter 3 describes the theory used to model the PL emission energies from quantum well structures. The important features of quantum wells are demonstrated by using a "particle in a box" model before the more sophisticated envelope-function approximation of Bastard (1981) is introduced. The behaviour of excitons in quantum wells is then analysed, indicating the additional selection rules that govern their luminescence.

Since the values of the band-edge discontinuities are essential parameters in calculating the stationary states in quantum wells and since their behaviour under pressure is of particular interest, the theory of band discontinuities in quantum wells is discussed in some detail.

3.2 Electronic Structure Of Quantum Wells

A semiconductor quantum well is formed when material of relatively narrow band-gap is sandwiched between material of larger band-gap. Provided the thickness of the narrow band-gap material (L_z) is sufficiently thin, quantum size effects will become apparent in the direction normal to the plane of the thin layer. A schematic band-diagram of such a system is shown in Fig.3.1. The problem of describing the behaviour of either electrons or holes in such a potential may be considered as analogous to the classic quantum mechanical problem of a
For the artificial case of an infinitely deep potential the one dimensional Schrödinger equation is,

$$-rac{\hbar^2}{2m} \frac{\delta^2 \psi(z)}{\delta z^2} = E \psi(z) \quad [3.1]$$

where $m$ is the mass of the particle in the direction of confinement. The energy eigenvalues $E_n$ are analytically given by,

$$E_n = \frac{\hbar^2}{2m} \left( \frac{n \pi}{L_z} \right)^2 \quad \text{for} \quad (n = 1, 2, 3, \ldots) \quad [3.2]$$

and where the wavefunctions are alternately cosine and sine functions whose amplitudes go to zero at the potential boundary. Equation 3.2 adequately illustrates one of the most beneficial features of a quantum
well system; the ability to tailor the energy of the confined states through the strong quadratic dependence of the well width $L_z$. An important consequence of the quantization in the quantum well is that the heavy-hole light-hole degeneracy in the valence band is broken by virtue of their different effective masses. In an unstrained quantum well the top of the valence-band is therefore always heavy-hole like in the $z$-direction.

By using finite barriers in the particle in a box problem and allowing them to be an adjustable parameter, Dingle (1974) fitted experimental PL data from GaAs/AlGaAs quantum wells of various widths to obtain the first estimate of the conduction- and valence-band potential depths. The approach has some obvious shortfalls, not least is ignoring the effective mass discontinuity that occurs at the two heterojunction interfaces that form the quantum well. Consequently Dingle's estimate has been shown to be inaccurate.

3.2.1 Envelope-Function Approximation

A more sophisticated and successful approach to modelling quantum wells is the envelope-function approximation developed by Bastard (1981). This technique not only accounts for the effective mass discontinuity but also allows the inclusion of higher lying energy bands. The model relies on realistic yet analytically useful wavefunctions shown below,

$$\Psi_{w,b}(k,r) = \sum_j C_j^{w,b}(k_{\perp}, k_z) U_j^{w,b}(r) e^{i(k_{\perp}.r_{\perp} + k_z.z)} \quad [3.31]$$
where the super or sub-scripts \( w \) and \( b \) refer to the wavefunction within the well and barrier respectively. The success of this form of wavefunction depends upon two factors. Firstly, the wavefunction is a sum of products of slowly varying functions, \( u^{w,b}(r) \), modulated at the scale of the host unit cells (the envelope functions) and quickly varying Bloch functions, \( C^{w,b}(k) e^{i k \cdot r} \), restricted to the first Brillouin zone. Since most host materials have similar band structures, the periodic parts of the Bloch functions will not differ significantly across a heterojunction interface. The principle of the approximation, therefore, is to assume that these may be ignored. Attention is focused instead on the Hamiltonian that governs the slowly varying envelope functions. The second feature of importance is that the wavefunction is summed over an appropriate number of energy bands (indexed by \( j \)). However, the summation is often reduced to a minimum by assuming that only a small fraction of the Brillouin zone contributes to the confined states. The summation also allows the approximation to be independent of how the band structure of the host materials is generated. Bastard (1981) used a multi-band Kane \( k.p \) analysis to describe the valence and conduction bands of the constituent materials, although a simple two-band model extending over the heavy-hole and electron bands at the \( \Gamma \) point will suffice to demonstrate the envelope approximation. This two-band model (as will be shown) is quite capable of accurately determining the ground state eigenvalues for quantum wells with a large conduction-band potential well.
3.2.1.1 Envelope-Function Two-Band Model

Identical Schrödinger-like equations may be written for the two bands, \( e \) for electrons and \( \text{HH} \) for heavy holes,

\[
\frac{i\hbar}{\partial z} \left[ \frac{1}{m_{e,\text{HH}}^*}(z) \frac{\partial}{\partial z} \right] U_{e,\text{HH}}(z) + (V_s(z) - E) U_{e,\text{HH}}(z) = 0
\]

where \( V_s(z) \) is the potential step in the conduction and valence band. The jump in effective mass across the interface is explicitly accounted for in Equ. 3.4. If it is assumed that the energy eigenstates are continuous across the interface, then integrating Equ. 3.4 across the interface provides the second boundary condition that the following quantity,

\[
\frac{1}{m_{e,\text{HH}}^*} \frac{\partial U_{e,H}}{\partial z}
\]

is also continuous across the interface. If the effective masses in the barrier and well are the same, the more familiar condition of \( \frac{\partial U_{e,H}}{\partial z} \) being continuous would be appropriate. Using these boundary conditions the following transcendental equations for both the conduction- and valence-band potentials must be solved, either graphically or numerically, to determine the eigenvalues.

\[
\tan \left[ \left( \frac{2m_{e,H}^* E}{\hbar^2} \right)^{1/2} \frac{L_z}{2} \right] = \left( \frac{m_{e,H}^*}{m_b^*} \right) \left( \frac{V_s - E}{E} \right)^{1/2}
\]

-even solutions and
the odd solutions. The subscripts $w$ and $b$ refer to the well and barrier effective masses respectively, of either holes or electrons. The number of electron bound-states is given by (Bastard 1986),

$$1 + \text{Int} \left[ \left( \frac{m^*_w V_0 L_z^2}{\pi^2 \hbar^2} \right)^{1/2} \right]$$

where Int refers to the integer value of the squared bracket. It is worth noting that there is always at least one bound state regardless of the well width or depth.

### 3.2.1.2 More Complex Models

The use of this two-band model does not give a comprehensive description of the valence band in real quantum well structures. A more realistic description is produced if a Kane $k.p$ three- or four-band model is used to describe the host bulk band structures (Bastard 1981, Bastard 1986). This set of $\Gamma$ point basis states includes the $s$-like spin up and spin down conduction-band states ($\Gamma^0_6$), the fourfold $p$-like $j = 3/2$ valence band-states ($\Gamma^7_8$) i.e. the $j_z = \pm 3/2$ heavy-hole and $j_z = \pm 1/2$ light-hole states, and the $j = 1/2$ spin-orbit split-off valence band ($\Gamma^7_7$) as shown in Fig.2.2. The index $j$ in Equ.3.3 now runs over these three or four bands, depending upon whether the spin-orbit split-off band is included. Coupling to higher bands has been included perturbatively by
Schuurman and 't Hooft (Schuurman 1985), who have shown that a four-band model is at least as accurate, to within a few percent, as sophisticated tight binding models.

If, as is normal, the [001] direction is taken as the quantization axis (i.e. the growth direction), then the effect of the quantum confinement is to immediately break the degeneracy of the $\Gamma_8$ states by virtue of the different effective masses. In the [001] direction the $j_z = \pm 3/2$ band is lowered in energy relative to the $j_z = \pm 1/2$ band. In the transverse directions, i.e. in the plane of the well, $k.p$ interactions cause a mass reversal, hence the dispersion relations for the [010] and [100] directions corresponding to the $j_z = \pm 3/2$ band become light-mass-like and heavy-hole-like for the $j_z = \pm 1/2$ band. From Fig.3.2 one would expect that for large values of $k_\perp$ a crossing of the two bands would occur, however, higher order $k.p$ interactions produce an anti-crossing behaviour as shown. Similar anti-crossing effects may be produced in bulk material by the application of uniaxial compressive stress, except the $j_z = \pm 1/2$ band becomes the higher lying band and therefore interacts with the $j_z = \pm 3/2$ in the direction of the applied stress.

If the minimum energy gap in a quantum well is the main variable of interest, it may then be shown that the simple two-band model is in fact quite adequate. When the confinement energy of an electron is much smaller than the band gap of the barrier or well materials and moreover the value of $k_\perp < L^{-1}_z$, then the conduction-band states ($\Gamma_6$) may be considered to be parabolic and de-coupled. They will then satisfy the Ben Daniel-Duke (1986) Hamiltonian of Equ.3.3. The heavy-hole states on the other hand are completely de-coupled (Bastard 1981), their curvature
Fig. 3.2 The effect of quantization of a quantum well upon the valence-band structure. (A) The bulk valence-band structure; the heavy \( j_z = \pm 3/2 \) and light hole \( j_z = \pm 1/2 \) valence-bands are isotropic. (B) The \( j_z = \pm 3/2 \) and \( j_z = \pm 1/2 \) bands are split due to the confinement potential in the \( z \) direction, i.e. the growth direction. (C) The valence-band structure perpendicular to the growth direction. The \( j_z = \pm 3/2 \) becomes light-hole-like, and the \( j_z = \pm 1/2 \) band becomes heavy-hole-like. (D) k.p interactions avoid the crossings indicated in (C) and produces an anti-crossing effect. The \( j_z = \pm 3/2 \) now has a light-hole "cap" for small values of \( k_x \) and \( k_y \).
being governed by remote bands not included in the four band k.p description. To determine the ground-state total confinement-energy it is then reasonable to revert to the two-band model described in section 3.2.1.1. Using this model Fig.3.3 shows the energy of the el to HH1 transition plotted against well width for a GaAs/Al$_{0.2}$Ga$_{0.8}$As single quantum well. Marsh (1986) and Nelson (1987) have shown that this restriction to two parabolic bands is quite adequate in predicting the ground state. From a comparison of the two-band parabolic model, a multi-band k.p model and a full psuedopotential formalism, Marsh (1986) shows that all these models give the ground state energy in quantum wells with widths from 5 to 50Å, to within 3% of one another.

It is also clear from these calculations, however, that to accurately describe higher lying confined states the inclusion of non-parabolicity is essential. Nelson (1987) accounts for this behaviour by considering the occupancy probability in the well and barriers for the various states. Although a n = 1 state in a narrow quantum well has a large confinement energy and may therefore be expected to be sensitive to non-parabolicity, the electron spends perhaps only 10% of its time in the well. The remaining 90% of the time is spent in the barriers where the wave number and hence the effect of non-parabolicity, is small. For a high lying state in a wide well both the probability of occupancy and confinement energy are high and hence the state becomes sensitive to non-parabolicity.
Fig. 3.3 The transition energy at 4K of the 1e to 1HH transition for a GaAs/Al$_{0.2}$Ga$_{0.8}$As single quantum well as a function of $L_z$. The transition energies have been calculated using the two-band envelope-function approximation as discussed in the text.
3.3 Two-Dimensional Density Of States

Another important implication of restricting the motion of carriers to two dimensions is the effect upon the density of states (DOS). The total energy for a two-dimensionally confined electron is given by,

\[ E_T = E_l(k_x, k_y) + E_\parallel \]  \hspace{1cm} [3.7]

corresponding to the sum of the kinetic energy in the plane of the well and the confinement energy in the growth direction. To determine the density of states it is necessary to sum over all states within the same energy interval. The total number of states from \( k = 0 \) to an arbitrary value of \( |k| \) per unit area is,

\[ G(k) = \left( \frac{1}{2 \pi} \right)^2 \pi k^2 \]  \hspace{1cm} [3.8]

alternatively, using the parabolic approximation \( E = \frac{\hbar^2 k^2}{2m^*} \), the total number of states may be expressed in terms of energy as;

\[ G(E) = \left( \frac{1}{2 \pi} \right)^2 \pi \frac{E}{\frac{\hbar^2}{m^*}} \]  \hspace{1cm} [3.9]

The density of states \( g(E) \) per unit energy interval is then obtained by differentiating Equ.3.9 with respect to \( E \) to give,

\[ g(E) = \frac{1}{2 \pi} \frac{m^*}{\hbar^2} \]  \hspace{1cm} [3.10]
for a given spin. The density of states is therefore independent of energy, hence the total density of states will have a step of $\frac{m^*}{2\hbar^2}$ per confined level in the well as shown in Fig. 3.4. This characteristic step-like density of states of a quantum well can be clearly observed in absorption or excitation spectra (Dingle 1974), since these measurements depend upon the product of the density of states and the square of the optical matrix element.

![Diagram](image)

Fig. 3.4 The characteristic two dimensional total density of states associated with quantum wells. Also shown for comparison is the bulk (three dimensional) density of states.
3.4 Excitons In Quantum Wells

The Bohr radius of a free exciton is given by,

$$a_b = \frac{4\pi e_0 e_r^2 h^2}{m_r^* q^2}$$ \[3.11\]

where $m_r^*$ is the reduced mass and $q$ the charge of an electron. Since the effective mass of the electron is so small, the Bohr radius is very large, usually greater than 100Å. It is clear that the exciton wave function will extend considerably further than this radius and hence if an exciton is confined by a potential whose size is comparable to the Bohr radius, the exciton binding energy will be significantly affected.

The Hamiltonian of a heavy-hole exciton in a quantum well may be written, using cylindrical co-ordinates, as

$$H = \frac{-\hbar^2}{2 m_e^*} \left( \frac{1}{\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right) - \frac{\hbar^2}{2 m_e} \frac{\partial^2}{\partial z_e^2}$$

$$+ \frac{\hbar^2}{2 m_{hh}^*} \frac{\partial^2}{\partial z_{hh}^2} - \frac{q^2}{4 e_0 |r_e - r_{hh}|} + V_{cb}(z_e) + V_{vb}(z_{hh})$$ \[3.12\]

where $r_e$ and $r_{hh}$ are the positions of the electron and hole and $V_{cb}$ and $V_{vb}$ the potential wells formed in the conduction and valence-band respectively. The exact solution of the above Hamiltonian is not possible, however Green (Green 1983, Green 1984) has used a variational approach to solve the problem in the specific case of GaAs wells.
Fig. 3.5 Exciton binding energy of both heavy-hole (a) and light-holes (b) in an AlGaAs/GaAs quantum well as a function of well width.
surrounded by infinitely thick $\text{Al}_{0.3}\text{Ga}_{0.7}$As barriers. Their calculation of the exciton ground-state of both heavy-hole and light-hole excitons as a function of the well width is shown in Fig.3.5. The figure shows some interesting features. Firstly, as the well width decreases the binding energy ($E_{bb}$) increases to a maximum of approximately 9.5meV compared to a bulk value of approximately 5meV and then falls quite rapidly. The initial rise in the binding energy is explained by the increased spatial confinement of the exciton wavefunction by the quantum well potential. However, as the well is narrowed further, an increasing proportion of the wavefunction exists in the barrier and hence the binding energy tends to that of an exciton in bulk AlGaAs. Another interesting feature is that for relatively large values of $L_z$, the binding energy of an exciton formed from a light-hole is greater than an exciton formed from a heavy-hole, while the situation is reversed for narrow wells. This reversal is caused by the light-hole exciton wavefunction spilling over into the barriers at a faster rate than the heavy-hole exciton as the well is narrowed.

The increased exciton binding energy due to the quantum confinement ensures that almost all optical processes that occur in quantum wells are dominated by excitons, either intrinsic or extrinsic. Room temperature PL from good quality GaAs/AlGaAs quantum wells originates from free exciton emissions involving both heavy and light holes (Dawson 1983). These emissions do not occur in the bulk material since the probability that an exciton is thermally ionized is given by a Boltzmann factor $\exp(-E_{ee}/k_BT)$, where $k_BT$ is about 26meV at room temperature.
3.5 Photoluminescence From Quantum Wells

3.5.1 Selection Rules

The optical matrix element for a quantum well has the form,

\[ M \sim \int_{\text{Crystal}} U_e(z) e^{i(k_e \cdot r)} C_{cb}(r) A_0 \cdot r U_h(z) e^{i(k_h \cdot r)} C_{vb}(r) \, dr \]

where \( U_e(z) \) and \( U_h(z) \) are the electron and hole (heavy or light) envelope wavefunctions, \( C_{cb}(r) \) and \( C_{vb}(r) \) the usual Bloch functions and \( A_0 \) the polarization vector of the emitted light. Using an infinite well approximation it may be shown (Dingle 1987) that this optical matrix element is the same as that of the bulk, provided transitions occur between electron and hole states with the same quantum number \( n \), i.e. \( \Delta n = 0 \). Quantum wells, therefore, obey the same selection rules as the bulk with the additional rule that \( \Delta n = 0 \). For finite potentials, however, this selection rule may be broken and "forbidden" transitions (such as the \( n = 1 \) electron to \( n = 3 \) heavy hole) although substantially weaker, may be observed in absorption spectra. Since the optical matrix element in two dimensions is the same as in three the major influence to the transition probability is through the two dimensional density of states. Absorption and PL excitation spectra tend to reflect the step-like nature of the density of states although they are often complicated by excitonic affects.
3.5.2 Photoluminescence Spectra

The PL spectrum from a quantum well is significantly different from that of bulk material of similar quality. In general the low temperature PL spectrum from a single quantum well will be dominated by a single narrow line with a Gaussian distribution (Bimberg 1986) and is usually free from the myriad of impurity related lines associated with bulk material. It is also very striking that the luminescence efficiency from a quantum well is substantially higher than bulk samples photoexcited in similar conditions. It is common, for example, to find the intensity of the quantum well emission to be at least an order of magnitude greater than the luminescence from the barrier material.

From the discussion of the previous section it is clear that the enhanced luminescence efficiency does not originate from optical matrix element considerations. Instead the enhancement is thought to be caused by a combination of the following factors. (i) Since little emission originates from the barrier material it is clear that the quantum wells, particularly at low temperature, are extremely efficient carrier collectors. (ii) Luminescence from quantum wells is invariably excitonic, due to the two dimensional confinement of the carriers. In general, however, the electron and hole forming the exciton do not have the same wave vector k and hence their collapse and emission is a forbidden process as dictated by the selection rules. Exciton scattering by energy fluctuations in the confining potential, caused by imperfections in the quantum well structure, lifts the k conservation rule and allows exciton mediated luminescence to become an efficient process. (iii) There is also some evidence to suggest that impurity gettering may occur in the
barriers during multilayer growth which decreases the number of non-radiative centres within the well and hence increases the probability of radiative transitions.

3.6 Theory of Band Offsets

One of the most important properties of a semiconductor to semiconductor interface (heterojunction) is the exact nature of the band structure at the interface. Since the fundamental band-gaps of the two semiconductors will in general be different, there will necessarily be a discontinuity in both the valence- and conduction-band edges at the interface. The various possibilities of how the energy difference between the two band gaps is distributed in the conduction and valence bands, forming the respective band discontinuities $\Delta E_c$ and $\Delta E_v$, is shown in Fig.3.6. From the figure the following simple relationships and definitions are derived.

$$
\Delta E_v (A,B) = E_v (A) - E_v (B) \quad [3.13a]
$$

$$
\Delta E_c (A,B) = E_c (A) - E_c (B) \quad [3.13b]
$$

$$
\Delta E_g = \Delta E_v + \Delta E_c = E_g (B) - E_g (A) \quad [3.13c]
$$

$$
Q_v = \Delta E_v / \Delta E_g \quad (The \ fractional \ valence-band \ offset) \quad [3.14a]
$$

$$
Q_c = \Delta E_c / \Delta E_g \quad (The \ fractional \ conduction-band \ offset) \quad [3.14b]
$$
It is clear that knowledge of the band-offset ratio is crucial for the successful design of any device containing a heterojunction. There is still, however, considerable debate concerning both the experimental and theoretical evaluations of the offsets.

The prediction of the band-offset ratio given any two semiconductors is a non-trivial problem. It is far from clear to what extent factors such as interface orientation, strain, or the presence of defects affect the band line-ups. Theoretical prediction is further exacerbated by lack of reliable experimental data, as demonstrated by the long held 85:15 "Dingle" rule for the offset ratio of GaAs/AlGaAs, now replaced by the more widely accepted value of 60:40.

There are two broad approaches to the theoretical investigation of band offsets. The first approach is a first principles numerical analysis of the electronic structure of a well defined interface. Once the Hamiltonian is fully specified, then in principle the electronic structure and hence the offsets will be found by solving a Schrödinger-like equation. The second approach uses "model" theories which involve defining a reference level as an intrinsic bulk property of a semiconductor. The band-edge discontinuities are then found by simply aligning the reference levels of the two semiconductors forming the interface. The simplest and most common model theory uses the Fermi level within a metal as a reference to determine the potential formed across a metal-to-metal interface.

There are both advantages and disadvantages associated with the two approaches described above. Numerical interface calculations make no
Fig. 3.6 Possible band structure configurations for a single quantum well. The configuration (c), where both electrons and holes are confined in the well material, is known as type-I. Where the electrons and holes are confined in different materials, as in (a) and (d), the configurations are known as type-II.
initial assumptions concerning the physics that determine the band line-ups, although many assumptions have to be made concerning the description of the problem, i.e. the use of ideal atomic geometries and the use of pseudopotentials to approximate atomic cores. Since it is not obvious what physical phenomena contribute to the line-ups, the calculated data tends to be treated like experimental data. Model theories, on the other hand, make assumptions about the essential physics involved and therefore require significantly less numerical computation compared with the previous method. The drawback, however, is that there is as yet no direct evidence that the simplifying assumptions are quantitatively or qualitatively correct, regardless of how accurately they fit to experiment. Nevertheless, there is some indirect experimental evidence which suggests the existence of reference levels that are themselves an intrinsic property of the bulk semiconductor. An implication of such reference levels is that band line-ups between different pairs of semiconductors are not independent and should therefore obey the transitivity rule. The transitivity rule states that the band offsets between two materials may be determined from the difference between the band offsets of each material with respect to a third, i.e.

\[ \Delta E_v(A, B) + \Delta E_v(B, C) = \Delta E_v(A, C) \]  

[3.15]

This rule also implies that band line-ups are independent of interface orientation, although it is conceivable that a reference level could be defined for any given orientation. The experimental evidence suggests (at least for the GaAs/AlGaAs system) that band line-ups are independent of
orientation (Wang 1985) and that the transitivity rule is obeyed (Katnani 1986).

3.6.1 The Theories of Van de Walle and Martin (1987)

In recent years there have been many attempts using the two approaches mentioned above to formulate a theory of band offsets (Mon 1981, Munoz 1987, Van Vechten 1985, Harrison 1985, Cardona 1987, Tersoff 1984 and Van de Walle 1987). As yet there appears to be little justification in prejudicing one theory in favour of another. The work of Van de Walle and Martin (Van de Walle 1987) is unique in that their model theory is derived from their own extensive first principle numerical calculations. In addition, their work is reviewed here firstly because they calculate band offsets as a function of pressure and secondly, that their model theory can easily incorporate strain effects (Van de Walle 1989). This aspect is discussed in further detail in chapter 6.

The problem of how the bands line up at a heterojunction is essentially one of determining the line-up of electrostatic potentials. The solution to the problem cannot be derived from the calculation of bulk band structures alone since this is normally performed on "infinite" crystals and consequently the band structure cannot be placed on an absolute energy scale, i.e. no vacuum level is present. The fundamental reason for this is that in an infinite crystal the long range nature of the Coulomb interaction does not allow a zero of energy to be defined, instead, all energies are calculated with respect to an arbitrary constant. It is the charge distribution at a surface or interface that determines in absolute terms the position of the bands. This problem is
common to both the first-principle and model-solid approaches. In the first case, Van de Walle and Martin overcome this problem by uniquely determining average potentials, $V_A$ and $V_B$, of the host materials A and B with respect to the charge distribution at their interface. For the model-solid theory, an average potential is uniquely determined with respect to a model surface for any given semiconductor. In both cases, bulk band structures may then be related to these average potentials in order to place them on an absolute scale and hence determine the various band-offsets. The problems caused by the infinite crystal in calculating band-offsets are also present in calculating absolute band-edge deformation potentials (Martin 1983, Mon 1981). In principle, any theory that places a band-structure on an absolute scale is also capable of determining how the various energy bands change as a function of crystal volume, i.e. the calculation of deformation potentials.

3.6.1.1 Van de Walle and Martin's Self-Consistent Calculation

The most accurate description of an interface is produced when the electron distribution is allowed to adjust itself to the local environment by finding self-consistent solutions of the charge density. From the calculation it is then possible to derive the shift in the average electrostatic potentials that occurs between the two materials at the interface. The calculations are performed on lattice-matched (110) interfaces where it is assumed that the two materials form an ideal zinc blende geometry throughout the system. The self-consistent calculation uses local-density-functional theory together with ab-initio pseudopotentials to determine the average potentials in the host
materials, \( \bar{V}_A \) and \( \bar{V}_B \). *Ab-initio* pseudopotentials are used in preference to empirical potentials to allow all the results from the different heterojunction systems to be treated on an equal footing and hence be analysed in an "experimental" fashion. Once the average potentials of the two host materials have been found, accurate standard bulk band-structures are also derived which may now be placed on the absolute energy scale. The valence-band energy is then given by an energy \( |E_{v,av}^A| \) above \( \bar{V}_A \). There are two important points to consider. Firstly, taken separately the band position with respect to the average potential and the average potential itself contain no physical information, they will depend upon the method of calculation and choice of pseudopotentials. Only the combination of the two carry any physical significance. Secondly, \( E_{v,av} \) is defined as the average valence-band energy, averaged over the three uppermost valence bands at the Brillouin zone centre, i.e. the light-hole, heavy-hole and spin split-off bands. This definition allows the position of the spin split-off band to be introduced in a simple posteriori fashion using Equ. 16.

\[
E_{v,s-o}^A = E_{v,av}^A - 2/3 \Lambda_0^A \quad [3.16]
\]

Hence the position of the light- and heavy-hole bands are given by,

\[
E_{v,HH, LH}^A = E_{v,av}^A + 1/3 \Lambda_0^A \quad [3.17]
\]

where \( \Lambda_0 \) is the experimentally determined spin-orbit splitting. Fig. 3.7 illustrates the line-up of the valence and conduction bands for a GaAs/AlAs (110) interface. The valence-band discontinuity, once
spin-orbit splitting has been included posteriori, is calculated to be 370 meV. Values for other important heterojunctions, together with other theoretical and experimental values for comparison, are given in table D.1 in appendix D. Van de Walle and Martin claim an accuracy of 50 - 100 meV, which in the case of the GaAs/AlAs valence-band discontinuity is slightly more than 30%. Emphasis is placed on calculating the valence-band offset since the band structure is generated using the local density approximation which is known to underestimate the value of the band gap. The conduction-band offset is therefore best calculated from the valence-band offset and an empirical value of the band-gaps.

The theoretical valence-band offsets from this self-consistent calculation have also been tested for transitivity as defined in Equ. 3.17. Table D.II in appendix D shows that the rule is satisfied to better than 60 meV, which is in the order of the claimed accuracy of the calculation. The interfaces considered are however all lattice matched and (110) orientated, the only orientation that avoids net dipoles across the interface. For the GaAs/AlAs heterojunction the (100) interface was also investigated. It is found that the valence-band discontinuity remains unchanged compared with the (110) interface, although increases to 390 meV for the (111) interface. Within certain limitations the authors believe that in general, the offset is independent of interface orientation. This result and the apparent satisfaction of the transitivity rule, strongly suggests that the band line-ups at heterojunctions are dependent upon some intrinsic property of the bulk materials involved.
Fig. 3.7 The band alignment in a GaAs/AlAs interface as calculated by Van de Walle (1987) using a self-consistent calculation. The valence-band discontinuity $\Delta E_v$ is calculated to be 0.37 eV.
3.6.1.2 Van de Walle and Martin's "Model-Solid" Theory

The model-solid theory allows the band structure of any given semiconductor to be placed on an absolute energy scale by relating it to the potential of a reference surface. This reference, or model surface, is formed from the superposition of neutral atoms where the electrostatic potential outside each atom goes exponentially to an absolute zero. As each atomic potential is rigorously defined with respect to the vacuum, then by superposition the average potential of the surface is also well defined. The band offset between the interface formed from two such "model" surfaces is determined therefore by the step in average potentials between the two surfaces \( \overline{V}_A - \overline{V}_B \). This model, by its very nature, does not allow the generation of dipoles across interfaces since the atoms are always considered to be neutral. Band offsets are then by implication independent of interface orientation in this model. The problem of calculating band offsets has once again been reduced to two separate problems; (a) the derivation of the absolute average electrostatic potential and (b), the generation of accurate band structure. Note that the comments concerning \( V_{av} \) made in the previous section apply equally to model-solid theory.

Using the tabulated values of \( E_{v,av} \) from the model-solid theory and experimental values of the spin-orbit splitting \( \Delta_0 \) given in table D.III in appendix D, finding the given valence-band discontinuity becomes trivial. For a heterojunction interface between semiconductors A and B, the discontinuity in the average valence-band energy \( \Delta E_{v,av}^{A,B} \) for binary semiconductors A and B is given by,
The quantity $\Delta E_{v,av}^{A,B}$ will be positive when the valence band is higher in material B. To obtain the position of the individual bands with respect to the average, the spin-orbit split-off energy $\Delta_0$ is introduced using Eqn.3.17. The valence-band discontinuity in the highest lying valence band is then given by,

$$\Delta E_{v,av}^{A,B} = (E_{v,av}^B + 1/3\Delta_0^B) - (E_{v,av}^A + 1/3\Delta_0^A)$$  \[3.19\]

For a GaAs/AlAs heterojunction the valence-band discontinuity is given by

$$\Delta E_v = (-6.92 + 1/3 0.34) - (-7.49 + 1/3 0.28) = 0.59\text{eV}$$

This particular estimate agrees exceedingly well with the recent experimental value of $0.535 \pm 0.012\text{eV}$ of Dawson (1987). As with the self-consistent calculation the conduction-band discontinuity is best found using experimental values of the band gaps.

Comparison of both the model-solid theory and the self-consistent calculations with experimental values is particularly difficult as extensive experimental investigations have only centred on a few of the many heterojunction permutations. Notably, both theories successfully predict the broken-gap line-up of InAs/GaSb (Sakaki 1977), where the conduction band of the InAs is lower in energy than the valence-band of GaSb.
Chapter 4

EXPERIMENTAL TECHNIQUES

4.1 Introduction

The aim of this chapter is to give a description of the experimental apparatus and techniques used in the course of this work. A description of the basic PL and PLE layout is presented, dwelling on some computer software features that are designed to improve the signal to noise ratio of the data collection. The remainder of the chapter covers the description of the two high pressure systems used to make the high pressure PL measurements, i.e. the 8kbar Be:Cu cell and the miniature diamond anvil cell.

Prior to this work, no high pressure PL facility was present at the University of Surrey. Hence in the course of this work a considerable fraction of time was invested by D.J. Dunstan and the author in the designing and commissioning of the 8kbar high pressure cell (Lambkin 1988b). Concurrently the miniature diamond anvil cell was being designed (Dunstan 1988) and commissioned by D.J. Dunstan and A.D. Prins.

4.2 Photoluminescence

Optical excitation may cause an electron, no longer in thermal equilibrium with the lattice, to occupy a high-energy state. The electron may then make a transition to an empty lower-energy state whereby all, or almost all, of the energy difference between the two states is emitted as a photon. The recording of the emitted radiation constitutes the photoluminescence (PL) spectrum of the given sample.
The organisation of the PL system is shown in Fig.4.1. The sample, approximately $1 \times 1 \text{cm}^2$, is placed in an Oxford Instruments flow cryostat fitted with optical windows. The transfer tube used with the cryostat is designed for use with both liquid nitrogen and helium. A useful feature of the flow cryostat is that it can operate quite normally in a horizontal position and is used in such a position for measurements with the high pressure apparatus. The sample is then excited with 10-250 mW of radiation from an argon ion laser. This laser power can produce a power density of up to $2.5 \times 10^3 \text{ W/cm}^2$ when focused to a spot size of approximately 100 $\mu$m with a 10 cm convex lens. The radiation is chopped at audio frequency and a reference signal sent to a lock-in amplifier. The sample is adjusted to prevent the specular reflected laser light from entering the detection optics. The PL emission from the sample may then be collected by appropriate refractive optics, analysed by a $1\text{m}$ Spex spectrometer and detected by a suitable photo-detector. For short wavelengths (400-900 nm) a relatively cheap silicon avalanche photodiode is used, while an ADC 403 liquid nitrogen cooled germanium PIN diode detector is used for wavelengths from 650 up to 1650 nm. The signal is then sent to a BBC microcomputer where it is corrected for the spectral response of the system, displayed on a V.D.U. and if required, stored on disc.

The Spex stepping motor, data collection, signal processing and display are all controlled by the BBC microcomputer. The software written by Dunstan (1987) has several ingenious features designed to remove extraneous signals due to cosmic rays and improve the signal to noise ratio, as described below.

(i) Running Mean and Standard Deviation (RMSD)

The monochromator stepping motor allows the spectrometer to be moved
Fig. 4.1 The experimental arrangement for a photoluminescence measurement.
rapidly between data points and to be kept stationary while each point is being measured. This enables checking and re-checking of points if necessary; the Spex is then advanced only when valid data has been recorded. This feature is especially useful when using the germanium detector since the detector is sensitive to cosmic rays that give rise to large positive or negative spikes during the course of a single scan. This anomalous data may be discriminated against by comparing a given point's value to the preceding data. A running mean $M_r$ and a running standard deviation $S_r$ of the last few data points $d_i$ are maintained. If the incoming datum point is outside three running standard deviations from the running mean $M_r \pm 3S_r$, the point is then rejected. When a point is rejected $M_r$ is updated, but $S_r$ is not. In this way a real change in the incoming data is accepted after a few attempts.

(ii) Signal Averager Discrepancy Detector (SADD)

In the case of poor signal to noise ratios, an averaged PL spectrum may be taken from several scans. During the first scan all the data are accepted. In subsequent scans, however, each datum point is compared with the average value of the previous scans and will only be accepted if it lies within three standard deviations. If the datum is rejected several more attempts are made to obtain a satisfactory result. If these fail, it is assumed that the average value stored is in error and a new value is obtained by remeasuring the point $N_s$ times, where $N_s$ is the scan number. The effect of these algorithmic signal processing techniques are shown in Fig. 4.2.
Fig. 4.2 The effect of the software features described in the text designed to reduce the signal to noise ratio of a photoluminescence measurement. (a) Shows the background noise generated by the Ge detector over 200 channels (where a change in channel is equivalent to a change in wavelength) at 300ms/channel. The large spikes are caused by cosmic rays. (b) Shows the effect of the RMSD on (a), while (c) shows the combined effect of the RMSD and SADD where $N_\gamma$ has a value of two.
4.3 Photoluminescence Excitation Spectroscopy (PLE)

A major disadvantage of PL experiments is that they merely probe the lowest occupied states, which are themselves located in the lowest end of the density of states. PLE measurements, on the other hand, do probe higher lying states and are a measure of the joint density of states of the conduction and valence bands. They also have an advantage over absorption experiments in that a narrow band-gap substrate does not hinder the measurement. The experimental arrangement for PLE is similar to PL with the exception that the spec is set at the PL emission wavelength of the sample, or alternatively, on its low energy tail and the intensity of the signal monitored as a function of the wavelength of the excitation source. The source is usually scanned from high energies down to the energy of the PL emission. Since the wavelength of the excitation source approaches the detection wavelength, great care must be taken to reject the maximum amount of specularly reflected laser light. This is achieved by positioning the sample at an oblique angle to the excitation source and collecting the luminescence almost normal to the sample.

When features of interest are in the 500-900nm range the excitation source used is a dye laser pumped by the argon ion laser, although a variety of dyes are needed to cover this wavelength range. For features at wavelengths greater than 900nm a tungsten lamp and a 0.25m monochromometer are used. Again the whole system is controlled by the BBC microcomputer, the additional software required having been written by A.D.Prins.
4.4 High Pressure Photoluminescence

There are two systems available for making high pressure PL measurements. Firstly, a 0-8kbar piston and cylinder system (Lambkin 1988a), suitable for both optical and transport measurements at high and low temperatures. Secondly, a miniature cryogenic diamond anvil cell (Dunstan 1988) to perform PL or absorption measurements to pressures in excess of 100kbars. Both systems have been used in the work presented here and are described below.

4.4.1 Portable High Pressure Piston And Cylinder System

4.4.1.1 Design Considerations

The high pressure cell, made of BeCu, is of conventional compound cylinder construction as shown in Fig.4.3. The BeCu is machined half hard and heat treated for 2 hours at 320°C, to a final hardness of 34 Rockwell C. The cell has an outside diameter of 19mm and therefore fits most commercial cryostats. The internal diameter of 5mm enables relatively large samples to be measured and can easily accommodate clover leaf samples for transport measurements. The cell is pressurised by a portable piston and cylinder intensifier via 0.025" I.D. stainless-steel capillary, as shown in Figs 4.4 and 4.7. The use of both BeCu and stainless-steel allows the system to be used in magnetic field applications.

The compound cylinder construction relies on the outer cylinder applying a compressive stress to the inner cylinder produced by an interference fit between the two, thereby reducing the stresses within
the inner cylinder when the cell is pressurised. The maximum internal pressure that is contained in such a system is given by Eq. 4.1,

\[ P_{\text{max}} = \frac{2 Y}{\sqrt{3}} \left[ \frac{b - a}{a} \right] = \frac{2 Y}{\sqrt{3}} \left[ \frac{\omega - 1}{\omega} \right] \tag{4.1} \]

where \( Y \) is the yield strength of the material, \( a \) the internal diameter of the inner cylinder, \( b \) the external diameter of the outer cylinder and \( c \) the internal diameter of the outer cylinder. A condition of the optimised design is that \( \omega = b/c = c/a \). This optimum pressure relies on the contact pressure at the interface of two cylinders being given by;

\[ P_{c}^{\text{opt}} = \frac{2 Y}{\sqrt{3 \omega}} \left( \frac{\omega - 1}{\omega + 1} \right) \tag{4.2} \]

with a required interference of;

\[ \delta_{\text{opt}} = \frac{2 a Y}{E} \left[ \frac{\omega - 1}{\sqrt{3 \omega}} \right] \tag{4.3} \]

For the 19mm cell made from BeCu with a yield strength of 10 kbars, the maximum operating pressure for elastic deformation is 8 kbars, requiring an interference fit of 20\( \mu \)m between the inner and the outer cylinders. The maximum operating pressure is thought to be a conservative estimate since the cell has been successfully tested over five cycles to over 13.5 kbars. The maximum pressure was limited by the piston-cylinder seals rather than a failure in the cell itself. It is thought that the relatively short working space (approx. 7mm) compared to the O.D. of the cell, makes end effects significant; the unpressurised ends giving

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considerable support to the short section of the cell under pressure. As a result, no expansion of the cell could be measured, to an accuracy of 10μm, when pressurised.

![Diagram of cell components]

Fig. 4.3 The high pressure 0-8kbar cell. (a) outer cylinder, (b) inner cylinder, (c) leak escape path, (d) backing pad, (e) bottom piston, (f) nylon chamfered ring, (g) rubber O-ring, (h) top piston with "Harwood" type sealing system.

The advantage of using the capillary feed (Harwood 1/8 inch O.D., 1/40 inch bore stainless-steel) is twofold. (i) It is possible to cool the cell down from room temperature to 77 or 4K without loss of pressure or developing uniaxial stresses within the cell. To achieve this it is necessary to freeze the cell from the bottom upwards and avoid premature freezing of the pressure fluid in the capillary. A satisfactory method uses two immiscible fluids with different freezing points, the higher in the cell, whilst the intensifier and capillary are filled with the lower. It was found that using a light vegetable oil (Carthamus tinctorius or safflower oil) in the cell (Lancefield 1987) and an n-pentane iso-pentane 50:50 mixture in the intensifier and capillary, enabled the pressure to be maintained to within ± 0.1kbar over the temperature range 300-4K.
Fig. 4.4 The three-way Harwood coupler, one arm being fed with high pressure fluid from the intensifier and hence to the cell. The third arm forms the wire/fibre feedthrough as shown in the inset and described in the text.
The second advantage to the capillary system is that the electrical and optical fibre feedthrough seal is made outside the cryostat and remains at room temperature. This eliminates the likelihood of a leak due to the thermal cycling of the seal. The seal is formed (Lancefield 1987) from a capillary stub, approximately 5cm long, into which the 0.07mm enameled copper wires and 140/100 optical fibres have been epoxied along with a nylon cylinder which provides added mechanical protection. The seal is shown in detail in the insert of Fig.4.4. The stub is filled with a low viscosity Araldite resin (MY750, HP905, and DY063) by alternate exposure to vacuum and atmospheric pressure. Once filled the resin is set by placing the stub in an oven at 120°C.

The stub is then sealed into a standard Harwood three-way coupler, the horizontal branch of which is connected to the intensifier while the straight-through outlet is connected to the top piston of the cell by suitable length of capillary. It is through this capillary and the cell’s top piston that the wires and fibre are fed from the stub into the cell. The capillary feed to the cell also acts as the support for the cell when in the cryostat. Several heat shields are also fitted at appropriate points along its length.

The intensifier is based on the Enerpac 14 ton double-acting hydraulic ram, acting on a 15mm piston and cylinder as shown in Fig.4.5. There is no frame or die-set, the components that normally make an intensifier system a massive device. Instead, the 14 ton ram screws directly into an extension of the high pressure cylinder. The high pressure seals are again O-rings and chamfered nylon rings.

For electro-optical experiments the fibre/wire feedthrough system is quite adequate. It was found, however, that using optical fibre for PL measurements had several disadvantages. Initially, the fibre from the
Fig. 4.5 The intensifier system. The hydraulic ram is a Enerpac 14 ton double-acting ram. The in-house built piston/cylinder system screws directly onto the ram.
high pressure cell was connected, using a mountable/demountable coupler, to one port of a three-way optical coupler. Excitation radiation was launched into the second port while the returning PL signal was collected from the third. It was found that the mounting of the sample onto the polished fibre-end in the cell was critical and that a PL signal was only obtained when the sample lay completely flush. Although attempts were made to design a mount that would meet this criterion, it became clear that a technique that relied on surface contact with the sample was also likely to damage the surface in the process.

To overcome this problem the optical fibre was replaced by a sapphire window. The window was made by simply substituting the BeCu bottom piston of the cell with one made from sapphire and using a backing pad suitable for optical access. This arrangement is shown in Fig.4.6.

Fig.4.6 Two designs of high-pressure sapphire windows. (a) Dual bottom piston and window design. (b) Traditional "Bridgeman" type window.
The sealing method remained unchanged. Although the optics of the system and the sample mounting were greatly improved, the sapphire windows were prone to fracture when under pressure. Nevertheless, some experiments were made using this system. The small aspect ratio of the window (width/length) requires that the end of the window be accurately square, otherwise non-uniform stress patterns arise as the window seats unevenly on the backing pad. Since fractures appeared to propagate from this end it suggested that the required degree of accuracy was not met.

This type of optical window has now been superseded by a more conventional design as shown in Fig.4.6b. The 2mm dia. x 1mm protrusion of the BeCu bottom piston has been replaced by a sapphire window of identical dimensions. The conical hole in the backing pad is extended into the piston itself and therefore causes no reduction in the optical aperture compared with the previous design.

The use of two immiscible fluids to successfully cool the cell to low temperatures, also requires the cell to remain vertical while cooling. Consequently a 90° prism was attached to the bottom of the cell allowing the excitation and PL collection to be made through a side window of the cryostat and enabling the cell to remain vertical, as shown in Fig.4.7. Keeping the cell versicle also has the advantage that the cell can be repeatedly removed from the cryostat without the windows becoming misted.
Fig. 4.7 Vertical arrangement of the 8kbar high pressure cell with the 90° prism for optical access.
4.4.1.2 Sample Preparation And Use

For electro-optical measurements such as photoconductivity, or more straightforward Hall measurements, the cell is large enough to accommodate standard clover leaf samples. The sample is usually secured to a simple platform mount that is screwed into the top piston and is positioned so that the fibre lies directly over the sample. To launch the maximum intensity of light down the fibre, the two ends are normally polished by using mountable/demountable couplers together with a polishing jig and diamond lapping film.

The sample mounting for the PL experiments is relatively simple. Several samples may be placed on the window and a piece of PTFE tape placed over them. The tape is then secured to the window by the rubber O-ring.

Once the pressure system has been assembled the cell is placed in the cryostat. The hydrostatic pressure in the cell may be measured directly by having a manganin resistive-wire gauge in the intensifier cylinder, although this requires another Harwood three-way coupler and an electrical feedthrough stub. Where possible the sample itself is used as a pressure gauge. III-V semiconductors and LDS structures usually contain layers of binary material for which the band-gap pressure coefficients are known. Signals from these layers may be used to determine the pressure. For PL experiments a piece of InP (for example) may easily be placed in the cell alongside the sample of interest to be used as a pressure gauge.

Standard safety precautions are observed when operating the system. Massive shields are placed around the cryostat and intensifier while the capillary is contained within a metal braid. Following standard practice
Spain 1977) all Harwood seals are vented to relieve pressure in the event of leaks.

4.4.2 The Miniature Cryogenic Diamond Anvil Cell

To generate pressures of 100 kbar or more, a diamond anvil cell (DAC) is used. The basic principle of the DAC is relatively simple, as illustrated in Fig. 4.8. A weak material, in a gap of large aspect ratio (diameter to thickness) between hard anvils will sustain pressures far in excess of its own strength. Diamond anvils with 700 μm culets squeezing a steel gasket of thickness 100 μm may generate pressures of a few hundred kbars in a sample hole provided in the centre of the gasket. The PL measurements are then made by passing the laser light through the diamond and collecting the luminescence in a back scattering configuration. There are a multifarious variety of DAC designs, a comprehensive review of which is given by Jayaraman (1986). A detailed description of the theory of pressure generation in a DAC is given by Dunstan (1989).

To date DACs have been characterised by their relatively large size, typically several cms in the outside diameter despite the small volume under pressure and usually require a large purpose built cryostat for low temperature work. A major design consideration is that forces of up to 1 tonne must be applied to the diamonds, which in turn must have accurate tilt and radial adjustment. This has historically been solved by using bulky drive mechanisms, or by clamping the cell when loaded and then removing the cell from the cryostat to increase the pressure. These problems have been overcome at Surrey by the design of a new miniature DAC as shown in Fig. 4.9. A full and detailed description of the cell is given by Dunstan (1987). The miniature DAC has an outside
Fig. 4.8 Principle of the diamond anvil cell.
diameter of 19mm and fits into the bore of an Oxford Instruments flow cryostat. The significant reduction in size is brought about by the drive force no longer being transmitted through the diamond alignment mechanisms and by the drive mechanism being a light-weight Bowden cable assembly.

4.4.2.1 Sample Preparation and Use

Since the available sample space in the DAC is a hole 250μm in diameter and 90μm in depth, the samples themselves must be significantly smaller. The samples are initially thinned to 30μm by mounting them with wax in a 30μm groove cut in a stainless steel block and then polishing away the substrate material using diamond lapping film. Once the sample has been demounted from the block it may then be cleaved into approximately 50μm x 50μm pieces by careful use of a scalpel blade. From a comparison of PL spectra of the samples before and after their thinning and cleaving, it is clear that the samples are completely unaffected by their ordeal. The identical process is used to prepare a similarly sized piece of ruby, needed for the pressure calibration (§4.3.2.3). The process is more problematic in that the ruby is almost transparent when 30μm thick and therefore invisible; and being a hard material also makes it considerably more difficult to cleave.

In order that the DAC may work safely to high pressures it is important that the two diamond faces are aligned accurately parallel and positioned diametrically opposite. Parallelism is found by adjusting the screws that tilt the bottom diamond plate and looking for optical fringes between the two diamond faces to six fringes or better. The radial alignment is obtained by adjusting the relevant screws while looking
Fig. 4.9 Miniature diamond anvil cell together with the Bowden cable drive mechanism.
through the two diamond faces using a microscope. This alignment may then be checked by inspecting the indented and drilled gasket to confirm that the gasket hole appears in the middle of both sides of the indent. The gasket is formed by indenting 0.5mm stainless steel to a thickness of less than 100μm and then drilling a 200-300μm hole in the centre of the indent using micro drills and a precision pillar drill.

The sample and ruby are handled and positioned, using a microscope, onto the top diamond culet using fine hypodermic syringe needles, the gasket is then placed into position. The sample space may then be filled with a suitable pressure transmitting fluid and the diamonds clamped together. A more thorough description of the operation and use of DACs is given by Spain (1989).

The choice of fluid is of some importance. It has been shown by Pieramarini (1985) that a 4:1 mixture of ethanol and methanol will remain hydrostatic at room temperature to a pressure of 100kbar. It was originally assumed that provided the pressure changes were made at room temperature, the alcohol mixture would remain hydrostatic down to liquid nitrogen and helium temperatures. However, when liquid argon was used as a pressure transmitting fluid, enabling pressure changes to be made at low temperature, anomalies were found between these measurements and those made with the alcohol mixture. Although neither the samples nor the ruby showed evidence of non-hydrostatic stress in excess of 3 kbars, the comparison with argon loading showed a systematic reduction in effective pressure recorded by the ruby, as shown in Fig.5.3. Indeed Cardona (1988) pointed out that anomalous low temperature pressure dependences in the literature (Olego 1980) probably resulted from the use of alcohol as the pressure medium. It may be conjectured that a pressure differential may arise on cooling caused by a larger coefficient of thermal expansion of
The loading of the DAC with liquid argon is relatively simple and in many respects less prone to failure than using alcohol. The cell, completely assembled with no load applied, is placed in a low pressure vessel and filled with argon to a pressure of 6bar. It is then immersed in liquid nitrogen while maintaining the over pressure of the argon. After half an hour at 77K the cell is loaded to 700psi and allowed to return to room temperature. Although a relatively large load has been applied, the room temperature pressure within the cell may only be 10 kbar or less and this may significantly reduce when cooled to low temperature.

Once loaded the DAC may be inserted into the flow cryostat, held in a horizontal position. The excitation and luminescence collection are made via the bottom window and bottom diamond. To gain the maximum signal it is important that the optics are properly aligned and that the laser radiation is brought to a sharp focus within the sample space. The laser spot may then be adjusted from one sample to another by using the micrometer screw gauges attached to the lens mount.

4.4.2.2 Pressure Calibration

The renaissance of diamond anvil cells may be traced to the development of the ruby fluorescence as a pressure calibration. The shift in the R lines \( R_1 \) and \( R_2 \) at 692.7 and 694.2nm respectively of 0.365Å/kbar has been shown to be constant up to pressures of 300kbars (Barnet 1973, Piermarini 1975). This shift has also been shown to be independent of temperature down to 4K (Noack 1979). There are, however, some disadvantages associated with its use. As the shift of 0.365Å/kbar
is so small that an accurate pressure measurement requires a high resolution, well calibrated spectrometer. This problem may be reduced by detecting the 692.95nm line from a neon lamp to act as a calibration marker, whilst simultaneously measuring the ruby.

The second and indeed more serious problem, is that the luminescence from the ruby is particularly intense and will interfere with and eventually swamp the emission from the sample as it approaches the ruby wavelength. This may be overcome by using a well characterised III-V sample, such as InP, as a pressure calibrant. This also has the advantage that the InP has a relatively large pressure coefficient (8.5meV/kbar) and is therefore more sensitive to small pressure changes. As a consequence its luminescence will almost always remain displaced from the emission of interest. Some samples will conveniently have their own internal pressure gauge in the form of a binary substrate or capping layer.

It should be noted that absolute pressure is rarely the variable of interest, but rather instead, the change in lattice spacing or change in band edge, both of which are related through the definition of the deformation potential. Pressure, therefore, can be considered as a dummy variable, itself related to the change in lattice constant through an equation of state. This aspect is examined in greater detail in chapter 5.
Chapter 5

THE HYDROSTATIC PRESSURE DEPENDENCE OF THE BAND-EDGE

PHOTOLUMINESCENCE OF In$_{0.53}$Ga$_{0.47}$As

5.1 Introduction

To understand the behaviour of quantum well structures under hydrostatic pressure it is essential that the behaviour of the individual host materials have first been thoroughly characterised. With the ultimate aim of considering the lattice matched In$_{0.53}$Ga$_{0.47}$/InP quantum well system under pressure, the band-edge PL of an epilayer of In$_{0.53}$Ga$_{0.47}$As was measured as a function of pressure.

Although a considerable amount of experimental data exists for the pressure behaviour of GaAs and InP, both at room and cryogenic temperatures, there has been some experimental controversy as to whether, firstly, the band-edge emission or absorption is linear or sub-linear with the applied pressure (Welber 1975, Yu 1978, Olego 1980, Wolford 1985, Goni 1987); and secondly, whether the pressure behaviour is also dependent upon temperature (Olego 1980). The results from the high pressure PL measurements on the InGaAs epilayer, together with data from Goni (1987) on GaAs show that the dependence is indeed sub-linear and temperature independent. These experimental conclusions were excellently predicted by Christensen (1984) for bulk GaAs using self-consistent relativistic band-calculations. It is interesting to note that the controversy over the linear or non-linear behaviour of the band-edge emission mainly concerns GaAs. This material becomes indirect at approximately 42kbar (Wolford 1985) beyond which the direct emission
becomes difficult to follow. InP and InGaAs on the other hand remain
direct to significantly higher pressures and therefore allow the
relatively small, but measurable, non-linear terms to become apparent.

Finally, the experimental data from the epilayer of the InGaAs is
used to derive a value for the band-gap deformation potential.

5.2 Experimental Results And Comment

Using the D.A.C. described in chapter 4, high pressure PL
measurements were made on a 4μm In\text{GaAs} \text{0.53Ga}_{0.47} lattice-matched epilayer,
grown by Metal Organic Vapour Deposition (MOCVD) on an InP substrate at
S.T.C. Technology Ltd.. The measurements were made both at room and
liquid nitrogen temperatures and the ruby scale used to measure the
pressure. Low pressure (0–8kbar) room temperature measurements were also
made on a larger sample using the BeCu cell described in chapter 4.
Typical spectra and the PL peak energies plotted as a function of
pressure for the different temperatures are shown in Fig.5.1 and Fig.5.2
respectively.

It is clear from Fig.5.2 that the curves for both room and liquid
nitrogen temperatures show a pronounced sub-linearity similar to that
observed in InP by Muller (1980) and Kobayashi (1981). A least squares fit
to the data gives the following quadratic expressions,

\[ E_g = 0.733 + 11.0 \pm 0.2 \times 10^{-3} p - 27 \pm 2 \times 10^{-6} p^2 \]

at 297K \hspace{1cm} [5.1]
Fig. 5.1 Typical luminescence of In$_{0.53}$Ga$_{0.47}$As are shown at 80K and room temperature and various pressures.
Fig. 5.2 The luminescence peak positions are shown as a function of hydrostatic pressure at 80K and room temperature. The solid curves are least squares fits (Equs 5.2 and 5.1 respectively).
and

\[ E_g = 0.796 + 10.9 \pm 0.2 \times 10^{-3} p - 30 \pm 2 \times 10^{-6} p^2 \]

at 77K \[5.2\]

where \( E_g \) is in eV, and \( p \) in kbars. The fits show that the pressure dependence, to within experimental error, is independent of temperature.

The low temperature data in Fig.5.2 were obtained using liquid argon as the pressure transmitting fluid. Initially however, measurements were made exclusively using a 4:1 methanol/ethanol mixture. It was considered at the time that provided changes in pressure were always made at room temperature, hydrostatic pressure would always be maintained, even on cooling to 77K. Fig.5.3 shows the low temperature peak energy versus pressure data measured using the alcohol mixture and liquid argon, together with the room temperature data. The figure clearly indicates the alcohol low-temperature data tends towards the room temperature values at high pressure. Such behaviour would be very difficult to explain since it implies a temperature dependent mechanism governing the fundamental band-edge deformation potentials. The higher pressure PL spectra taken at low temperature using the alcohol mixture showed a broadening consistent with the presence of non-hydrostatic stresses of approximately 3kbar. This uniaxial component is not great enough however, to explain the apparent systematic discrepancy of some 10% between the argon and alcohol pressure coefficients. A possible explanation for the anomaly may lie in the alcohol mixture freezing to a solid with a relatively smaller coefficient of thermal contraction compared to the ruby. On cooling the ruby may then experience a reduced hydrostatic pressure in comparison with that generated in the alcohol. This type of behaviour probably
Fig. 5.3 The luminescence peak positions as a function of pressure for (a) at 80K with liquid argon, (b) at 80K with alcohol and (c) at room temperature with alcohol.
accounts (Cardona 1988) for the temperature dependence of the pressure measurements made on highly doped GaAs reported by Olego (1980).

The luminescence intensity, at both temperatures, tends to quench at pressures above 40kbar. This observation still requires an adequate explanation. A direct role for the X and L minima can be ruled out on the grounds that even at these pressures they lie at significantly higher energies than the $\Gamma$. One possible cause may involve a deep state associated with the X-minima, which with the application of high pressure begins to cross the $\Gamma$ minima at approximately 40kbar.

### 5.3 Determination Of The Hydrostatic Band-Gap Deformation Potential

Since the PL emission from the bulk InGaAs is a measure of the difference in energy between the conduction and valence bands, it is evident that its pressure dependence can only provide information on the value of the band-gap deformation potential, and not the absolute values of the conduction and valence bands. To relate the applied hydrostatic pressure to the resulting change in lattice constant, a suitable equation of state is needed. A commonly used empirical equation of state is the Murnaghan equation (Murnaghan 1944) given in Eq.5.3,

\[
\left( \frac{\Delta a}{a_0} \right)_T = 1 - \left[ \left( \frac{B'}{B_0} \right) p + 1 \right]^{-1/3B_0} \quad [5.3]
\]

Where $B_0$ is the bulk modulus and $B_0'$ the derivative of $B_0$ with respect to pressure. The equation is non-linear and requires a knowledge of the bulk modulus of the material and its pressure derivative. The equation shows
Fig. 5.4 The luminescence peak positions are replotted against change in lattice constant. The straight lines are linear least squares fit to the data.
that if the change in energy is linear with strain as it is defined in Equ.2.12, then the change in energy must be non-linear with pressure.

The InGaAs epilayer is commensurate with the InP substrate in two dimensions and is free in the third; thus, neglecting any effects of biaxial strain on the band-gap, it is appropriate to use a bulk modulus for the epilayer given by,

\[ B_0^{\text{epi}} = \frac{2}{3} B_0^{\text{InP}} + \frac{1}{3} B_0^{\text{InGaAs}} \]  \hspace{1cm} [5.4]

No measurements have been made of \( B_0 \) or \( B_0' \) for InGaAs. A value for \( B_0 \) may be found however, by using the Keyes' empirical scaling rule (Keyes 1962). According to this rule, the second-order elastic constants \( C_{1,j} \) vary as the inverse fourth power of the lattice constant. Using GaAs as the basis material, the bulk modulus of the InGaAs can be determined from the following;

\[ C_{1,j}^{\text{GaAs}} = C_{1,j}^{\text{(GaAs)}} \left( \frac{a_0^{\text{(GaAs)}}}{a_0^{\text{(InGaAs)}}} \right)^4 \]  \hspace{1cm} [5.5]

and

\[ B_0 = \frac{C_{1,1} + 2 \times C_{1,2}}{3} \]  \hspace{1cm} [5.6]

where \( C_{1,1}^{\text{(GaAs)}} = 1187.7 \text{kbar}, \quad C_{1,2}^{\text{(GaAs)}} = 537.2 \text{kbar} \).

Using the above scaling law, \( B_0 \) for InGaAs is calculated to be 650 kbar. Values for the elastic constants and bulk moduli for other binary semiconductor materials are tabulated in Table B.1 in appendix B. Since most III/V semiconductors appear to have a similar value of the differential
bulk modulus, $B'_0$ for InGaAs is assumed to have a value of 4. Another approach is to assume that the bulk modulus of the InGaAs is the same as that of InP. Relative spectroscopic measurements of the bulk modulus of Ga\textsubscript{x}In\textsubscript{1-x}As\textsubscript{y}P\textsubscript{1-y} with $y = 0.83$ lattice-matched to InP by Prins (1988) yielded a value to within 1% of InP, which in principle agrees with Keyes' empirical rule if InP is used as the basis material. This result would suggest that for the InGaAs epilayer $B_0$ and $B'_0$ may be taken to have the InP values, $B_0 = 760 \pm 40$ kbar and $B'_0 = 4.0 \pm 0.2$ (Menoni 1987). Using these values, the 300K experimental data, as a function of pressure, can be transformed by use of Equ. 5.3 to data as a function of the change in lattice constant $\Delta a/a_0$ and is thus plotted in Fig.5.4.

For the 80K data it is necessary to correct the equation of state for the low temperature. A rigorous treatment is given by Spain (1977), although for the purposes here it is sufficient to correct $B_0$ by the change in lattice constant due to thermal expansion. The change in lattice constant in going from 80K to 300K is approximately $8.3 \times 10^{-4}$ (Landolt-Bornstein 1979) and corresponds to a thermal pressure of $P_T = 1.6$ kbar at 80K with reference to 300K. At 80K therefore, $B_0$ becomes $B_0 + P_T B'_0 = 766.4$ kbar. Using this value in the Murnaghan equation, the 80K data are replotted against change in lattice constant as in Fig.5.4. Within experimental error both the 300K and 80K data may be fitted with straight lines, the gradients of which correspond to a $1/3$ of the hydrostatic band-edge deformation potential as defined in Equ.2.12. The factor of $1/3$ arises since the deformation potential is defined in terms of change in volume rather than change in lattice constant. Using the InP values of $B_0$ and $B'_0$ the deformation potentials are $-8.3 \pm 0.1$ eV at 300K and $-8.2 \pm 0.1$ eV at 80K. As would be expected the deformation potentials
are the same to within experimental error, hence a mean value may be taken to be $-8.25 \pm 0.1\text{eV}$. If the interpolated values of the bulk modulus is used instead, the deformation potentials are found to be $\Sigma_{300\text{K}} = -8.0 \pm 0.1\text{eV}$ and $\Sigma_{800\text{K}} = -7.8 \pm 0.1\text{eV}$. The errors quoted correspond to random scatter in the data and do not include systematic errors due to the uncertainty in $B'_0$ and $B''_0$. The results are presented in this fashion so that they can be subsequently corrected when accurate values of $B'_0$ and $B''_0$ become available.

The assumption of neglecting the effects of uniaxial stress due to the difference in bulk moduli between the epilayer and substrate can be analysed in more detail. Since the bulk modulus of InGaAs is interpolated to be smaller than InP, under pressure an epilayer of InGaAs will experience a tetragonal distortion in the $<001>$ direction. The strain in the plane of the interface $\varepsilon_{\parallel}$ generated under a particular pressure $p$ is given by,

$$\varepsilon_{\parallel}(p) = \left[ \left( \frac{\Delta a}{a_0} \right)_{\text{InP}} - \left( \frac{\Delta a}{a_0} \right)_{\text{InGaAs}} \right]$$  \[5.7\]

The change in lattice constants in Equ.5.7 for a given pressure $p$ can be found from the Murnaghan equation of state using the interpolated value of $B'_0$ for the InGaAs. At a pressure of 35kbars, for example, the induced strain is $+0.156\%$, where the positive sign implies a biaxial tensile stress. The strain experienced in the InGaAs perpendicular to the interface $\varepsilon_{\perp}$ is related to the in-plane strain by Equ.5.8, where $c_{11}$ and $c_{12}$ are the elastic constants of the InGaAs,

$$\varepsilon_{\perp} = -2 \times \frac{c_{12}}{c_{11}} \varepsilon_{\parallel}$$  \[5.8\]
At a pressure of 35 kbars this perpendicular strain is estimated to be -0.156% and hence the total change in volume is given by,

$$\frac{\Delta V}{V_0} = 2\varepsilon_\parallel + \varepsilon_\perp$$  \[5.9\]

$$= +0.00156 \text{ at 35 kbars}$$

Using an interpolated theoretical value of the band-gap deformation potential for InGaAs of -7.14 eV (Van de Walle 1989), the decrease in the band-gap at this pressure due to the dilatational component of the induced strain is given by the product of the deformation potential and the change in volume, giving a value of 11.1 meV, equivalent to a reduction in hydrostatic pressure of approximately 1 kbar.

The induced splitting of the light- and heavy-hole valence bands caused by the deviatoric component of the strain is given by Equ.s 2.14 and 2.15; again using an interpolated value for the shear deformation potential the change in energy of the light-hole band from its unstrained position is +5.3 meV and hence tends to reduce the band-gap. The net reduction in the band gap due to the uniaxial strain is therefore 16 meV at 35 kbar. The net effect of the different bulk moduli for the epilayer and substrate is to decrease the band-gap by an "apparent" hydrostatic pressure of 1.5 kbar at 35 kbars, which is marginally outside the experimental error of ± 1 kbar for the measurement of the absolute pressure using the ruby scale. It is reasonable therefore, to neglect the effects of uniaxial strain. This conclusion drawn from the simple calculation above also indicates why the surprising experimental result of Prins and Dunstan (1988); that the pressure dependence of the
band-to-band luminescence from an epilayer of GaInAsP on and off the InP substrate is the same to within 1/3%, is not as surprising as they suggest.

5.4 Comparison Between Experiment And Theory

People (1988) has measured the pressure dependence of the direct band-gap of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ using stimulated emission at room temperature. Their sample consisted of 0.3μm of $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ on 1.7μm of $\text{In}_{0.63}\text{Ga}_{0.47}\text{As}$ (active layer) on an (001) InP substrate. Using similar experimental and analytical techniques to those described above they found that the PL emission pressure data was best fit by a quadratic expression with a linear term of $12.44\text{meV/kbar}$ and a squared term of $-68.0 \times 10^{-3}\text{meV/kbar}^2$. The band-gap deformation potential is estimated to be $-7.79 \pm 0.4\text{eV}$. It should be noted that the difference in pressure coefficients is within the experimental spread that was found in the measurement of the band-gap pressure dependence of GaAs.

These experimental values for the band-gap deformation potential agree satisfactorily with theoretical prediction. Linearly interpolating between the theoretical values for GaAs and InAs, Van de Walle (1989) predicts a value of $-7.1\text{eV}$, Cardona (1987) a value of $-6.9\text{eV}$ and Camphausen (1971) a value of $-7.6\text{eV}$. It is noteworthy that all these values tend to underestimate the experimental values and may indicate that linearly interpolating values of the deformation potential is not an accurate assumption.
Chapter 6
PRESSURE DEPENDENCE OF THE BAND-EDGE DISCONTINUITIES IN ISOLATED
InGaAs\textsubscript{X}InP AND Al\textsubscript{x}Ga\textsubscript{1-x}As\textsubscript{X}GaAs QUANTUM WELLS

6.1 Introduction

A considerable amount of effort has been invested in recording PL emissions from quantum wells under high pressure, particularly in the GaAs\textsubscript{X}Al\textsubscript{1-x}Ga\textsubscript{As} system (Venkateswaran 1985, 1986, Lefebvre 1987, Gell 1987, Wolford 1987 and Prins 1987). In this chapter the pressure dependence of the PL emissions from InGaAs\textsubscript{X}InP and GaAs\textsubscript{X}AlAs quantum well structures are investigated in detail. From such measurements it is possible to deduce the pressure dependence of the band-edge discontinuities by two distinct approaches. The basic methodology behind the two approaches is discussed, demonstrating how one technique is sensitive to the conduction-band discontinuity, while the other is sensitive to the valence-band discontinuity. No attempt is made in these descriptions to account for additional factors that can affect quantum wells under pressure; these are covered when the two methods are applied to specific experimental data.

From the analysis of the high-pressure PL experiments on InGaAs\textsubscript{X}InP and GaAs\textsubscript{X}AlAs quantum well structures, it is found that in both cases the band-offset ratio changes with pressure. This is the first observation of this phenomenon which had previously been thought too small to be of any consequence, or alternatively, had been simply ignored.

Finally, these results are compared to theoretical calculations. Excellent agreement is found with the calculations of Van de Walle (1987)
and Cardona (1987) for both quantum well systems. It is concluded that these measurements tend to support the assumption that band-offsets are determined by properties of the bulk host materials.

6.2 Methodology

The behaviour of quantum wells under hydrostatic pressure is complex. The PL emissions from isolated quantum wells will be affected by the pressure dependence of some or all of the following factors: i) the bulk band-structure of the host materials, ii) the effective masses of the holes and electrons, iii) the exciton binding energy, iv) the well width, v) mixing between Γ and X-like states, vi) the magnitude of the optical matrix element and vii) the band-offset ratio. Although the problem is complex in detail, two methods involving high pressure PL measurements can be successfully used, in a relatively simple fashion, to accurately determine the pressure behaviour of the conduction and valence-band offsets.

The first method analyses luminescence from type-I quantum wells and is particularly sensitive to the conduction-band discontinuity. The second method analyses luminescence from type-II quantum wells and is as a consequence sensitive to the valence-band discontinuity. The basic principles behind the two methods and the distinction between type-I and type-II quantum wells can be clearly demonstrated in Fig.6.1. The figure shows the relative positions, as a function of pressure, of the important band edges with respect to the top of the valence band in the well material of a typical quantum well. The exciton binding energy and hole confinement energy have been ignored for simplicity since their pressure
Fig. 6.1 The figure indicates how a possible band structure configuration of a type-I quantum well can change with pressure. The conduction-band offset $\Delta E_c$ decreases with pressure, while the valence-band offset $\Delta E_v$ increases slightly. Shown is how the ground state confinement energies from wells of three different widths also reduce with pressure. At sufficient pressure the various wells will become type-II as the $X$ minima in the barrier material falls below the $\Gamma$ confined state in the well material.
dependence are considered to be relatively small. The figure has been constructed showing the conduction-band discontinuity decreasing with pressure while the valence-band discontinuity increases slightly. The diagram is conveniently divided into two regions, type-I and type-II, representative of the band structures associated with these respective types of quantum well. Schematic band diagrams of these quantum wells are shown in Fig.s 6.2 and 6.7.

6.2.1 Type-I Quantum Well Method

In the type-I region of Fig.6.1 transitions are direct in both momentum and real space. Also shown in this region are three confined states formed from isolated wells of three different widths. If, as is shown in Fig.6.1, the electron confining potential i.e. the conduction-band discontinuity, goes to zero with pressure, it is then clear from an elementary treatment of a "particle in a box" that the confinement energy of the higher energy states must decrease at a faster rate than the lower energy states. The net effect is that the pressure coefficients of transition energies from the higher lying confined states must always be smaller than the pressure coefficient of the band gap of the well material; and necessarily decrease with decreasing well width. Conversely, if the conduction-band discontinuity were to increase with pressure Fig.6.1 would indicate, mutatis mutandis, that the pressure coefficients of the transition energies would be, ceteris paribus, greater than the coefficient of the well material band-gap and increase with decreasing well width. By modelling the pressure dependence of the transition energies from wells of various widths and using the electron
confining potential as a variable, it should be possible to estimate a value for the pressure dependence of the conduction-band discontinuity. This approach is applied to InGaAs\/InP high pressure PL data in §6.3.

6.2.2 Type-II Quantum Well Method

Again referring back to Fig. 6.1, it is clear that as the pressure is increased, the X-state in the barrier material will approach the bottom of the barrier conduction-band. At a sufficient pressure the confined Γ-state in the well and X-state in the barrier will become degenerate, a further increase in pressure will cause the X-state to become the lowest lying conduction-band level in the entire quantum well system. In such a staggered band alignment, shown in Fig. 6.7, holes remain confined in the well material while electrons become confined in the barriers. This arrangement of band-structure forms a type-II quantum well. Although possible optical transitions in type-II systems are indirect in both real and momentum space, they can still occur. These transitions are discussed in greater depth in §6.4.1.

It should be stressed that this arrangement of bands forming a type-II system is not unique. It is possible to produce an alternative system where electrons are confined in the well and holes in the barriers. It should also be noted that type-II band structures can be generated by means other than the use of high pressure. Some alternative methods are described in §6.4.1.

In the type-II region of Fig. 6.1 it is seen that a simple estimate for the valence-band discontinuity at a given pressure \( \Delta E_v(p) \) is given by,
where $E^X_b(p)$ is the indirect band-gap of the barrier material and $E^\text{II}_{\text{PL}}(p)$ the energy of the type-II emission. This approach is used to analyse high-pressure PL data from a AlAs\GaAs superlattice in §6.4.

By extrapolating the type-II recombination energy $E^\text{II}_{\text{PL}}$ to $p = 0$ Wolford (1986) and Venkateswaran (1986) were able to determine the fractional valence-band offset $Q_v$ for Al$_x$Ga$_{1-x}$As\GaAs superlattices at atmospheric pressure. Wolford (1986) reports a value of $Q_v$ of 0.32 ± 0.2 for $x = 0.28$ and 0.7, while Venkateswaran (1986) gives a value of 0.30 ± 0.04 for $x = 0.25$.

If for some reason it is not possible to measure a type-II emission, then a third, although related technique, is to measure the pressure dependence of the extinction of type-I emissions from wells of various widths, as suggested by Fig.6.1. The drawback with this method is the type-I emissions should be spaced over a fairly large energy range in order to see the well emissions extinguish sequentially. This can in practice be difficult to realise. Conceivably all three techniques could be applied to a single sample. In practice, however, it is prudent to design the sample for the specific technique. Strong type-II emissions are found for example in superlattice material and are usually significantly weaker in the isolated quantum well samples.

The two methodologies outlined in the two preceding sections are now applied to two specific quantum well systems.
6.3 Pressure Dependence Of The Conduction-Band Discontinuity In In$_{0.53}$Ga$_{0.47}$As/InP Isolated Single Quantum Wells.

Type-I Method

6.3.1 Introduction

The lattice matched In$_{0.53}$Ga$_{0.47}$As/InP quantum well system is type-I as described in §6.2.1, a schematic band diagram of which is given in Fig.6.2, defining the notation used in the text.

![Schematic Band Diagram](image)

**Fig.6.2** A schematic band diagram of an isolated InGaAs/InP quantum well defining the notation used in the text.

6.3.2 Experimental

The multiple quantum well sample grown by Metal Organic Chemical Vapour Deposition (MOCVD) at STC Technology Ltd., consisted of four In$_{0.53}$Ga$_{0.47}$As isolated wells labelled A-D with widths 15, 40, 68, and
96Å respectively, separated by 200Å of InP. The sample also contained a 0.1μm layer of InGaAs, labelled E, which is assumed to behave as the bulk material. In addition to the quantum well sample, a piece of the epilayer of InGaAs already discussed in chapter 5, was also measured during the course of the experiment. This acted as an additional reference for the behaviour of the bulk well material. Both samples were loaded into the DAC as described in chapter 4; liquid argon was used as the pressure transmitting fluid. All measurements were made at liquid nitrogen temperatures.

PL was excited by 10-100mW of 514nm argon ion laser radiation and detected by the germanium PIN diode detector. All the spectra were corrected for the response of the system.

6.3.3 Results

The PL spectrum of the quantum well sample at 8kbars is shown in Fig.6.3, together with a schematic band-diagram of the sample itself. This spectrum shows luminescence from the n = 1 level in the conduction band to the n = 1 heavy-hole level in the valence band. The linewidth of the peaks tend to increase with decreasing well width indicating the greater sensitivity of the thinner wells to well width fluctuations. Also shown is the PL spectrum of the InGaAs epilayer, labelled F, which lies slightly lower in energy than the 0.1μm layer contained in the multiple quantum well structure.

Fig.6.4 shows PL spectra at various pressures. As the pressure is increased all the peaks move to higher energies, although the rate of increase is clearly smaller for the narrower wells. A consequence of this
Fig. 6.3 The luminescence spectrum at 8 kbar of the InGaAs/InP multiple quantum well sample. Also shown is the spectrum (F) of the 4 \( \mu \)m epilayer of InGaAs.
Fig. 6.4 Luminescence spectra of the multiple quantum well sample shown at several different pressures. These spectra clearly show how the resolution of peaks C, D, and E is lost as the pressure is increased. The spectrum from the InGaAs epilayer (F) is also shown at 8 and 66 kbar. The intensity of peak A has reduced by an order of magnitude by the highest pressure.
behaviour is that it becomes increasingly more difficult to resolve peaks from the thicker wells as the pressure is increased. This results in a PL spectrum at 66kbars containing two resolved peaks A and B, and a third peak constructed from the superposition of peaks C, D, and E. To continue to provide a clear reference for the behaviour of the well material at high pressure it was necessary to place the epilayer of InGaAs in together with the quantum well sample. It is also worth noting that a below band-edge emission appears at pressures greater than 45kbars and that the relative intensity of the peaks changes with increasing pressure.

As Venkateswaran (1986) pointed out, a more accurate method of investigating the difference in pressure coefficients between different wells is to plot the difference in energy between any two peaks as a function of pressure. This prevents the statistical error due to the uncertainty of the pressure measurement (± 1kbar) deduced from the ruby scale from being compounded. It is perhaps more physically meaningful and certainly more accurate, however, to treat pressure as a dummy variable and to plot the total confinement energy of a given well against the change in the well material’s fundamental band-gap. Ignoring the exciton binding energy, a quantum well transition energy may be written,

\[ E_{1\text{HH}} = E_2^{\text{(InGaAs)}} + A_1^\Gamma + A_{1\text{HH}}^\Gamma \]  

[6.2]

where \( A_1^\Gamma \) and \( A_{1\text{HH}}^\Gamma \) are the electron and heavy hole confinement energies in the conduction and valence-bands respectively, as shown in Fig.6.2. The total confinement energy \( E_{\text{con}} \) may then be estimated from the PL data by,
\[ E_{\text{con}} = \Delta_{1e}^\Gamma + \Delta_{1\text{HH}}^\Gamma \]

\[ \approx \text{PL} \left( E_{1H}^{1a} \right) - \text{PL} \left( E_q^{(\text{InGaAs})} \right) \tag{6.3} \]

Using the above approximation, the total confinement energies for the different wells are plotted against the energy of the PL emission from the 4μm epilayer of InGaAs as shown in Fig.6.5. The relationships are remarkably linear. The magnitude of the gradient \(-dE_{\text{con}}/dE_q\), given by a least squares fit, decreases with increasing well width, i.e. \(dE_{\text{con}}/dE_q = -0.155, -0.113, -0.075\) and \(-0.035 \pm 0.5\%\) for the 15, 40, 68 and 96Å wells respectively. In terms of linear pressure coefficients it is clear that they increase with increasing well width. Assuming that InGaAs has a linear pressure coefficient \(dE/dp\) of 10.9meV/kbar as found in chapter 5, then \(dE_{1H}^{1a}/dp = 9.21, 9.45, 10.08, 10.51 \pm 0.01\text{meV/kbar}\) for the 15, 40, 68, and 96Å wells respectively.

### 6.3.4 Theoretical Model

The experimental results presented above strongly suggest that the conduction-band discontinuity decreases with pressure as described in §6.2.1. In order to make quantitative comments on the magnitude of the effect and the influence of other factors, it is necessary to develop a suitable theoretical model.

The model consists of calculating the total confinement energy using the two band envelope-function approximation (as described in chapter 3 §3.2.1.1) as a function of the fundamental band-gap of \(E_q^{(\text{InGaAs})}\). In
Fig. 6.5 The confinement energy $E_{\text{con}}$ for the various well widths as a function of the fundamental band-gap of InGaAs $E_g$. The broken lines represent theoretical fits assuming a constant band-offset ratio, while the solid lines are calculated assuming the valence-band discontinuity remains constant with pressure.
practice this is done by using pressure as a dummy variable in a computer code to estimate the values of the various parameters for incremental values of pressure $p$.

The affect of pressure on a quantum well system has been discussed in some detail by Lefebvre (1987). The authors point out that there are three major contributions to the behaviour of the confinement energy as a function of pressure, all of which are included in the model.

(i) Due to the different pressure coefficients of the band gaps of the well and barrier materials, the conduction- and valence-band discontinuities ($\Delta E_c$ and $\Delta E_v$ respectively) will also vary with pressure.

The pressure dependence of $E_g$ (InGaAs) at liquid nitrogen temperatures has been measured and is given by Equ. 5.2 in chapter 5. The pressure dependence of $E_g$ (InP) has also been determined from PL measurements (Muller 1980) as,

$$E_g^{\text{(InP)}} = 1.420 + 8.5 \pm 0.2 \times 10^{-3} p - 18 \pm 2 \times 10^{-6} p^2$$

with $E_g$ in eV and $p$ in kbars. The values of $\Delta E_c(p)$ and $\Delta E_v(p)$ at a given pressure will also depend upon the value of the band-offset ratio as defined in Equ.s 3.16. The ratio is initially assumed to be 0.38:0.62 (Skolnick 1986) and is assumed to remain constant with pressure.

(ii) Since the effective mass of electrons and their fundamental band-gap are related by $k.p$ theory (as described by Equ.2.6 in chapter 2), an increase in the band gap caused by the hydrostatic pressure will also increase the effective mass. This phenomenon *ceteris paribus*, will tend to reduce the confinement energies with pressure. The increase in effective mass with $E_g$ for electrons in both InP (Shantharama 1984) and
InGaAs (Adams 1986) have been experimentally determined to be,

\[ \frac{m_e^*}{dE} = 0.074 \pm 0.005 \text{ m}_0 \text{eV}^{-1}, \]

and

\[ \frac{m_e^*}{dE} = 0.049 \pm 0.002 \text{ m}_0 \text{eV}^{-1}. \]

The effect of pressure upon the heavy-hole effective masses is negligible since its value depends upon interactions of high lying bands that remain relatively unperturbed by high pressure. Their values are therefore assumed to remain constant with pressure. The following values of the effective masses at atmospheric pressure are used in the model,

\[ m_e^* = 0.041m_0 \text{ (Nicholas 1979)}, \]
\[ m_{\text{HH}}^* = 0.465m_0 \text{ (Alavi 1980)}, \]

and

\[ m_e^* = 0.0789m_0 \text{ (Eaves 1971)}, \]
\[ m_{\text{HH}}^* = 0.56m_0 \text{ (Stradling 1975)}. \]

(iii) The decrease in the well width \( L_z \) with pressure will cause, ceteris paribus, the confinement energies to increase. The change in \( L_z \) may be estimated from the Murnaghan equation of state as described in chapter 5 (Equ.5.3). From the discussion in chapter 5 appropriate values for the bulk modulus and differential bulk modulus of InGaAs are \( B_0 = 766 \pm 40 \text{kbar} \) and \( B'_0 = 4.0 \pm 0.2 \). No attempt at this stage is made to account for the possible generation of uniaxial stresses.
Using the model as described above, the total confinement energy can be calculated as a function of $E_{\text{g}}^{\text{InGaAs}}$ for the various well widths, as shown by the dashed lines in Fig. 6.5. The calculated fits underestimate the experimental values of $dE_{\text{con}}/dE_{\text{g}}$ by approximately 50%.

6.3.5 Discussion

The major factor responsible for the poor fit to the experimental data must be an inaccurate value for the rate of change of the conduction-band discontinuity $dAE_c/dE_g$. This is deduced from the following argument. Fig. 6.1 clearly shows that $dE_{\text{con}}/dAE_c$ for all confined states must always be less than 1, i.e. the confinement energy will not decrease more rapidly than the offset. This implies that the magnitude of $dAE_c/dE_g$ must be greater than $|0.155|$ (the value of $dAE_c/dE_g$ for the highest transition energy), compared to a value of $|0.077|$ when a constant band-offset ratio is assumed. It is not surprising, therefore, that the calculated fits grossly underestimate the experimental data.

The need for a large magnitude of $dAE_c/dE_g$ is also emphasised by considering the effect of the pressure dependence of $m_e^*$, the only other parameter that could potentially have a significant effect on $dE_{\text{con}}/dE_g$. It is found that even doubling the experimental value of $d(\text{InGaAs})/dE_g$ will only increase $dE_{\text{con}}/dE_g$ in magnitude by approximately 3.5%. This test demonstrates the need for a pressure dependent offset ratio and gives an indication that the assumption of parabolic bands in the model is adequate for the accuracy of this calculation.

If the value of $dAE_c/dE_g$ is now considered as a variable parameter
it is found that good fits are produced, as shown by the solid lines in Fig.6.5, when it takes a value of -0.215. This is equivalent to assuming that the valence-band discontinuity remains constant with pressure, \( \frac{d\Delta E_v}{dp} = 0.0 \text{meV/kbar} \) and the conduction-band discontinuity decreases at approximately \( \frac{d\Delta E_c}{dp} = -2.3 \text{meV/kbar} \). This also implies that the band offset ratio \( Q_c : Q_v \) changes as a function of pressure, i.e. \( Q_c \) decreases at an initial rate of \(-0.0023 \text{kbar}^{-1}\), while \( Q_v \) increases at the same rate.

The solid lines in Fig.6.5 have the following gradients, -0.157, -0.080, -0.045 and -0.029 for the wells A, B, C and D respectively. Excellent agreement is reached with the 15 and 96Å wells and to a lesser extent with the 40 and 68Å wells. In terms of pressure coefficients, again assuming a linear pressure coefficient for InGaAs, these lines have the following coefficients 9.18, 10.03, 10.41 and 10.58meV/kbar for the wells A, B, C and D respectively. In these perhaps more amenable terms the maximum error between the theoretical and the experimental values is only 0.6meV/kbar for the 68Å well.

Fig.6.6 is a plot of the theoretical dependence of \( \frac{dE_{con}}{dE} \) against \( E_{con}(p = 0) \) assuming that \( \frac{d\Delta E_c}{dE} = -0.215 \), together with the experimental data. It can be seen from the figure that the line shape generated by the model is incapable of giving an exact fit to all the experimental data simultaneously. Although the exciton binding energy has been ignored in the model, the work of Lefebvre (1987) suggests that this a small contribution and incapable of improving the theoretical fit. A perhaps more plausible explanation is that the affect of strain has been ignored in the calculation. Strains could possibly arise from unintentionally lattice mismatch caused by fluctuations in the indium concentration during growth, exacerbated by the difference in the host
Fig. 6.6 A plot of the theoretical dependence of $\frac{dE_{\text{con}}}{dE}$ against $E_{\text{con}}$ at ambient pressure at 80K, assuming $\frac{dA_{c}}{dE_{g}} = -0.215$. Also shown are the experimental data.
materials' compressibilities. From the discussion in chapter 5 §5.3 small strains caused by the difference of 100kbars in the bulk moduli of InGaAs and InP could cause an apparent reduction in the pressure coefficient of the InGaAs of approximately 0.5meV/kbar (at 35kbars). Both the 40 and 68Å wells appear to have pressure coefficients that are reduced by a similar amount when compared to the theoretical values. It is not inconceivable therefore, that the discrepancy between the theoretical and experimental values may be accounted for by the presence of small strains within particular wells.

Bearing all these considerations in mind the variations in the band-edge discontinuities with the band-gap are:

\[
\frac{d\Delta E}{dE} = -0.215 \pm 0.05, \quad \frac{d\Delta E}{dE} = 0.0 \pm 0.05
\]

or in terms of pressure,

\[
\frac{d\Delta E}{dp} = -2.3 \pm 0.6\text{meV/kbar} \quad \frac{d\Delta E}{dp} = 0.0 \pm 0.6\text{meV/kbar}.
\]

It is possible, therefore, within the limits of the accuracy of the experiment, that the valence-band discontinuity could increase with pressure.

6.3.6 Comparison With Theory

The "model-solid" theory of Van de Walle (1987) is particularly suited to the problem of theoretically determining the pressure dependence of the band-edge discontinuities. For a given change in
volume, the energy of the average valence-band level in the host materials are shifted according to the values of their deformation potentials and bulk moduli. Since all these values are similar for both InP and InGaAs the rate of change in the valence-band discontinuity with pressure (as shown in appendix E) is very small i.e. \( \frac{d\Delta E}{dP} = +0.25\text{meV/kbar} \) assuming no difference in bulk moduli, or a value of +0.017meV/kbar for a bulk modulus of 650kbar for InGaAs. These values are in excellent agreement with the experimental value. Using the theoretical values of the conduction-band deformation potentials, \( \frac{d\Delta E_c}{dP} \) is estimated to be -1.3meV/kbar. Van de Walle and Martin suggest, however, that the conduction-band discontinuity is best determined from the calculated value of the valence-band discontinuity and experimental values of the host band-gaps. This implies ipso facto, a value of \( \frac{d\Delta E_c}{dP} = -2.65\text{meV/kbar} \) that will be in excellent agreement with experiment. The above calculations for the InGaAs/InP system is covered in detail in appendix E.

It should be noted that the Van de Walle and Martin theory is not unique in giving satisfactory agreement with the observed pressure dependence of the offset ratio. Using the Dielectric-Midgap-Point (DME) theory of Cardona (1987), \( \frac{d\Delta E_v}{dP} \) is estimated to be +0.56meV/kbar, which is also within the quoted experimental error.
6.4 Pressure Dependence Of The Valence-Band Discontinuity In GaAs/AlAs
And GaAs/Al$_{x}$Ga$_{1-x}$As Quantum-Well Structures

Type-II Method

6.4.1 Introduction

The type-II band alignment described in §6.2.2 and shown in Fig.6.7 was first experimentally observed by Wilson (1986) in Al$_{x}$Ga$_{1-x}$As/AlAs multiple quantum well structures using PL. Provided the aluminium concentration is greater than 0.26, the $\Gamma$-minima in the AlGaAs (which remains direct gap) lies above the X-minima in the AlAs. The characteristic signature from such a band alignment is a transition energy that is smaller than the lowest confined type-I transition from the well region.

There are three possible approaches to forming a type-II quantum well in the AlGaAs/GaAs system. As indicated in §6.2.2, the application of sufficient hydrostatic pressure will cause a transition from a type-I to a type-II band alignment, as will the application of an electric field (Meynadier 1988). A third approach is to allow the GaAs well to become sufficiently thin such that the first confined electron state will lie above the conduction-band minima of the AlGaAs barriers. For example, a GaAs/AlAs superlattice will be type-II when the thickness of the GaAs is less than 35Å, and the AlAs barriers greater than 15Å (Dawson 1987).

Although it is clear that a type-II configuration is possible, it is not immediately obvious why optical transitions should also occur. The band-structure and related optical matrix elements of GaAs/Al$_{x}$Ga$_{1-x}$As...
Fig. 6.7 A schematic band diagram of a GaAs/AlAs type-II superlattice, defining the notation used in the text.
type-II superlattices and quantum wells have been given considerable theoretical attention (Ting 1987, Gell 1987), both as a function of alloy composition and hydrostatic pressure. In a short period superlattice the X-like conduction-band state maps onto the reduced Brillouin zone centre due to zone folding effects, caused by the increased periodicity of the superlattice. This strictly occurs only when the period of the superlattice includes an even number of zincblende elementary cells. This implies that a X to \( \Gamma \) transition would be pseudodirect and would hence have a significant oscillator strength. From pseudopotential calculations Gell (1987) shows that finite oscillator strengths can also occur in multiple quantum wells (where the superlattice periodicity is not present) due to \( \Gamma - X \) mixing between \( \Gamma \) confined states and Bloch bulk X-like states in the barriers. It is possible, therefore, to observe momentum conserving zero-phonon type-II recombinations in both superlattice and quantum well systems.

The nature of this \( \Gamma - X \) mixing has been experimentally investigated by Skolnick (1989) using high-pressure PL whereby a type-I GaAs/AlAs superlattice is "forced" type-II by the pressure. From such measurements the authors were able to show that both the phonon and zero-phonon recombinations are mediated through the same intermediate \( \Gamma \) state.

6.4.2 Experimental

The GaAs/AlAs superlattice used in this experiment was grown by molecular-beam epitaxy at Philips Research Laboratories, Redhill, and consisted of 60 periods of GaAs and AlAs. The GaAs thickness was measured by PL and transmission electron microscopy to be 30 ± 2Å and the AlAs to
Fig. 6.8 The 8K luminescence spectrum of the GaAs/AlAs superlattice at atmospheric pressure.
be 68 ± 2Å (Dawson 1987). The 8K PL spectrum is shown in Fig. 6.8. The spectrum consists of five peaks, peak A being a relatively weak type-I recombination emission. Peak B has been assigned as a type-II emission involving the zero phonon recombination of localised excitons formed from the $X_2$ minimum in the AlAs and heavy holes in the GaAs. The remaining peaks, C, D, and E, are X or $\Gamma$-related phonon assisted emissions. Skolnick (1989) has assigned these as follows; C is the phonon satellite associated with the LA(X) energy of AlAs and GaAs; D and E lie in the range of the optic phonon branches of GaAs and AlAs respectively, although they cannot be unambiguously assigned to the $\Gamma$ or X points. The sample and a piece of bulk GaAs were mounted in the 0-8 kbar BeCu high-pressure cell, described in §3.3.1. The cell was inserted into the flow cryostat, however, changes in pressure were only made at room temperature to ensure hydrostatic conditions.

The PL was excited by 10-100 mW of focused 514 nm argon ion laser radiation (approximately $5 \times 10^2$ W cm$^{-2}$) and detected using the cooled germanium detector. For reasons already explained in §3.3.2.3 the pressure induced shifts in the spectra were recorded as a function of the bulk GaAs band-edge emission. Any pressure coefficients quoted therefore assume a direct-gap pressure coefficient of GaAs to be 10.7 meV/kbar (Wolford 1985).

6.4.3 Results

The PL peaks B, C, D, and E shift to lower energies by $-2.3 \pm 0.1$ meV/kbar with hydrostatic pressure, as shown in Figs 6.9 and 6.10. To within experimental error the separations of the peaks remain constant.
Fig. 6.9 Typical luminescence spectra of the GaAs/AlAs superlattice, together with bulk GaAs, at 8K and elevated pressures.
At these elevated pressures the type-I emission was no longer detectable. If it is assumed that the type-I recombination has a pressure coefficient similar to that of bulk GaAs, then the Γ and X-related are separating at approximately 13meV/kbar. At 2.6kbars the separation between the two states has increased from 100meV to 133meV. It is probable that the type-I recombination no longer occurs because of this increased separation, or at least the reduction in intensity places the type-I emission below the poorer signal-to-noise ratio of the pressure cell system.

Since the bulk moduli of the GaAs and AlAs are very similar (Van de Walle 1987) it is assumed that the measured pressure effects are caused only by hydrostatic pressure and that the effect of uniaxial stress is negligible. This assumption is further supported by a comparison of the hydrostatic pressure data with data from recent uniaxial stress measurements (Lefebvre 1989) performed on a similar GaAs/AlAs superlattice. This work showed that the relative spacings of the peaks and the intensity of peak B are very sensitive to the application of uniaxial stress.

The measured pressure coefficients \( \frac{dE_{pl}}{dp} \) of type-II emissions from Wolford (1986) and Venkateswaran (1986) for various AlGaAs/GaAs superlattices with different alloy compositions and structures, together with the measurement presented here, are plotted against the aluminium concentration, shown in Fig.11. The dependence is linear. The low scatter across the alloy range supports the assumption that uniaxial stresses are negligible since the data comes from different samples in different experiments.
Fig. 6.10 The luminescence peak positions of the superlattice plotted against the peak energy of the GaAs. The solid lines are least squares fits to the data.
6.4.4 Discussion

While the pressure measurements confirm the X-like nature of the PL spectra at low temperature, the pressure coefficient obtained is different from the reported value of $-1.3 \pm 0.1 \text{meV/kbar}$ (Wolford 1986) for the indirect gap in bulk GaAs. Since the measurements are made with respect to the bulk GaAs band-edge, this small difference is significant and well outside experimental error.

As was indicated in §6.2.2 an important feature of type-II systems is that the recombination energy depends directly on the valence-band discontinuity $\Delta E_v$. A schematic band-diagram of a GaAs/AlAs type-II superlattice is shown in Fig.6.7 from which it is clear that $\Delta E_v$ is given by,

$$\Delta E_v = E_{\Gamma}^{X,b} - E_{\Gamma}^{II} + \Delta_{1HH}^{\Gamma} + \Delta_{1e}^{X} - E_{EB}$$  \[6.5\]

where $\Delta_{1HH}^{\Gamma}$ and $\Delta_{1e}^{X}$ are the hole and electron confinement energies respectively, $E_{\Gamma}^{X,b}$ the indirect gap of the barrier material, $E_{EB}$ the exciton binding energy, and $E_{\Gamma}^{II}$ the energy of the observed type-II recombination emission. The effective masses of the electrons (Dawson 1987) ($m^* = 1.1m_0$) and holes (Miller 1984) are relatively large and hence the confinement energies are relatively small compared with the valence-band discontinuity, and tend to be canceled by the small exciton term. A good estimate for $\Delta E_v$ may be obtained from just the measured value of $E_{\Gamma}^{II}$ and knowledge of $E_{\Gamma}^{X,b}$ (Dawson 1987). Similarly, the pressure dependence of $\Delta E_v$ can be obtained from the pressure dependence of the observed emission and indirect band-gap of the barrier material i.e.
The value of $dE^*_{(Al\ Ga\ As)}/dp$ for $x = 1$ has not been experimentally determined, however, it is not unreasonable to assume that the pressure coefficient of the indirect-gap in $Al\ Ga\ As$ is independent of $x$ and equal to its value in bulk GaAs, i.e. $-1.3 \pm 0.1$ meV/kbar. This assumption is supported by one measurement on bulk $Al_{0.3}Ga_{0.7}$As which gave approximately $-1.0$ meV/kbar (Roach 1988). For the GaAs/AlAs superlattice therefore, $d\Delta E_v/dp = +1.1 \pm 0.2$ meV/kbar. Furthermore, as shown in Fig.6.11, $dE^\Gamma_{I}/dp$ is linear with alloy composition ($x$) and so the constant value of $dE^x_{I}/dp$ implies that the pressure coefficient $d\Delta E_v/dp$ is also linear in $x$, i.e.,

$$d\Delta E_v/dp = 1.1x \ (meV/kbar) \quad [6.7]$$

which is represented by line B in Fig.6.11.

Given the pressure dependence of the valence-band discontinuity, the conduction-band discontinuity pressure coefficient is given by,

$$d\Delta E_c/dp = (dE^\Gamma_{I}/dp - dE^\Gamma_{II}/dp) - d\Delta E_v/dp \quad [6.8]$$

where $E^\Gamma_{I}$ and $E^\Gamma_{II}$ are the direct band-gaps of the host barrier and well materials respectively. Since $dE^\Gamma_{I}/dp(x = 1)$ is not known, no conclusions for $AE_c$ can be given for the GaAs/AlAs superlattice. However, for the alloy $Al_{0.3}Ga_{0.7}$As, the direct-gap pressure coefficient has been measured to be $+9.9$ meV/kbar (Venkateswaran 1986). From this and Equ.6.7, a superlattice with this ternary material in the barriers will have a
value of $d\Delta E_v/dp$ of $-1.1 \pm 0.4$ meV/kbar. This can be expressed as the pressure dependence of the fractional valence and conduction-band offsets, i.e., $Q_v(x = 0.3)$ increases at $0.0013 \pm 0.0008$ kbar$^{-1}$, and $Q_c(x = 0.3)$ decreases at the same rate.

The change in $\Delta E_v$ with pressure is an order of magnitude smaller than the change in the direct-gap of either the well or barrier materials. Nevertheless, the change is significant in analysing the behaviour of quantum wells over the range of several tens of kbars. It has, for example, significant implications in modelling the behaviour of type-I emissions in GaAs/Al$_x$Ga$_{1-x}$As quantum wells. The trend of a decreasing pressure coefficient for confined states with increasing well width, (already discussed earlier in this chapter for the InGaAs/InP system), was first observed by Venkateswaran (1986). Both Lefebvre (1987) and Gell (1986) have attempted to model this trend with an assumption of
a pressure independent $Q_p$ and in the case of Gell et al with the fallacious assumption that both the pressure coefficients of the $\Gamma$ and $X$ band-gaps of $Al_{x}Ga_{1-x}As$ are the same as those of GaAs. Their fits, although indicating the correct trend caused by the increasing effective mass of the electrons, are qualitatively unsatisfactory.

This reduction in the conduction-band discontinuity with applied hydrostatic pressure is contrary to the experimental result of Piotrzkowski (1988). From measuring the two-dimensional electron concentration in a $Al_{x}Ga_{1-x}As/GaAs:Si$ heterojunction as a function of pressure, they concluded that the conduction-band discontinuity is pressure independent. Since this result does not appear to be supported by theory (discussed in the following section) it suggests more credence be given to the interpretation presented above.

6.4.5 Comparison With Theory

The pressure dependence of the valence-band discontinuity in the AlAs/GaAs superlattice is supported by the theoretical calculations of Van de Walle and Martin. Using the self-consistent model described briefly in §3.5.1.1, these authors predict a value of $d\Delta E/dp$ for a AlAs/GaAs superlattice of +0.8meV/kbar (Van de Walle 1987), in excellent agreement with the above interpretation of the experimental data. Using the "model-solid" theory (as shown in appendix E) a larger value of +1.8meV/kbar is predicted. Not surprisingly, the linear dependence on $x$ may be reproduced by the theory if the band-gaps and valence-band deformation potentials of the ternary materials are deduced by linear interpolation.
The DME theory of Cardona (1987) also predicts that the valence-band discontinuity will increase with pressure, i.e. $\frac{d\Delta E}{dp} = +1.6\text{meV/kbar}$ (Cardona 1988) despite the deformation potentials being of opposite sign. The problem in drawing any conclusions concerning the relative merits of the Van de Walle and Martin "model-solid" theory over the Cardona and Christensen DME formalism, from such a small experimental data set, is that in both cases the theoretical value of the measurable quantity requires taking the difference between two valence-band deformation potentials that are both small in magnitude. PL is a measurement of energy between two bands and hence the pressure experiments are incapable of determining the sign or value of the valence-band deformation potentials. By virtue of the same argument, however, the pressure dependence of Type-II emissions are an exceedingly sensitive measurement of the difference between deformation potentials, and as such, presents a significant challenge for band-offset calculations.

The success of the Van de Walle and Martin "model-solid" theory does tend, however, to suggest that the pressure behaviour of quantum wells is determined by the bulk deformation potentials, and hence supports the assumption that band-offsets are also determined by properties of the bulk host materials.
Chapter 7
CONCLUSION

During the course of this work two new pressure systems have been commissioned, the portable high pressure piston and cylinder system (Lambkin 1988a); and the miniature cryogenic diamond anvil cell (Dunstan 1988). The results presented in this thesis are an affirmation of their success, particularly the diamond anvil cell.

The hydrostatic pressure dependence of the band-edge PL of an epilayer of In$_{0.53}$Ga$_{0.47}$As on InP has been measured at both room and liquid nitrogen temperatures. The initial pressure coefficient of the band-gap is measured to be 10.95 ± 0.1meV/kbar. Notably, and contrary to some measurements on GaAs (Wolford 1985 and Gell 1987), the pressure dependence is found to be non-linear. The dependence of the band-gap on lattice constant is, however, found to be linear, described by a deformation potential of -8.25 ± 0.1eV for a bulk modulus of 760kbar. Significantly the pressure dependence is observed to be independent of temperature. Initial results that tended to suggest otherwise are probably due to the generation of uniaxial stresses caused by an inappropriate choice of hydrostatic pressure fluid (Cardona 1988). It is advised that for the generation of high hydrostatic pressures in a diamond anvil cell, liquid argon or helium should be used as the pressure transmitting fluid.

Rather than analyse the emissions from quantum well structures as a function of pressure, it is more accurate and indeed more meaningful, to analyse the emissions as a function of the band-gap of the well material. Pressure is therefore treated as a dummy variable in order to vary the
band-gaps of the host materials. Pressure is similarly treated in the calculations made to model the experimental data.

The PL from an InGaAs/InP multiple quantum well structure has been measured as function of pressure at 80K. It is observed that the confinement energies decrease with pressure, the effect being more marked in narrow wells. In order to explain these results in terms of the pressure behaviour of the barrier heights, effective masses and well widths, it is necessary to include a pressure dependence of the band-offset ratios. It is deduced that the valence-band discontinuity is virtually independent of pressure, while the conduction-band discontinuity decreases at approximately $2.3 \pm 0.6 \text{meV/kbar}$. The pressure dependence of type-II recombinations in a AlAs/GaAs superlattice has been measured in the piston-cylinder system at liquid helium temperatures. Such emissions are sensitive to the valence-band discontinuity, hence their measurement as a function of pressure give an estimate for the pressure dependence of the valence-band discontinuity of $+1.1 \pm 0.2 \text{meV/kbar}$. Analysis of reported data for quantum wells with the ternary alloy $\text{Al}_x\text{Ga}_{1-x}\text{As}$ in the barriers suggests that the pressure coefficient $\frac{d\Delta E_v}{dP}$, where $\Delta E_v$ is the valence-band discontinuity, is linearly dependent upon $x$, i.e. $d\Delta E_v/dP = 1.1x \text{(meV/kbar)}$.

It is found that the experimental results described above are adequately predicted by at least two theories, Cardona and Christensen’s DME theory (Cardona 1987) and Van de Walle and Martin’s Model-Solid theory (Van de Walle 1987). Although the experimental data does not prejudice any one theory over any other, agreement with such theories does tentatively suggest that the physics that governs band-edge discontinuities depends on the properties of the bulk host materials and
not, for example, on the detailed nature of the interface, such as the interface orientation or presence of impurities.

As was indicated in chapter 6 high pressure PL techniques are not sensitive to the sign or magnitude of the host materials' deformation potentials, they are however, sensitive to the difference between the two. This suggests therefore, that such techniques may be suitable to rigorously test the dependence of the band-edge discontinuities upon such factors as interface orientation, the presence of doping or strain.

An interesting extension to the high pressure PL measurements described in this work would be the successful development of high pressure photoluminescence excitation spectroscopy. Using such measurements it would be possible to study the behaviour of the higher lying confined levels in a quantum well, which are themselves intrinsically more sensitive to the band-edge discontinuities. It would be interesting, for example, to follow a high lying confined state in an InGaAs/InP quantum well as it becomes a virtual state as the conduction-band well decreases with pressure.

A major problem with such an experiment, apart from the difficulties associated with a back scattering configuration needed for the diamond anvil cell, is finding a suitable excitation source. The very low power density generated from the dispersed light of a tungsten lamp, together with the small size of the sample, make such a source impractical. A drawback with using a dye laser is that any given dye has a relatively short wavelength range. This problem was encountered when some preliminary PLE measurements were made at the Laboratoire de Physique du Solide et Energie Solaire, CNRS, Valbonne. A possible alternative source is the relatively new Ti-Sapphire laser, capable of producing a maximum
power of some 20\% of that of the pump beam, and tunable up to 1.2\mu m.
### TABLE A.I

<table>
<thead>
<tr>
<th>Material</th>
<th>GaAs</th>
<th>AlAs</th>
<th>InAs</th>
<th>InP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_T^e$ (eV) 300K</td>
<td>1.43 (a)</td>
<td>3.003 (h)</td>
<td>0.36 (m)</td>
<td>1.35 (p)</td>
</tr>
<tr>
<td>$E_T^e$ (eV) 4K</td>
<td>1.519 (b)</td>
<td>3.099 (h)</td>
<td>0.41 (m)</td>
<td>1.423 (p)</td>
</tr>
<tr>
<td>$E_T^x$ (eV) 300K</td>
<td>1.98 (c)</td>
<td>2.16 (j)</td>
<td>2.17 (u)</td>
<td>1.90 (s)</td>
</tr>
<tr>
<td>$E_T^x$ (eV) 4K</td>
<td>2.010 (d)</td>
<td>2.24 (j)</td>
<td>2.32 (t)</td>
<td></td>
</tr>
<tr>
<td>$E_T^l$ (eV) 300K</td>
<td>1.81 (c)</td>
<td></td>
<td></td>
<td>1.90 (s)</td>
</tr>
<tr>
<td>$E_T^l$ (eV) 4K</td>
<td>1.84 (d)</td>
<td>2.661 (k)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_0$ (eV)</td>
<td>0.341 (e)</td>
<td>0.29 (l)</td>
<td>0.38 (n)</td>
<td>0.11 (u)</td>
</tr>
<tr>
<td>$m^*$ ($m_0$)</td>
<td>0.0665 (f)</td>
<td>0.143 (k)</td>
<td>0.023 (m)</td>
<td>0.0789 (v)</td>
</tr>
<tr>
<td>$m^*$</td>
<td>0.067 (g)</td>
<td>0.22 (g)</td>
<td>0.023 (g)</td>
<td>0.089 (g)</td>
</tr>
<tr>
<td>$m_{LH}$ ($m_0$)</td>
<td>0.094 (f)</td>
<td>0.22 (l)</td>
<td>0.024 (m)</td>
<td>0.12 (p)</td>
</tr>
<tr>
<td>$m_{HH}$ ($m_0$)</td>
<td>0.34 (f)</td>
<td>0.4 (g)</td>
<td>0.34 (g)</td>
<td>0.56 (w)</td>
</tr>
<tr>
<td>$m_{s-c}$ ($m_0$)</td>
<td>0.15 (g)</td>
<td>0.24 (g)</td>
<td>0.14 (n)</td>
<td>0.21 (p)</td>
</tr>
</tbody>
</table>

Band structure parameters of some relevant binary semiconductors.
<table>
<thead>
<tr>
<th>Material</th>
<th>In$<em>{0.53}$Ga$</em>{0.47}$As</th>
<th>Al$<em>x$Ga$</em>{1-x}$As</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^\Gamma_T$ (eV) 300K</td>
<td>0.73 (x)</td>
<td>$1.425 + 1.35x$ (i)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.423 + 1.36x + 0.22x^2$ (h)</td>
</tr>
<tr>
<td>$E^\Gamma_T$ (eV) 4K</td>
<td></td>
<td>$1.514 + 1.45x$ (i)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.5194 + 1.36x + 0.22x^2$ (h)</td>
</tr>
<tr>
<td>$E^X_T$ (eV) 300K</td>
<td></td>
<td>$1.911 + 0.005x + 0.245x^2$ (bb)</td>
</tr>
<tr>
<td>$E^X_T$ (eV) 4K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^L_T$ (eV) 300K</td>
<td></td>
<td>$1.734 + 0.574x + 0.055x^2$ (bb)</td>
</tr>
<tr>
<td>$\Delta_0$ (eV)</td>
<td>0.36 (z)</td>
<td>0.341 - 0.05x (z)</td>
</tr>
<tr>
<td>$m_e^<em>$ ($m_0^</em>$)</td>
<td>0.041 (aa)</td>
<td>0.067 + 0.083x (z)</td>
</tr>
<tr>
<td>$m_{lh}^<em>$ ($m_0^</em>$)</td>
<td>0.086 (z)</td>
<td>0.074 + 0.076x (z)</td>
</tr>
<tr>
<td>$m_{hh}^<em>$ ($m_0^</em>$)</td>
<td>0.56 (y)</td>
<td>0.62 + 0.14x (z)</td>
</tr>
<tr>
<td>$m_{s-e}^<em>$ ($m_0^</em>$)</td>
<td>0.16 (z)</td>
<td>0.15 + 0.09x (z)</td>
</tr>
</tbody>
</table>

Band structure parameters for In$_{0.53}$Ga$_{0.47}$As and Al$_x$Ga$_{1-x}$As alloys.
References for tables A.I and A.II.

(a) Sell (1974)  
(b) Thurmond (1975)  
(c) Aspens (1976a)  
(d) Wolford (1985)  
(e) Aspens (1976b)  
(f) Miller (1984)  
(g) Lawnaetz (1971)  
(h) Bosio (1988)  
(i) Olegart (1987)  
(j) Lorentz (1970)  
(k) Gell (1987)  
(l) Braunstein (1962)  
(m) Adachi (1968)  
(n) Pidgeon (1967)  
(o) Matossi (1958)  
(p) Rochon (1975)  
(q) Turner (1964)  
(r) Varshni (1967)  
(s) Kobayashi (1981)  
(t) Onton (1972)  
(u) Cardona (1967)  
(v) Eaves (1971)  
(w) Stradling (1975)  
(x) Orelego (1982)  
(y) Alavi (1980)  
(z) Interpolated from values in Table A.I.(b)  
(aa) Nicholas (1979)  
(bb) Lee (1989)  

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APPENDIX B

Table B.I

<table>
<thead>
<tr>
<th></th>
<th>GaAs</th>
<th>AlAs</th>
<th>InAs</th>
<th>InP</th>
<th>InGaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$</td>
<td>5.65 (a)</td>
<td>5.65 (a)</td>
<td>6.08 (a)</td>
<td>5.87 (a)</td>
<td>5.87 (a)</td>
</tr>
<tr>
<td>$a_v$</td>
<td>1.16 (a)</td>
<td>2.47 (a)</td>
<td>1.00 (a)</td>
<td>1.27 (a)</td>
<td>1.075 (f)</td>
</tr>
<tr>
<td>$a_c^\Gamma$</td>
<td>-7.17 (a)</td>
<td>-5.64 (a)</td>
<td>-5.08 (a)</td>
<td>-5.04 (a)</td>
<td>-6.06 (f)</td>
</tr>
<tr>
<td></td>
<td>-9.3 (b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^{\Gamma-\Gamma}_c$</td>
<td>-8.33 (a)</td>
<td>-8.11 (a)</td>
<td>-6.08 (a)</td>
<td>-6.31 (a)</td>
<td>-7.14 (f)</td>
</tr>
<tr>
<td></td>
<td>-8.66 (c)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_c^\times$</td>
<td>4.09 (a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^{\Gamma-\times}_c$</td>
<td>1.99 (c)</td>
<td>1.62 (a)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_1$</td>
<td>10.8 (c)</td>
<td>-1.35</td>
<td>10.2 (g)</td>
<td>8.5 (i)</td>
<td>10.9 (i)</td>
</tr>
<tr>
<td>$E_2$</td>
<td>-14.0 (c)</td>
<td></td>
<td></td>
<td>-18.0 (i)</td>
<td>-30.0 (i)</td>
</tr>
<tr>
<td>$b$</td>
<td>-1.7 (d)</td>
<td>4.55 (d)</td>
<td>-1.8 (h)</td>
<td>-2.0 (j)</td>
<td></td>
</tr>
<tr>
<td>$d$</td>
<td>-4.55 (d)</td>
<td></td>
<td>3.6 (h)</td>
<td>-5.0 (j)</td>
<td></td>
</tr>
<tr>
<td>$B_0$</td>
<td>746.6 (e)</td>
<td>772.6 (h)</td>
<td>580.7 (n)</td>
<td>760 (k)</td>
<td>650.0 (m)</td>
</tr>
<tr>
<td>$B'_0$</td>
<td>4.67 (e)</td>
<td></td>
<td>4.0 (k)</td>
<td>4.0 (f)</td>
<td></td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>1187.7 (e)</td>
<td>1250.0 (h)</td>
<td>833.0 (o)</td>
<td>1022.0 (p)</td>
<td>1023.1 (m)</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>537.2 (e)</td>
<td>534.0 (h)</td>
<td>453.0 (o)</td>
<td>576.0 (p)</td>
<td>462.7 (m)</td>
</tr>
</tbody>
</table>

Deformation potentials, pressure coefficients and related parameters for relevant semiconductors.

The parameters have the following units:

- $a_0$ (Å);
- $a_v$, $a_c^\Gamma$, $E^{\Gamma-\Gamma}$, $a_c^\times$, $E^{\times-\Gamma}$, $b$, $d$ (eV);
$E_1$ (meV/kbar);
$E_2$ (1x10^{-3}meV/kbar);
$B_0$ (kbar);
$B_0$' (Dimensionless);
$C_{1,1}$ (kbar);
$C_{1,2}$ (kbar).

References for table B.I

(a) Van de Walle (1989)
(b) Nolte (1987)
(c) Gonl (1987)
(d) Chandrasekhar (1977)
(e) McSkimin (1967)
(f) Interpolated from values in the table.
(g) Tsay (1974)
(h) Wiley (1975)
(i) Trommer (1980)
(j) Camassel (1980)
(k) Menoni (1987)
(l) Lambkin (1988b)
(m) Interpolated from Keyes (1962) empirical scaling rule.
(n) Burenkov (1975)
(o) Gerlich (1963)
(p) Hickernell (1966)
Temperature dependence of GaAs, InP and InAs, fitting the following empirical relation,

\[ E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \]

The above values are taken from Varshni (1967).
Heterojunction valence-band lineups ($\Delta E_v$) for lattice matched (001) interfaces, obtained by the Self Consistent Interface Calculation (SCIC), and the "Model-Solid" approach. These values are taken from table II in reference Van de Walle (1987). Also shown for comparison are values determined by calculating the Dielectric Midgap Energy (DME), the method adopted by (Cardona 1987).

<table>
<thead>
<tr>
<th>Heterojunction</th>
<th>SCIC</th>
<th>Model-Solid</th>
<th>DME</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlAs/Ge</td>
<td>1.05 eV</td>
<td>1.19 eV</td>
<td>0.84 eV</td>
</tr>
<tr>
<td>GaAs/Ge</td>
<td>0.63</td>
<td>0.59</td>
<td>0.45</td>
</tr>
<tr>
<td>AlAs/GaAs</td>
<td>0.37</td>
<td>0.60</td>
<td>0.39</td>
</tr>
<tr>
<td>AlP/Si</td>
<td>1.03</td>
<td>1.16</td>
<td>0.91</td>
</tr>
<tr>
<td>GaP/Si</td>
<td>0.61</td>
<td>0.45</td>
<td>0.57</td>
</tr>
<tr>
<td>AlP/GaP</td>
<td>0.36</td>
<td>0.7</td>
<td>0.34</td>
</tr>
<tr>
<td>ZnSe/GaAs</td>
<td>1.59</td>
<td>1.48</td>
<td>1.13</td>
</tr>
<tr>
<td>ZnSe/Ge</td>
<td>2.17</td>
<td>2.07</td>
<td>1.57</td>
</tr>
<tr>
<td>InAs/GaSb</td>
<td>0.38</td>
<td>0.58</td>
<td>0.54</td>
</tr>
<tr>
<td>AlSb/GaSb</td>
<td>0.38</td>
<td>0.49</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Table D.IIa

<table>
<thead>
<tr>
<th>$\Delta E_v(A,B)$</th>
<th>$\Delta E_v(B,C)$</th>
<th>$\Delta E_v(A,B) + \Delta E_v(B,C)$</th>
<th>$\Delta E_v(A,C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.37 eV</td>
<td>0.63 eV</td>
<td>1.00 eV</td>
<td>1.05 eV</td>
</tr>
<tr>
<td>0.36</td>
<td>0.61</td>
<td>0.97</td>
<td>1.03</td>
</tr>
<tr>
<td>1.59</td>
<td>0.63</td>
<td>2.22</td>
<td>2.17</td>
</tr>
</tbody>
</table>

where A, B and C are the following semiconductors.

Table D.IIb

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlAs</td>
<td>GaAs</td>
<td>Ge</td>
</tr>
<tr>
<td>AlP</td>
<td>GaP</td>
<td>Si</td>
</tr>
<tr>
<td>ZnSe</td>
<td>GaAs</td>
<td>Ge</td>
</tr>
</tbody>
</table>

Examination of transitivity using Equ. 3.15a. The values in the table are from the self-consistent calculations of Van de Walle (1987) tabulated in Table D.I. The values in the last two columns of Table D.IIa are equal to within the numerical accuracy of the calculation, showing that transitivity is satisfied.
Band structure parameters used to determine the band line-ups in quantum well systems using Van de Walle's "model-solid" theory (Van de Walle 1987). The values in the above table are taken from Table II in reference Van de Walle (1989).
APPENDIX E

The determination of the pressure dependence of the valence-band discontinuity in a quantum well using the Van de Walle "model-solid" theory (Van de Walle 1989).

The valence-band discontinuity at ambient pressure for a heterojunction $A/B$ is given by,

$$\Delta E_{v}^{A,B} = (E_{v,av}^{B} + 1/3\Delta_{0}^{B}) - (E_{v,av}^{A} + 1/3\Delta_{0}^{A})$$

The valence-band discontinuity $\Delta E_{v}$ will be positive when the valence band in $B$ is higher in energy than the valence band in $A$. For a given fractional change in the volume $\Delta V/V_{0}$, the valence-band discontinuity now becomes, (assuming that the spin orbit splitting remains constant)

$$\Delta E_{v}^{A,B}(\Delta V/V_{0}) = (E_{v,av}^{B} + a_{v}^{B}\Delta V/V_{0} + 1/3\Delta_{0}^{B}) - (E_{v,av}^{A} + a_{v}^{A}\Delta V/V_{0} + 1/3\Delta_{0}^{A})$$

If it is assumed, at least at low pressure, that the equation of state is linear, i.e. $\Delta V/V_{0} = -1/B_{0} \times p$, then the change in the valence-band discontinuity as a function of pressure is simply given by,

$$\frac{d\Delta E_{v}^{A,B}}{dp} = a_{v}^{A} 1/B_{0}^{A} - a_{v}^{B} 1/B_{0}^{B}$$
AlAs/GaAs Quantum Well:
Using the values for the deformation potentials and bulk moduli given in table B.1, the value of $d\Delta E^A_B/d\rho$, where $A$ and $B$ are AlAs and GaAs respectively, is $+1.8\text{meV/kbar}$.

InP/InGaAs:
Using the InP value of the bulk modulus ($760\text{kbar}$) for the bulk modulus of InGaAs, and the values of the deformation potentials in table B.1, the value of $d\Delta E^A_B/d\rho$ is $+0.25\text{meV/kbar}$. If however, the interpolated value of $650\text{kbars}$ for the InGaAs bulk modulus is used instead, $d\Delta E^A_B/d\rho$ is $+0.017\text{meV/kbar}$.
References


