HIGH PRESSURE PHOTOLUMINESCENCE OF SEMICONDUCTOR STRUCTURES

BY

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ABSTRACT

High pressure photoluminescence has been used to study semiconductor structures. The measurements have been made in a miniature cryogenic diamond anvil cell (DAC). The results reported cover a wide range of materials and many different aspects are discussed. This in part serves to demonstrate the versatility and importance of the technique. New developments in DAC technology are fully described, in particular the introduction of electrical feedthroughs and the importance of the gasket geometry.

The technologically important material system GaAs/Al$_{1-x}$Ga$_x$As has been studied under hydrostatic pressure. Band offsets and their pressure dependencies are determined with spectroscopic accuracy and show interesting deviations from the expected behaviour. The effect of substrate orientation on the band offsets has also been investigated. The binding energy of excitons in GaAs/AlAs superlattices in the vicinity of Γ-X (Type I to Type II) crossover is measured for the first time.

The emerging new material systems containing strained layers have been studied, particularly In$_x$Ga$_{1-x}$As grown pseudomorphically on GaAs. In this system the pressure coefficients of the PL from strained quantum wells are found to have an unexpected dependence on the composition. Comparison with strained InAs/InP quantum wells suggests that this is in fact a strain effect rather than alloy. The band line-up in In$_x$Ga$_{1-x}$As/GaAs and In$_x$Ga$_{1-x}$As/Al$_y$Ga$_{1-y}$As quantum well structures is

(1)
determined from the crossing of $\Gamma$ and $X$ states.

A preliminary study of the dilute magnetic semiconductor $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ is made. High pressure magnetic field measurements on this material are expected to yield information on the nature of the exchange interactions. To this end $\text{CdTe}/\text{CdMnTe}$ superlattices have been characterised under hydrostatic pressure.

Films of $\text{a-Si:H}$ are studied under pressure. The intensity of the PL is found to be maintained up to $\sim 90$ kbar, in contrast with previous published data. The PL exhibits a small red shift of $1.9$ meV/kbar which is compared with the pressure coefficients of the PL from other amorphous materials.
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Chapter 1

INTRODUCTION

Recent years have seen the rapid development of the semiconductor growth techniques Metal Organic Chemical Vapour Deposition (MOCVD) and Molecular Beam Epitaxy (MBE). These techniques are capable of depositing ultra-thin layers of semiconductor and of growing coherent crystalline structures with alternating layers of different materials. Initially the materials had the same natural lattice constant but more recently pseudomorphic growth of materials with different lattice constants has been successfully demonstrated. Layers are sufficiently thin to show quantum effects of low dimensionality. The characterisation of these low dimensional structures (LDS) is currently of great interest. In this thesis LDS are studied by high pressure photoluminescence (PL). The application of hydrostatic pressure reduces the lattice constant but maintains the symmetry of the crystal; small changes in lattice constant may have large electronic effects. Hydrostatic pressure therefore provides a unique means by which to perturb the band structure and thereby obtain insight into the fundamental physics. High pressure studies have made a significant contribution to the understanding of bulk semiconductors and are now being found to be of considerable utility in revealing the nature of LDS. Of particular importance, for device engineering with LDS, is a knowledge of the nature of the interface between the constituent materials and in particular the
line-up of the band structures at the interface. High pressure PL has been shown to be a powerful technique for making accurate spectroscopic measurements of the valence-band offset in the GaAs/AlGaAs system (Wolford et al 1986, Venkateswaren et al 1986). The determination of the band offsets in LDS is the primary concern of this thesis. The technique of Wolford has been used to study the GaAs/AlGaAs system further and has been developed to study the strained system InGaAs/AlGaAs.

The thesis is arranged as follows; in chapter 2 the effect of hydrostatic pressure on bulk semiconductors is described, including the effect on the band structure and on the effective masses of the carriers. In particular, chemical trends are discussed. This serves as an introduction to chapter 3 where LDS under pressure are discussed. A method for modeling quantum confined states under pressure is described. In chapter 4 the diamond anvil cell (DAC) high pressure techniques used are described in detail. Much has been learnt about operation of the DAC and details are given here. Electrical feedthroughs for the DAC have been developed; the method is described.

Chapters 5-8 detail the experimental work carried out. Chapter 5 discusses the high pressure techniques for determining band offsets and considers GaAs/Al\(_x\)Ga\(_{1-x}\)As structures. The band offsets in this system are measured using the crossing of the confined \(\Gamma\) state in the well with the barrier \(X\) states to determine the valence band offset with spectroscopic accuracy. The pressure coefficient of quantum well emission is modeled to determine the pressure dependence of the band offsets. The effect of crystal orientation on the band offsets is also considered. Exciton binding energies are studied in GaAs/AlAs superlattices in the vicinity of \(\Gamma\)-\(X\) crossover or in other words as
pressure turns the structure from Type I to Type II. In chapter 6 strained layer InGaAs/GaAs structures are studied. The pressure dependence of the PL from these layers shows an unexpected dependence on composition or strain. The related strained system InAs/InP is studied for comparison and shows that the anomaly is strain rather than composition related. The pressure induced \( \Gamma - X \) crossovers in InGaAs/GaAs and InGaAs/AlGaAs quantum wells have been studied. This has allowed the nature of the crossovers to be identified as Type I (crossover with \( X \)-minima in well) for structures with GaAs barriers but Type II for structures with sufficiently high aluminium content barriers. Following this identification the band-offset ratio is accurately determined and the energy of the \( X_{x,y} \) minima in strained InGaAs measured as a function of composition.

In chapters 7 and 8 we move away from III-V semiconductors and look at two very different material systems. Chapter 7 details preliminary results from CdTe/CdMnTe superlattices. The constituent materials and the superlattices are characterised as a function of pressure. This will allow subsequent magneto-optical experiments to be analysed, where the exchange interaction will be studied as a function of pressure (mean Mn-Mn separation) and magnetic field. Chapter 8 reports on the behaviour of the PL from a-Si:H films under hydrostatic pressure. It is found that the films are sufficiently homogeneous to withstand pressures upto \( \sim 90 \) kbar without quenching of the PL intensity. The pressure coefficient of the PL is almost identical to that of c-Si, this is explained in terms of a density of states argument which is supported by the pressure coefficients of other amorphous materials. Finally, in chapter 9, some conclusions are drawn.
Chapter 2

BAND STRUCTURE AND THE PERTURBING INFLUENCE OF
HYDROSTATIC PRESSURE

2.1 Introduction.

In this chapter the basic properties of bulk semiconductor materials are briefly described in terms of their band structure. The perturbing influence of hydrostatic pressure on the band structure is then discussed. This serves as an introduction to the following chapter, where low-dimensional structures and their behaviour under pressure are considered, and an understanding of the bulk behaviour will be essential.

2.2 Band Structures of the Tetrahedrally Bonded Semiconductors.

2.2.1 Introduction.

The band structure, or E(k) relationship, of a semiconductor is determined by its constituent atoms and its crystalline structure. It is only the band structure along certain high symmetry directions, where minima in the conduction band occur, which usually interests us. A full discussion of band structures is beyond the scope of this thesis, however some basic concepts are essential to the understanding of the
behaviour of band structures under pressure.

2.2.2 Band Structure and the Tight Binding Approximation.

In the present context it is more convenient to consider the band structure in terms of the wavefunctions of the electrons of the constituent atoms, in contrast to the nearly-free electron model where the atomic character is disregarded. This method is known as the tight-binding approximation, or the linear combination of atomic orbitals (LCAO).

The tight-binding approximation deals with the case in which the overlap of the atomic wavefunctions is sufficient to require corrections to the picture of isolated atoms, but not so much as to render the atomic description completely irrelevant. In the tight-binding approximation the electron wavefunction is constructed from a linear combination of the atomic orbitals. The simple example of just two adjacent atoms is illustrated in fig. 2.1. The wavefunctions of the isolated atoms $\Psi_A$ and $\Psi_B$ form linear combinations of the form:

$$\Psi_1 = a\Psi_A + b\Psi_B$$

and

$$\Psi_2 = b\Psi_A - a\Psi_B \quad \text{(as described in Harrison (1980))} \quad [2.1]$$

giving rise to the bonding and anti-bonding states, whose energy is lowered and raised respectively from the free atom energy level, as shown. If $N$, rather than two atoms, are brought together then there will be $N$ distinct linear combinations and $N$ energy levels.
Fig. 2.1 The formation of bonding and anti-bonding combinations of atomic orbitals for two atoms, and the corresponding energy level diagram (after Harrison 1980).

Fig. 2.2 The figure shows the successive transformation of energy levels from the free atom atomic s and p levels on the left, to the sp hybrids and the bonding/antibonding orbitals and finally to the band states, (after Harrison 1980).
In the tetrahedrally bonded semiconductors the same principle applies. For example in crystalline Si each atom contributes four valence electrons, one s and three p electrons. Four orthogonal $sp^3$ hybrids may be picked which are constructed from linear combinations of atomic orbitals as follows

\[ h_1 > = \frac{1}{2} \left( |s> + |p_x> + |p_y> + |p_z> \right) \]
\[ h_2 > = \frac{1}{2} \left( |s> + |p_x> - |p_y> - |p_z> \right) \]
\[ h_3 > = \frac{1}{2} \left( |s> - |p_x> + |p_y> - |p_z> \right) \]
\[ h_4 > = \frac{1}{2} \left( |s> - |p_x> - |p_y> + |p_z> \right) \]  \[2.2\]

These hybrid states are highly directional orbitals, whose amplitude is predominantly along the direction to a specific nearest neighbour (i.e. along [111], [\bar{1}1\bar{1}], [\bar{1}1\bar{1}], [\bar{1}1\bar{1}] respectively). A hybrid interacts strongly with one hybrid on a neighbouring atom to form bonding and anti-bonding states. Interactions between all of the hybrids broaden these levels into bands, namely the conduction and valence bands. This is shown schematically in fig. 2.2.

In fig. 2.3 the broadening of the bands as a function of atomic separation is illustrated. This is a useful picture for high-pressure work where the only physical effect of the application of hydrostatic pressure is to change the atomic spacing. Moreover, the figure illustrates that small changes in the lattice constant can have large electronic effects.

Highly accurate calculations of band structures, along the high
Fig. 2.3 The energy bands of a tetrahedrally bonded semiconductor are illustrated as a function of atomic separation (after Kimball 1935).
symmetry directions, for many of the elemental and binary semiconductors have been carried out (see for example, Chelikowsky and Cohen 1976); also more recently calculations for the ternaries and quarternaries (see, for example, Aymerich 1982, Ling and Miller 1988, Stampfl et al 1989) have been performed. Experimental verification of these band structures is often only possible at extrema. Examples of some of these band structures are shown in fig. 2.4.

In the tight binding picture it is evident that it is the outer electrons and the symmetry of the lattice which predominantly determine the band structure of the material. Consequently one would expect all the tetrahedrally bonded semiconductors to have similar band structures and this is indeed seen to be the case (fig. 2.4). However, we would also expect some systematic trends with position in the periodic table, the periodic table is shown in appendix A. Returning for a moment to consider the two atom case, the energy gap between the bonding and anti-bonding levels \( E_g \) is given by

\[
E_g^2 = (E_1 - E_2)^2 + (2V)^2 \tag{2.3}
\]

(Harrison 1980) where \( E_1 \) and \( E_2 \) are the atomic orbital energies of atoms 1 and 2 respectively and \( V \) is a measure of the strength of the interaction between atoms 1 and 2. Thus there are two contributions to the average band gap of a semiconductor, a covalent term \( E_h^2 \propto (2V)^2 \) which is determined by the overlap of the atomic orbitals and an ionic term \( C^2 \propto (E_1 - E_2)^2 \) due to the difference in the atomic energy.

\[
E_g^2 \propto E_h^2 + C^2 \tag{2.4}
\]
Fig. 2.4 Calculated band structures for some common semiconductors. The calculations were performed using the Empirical Pseudopotential method (Chelikowsky and Cohen 1976). The figures illustrate the chemical trends discussed in the text.
We therefore expect to see increasing band gaps with increasing ionicity (e.g., Ge - GaAs - ZnSe) since $C \propto \Delta Z$ in a given row of the periodic table. The covalent contribution to $E_g$, $V$, is reduced with increasing bond length i.e., for elements lower down a column in the periodic table, so for example, we would expect and do observe decreasing average band-gaps going from, for example, Si to Ge to Sn ($E_g^2$ is proportional to $1/(\epsilon_r-1)$ and is therefore measurable). $E_g$ is only an average band gap and the minimum optical gap will not necessarily follow these trends.

All of the tetrahedrally bonded semiconductors have a valence band maximum at the Brillouin zone centre but the conduction band minima are not necessarily at $k=0$. An important trend is the drop of the $\Gamma$ minimum in the conduction band with respect to the $X$ and $L$ minima with increasing covalent radius and increasing ionicity. Thus in general we may say that the minimum gap between the conduction band and the valence band tends to be at $\Gamma$ (a direct gap semiconductor) but that at small covalent radius and low ionicity this need no longer be so. Technologically important examples of indirect semiconductors are Si, where the conduction band $X$ minima lie lowest and Ge where the $L$ minima lie lowest.

2.3 The Effect of Hydrostatic Pressure on the Band Structure.

2.3.1 Introduction.

The effect of hydrostatic pressure on a semiconductor is to reduce its lattice constant whilst maintaining its structural symmetry
(provided a structural phase transition is not induced). Pressures of the order 100 kbar will reduce the lattice constant by approximately 3%. Early studies (Paul and Warschaucer 1963, Keyes 1968, Pitt 1977, Zallen and Paul 1967 and Camphausen et al 1971) showed that the energy of levels could depend, often sensitively, on the pressure induced changes in the interatomic distance. The application of hydrostatic pressure has two principal effects on the electronic structure, the closer proximity of adjacent hybrid orbitals increases the interaction between them leading to an increase in the energy separation between the bonding and anti-bonding states and a broadening of the bands. The first effect will increase the direct gap while the second effect will tend to work in the opposite direction and decrease the gap.

Experimentally it is observed that the pressure coefficient of the energy difference between two states of a given symmetry in most of the semiconductors (Paul 1961) is very similar. However the pressure coefficients of states of different symmetry are very different (Camphausen et al 1971 and Paul 1958). A schematic of the band structure of a typical semiconductor is shown in fig. 2.5 with approximate figures for the pressure induced shifts, with respect to the top of the valence band, for each of the symmetry points. The figures are a good guide for all of the tetrahedrally bonded semiconductors with only small variations between materials which will be discussed later. These characteristic shifts have made high pressure a useful tool for identifying the nature of states. The ability of pressure to change the ordering, in energy, of the conduction band minima has made accurate determination of the energies of the higher minima possible. See for example, Wolford and Bradley (1985) who accurately determined the ambient pressure energy of the GaAs X minima or Adams et al (1977) and
Fig. 2.5 A schematic diagram of the band structure of the tetrahedrally bonded semiconductor showing the characteristic pressure coefficients of the high symmetry points with respect to the top of the valence band.
Vinson et al (1976) who first correctly determined the ordering of the conduction band valleys in GaAs to be \( \Gamma, L, X \). High pressure has also been used extensively to study the nature of impurity states; see for example Thomas and Hopfield (1966), Wolford et al (1982), and Wolford et al (1984). Hydrostatic pressure is currently proving to be a powerful tool in the elucidation of the band structure of microstructures, which is the primary concern of this thesis and will be discussed in detail in the following chapters.

2.3.2 Trends in Pressure Coefficients.

Although there is remarkable similarity between the pressure coefficients of chemically different materials there are trends to be noted. As in the case of the average band gap, systematic trends within the periodic table (appendix A), with ionicity and covalency are expected. Since hydrostatic pressure changes the bond lengths it will affect the covalency but have little affect on the ionicity. For an infinitely deep well of width \( d \), the energy levels are proportional to \( 1/d^2 \), therefore covalent interactions will scale approximately as \( (\text{bond length})^2 \). Thus we expect materials such as Si which are purely covalently bonded to have a higher average pressure coefficient than materials such as CdTe which are relatively ionic. A semiempirical theory of the fractional ionic or covalent character of a bond in a dielectric crystal has been developed with considerable success (Phillips, 1973). The fractional covalent character of the bonds in some binary crystals given by this theory are given in table 2.1 and correlated with the direct gap pressure coefficient (as a rough estimate of \( dE_0/dP \)) of these materials showing clearly the predicted trend.
Table 2.1 The fractional covalent character (Phillips 1973) of the bonds for some binary materials are compared with the direct-gap pressure coefficient of the material. The table shows the trend to lower pressure coefficients with increasing ionicity.

<table>
<thead>
<tr>
<th>Material</th>
<th>Fraction Covalent character</th>
<th>Direct-gap pressure coefficient (meV/kbar)</th>
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<tr>
<td>Si</td>
<td>1</td>
<td>- (a)</td>
</tr>
<tr>
<td>GaSb</td>
<td>0.74</td>
<td>14.5 (b)</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.69</td>
<td>10.7 (c)</td>
</tr>
<tr>
<td>InAs</td>
<td>0.64</td>
<td>10.2 (d)</td>
</tr>
<tr>
<td>InP</td>
<td>0.58</td>
<td>8.5 (e)</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.39</td>
<td>10.4 (f)</td>
</tr>
<tr>
<td>CdTe</td>
<td>0.33</td>
<td>6.5 (g)</td>
</tr>
</tbody>
</table>

(a) N/A
(b) Noak and Holzapfel (1978)
(c) Wolford and Bradley (1985)
(d) Tsay et al (1974)
(e) Muller et al (1980)
(f) Strossner et al (1987)
(g) Dunstan et al (1988)
It is in fact more physically meaningful to compare deformation potentials than pressure coefficients, since the bond lengths do not vary linearly with pressure, and it is of course the variation of band gap with lattice constant (or wavefunction overlap) rather than with pressure which is the fundamental property. Hydrostatic deformation potentials are discussed in the next section. The change in lattice constant may be derived from the applied pressure by a suitable equation of state. A commonly used equation of state is the Murnaghan equation (Murnaghan 1944)

\[-\left( \frac{\Delta a}{a_0} \right)_T = 1 - \left[ \left( \frac{B'_0}{B_0} \right) P + 1 \right]^{-1/(3B'_0)} \]  

[2.5]

where $B_0$ and $B'_0$ are the bulk modulus and its derivative with respect to pressure respectively. From equation 2.5 it is clear that the lattice constant does not change linearly with pressure. Experimentally the direct-gap coefficients of most semiconductors are observed to increase non-linearly with pressure and are well described by a quadratic expression of the form

\[ E_g(P) = E_g(0) + \alpha P + \beta P^2 \]  

[2.6]

where $\alpha$ and $\beta$ are constants, $\alpha$ is approximately 10 meV/kbar as already discussed (section 2.3) and $\beta$ is negative and of order $10^{-2}$ meV/kbar$^2$. 
2.4 Hydrostatic Deformation Potentials.

A deformation potential may be defined as the energy shift of a level per unit strain. The perturbed energy after hydrostatic dilation is given by

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

[2.7]

where 'a' is the hydrostatic band-edge deformation potential and the dilation, \( \Delta \), is given by

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

[2.8]

where \( \varepsilon_{11} \) are the cartesian strain tensors.

It is in fact difficult to measure an absolute shift in energy experimentally. We therefore define a band-gap deformation potential, which gives the relative change in energy between two electronic states \( E_c \) and \( E_v \), with band-edge deformation potentials \( a_c \) and \( a_v \) respectively. The energy difference is given by

\[ E_0(\Delta) = E_c(\Delta) - E_v(\Delta) \]

\[ = E_0 + (a_c - a_v) \frac{\Delta V}{V_0} \]

\[ = E_0 + \Xi \frac{\Delta V}{V_0} \]  

[2.9]

where \( \Xi \) is the band-gap deformation potential.

Thus the band-gap deformation potential may be determined from the
pressure coefficient, provided that the bulk modulus of the material is known:

\[
\frac{dE}{dP} = -\frac{\Xi}{B_0} \tag{2.10}
\]

Band-gap deformation potentials may be determined from, for example, the pressure coefficient of band edge luminescence. The band-edge deformation potentials can not of course be obtained from this data alone, only their difference.

2.5 The Pressure Dependence of the Effective Mass.

2.5.1 Introduction.

We have seen how the band extrema are affected by pressure but we shall also require to know the influence of pressure on the curvature of these bands, at least close to the extrema, since this describes the effective mass of the carriers. This is particularly important for modeling confined states and confined states under pressure. The k.p \texttrade; method, developed by Kane \texttrademark; has been used successfully for this purpose.

2.5.2. k.p Theory.

The k.p theory is primarily a method to explore the band structure in the vicinity of a given point, k\textsubscript{0}, in great detail. In our case we are concerned with the curvature of the bands at the conduction band minima and at the valence band maximum.
The k.p method is based on the k.p representation which can be used to provide complete band structures throughout the Brillouin zone. Some such calculations have been made; see, for example, Cardona and Pollak (1966).

The essentials of the k.p method are outlined in this section. Starting from the Schrödinger equation

\[ H\Psi(r) = E\Psi(r) \]  \hspace{1cm} \text{[2.11]}

and using the one-electron Hamiltonian,

\[ H = \frac{p^2}{2m} + V(r) \]  \hspace{1cm} \text{[2.12]}

where \( V(r) \) is the potential energy and \( \frac{p^2}{2m} \) is the kinetic energy given by,

\[ \frac{p^2}{2m} = \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \]  \hspace{1cm} \text{[2.13]}

we consider the Bloch functions of the form

\[ \Psi_k(r) = \sum_{L \in K} \exp\{i(k+K).r\} = \exp(ik.r) \ u_k(r) \]  \hspace{1cm} \text{[2.14]}

where \( K \) is a reciprocal lattice vector and \( u_k(r) \) is a function which has the periodicity of the lattice ie

\[ u_k(r+a) = u_k(r) \]  \hspace{1cm} \text{[2.15]}

where \( a \) is any vector of the Bravais lattice.
Substitution of equation 2.14 into the Schrödinger equation 2.11 yields an equation for the periodic function $u_{nk}(r)$ associated with the $n^{th}$ energy level with wavevector $k$, $E_n(k)$; namely

$$\left[ \frac{\hat{p}^2}{2m} + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p} + \frac{\hbar^2 k^2}{2m} + V(r) \right] u_{nk}(r) = E_n(k) u_{nk}(r)$$ \hspace{1cm} [2.16]

where $\mathbf{p}$ is the momentum operator $-i\hbar \nabla$.

If we now consider any point $k=k_0$, equation 2.16 has a complete set of eigenfunctions $u_{nk_0}(r)$; this set of states is called the $k.p$ representation. Rewriting the Schrödinger equation of equation 2.16 in terms of a new Hamiltonian $H_{k_0}$ gives

$$\left[ H_{k_0} + \frac{\hbar}{m} (k-k_0) \cdot \mathbf{p} + \frac{\hbar^2}{2m} (k^2-k_0^2) \right] u_{nk}(r) = E_n(k) u_{nk}(r)$$ \hspace{1cm} [2.17]

and writing $u_{nk}(r)$ in terms of $u_{nk_0}(r)$

$$u_{nk}(r) = \sum_{n'} c_{n'n} u_{nk_0}(r)$$ \hspace{1cm} [2.18]

multiplying equation 2.17 on the left by $u_{nk_0}(r)$ and integrating over the unit cell we obtain

$$\sum_{n'} \left\{ \left[ E_n(k_0) + \frac{\hbar}{2m} (k_0^2-k_0'^2) \right] \delta_{nn'} + \frac{\hbar}{m} (k-k_0) \cdot \mathbf{p}_{nn'} \right\} c_{n'n'} = E_n(k) c_{nn}$$ \hspace{1cm} [2.19]
where \( p_{nm} = \int_{\text{unit cell}}^{} u^*_{n k_0}(r) p u_{n' k_0}(r) dr \) \[ 2.20 \]

Equations 2.18, 2.19 and 2.20 define the \( k_0 p \) representation, at this point the representation is exact and, as already mentioned, may be used to calculate \( k \) at any point in the Brillouin zone. In practice the \( k p \) method is usually used for exploring the band structure in the vicinity of a given point \( k_0 \), either by perturbation theory or by diagonalization of a small number of bands whose eigenvalues lie close together.

2.5.3 \( k p \) Perturbation.

A perturbation method may be applied to \( k \) values in the vicinity of a general point \( k_0 \). For example equation 2.16 may be rewritten as

\[
\left[ \frac{-p^2}{2m} + V(r) + \frac{\hbar}{m} k.p \right] u_{nk}(r) = \lambda_{nk} u_{nk}(r) \tag{2.21}
\]

where

\[
\lambda_{nk} = E_n(k) - \frac{\hbar^2 k^2}{2m}
\]

If \( k=0 \) then equation 2.21 becomes

\[
\left[ \frac{-p^2}{2m} + V(r) \right] u_{nk}(r) = \lambda_{00} u_{00}(r) = E_n(0) u_{00}(r) \tag{2.22}
\]

Comparing equations 2.21 and 2.22 we may consider the term \( \frac{\hbar}{m} (k.p) \) as a small perturbation. 

ie

\[
H u_{nk}(r) = (H_0 + H') u_{nk}(r) = \lambda_{nk} u_{nk}(r) \tag{2.23}
\]

21
where $H_0$ is the unperturbed Hamiltonian ($\left[ (-\hbar^2/2m) \nabla^2 + V(r) \right]$) and $H'$ is the perturbation ($\left( \hbar/m \right) k.p$). In fact the problem can be treated more generally, where any point $k_0$ can be considered, the perturbation then becomes

$$\frac{\hbar}{m} (k-k_0).p$$  \hfill [2.24]

In the case of a single band treated by perturbation theory, we obtain

$$E_n(k) = E_n(k_0) + \frac{\hbar}{m} (k-k_0).p + \frac{\hbar^2}{2m} (k^2-k_0^2)$$

$$+ \frac{\hbar^2}{m^2} \sum_{n'} \frac{|(k-k_0).p_{nn'}|^2}{E_n(k_0) - E_n'(k_0)} \hfill [2.25]$$

Thus the energy for the nth band is given in terms of the known energies at $k=k_0$ and is valid provided that the value of $k$ is not too far from $k_0$. The $k.p$ method is therefore a semiempirical technique in the sense that measured values of such parameters as energy gaps and effective mass at $k_0$ must be incorporated in the theory if it is to yield quantitative results.

2.5.4 Three Band Approximation.

For a realistic description of the bands in a semiconductor the coupling between the bands must be considered and the degeneracies at the top of the valence band taken account of. In most cases accurate solutions may be obtained by considering only a few bands close in energy. A full treatment of the band structure at the $\Gamma$ point, $k=0$,
considering the lower-lying states has been given by Kane (1966) and leads to the following secular equation

\[(E - E_c) (E - E_v) (E - E_v + \Delta) - k^2 P^2 (E - E_v + \frac{2}{3} \Delta) = 0 \]

where \( P^2 \) is the momentum matrix element describing the coupling \( \Gamma_{1c} \) and \( \Gamma_{5v} \). Solutions to this equation have been given by Long (1968) and are as follows:

\( \Gamma_{1c} \) Conduction band

\[ E_c (k) = E_o + \frac{\hbar^2 k^2}{2 m} \quad ; \quad \frac{m^*}{m} - 1 = \frac{E_p}{E_o} \left[ \frac{2}{3} \frac{E_o}{E_v} + \frac{1}{E_o + \Delta} \right] \]

[2.27]

Heavy-hole valence band

\[ E_{hh} (k) = \frac{\hbar^2 k^2}{2 m_{hh}} \quad ; \quad \frac{m}{m_{hh}} = 1 \]

[2.28]

Light-hole valence band

\[ E_{lh} (k) = -\frac{\hbar^2 k^2}{2 m_{lh}} \quad ; \quad \frac{m}{m_{lh}} = (2E_p/3E_o) - 1 \]

[2.29]

Spin-orbit split-off valence band

\[ E_{so} (k) = -\Delta - \frac{\hbar^2 k^2}{2 m_{so}} \quad ; \quad \frac{m}{m_{so}} = \frac{E_p}{3(E_o + \Delta)} - 1 \]

[2.30]
where \( E_p = \frac{2mP^2}{h^2} \) and energies are given with respect to the top of the valence band.

Thus k.p perturbation theory gives an accessible means of predicting the effective mass dependence in the bands as a function of the band gap, with \( m^* \) varying approximately proportionally with band gap. This is a particularly useful form for predicting the effective mass change under pressure.

The pressure dependence of the effective mass has been measured experimentally by Adams et al (1986) for some materials. They give the following values for \( \frac{dm^*}{dE_0} \): for GaAs, 0.045 \( m_e \) eV\(^{-1} \) and for InP, 0.049 \( m_e \) eV\(^{-1} \), which agree well with k.p theory.

2.6 Temperature Dependence of the Band Gap.

Experimentally it is observed that the band gaps of semiconductors increase with decreasing temperature. Two effects are responsible for this. Firstly the reduction in temperature causes the lattice to contract, or in other words the atoms vibrate about equilibrium positions which are now closer together. This is analogous to an applied hydrostatic pressure which we have already seen increases the direct band gap. This effect accounts for much less than half of the increase; the remainder is accounted for by the electron-phonon interaction. At high temperatures, phonons cause regions of compression and rarefaction in the lattice, leading to regions of high and low pressure, or high and low band-gap. The low (or negative) pressure regions therefore lead to a reduction in the band edge energy. Conversely as the temperature is
reduced towards 0 K and the phonon density decreases the band gap increases.

The temperature dependence of the band gap of many semiconductors has been fitted by the following empirical relation (Varshni 1967)

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}$$  \[2.31\]

where $E_g(0)$ is the value of the band gap at 0K and $\alpha$ and $\beta$ are constants given by Varshni for some common materials.
Chapter 3

LOW DIMENSIONAL STRUCTURES UNDER PRESSURE

3.1 Introduction.

Much of the experimental work reported in this thesis is concerned with the energy of quantum-confined states in low-dimensional structures (LDS) and their behaviour under pressure. In this chapter, following an introduction to the basic ideas of heterojunction band offsets, quantum wells and superlattices, a model for determining the energy and wavefunctions of quantum-confined states, the 'envelope function approximation', is described. A method, used throughout this thesis for modeling confined states under pressure is then discussed.

Significant effects on the band structure brought about by confinement and by built-in strain (in lattice mismatched systems) are also described.

Finally the photoluminescence process in bulk and LDS structures is discussed.

3.2 Heterojunctions.

3.2.1 Introduction.

A heterojunction is formed at the interface between two different
semitconductor. Where the two materials have different band gaps a band-edge discontinuity is inevitable. In fig. 3.1 the band gaps of some important semiconductors are plotted against their lattice constant. Materials of equal or similar lattice constant and ionicity may generally be epitaxially grown to form a heterojunction in a single crystal. The most technologically important example is probably GaAs/AlGaAs. In this system, we see from the figure that the lattice constant hardly varies across the alloy range, so that AlGaAs of any composition may be grown epitaxially on GaAs. Other important examples include InGaAs lattice-matched to InP and CdTe which is roughly lattice-matched to InSb. In recent years it has been shown to be possible to grow layers where there is significant mismatch in the lattice constant (Kirby et al. 1989, Eng et al. 1989) provided the layers are below a critical thickness (Matthews and Blakslee 1974, 1975 and 1976, People and Bean 1985, Dixon and Goodhew 1990). This causes strain in one or both of the layers, depending on the substrate, relaxation and relative thicknesses of the layers. Examples of such systems which have been grown are InGaAs/GaAs, InGaAs/InP and CdTe/ZnTe. Strained layers are discussed more fully later in this chapter (section 3.10).

3.2.2 Heterojunction Band Line-up.

The alignment of the band structures of two bulk materials as they come together to form a heterojunction is the subject of intensive research, both theoretical and experimental (for a review see, Capasso and Margaritondo 1987). Three broad classes of alignment are recognised (Esaki 1986), these are illustrated in fig. 3.2 and the meaning of the terms conduction-band and valence-band offset (ΔEc and ΔEv) indicated. A
Fig. 3.1 The room temperature band gaps of semiconductors are plotted against their lattice constant. Materials of similar lattice constant and ionicity may generally be grown to form a heterojunction (after Sze 1981).

Fig. 3.2 A schematic diagram of the three types of quantum well alignment, Type I, Type II and Type III. The figure illustrates the meaning of the terms conduction-band and valence-band offset (after Esaki 1986).
Type I structure is one in which the lowest state for electrons and holes is in the same material, and a Type II structure is one in which the lowest energy states for the carriers are in the different materials, so that the electrons and holes are spatially separated. The third class, Type III structures, involve a heterojunction with a semimetal. These definitions are used rather loosely and consequently, sometimes ambiguously. For example a structure may be Type I for direct (in k space) transitions but Type II for indirect transitions or Type I for electron to heavy-hole transitions but Type II for electron to light-hole transitions. The exact meaning of these terms will be made clear where they are used.

3.3 Quantum Wells and Superlattices.

3.3.1 Introduction.

Optical investigation of heterojunctions nearly always involves, in fact, the study of optical transitions in quantum wells (two back to back heterojunctions) or superlattices since this leads to carrier confinement and observable transitions. Consequently, to study the heterojunctions in this way, it is important to understand the effect of the quantum-well potential on the band structure and to be able to model successfully the confinement energies in the well or superlattice.

Figure 3.3(a) shows a schematic of the band structure of a Type I quantum well with a narrow band gap material, A, surrounded by a wider band gap material, B. This could be for example GaAs (A) and AlGaAs (B). The solid line represents the Fermi extrema in the conduction or valence
Fig. 3.3 (a) A schematic diagram of a Type I quantum well constructed from a narrow band-gap material (A) and a wider band-gap material (B). The energy and wavefunction of some of the confined states are illustrated. (b) The construction of the total energy of an electron in the conduction band of a quantum well structure; $z$ is the direction perpendicular to the interface. Also shown is the two dimensional density of states $\rho(E)$ (the broken line indicates the form of $\rho$ for a bulk crystal).
bands. The wavefunctions and energies of the confined states are indicated. Note that in the valence band there are two sets of energies associated with the light and heavy hole bands.

The energy levels in the growth direction are quantised by the confinement potential. In the perpendicular direction, in the plane of the well, there is no such effect and the dispersion curves remain that of the bulk material so that, for example, the total energy of an electron in the first confined state may be written as

\[ E + \frac{\hbar^2 k_{\|}^2}{2 m_1} \]

[3.1]

where \( k_{\|} \) is the wave vector in the plane of the well and \( E_1 \) is the confinement energy found by solving the one-dimensional Schrödinger equation, written with respect to the bulk conduction band edge. This is illustrated in fig. 3.3(b). This combination of discrete energy levels and free electron-like dispersion curves leads to a step density of states, also illustrated in fig. 3.3(b), each step originating from the onset of a sub-band. The three-dimensional density of states goes as \( E^{1/2} \) and is illustrated by the dashed line. An important consequence of this is that the density of states at the bottom of the conduction band in a quantum well system is finite whereas in a bulk material it is zero. This has important, beneficial consequences for some devices such as lasers.

Figure 3.4(a) is a schematic diagram of the band structure of a superlattice, this is the limiting case of many adjacent quantum wells.
Fig. 3.4 A schematic diagram of a superlattice showing, on the left, the overlap of the carrier wavefunctions from adjacent wells. On the right the broadening of the lowest confined state of a single quantum well into a band is shown. \( \pi/d \) is the Brillouin zone boundary of the superlattice.
with thin barriers so that the tails of the wavefunctions associated with the states confined in the wells penetrate the barriers and overlap. An electron in such a system is free to travel from one well to the next. The wavefunction overlap leads to a broadening of the discrete energy levels into bands. Figure 3.4(b) illustrates the broadening of the lowest localised state of the single well into a band. $\pi/d$ is the Brillouin zone boundary of the superlattice if $d$ is the superlattice period.

Considering the case of an infinitely deep quantum well (a particle in a box) the confined states in the well are given by solutions of the Schrödinger equation:

$$\left( -\frac{\hbar^2}{2m} \right) \frac{d^2\Psi}{dz^2} = E \Psi$$  \[3.2\]

with the boundary condition that $\Psi$ must be zero at the interface, required by continuity of $\Psi$ since $\Psi$ is zero in the confining layers. This leads to solutions of the form:

$$\Psi_n = A \sin \left( \frac{n \pi z}{L_z} \right)$$  \[3.3\]

with energy

$$E_n = \frac{\hbar^2}{2m} \left( \frac{n \pi}{L_z} \right)^2 \quad n = 1, 2, 3, \ldots$$  \[3.4\]

This result is modified for real quantum well structures by such things as the finite potential step and the different effective masses in the constituent materials. In this thesis the confined states of real
quantum-wells are modeled using the envelope function formalism following the approach of Bastard (1981).

3.3.2 The Envelope Function Approximation.

The essential point of the model is to neglect any phenomena which are rapidly varying at the atomic scale and to focus on the effective Hamiltonian which governs the slowly varying envelope function. The superlattice features are then incorporated into a Kane-type analysis.

Considering the general case of a superlattice made of materials A and B (a quantum well being the limiting case of a superlattice with thick barriers), the wavefunction in each material takes the form

\[ \Psi_{A,B}^{A,B}(r) = \sum_j F_j^{A,B}(r)u_j^{A,B}(r). \]  

[3.5]

where \( F_j(r) \) are the slowly varying envelope functions and \( u_j \) is the periodic part of the Bloch functions at \( k=0 \).

The band structures of the host materials in the vicinity of \( k=0 \) are described by the Kane model (Kane 1957). It is assumed that the interface potential is strongly localised and that the interface potential does not mix but only shifts the states. The envelope functions \( F_1 \) and \( F_2 \) are assumed continuous at the interface. Two further boundary conditions are obtained by Bastard (1981) and require the expressions of eqn. 3.6 be to continuous at the interface, where \( V_p \) is the shift of the P levels at the \( \Gamma \) point when going from material A to material B in the z direction (axis of superlattice).

\[ \frac{1}{E_A + \lambda - V_p(z)} \left( -\sqrt{2} \frac{d}{dz} \frac{F_1-\frac{1}{2}(k+F_2)}{d} \right) \]
and

$$\frac{1}{E_A + \lambda - V_p(z)} \left( -\sqrt{2} \frac{d F_2 + (ik-F_1)}{dz} \right)$$

$$k = \sqrt{2} \frac{(k \pm ik_y)}{\sqrt{2}}$$ \[3.6\]

where $\lambda$ is the energy and $E_A$ is the energy gap in material A.

The long range behaviour of $F_{1,2}$ is governed by the Bloch theorem

$$F_{1,2}(z+md) = \exp(iqmd) F_{1,2}(z)$$ \[3.7\]

where $d$ is the period of the superlattice and $q$ is the superlattice wave vector along the superlattice axis.

Bastard gives results for the application to GaAs/AlGaAs superlattices which hold for similar systems:

$$\frac{1}{E_A} \frac{d F_{1,2}^{(A)}}{dz} = \frac{1}{E_B} \frac{d F_{1,2}^{(B)}}{dz}$$ \[3.8\]

In the Kane model $E \propto m$ so eqn. 3.8 may be written as

$$\frac{1}{m_A} \frac{d F_{1,2}^{(A)}}{dz} = \frac{1}{m_B} \frac{d F_{1,2}^{(B)}}{dz}$$ \[3.9\]

This is slightly different from the more usually used boundary condition, $dF/dz$ continuous, but may in fact be shown to be essential to conserve probability current if there is an effective mass jump at the interface. Or, in other words, to ensure that the eigenstates are stationary. Taking $F$ to be linear combinations of plane waves with
opposite wave vectors inside each material and using the boundary conditions of equations 3.7 and 3.9 the dispersion relations \( \lambda(q) \) are given by:

\[
\cos(qd) = \cos(k_A l_A) \cos(k_B l_B) - \frac{1}{2} \left[ x + \frac{1}{x} \right] \sin(k_A l_A) \sin(k_B l_B)
\]

\[
k_A^2 = \frac{2 m_A}{h^2} \lambda - k_{\perp}^2
\]

\[
k_B^2 = \frac{2 m_B}{h^2} \left( \lambda - V_s \right) - k_{\perp}^2
\]

\[x = \frac{m_A k_B}{m_B k_A} \tag{3.10}\]

where \( k_{\perp} \) is the magnitude of the in-plane wavevector and where \( \lambda < V_s \), \( k_B \) is imaginary. We substitute \( ik_B = \mu \) and equation 3.10 then becomes

\[
\cos(qd) = \cos(k_A l_A) \cosh(\mu l_B) - \frac{1}{2} \left( \frac{\mu^2 - k_A^2}{k_A \mu} \right) \sin(k_A l_A) \sinh(\mu l_B) \tag{3.11}
\]

This differs from the more usual Kronig-Penney result, since \( x \) explicitly depends on \( m_A \) and \( m_B \).

We see that the detail of the rapidly varying part of the wavefunction is lost from the result and only the 'envelope' behaviour is left.
3.3.3 Non-Parabolicity.

Coupling between the bands causes them to deviate from the parabolic form. Non-parabolicity in the lowest-lying conduction band is caused primarily by coupling with the light-hole band. This is particularly important for quantum wells where the states may be made up from high $k$ values.

Nelson et al (1987) introduced the concept of an energy-dependent effective mass to describe the dispersion relation in a non-parabolic band. Hence the dispersion relation in the well is written as

$$E = \frac{\hbar^2 k_w^2}{2 m_w^*(E)}$$  \[3.12\]

and in the barrier as

$$E = V - \frac{\hbar^2 k_b^2}{2 m_b^*(E)}$$  \[3.13\]

Non-parabolicity may thus be introduced into the envelope function approximation in a very natural way via an energy-dependent effective mass in the Kane model.

3.3.4 The Effect of Quantum Confinement on the Valence Band Structure.

In the bulk material the valence band is fourfold degenerate at the \( \Gamma_b \) point, \( J = \frac{3}{2} \), so that \( J_z = \pm \frac{3}{2} \) and \( J_z = \pm \frac{1}{2} \) (the spin-orbit split-off valence band, \( J = \frac{1}{2} \), is at lower energy in the bulk). The effect of quantum confinement is to lift the fourfold degeneracy of these levels.
Fig. 3.5 The effect of quantum confinement on the valence band structure. The effect is illustrated in a simplified manner by means of successive perturbation. (a) the four bands are degenerate at $k=0$. (b) the degeneracy of the $J = \pm \frac{3}{2}$ and $J = \pm \frac{1}{2}$ bands is lifted by the quantum well potential. (c) the dispersion in the $y$ direction is illustrated. (d) $k.p$ interactions lead to anti-crossing effects.
The dimensional perturbation splits the levels and $k.p$ perturbations lead to dispersion. These two effects should be treated on an equal footing for an accurate solution of the valence band states by diagonalisation of a perturbative Hamiltonian:

$$H = H_{k.p} + H_{QW}$$  \[3.14\]

However a qualitative picture may be obtained by considering the quantum well potential as a first perturbation, this lifts the degeneracy between $J_z = \pm \frac{3}{2}$ and $J_z = \pm \frac{1}{2}$ since they correspond to different masses. $k.p$ interactions affect the dispersion of the bands in the plane of the well. This is illustrated in fig. 3.5. Figure 3.5(a) shows the four degenerate bands at $k=0$, in fig. 3.5(b) the degeneracy is lifted by the quantum-well potential so that the $J_z = \pm \frac{3}{2}$ 'heavy hole' bands lie higher in energy than the $J_z = \pm \frac{1}{2}$ 'light hole' bands. $k.p$ interactions then lead to dispersion in the plane of the well, Figure 3.5(c) shows the dispersion in the $y$ direction, the $J_z = \pm \frac{3}{2}$ bands now have a light mass and the $J_z = \pm \frac{1}{2}$ bands have a heavy mass. Anti-crossing effects result from higher order $k.p$ interactions and lead to the dispersion illustrated in fig. 3.5(d).

3.4 The Effect of Hydrostatic Pressure on Quantum-Confined States.

In chapter 2 the behaviour of the bulk states under pressure was described in detail. In a quantum well the states have the same characteristic; however, to successfully model the confined states under pressure five important effects must be considered.
The dominant effect is usually the difference in the pressure coefficients of the well and barrier materials, which means that the confining potential is changing with pressure. For example, in GaAs quantum wells with AlGaAs barriers the pressure coefficient of AlGaAs is less than that of GaAs. If it is assumed that the band offset ratio remains constant with pressure then both electrons and holes see a reduced potential barrier leading to a lower confinement energy. Hence, from this argument alone, the pressure coefficients of the confined states would be expected to be less than that of bulk GaAs.

A second important effect is the variation of the band offset ratio with pressure. In the GaAs/AlGaAs example the total offset is decreasing with pressure but the conduction band and valence band offsets could be changing in either direction. Exactly how the division of the offset varies with pressure will make a significant difference to the pressure coefficient of the PL energy observed. This is primarily because the electron confinement energy is sensitive to changes in the conduction-band offset (the heavy-hole is much less sensitive to changes in the valence-band offset because of its greater effective mass). In fact it has been shown (Lambkin et al 1989) that in the GaAs/AlGaAs system the valence-band offset increases at 1.1x meV/kbar, rather than decreasing as would be the case for constant offset ratio. This means that the offset in the conduction band must fall even faster causing the pressure coefficient again to drop well below that of bulk GaAs, this is discussed further in chapter 5. An even more striking example of this effect is seen in InGaAs/InP quantum wells (Lambkin et al 1988) where the conduction band offset is decreasing at 2.3 meV/kbar and for wells of 15Å the pressure coefficient of the PL is only 9.2 meV/kbar compared with 10.95meV/kbar for bulk InGaAs.
Both of these first two effects depend on well width and confinement energy. The effects are largest in narrow wells, where the confined state is close to the top of the well.

The k.p interaction is used to describe the mass of confined carriers under pressure in the same way as the bulk states. Since the Kane model describes the mass as a function of the energy gap we may easily rewrite (eqs. 2.27 - 2.29) in terms of the pressure. We use the following expressions for the masses in the well:

\[
\frac{m_e(P)}{m_e(0)} = \frac{E_g + E_g' P}{E_g} \frac{E_g + E_g' P + \Delta}{E_g + \Delta} \frac{2\Delta + 3E_g}{2\Delta + 3(E_g + E_g P)}
\]

\[3.15\]

\[
\frac{m_{hh}(P)}{m_{hh}(0)} = 1
\]

\[3.16\]

\[
\frac{m_{lh}(P)}{m_{lh}(0)} = \frac{E_g + E_g' P}{E_g}
\]

\[3.17\]

where \( E_g' = \frac{dE_g}{dP} \)

Similar equations describe the masses in the barrier material. These equations assume that the bands are parabolic so that the masses are independent of the confinement energy and depend only on pressure. In the case of non-parabolic bands the appropriate masses will depend on the degree of confinement (or well width). However, the effective mass enters into the solution of the Schrodinger equation for the confinement energy, therefore solutions to the envelope function calculation for non
parabolic bands must be made iteratively.

The masses increase with pressure in both the well and the barrier; the effect of increased mass in the well is to reduce the confinement energy. However, since the wavefunctions must be matched at the interface and the masses will be increasing at different rates in the two materials, the real space extension of the wavefunction will be modified and this may lead to a tendency for the levels in the well to rise depending on the material system considered.

The physical effect of the well width diminishing under pressure need scarcely be taken into account. This effect will make the confined states rise in the well. The pressure-dependent well width may be written as:

\[ L_z(P) = L_z(0) [ 1 - (S_{11} + 2S_{12}) P ] \]  \[3.18\]

where \( S_{11} \) and \( S_{12} \) are the elastic constants for the well material. Experimental values are known for most of the common materials and the correction to the confinement energy is very small.

The final effect which must be considered when measuring the quantum well band gap by photoluminescence and by many other techniques is the binding energy of the exciton. This reduces the observed energy gap and changes with well width, effective masses and dielectric constant. Lefebvre et al (1986) gives an expression for the variation of the 3D Rydberg with pressure

\[ R^*_z(P) = R^*_z(0) \exp(2kP) \mu(P)/\mu(0) \]  \[3.19\]
where $k$ describes the change in dielectric constant with pressure $k = (1/e)(dc/dP)$. The pressure dependence of the exciton binding energy in quantum well systems and especially in the vicinity of $\Gamma$-$X$ crossover is a subject of research in this thesis and is discussed more fully in chapter 5.

This model has been used extensively to analyse some of the experimental data presented in chapters 5-7, where a fuller discussion of the implications of some of these effects will be found.

### 3.5 Strained Layer Structures.

#### 3.5.1 Introduction.

The growth of lattice-matched and strained epitaxial layers has been briefly discussed in section 3.2.1. Chapter 6 of this thesis is concerned solely with the behaviour of strained layers and so an introduction to their properties is given here. A review of this area has been given by O’Reilly (1989).

#### 3.5.2 Growth and Critical Thickness.

In recent years it has been shown possible to grow high-quality crystalline epilayers which are not lattice matched to their substrate (section 3.2.1). The epitaxial layer will have the in plane lattice constant of the substrate material and all of the strain will be contained within the layer. This is illustrated in fig. 3.6 where the layer is seen to be under biaxial compression. High-quality growth can
Fig. 3.6 A strained layer under biaxial compression is illustrated with the example of InGaAs grown pseudomorphically on GaAs. The strained material has a natural lattice constant greater than that of the substrate. The layer takes the in-plane lattice constant of the substrate and relaxes along the growth direction.

Fig. 3.7 The stored energy per unit area ($E_{st}$) and the energy per unit area required to relieve the strain by dislocations ($E_{dis}$) are compared (after O'Reilly 1989).
be maintained only up to a certain critical thickness after which dislocations will form and relieve the strain. The thin non-equilibrium layers can exist only because the dislocation energy required to relieve the strain is greater than the strain energy itself. This is illustrated in fig 3.7. The cost of strain per unit area is given by

\[
E_{st} = 2G \left( \frac{1 + \sigma}{1 - \sigma} \right) \varepsilon_{||}^2 h
\]  

[3.20]

where \( h \) is the layer thickness, \( G \) is the shear modulus and \( \sigma \) is Poisson's ratio so that for a given system the strain energy increases linearly with layer thickness. In contrast the cost of a dislocation is roughly constant, being high for thin layers and only increasing slowly (logarithmically) with \( h \). The exact form of the expression for the energy of dislocation is arguable. At some critical thickness the energy of dislocation is less than that of the strain energy and hence it is energetically favourable to relieve the strain via dislocations.

The problem of critical thickness was first studied by Frank and Van der Merwe (1949) and more recently there have been a number of further calculations (People 1986, Matthews and Blakeslee 1975 and 1976, People and Bean 1985 and Voisin 1988). Attempts to determine the critical thicknesses for the strained system \( \text{In}_{x} \text{Ga}_{1-x} \text{As/GaAs} \) have been carried out by Andersson et al (1987) and Dixon et al (1990).

A superlattice stack may be grown to any thickness if both the well and barrier are mismatched to the substrate, alternate layers being in tension and compression.
3.5.3 Strain.

The strains in the pseudomorphic layer can be determined, knowing that the in-plane lattice constant is equal to that of the substrate.

\[ a_\parallel = a_{\text{sub}} \quad [3.21] \]

Then the in-plane strain is given by;

\[ \varepsilon_\parallel = \varepsilon_{xx} = \varepsilon_{yy} = \frac{a_\parallel}{a} - 1 \quad [3.22] \]

where \( a \) is the equilibrium lattice constant of the constrained layer. In response to the biaxial stress the layer relaxes along the growth direction, so that

\[ a_\perp = a \left[ 1 - D \left( \frac{a_\parallel}{a} - 1 \right) \right] \quad [3.23] \]

where the constant \( D \) depends on the elastic constants and the interface orientation. For growth along the (001) direction \( D = 2(c_{12}/c_{11}) \).

The strain along the growth direction is given by

\[ \varepsilon_\perp = \varepsilon_{zz} = \frac{a_\perp}{a} - 1 \quad [3.24] \]

and

\[ \varepsilon_\perp = -\frac{2\sigma}{1-\sigma} \varepsilon_\parallel \quad [3.25] \]

For tetrahedral semiconductors \( \sigma \) is approximately 1/3 so that \( \varepsilon_\perp \approx -\varepsilon_\parallel \).

The total strain may be resolved into two parts, a hydrostatic
It is convenient to analyse strained layers in terms of the hydrostatic component and the axial component of the strain, since the hydrostatic and axial deformation potentials have been measured for many materials. The hydrostatic component of the strain will act to increase the direct band gap (section 2.3) whilst the axial strain produces splitting of degenerate levels.

For bulk semiconductors it is usual to consider only relative shifts in the conduction and valence bands. However in the strained-layer case we will always be concerned with a heterojunction since the layers cannot exist in bulk form. The strain effects on the band structure are therefore calculated in terms of absolute energy positions and shifts, this has the advantage that the band line up in the system is immediately evident. This is done by implementation of the Model-Solid theory of Van de Walle and Martin (Van De Walle and Martin 1986 and 1987, Van de Walle 1989). In the model an absolute energy is calculated for the average valence band position, \( E_{v,av} \); all shifts can then be referenced to this. When the material is strained \( E_{v,av} \) will be
shifted due to the hydrostatic component, the shift is given by

\[ \Delta E_{v,av} = a_v \frac{\Delta V}{V} \]  

[3.28]

where \( \Delta V/V \) is given by equation 3.26 and \( a_v \) is the hydrostatic deformation potential for the valence band. Similarly

\[ \Delta E_c = a_c \frac{\Delta V}{V} \]  

[3.29]

Even in the case of no strain and no quantum confinement the valence band is split due to spin-orbit effects. The position of the topmost valence band, \( \Gamma_{8'} \), is then given by

\[ E_v = E_{v,av} + \frac{\Delta}{3} \]  

[3.30]

where \( \Delta \) is the spin-orbit splitting. Where strain is present, shear components of the strain lead to additional splittings, which interact with the spin-orbit splittings to produce the final valence-band positions. The strain splittings are proportional to the magnitude of the strain, at least for small strains. For strain along [001] the following shifts are calculated with respect to the average \( E_{v,av} \):

\[ \Delta E_{v,2} = \frac{1}{3} \Delta - \frac{1}{2} \delta E_{001} \]  

[3.31]

\[ \Delta E_{v,1} = -\frac{1}{6} \Delta + \frac{1}{4} \delta E_{001} + \frac{1}{2} \left[ \Delta^2 + \Delta \delta E_{001} + \frac{9}{4} \left( \delta E_{001} \right)^2 \right]^{1/2} \]  

[3.32]
Fig. 3.8 The figure illustrates how the hydrostatic and biaxial component of the strain shift and split the important energy levels. The approximate magnitude of these effects is indicated in terms of the relevant band gap deformation potentials. Figure (a) shows the unstrained case. (b) illustrates the effect of the hydrostatic component of the strain on the energy levels. (c) shows the effect of the uniaxial component of the strain. The figure illustrates the case for biaxial compression.
\[
\Delta E_{v,3} = - \frac{1}{6} \Delta + \frac{1}{4} \delta E_{001} - \frac{1}{2} \left[ \Delta^2 + \Delta \delta E_{001} + \frac{9}{4} (\delta E_{001})^2 \right]^{1/2}
\]

[3.33]

where \( \delta E_{001} = 2b(e_{zz} - e_{xx}) \) and \( b \) is the shear deformation potential which is negative for all the materials considered here. The valence-band labels \( E_{v,1}, E_{v,2}, E_{v,3} \) refer to the \( \Gamma_8 \) light and heavy hole and the \( \Gamma_7 \) spin split-off band respectively.

A similar procedure may be used for the conduction bands. The conduction band is non-degenerate at the \( \Gamma \) point and is therefore subject only to hydrostatic shifts which are given in eqn. 3.29 where \( a_c \) is the band edge deformation potential at the \( \Gamma \) point. For the satellite valleys, the \( X \) and \( L \) minima, there are six and four equivalent minima respectively (because there are six and four \(<001>\) and \(<111>\) directions). These minima coincide in energy in the bulk but are split by strain in the appropriate direction: \((001)\) strain splits the \( X \) in \( X_{x,y} \) and \( X_{z} \), while leaving \( L \) degenerate. The opposite applies to a \((111)\) strain. The absolute energy of the levels in the bulk may be taken as the average, or centre of gravity, energy, which is shifted by the hydrostatic component of the strain as for the \( \Gamma \) point but with the appropriate deformation potential. The splitting of the bands may then be expressed with respect to this average. For uniaxial strain along [001] the splitting of the \( X \) minima may be written as:

\[
\Delta E^0_{c} = \frac{2}{3} \varepsilon_{u} \varepsilon_{zz} (e_{zz} - e_{xx})
\]

[3.34]

\[
\Delta E^{100,010}_{c} = - \frac{1}{3} \varepsilon_{u} \varepsilon_{zz} (e_{zz} - e_{xx})
\]

[3.35]

Thus the strain splitting of energy levels and their absolute
Fig. 3.9 A schematic representation of the strained layer band structure is shown. (a) the band structure of the unstrained material. (b) A layer under biaxial compression, the band gap is increased by the effect of strain and the light-hole like nature of the highest lying valence band in the plane of the well is illustrated. (c) a layer under biaxial tension. (after O'Reilly 1989).
energy in the model solid can be calculated from deformation potentials, most of which are known for the important materials. Figure 3.8 shows a schematic of the effect of strain on the energy levels, indicating the magnitude of the effects.

Besides splitting the valence bands at $\Gamma$, axial strain also introduces anisotropy. This follows from the lifting of the degeneracy and can be understood via $k.p$ theory; this has been discussed by Pikus et al (1959 and 1974), Blacha et al (1984) and O'Reilly (1986). Figure 3.9 illustrates this anisotropy. Fig. 3.9(a) shows the unstrained band structure, with the heavy and light hole bands degenerate at $\Gamma$. The spin split-off band lies $\Delta$ lower in energy. In fig. 3.9(b) the material is under biaxial compression and the mean band gap increases due to the hydrostatic component. The valence bands split and become anisotropic so that the highest band is heavy hole like along the strain axis ($k_\parallel$) and light hole like along $k_\perp$. Figure 3.9(c) shows the situation for a material under biaxial tension. The mean band gap is reduced by the negative hydrostatic pressure. The valence bands are again split with the highest lying valence band being light hole like along the strain axis and heavy in the plane perpendicular to it.

3.6 Photoluminescence.

3.6.1 Introduction.

Photoluminescence has been used throughout the work reported in this thesis as a tool for studying the behaviour of the electronic structure of semiconductor samples under pressure. It is therefore
important to say a few words about the process itself, since an understanding of this is important for the interpretation of the experimental results.

3.6.2 PL in Bulk Semiconductors.

Broadly speaking PL means the emission of photons brought about by optical excitation. Since the time taken for radiative recombination ($\approx 10^{-9}$s) is much greater than that of thermal relaxation ($\approx 10^{-12}$s), emission will normally be from the lowest energy states. Thus in general PL from semiconductors gives information about the lowest band gap. Figure 3.10 shows a schematic of the PL process. An electron and hole pair is created by a high energy photon, usually of a much higher energy than the semiconductor band gap. The carriers quickly thermalise to the band edge by emission of phonons. Any or all of the six phonons may take part in this process, however the LO phonon is generally favoured since it produces the greatest change in potential per unit displacement (Pankove 1971). Once at the band edge the electron-hole pair may recombine radiatively. The finite width of the resulting PL peak represents, on the high energy side, the temperature of the sample, and on the low energy side the density of states.

Phonons are obviously required to conserve momentum in indirect transitions and may also play a role in direct transitions. Figure 3.11(a) illustrates the conserving momentum role of phonons in an indirect transition and fig. 3.11(b) illustrates the role of optical phonons (an optical phonon being possible at $k=0$) in a direct transition showing a one and two phonon process. These transitions are less likely but are possible and give replication of the zero-phonon spectrum at
Fig. 3.10 A schematic representation of the process of photoluminescence. The carriers are excited by an incoming photon of greater energy than the band gap. The carriers subsequently recombine, emitting a photon whose energy is approximately equal to the band gap.

Fig. 3.11 Figure (a) illustrates excitonic recombination. A direct transition is shown on the left and on the right the role of phonons in indirect transitions is illustrated. $E_x$ represents the exciton binding energy. Figure (b) illustrates the role of phonons in direct transitions, showing a one and a two phonon process.
lower energy by amounts equal to an integer multiple of the phonon energy. These peaks are known as phonon replicas.

PL is not always observed between the two band edges; indeed, usually it is not. In high-quality undoped samples the emission is usually excitonic in nature, so that the PL energy is reduced by the exciton binding energy. The excitons may be free or bound to an impurity. PL may also be observed between conduction band and acceptor levels, valence band and donor levels or transitions to deep levels, to name just a few.

The intensity of the luminescence is dictated by the transition probability and also by other competing recombination paths. The transition probability between two states \( k \) and \( n \) may be expressed in terms of the optical matrix element.

\[
M \sim \frac{1}{m} \langle k|p|n \rangle = i \omega_{kn} \langle k|r|n \rangle \sim \int u_k^* \nabla u_n \, dr^3 \tag{3.36}
\]

The observed PL intensity is not necessarily a measure of how much the transition is allowed, often it is a question of alternatives. If there is no other competing non-radiative recombination path then all that prohibition does is lengthen the radiative lifetime.

The shape and width of a PL spectrum can be a useful indicator of the type of transition and the quality of the material. As far as pressure coefficients are concerned, it is found (Wolford and Bradley 1986, Leroux et al 1985) that shallow levels (eg acceptors and donors
where the binding is coulombic) follow the band edge almost exactly, whilst deep levels (by which is meant a localised level with a short range binding potential which may not necessarily be deep in the band gap) will have their own distinct pressure coefficient.

3.6.3 PL in Quantum Wells.

In a quantum well, PL is observed between the lowest confined electron state and the highest confined hole state. The emission is usually excitonic in nature, the exciton binding energy being greatly increased by the quantum confinement (see, for example, Dawson et al 1986) up to a theoretical maximum of four times the bulk binding energy (Ralph 1965). Since PL gives information on the lowest energy states, if fluctuations in the well width exist, the PL will tend to be emitted from the lowest energy (widest) part of the well. If the fluctuations in the well width are larger than the diameter of the exciton the PL peak will not be broadened but will be 'Stokes' shifted to a lower energy than would be expected for the average width of the quantum well. If the fluctuations are smaller than the exciton diameter then the exciton is sampling several randomly chosen well widths and this will lead to a broadening of the PL spectrum. Fluctuations in well width are quite intrinsic to epitaxial growth since monolayer steps are unavoidable. Peaks can be shown to be Stokes-shifted if they are not coincident with the corresponding peak in the absorption spectrum.

As in the bulk case the optical transitions are governed by selection rules. The optical matrix element for the quantum well transitions may be written as
\[ M \sim \langle k | z | n \rangle \]

\[ = \int_{QW} f_k^*(z) \left[ u_k^*(z) z u_n(z) \right] f_n(z) \, dz \]  \hspace{1cm} [3.37]

where \( f(z) \) are the slowly varying envelope functions and \( u(z) \) are the bulk wavefunctions which vary rapidly on the atomic scale. Integrating over one unit cell where \( f(z) \) is approximately constant the integral becomes:

\[ f_k^* f_n \int_{QW} u_k^*(z) z u_n(z) \, dz \]  \hspace{1cm} [3.38]

what remains inside the integral is the bulk optical matrix element; if this is zero in the bulk then the quantum well transition will also be forbidden. If however the bulk transition is allowed with probability \( P \) then

\[ M \sim P \int f_k^*(z) f_n(z) \, dz \]  \hspace{1cm} [3.39]

so that if the bulk transition is allowed then the quantum well transition is also allowed provided there is a finite overlap between the envelope functions. The quantum-well potentials are symmetric under real-space reflections and so the envelope functions are characterized by their even or odd character under reflection. Thus from eqn. 3.39 it is clear that transitions will be allowed if two states have the same parity. In his original paper, Dingle (1974) stated that in the infinite well approximation, due to the orthogonality of the envelope wave functions only transitions between confined conduction and valence band
states of the same quantum number $n$ were allowed ($\Delta n = 0$ rule). Whilst these are the strongest features in the absorption and excitation spectra, in finite quantum wells the envelope functions are not exactly orthogonal, which leads to the observation of transitions with different $n_{eg}$ electron $n = 1$ to heavy hole $n = 3$. Even breaking of the parity selection rule has been observed (Miller et al 1981, Pinczuk et al 1984). In real quantum wells asymmetries such as the interfaces, alloy fluctuations and compositional variations may break the selection rules and forbidden transitions may be observed (Lambkin et al 1990a, Miller et al 1981, Xu et al 1983) even in photoluminescence.

When two states are brought close together, for example by quantum confinement or by the application of hydrostatic pressure the states will tend to be mixed and this again can lead to a breaking of the selection rules for pure states. For example in the vicinity of a pressure-induced $\Gamma$-$X$ crossover PL with $X$-like characteristics is observed; however, the $X$ emission would be almost prohibited ($M$ very small) on the grounds of $k$ conservation. As the $\Gamma$ and $X$ levels are driven past each other (in fact they anticross) and the mixing is reduced the PL intensity rapidly diminishes. In Type II superlattices, the real-space overlap of the wavefunctions can be very small. For example, in GaAs/AlGaAs superlattices where a crossover between the $\Gamma$ minimum in the well and the barrier $X$ minima may be induced by pressure, the electrons are confined in one material and the holes in another. The optical transition is strongly prohibited by the small wavefunction overlap both real and $k$-space. However, the transition is observed (see, for example, Wolford et al 1986).
4.1 Introduction

In this chapter the experimental apparatus and techniques used and developed in the course of this work will be described. Photoluminescence of semiconductors is a reasonably standard technique and will therefore be described only briefly with the emphasis on special high pressure requirements. Conversely, high pressure photoluminescence is a more specialised technique. In this work high pressures are generated using a diamond anvil cell (DAC). The design and operation of the DAC will be described in detail. Much experience and new understanding of the behaviour of the cell has been obtained during the course of this work. Following the success of optical measurements in a DAC, a method for incorporating electrical feedthroughs into the cell has been developed and is described here.

4.2 Photoluminescence

The experimental set up is shown in Fig. 4.1. The arrangement is similar to a standard PL setup with the essential difference being that the PL must be collected in the back scattering geometry (as illustrated) because of the design of the diamond anvil cell. The setup basically consists of an excitation source, some focusing and collecting
Fig. 4.1 A schematic diagram of the layout of the PL system.

Fig. 4.2 The spectral response of the detectors used. The curves are not to scale. The Si detector has a maximum quantum efficiency of almost one as does the Ge detector whilst the PM tube has a quantum efficiency of only about 0.2.
optics, a spectrometer and a detector. An Argon ion laser (514nm) is used to excite the PL, having a much higher energy than any of the semiconductor band gaps under consideration. The laser beam is focused onto the sample after passing through a notch filter to clean up the laser line (remove plasma lines), the emitted PL is collected by the same focusing optics and focused onto the slits of a 1m spectrometer. Because of the back-scattering geometry a large amount of scattered laser light reaches the spectrometer, this can be eliminated largely by the use of a long pass filter placed in front of the slits. The dispersed light is detected using an appropriate detector. The useful spectral range and response of the detectors used are shown in fig. 4.2. In most cases lock-in detection is used, this means that the PL is distinguished from other background sources of light by passing the incoming laser beam through a light chopper and connecting the detector and chopper to a lock-in amplifier, which selects signals only at the chopping frequency. For more sensitive work in the PM region, photon-counting is used; in this case background light must be eliminated. The amplified signal from the detector is connected directly to a BBC microcomputer, which controls the spectrometer and records the spectra. Spectra can be corrected for the spectral response of the detection system in the computer.

Details of some of the optics are indicated in fig. 4.1. For this work the sample is generally inside the DAC which is in a cryostat. The laser beam enters the DAC via a small mirror placed on the optical axis of the experiment, so that the beam is parallel to the optical axis. The beam is focused by a short focal length lens, just outside of the cryostat (not shown). The emitted PL, collected by the same lens, becomes a parallel beam which is then focused on to the spectrometer.
slits by a lens which is also not shown. The mirror obscures only a small part of the beam. The use of the same lens for focusing the laser beam and collecting the PL has been found to be the most successful technique since optimisation of the focusing optics necessarily implies optimisation of the detection optics and visa versa. Accurate optical alignment of the experiment is critical but is not easy for two main reasons; the sample is very small (~50μm square) and inaccessible, and the emitted PL is usually invisible to the naked eye. Both these problems are aided by using an optical fibre butted up against the back diamond (section 4.4.3). This serves two main purposes, white light can be passed down the fibre so that the detection optics can be optimised, since the only light passing out of the cryostat has passed through the gasket hole (approximately the position of the sample). The laser light should now be focused in the correct plane and traversing the focused spot, using micrometers on the focusing lens mount, until light is seen coming out of the optical fiber ensures that the beam is very close to the sample. Only minor adjustment to this lens should now be necessary to detect the luminescence. An alternative approach is to use a small ruby chip glued to the inside of the cell, luminescence from which is in the visible. The laser beam can then be brought close to the sample and approximately correctly focused by eye. If there is a ruby chip in the gasket hole for pressure calibration purposes, this can be used for finer adjustment once the optical arrangement is approximately correct. Final optimisation always involves maximisation of the PL signal from the sample itself. A useful addition being investigated for this setup is a microscope capable of viewing the gasket hole from outside the cryostat which would allow, amongst other things, the position of the laser spot to be monitored.
4.3 Cryogenic Temperatures

Much of the work is carried out at cryogenic temperatures. Two types of cryostat are used, either a flow cryostat or a bath cryostat. Either liquid nitrogen or liquid helium may be used as the cryogenic fluid. In a flow cryostat the cryogenic fluid is pumped continuously from its dewar via a transfer tube into the cryostat, so that the sample is surrounded by cold gas. A heater is also incorporated so that the sample may be maintained at any temperature from that of the liquid in the dewar up to a temperature somewhat above room temperature. This range of temperature can be useful for some experiments and is not available in a bath cryostat where the temperature is essentially fixed. In a bath cryostat the sample sits in a bath of the cryogenic liquid, usually helium. This means that the temperature of the sample is more stable than in a flow cryostat and usually lower since in practice few flow cryostats will reach the temperature of the cryogenic liquid.

4.4 High Pressures

Many devices for generating high pressures have been developed. The most successful device for optical work is the diamond anvil cell. A large variety of DACs have been designed, for reviews see Jayaraman (1983) and Dunstan and Spain (1989). For the high pressure work reported in this thesis a miniature cryogenic DAC designed and built by Dunstan and Scherrer (1988) is used. Later improvements to the design are described in Dunstan and Wilkinson (1990).
Fig. 4.3 A schematic diagram illustrating the principle of the diamond anvil cell.
4.4.1 The Diamond Anvil Cell

The principle of the diamond anvil cell is illustrated in fig. 4.3. The essential items are two opposing anvils, with a metal gasket between to contain the pressure volume. The sample is surrounded by a hydrostatic medium in the gasket hole. A moderate force is applied to the anvils which by virtue of the small culet area (~0.5 mm²) generates high pressures (typically ~0-200 kbar but in principle up to at least 5 Mbar) in the gasket hole.

The remainder of the cell must provide support for the diamonds and allow force to be applied to them. There must be some means of aligning the diamonds accurately opposite and parallel which will maintain alignment at high pressures, and of course unobscured optical access is essential.

4.4.2 Diamond Anvils

Diamond anvils are used because of their strength and their transparency to photons over a wide energy range. The design of diamond commonly used in DACs is shown in fig. 4.4 alongside the brilliant cut diamond for comparison (for details of design criteria see Seal (1984)). The table area of the diamond is increased for high pressure work, as is the anvil angle and waist. Typical culet diameters are 750μm or 500μm, the choice of culet size will be discussed later (section 4.7.3).

Optical quality is an important factor in the choice of diamonds and is discussed fully by Seal (1984). Standard diamonds (Type I) are slightly yellow, resulting from Nitrogen impurity. Type IIa diamonds are white and do not absorb as strongly in the infra red (but are much
Fig. 4.4 The design of diamond anvil used is shown in (b). (a) shows the design for a brilliant cut diamond for comparison (After Dunstan and Spain 1989).

Fig. 4.5 The miniature cryogenic diamond anvil cell. The principal components marked on the vertical section C-C are (1) top plate, (2) piston, (3) body, (4) pad, (5) base plate. The hole marked in the bottom projection are for (a) the tension wires, (b) the clamp bolts, (c) the stand-off screws, and (d) the securing screws. The holes marked in the transverse section are for (e) the X-Y adjustment and the pad securing screws and (f) the piston guide screw. (After Dunstan and Scherrer 1988.)
more expensive). Diamonds are also chosen for low fluorescence.

4.4.3 The Dunstan Cell

Full details of this cell have been published (Dunstan and Scherrer 1988, Dunstan and Wilkinson 1990a and Dunstan and Wilkinson 1990b) and only the essential details will be described here. The cell is illustrated in fig. 4.5. It is designed to fit down the bore of a standard cryostat and has a maximum O.D. of 19mm. It is made out of hardened Be:Cu. The diamond anvils are secured to the piston and the pad. The pad is held against the back plate and x-y movement is achieved by means of the three grub screws. The back plate and hence the diamond can be tilted with respect to the body by means of three stand-off screws and secured by three more retaining screws. The piston is a close fit with the bore to maintain alignment in the cell. Load is applied to the diamonds via the drive mechanism, this is illustrated in fig. 4.6. The drive is of course also designed to fit down a standard cryostat bore and to allow pressure changes whilst the cell is in the cryostat. The drive mechanism is a Bowden cable device; the steel tubes butt up to the top plate whilst two cables run down the tubes and wrap around the base of the cell, arches are provided at the base to prevent the wires turning through a sharp corner and a brass base plate protects the screw heads in the base of the cell. At the top of the drive mechanism the tubes end at and are soldered to the thrust plate, while the wires pass through the thrust plate. Friction clips are attached to the wires and a hydraulic ram is used to push on the thrust plate and pull on the wires thus loading the cell. A ball bearing between the ram and thrust plate ensures symmetrical loading of the drive mechanism. Heat shields are
Fig. 4.6 The Bowden cable drive mechanism with the DAC in position.
added along the length of the tubes to minimise the thermal loading of the cryostat. 'O' rings seal the wires to the thrust plate make the whole device vacuum tight, as required for work in the cryostat. An optical fibre whose function has already been described can be threaded down the centre of the drive mechanism. Capacity for electrical feedthroughs is also provided.

4.5 DAC Operation

4.5.1 DAC Assembly

The first step in assembly of the DAC is to attach the diamonds to the pad and piston. They must be secured flat against the Be:Cu and centred over the holes provided for optical access (fig. 4.5). A jig designed for carrying out this procedure is shown in fig. 4.7(a). The diamonds, pad and piston are first thoroughly cleaned in solvents, the diamond is then clamped onto the pad or piston in the jig. The diamond culet sinks slightly into the perspex sheet, the screws then allow independent movement of the pad (piston). The diamond culet is viewed through the optical access hole using a monocular microscope and the pad (piston) positioned so that the culet is in the centre of the hole. A small drop of cyanoacrylate glue is then applied to the side of the diamond at the base, this is drawn in by capillary action and sets in seconds, securing the diamond. The pad (piston) can then be removed from the jig and a ring of rapid Araldite placed around the diamond to give it added security.
Fig. 4.7 (a) The diamond aligning jig shown in section. The diamond anvil is shown sitting on top of the DAC piston and held in place by a clamped down perspex sheet. Four screws allow independent X-Y movement of the piston whilst the diamond is held stationary by the perspex. (b) The sample thinning jig. Samples are placed in the groove which is ~30µm deep.

Fig. 4.8 The setup for loading argon into the diamond anvil cell (After Spain and Dunstan 1989).
4.5.2. Diamond Alignment

The diamond anvils must be aligned accurately opposite and parallel in the DAC for successful high pressure operation. In the DAC described, the piston diamond is fixed and the pad diamond must be aligned with respect to it. Three grub screws in the side of the cell allow X-Y translation of the pad and hence the diamond, when tightened against the sloping edges of the pad they secure the pad against the back plate. Observation of the two culets in contact, viewed through a microscope, allow the diamonds to be positioned accurately opposite. The orientation of the diamond is altered by changing the tilt of the back plate with respect to the body of the cell; for this purpose there are three stand-off screws in the base of the cell. Parallelism is checked by assembling the cell with the diamond culets in contact and observing white light interference fringes between the two culets. The base plate must be aligned so that only two or three fringes are seen. If no fringes are observed the cell is either very badly aligned or there is dirt between the diamond culets which should be removed. Good alignment of the cell is checked during the gasket indentation process.

4.5.3 The Gasket

The standard gasket material used for this work is 0.5mm stainless steel sheet, other materials such as Inconel may also be used. Pre-indented gaskets are always used. The first step is to drill two holes so that the gasket can be passed over the gasket guide pins, and to trim the metal so that it does not protrude past the edge of the piston. The gasket is then ready for indentation. The cell is assembled
and load applied by the hydraulic ram in a specially designed indenting jig. The load is increased in small steps and the gasket inspected and cell alignment checked, before each increase. If the cell starts to move out of alignment the cause must be identified and the cell realigned. The thickness to which the gasket is indented is determined by the required pressure range for the experiment, this will be discussed later in section 4.7. The thickness of the indentation is measured using a ball ended micrometer. A small hole is drilled in the centre of the indentation to form the pressure volume. Micro drills (small engineers' twist drills) with diameters in the range 150-300\(\mu m\) are used. Ideally the hole diameter should be about \(1/3\) of that of the diamond culet, and never more than \(1/2\). A vertical drilling machine is used to drill the hole; the drill bit is positioned centrally over the indentation with the aid of a microscope and an X-Y stage with micro positioners. Normally several gaskets are preindented to allow for failures in drilling the hole sufficiently centrally.

4.5.4 Sample Preparation and Loading

Typical gasket hole dimensions are \(~\text{dia. 300}\mu m\) and thickness \(100\mu m\) and the sample must be prepared accordingly. Samples are first thinned to \(~30\mu m\) thickness; a jig for doing this is shown in fig. 4.7(b), the sample is secured face down in the \(30\mu m\) deep groove with melted wax. It is then mechanically thinned using \(\text{Al}_2\text{O}_3\) abrasive paper until all of the protruding sample has been removed. Ruby chips are prepared in the same manner but require a carborundum wheel to thin them. The sample is then removed and cleaned in solvents after which it may be cleaved, to the correct size using a razor blade or scalpel blade under a microscope.
The small samples tend to fly off, never to be seen again; this can be avoided largely by covering the sample in a drop of water or alcohol before cutting or by cutting the sample on a damp filter paper. Once cut to the correct size the sample can be loaded into the DAC. Usually two or three samples are loaded together (one or two being pressure gauges); they are picked up and placed face up on the piston diamond. They are transported on the end of a fine needle or wire, to which they are attracted electrostatically (gravitational forces being insignificant on such tiny objects). Once on the diamond culet the samples can be pushed around until they are entirely within the area to be covered by the gasket hole. The gasket is lowered over the guide pins and on to the diamond. Back illumination allows the samples to be observed through the gasket hole as the gasket is lowered, so that one can be certain that the metal will not touch the samples. Throughout the preparation and loading sequence great care is taken to ensure that the sample and diamonds are maintained grease free, since at low temperatures frozen grease can lead to stresses.

4.5.5 Pressure Media

Two pressure media have been used in this work. Early work used a 4:1 methanol:ethanol solution. This had two main disadvantages: the solution was frozen at cryogenic temperatures so that pressure changes had to be made at room temperature, this led to lengthy experiments, and the pressure was only hydrostatic up to about 100kbar at low temperatures. There is also evidence to suggest that the pressure is inhomogeneous in the gasket hole for pressures >60kbar (Lambkin 1989). In later work liquid argon was used exclusively as the pressure
transmitting medium. Due to its very weak van der Waals bonding the pressure can be changed at low temperatures without introducing appreciable stresses or non-hydrostatic conditions.

4.5.6. Pressurising the Cell

The method of pressurising the cell depends on the medium used. For loading with methanol:ethanol a small drop of the solution is placed in the gasket hole and indentation using a syringe. After checking that there are no bubbles caught in the hole the cell is quickly assembled (before the alcohol evaporates) and clamped with the clamp bolts; the cell should now be at a pressure of a few kbar.

Loading with argon is more involved, but easier, because the argon must be liquefied. The cell is loosely assembled and inserted in the drive mechanism. The cell is then sealed inside the loading bomb. The loading bomb is illustrated in fig. 4.8. The seal is at the top of the drive mechanism in the same place as the cryostat seals (Prins et al 1989). The bomb is filled with gaseous argon at about 100psi. A vacuum pump can be used to evacuate the system first to help ensure that pure argon forms the pressure transmitting fluid. The gas is liquefied by immersing the bomb in a dewar of liquid nitrogen. When everything is cold it takes about 10-20 mins. for the bomb to fill, the cell is then completely surrounded with liquid and hopefully the gasket hole is filled. The cell can now be sealed by applying load with the hydraulic ram. The gas is then vented, the bomb warmed up and the cell and drive removed. The cell will now usually be at a pressure of 10-20 kbar at room temperature. PL must be collected from one of the samples to verify that the cell is under pressure.
4.6 Pressure Calibration

Ruby is the most commonly reported pressure calibrant. The luminescence from the R1/R2 lines is used and their shift is known to be linear (0.365 Å/kbar) with pressure up to ~200 kbar (Barnett et al 1973). It is particularly advantageous because the luminescence is bright even at room temperature which is not the case for many semiconductor samples, and because it scarcely moves with pressure so is easy to find. The brightness of the luminescence is a great disadvantage if the sample luminescence is in the same spectral region as the ruby when it becomes difficult to eliminate the ruby emission from the spectrum. The pressure induced shift is small, leading to error in the pressure measurement. A zero kbar reference ruby experiencing the same temperature is always used to correct for fluctuations in temperature and error in the spectrometer.

Direct gap semiconductors such as GaAs and InP are often preferred as pressure gauges because they have large pressure coefficients ~10 meV/kbar. Even allowing for uncertainty in the pressure coefficients these are usually more accurate than ruby. Their PL is dimmer and may usually be spectrally and spatially resolved from other samples. An appropriate pressure gauge must be chosen for each experiment; important considerations are: the spectral region, the pressure at which the gauge material becomes indirect (e.g. GaAs Γ-X crossover at ~40 kbar) and the phase transition pressure. Often the ideal gauge does not exist and it may even be necessary to employ two gauges to cover the pressure range of the experiment. Indirect semiconductors are not suitable as pressure gauges.

The most accurate results are obtained by using a layer within the
sample of interest as the pressure gauge. In this way differences in energy can be studied without any need to introduce errors by converting to pressure. The effects of any inhomogeneities in the pressure medium are also reduced.

4.7 The Gasket and Force Pressure Plots

4.7.1 Introduction

Great effort has been directed at the development of diamond anvil cells and also at the selection or manufacture of diamond anvils, however, little attention has been paid to the gasket. During the course of the work reported in this thesis much experience has been gained and the importance of the gasket has been realised. In the pressure range of interest (0-200 kbar) with diamonds of typical culet diameter ~750μm the geometry and material of the gasket are important parameters in determining the performance of the cell. These parameters can be used to tailor the pressure range of the cell to the experiment.

4.7.2 The Force Pressure Relationship

The force pressure relationship is routinely monitored during an experiment and is found to be a useful diagnostic tool. The relationship is not a linear one but takes the form of a slow rise in pressure from the initial loading pressure, followed by a rapid increase and finally a turnover to sublinear behaviour at the highest pressures. This form is shown, for example, in fig. 4.9. The behaviour of the gasket has been
modeled theoretically (Dunstan 1989), based on theory worked out long ago by Schroeder and Webster (1949) in the completely different context of press forging and coining. The application of this theory to the problem of the DAC gasket has been very successful. Some important results from this work are given in appendix B. The general form of the curve observed experimentally is predicted theoretically. However empirical measurements remain the only sufficiently accurate way of predicting the force pressure relationship for experimental purposes.

4.7.3 Gasket Geometry

The relationship between the force-pressure characteristic and the gasket geometry have been studied in some detail. For a given gasket material and pair of diamonds the most important geometrical parameter is the thickness to which the gasket is preindented. Figure 4.9 shows the force-pressure relationship for a cell with anvils of 500μm diameter culets and 0.5mm steel gaskets operating at room temperature. Results for three gasket thicknesses 60μm, 30μm and 13μm are shown. The highest pressures obtained were ~110, 135 and 260 kbar respectively. For the thinnest gasket, while high pressures were obtained, the gasket was too thin to be of much practical use (a stronger gasket material is required to allow thicker gaskets for the same pressures). Each pressure run was terminated at the onset of sublinear behaviour, except for the thinnest gasket where insufficient force was available to reach this part of the curve. From fig. 4.9 it is seen that the onset of sublinear behaviour occurs at higher pressures for thinner gaskets. This is predicted (Dunstan 1989) to be the point at which the gasket hole stops
Fig. 4.9 Force-pressure plots at 300K are shown for three gaskets pre-indentated to different thicknesses, using diamonds with 500µm culets. In (a) the indentation thickness was 60µm; this curve shows sublinearity very clearly at a relatively low pressure. In (b) the thickness was 30µm. In (c) the thickness was only 13µm and the highest pressure of 260 kbar could be reached.

Fig. 4.10 Force-pressure plots at 300K are shown for two sizes of diamond culet, 500µm and 750µm. The gasket dimensions were scaled accordingly to obtain the same geometry. Note that it is the force which is changed in proportion to the area, not the pressure.
Fig. 4.11 Force-pressure plots at 300K and 80K are shown for 750μm ouletts and the same gasket dimensions.

Fig. 4.12 A typical force-pressure plot from an experiment in which the pressure was cycled a few times. Note the large hysteresis. Pressure changes were made at room temperature, crosses indicate room temperature pressures and open circles show the pressure obtained when the cell was cooled to 80K.
contracting and starts to enlarge, and indeed this enlargement of the gasket hole is observed. This is the onset of gasket failure. Any asymmetries in the system, such as slight misalignment of the diamonds exacerbates the situation, for example, the hole may elongate rapidly or drift radially. At this point the diamonds are at risk and the experiment should be terminated.

Higher pressures can be generated for the same force by reducing the culet area of the diamonds, as expected. Figure 4.10 shows the force-pressure relationship for two different culet diameters 500µm and 750µm measured at 300K. The gasket is again steel and its dimensions are scaled with the culet diameter (500µm culets; thickness 60µm, hole diameter 200µm, 750µm culets; thickness 90µm, hole diameter 300µm).

The cell behaves much as expected at 300K. However at low temperatures a much reduced pressure range for the available force is found, this is illustrated in fig. 4.11 where the results for a cell with 750µm culets are shown. In each case the gasket was similar, a dramatic difference is seen between the behaviour at room temperature and at cryogenic temperatures. This was unexpected and from the point of view of making measurements disappointing. This was initially thought to be a problem with the cell and/or drive mechanism, whereby some of the force was lost in friction and not transmitted to the diamonds. However, a comparison of the force-pressure plots for 500µm and 750µm culets, at 300K and 80K, shows that this is not the case and that the reduced pressure range at low temperature is in fact intrinsic to the diamond and gasket system, since it is the applied force which scales with culet area and not the generated pressure. Higher pressures for a given gasket thickness are expected to be obtained by using a stronger material. Experiments are planned on hardened Inconel. Tests on
untreated Inconel achieved a somewhat lower ultimate pressure than a steel gasket of the same dimensions.

Figure 4.12 shows the force-pressure relationship for a cell with diamonds with 750µm culets and a steel gasket preindented to 80µm. In this case methanol:ethanol was used as the pressure transmitting medium, so pressure changes were made at room temperature. The figure illustrates the hysteresis which the cells suffer, especially when unloading from high pressures. The figure also shows that significant pressure changes occur when the cell is cooled from room temperature to 80K. This can cause problems where very detailed work is being carried out.

In summary, it has been shown that an understanding of the force-pressure relationship is important for successful operation of the DAC. The gasket thickness and culet size must be chosen correctly at the beginning of the experiment so that a suitable pressure range is available during the experiment. It should be noted that this does not just mean that the highest pressure required will be reached, but also that the lowest pressure will be reached and preferably that the steep part of the characteristic does not coincide with a region in pressure where a detailed study of the sample is required. Monitoring the force-pressure plot during an experiment gives the experimenter some predictability when changing pressure, fine adjustments to the pressure are usually done by monitoring the luminescence feature of interest while changing the force. The plot also allows the experimenter to know when the gasket hole begins to enlarge, for low temperature work, where the cell is in a cryostat, this is the only practicable method of monitoring the cell and avoiding destruction of the diamonds at high pressures.
4.8 Experimental Procedures

From experience gained while using the DAC, the following additional comments on experimental procedure are thought worthy of note:

Since the cells exhibit large hysteresis on unloading it is desirable to start the experiment at the lowest pressure required and only to increase pressure during the experiment. A final measurement at 0 kbar is nearly always possible. (However, some data points taken during unloading are highly desirable to confirm reversibility and are taken where possible). Pressure is best decreased at room temperature whilst monitoring the PL, a sample with room temperature luminescence may be loaded especially for this purpose where the sample itself does not luminesce at room temperature. With argon-loaded cells the pressure is expected to fall by some 5-10 kbar during cooling from room temperature and this should be allowed for. This applies to pressures less than \( \sim 30 \) kbar, at higher pressures the pressure is less sensitive to temperature. Similar changes can be expected with methanol:ethanol but are less predictable.

Since pressure and temperature are not independent variables in the DAC the use of argon as a pressure transmitting medium, where pressure changes are made at the temperature of the experiment, has greatly improved the controllability of experiments.

It has been shown possible, under conditions of accurate laser focusing, to spatially resolve signals from two, or more, different samples in the gasket hole, even when they are emitting PL at the same wavelength (Prins 1989, Prins and Dunstan 1989). However this is
difficult and potentially controversial and should be avoided where ever possible e.g. by the choice of a pressure gauge emitting in a different region of the spectrum.

During an experiment pressure changes are usually made while monitoring the luminescence feature of interest (rather than the pressure gauge). The force is changed so that the signal is halved, then if the signal can not be recovered by repositioning the laser spot, the PL peak must have moved under pressure (or quenched). This method of changing pressure ensures that sample emission does not change unexpectedly and a feature of interest missed e.g. the quenching energy of a quantum well emission. This is particularly important in light of the difficulty of reducing pressure to recover the missed data. This method allows pressure changes as accurate as 1/10 kbar when required.

Non-hydrostatic conditions are sometimes observed during high pressure experiments, this causes the PL peaks to broaden or even split. Half widths should be monitored during an experiment to ensure the validity of any data. These events are rare but usually occur at low temperatures and are more common on unloading pressure than on loading. These conditions can sometimes be removed by tapping the drive mechanism but usually require the cell to be warmed up and re-cooled.

4.9 Electrical Feedthroughs in a DAC

The success of the DAC for optical work has led several groups to investigate the possibility of introducing electrical feedthroughs into the DAC. This would allow electrical and electro-optical measurements. Difficulties arise for two main reasons. Firstly the electrical wires
must be brought into the sample space without shorting to the metal gasket and the wires must withstand the high pressures without breaking. Secondly the sample must be very small, ~50-100μm square, which means making electrical contacts is extremely difficult.

Several groups have reported the successful introduction of feedthroughs in the DAC. Patel et al (1986) have reported on a method using Al₂O₃ coated gaskets to act as the insulation and beveled diamonds. Gonzalez et al (1986) have reported on a similar technique. Despite these and other reports of successful methods very little actual data, obtained by these methods, has been published, suggesting that the methods may not be very reliable. The deposition of Al₂O₃ is a rather specialised technique which is not available to all laboratories. The deposition must be carefully controlled for use on the gaskets. A much simpler technique, which will be generally available to all laboratories, has been developed. This involves the use of epoxy as the insulating layer. The technique is briefly described here.

Diamonds with rounded edges are used to avoid cutting the wires (double beveled diamonds have yet to be evaluated for this purpose). The gaskets are made of steel as usual and preindented and drilled in the normal manner. The gaskets are then covered with an epoxy insulating film (Araldite CY1301/HY1300). The epoxy is spun onto cleaned gaskets and then cured in accordance with the manufacturers instructions. The gasket hole is then redrilled to clear out the epoxy. The cell may then be loaded with a suitably prepared sample. Wires from the sample are connected with conducting epoxy to pins which pass through the piston and out of the cell. The pins are insulated from the piston by PTFE sleeving and securely glued in place. The current design of DAC allows for four pins.
Initial tests involved placing a single wire (rather than a sample) across the gasket hole and connecting it to a pin at either end. Electrical continuity was then checked as the pressure was increased, at the same time it was ensured that the wire was not shorted to the gasket. Room temperature measurements using pentane as the pressure transmitting medium were attempted first. The feedthroughs were shown to operate successfully up to 75 kbar. This limit being set by the available force rather than being a limit of the technique itself. Argon loading has also been shown to be possible suggesting that the technique will also be successful for low temperature measurements.

Other workers in collaboration with this project have developed techniques for producing small samples with electrical leads suitable for use in the cell. At Surrey a method involving bonding wires onto small samples has been developed (Leong 1990). The samples are first thinned in the normal manner and then supported on a Si wafer. The samples are mechanically masked prior to the evaporation of metallic contact pads. Wires are then attached by bonding to the evaporated pads. The samples are removed from the Si wafer and cleaved to the appropriate size for loading. A completely different method, using photolithography and plating techniques has been developed at the University of Birmingham. This method has also produced suitable samples (Childs 1990). Leong (1990) has demonstrated room temperature photoconductivity at various pressures using the technique described here.
Chapter 5

BAND LINEUPS AND EXCITON BINDING ENERGIES IN GaAs/AlGaAs
QUANTUM WELLS.

5.1 Introduction

This chapter is concerned with the band line-up in GaAs/AlGaAs heterojunctions. The exact values of the offsets in this system have been controversial for many years. This has generally been believed to be because of difficulties with the different measurement methods used. Work by Wolford et al (1986) and others (Venkateswaren et al 1986) established the high pressure technique for making accurate spectroscopic measurements of the valence-band offset. In this chapter Wolford's method and variations on his technique are discussed in detail. Difficulties with the techniques are also discussed. One such difficulty is the accurate extrapolation of measurements made at high pressures to ambient pressure. The behaviour of quantum wells under pressure has been studied in detail, making this extrapolation more reliable. A limitation of the technique for determining the band offsets is uncertainty in the value of the exciton binding energy, and in particular its value at Γ-X crossover. The binding energies are measured in GaAs/AlAs quantum wells as a function of pressure up to the Γ-X crossover. The effect of crystal orientation is also studied.

Despite the simplicity and accuracy of the high pressure technique, the work reported here has not helped to settle the controversy of the
value of the band offsets in GaAs/AlGaAs heterojunctions. It now appears that the band offsets may vary considerably from sample to sample. The results of some theoretical predictions of the band lineup are considered.

5.2 Band Offsets in GaAs/AlGaAs Heterojunctions

The GaAs/AlGaAs system is the most technologically important semiconductor system after Si. Consequently the band offsets have been extensively studied. A heterojunction between two similar materials with the same lattice constant represents the most simple heterojunction imaginable and yet the values of the band offsets remain controversial.

Early work by Dingle (1975) and Dingle et al (1974) measured the 2K absorption spectra of a number of quantum well structures. By fitting the data to a simple square well model the band offset ratio was determined to be 85:15. Despite the fact that these measurements were made only on GaAs/Al$_{0.2}$Ga$_{0.8}$As samples, the 85:15 'Dingle' rule became widely accepted as the correct value across the alloy range. This value remained largely uncontested for over a decade.

In 1984 Miller et al studied the PLE spectra of synthesized 'parabolic' quantum wells and determined the offset ratio to be ~50:50. Spectroscopic measurements by Dawson et al (1985) on narrow (~55Å) GaAs quantum wells, where the well width and conduction band offset are left as adjustable parameters, determined the offset ratio to be ~75:25 at 8K for Al fractions in the range 0.25<x<0.36. Recent studies by Meynadier et al (1985) give a ratio of 60:40 for GaAs/Al$_{0.13}$Ga$_{0.87}$As quantum wells. They use PLE to study $\Delta n=0$ transitions in symmetric and asymmetric quantum wells. Results on intrasubband transitions measured by
Fig. 5.1. A summary of experimental values for (a) the valence-band offset and (b) the fractional valence-band offset for GaAs/AlGaAs heterojunctions. Data are from Wang and Stern (1985) and references therein. In (a) the upper dashed line corresponds to $\Delta E_v = 0.4 \Delta E_g$ and the lower dashed line corresponds to $\Delta E_v = 0.15 \Delta E_g$. 
Raman scattering gives a value of $Q_v = 0.31$ (Menendez et al 1986).

Determination of the valence band offset from Type II GaAs/AlAs structures by Dawson et al (1987) yields a fractional valence band offset of 0.33-0.34. High pressure measurements to determine the valence band offset (by the Type II method described below) have yielded the following values for the fractional valence band offset, $Q_v$: $Q_v = 0.31 \pm 0.03$ (x=0.28), $Q_v = 0.34 \pm 0.02$ (x=0.70) (Wolford et al 1986) and $Q_v = 0.30 \pm 0.04$ (x=0.25, 0.33) (Venkateswaran et al 1986).

All of the above are spectroscopic measurements although only those measuring Type II transitions can claim to be making a direct spectroscopic measurement of the offsets. Electrical measurements, such as C-V profiling and the charge transfer method, have also been performed. Wang and Stern report a value for $Q_v$ of 0.38 for x=0.5 and 0.28 for x=1 determined from the latter technique. These techniques have been reviewed by Kroemer (1983).

Additional data supporting non commutativity further complicates the comparison of results. Waldrop et al (1981) found that, for (110) interfaces, on average $\Delta E_v = 0.40$ eV for GaAs grown on AlAs but only 0.15 eV for AlAs grown on GaAs. However Wantanabe et al (1984) find Al$_{0.33}$Ga$_{0.67}$As/GaAs (100) interfaces to be commutative within experimental error. Commutativity is assumed in the analysis of results from most of the above techniques. Wang and Stern (1985) have compared the valence band offsets measured by a number of authors; their graphs are reproduced in fig. 5.1. The results mentioned here represent only a small fraction of the effort which has been directed at determining the band offsets in the GaAs/AlGaAs system. Considering the data discussed here and giving equal weight to the reliability of each of the values, it may be concluded that the Type I alignment of GaAs/AlGaAs quantum
wells is not under debate but that little can be said with certainty about the values of the offsets, except perhaps that $Q_v = 0.5$.

5.3 Interpretation of High Pressure Data.

5.3.1 Introduction

The data which may be obtained from high pressure photoluminescence experiments, falls into two categories. Namely, data from Type I and Type II transitions. Figure 5.2(a) is a schematic diagram of a GaAs/AlGaAs quantum well, illustrating a Type I transition. Figure 5.2(b) illustrates the situation at high pressure, where the just structure has been turned Type II. Structures may be grown Type II, in the GaAs/AlGaAs system, by an appropriate choice of well width and barrier composition (see, for example, Dawson et al 1987). Type I transitions are sensitive to movements of the conduction band offset under pressure but not to the absolute value, whilst Type II transitions are sensitive to both the absolute value and movements of the valence band offset. Of course knowledge of one offset automatically implies a knowledge of the other if the band gaps and their pressure dependencies are known for the constituent materials.

5.3.2 Type I Data

Factors affecting the pressure coefficients of confined quantum well states have been discussed in detail in chapter 3. They include, for example, the pressure coefficients of the well and barrier materials
Fig. 5.2. The figures are schematic diagrams of quantum wells with the two types of band alignment discussed in the text. (a) illustrates a Type I quantum well, where electrons and holes are both confined in the same material. (b) illustrates the situation at crossover. Any further increase in pressure will turn the quantum well Type II, in this case the electrons will be confined in the barrier X-states and the holes will be spatially separated in the well material. The figures define the notation used in the text.
and the pressure dependence of the effective masses. These are properties of the bulk materials and have been well characterised. One parameter to which the pressure coefficient of the Type I transition is particularly sensitive is the pressure dependence of the conduction band offset. In most quantum well systems the pressure coefficients of the direct gaps of the constituent materials are not equal. This means that under pressure the value of the band gap discontinuity must change. In the GaAs/AlGaAs system GaAs has a higher pressure coefficient than AlGaAs, thus the total band gap discontinuity must decrease with pressure. However, this tells us nothing about how the individual offsets are changing. In previous modeling of quantum well transitions under pressure, the offset ratio has been assumed to remain constant (Lefebvre et al 1987, Gell et al 1987). Recent work by Lambkin et al (1988) on Type I transitions in InGaAs/InP quantum wells shows striking results, dispelling this assumption. The pressure dependence of the offsets can be obtained from the high pressure data because the energy of the Type I transition is sensitive to changes in the electron confinement energy. Thus if, for example, the conduction band offset decreases under pressure, the electron confinement energy will also decrease. A measurement of the PL energy made relative to the band gap of the well material as the pressure is increased is able to accurately detect small changes in the electron confinement energy and hence the pressure dependence of the offset. The valence band offset must also be changing but because the heavy hole is ~ 5 times heavier than the electron its confinement energy is less sensitive to the offset and is relatively unchanged. A full solution of the envelope function model, described in chapter 3, is required to fit the data and to determine the pressure dependence of the conduction band offset. The pressure
dependence of the valence band offset then follows from the pressure coefficients of the bulk materials.

In contrast to the sensitivity of the Type I transition to changes in the band offsets under pressure the absolute energy of the Type I PL transition is rather insensitive to the division of the band-gap discontinuity between the conduction and valence bands. The uncertainties associated with the exciton binding energies and the well widths means that this type of data cannot provide useful information on the band offsets. Spectroscopic measurements which use direct transitions to derive the band offsets involve fitting data from higher confined states to increase the accuracy. Such methods should still be considered dubious for the reasons given above.

5.3.3 Type II Data

Since the \( \Gamma \) and \( X \) minima have characteristic pressure coefficients of different sign, in some materials they may be caused to cross. In bulk GaAs, for example, the \( \Gamma \)-\( X \) crossover occurs at \( \sim 40 \) kbar. In many materials however the \( \Gamma \) and \( X \) states are separated by too great an energy for the crossover to occur at a pressure below the phase transition pressure. In GaAs/AlGaAs quantum wells it is possible to induce a crossover between the confined \( \Gamma \) state in the well and the \( X \) minima in the barrier. The observed photoluminescence then results from recombinations between electrons confined in the GaAlAs barriers (\( X \) minima) and holes confined in the GaAs. The transitions are therefore indirect in both real and \( k \) space. When this occurs a very accurate, spectroscopic, determination of the valence band offset is possible. The valence offset is then given by
where the notation is defined in fig. 5.2(b). The indirect gap of the barrier material, $E_B$, and its pressure dependence are usually well known. The heavy hole confinement energy can be calculated using the envelope function approximation. Whilst this will depend on the value of the valence band offset it is not particularly sensitive to it, at least for wide wells, thus absolute errors will be small. The exciton binding energy, $E_{EB}$, can again be calculated without much absolute error. The value of the exciton binding energy at $\Gamma$-$X$ crossover is discussed in section 5.6. For superlattice samples where the barrier layers are thin the effect of confinement of the barrier $X$ electrons should be taken into account. Wolford et al (1986) and Venkateswara et al (1986) determined the valence band offsets in quantum well samples by extrapolating the Type II emissions back to atmospheric pressure. If Type II luminescence is not observed the valence-band offsets may be determined from the quenching of the Type I emissions at $\Gamma$-$X$ crossover. It is often this related technique which is most useful in practice since the Type II emission are usually weak, if detected at all, and are often not trackable over a large pressure range which makes extrapolation unreliable. If the sample contains wells of different widths then the wells will quench sequentially as the pressure is increased, pin-pointing the position of the barrier $X$ minima with respect to the GaAs valence band at several pressures (just as the Type II transitions do). Ideally the pressures at which the wells have crossovers will be spread out. In practice this may be difficult to arrange, making extrapolation difficult. The use of narrow wells means
that the heavy hole confinement energy becomes significant and more importantly significantly affected by the choice of valence band offset. This makes determination of the band offset for narrow wells rather unreliable. This is discussed further when the experimental results are analysed, where it is shown how this effect can be used to advantage.

The pressure coefficient of the Type II transitions will also give the pressure dependence of the valence band offset:

\[
\frac{d\Delta E_v}{dP} = \frac{dE^X}{dP} - \frac{dE_{PL}}{dP} \quad [5.2]
\]

This in theory offers a more direct measure of the pressure dependence of the band offsets than the Type I method but relies on being able to observe the Type II transitions and accurate knowledge of the pressure coefficients of barrier X minima. Lambkin et al (1989) have determined the pressure coefficient of the valence band offset in GaAs/Al_0.63Ga_{0.37}As heterojunctions to be +1.1x meV/kbar, this result assumes that the pressure coefficient of the X minima in AlGaAs is equal to that of GaAs (-1.34 meV/kbar). However Prins (1989) makes the same measurement in a GaAs/Al_0.37Ga_{0.63}As quantum well where spatially direct X emission from the AlGaAs barrier layers is also observed. He finds that the pressure coefficient of the AlGaAs indirect gap is -2.33 meV/kbar whilst that of the Type II transition is -1.72 meV/kbar, implying an decrease in the valence band offset under pressure of 0.61 meV/kbar. (An independent measurement of the pressure coefficients of the indirect gaps of GaAs and AlGaAs needs to be made.)
<table>
<thead>
<tr>
<th>Sample</th>
<th>Well width (Å)</th>
<th>Barrier width (Å)</th>
<th>Barrier composition, x</th>
<th>Substrate orientation</th>
<th>Growth temperature (°C)</th>
<th>Growth laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>15</td>
<td>450</td>
<td>0.242</td>
<td>(100)</td>
<td>600</td>
<td>Optoelectronic Joint Research Laboratory, (OJRL), Kawasaki.</td>
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Table 5.1 Sample details.
5.4 Experimental Determination of the Band-Lineup in GaAs/AlGaAs Quantum Wells with Various Substrate Orientations

5.4.1 Experimental Details

New results from four samples are reported here. Samples A, C and D each consisted of five quantum wells of various widths. The barriers were Al\textsubscript{x}Ga\textsubscript{1-x}As with x = 0.24. Sample B was a GaAs/AlAs superlattice with 40 Å wide wells. For samples A-D the substrate orientations were (100), (100), (311)A and (311)B respectively. The sample details are summarised in table 5.1. The samples were all nominally undoped. The well widths were determined from the growth time. This was precalibrated from the measured thicknesses of thick layers. In the case of samples A, C and D the Al\textsubscript{x}Ga\textsubscript{1-x}As barrier compositions were determined precisely from the 1.8 K PL energy of the neutral acceptor bound exciton (A\textsuperscript{0}-X) in AlGaAs (Fukunaga et al 1987).

In each case strong excitonic emission from each of the quantum wells is observed, except from the widest well (~240 Å) in samples A, C and D where the emission is not resolved from that of the GaAs substrate. Clear GaAs substrate or capping layer emission is seen in all the samples. The PL spectra for samples A, C and D, measured at 80 K, are shown in fig. 5.3. Sample B is discussed more fully in the second half of this chapter in connection with the exciton binding energies and so data from that sample are presented there. The 10 K PL spectrum can be seen in fig. 5.11.

High pressure experiments were conducted as described in chapter 4. Argon was used as the pressure transmitting medium. Experiments were conducted at 80 K, ~10 K or at 2.2 K as specified. Emission from the
Fig. 5.3. Photoluminescence spectra, recorded at 80K and ambient pressure are shown for (a) sample A, (b) sample C and (c) sample D. Each sample shows four distinct peaks associated with quantum wells of different widths. Also seen at low energy is the substrate emission.
GaAs substrate served as the pressure gauge in each of the experiments. The band gap of GaAs is known to increase at 10.7 meV/kbar (Wolford and Bradley 1985). Whilst the exact pressure coefficient of GaAs may be under debate, in this series of experiments all of the pressure coefficients quoted are derived from comparative measurement with GaAs. This means that highly accurate values for the differences between pressure coefficients are obtained. These differences are significant even from sample to sample.

5.4.2 Results

Figure 5.4 shows the PL spectra from sample A, taken at 80 K, at various pressures. As the pressure is increased the PL peaks, associated with each quantum well, move to higher energy at approximately 10 meV/kbar, the rate which is characteristic of $\Gamma$-$\Gamma$ transitions. The first spectrum shows the situation at ~16 kbar, where the emission from the thinnest well is almost completely quenched. By ~21 kbar the emission from the next thinnest well has almost quenched. By ~29 kbar only the emission from the GaAs substrate remains. In each case as the intensity drops off the pressure coefficient of the emission is simultaneously reduced. At 80 K the intensity drops from its initial value to an undetectable level over a ~5 kbar range. The substrate emission will be quenched too by the bulk $\Gamma$-X crossover at ~40 kbar (Goni et al 1987). On unloading the pressure, full initial intensity of all the peaks is recovered. Samples B-D behave in a similar manner. For the data recorded at 2.2 K the high pressure cut off of the PL intensity is much sharper, occurring over a ~2 kbar range. Figure 5.5 shows the behaviour of the PL emission for sample C under pressure. The data are
Fig. 5.4. PL spectra from sample A, recorded at various pressures, are shown. The spectra were recorded at 80K. The sequential quenching of the wells as the pressure is raised is illustrated.
Fig. 5.5. The difference between the PL energy and the GaAs energy is plotted against the GaAs pressure gauge energy for each of the observed wells in sample C.
plotted as the difference between the quantum well emission energy and the GaAs emission energy (the confinement energy) against the GaAs energy. This method of plotting the data is the most convenient way in which to observe differences in the pressure coefficients of the different wells. The narrow wells are seen to have lower pressure coefficients than the wide wells. At high pressures the confinement energy is seen to drop rapidly with pressure for some of the wells. This is characteristic of the mixing of the $\Gamma$ and $X$ states and marks the onset of the true Type II transitions, which are too weak to observe in these samples. The other samples behave in a similar manner (data from sample B is shown in fig. 5.12). Figure 5.6 shows the corresponding intensity of the PL emission, for sample C, plotted against the GaAs energy. The arrows indicate the energy of the GaAs (or pressure) at which $\Gamma$-$X$ crossover occurred. Quenching curves were obtained for each sample. The pressure coefficients and the energies of crossover, for each of the samples, are tabulated in table 5.2.

Figure 5.7 shows the measured Type I pressure coefficients as a function of the ambient pressure transition energy for each of the samples studied. Figure 5.8 shows the energy of crossover for each of the wells as a function of the transition energy at 0 kbar.

5.4.3 Analysis and Discussion

In figure 5.7 it is seen that the pressure coefficients of the Type I transitions decrease monotonically with decreasing well width (increasing PL energy). This is to be expected. In the limit of infinitely wide wells the pressure coefficients must tend to 10.7 meV/kbar, the value for bulk GaAs. For infinitely narrow wells the
Fig. 5.6. The intensity of the PL from sample C is shown plotted against the GaAs emission energy. The sudden quenching of the intensity at Γ-X crossover is seen for each of the wells. The energy of the crossover may be found by comparison with fig. 5.5.
<table>
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<tr>
<th>Sample</th>
<th>Wall width (Å)</th>
<th>( E_{k0} )</th>
<th>( \frac{dE_{k0}}{dP} ) (meV/kbar)</th>
<th>Energy at crossover (eV)</th>
<th>Pressure at crossover (kbar)</th>
<th>Temperature of measurement (K)</th>
<th>( \Delta E(P) ) (meV)</th>
<th>( \Delta E_0(0) ) (meV)</th>
<th>( Q_0(0) )</th>
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Table 5.2 Summary of experimental results for samples A to D.
Fig. 5.7. The pressure coefficient for each of the wells studied is plotted against its ambient pressure PL energy. (Similar to a plot against inverse well width.) The symbols refer to: +, sample A, solid circle, sample B, x, sample C and open circles, sample D. The lines are theoretically derived from envelope function calculations and are described in the text.
Fig. 5.8. The figure shows the energy of the PL at \( \Gamma-X \) crossover, as derived from the quenching curves, against the ambient pressure PL energy. Symbols have the same meaning as in fig. 5.7. The dashed lines are guides for the eye.
pressure coefficient must be that of the barrier material (9.9 meV/kbar for \( \text{Al}_{0.25}\text{Ga}_{0.75}\text{As} \)) (Chandrasekhar et al 1986). The modeling of the pressure coefficients of quantum well transitions has been discussed in chapter 3. Accounts have also been given by Lefebvre et al (1987) and Gell et al (1987). The solid curve shows the predicted trend for GaAs/Al\(_{0.24}\text{Ga}_{0.76}\) As quantum wells, assuming a constant valence-band offset under pressure, with an initial offset ratio of 70:30 (CB:VB). Table 5.3 lists the material parameters used in the calculation. Since the pressure coefficients of the Type I transitions are almost completely insensitive to the initial band-offset ratio, it is possible to neglect the fact that the samples may have different band-offset ratios and concentrate on the pressure dependence of the band offsets.

Sample A is considered first. This was grown on a (100) oriented substrate. Such wells have been extensively studied and reported on in the literature (Wolford et al 1986, Venkateswaren et al 1985, Venkateswaren et al 1986). In fig. 5.7 the solid curve (constant valence-band offset) is seen to under-estimate significantly the experimentally observed pressure coefficients in sample A. As discussed above, Type I pressure coefficients are most sensitive to changes, under pressure, of the conduction band offset. An attempt is made to fit the data by allowing the conduction band offset to increase under pressure in the model. The broken line shows the fit assuming that the conduction band offset is increasing at 1.8 meV/kbar. This implies that the valence band offset must decrease at 1 meV/kbar. This gives a reasonable fit to the data although still significantly underestimates the pressure coefficient of the narrowest well. Data from sample B, with AlAs barriers cannot be analysed in this manner because the pressure coefficient of the direct gap of AlAs is not known. The -1 meV/kbar
### Material Parameters

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<th>Parameter</th>
<th>GaAs</th>
<th>AlGa&lt;sub&gt;x&lt;/sub&gt;As&lt;sub&gt;1-x&lt;/sub&gt;</th>
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<td>2.96&lt;sup&gt;(b)&lt;/sup&gt;</td>
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<td>2.01&lt;sup&gt;(c)&lt;/sup&gt;</td>
<td>2.01+0.005x&lt;sup&gt;(c),(d)&lt;/sup&gt;</td>
<td>2.24&lt;sup&gt;(e)&lt;/sup&gt;</td>
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<tr>
<td>( \Delta E (\Gamma-\Gamma)/dP_g ) meV/kbar</td>
<td>10.7&lt;sup&gt;(c)&lt;/sup&gt;</td>
<td>9.9 (x=0.25)&lt;sup&gt;(f)&lt;/sup&gt;</td>
<td>9.0</td>
</tr>
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<td>( \Delta E (X-\Gamma)/dP_g ) meV/kbar</td>
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<td>-1.34</td>
<td>-1.34</td>
</tr>
<tr>
<td>( m_e^* (m_o^*) )</td>
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</tr>
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<td>-0.34</td>
<td>0.40&lt;sup&gt;(j)&lt;/sup&gt;</td>
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<td>( \Delta E ) (eV)</td>
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<td>0.275&lt;sup&gt;(m)&lt;/sup&gt;</td>
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</table>

- <sup>(a)</sup> Thurmond (1975)
- <sup>(bb)</sup> Landolt and Bornstein (1982)
- <sup>(b)</sup> Olegart et al (1987)
- <sup>(c)</sup> Wolford and Bradley (1985)
- <sup>(d)</sup> Lee et al (1989)
- <sup>(e)</sup> Lorentz et al (1970)
- <sup>(f)</sup> Chandrasekhar et al (1986)
- <sup>(g)</sup> El Jari et al (1985)
- <sup>(h)</sup> Dumke et al (1972)
- <sup>(i)</sup> Miller et al (1984)
- <sup>(j)</sup> Lawaetz (1971)
- <sup>(k)</sup> Aspnes et al (1973)
- <sup>(l)</sup> Linearly interpolated between GaAs<sup>(k)</sup> and AlAs<sup>(m)</sup>
- <sup>(m)</sup> Onton (1970)

Table 5.3 Material parameters used in the modeling of the high pressure data (see text).
value for the pressure dependence of the valence band offset for sample A is contrasted with the previous results of Lambkin et al (1989), +0.26 meV/kbar, and Prins (1989), ∼-0.6 meV/kbar, discussed in section 5.3.3. In fig. 5.9 the pressure coefficient data from sample A are plotted together with other data taken from the literature for GaAs/Al$_x$Ga$_{1-x}$As quantum wells with $x=0.30$. All the samples had (100) substrate orientations. Whilst the absolute pressure coefficients may not be directly comparable, due to the use of different pressure gauges, the trend with well width in each sample should be comparable. It is seen that for (100) samples quite different trends have been observed in samples which would otherwise be considered identical.

This is a most unexpected result if we are to believe that band offsets are determined by the lineup of reference levels in the two materials and that these reference levels are a property of the bulk material. In this case the arbitrary movement of the reference levels would not be expected. These results would therefore suggest that, in some samples at least, the movement of the band offsets under pressure is determined by some interface property.

The possibility of the PL being affected by interface properties must also be considered. The greatest differences in pressure coefficients of the PL, from sample to sample, are found in narrow wells. These wells are taken to give the best measure of the pressure dependence of the offsets because the confinement energies in these wells are most sensitive to the offsets. However the confined states are also most sensitive to the interfaces in these wells. The exact mechanism by which an interface property could dominate the pressure coefficient of apparently free excitonic emissions is not clear but the possibility should not be overlooked.
Fig. 5.9. Results from the literature and this work for the pressure coefficients of the PL from (001) GaAs/Al\(_x\)Ga\(_{1-x}\)As quantum wells where \(x \approx 0.30\) are shown. The figure illustrates the discrepancy in values which exists. The data are taken from the following sources: diamonds, this work, squares and crosses, Venkateswaram et al (1986) and circles, Wolford (1986).
Samples C and D are now considered. Their data fall below the solid line (constant valence-band offset) in fig. 5.7 showing that in these samples the conduction-band offset is decreasing with pressure. The dashed line shows the predicted behaviour for the conduction band offset decreasing at 1.8 meV/kbar. The experimental data is best fitted by allowing the conduction band offset to fall at 1.6 meV/kbar for sample C and at 1.0 meV/kbar for sample D. This implies an increase in the valence band offset of 0.8 meV/kbar and 0.2 meV/kbar for sample C and D respectively. The same modeling parameters are used for these (311) orientated samples as for the (100) samples. The heavy hole masses are expected to be slightly different along the (311) direction; Fukunaga et al (1987) report a value of 0.5 $m_0$ for these samples. However this would make only a very small difference to the calculation.

In summary it can be said that the new data reported here and existing data in the literature show that the pressure coefficients of Type I transitions in GaAs/AlGaAs quantum wells behave in quite different ways in different samples. This is interpreted as a difference in the pressure dependencies of the band offsets, to which the Type I transitions are sensitive.

The high pressure crossovers are now considered. In section 5.3.3 the method by which the valence band offset may be determined from a Γ-X crossover was described. Table 5.2 gives the energies and pressures of the crossovers for each of the wells. Figure 5.8 shows the energies of these crossovers, again a large variation is observed for each of the similar samples (A, C and D with AlGaAs barriers of similar compositions). The valence band offset is determined for each of the wells using equation 5.1. The heavy hole confinement energy is estimated by first determining the valence band offset approximately from the
widest well where this energy is very insensitive to the absolute value of the offset and then by using this value to calculate the hole confinement energy for each of the other well widths. The exciton binding energy, at Γ-X crossover, is taken as 16 meV as measured in sample B (section 5.6). The determined valence band offsets are given in table 5.2 and are plotted in fig. 5.10 as a function of the crossover pressure. The data are extrapolated to zero to give the ambient pressure valence band offset. Accurate extrapolation to 0 kbar is obviously difficult, its accuracy is increased by fitting the data with a line whose slope (the pressure dependence of the valence band offset) has been determined from the Type I data. The valence-band offset may be expressed as a fraction of the total band-gap discontinuity. The values of the direct gaps used are given in table 5.3. The fractional valence-band offset, $Q_v$, for each of the samples is given in table 5.2.

Considerable variation in the value of the valence band offset is found between the samples. Again, this would not be expected if band offsets are determined by the lineup of intrinsic reference levels of the two material. A difference may be expected for different crystal orientations due to interface dipoles or perhaps the reference levels may be orientation dependent. However we note that there are considerable differences between samples of the same crystal orientation. Also that samples C and D give offsets which agree well with those determined by Wolford and Venkateswaren by the same technique on (100) orientated samples.

The nature of the crossover has not been questioned until now. The cause of the quenching of the Type I PL transitions is assumed to be due to crossover between the first confined electron state in the GaAs well and the X minima in the AlGaAs barrier. The mixing of the states in
Fig. 5.10. The valence-band offsets derived at the point of $\Gamma$-X crossover are plotted against the pressure at crossover. The solid lines show the extrapolation to ambient pressure using the previously determined pressure coefficient of the valence band offset. The symbols have the same meaning as in figs. 5.7 and 5.8.
the vicinity of crossover strongly supports the assumption that crossover is with an X-related state. However it cannot be certain that this is the band edge state as other X-related states are known to exist below the band edge (see, for example, Wolford and Bradley 1985). Such an error in assignation would lead to an over estimate of the valence-band offset by an amount equal to that by which the state lies below the band edge. The data from wells of different width can aid in determining whether a below band edge state is involved in the quenching as long as we assume that all the wells in one sample have the same valence-band offset. If quenching is caused by a state below the band edge (X) then in wide wells the valence band offset will be overestimated. This in turn will lead to an over estimate in the calculation of the hole confinement energy for narrow wells and lead to such wells appearing to have even greater valence band offsets. Thus consistency for the different well widths in the sample indicates that the true band offset is being measured. The consistencies observed in the samples reported here suggest that this is the case.

5.5 Theoretical Predictions of the Band Offsets in GaAs/AlGaAs Quantum Wells and Crystal Orientation Dependence

The intense experimental interest in determining the band offsets has been equaled by theoretical investigation. Current theories fall into two broad categories. The theories either involve a full numerical analysis of the electronic structure of a well defined interface or they consist of a simplified model, in which a reference level is assigned to each bulk material.
The 'model solid' theory of Van de Walle and Martin (Van de Walle and Martin 1986 and 1987, Van de Walle 1988) falls into the latter category. This theory is mentioned here because it is particularly adapted to describing quantum well structures under pressure (and also under strain, section 3.5.4, section 6.9). In the model solid theory an accurate band structure is first generated and then aligned on an absolute energy scale. The band structures are derived from density-functional calculations (Hohenberg and Kohn 1964). The best known deficiency of density-functional theory is its failure to predict the correct band gaps. The model solid theory therefore calculates the valence band position and adds on the experimentally determined band gap to obtain the conduction band position. A common reference level is accomplished by modeling the solid as a superposition of neutral atoms. In each atom the electrostatic potential is rigorously defined with respect to the vacuum level. The average electrostatic potential in the 'model solid' is therefore also well defined on an absolute energy scale. The valence band offset between two 'model solids' is then readily found. The conduction band offset is best found from the experimental values of the band gaps, following determination of the valence band offset. The valence band offset for a GaAs/AlAs heterojunction is determined as an example of the technique. The absolute energies of the 'average' valence band for GaAs and AlAs are determined in the theory (Van de Walle 1988) and are as follows:

\[
\begin{align*}
\text{GaAs} & \quad E_{v,\text{av}} = -6.92 \text{ eV} \\
\text{AlAs} & \quad E_{v,\text{av}} = -7.49 \text{ eV}
\end{align*}
\]

It is the offset between the highest lying valence bands, which are lifted from the average by \(1/3 \Delta_0\), which is of interest. The valence band offset for a GaAs/AlAs heterojunction is therefore given by
\[ \Delta E_v = \left( -6.92 + \frac{1}{3} \times 0.34 \right) - \left( -7.49 + \frac{1}{3} \times 0.275 \right) = 0.59 \text{ eV} \]

This is in good agreement with the value reported here for sample B (0.58 eV). A summary of the predictions, for the same valence band offset, of some other prominent theories is given in table 5.4. Most of the theories predict the valence band offset reasonably well, but given the experimental uncertainties there is little evidence to promote a preference for one theory over another.

<table>
<thead>
<tr>
<th>GaAs/AlAs Valence-Band Offset (eV)</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCIP(^{(a)})</td>
<td>0.25</td>
</tr>
<tr>
<td>HAO(^{(b)})</td>
<td>0.04</td>
</tr>
<tr>
<td>Tersoff(^{(c)})</td>
<td>0.35</td>
</tr>
<tr>
<td>FKP(^{(d)})</td>
<td>0.3</td>
</tr>
<tr>
<td>VW1(^{(e)})</td>
<td>0.37</td>
</tr>
<tr>
<td>VW2(^{(f)})</td>
<td>0.59</td>
</tr>
</tbody>
</table>

(a) Self consistent interface potential (Pickett et al 1978)
(b) Harrison atomic orbital (Harrison 1977)
(c) Tersoff (1984)
(d) Frensley-Kroemer pseudopotential (Fresley and Kroemer 1977)
(e) Van de Walle and Martin, self-consistent calc. (1987)
(f) Van de walle and Martin, Model Solid Theory (1988)

Table 5.4 A comparison of theoretical predictions of the valence band offset in GaAs/AlAs heterojunctions.

The methods of Van de Walle and Martin are also able to make predictions of the pressure dependence of the offsets. For GaAs/AlAs heterojunctions, the self-consistent model predicts a value for the pressure dependence of the valence-band offset as +0.8 meV/kbar. The 'model-solid' theory predicts a value of 1.8 meV/kbar. These values are of the same order as the experimental values reported here.
The 'model-solid' theory is one theory which has considered the effect of crystal orientation on the band offsets (Van de Walle and Martin 1987 and 1988). The authors find no orientation dependence for non-polar interfaces within the accuracy of the model. For polar interfaces it has been shown that the rearrangement of atoms can change the band offsets (Kunc and Martin 1981). This is supported by experimental evidence on the two-dimensional hole densities in $\text{Al}_{0.26}\text{Ga}_{0.74}\text{As/GaAs}$ heterojunctions. Wang et al (1985) studied (100) and (311) interfaces and found the offsets to be orientation independent. This is in contrast to some systems, such as Ge/GaAs interfaces, where there is strong evidence of orientation dependence (Grant et al 1978, Bauer et al 1983).

5.6 Exciton Binding Energies in GaAs/AlAs Quantum Wells

5.6.1 Introduction

Much work has been done to determine the exciton binding energies in quantum wells. GaAs/AlGaAs quantum wells have received particular attention both experimentally and theoretically. In this section the binding energies of the exciton in the vicinity of $\Gamma$-$X$ crossover are investigated. This is an important parameter in determining the band offsets from Type II luminescence (eqn. 5.1) and so is of interest here. Results from Type I and Type II quantum well systems have been reported in the literature. This is, however, the first work to report on the transition region and to consider the effect of $\Gamma$-$X$ mixing on the binding energies.
The binding energies are found, in this work, by measuring the energy separation between the ground state (1S) luminescence peak and that of the first excited state (2S) of the exciton. The 2S binding energy may be calculated and hence the 1S binding energy accurately determined. The Γ-X crossover is induced by hydrostatic pressure.

5.6.2 Experimental Details

The GaAs/AlAs superlattice samples were grown by MBE at the Philips Research Laboratories, Redhill. Each consisted of several periods of GaAs wells with 75Å wide AlAs barriers. Sample B has been described in section 5.4.1, sample E was similar but with 60Å wide wells.

The high pressure experiments were conducted as previously described. Argon was used as the pressure transmitting medium. GaAs substrate emission from the sample itself served as the pressure gauge. Detection of the weak 2S feature in the DAC proved difficult. This was partly due to the reduced signal to noise ratio. The use of a high laser intensity was not possible as this caused the 1S feature to broaden and obscure the 2S feature. The samples were also found not to be uniform, with some parts of the sample exhibiting no 2S feature at all or only a weak feature. PL at ~10K therefore had to be performed on a number of DAC size (50μm by 50μm) pieces to select one suitable for the experiment before loading. PL in the high pressure experiments was detected using a GaAs photomultiplier tube and photon counting. This provided sufficient sensitivity to detect the 2S feature.
5.6.3 Experimental Results

The ambient pressure spectra, recorded outside the DAC, are shown in fig. 5.11. In each case a strong luminescence feature characteristic of quantum well emission is observed with a weaker peak to higher energy. These are assigned as the 1S and 2S luminescence features of the exciton respectively. Table 5.5 summarises the sample details and the spectral features.

Figure 5.12 shows the behaviour of sample B under pressure. The PL energy of the 1S and 2S features and a low energy feature are plotted against the GaAs substrate emission energy. Figure 5.13 shows the intensity of the 1S and 2S features as a function of the GaAs energy. The intensity cuts off sharply at ~1.5 kbar and is reduced to an undetectable level by about 8 kbar. This cut off is assigned as a \( \Gamma - X \) crossover as previously discussed for this sample in section 5.4. The intensity of the 2S feature stays roughly in proportion with the 1S feature and is soon (~1 kbar) undetectable. No Type II luminescence is observed, although some evidence of \( \Gamma - X \) mixing may be being seen at around 1.502 eV (GaAs emission energy). The pressure coefficient of the 1S peak is measured to be 10.4 meV/kbar. The 2S feature rises in energy, with pressure, but less rapidly than the 1S.

To lower energy a rather strong luminescence feature is observed (not shown in fig. 5.11). This feature maintains approximately constant intensity throughout the pressure range studied. At ambient pressures its intensity is much less than that of the 1S feature. However as the 1S, emission quenches this feature begins to dominate the PL spectrum. The pressure coefficient of the feature is found to be 8.6 meV/kbar.
Fig. 5.11. Photoluminescence spectra measured at 10K for samples (a) B and (b) E. The strong 1S feature is shown on the left with the corresponding weak 2S feature on the right.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Well Width (Å)</th>
<th>PL Features(eV)</th>
<th>1S-2S Splitting (meV)</th>
<th>1S Binding Energy (meV)</th>
<th>Calculated B &amp; G Dawson Ghiti (Γ)</th>
<th>Ghiti (X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B (G167)</td>
<td>40</td>
<td>1.683</td>
<td>1.700</td>
<td>17</td>
<td>19</td>
<td>10.5</td>
</tr>
<tr>
<td>E (G171)</td>
<td>60</td>
<td>1.613</td>
<td>1.626</td>
<td>13</td>
<td>14.6</td>
<td>9.8</td>
</tr>
</tbody>
</table>

B & G - Green and Bajaj (1983)
Dawson - Dawson et al (1986)
Ghiti (Γ and X, see text) - Ghiti (1990a)

Table 5.5 The table summarises the ambient pressure data from samples B and E. The energies of the 1S and 2S spectral features and the inferred exciton binding energies are given. On the right some theoretically determined 1S binding energies are given for comparison.
Fig. 5.12 The energies of the emissions from sample B are shown as a function of pressure (GaAs emission energy). At high energy the features assigned to the 1S and 2S states of the exciton are shown. At low energy the emission from an unassigned feature, moving at 8.6 meV/kbar, is shown.
Fig. 5.13. The intensities of the 1S and 2S emissions shown in fig. 5.12 are plotted against the GaAs emission energy.
5.6.4 Analysis and Discussion.

The assignment of the spectral features is considered first. The main spectral feature at ambient pressure is an intense sharp peak, characteristic of excitonic quantum well emission. This peak is at the expected energy for el-hhl transitions, for the given well widths. It is therefore assigned as the ground state (1S) of the heavy-hole exciton.

Workers at Philips Research Laboratories have studied the high energy feature and assign this as the excited state (2S) of the exciton (Moore et al 1986, Dawson et al 1986). Using PL and photoluminescence excitation spectroscopy, with polarised light, they have confirmed the heavy-hole nature of the transition. To date their work has been principally concerned with GaAs/Al\(_{0.30}\)Ga\(_{0.70}\)As structures, in these samples the energy of the 2S feature agrees well with their calculations (Dawson et al 1986, Duggan et al 1985) of its energy, further confirming the assignment. From the PL and PLE spectra the Stoke's shift in these samples is found to be < 1 meV; this allows confident determination of the 1S-2S splitting.

Other transitions, of similar energy, which could conceivably be assigned to the '2S' feature are briefly considered. It is found that none of them are consistent with all of the data. Firstly, the el-lhl transition, this is calculated to be at too high an energy and in any case would not be consistent with the polarisation experiments (heavy-hole transition). Secondly, Type II transitions between the barrier X minima and the GaAs heavy-hole state. For sample B the ambient pressure energy would be approximately correct. However the feature moves up in energy with increasing pressure, which would not be expected for an X-related transition (even considering \(\Gamma-X\) mixing, see
fig. 5.16). Although such a transition is strongly prohibited and emission from such a state most unexpected when it is above the well state in energy, such emissions have been reported (Meynadier et al 1988). Meynadier et al use an electric field to switch the GaAs/AlAs superlattice from Type I to Type II. In their case the intensity of the Type II luminescence then increases as would be expected. The opposite is observed for our '2S' feature. Finally, we consider the effect of well width fluctuations on the PL. A narrowing of the well by ~2 monolayers would account for the energy of the '2S' feature in these two samples but not in other wide well samples studied at Philips (see fig. 5.14). It may therefore be concluded that the 2S assignment made by Dawson et al (1986) and Moore et al (1986) is most likely correct. The low energy luminescence feature has not been assigned, this may be a deep level of some sort. The deep level assignment is supported by the pressure coefficient of this feature, 8.6 meV/kbar.

Figure 5.14 shows the results from a series of samples studied at Philips, giving the 1S-2S splitting for samples with various well widths and barrier compositions. The new data from samples B and E have been added. The exciton binding energy is determined from the 1S-2S splitting by adding the binding energy of the 2S state. This has been calculated by the Philips group (Dawson et al 1986). The results are shown in fig. 5.15(b) for two different in-plane heavy hole masses. It is seen that the 2S binding energy is much less than the 1S-2S splitting. This means that absolute errors in the calculation will be small. An accurate determination of the 1S binding energy is therefore possible. The values calculated by Duggan et al (1985) for binding energies as a function of well width are also shown in the figure. The 1S-2S splitting and binding energies are given in table 5.5. Calculated values for the 1S binding
Fig. 5.14. Values of the 1S-2S splittings from a series of GaAs/Al$_x$Ga$_{1-x}$As samples are shown as a function of well width. The solid squares represent the new data reported here for GaAs/AlAs superlattices. The remaining data are taken from Moore et al (1986): solid circles, $x = 0.35$, crosses, $x = 0.40$ and open square, $x = 1$. 
Fig. 5.15. The calculated dependence of (a) the 1S and (b) the 2S binding energies of the heavy-hole exciton as a function of well width. The figures are taken from Dawson et al (1986). The figures show that the 2S binding energy is much smaller than the 1S. The two curves in each figure show the sensitivity of the calculation to the value of in-plane heavy-hole mass used (solid curve 0.18m₀, dashed curve 0.25m₀).
energies are also given in the table for comparison. Values taken from Greene and Bajaj (1983) for infinite potential wells, from Dawson et al (1986) for GaAs/Al$_{0.30}$Ga$_{0.70}$As for the same well widths and from Ghiti (1990a) for GaAs/AlAs quantum wells. In the case of Greene and Bajaj the use of infinite barriers in the calculation should provide an upper bound for the binding energies. In addition their calculations are by a variational method, this results in the variational binding energies being rigorous upper bounds for the true binding energies. The calculations of Dawson et al are different in that they include light- and heavy-hole mixing and non-parabolicity in the conduction band and the calculations are not made by a variational approach (details are given in Duggan et al 1985). Their results on the binding energies are expected to be increased by ~1 meV (Greene and Bajij 1983) for GaAs/AlAs structures, giving a predicted value of approximately 14.5 meV for sample B and 13 meV for sample E. The calculations of Ghiti follow the approach of Ekenberg and Altarelli (1987) and have been fully described in Ghiti (1990b).

The calculated values somewhat underestimate the experimentally determined values. In fact the measured 1S binding energies are more characteristic of excitons found in indirect bulk III-V semiconductors eg 20.5 meV in GaP (Humphreys et al 1978). Miller et al (1981) have also measured binding energies from 1S-2S splitting and report similar large values. Although the 2S feature was not as clearly defined in their spectra as in those shown here, leading to doubt about the assignment.

In fig. 5.12 the binding energy of the 1S exciton is seen to drop from ~19 meV at ambient pressure to ~16 meV at Γ-X crossover, as determined from the PL intensity. Calculations by Salmassi and Bauer (1989) predict the Type II binding energy of sample B to be ~12 meV. We
find a value of \(-16\) meV at \(\Gamma-X\) crossover when the structure is just turning Type II. Hodge et al (1990) have experimentally determined the Type II binding energies for several GaAs/AlAs structures, using a novel induced far-infrared absorption technique, and find good agreement with the theory of Salmassi and Bauer. For example for a 25.4/39.6 Å GaAs/AlAs superlattice they find that the Type II exciton has a binding energy of 13.2 meV compared with a calculated value of 14 meV. Ghiti (1990a) has estimated an upper bound for the Type II binding energy, by using the method described above for Type I binding energies, for the structure at 0 kbar. The AlAs X-minima mass and a confining potential given by the difference in energy of the X levels in the well and barrier are used in the calculation. However a Type I alignment has to be assumed; this then gives an upper bound for the exciton binding energy since in the true Type II alignment the energy will be reduced by the spatial separation of the carriers. At ambient pressure this gives values of 19.2 meV for the 40 Å wells and 16.9 meV for the 60 Å wells. These values are included in table 5.5 for comparison.

Theoretical investigations to date have considered only Type I and recently Type II excitons. These calculations have not considered the influence of \(\Gamma-X\) mixing in the conduction band nor modeled the transition from Type I to Type II. We are not currently able to make quantitative predictions but we may consider qualitatively what the influence of these effects would be. If the exciton is considered as a 'Hydrogen-like' molecule, moving in the periodic crystal, the only effect of which is to provide the electron and hole with their effective masses. The binding energy may then be expressed as

\[
E_B = \frac{\mu e^4}{2 \hbar^2 e^2} \quad [5.3]
\]
where \( \mu \) is the reduced mass and \( \varepsilon \) is the dielectric constant of the crystal. If the \( \Gamma \) and \( X \) states mix the electron mass will increase towards that of the \( X \) electron. Substitution of the \( X \) mass for the \( \Gamma \) mass in eqn. 5.3 increases the binding energy by a factor 5. The degree of \( \Gamma-X \) mixing under pressure may be simply modeled as follows. Away from the crossover the wavefunctions are described in the envelope function approximation as

\[
\Psi_{\Gamma} = F_{\Gamma}(z) \ u_{\Gamma}(r) 
\]

and

\[
\Psi_{X} = F_{X}(z) \ u_{X}(r) \quad [5.4] 
\]

where \( F_{\Gamma} \) and \( F_{X} \) are the slowly varying envelope functions and \( u_{\Gamma} \) and \( u_{X} \) are the Bloch states. The simplifying assumption is made that the only relevant interaction is between one \( \Gamma \) and one \( X \) state. This leads to familiar results for the general two state problem (Feynman 1965). The wavefunction of the mixed states is expressed as

\[
\Psi(r) = a_{1}\Psi_{\Gamma} + a_{2}\Psi_{X} \quad [5.5] 
\]

The Hamiltonian is

\[
H = \begin{pmatrix}
E_{\Gamma}\varepsilon & E_{\Gamma} \\
\varepsilon & E_{X}
\end{pmatrix}
\]

where \( \varepsilon \) is the interaction potential. The eigenvalues are
Despite the restricted assumptions, this model represents the essential elements of the problem. Figure 5.16 shows the calculated eigenvalues of the states for the sample B as a function of pressure. The value of $\varepsilon$ is taken as 3 meV (Meynadier et al 1988). The confinement energies and their pressure dependencies are derived from the envelope function model described in chapter 3. The pressure coefficient of the direct gap of AlAs is not known, a value of 9 meV/kbar is assumed. The pressure dependence of the valence band offset is taken as +1.1 meV/kbar. This choice of pressure coefficients predicts a coefficient of 10.3 meV/kbar for the $\Gamma$ state, very close to the value of 10.4 meV/kbar observed experimentally. From fig. 5.16 it is seen that at ambient pressure the states are barely mixed and so we would not expect any significant contribution to the binding energy. At $\Gamma$-X crossover the states are strongly mixed and we would expect an increase in the binding energy due to the increased mass. The mass of the electron also increases with pressure, as described by k.p theory but this is a very small effect at the low pressures being discussed here. The effect of confinement on the exciton is now considered. The effect of the closer proximity of the electron and hole is to increase their binding energy. This may not be expressed simply. Methods for determining the influence by the variational approach, for example, are described by Greene and Bajaj (1983) and Greene et al (1984). In this case, when there is little $\Gamma$-X mixing the exciton is confined by the conduction band and valence band offsets. When $\Gamma$-X mixing occurs the appropriate confining potential in
Fig. 5.16. The result of a calculation of the mixing of the $\Gamma$ and $X$ states, as discussed in the text, for sample B is shown. The figure shows the $\Gamma$-$X$ crossover at $\sim$2 kbar. The figure shows that the states at 0 kbar are not significantly mixed since they have the distinct pressure coefficients characteristic of the pure states.
the conduction band is not clear. When the $\Gamma$ and $X$ states are coincident in the superlattice and the states are mixed by the interface potential there will be no potential barrier in the conduction band. The effective confining potential must then fall as $\Gamma$-$X$ crossover is approached. This tends to reduce the exciton binding energy as the wavefunction overlap is reduced. There are therefore two competing effects which determine the 1S exciton binding energy, the electron mass and the confining potential. Which of these effects should dominate is not clear without a full calculation. However current methods for calculating binding energies are not particularly suitable for considering mixed states. Experimentally it appears that the effect of the confining potential is most important.

5.7 Summary and Suggestions for Further Work.

Techniques for determining the band offsets in quantum well structures and their pressure dependencies by high pressure PL have been described in detail. Direct spectroscopic measurement of the valence band offset has shown that this parameter can vary considerably from sample to sample. This is an important result for device manufacturers. The data presented here are insufficient to speculate on the underlying cause of this discrepancy. A larger data set is required so that such factors as growth temperature, growth technique, impurities etc can be correlated. The question of orientation dependent band-offsets must remain open until this matter is settled.

Exciton binding energies as a function of pressure in the vicinity of $\Gamma$-$X$ crossover have been measured for the first time. The binding
energy is found to fall slightly as the Type I-Type II crossover is approached. The binding energies are found to be higher than predicted theoretically even when little $\Gamma$-X mixing is expected. The high pressure data from sample E, where the $\Gamma$ and X states are separated by a greater energy at ambient pressure, should prove more informative. This may show that it is indeed $\Gamma$-X mixing which is responsible for the high values of the 1S binding energy. A full theoretical calculation is still required to describe the binding energy in the transition region from Type I to Type II lineups. Experiments are in hand to study the binding energy of Type I X excitons for the first time. This will be done in an InAlGaAs/AlGaAs superlattice where X is the lowest conduction band state throughout the structure. This data may shed some light on the results reported here.
Chapter 6

HIGH PRESSURE PHOTOLUMINESCENCE OF InGaAs/AlGaAs
STRAINED-LAYER QUANTUM WELL STRUCTURES

6.1 Introduction

In this chapter the effects of pressure on the PL of strained In\textsubscript{\textit{x}}Ga\textsubscript{\textit{1-x}}As layers, grown pseudomorphically on GaAs, are discussed. The hydrostatic pressure coefficients of the photoluminescence of strained-layer quantum wells are found to be unexpectedly low, and to depend linearly on composition. A related strained system, InAs grown pseudomorphically on InP, is found to exhibit low coefficients also. A small reduction in the pressure coefficient of the strained layers, compared to the bulk alloy, is predicted but is not sufficient to account for the experimental results.

At high pressures $\Gamma$-X crossovers are observed. A study involving In\textsubscript{\textit{x}}Ga\textsubscript{\textit{1-x}}As/GaAs and In\textsubscript{\textit{x}}Ga\textsubscript{\textit{1-x}}As/AlGaAs samples allows the nature of the crossovers to be identified. In the InGaAs/GaAs structures $\Gamma$-X crossovers are assigned as Type I crossings with the well X minima. This allows, for the first time, a direct measure of the position of the X minima in a strained material. In the InGaAs/AlGaAs structures the crossovers are assigned Type II crossings with the AlGaAs barrier X minima. This allows accurate determination of the band-offset ratio for
6.2 Motivation for the Work

Strained layers, in particular InGaAs grown pseudomorphically on GaAs, are currently of great interest (Kirby et al 1989, Eng et al 1989, O'Reilly 1989). However little is known of the fundamental parameters in this material system. This chapter is concerned with the characterisation of this system by high-pressure PL. This work constitutes part of a program at Surrey, coordinated by the Strained-Layer Structures Research Group. The group is principally concerned with the development of strained-layer lasers operating at 1.55μm, where losses in optical fibres are at a minimum. The InGaAs/GaAs material system offers the possibility of the required wavelength at the right composition, together with improvements in device performance due to strain. Strain is predicted to reduce Auger and inter-valence band absorption (Adams 1986), which are the primary loss mechanisms in long wavelength lasers. Figure 6.1 illustrates these loss mechanisms. The effect of compressive strain on the valence band is to give it a 'light-hole like' cap. This confines the holes near k=0 and is therefore predicted to reduce these losses. The affects of strain are expected to be beneficial for other devices, for example, high speed complementary logic.
Fig. 6.1 Schematic diagrams of the major loss mechanisms in long wavelength lasers, (a) Auger recombination, (b) IVBA. These losses are predicted to be reduced by the strain induced modification of the valence band.
6.3 Hydrostatic Pressure Coefficients of the Photoluminescence of InGaAs/GaAs Strained-Layer Quantum Wells

6.3.1 Introduction

The PL of strained InGaAs quantum wells has been studied under hydrostatic pressure. The pressure coefficient of the PL is found to decrease strikingly with increasing indium content or well width. This is not predicted theoretically; the pressure coefficient of the direct gap of In\(_{x}\)Ga\(_{1-x}\)As is expected to be approximately constant across the alloy range. Low values for the pressure coefficients of the PL from strained InGaAs layers have been reported previously (Wang et al 1989, Hou et al 1990).

This has led to an examination of whether either the hydrostatic deformation potential 'a' or the axial deformation potential 'b' should be strongly strain dependent. The effects of disorder and strain in the alloy are discussed. The pressure coefficients of InAs strained-layer quantum wells grown pseudomorphically on InP have also been studied. This gives a useful comparison with the InGaAs wells since composition and strain have been varied independently. Additionally the well material is no longer an alloy so that the effects of alloy disorder, which are difficult to quantify, can be neglected. These data also show low pressure coefficients. The two sets of results are shown to be consistent if strain is assumed to be the cause of the anomaly. Results from the literature, on other strained-layer material systems are discussed.
<table>
<thead>
<tr>
<th>Sample Parameters</th>
</tr>
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<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>InGa\textsubscript{x}Al\textsubscript{1-x}As/GaAs Samples</td>
</tr>
<tr>
<td>A (ME482)</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
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<tr>
<td>B (ME501)</td>
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<tr>
<td></td>
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<td></td>
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</tr>
<tr>
<td>C (ME566)</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td>InAs/InP Samples</td>
</tr>
<tr>
<td>D (M115) (univ. of Sheffield)</td>
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<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>E (C169) (STC)</td>
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<tr>
<td></td>
</tr>
<tr>
<td>InGa\textsubscript{x}Al\textsubscript{1-x}As Samples</td>
</tr>
<tr>
<td>F (ME673)</td>
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<td></td>
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<td></td>
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<tr>
<td>G (ME613)</td>
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</tbody>
</table>

Table 6.1 The sample parameters
6.3.2 Experimental Details

The InGaAs/GaAs samples were grown by MBE in a Vacuum Generators V80H reactor at the Royal Signals and Radar Establishment. The compositions predicted by the RHEED oscillations had been previously confirmed by several techniques (Energy-dispersive x-ray microprobe, Rutherford backscattering, optical absorption and double crystal x-ray diffraction) on thick relaxed layers. The compositions predicted by the RHEED oscillations are therefore taken as correct for the quantum wells. The InAs/InP samples were grown by MBE at the SERC growth facility, University of Sheffield and by MOCVD at STL. The InGaAs/GaAs series of samples consisted of two samples with several quantum wells of varying width, each with a different \( \text{InGaAs} \) composition (sample A, ME482 \( x = 0.15 \) and sample B, ME501 \( x = 0.20 \)) and a third sample with wells of constant width but with varying composition (sample C, ME566). In each case the GaAs barriers were 500Å wide so that the wells were both electronically and structurally isolated from each other. The well widths and compositions were chosen so that each well was below critical thickness as determined by theory (Matthews and Blakeslee 1974, 1975, 1976, People and Bean 1985) and by TEM measurements (Dixon and Goodhew 1990). The combined structures were also below critical thickness. The samples were not intentionally doped, the background doping was about \( 10^{14} \) cm\(^{-3}\). The InAs/InP samples consisted of several InAs wells of varying thickness (sample D, M115 and sample E, C169). The sample parameters are summarised in table 6.1.

PL spectra, taken at 10-20K, for each of the InGaAs/GaAs samples are shown in fig. 6.2. In each case a sharp peak is observed for each quantum well in the sample. This is characteristic of
Fig. 6.2 PL spectra from the InGaAs/GaAs samples recorded at 10K-20K, (a) sample A at ambient pressure, (b) sample B at ambient pressure and (c) sample C at 5 kbar. In (c) the emission from the GaAs pressure gauge is also shown.
Fig. 6.3 PL spectra from the InAs/InP samples. (a) sample D, recorded at 10K and 0 kbar. (b) sample E, recorded at 80K and 32 kbar.
free-exciton quantum well emissions and indicates the quality of the strained layers. PL spectra for the InAs/InP samples are shown in fig. 6.3. Sample D shows sharp excitonic emission although the FWHM are greater than for the InGaAs quantum wells. Sample E, containing two quantum wells, shows a single broad emission. The width of the emission in both of these samples is probably attributed to a combination of effects (well-width fluctuations, partial strain relaxation, defect emissions).

The sample preparation and high pressure experiments were conducted as previously described (chapter 4). Argon was used as the pressure transmitting medium and all spectra were recorded at ~10K, except for sample E where measurements were made at 80K.

The emission from another semiconductor was used as a pressure gauge in each of the experiments, except in the case of sample E where ruby luminescence was used. The most precise measurements of pressure coefficients are obtained by plotting the PL peak energies against an emission band whose pressure coefficient is already known (Lambkin et al 1988), and preferably a band which is of physical significance to the problem. For the InGaAs/GaAs samples (A–C) GaAs was used as the pressure gauge up to about 40kbar where the PL is quenched by the Γ-X crossover. Above this pressure a piece of InP was used to provide the pressure gauge. The GaAs band edge emission shifts at 10.7 meV/kbar (Wolford and Bradley 1985), InP shifts at 8.5 meV/kbar–0.018 meV/kbar² (Muller et al 1981). Above the GaAs Γ-X crossover the GaAs band gap may be estimated from the InP emission taking account of the nonlinearity in the GaAs pressure coefficient (-0.014 meV/kbar²) (Goni et al 1987), which becomes significant at these pressures. The GaAs coefficient is of obvious physical significance to the problem. InP is simply used as a convenient
pressure gauge. For the InAs/InP sample D the InP capping layer provides a convenient pressure gauge. This is the best pressure gauge possible, not only does it provide a gauge over the entire range of the experiment but it is also of physical significance in the experiment, being the barrier layer, and furthermore is actually in the sample, thus eliminating fears of pressure differences in the sample space.

6.3.3 Experimental Results from InGaAs/GaAs Structures

Figure 6.4 shows the difference between the emission peak energy for each quantum well and the GaAs emission plotted against the GaAs emission energy for sample C. Samples A and B behaved in a similar manner. The arrow in fig. 6.4 indicates where the GaAs emission was quenched; at higher pressures the GaAs band gap has been estimated from the InP energy. Plotting the data in this way allows an accurate measure of differences in pressure coefficients, whilst accurate knowledge of the GaAs pressure coefficient is not necessary. Since the GaAs emission is weaker and broader than the quantum well emissions error in determining its position show up as scatter in the data with the same scatter for each well, this is seen in fig. 6.4.

Figure 6.5 shows PL and absorption spectra (Allegre 1990) for an In$_{0.15}$Ga$_{0.85}$As quantum well, similar to the ones studied here. The Stoke's shift is ~1-2 meV, indicating the high quality of the material.

At low pressures direct $\Gamma_6$-$\Gamma_8$ quantum well luminescence is observed with the characteristic ~10 meV/kbar pressure coefficients. At higher pressures the PL is strongly quenched, the pressure coefficients are reduced and finally move down in energy with increasing pressure at a
Fig. 6.4 The difference between the InGaAs quantum well PL energy and the GaAs (pressure gauge) emission energy is plotted against the GaAs emission energy. The figure shows Γ-like behaviour at low pressure turning into Χ-like behaviour at higher pressures. The arrow indicates the pressure above which the GaAs energy has been inferred from the InP emission (see text).
Fig. 6.5 The PL, absorption and reflectivity spectra are shown for an In$_x$Ga$_{1-x}$As/GaAs 110Å quantum well. Comparison of the PL and absorption spectra reveals a very small Stoke’s shift, ~1-2 meV  (Allegre (1990)).
rate characteristic of the X minima. This is observed most clearly in sample C as seen in fig. 6.4. These Γ-X crossovers give detailed information on the electronic structure of the system. This is discussed fully in the second half of this chapter, we are initially concerned only with the direct gap pressure coefficients.

6.3.4 Analysis of InGaAs/GaAs Results

It is found that the pressure coefficient of the PL decreases strikingly when either the well width or the indium content is increased. First, the data from samples A and B, where the composition is constant in each well but the well widths vary, are considered. In figure 6.6(a) the pressure coefficients of the PL from each well is plotted against well width whilst fig. 6.6(b) shows the same data plotted against inverse well width. It has already been seen, in chapter 5, that in GaAs/AlGaAs quantum wells the pressure coefficient of the PL increases with increasing well width. Conversely, we see here that in InGaAs/GaAs structures the pressure coefficient decreases with increasing well width. Factors affecting the pressure coefficient of quantum well transitions have been discussed in chapters 3 and 5 and are not reiterated here, except to say that in the wide well limit, when confinement effects become negligible, the pressure coefficient of the PL must tend to the bulk material value. For example in GaAs/AlGaAs quantum wells, the wide well limit is 10.7 meV/kbar, the pressure coefficient of bulk GaAs. By plotting the data against inverse well width, as in fig. 6.6(b), we are able to extrapolate to infinite well width to obtain the pressure coefficient of bulk strained InGaAs. These values are found to be 9.4 meV/kbar for x=0.15 and 9.1 meV/kbar.
Fig. 6.6  (a) The pressure coefficients of the PL from samples A (triangles) and B (solid circles) are plotted against well width. (b) The same data is replotted against inverse well width; this allows extrapolation to infinite well width to determine the pressure coefficient of bulk strained InGaAs.
for $x=0.20$. In GaAs/AlGaAs quantum wells the increase in pressure coefficient with well width is described, to first order, by the difference in pressure coefficients of the well and barrier material and the proportion of the carrier wave function in each. The barrier material has a lower pressure coefficient than the well material. As the well gets narrower and more of the wave function is in the barrier the pressure coefficient of the quantum well emission consequently drops. Thus if we are to believe the extrapolations of fig. 6.6(b), in the InGaAs/GaAs system the pressure coefficient of the well material is lower than that of the barrier and therefore a reversed trend is to be expected. However other effects can determine the pressure coefficient of a confined state, in particular, in narrow wells the confinement energy can be very sensitive to changes in the band offsets under pressure. In fig. 6.7 the data from sample B are replotted and an attempt is made to fit the well width dependence of the pressure coefficient. The solid curves are theoretical predictions based on the following assumptions. In each case an initial 60:40 (CB:VB) offset ratio is assumed. The effective mass of the electron is assumed to increase linearly with pressure or increasing band gap. For curve a, it is assumed that the pressure coefficient of the well material is equal to that of the GaAs barrier, 10.7 meV/kbar and that the band offsets do not vary under pressure. In this case the predicted pressure coefficient of the PL remains approximately constant with well width. The small deviation from 10.7 meV/kbar is due to the increase in effective mass with pressure which decreases the confinement energy slightly. In curve b, we show that it is not possible to get the required reduction in the pressure coefficient by varying the band-offset ratio with pressure while keeping the pressure dependence of the quantum-well band gap
Fig. 6.7 The pressure coefficients from sample B are replotted against well width and a theoretical fit is attempted. The solid curves show the predicted behaviour for different models as described in the text.
constant at 10.7 meV/kbar. The valence-band heavy-hole band offset is increased at 1.5 meV/kbar. This accounts for the data relatively well in thin wells but considerably over estimates the pressure coefficients for wide wells. This must evidently be the case, since it is the wide wells which exhibit the most surprising pressure coefficients; these wells are least sensitive to the band offsets. In curve c, we obtain excellent agreement with the experimental data by allowing the pressure coefficient of the well material to be equal to that of the wide well extrapolation (9.4 meV/kbar). The valence band offset is assumed to be independent of pressure. We see, that for each of the three models, the data is reasonably well fitted for narrow wells, tending to the GaAs pressure coefficient at L =0. This is to be expected; when the well is infinitely narrow all of the wave function is in the GaAs barriers. However the wide well behaviour can only be described by assuming that the pressure coefficient of the well material is indeed significantly lower than that of GaAs.

The data from sample C are able to show how the pressure coefficient of bulk strained InGaAs varies with indium content x. In this sample the wells are wide (100Å) and the pressure coefficients are therefore a good approximation to that of the bulk material. The well width remains below critical thickness. Note that in fig. 6.7, curve c, the pressure coefficient of 100Å wells is only 0.1 meV/kbar greater than that of the bulk material. Data from sample C are plotted in fig. 6.8 where the variation of pressure coefficient with alloy composition is seen to be linear. Also shown are the values for bulk InAs (Tsai et al 1974) and for In_{0.53}Ga_{0.47}As (Lambkin and Dunstan 1988) lattice matched to InP. The data indicate that the pressure coefficient of the PL varies as (10.7-6.0x) meV/kbar for strained InGaAs. In contrast the values
Fig. 6.8 The pressure coefficients from sample C are plotted against the well InGaAs composition. The line illustrates the empirically determined behaviour of 10.7-6.0x meV/kbar.
for the bulk unstrained materials suggest that the pressure coefficient should be approximately constant across the alloy range.

This result is most surprising. The analysis so far has shown that the unexpected pressure coefficients arise from the strained InGaAs well material itself and are not an artifact of the system under pressure, such as rapidly varying band offsets. We are thus forced to consider the influence of higher-order elastic constants and strain-dependent deformation potentials on the pressure coefficients. This analysis (E.P. O'Reilly 1990) is given in appendix C. The important results are reiterated here and compared with the experimental data.

The pressure dependence of the band gap may be expressed as

$$\frac{dE_g}{dP} = a \frac{d}{dP} (3 \epsilon_{||}) + (a + b) \frac{dc_{ax}}{dP}$$  [6.1]

where $a$ and $b$ are the hydrostatic band-gap deformation potential and the axial deformation potential respectively. Assume, for the moment, that the deformation potentials are independent of strain. The strained well pressure coefficient may be written in terms of the unstrained alloy coefficient,

$$\frac{dE_g}{dP} = \frac{B_x}{B_s} \frac{dE_g^0}{dP} + (a + b) \frac{dc_{ax}}{dP}$$  [6.2]

The values of the terms on the right hand side of equation 6.2 may be estimated as follows. The bulk modulus of In$_x$Ga$_{1-x}$As has not been measured; however for a wide range of materials $B$ is observed to follow the empirical relationship $B \propto a^{-4}$, where $a$ is the alloy lattice constant (Prins and Dunstan 1988). We therefore estimate $B_x/B_s$ as
\[ \frac{B_x}{B_u} = \left( \frac{a_x}{a_u} \right)^4 \approx 1 + 4\varepsilon_0^0 \]

\[ \approx 1 - 0.28x \]  

where \( \varepsilon_0^0 \) is the in-plane strain at \( P=0 \), and depends on the composition \( x \) as \( \varepsilon_0^0 \approx -0.07x \) for InGaAs lattice matched to GaAs. The pressure coefficients of the bulk unstrained alloys is taken to be 10.7 meV/kbar, the value for GaAs, independent of composition. This is justified by existing measurements for bulk InAs (10.2 meV/kbar) and In\(_{53}\)Ga\(_{47}\)As on InP (10.95 meV/kbar) which suggests that the pressure coefficient is not strongly composition dependent in the unstrained alloy.

The pressure dependence of the axial strain can be estimated using elasticity theory. This is given in appendix C and yields the result

\[ \frac{dE_x}{dP} = \frac{4}{3} \left( \frac{b}{a} \right) \varepsilon_0^0 \frac{1 + \sigma_x^0}{1 - \sigma_x^0} \frac{dE_0^0}{dP} \]

\[ \approx -\frac{10}{3} \varepsilon_0^0 \frac{dE_0^0}{dP} \]  

where typical values of \( \sigma_x = \frac{1}{3} \) and \( b/a = \frac{1}{4} \) are taken.

Substitution of these estimates in eqn. 6.2 gives a value for the pressure coefficients of the strained layers assuming strain-independent deformation potentials of

\[ \frac{dE_g}{dP} = \left( 1 + 4\varepsilon_0^0 \right) \frac{dE_0^0}{dP} + \left( -\frac{10}{3} \varepsilon_0^0 \frac{dE_0^0}{dP} \right) \]  

The first term on the right of eqn. 6.6 acts to decrease the pressure
coefficient below that of the unstrained alloy whilst the second term acts in the opposite direction. The combined effect is expressed by

\[
\frac{dE(x)}{dP} = \left(1 + \frac{2}{3} \varepsilon^0_{||}\right) \frac{dE^0_{||}}{dP}
\]

\[
= 10.7 - 0.5x \text{ meV/kbar} \quad [6.7]
\]

Whilst this predicts an overall reduction in the pressure coefficients of the strained-layers with alloy composition, the magnitude of the variation is nowhere near sufficient to describe the experimental data.

The influence of the inclusion of third order elastic constants and strain dependent deformation potentials on the result of equation 6.7 has also been investigated (E.P. O'Reilly 1990). The full set of third-order elastic constants have been measured for GaAs (Drabble and Brammer 1966, McSkimmin and Andreatch 1967). The elastic constants for In\textsubscript{1-x}Ga\textsubscript{x}As are assumed to vary as \( \varepsilon_{||}^0 \), \( \varepsilon_{||}(P) \) and \( \varepsilon_{\perp}(P) \) are evaluated numerically. The inclusion of third order elastic constants approximately halves the pressure dependence of the axial strain, so that

\[
(a + b) \frac{dE_{ax}}{dP} \approx -\frac{5}{3} \varepsilon_{||}^0 \frac{dE^0_{||}}{dP}
\]

\[ [6.8] \]

and

\[
\frac{dE(x)}{dP} = 10.7 - 1.7x \text{ meV/kbar} \quad [6.9]
\]

This is still a factor of three down on the experimentally observed composition dependence.

We turn now to consider the effect of strain-dependent deformation
potentials. Consider first, the hydrostatic deformation potential, \( a \). Strain dependence can be allowed for by expressing the band gap variation with hydrostatic and axial strain as

\[
E_g = E^0_g + a_{\text{vol}} \varepsilon + a_{\text{ax}} \varepsilon^2 + a_{\text{vol}} \varepsilon^2
\]  

[6.10]

thus introducing higher order deformation potentials. The band-gap pressure dependence is then given by

\[
\frac{dE}{dP} = (a + 2a_{\text{vol}}) \frac{d\varepsilon_{\text{vol}}}{dP} + 2 a_{\text{ax}} \frac{d\varepsilon_{\text{ax}}}{dP}
\]  

[6.11]

Experiments and calculations suggest that \( a_{\text{vol}} \approx 0 \) in GaAs (Goni et al. 1989), so that the second order volume deformation potential will act, if anything, to increase the pressure coefficient of the band gap. The value of \( a_{\text{ax}} \) is not known for GaAs, however \( a_{\text{ax}} \) has been calculated for strained GaSb (Qteish and Needs 1990) using self-consistent local-density calculations, where a value of \( a_{\text{ax}} = -8.69 \) is found. The value of \( a_{\text{ax}} \) in strained In\(_x\)Ga\(_{1-x}\)As is not expected to differ greatly, but most significantly, it is expected to be negative also. Thus the second term on the RHS of equation 6.11 would be expected to act to increase slightly the pressure dependence of the band gap.

Consider now the strain dependence of the axial deformation potential \( b \). This has been calculated to have only a weak dependence on strain in GaSb (Qteish and Needs 1990), and shows little variation between different III-V semiconductors (O'Reilly 1989). It is therefore unlikely that a strain dependent \( b \) could account for the observed pressure coefficients. To account for the data \( b \) must increase rapidly with pressure at a rate of \(-1\%/\text{kbar}\) (50\% for a 3\% change in volume),
this would be most surprising.

6.4 Hydrostatic Pressure Dependence of the Photoluminescence of InAs/InP Quantum Wells.

6.4.1 Introduction

The pressure coefficients of $\text{InGa}_x\text{As}$ quantum wells grown pseudomorphically on GaAs have shown a strong dependence on indium content $x$. This dependence has not been successfully described by current theory in terms of pure crystal properties. Arguments of alloy disorder and anomalous strain values may be invoked in an attempt to explain the experimental results. Another strained system provides a convenient test for some of these ideas, that of InAs grown pseudomorphically on InP. In this system the well and barrier materials are both binaries, so that considerations of alloy disorder do not apply (see below). In this work we seek to find whether such structures also exhibit unexpected pressure coefficients and if so whether this reveals anything further about the origin of such anomalies. InAs is related to $\text{InGa}_{1-x}\text{As}$, being one extreme of the alloy range. Thus we may expect our predictions for the pressure coefficients of strained $\text{InGa}_{1-x}\text{As}$ to apply to strained InAs. From the data so far it is not possible to predict whether the observed composition dependence for $\text{InGa}_x\text{As}$ grown on GaAs (10.7–6.0x meV/kbar) is in fact a strain dependence, since the strain varies linearly with composition. InAs/InP structures thus provide a system in which to test this. In the strained InAs/InP system the well
composition and the strain have been independently varied.

6.4.2 Experimental Results from InAs/InP Structures

Sample D consisted of four narrow quantum wells. In this system, with 3.6% strain, it is necessary to keep the wells narrow to be below critical thickness, despite the fact that wide wells give more conclusive results. The FWHM of the PL peaks, shown in fig. 6.3(a) are slightly wider than those obtained of InGaAs on GaAs. This may suggest some partial relaxation. However the FWHM are greater for the narrower wells suggesting that well width fluctuations may be dominating the peak width. Figure 6.9 shows the difference between the emission peak energy and the InP emission, plotted against the InP emission energy, for each of the wells in sample D. The pressure coefficients are all approximately 8.5 meV/kbar. At approximately 50 kbar the PL from all of the wells quenched and was not recoverable. The highest energy (thinnest) wells quenched slightly earlier than the lower energy wells.

The irreversible quenching of the PL at high pressure suggests that the sample suffered permanent structural damage. The most likely explanation is that the structure underwent a phase transition. However this pressure is considerably lower than the phase transitions pressure in the two bulk materials. InAs has a phase transition at ~80-100 kbar (Minomura and Drickamer 1962 (84 kbar), Jamieson 1963 (102 kbar)) and InP has a phase transition at ~105-135 kbar (Minomura and Drickamer 1962 (105-110 kbar), Jamieson 1963 (133 kbar).

The pressure coefficient of the single emission from sample E was found to be 6.2 meV/kbar. The PL from this sample is very broad and the
Fig. 6.9 The difference between the InP (pressure gauge) capping layer emission energy and the quantum well PL energy is plotted against the InP energy for sample D. The wells are seen to all have very similar pressure coefficients approximately equal to that of the barriers.
two quantum wells are not resolved, even at 10K. TEM on this sample has shown that the wells were severely dislocated. This sample was grown by MOCVD and there is some uncertainty in the exact well widths. The PL and TEM data together suggest that there is significant relaxation in this structure. The intensity of the PL in such a structure is mysterious, however high intensity PL from relaxed InAs layers has been observed elsewhere (David 1990). Bright luminescence is observed up until 115 kbar where it is suddenly quenched and not recovered by reducing pressure. This is almost certainly due to a phase transition in one of the materials. This result makes the loss of intensity in sample D, at lower pressures, all the more surprising.

6.4.3 Analysis of InAs/InP Results.

The analysis is concerned only with sample D, where high quality strained-layer quantum wells are found. The behaviour of the significantly relaxed wells in sample E will be discussed in section 6.5. Figure 6.10 shows the pressure coefficients, from the wells in sample D, plotted against well width. The wide well limit is seen to be 8.5 meV/kbar. The wells are much narrower than would be ideal for this kind of extrapolation, since the pressure coefficients are very sensitive to the behaviour of the band offsets. Figure 6.7, curve b showed than in the InGaAs/GaAs structures the narrow well data could be fitted reasonably well by making the band offsets move quickly with pressure.

Much is now known about the behaviour of band-offsets under pressure and we can therefore make reasonable assumptions in order to fit the data. For a large number of systems, which have been studied,
Fig. 6.10 The pressure coefficients from sample D are plotted against well width. The curves are models for the predicted behaviour assuming the pressure coefficients of the well material indicated. The models are discussed in the text.
the valence band offset is known not to change significantly under pressure. A pressure independent valence band offset is therefore assumed in the first instance. The pressure coefficients of Type I transitions are not particularly sensitive the the initial choice of offset ratio, a 60:40 (CB:VB) ratio is therefore taken as a good approximation. In figure 6.10 the solid curves are models for the well width dependence calculated using the above assumptions by the method discussed in chapter 3. Curve a is calculated assuming that the pressure coefficient of the strained InAs well material is equal to that of the bulk material (10.2 meV/kbar). This significantly overestimates the observed pressure coefficients. Curve b accepts the wide well extrapolation of 8.5 meV/kbar as the pressure coefficient of the well material. This gives excellent agreement with the data. The pressure coefficient of the InP barriers is also 8.5 meV/kbar, thus accounting for the apparent well width independence of the fit. In curve d the pressure coefficient of the well material is assumed to be given by the composition dependence observed in the InGaAs/GaAs structures (10.7-6.0x) meV/kbar, ie 4.7 meV/kbar. This significantly underestimates the pressure coefficients. In curve c the pressure coefficient of the InAs is derived as follows: It is assumed that the (10.7-6.0x) meV/kbar dependence is in fact a strain dependence. The in-plane strain for InGaAs grown pseudomorphically on GaAs may be expressed as

$$\varepsilon_{\parallel}^{(x)} = \frac{a(\text{GaAs})}{a(\text{InGa}_{1-x}\text{As})} - 1$$  \[6.12\]

The lattice constant of InAs is 6.08 Å and of GaAs, 5.65 Å. The lattice constant of the alloy a(InGa_{1-x}\text{As}) is linearly interpolated between
these two values. The pressure dependence of strained In\textsubscript{\(\text{Ga}_{1-x}\text{As}\)} layers may then be expressed as

\[
10.7 + 6.0 \left( \frac{13 \, \epsilon^0_{\parallel}}{\epsilon^0_{\parallel} + 1} \right) \tag{6.13}
\]

The lattice constant of InP is 5.87\(\text{Å}\), \(\epsilon^0_{\parallel}\) for InAs lattice matched to InP is therefore \(-0.0345\). Substitution of this value in equation (6.13) gives a pressure coefficient of 8 meV/kbar. This agrees with the experimentally determined coefficient of 8.5 meV/kbar to within 0.5 meV/kbar.

The InAs/InP structures therefore provide another example of unexpected pressure coefficients in strained-layer systems. The pressure coefficient of the bulk strained material is found to be 8.5 meV/kbar, significantly lower than the bulk value of 10.2 meV/kbar. This serves to discount suggestions that the anomaly is due to alloy fluctuations and ensuing strain anomalies. However the following comments are made on this point. Firstly, the possibility of the inclusion of phosphorous in the InAs layers can not be excluded. This is a well known phenomenon and is the reason that InP based materials are not usually grown in the same MBE machine as GaAs based materials. It is therefore likely that a few per cent phosphorus is present in the well making it a weak alloy. Secondly, since the wells are narrow, the PL will be sensitive to the interfaces. The interfaces cannot be perfect and must represent disorder to some degree.

The InGaAs/GaAs results and the InAs/InP results are seen to be consistent if strain is assumed to be the cause of the anomaly rather than composition. This is an interesting result. The excellent agreement between two quite different systems where the strain and composition
have been varied independently, and where one well material is an alloy while the other is not, supports strongly a conclusion that this is a real effect and not an artifact of defects or deviations from the pure crystal picture. In section 6.6 results from the literature on other strained systems are discussed and shown to be consistent also.

6.5 Pressure Coefficients in Partially Relaxed Strained-Layer Quantum Wells

One result brings the above interpretation of the unexpectedly low pressure coefficients into doubt. That is the pressure dependence of partially relaxed layers. Sample E (InAs/InP) exhibits a very low pressure coefficient of 6.2 meV/kbar. Envelope function calculations for wells of this width (20-30 Å) give ~5 meV/kbar as the coefficient of the well material. The quantum wells were obviously relaxed to some degree and the layers heavily dislocated. The high intensity of the PL may indicate 3-D growth. A quantum well of In$_{0.3}$Ga$_{0.7}$As/AlGaAs, 100 Å wide, has been grown as one of a stack of quantum wells (sample F in the second half of this chapter). The use of AlGaAs barriers does not significantly change the strain since the lattice constant of Al$_y$Ga$_{1-y}$As is almost exactly constant across the alloy range. The PL from this well was broad, again indicating partial relaxation. This too showed an anomalous pressure coefficient (8.8 meV/kbar). This is slightly lower than would be expected from the observed trend in unrelaxed wells.

In figure 6.11 all of the Type I pressure coefficients measured to date are shown, these include data from InGaAs/AlGaAs samples (samples F
Fig. 6.11 A summary of the pressure coefficients of Type I transitions in wide strained layer quantum wells. The pressure coefficients are plotted against the InGaAs composition of the well or against the corresponding composition for the same strain for the InAs/InP samples. Small + sample C, x sample F, circles sample G and large + InAs/InP samples D and E.
and G) which have not yet been discussed. Data from the InAs/InP structures are plotted at an InGa\textsubscript{1-x}As composition x which corresponds to the same in-plane strain as given by equation 6.13. The extrapolated wide well values of the pressure coefficients are given. The figure confirms that all strained wells consistently follow the empirical relationship (10.7-6.0x) meV/kbar, whilst partially relaxed wells do not and exhibit even more anomalous behaviours. Note that the strain in the relaxed layers has not been measured, these data are plotted at the composition /strain determined for the unrelaxed case.

These results may suggest that the anomalous pressure coefficients are not due to pure crystal properties but due to defects of some form. However, it is not possible to say, from the data so far, whether the anomalies in strained and relaxed wells are derived from the same mechanism. Or that crystal distortions (tetragonal distortions) in the unrelaxed strained layers are not accentuated in the partially relaxed layers due to, for example, the strain field of the dislocations. Only limited results are available from partially relaxed layers, this obviously represents an area of continuing interest. Further data will be required to identify the mechanism determining the pressure coefficients in these layers.

6.6 Pressure Coefficients In Other Strained-Layer Systems

The pressure coefficients of some other strained-layer systems have been reported in the literature.

In the GaAsSb/GaAs system the pressure coefficients of GaAs\textsubscript{0.88Sb0.12} quantum wells have been studied as a function of well width.
(Prins et al 1990). The results are shown in figure 6.12 and show a striking similarity with fig. 6.7. The wide well width limit of the pressure coefficient is ~9.4 meV/kbar. Again this is most surprising since the pressure coefficient of GaSb is known to be 14.5 meV/kbar (Noak and Holzapfel 1978). Taking a linear interpolation between GaAs (10.7 meV/kbar) and GaSb, the pressure coefficient of unstrained GaAs$_{0.88}$Sb$_{0.12}$ is expected to be approximately 11.2 meV/kbar. Quantitative comparison with the InGaAs data is difficult since GaAsSb and InGaAs are quite distinct materials, unlike the InAs/InP data where comparison could be readily made since the well materials were different compositions of the same alloy. However a rough comparison can be made by comparing the strains. The lattice constant of GaSb is 6.08 Å, a(GaAs$_{0.88}$Sb$_{0.12}$) is therefore linearly interpolated to be 5.70Å. The in-plane strain, $\varepsilon_0^0$ is then -0.0091. The equivalent In$_x$Ga$_{1-x}$As composition, lattice matched to GaAs, for this strain is also $x=0.12$. The pressure coefficient of strained In$_{0.12}$Ga$_{0.88}$As is 10 meV/kbar compared with the GaAs$_{0.88}$Sb$_{0.12}$ value of 9.4 meV/kbar. Note that Prins et al. used In$_{0.53}$Ga$_{0.47}$As, lattice matched to InP, as a pressure gauge in their experiments, the pressure coefficient of which is not known to better than ±0.5 meV/kbar. Bearing in mind this uncertainty and the difference in the pressure coefficients of the unstrained well materials it may be concluded that GaAs$_{0.88}$Sb$_{0.12}$ strained-layer quantum wells exhibit the same strain dependence of the PL pressure coefficients, within error, as the InGaAs/GaAs and InAs/InP structures studied.

Warburton et al (1989) have studied highly strained GaSb/GaAs quantum wells. The wells were 15Å wide, which is expected to be below critical thickness. The PL exhibited linewidths of ~20 meV indicating
Fig. 6.12 The pressure coefficients from GaAs$_{0.88}$Sb$_{0.12}$/GaAs strained layer quantum wells as a function of well width reported by Prins et al (1990). The figure is shown to indicate the strong similarly with the InGaAs/GaAs data, see figure 6.7 for example.
that the strained layer is of reasonable quality. Pressure coefficients of 8.9 ± 1.0 meV/kbar for a single quantum well and 9.4 ± 1.0 meV/kbar for a five period superlattice are reported. The in-plane strain is estimated to be -0.071. This is the highest strain discussed so far, our empirical relationship would therefore predict a large reduction in the pressure coefficient from the unstrained value. We estimate the pressure coefficient of strained GaSb to be ~8.5 meV/kbar. In the 15Å wide wells the pressure coefficient of the PL is expected to be intermediate between 8.5 meV/kbar and 10.7 meV/kbar (GaAs barriers) consistent with the data. If the well material were to have the pressure coefficient of the unstrained GaSb (14.5 meV/kbar) a value intermediate between 14.5 and 10.7 meV/kbar would be expected. This is clearly outside the range of experimental error.

Warburton et al (1990) have studied wide (93Å) Ga$_{0.85}$In$_{0.15}$Sb quantum wells grown pseudomorphically on GaSb. They find that the pressure coefficient of the PL is 0.98 times that of bulk GaSb. We would predict a reduction in pressure coefficient of ~0.75 meV/kbar ($\varepsilon_1^0 = -0.0096$) from that of GaSb. This agrees with the data to within experimental error, assuming that the unstrained value of the pressure coefficient of Ga$_{0.85}$In$_{0.15}$Sb is equal to that of GaSb, but is not very conclusive.

Results from III-V strained layers studied so far all appear to follow the same trend with strain. However work on strained II-VI materials shows no such behaviour. Gil et al (1989) have studied CdTe/ZnTe 'freestanding' superlattices. In these structures the CdTe layers are under compression and the ZnTe layers are under tension giving typical values of in-plane strain of $\varepsilon_1^0 = -0.039$ and $\varepsilon_1^0 = +0.020$ respectively for the layer thicknesses measured. Gil et al have
obtained good fits to their data using bulk values for the pressure coefficients whilst the strains are sufficiently high for the effects seen in III-V systems to be noticeable. However, in this material system the bulk moduli are very different, this needs to be accounted for in the analysis. A pressure dependent valence-band offset has also been invoked. It is therefore difficult to deduce the pressure coefficients of the constituent strained materials accurately. Further studies of strained II-VI materials will be necessary before conclusions can be drawn about whether or not these materials exhibit strain dependent pressure coefficients as in III-V materials. Of course we do not yet know what effect tensile stress will have on the pressure coefficients.

6.7 Summary of Type I Transition Pressure Coefficients.

The pressure coefficients of the PL of \( \text{InGa}_x\text{As} \) quantum wells grown pseudomorphically on GaAs have been shown to depend strongly on indium content \( x \) as \((10.7 - 6.0x) \) meV/kbar. Data from InAs quantum wells grown on InP can be correlated with this dependence if it is rewritten as a strain dependence. Strain dependent pressure coefficients are supported by other data in the literature.

These results have not been explained theoretically in terms of strain dependent elastic constants or deformation potentials. The results from partially relaxed wells must still leave open to debate the possibility that the experimentally observed results are not due to pure crystal properties. However the apparent universality of the strain dependence in III-V materials, the high quality of the PL (intensity, narrow line widths) and the small Stokes shifts, suggest that a
fundamental property of tetragonally distorted lattices is being observed, which has yet to be accurately described by theory.

6.8 The Band Structure of InGaAs/GaAs Strained-Layer Quantum Wells.

6.8.1 Introduction

In chapter 5 methods for determining the band offsets in quantum wells by high pressure photoluminescence were fully discussed. Given the current interest in strained InGaAs/GaAs based devices it is important to determine the band offsets, knowledge of which is essential for device engineering. The high pressure method for determining the valence band offset in structures where a Type II $\Gamma$-X crossover (a crossover between the confined electron $\Gamma$-state and the X level in the barrier material) can be induced is highly accurate, since a spectroscopic measurement is being made. There is considerable uncertainty in the literature as to the correct value for the offset ratio. A large range of values is reported, 83:17 (Andersson et al 1988), 60:40 (Reithmaier et al 1990), and 52:48 (Hou et al 1990) to name just a few. Additionally, there is some doubt as to whether the band offset ratio should be composition or strain dependent. The high pressure measurements are therefore desirable but can only be made if the first confined electron $\Gamma$ state in the well crosses with the barrier X minima before crossing against the X levels in the well. The relative energies of the well and barrier X minima in the quantum well structure are determined by the valence band offset, the value of which is uncertain, and by the strain splitting of the X minima in the strained...
In Ga As, which is unknown. It is not then possible to predict with certainty which $X$-minima lie lowest in the structure. Indeed, we shall see below that the well and barrier $X$ minima have quite different pressure coefficients, and this also affects the $\Gamma$-$X$ crossovers.

InGa$_{1-x}$As quantum wells grown on GaAs and AlGaAs have been studied. The nature of the $\Gamma$-$X$ crossovers in InGaAs/GaAs quantum wells has thereby been shown to be due to crossovers with the well $X$-minima (Type I). These do not allow determination of the band offsets. However they do give a direct measure of the energy of the $X_{x,y}$ minima in strained InGa$_{1-x}$As, as a function of composition $x$. No other experimental determinations of those values have been reported. In InGaAs/AlGaAs quantum wells Type II crossovers have been observed. This allows accurate determination of the band offset ratio for InGaAs/GaAs heterojunctions. Values for band offset ratios for InGaAs/AlGaAs heterojunctions are also obtained.

The results allow comment on transitivity in the strained (InAlGa)As system and on strain dependence of the band offset ratio. Knowledge of the ground state alignment allows prediction of the alignment of higher lying levels.

6.8.2 Experimental Details

The samples were grown by MBE at RSRE by the SLS group. The results from three samples are described here. Sample C which has already been discussed, consisted of three quantum wells each of different InGaAs composition with GaAs barriers. Samples F and G were similar but with more wells and with Al$_{0.1}$Ga$_{0.9}$As and Al$_{0.24}$Ga$_{0.76}$As barriers respectively. All wells were nominally 100 Å wide with 500 Å barriers
to isolate them both electronically and structurally. Details of the sample parameters are given in table 6.1. Note that both samples F and G contained a GaAs quantum well, giving a reference to the known GaAs/AlGaAs system. None of the samples were intentionally doped; the background doping was about $10^{14}$, n-type. All of the structures were below critical thickness, both for each individual strained-layer quantum well and for the structure as a whole, except for the $\text{In}_{0.3} \text{Ga}_{0.7} \text{As}$ well in sample G. The one well above critical thickness, which is partially relaxed, has been commented on in section 6.5 and need not be discussed further here.

The high pressure experiments were conducted as previously described (chapter 4). Argon was used as the pressure transmitting medium. The experiments were conducted at 10K or 20K.

As usual other semiconductors were used to act as pressure gauges. For sample C, a piece of GaAs provided the gauge up until its $\Gamma$-X crossover at ~40 kbar, and a piece of InP provided the gauge above this pressure. For samples F and G the GaAs quantum well provided the pressure gauge until its luminescence was quenched by the $\Gamma$-X crossing with the barrier; at higher pressures a piece of $\text{In}_{0.53} \text{Ga}_{0.47} \text{As}$ epilayer was used. The PL from these gauges have known pressure coefficients (Wolford and Bradley 1985, Lambkin and Dunstan 1988); however, in these experiments pressure is only a dummy variable. Its absolute value is irrelevant to the analysis, and it is only necessary when pressure coefficients are quoted.

6.8.3 Experimental Results

Figure 6.13 shows a typical spectrum for samples F and G (sample C
Fig. 6.13 PL spectra from the InGaAs/AlGaAs samples, F and G. The spectra were recorded at the temperatures and pressures indicated.
is shown in fig. 6.2). The spectra were recorded at the temperature and pressure indicated. For each sample characteristic quantum-well free-exciton emissions are seen, indicating the high quality of the strained-well material. The behaviour of the quantum well emissions under pressure for sample C have already been shown in fig. 6.4. The \( \Gamma-\Gamma \) transitions have been discussed in detail, the crossover to \( X \)-like behaviour is of interest here. Fig. 6.4 shows that at high pressures the pressure coefficients of the \( \Gamma-\Gamma \) transitions begin to reduce and finally become negative, characteristic of \( X \)-related transition. Simultaneously the intensity of the PL is drastically reduced. The transitions now have a pressure coefficient of \(-2.6 \text{ meV/kbar}\); within experimental error no difference in the coefficients for each of the wells is observed.

Samples F and G behave in a similar manner. Although no \( X \)-related transitions are observed, the transitions show signs of band mixing (reduced pressure coefficients) while the PL is strongly quenched, finally becoming undetectable. In fig. 6.14 the crossover energies are plotted against the peak energy of the PL at ambient pressure. For sample A where \( X \)-related emissions are observed over a reasonable pressure range the crossover energy can be readily derived from fig. 6.4. For samples F and G where no pure \( X \)-behaviour is observed the crossover energy can be determined from the cut-off in PL intensity. Figure 6.15 shows characteristic quenching curves for sample G. These crossover energies give information on the electronic structure of the quantum wells. In the next section the significance of a plot of the type of fig. 6.14 is discussed, and in particular how it can reveal the band offsets.
Fig. 6.14. The crossover (from $\Gamma$ to X-like behaviour) energies for the quantum wells in samples C (solid circles), F (diamonds) and G (squares) are plotted against their ambient pressure transition energies. The open circle indicates the crossover energy of bulk GaAs. The solid lines are least squares fits to the data whilst remaining lines are theoretical models, discussed in the text, for the behaviour of sample C. The dashed line shows the expected behaviour for a Type I crossover (with X-states in the well) whilst the broken and chain-dotted lines show two models for Type II crossovers (crossing with the barrier X-states). The broken line assumes that the valence band offset remains constant under pressure whilst the chain-dotted line assumes that the valence-band offset increases at 1.3 meV/kbar. The data from sample C are seen to be closely described by a Type I crossing model. Fits to the data from samples F and G have slopes characteristic of Type II crossings, the slope of these lines gives the fractional valence-band offset. For sample F (diamonds) the crossover from Type I to Type II behaviour is observed.
Fig. 6.15 The figure shows typical quenching curves, in this case for sample G. The curves show the cut off of the intensity of the PL as the $\Gamma$ and $X$ states cross. These are used to determine the point at which $\Gamma$-$X$ crossover occurs if pure $X$-related emissions are not observed.
6.8.4 Analysis and Discussion

The pressure coefficients of the direct transitions have been plotted in fig. 6.11, where the InGaAs/AlGaAs samples are seen to exhibit the same behaviour as the InGaAs/GaAs samples.

At higher pressure the transitions are seen to take on an X-like characteristic, i.e. to move with a small negative pressure coefficient, measured to be -2.6 meV/kbar. This is about twice the coefficient of the X minima in GaAs which move at -1.34 meV/kbar (Wolford and Bradley 1985). X-related coefficients have been measured previously in InGaAs/GaAs strained-layer quantum-well structures (Wang et al 1989, Hou et al 1990) where a value of -2.6 meV/kbar is also reported. Like the pressure coefficient of the \( \Gamma \) minimum, the coefficient of the X minima in InGaAs is not expected to be strongly composition or strain dependent. However, the observed unexpectedly low values for the direct transitions suggest the possibility that the X-minima values might be anomalous, too. Since the origin of the anomaly is unknown the X pressure coefficient cannot be theoretically predicted quantitatively, in either magnitude or sign.

High values of pressure coefficients of X-related transitions have been observed in the GaAs/AlGaAs system. This occurs with Type II transitions (Lambkin et al 1989, and references therein) and is due to an increase in the valence-band offset under pressure. For GaAs/AlAs a value of -2.4 meV/kbar (Lambkin et al 1989) is reported, similar to the value found in InGaAs/GaAs. However, we shall proceed to show that the observed X-related transitions are due to levels entirely within the wells, and the high coefficient cannot therefore be explained by changes in the valence band offset.
Over the elbow between the $\Gamma$ and X-like behaviours the transitions have intermediate pressure coefficients. This is expected as the $\Gamma$ and X states mix in the vicinity of crossover, and has been observed previously in other material systems.

In samples F and G, which have AlGaAs barriers, no pure X-related emissions are observed. The PL is quenched by crossover, and evidence of band mixing is observed, but the PL is quenched beyond detection before the onset of true X-like behaviour. If these transitions are Type II, as we propose, we expect the PL to be weak since the carriers are spatially separated in real space as well as in k-space.

Previous authors have determined the band offsets for InGaAs/GaAs by high-pressure PL, following the procedure first used by Wolford et al. (1986) and described in chapter 5. Their analysis depends on the assignation of the X-related transition to a Type II recombination between the barrier X level and the InGaAs valence band. However, because of uncertainty in the valence-band offsets in these structures, and given the similarity of the well and barrier materials especially for low indium contents, it is not certain which X level, well or barrier, is being observed in the transition. The position of the X minima in InGaAs across the alloy range is uncertain, and any difference in pressure coefficients of the GaAs and the InGaAs X-minima must also be considered. It is therefore essential, for a determination of the band-offset ratio from the crossovers, that the true nature of the crossovers be determined.

In the proceeding analysis the crossovers in the InGaAs/GaAs quantum-well structures are shown to be due to crossings against the X minima in the strained wells. This is determined by comparison with samples containing aluminium in the barriers. In fig. 6.14 the dashed
line shows the expected behaviour for sample C (GaAs barriers) if crossover is with the X levels in the wells. The well X minima position is calculated for each InGaAs alloy composition by interpolation between theoretically determined values (Chelkowsky and Cohen 1976) for the binaries GaAs and InAs. Since the layer is under strain, the free-standing alloy band-structure is modified. The effect of (001) strain on the X minima is to lift their degeneracy, with the $X_{x,y}$ minima lower than the $X_z$. The shifted X position can then be expressed as a function of strain as follows (Van de Walle 1989): The centre of gravity of the X minima is shifted due to the hydrostatic component of the strain and the shift is expressed as

$$\Delta E_{\text{cg}}^X = a_x \left( \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \right)$$  \[6.14\]

where $a_x$ is the band-gap deformation potential and $\varepsilon_{xx}$ and $\varepsilon_{zz}$ are components of the strain tensor. The value of $a_x$ is not known for InGaAs, GaAs or InAs and we therefore use a calculated value for AlAs (Van de Walle 1989) (1.62 eV). The $X_{x,y}$ and $X_z$ states splitting, due to the uniaxial component of the strain, shifts the $X_{x,y}$ states downwards:

$$\Delta E_{XX,Y} = -\frac{1}{3} \frac{\varepsilon_{xx}}{\varepsilon_{zz}} \left( \varepsilon_{xx} - \varepsilon_{zz} \right)$$  \[6.15\]

the value of the deformation potential $\varepsilon_{xx}^\Delta$ is not known for InGa$_{1-x}$As, or the binaries, however it has been calculated for GaAs (8.61 eV) and InAs (4.50 eV) (Van de Walle 1989) and we therefore use a linearly interpolated value for each InGaAs composition. The uniaxial component of the strain also splits the valence bands; the shift of the highest lying valence band is expressed as
\[ \Delta E_{VB} = -b \left( \varepsilon_{zz} - \varepsilon_{xx} \right) \]  \[6.16\]

The indirect band gap of InGaAs is therefore readily obtained. The expected crossover energies may then be calculated using the experimentally determined pressure coefficients. The broken line in fig. 6.14 shows the expected trend, for sample C, for crossing against the X minima in the barrier assuming a 60:40 offset ratio with no pressure dependence of the valence-band offset. The chain-dotted line shows the expected behaviour if the -2.6 meV/kbar X coefficient is assigned as a Type II transition; this implies that the valence band offset is increasing under pressure. It is seen in fig. 6.14 that the predicted trends for Type I and Type II crossovers are quite distinct and the excellent agreement with the Type I crossing model confirms this assignment. Also shown in fig. 6.14, along with the sample A data, is the \( \Gamma-X \) crossover energy for bulk GaAs (open circle). Deviations of the Type I model (dashed line) from the data towards low indium content are probably due to an over estimate of the X minima coefficient (-2.6 meV/kbar), which must in fact tend to the GaAs value of -1.34 meV/kbar in this region. In contrast, for sample G, where we have changed the barrier material from GaAs to \( \text{Al}_{0.1}\text{Ga}_{0.9}\text{As} \), the behaviour is quite different, being that expected for crossing against a level in the barrier. If the quenching of the PL in this sample was due to a crossover in the well it would be expected to follow the same behaviour as sample C, since the wells are wide and the confined states are negligibly affected by the increased heterojunction barrier height. The lattice constant of AlGaAs is essentially independent of composition so that the strain in these structures is not altered by the choice of
barrier material. For certain compositions of AlGaAs in the barriers it is expected that both types of crossover will be observed in one sample. It is already known that GaAs/AlGaAs quantum wells cross Type II with the AlGaAs X minima (Wolford et al 1986, Venkateswaren et al 1986) and this must also be the case for sufficiently low indium content wells. As the indium content is increased and the wells deepen with respect to the barriers the crossover is expected to occur against the well X-states. This is seen in the case of sample F where the GaAs and low indium content wells follow the Type II crossing trend of sample G whilst the highest indium content well fits the Type I crossing line of sample C.

The Type I crossovers of sample A cannot give information on the band offsets, except to give an upper bound for $Q_v$. For large enough values of $Q_v$ the crossovers would have occurred at lower pressures as a Type II crossover against the barrier X-states. This limit depends on the strain splitting of the InGaAs X states and on any changes in the valence band structure under pressure but is about $Q_v < 0.75$. However the data provide a good determination of the positions of the strained $X_{x,y}$ minima as a function of composition. Extrapolation of the X-related transition lines to ambient pressure gives the energy of these levels, following corrections for the confinement and binding energies. The result of these extrapolations is shown in fig. 6.16; the solid line is a theoretical prediction derived from the method described earlier in this section. This good agreement with theory indicates that the interpolation between the binaries is an accurate method for deriving X level energies at least for In$_x$Ga$_{1-x}$As compositions up to $x = 0.25$ and confirms the values of the deformation potentials used. The additional X related features seen in fig. 6.4 are probably phonon related; these are commonly observed in the spectra of indirect PL transition. No further
Fig. 6.16 The positions of the strained $X_{x,y}$ minima in InGaAs, determined by extrapolating the X-related transitions, are plotted as a function of indium content. The solid curve is the theoretically expected behaviour derived as described in the text.
attempt to assign them is made here. Photoluminescence selective excitation experiments are planned in order to help identify these levels.

In samples F and G the Type II crossovers can be used to determine the fractional valence-band offset of InGaAs/GaAs heterojunctions. The combined movement of the conduction-band and valence-band edges as the indium content is increased from zero (GaAs) is determined by measuring the PL energy in these samples to give a measure of the band gap, while the movement of the valence-band edge alone is given by the energy of the PL at crossover. The crossover energy for each well thus provides a direct measure of the movement of the valence band in the strained InGaAs, relative to the GaAs band structure, with indium content. This is most easily seen by making initially some simplifying assumptions. The barrier level, whose identity is considered unknown for the moment, is assumed to be stationary with pressure. The valence-band structure is also assumed to be unchanged by pressure. Small changes in the hole confinement energies and the exciton binding energies are neglected. The change in energy of the conduction band of the InGaAs with indium content does not affect the PL energy at crossover. On the other hand, the change in energy of the valence band of the InGaAs with indium content does not affect the crossover pressure but it does determine directly the PL energy at crossover. Thus a plot of the crossover energy against the PL energy at ambient pressure gives a line whose gradient is the fractional valence-band offset, $Q_v$. That is, the slope of the lines for samples F and G shown in fig. 6.14 is the fractional valence-band offset for InGaAs/GaAs heterojunction.

Corrections to this value are necessary since the simplifying assumptions are approximations. Since the wells are wide the confinement
energies are small and can be calculated without much absolute error, as can the exciton binding energies. Thus an accurate measure of the strained InGaAs band-gap can be made. Next, the energy of the barrier level probably does not remain constant under pressure. We must first identify the level; this is facilitated by the presence of the GaAs/AlGaAs wells in each structure; in these wells the band lineup is assumed to be that given by Wolford et al (1986) and VenkateswaraReddy et al (1986) i.e a band offset ratio of ~70:30. The crossovers in these wells tells us that the crossover is not with the AlGaAs X level but with a level ~60 meV below this in both samples. Since this is close to the X minima and follows it with aluminium composition, it is assumed that this is an X-related state. Consequently it is assigned the pressure coefficient of the AlGaAs minima which is assumed equal to that of GaAs. The final assumption was that the valence-band offsets do not change under pressure. This known to be a good approximation in other material systems where the pressure dependence of the valence-band offset has been studied (Lambkin et al 1989, Lambkin et al 1988, Wilkinson et al 1990, Lambkin et al 1990). In the case of GaAs/AlGaAs structures, \( \Delta E_v \) has been shown to move at 1.1y meV/kbar (Lambkin et al 1989). Clear Type II luminescence is required to determine the pressure dependence of the valence band offset, but data are not available. Further superlattice experiments are in hand to determine these values for InGaAs/AlGaAs heterojunctions. For the purposes of this work \( \Delta E_v \) is assumed to have a pressure coefficient determined solely by the aluminium content y. This dependence on aluminium content is sufficient to account for the difference in slope found for samples F and G, to within experimental error, and is then extrapolated to zero aluminium content.
Applying these corrections for the pressure dependence of the barrier level and of the valence-band offset leads to a value for the slopes of $0.40 \pm 0.02$ and this gives the value of 60:40 (CB:VB) for the band-offset ratio. The high accuracy of this result arises due to the spectroscopic nature of the measurement. The quoted error does however assume that assumptions discussed in the text, such as the value of the pressure dependence of the valence-band offset, are correct.

The data also give information on the composition dependence of the band offset ratio in InGaAs/GaAs. Some authors have suggested that the ratio may vary considerably with indium content (Joyce et al 1988). In the range of compositions studied ($0 \leq x \leq 0.25$), the data shows that the ratio is independent of indium content. This is because (under the simplifying assumptions made earlier) it is the gradient of the curve in fig. 6.14 which is the differential band-offset ratio between InGaAs and InGaAs of infinitesimally different compositions. The best fit to the data is a straight line. The various corrections made are all linear with indium content; consequently the band-offset ratio is constant over the composition range studied, and therefore independent also of strain. This is supported by other workers who also report composition independent band offset ratios (Reithmaier et al 1990, Niki et al 1989, Zou et al 1990).

Whether band offsets in the strained (InAlGa)As system are transitive is another question to which the data provides an answer, within the composition range studied. Having obtained the value of 60:40 for the band offset ratio in InGaAs/GaAs and taking the literature value of 70:30 for the ratio in GaAs/AlGaAs, the ratio for an InGaAs/AlGaAs heterojunction may be calculated. This is done by assuming transitivity and using the following expression to determine $\Delta E_v$:

\[
\begin{align*}
\Delta E_v (\text{AlGaAs/InGaAs}) & = \Delta E_v (\text{InGaAs/GaAs}) + \Delta E_v (\text{GaAs/AlGaAs}) \quad [6.17]
\end{align*}
\]

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The curves for the AlGaAs compositions studied are shown in fig. 6.17, together with the experimental data. The data support transitivity, within experimental error. A more rigorous test of transitivity will be possible when the values of $Q_v$ can be determined more accurately, following the determination of the pressure dependence of the valence-band offset, as described above. Also when data from a greater composition range are available.

Finally from the band lineup of the ground state levels, the alignments of higher lying states may be inferred. The experimental results require the InGaAs/GaAs X valley alignment to be Type I at the crossover pressures. From the determined $\text{InGa}_x\text{As}_{1-x}$ X positions and the fractional valence-band offset, the ambient pressure alignment of the X valleys is found to be Type I also. Note that the well and barrier X minima lie within 20 meV of each other in the quantum well structures so that within the errors quoted for $Q_v$, $E^{Xx,y}$ and the uncertainty in the indirect gap of GaAs (Aspnes et al 1976, Chelkowsky and Cohen 1976, Wolford and Bradley 1985), the X valley alignment could be just Type II. In the valence band, the light hole alignment also follows from the determined band-offset ratio. The light-hole heavy-hole splitting may be readily determined (Van de Walle 1989) using accepted values for the shear stress deformation potential $\beta$. For example for $x=0.25$ and taking $\beta=-1.7$ eV (Chandrasekhar and Pollak 1977) we find a splitting of 103 meV, a value of $Q_v = 0.40$ therefore implies that the light hole alignment is Type I, since the lh-hh splitting is less than the heavy-hole valence band offset. Again uncertainty in $Q_v$ but more significantly $\beta$ (Bhargarva and Nathan 1967, Balshev 1969), may alter the predicted alignment. A type II light-hole alignment has been suggested
Fig. 6.17 The fractional valence-band offsets, derived from the Type II crossovers in the InGaAs/AlGaAs quantum wells, are shown. Diamonds are for sample F with 10% AlGaAs barriers and squares are for sample G with 24% AlGaAs barriers. The curves are calculated, as described in the text, for the AlGaAs compositions indicated assuming transitivity.
by several authors (Andersson et al 1988, Marzin et al 1985, Ji et al 1987); this would imply a larger splitting, $b \leq -1.7$ eV.

6.8.5 Summary

The photoluminescence of InGaAs/GaAs and InGaAs/AlGaAs strained-layer quantum wells have been studied under high hydrostatic pressure. The crossover to X-related behaviour in InGaAs/GaAs wells is shown to be Type I, by comparison with Type II crossovers in InGaAs/AlGaAs structures. From the Type I crossovers a direct measurement of the position of the lowest lying X minima ($X_{x,y}^x$) in strained InGaAs is made. From the Type II crossovers an accurate determination of the valence-band offset ratio for InGaAs/GaAs heterojunctions is made and found to be $40 \pm 2\%$.

6.9 Theoretical Prediction of the Band Lineup in Strained InGaAs/GaAs Heterojunctions

The Model Solid theory of Van de Walle and Martin has been discussed in chapter 5, where it was shown to be a good guide to the band line up in the GaAs/AlGaAs system. The application of the model to strained layer systems has been discussed in chapter 3. The model is solved here for the strained system In$_x$Ga$_{1-x}$As/GaAs and is shown to agree well with the experimental results.

The non zero components of the strain tensor ($\epsilon_{xx}$, $\epsilon_{yy}$ and $\epsilon_{zz}$) are calculated as in equations 3.22 and 3.24. The values for the unstrained lattice constants of the alloys, $a$, are derived by linear interpolation
between the binaries (GaAs 5.65 Å, InAs 6.08 Å). The constant D (eqn. [3.23]) is given for GaAs and InAs (Van de Walle 1989) and is also linearly interpolated for the alloys.

The absolute energy of the average valence band position is calculated in the model solid theory. Van de Walle gives the following values for InAs, -6.67 eV, and GaAs, -6.92 eV (Van de Walle 1989). The absolute energy of the average valence-band position, for the alloys, is computed using the following expression (Cardona and Christensen, 1988):

\[ E(x) = x E(AC) + (1-x)E(BC) + 3x(1-x)[-a_x(AC) + a_x(BC)] \frac{\Delta a_x}{a_0} \]

where \[ \Delta a = a_x(AC) - a_x(BC) \]
and \[ a_x = x a_x(AC) + (1-x) a_x(BC) \]

This is a general expression which is used to calculate the positions of energy levels in alloys \( (A_x B_{1-x} C) \) where the constituent binary materials are not lattice matched. In this case a strain contribution should be considered since one material is effectively compressed whilst the other is expanded. \( E \) can be any energy level and \( a_x \) the appropriate deformation potential. In this case \( E \) is \( E_{x,\text{av}} \), the average position of the valence band, and \( a_x \) is \( a_{\text{v},x} \), the hydrostatic band-edge deformation potential of the valence band. Values for \( a_{\text{v},x} \) are calculated in the model solid theory (Van de Walle 1989). The model solid theory has thus been used to give the absolute energy of the average valence band position for \( (In_x Ga_{1-x} As) \) and GaAs. In an unstrained system the band offsets could then be immediately deduced. In the strained system the shift of the bands due to the strain must first be calculated. The shifts of the average valence band position and the conduction band minima, with the
hydrostatic component of the strain are given by equation 3.28 and 3.29.
In the conduction band the $\Gamma$ minimum is only affected by the hydrostatic
component of the strain (eqn. 3.29); the conduction band-edge
deformation potential, $a_c$ is interpolated for the alloys between the
GaAs (-7.17 eV) and InAs (-5.08 eV) values. The X minima are shifted due
to the hydrostatic component and also split by the uniaxial component
(eqns. 3.34 and 3.35) of the strain. The X-minima band-edge deformation
potential is taken as 4.09 eV for each composition. This value has been
calculated (Van de Walle 1989) for AlAs and is not expected to vary
greatly for different III-V semiconductors. The uniaxial component of
the strain also lifts the degeneracy of the valence bands as described
by equations 3.31-3.33. Here, $b$ is taken as a linearly interpolated
value between -1.9 eV, GaAs and -1.55 eV, InAs, as calculated in the
model solid theory, for each composition. In the unstrained GaAs the
degeneracy of the valence bands is also lifted due to spin-orbit
effects. The highest lying valence states being lifted from $E_{v,av}$ by
$\Delta_0/3$, where $\Delta_0$ is the spin orbit splitting, taken as 340 meV (Aspnes et
al 1973). The positions of all the energy states of interest have now
been calculated on an absolute energy scale. Hence the alignment of
levels in the quantum well structure are determined and the band offsets
obtained. Figure 6.18 shows the calculated positions of the energy
levels as a function of alloy composition, for the range of alloys
studied.

The fractional valence-band offset is found to be 40% in excellent
agreement with the experiments reported here. A Type I alignment of the
$X$-$X_{x,y}$ valleys in GaAs/InGaAs heterojunctions is also predicted, in
agreement with experiment. The light hole level is predicted to be
approximately coincident with the GaAs valence band, consistent with the
Fig. 6.18 The band structure of strained InGaAs is calculated on an absolute energy scale using the 'Model-Solid' theory of Van de Walle and Martin for the range of compositions studied.
6.10 Future Work

Much work remains to be done in characterising this new material system. The research reported in this chapter has probably raised more questions than it has answered. The anomalous pressure coefficients remain unexplained. High pressure experiments, on layers of InGaAs grown on InP under tensile stress and on In$_{x_1}$Ga$_{1-x_1}$As/In$_{x_2}$Ga$_{1-x_2}$As structures are planned. This will hopefully reveal more about the relationship between strain and the pressure coefficients. Further studies on very different strained materials, such as II-VIs for example, will be interesting. Further theoretical analysis is also required.

The determination of the band-offset ratio for InGaAs/GaAs heterojunctions has been limited in accuracy by uncertainty in the pressure dependence of the valence-band offset. InGaAs/AlGaAs superlattice experiments are planned, where clear Type II luminescence is more likely to be observed. This will allow a direct determination of the pressure dependence of the valence-band offset. X-related features in the PL of InGaAs/GaAs structures remain unassigned at present. Photoluminescence selective excitation experiments are in hand to identify these levels. Such experiments may also reveal the position of higher lying states, such as the $X_{z}$ minima in strained In$_{x}$Ga$_{1-x}$As.
7.1 Introduction

In this chapter preliminary results of a study of dilute magnetic semiconductors (DMS) under high pressure are reported. Superlattices of CdTe/CdMnTe have been concentrated on. Dilute magnetic semiconductors, such as CdMnTe, have the interesting property that their band gaps are dependent on the external magnetic field. High pressure provides a powerful tool for studying the form of the magnetic interactions which are responsible for this effect. In semimagnetic materials these transitions will be influenced by the mean magnetic-ion separation. The average Mn-Mn separation, for example, could of course be varied from sample to sample to study this effect. High pressure, however provides a controllable manner in which to make this change in one sample. This eliminates other quantities that may vary from sample to sample from the analysis.

An essential preliminary step for such a study of the SL samples under high pressure and magnetic fields is to verify the pressure dependence of the constituent materials in the absence of a magnetic field and to determine the magnetic field dependence in the absence of pressure. This work has been carried out in collaboration with the DMS semiconductor group at the University of Hull. This group has
characterised the materials as a function of magnetic field. In this chapter the behaviour of the SL samples under pressure are described. A full study of the samples under pressure and magnetic field has yet to be completed and will be published elsewhere.

7.2 Dilute Magnetic Semiconductors

A few words are said here about the DMS Cd$_{1-x}$Mn$_x$Te since it has not been mentioned elsewhere in this thesis. The addition of Mn to the II-VI semiconductor CdTe, increases its band gap. Mn may be added up to a composition of ~70% (Giriat and Furdyna 1988). The band structure in zero magnetic field is qualitatively similar to CdTe itself. The energy of the direct gap of Cd$_{1-x}$Mn$_x$Te is shown in fig. 7.1 as a function of Mn content x and temperature (Lee and Ramdas 1984). Above about 40% Mn content the optical absorption no longer increases with composition but becomes pinned at ~2.2 eV (10K), this is due to an internal (a spin flip within the 3d$^5$ level) Mn transition (Khoi and Gaj 1977). The band structure of CdMnTe is significantly altered when a magnetic field is applied principally because a large Zeeman splitting occurs in the conduction and valence bands. The splitting is proportional to the magnetic field for low fields. Magnetism in DMS has been excellently reviewed by Furdyna (1988) and Furdyna and Kossut (1988) where exchange interactions (Mn-Mn exchange interaction and the exchange interaction between the magnetic ions and the electrons and holes) are discussed. This is not repeated here except a brief description of the effect on the band gap. The approximate splitting (small terms have been neglected) of the conduction and valence bands can be expressed simply
Fig. 7.1 The energy of the direct gap of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ as a function of Mn content and temperature (after Lee and Ramdas 1984).

\[ \text{Cd}_{1-x}\text{Mn}_x\text{Te} \]

\[ \begin{array}{c}
\text{Energy of Features A and B (eV)} \\
\text{Manganese Mole Fraction (x)}
\end{array} \]

Fig. 7.2 The figure illustrates the magnetic field induced splitting of the conduction and valence bands of a DMS.

$\Delta E_c$  
$\Delta E_v$

1/2  
-1/2

$E_g$  
$E_g(B)$

$-3/2$  
$-1/2$  
$1/2$  
$3/2$

$m_j$

B=O  
B>O
as follows

$$\Delta E_c = g_e^* \mu_B B$$

and

$$\Delta E_v = g_h^* \mu_B B$$  \[7.1\]

where $g_e^*$ and $g_h^*$ are effective $g$ factors. This is illustrated in fig. 7.2. The band gap in a field $B$ is then given by

$$E_g(B) = E_g(0) - \frac{1}{2} \left( \Delta E_c + \Delta E_v \right)$$  \[7.2\]

$$= E_g(0) - \frac{1}{2} \left\{ x \, N_0 (|\alpha| + |\beta|) \, <s_z> \right\}$$  \[7.3\]

where $\alpha$ and $\beta$ are the exchange constants between the electrons and the Mn ions and the holes and the Mn ions respectively, $N_0$ the number of cations per unit volume and $<s_z>$ the average spin component of the Mn ions. Experimentally determined values of the sp-d exchange constants for Cd$_{1-x}$Mn$_x$Te are $N_0\alpha = 0.22$ eV and $N_0\beta = -0.88$ eV (Furdyna 1988). Evaluation of eqn. 7.3 shows that the band gap will be strongly dependent upon the magnetic field.

7.3 Experimental Details

The samples were grown by MBE at the University of Hull in a VG80 machine. Two superlattice samples have been studied, their details are given in table 7.1. In each case the substrate material is InSb which is roughly lattice matched to CdTe. The pressure dependence of the superlattice emission has been studied for both samples. In the case of sample A, ruby was used as the pressure gauge. For sample B InP was used. In sample B clear CdMnTe capping layer emission was also observed.
### Sample Details

<table>
<thead>
<tr>
<th>Sample</th>
<th>CdTe well width width (Å)</th>
<th>CdMnTe barrier width (Å)</th>
<th>CdMnTe composition (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (M92)</td>
<td>72</td>
<td>77</td>
<td>0.25</td>
</tr>
<tr>
<td>B (M104c)</td>
<td>25</td>
<td>25</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Table 7.1 The sample parameters.

### Material Parameters

<table>
<thead>
<tr>
<th></th>
<th>CdTe</th>
<th>Cd_{1-x}Mn_{x}Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g^{(\Gamma-\Gamma)}$ (eV)</td>
<td>1.606$^{(a)}$</td>
<td>1.606 +1.592x$^{(a)}$</td>
</tr>
<tr>
<td></td>
<td>1.606</td>
<td>1.606 +1.477x</td>
</tr>
<tr>
<td>$\frac{dE}{dP}$ _g (meV/kbar)</td>
<td>6.5$^{(b)}$</td>
<td>8.2$^{(c)}$</td>
</tr>
<tr>
<td>$m_e^{*}$ (m_0)</td>
<td>0.096</td>
<td>0.096</td>
</tr>
<tr>
<td>$m_{hh}^{*}$ (m_0)</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>$\Delta E_v$ (meV)</td>
<td>34</td>
<td></td>
</tr>
</tbody>
</table>

(a) Lee and Ramdas (1984)  
(b) Dunstan et al (1988)  
(c) This work

Table 7.2 The material parameters used for modeling the high pressure data.
allowing determination of the pressure coefficient of Cd$_{0.75}$Mn$_{0.25}$Te. Experiments on sample A were conducted at 80 K and on sample B at 4 K.

7.4 Experimental Results

Photoluminescence spectra for samples A and B at various pressures are shown in fig. 7.3 and fig. 7.4 respectively. For sample A sharp luminescence peaks are seen, measured at 10 and 40 kbar. This shows that the intensity of the PL remains roughly constant upto ~40kbar. Above ~40 kbar the PL is quenched and not recoverable. This is probably due to a phase transition in the CdTe or CdMnTe. This is roughly consistent with phase transition pressures reported in the literature, for example Shan et al (1985) report a value of ~35 kbar for Cd$_{1-x}$Mn$_x$Te, x<.3. Figure 7.5 shows the energy of the emission as a function of pressure. The pressure coefficient of the SL emission is found to be 6.6 meV/kbar. For sample B SL and capping layer emission is seen. Figure 7.6 shows the energy of the emission from sample B plotted against the InP emission energy. The high energy emission is from the CdMnTe capping layer whilst the lower energy emission is from the SL. Taking the pressure coefficient of InP to be 8.5 meV/kbar (Muller et al 1981) the pressure coefficient of the SL emission is found to be 8.3 meV/kbar and that of the capping layer to be 8.2 meV/kbar. The data of figure 7.6 are best fitted by a linear coefficient, this implies that the transitions have approximately the same bowing with pressure as InP (0.018 meV/kbar$^2$). The intensities of the emissions from sample B show an interesting behaviour and are plotted in fig. 7.7.

The magnetic field dependence in these samples has been studied at
Fig. 7.3 PL spectra from sample A measured at 80 K and at the pressures indicated.
Fig. 7.4 PL spectra from sample B measured at 4K and at the pressures indicated. The high energy emission is from the CdMnTe capping layer and the low emission is from the CdTe/CdMnTe superlattice. The spectra illustrate the pressure induced quenching of the emissions.
Hull. Figure 7.8(a) shows the magnetic field dependence of the PL from a Cd$_{0.8}$Mn$_{0.2}$Te layer. The band gap is seen to be decreased by about 40 meV in a field of 10T. Figures 7.8(b) and (c) shows the magnetic field dependence of the PL from the samples studied here (Gregory 1990). The magnetic field effects are reduced in the superlattice samples but are still significant, especially in the narrow well samples.

7.5 Analysis and Discussion

The magnetic field results supplied by the Hull group show that the SL PL energy is significantly affected by magnetic field changes in the barrier material. This shows that it will be possible to use the SL emission as a probe of these magnetic field effects under pressure.

To interpret magnetic field data under pressure it will be essential to have fully characterised the SL structures under pressure. Wide and narrow well samples have therefore been studied. In the wide well sample the emission is sensitive mainly to the pressure coefficient of the well material. In the narrow well sample the emission is principally sensitive to the relative coefficients of the two materials and movements of the band offsets under pressure. The magnetic field experiments will be performed on narrow well samples to increase the proportion of the electron and hole wavefunctions penetrating the barrier and hence enhance the magnetic field effects. It is therefore particularly important to characterise such samples. The pressure coefficients of the SL PL have been fitted using the envelope function model described in chapter 3. Sample A is discussed first. In this sample the wells are wide and the emission relatively insensitive to
Fig. 7.5 The energy of the PL emission from sample A as a function of pressure.

6.6 meV/kbar
Fig. 7.6 The energy of the PL emissions from sample B as a function of the InP (pressure gauge) energy.
Fig. 7.7 The intensity of the PL from sample B is plotted as a function of the InP energy. Circles show the behaviour of the CdMnTe capping layer and crosses show the behaviour of the superlattice emission.
movements of the band offsets under pressure, so that the valence band offset can be assumed to remain constant. The parameters used in the model are given in table 7.2. Whilst the pressure coefficient of CdTe has been measured previously there is some controversy as to its exact value (for example, 11.4 meV/kbar - Thomas 1961, 8.0 meV/kbar - Langer 1964 and 7.9 meV/kbar - Babonas et al 1971). Good agreement is obtained using the value of 6.5 meV/kbar reported by Dunstan et al (1988) in the calculation. This is therefore accepted as the correct value for CdTe. The pressure coefficient of CdMnTe is also under debate in the literature but its value has been measured directly in this work to be 8.2 meV/kbar for Mn content ~0.25. The valence band offset is assumed to remain constant under pressure in the envelope function calculation which then yields a value of 6.5 meV/kbar as expected for wide wells. For sample B the pressure coefficient of the CdMnTe capping layer and the superlattice are found to be the same within error. This is a surprising result since the well and barrier materials have quite different pressure coefficients and the electron is confined in a deep well. For example, calculations assuming that the valence band offset remains constant under pressure predict a value of 6.9 meV/kbar for the pressure coefficient of the superlattice band-gap. This probably suggests that the pressure coefficient of one of the constituent materials is slightly in error, rather than that the band offsets are varying rapidly. Before further characterisation of this system, under pressure, can be carried out the pressure coefficients of CdTe and CdMnTe should be measured against the same pressure gauge (or each other). The results shown in fig. 7.6 suggest that the two coefficients are very similar. However knowledge of the superlattice PL pressure dependence, in the absence of a magnetic field, should allow the
Fig. 7.8 The magnetic field dependence of the band-gap in DMS is illustrated. (a) shows the dependence for a bulk $\text{Cd}_{0.8}\text{Mn}_{0.2}\text{Te}$ layer. (b) and (c) illustrate the dependence for the superlattice samples A and B (after Gregory 1990).
magnetic effects to be studied.

The intensities of the emissions from sample B are shown in fig. 7.7. As the pressure is increased the intensity of the superlattice emission drops off, whilst that of the CdMnTe capping layer rises to a maximum and then falls off. The intensities are recovered on unloading pressure. The intensity of the capping layer reaches a maximum when the emission is at approximately 2.04 eV. This is close to the energy of the internal Mn-Mn transition mentioned in section 7.2 (2.2 eV at 10K). Shan et al (1985) have studied the absorption edge of CdMnTe under pressure. For composition above x=0.5 they observe a negative pressure coefficient of the edge. This is assigned as effects involving the Mn\(^{2+}\) levels. The pressure coefficients they measure are around -5 meV/kbar. In sample B the intensity maximum occurs at around 12 kbar. Using the data of Shan et al the energy of the Mn-Mn transition is calculated to be 2.14 eV at this pressure, in reasonable agreement with the observed energy. The linear nature of the emission energy with pressure suggests that the PL continues to come from the same states in the CdMnTe. This is therefore not a crossover to the Mn level but some sort of resonance with the Mn-Mn transition energy. Vecchi et al (1981) have shown that the first excited state sits only 1.18 eV above the top of the valence band a crossover under pressure is not therefore to be expected. The reason for the apparently linear decrease of the superlattice emission intensity is not clear at present.

7.6 Summary

Preliminary results of magneto-optical studies on CdTe/CdMnTe superlattices have been reported. These constitute a characterisation of
the system as a function of pressure. This characterisation will allow the results from the magnetic field experiments at high pressure to be analysed, to study the magnetic interactions as a function of Mn-Mn separation. Further high pressure work is required to fully characterise the system under pressure, for example, to determine the pressure dependence of the band offsets.

The intensity of the emission, from the CdMnTe layer, has shown an interesting behaviour. Further work is required to confirm the assignment suggested here.

End Note

Prakash et al (1990) have recently reported on CdMnTe under hydrostatic pressure. They have studied the binding energy of the bound magnetic polaron (BMP) and find that volume changes alone cannot account for the changes in the BMP binding energy which they observe. They therefore conclude that the exchange energy $J_{\text{Nox}}$ has to change with the exchange constant, pressure and furthermore that $J_{\text{Nox}}$ itself changes with pressure.
8.1 Introduction

In this chapter the behaviour of the PL of a-Si:H under hydrostatic pressure is investigated. The intensity of the PL is of particular interest here, where it is taken as a indicator of structural damage in the sample. The PL intensity is found to be maintained upto high pressures (~90 kbar) and then to be quenched suddenly. The intensity is then recoverable on unloading pressure. The energy of the PL is found to have a small red shift with pressure similar to that of crystalline silicon. Pressure coefficients from other amorphous and crystalline materials are discussed in the light of this result.

Since amorphous materials have not been discussed elsewhere in this thesis a few comments, particularly on PL in a-Si:H, are made in the following section.

8.2 Amorphous Silicon

8.2.1 Structure of Amorphous Silicon

A-Si is deposited by one of the following techniques: glow
discharge, sputtering or CVD (chemical vapour deposition) and the amorphous nature of the material has been verified by many techniques. The material has a well-preserved first-neighbour separation i.e. little change in bond length from crystalline silicon, but second-neighbour separations are modified due to variations of about ±5% of the bond angle. Structurally the material can therefore be considered as similar to c-Si but lacking the long range order. The effect of this on the electronic and optical properties of the material is the subject of intensive research.

Experimentally it is found that the electronic properties of the material are greatly enhanced by hydrogenation. A hydrogen content of between 2 and 16 atomic per cent is required. There is considerable evidence that, within the amorphous network, there exist structural inhomogeneities specifically voids and microcracks.

8.2.2 Photoluminescence in Hydrogenated Amorphous Silicon

In early studies of a-Si, luminescence was undetectable because the density of defects was so large that non-radiative recombination was dominant. Hydrogenation by glow discharge or by reactive sputtering reduced the defect density, and it was quickly discovered that this material had strong luminescence (Engemann and Fischer 1973).

Two main bands of luminescence are observed in a-Si:H. The highest energy band is at about 1.4 eV and is believed to be due to recombination of carriers trapped in the band tails (Street 1981) and so is a consequence of the intrinsic disorder of the material. A schematic of the density of states for an amorphous semiconductor is shown in fig. 8.1. The important features for PL are the localised band edge.
Fig. 8.1 Schematic density of states diagram for an amorphous semiconductor showing the extended states separated from the localised band tail states by the mobility edge and defect states in the gap.

Fig. 8.2 A model for the luminescence transitions showing the 1.4 eV band-tail transition, non-radiative tunneling to defects, and the subsequent recombination that is proposed to explain the 0.9 eV luminescence.
states and the defects states within the gap. The exact position of the luminescence peak varies from sample to sample depending on the deposition conditions. This is believed to be due to changes in the band gap and disorder because of differences in the microstructure, hydrogen content etc., rather than different origins of the PL. The second band at 0.9 eV has been less extensively studied and is less well understood but is believed to be defect-related. A model for the luminescence in a-Si:H is shown in fig. 8.2. Excited carriers thermalize to the localized band tail states and recombine radiatively, giving rise to the 1.4 eV luminescence spectrum. Non radiative tunneling to a defect, followed by radiative recombination is proposed to explain the 0.9 eV luminescence. Other luminescence bands have been observed in some samples but will not be discussed here. A review of luminescence and recombination in a-Si:H has been given by Street (1981).

It is the 1.4 eV emission with which we are primarily concerned here, this gives rise to a broad relatively featureless spectrum, considerably lower in energy than the optical gap, at about 1.9 eV, determined from optical absorption experiments (Street 1978). Examples of complementary PL, PLE and absorption spectra are shown in fig. 8.3 (Street 1978) showing the general form of the PL spectra and its position relative to the absorption edge. The energy of the emission relative to the band gap and the high density of recombination centres indicate that the states are close to the band edges. In addition, the peak is most intense in samples in which the defect density is lowest, which implies that intrinsic states (e.g. band tails) are involved. Similar pressure coefficients of the PL emission and the absorption edge (see later) are observed, suggesting further that the PL is derived from the intrinsic band edge states.
Fig. 8.3 Examples of complimentary PL, PLE and absorption spectra (Street 1978) showing the general form of the PL spectrum and its position relative to the absorption edge.

Fig. 8.4 The relative luminescence intensity is shown as a function of the dangling bond density as measured by ESR in undoped a-Si:H (Street et al. 1978). The fits relate to a tunneling formula (Tsang and Street 1978), where $R_c$ is a critical transfer distance.
It is clear from the long decay times observed that localised rather than extended states are involved. Decay rates have been reported by many authors (Tsang and Street 1979, Austin et al. 1979, Kurita et al. 1979, Shah and DiGiovanni 1981). The decay contains components that extend from $10^{-8}$ upto $10^{-2}$ sec. and in fact response can be observed up to 1 sec. These long decay times, compared with typical exciton decay times of $10^{-8}$-$10^{-9}$ sec., indicate that recombination occurs through well-separated electrons and holes by a tunneling process.

Figure 8.4 shows the relation between the dangling bond density $N_s$ and the luminescence intensity $I$ for measurements at 10K (Street et al. 1978). Provided $N_s$ is below $10^{17}$cm$^{-3}$, $I$ is large and more or less independent of $N_s$. However, when $N_s$ exceeds $10^{17}$cm$^{-3}$ $I$ decreases rapidly, becoming undetectable for $N_s > 10^{18}$cm$^{-3}$. Since unhydrogenated a-Si typically has dangling-bond densities of about $10^{19}$cm$^{-3}$, it is not surprising that this material does not exhibit luminescence, indeed it is only the localised nature of the band tail states that allows such intense luminescence in a-Si:H at defect densities of $10^{17}$cm$^{-3}$.

8.3 A-Si:H Under Hydrostatic Pressure

8.3.1 Experimental Details

The a-Si:H sample was grown at Dundee University by glow-discharge (g.d.) deposition onto a quartz substrate held at 300°C. The sample was 1.2μm thick with a room temperature conductivity of about $1 \times 10^{-9}$Ω$^{-1}$cm$^{-1}$ and activation energy $=0.75$ eV. The sample and a piece of ruby, for pressure calibration, were prepared and loaded into the DAC in the
manner described in chapter 4. A 4:1 methanol:ethanol solution was employed as the pressure transmitting medium. The PL intensity is strongly quenched at temperatures above -100K, hence measurements were carried out at 80K. To avoid axial stresses, all pressure changes were made at 300K.

The high pressure experiments were conducted as previously described, the excitation power was kept low (20-50mW) to minimize heating the sample and the PL detected by a cooled Ge detector. The spectra were corrected for the spectral response of the detection system. The luminescence from the ruby in the cell and from a reference ruby on the outside of the cell was used for conventional pressure calibration.

A comparison of intensities from PL spectra obtained in a DAC is difficult because of the difficult optical alignment and possible movements of the sample within the cell. For each pressure we have taken the most intense spectrum recorded as the best measure of the sample's PL intensity, since less intense spectra merely indicate that some of the PL intensity has not been collected by the optics. In view of these difficulties a measurement of relative intensity cannot be considered more accurate than to within a factor of two and to achieve this accuracy requires some care. However, this degree of accuracy is quite adequate for our present purposes since, as discussed in section 8.2.2, structural damage leading to defect densities as low as $10^{18} - 10^{19} \text{cm}^{-3}$ will quench the PL by orders of magnitude (Street 1978) so that quenching by a factor of two would be regarded as insignificant.
8.3.2 Results

Figure 8.5 shows typical PL spectra measured at the pressures indicated and at a temperature of 80K. In order to maintain standard growth conditions, the substrate was not roughened before growth of the a-Si:H film; therefore characteristic interference fringes are seen on the otherwise approximately Gaussian spectrum. Figure 8.6 is a plot of relative PL intensities against pressure, obtained by integrating the spectra. The results of four separate experiments are shown; for each experiment a new piece of the same sample was used. Measurement were taken while increasing and decreasing pressure in order to observe any irreversibility. The plot clearly shows that, within experimental error, there is no pressure quenching up to ~90 kbar. Above ~90 kbar some sudden quenching is seen but the PL is still observable at ~100 kbar. At 126kbar the PL is quenched beyond detection. For unloading from pressures up to ~90 kbar the intensity is maintained. Measurements made while decreasing pressure from 126 kbar are indicated by circled points. The intensity is seen to recover, with some hysteresis, so that at 0 kbar almost full initial intensity is observed.

Owing to the presence of the interference fringes, the PL peak position for each intensity against energy spectrum was taken as the energy corresponding to equal integrated intensities on each side. The shifting of the PL peak to lower energies with pressure can be seen in fig. 8.5. This red shift is plotted in fig. 8.7 where circled points have the same meaning as in fig. 8.6. From fig. 8.7 it is seen that the shift for pressures up to ~90 kbar is independent of the direction of pressure change and is found to be \(-1.9 \pm 0.1\) meV/kbar. At pressures greater than ~90 kbar, when the PL is heavily quenched, the peak is seen
Fig. 8.5 Typical PL spectra of a-Si:H measured at the pressures indicated and at a temperature of 80K. Spectra are corrected for the response of the detection system.
Fig. 8.6 The PL integrated intensity is shown as a function of hydrostatic pressure. The curves are guides to the eye showing the behaviour of data within experimental error. The circled data points were obtained, while deceasing pressure, from a sample which had been subjected to 126 kbar.
to shift rapidly to longer wavelengths. For the sample that experienced a maximum pressure of 126 kbar, some of the shift is irreversible. When decreasing the pressure on this sample the shift was found to be 

\[ -1.8 \pm 0.2 \text{ meV/kbar} \]

which is the same, within experimental error, as for increasing pressure, but with the peak position permanently shifted to lower energy by \(-35 \text{ meV}\).

8.3.3 Discussion

The PL intensity has been shown not to be significantly quenched by hydrostatic pressure up to \(-90 \text{ kbar}\). In an amorphous material, voids and other weak or low density regions are expected to collapse at pressures much lower than the corresponding crystalline phase transition, causing structural changes to the amorphous network. Since in a-Si:H the PL is strongly quenched by defect densities above \(10^{17} \text{ cm}^{-3}\), it provides a sensitive measure of structural damage. The results reported here are in strong contrast to previous work on g.d. material, deposited at 250°C (Weinstein 1981). Weinstein reported a strong quenching of the PL intensity with pressure throughout the range 0-42 kbar. The emission was quenched beyond a detectable level at 75 kbar. He also observed that, on unloading pressure, the intensity was only partially recovered. This was interpreted as an increase in defect density and some form of permanent structural damage under compression. Clearly the effect of pressure is sample dependent, and our data shows that it is possible to produce high quality material which is not damaged by hydrostatic pressure up to at least 90 kbar and consequently in which the PL intensity is not significantly affected. This pressure is close to the c-Si phase
Fig. 8.7 The PL energy (determined as described in the text) is plotted as a function of hydrostatic pressure. The circled data points have the same significance as in fig. 8.6.
transition at 125 kbar (Weinstein and Piemarini 1975, Welber, Kim, Cardona and Rodriguez 1975). We report a reversible shift of 
$-1.9 \pm 0.1 \text{ meV/kbar}$ for pressures less than ~90 kbar. Other authors have reported similar shifts at low pressures (less than 50 kbar). Weinstein (1981) reported a shift of $-2.0 \pm 0.5 \text{ meV/kbar}$. Welber and Brodsky (1977) and Minomura (1981), observing not the PL but the absorption edge, reported $-0.7$ to $-2.0 \text{ meV/kbar}$ and $\sim -1 \text{ meV/kbar}$ respectively. For pressures above ~90 kbar we observe a permanent red shift. Welber and Brodsky (1977) have reported a similar irreversibility for pressures above 50 kbar. Minomura (1981) found that the rate of shift increased above 50 kbar and that the films showed a large hysteresis which became larger with increased applied pressure. He also found that the optical gap shrinks to zero; that is, a transition to the metal state occurs, at about 130 kbar. It is at pressures approaching this value that we observe complete quenching of the PL.

In a-Si quenching of the PL by any mechanism such as temperature or defect density is often associated with a large red shift of the order 100 meV per decade (Street 1981, Dunstan and Boulitrop 1984). It is possible that this effect is seen in figs. 8.6 and 8.7 for the points at 94 and 101 kbar, however the nature of the quenching mechanism is not clear since the recovery of the PL intensity on release of pressure indicates that the samples have not been structurally damaged. An alternative possibility is that the band tail emission has been completely quenched at ~90 kbar and the spectra seen at higher pressures are due to the defect related emission reported at ~0.9 eV at 0 kbar (Street 1981, Dunstan and Boulitrop 1984). If this is so the absence of this emission after unloading is surprising.

Since quenching of the PL is associated with a red shift the
determination of an intrinsic pressure coefficient when quenching is simultaneously observed is impossible; any red shift due to the quenching will be added to the pressure induced shift. Since we observe no quenching over the range 0-90 kbar we are able to identify our value of -1.9 ± 0.1 meV/kbar as the pressure coefficient of the tail states responsible for the PL (Street 1981, Dunstan and Boulitrop 1984). It is interesting to note that Weinstein (1981) observed an essentially identical coefficient (-2.0 ± 0.5 meV/kbar) despite observing quenching over the entire pressure range. The most obvious explanation for this is that quenching was complete in collapsed parts of the sample whilst completely unquenched PL was observed from undamaged parts of the sample; this is consistent with the only partial recovery of the PL intensity on release of pressure in his samples. A similar effect may be responsible for the similar behaviour of the circled points in fig. 8.7.

At high defect densities (≈ 10^{18} cm^{-3}) the exponential absorption tail in a-Si:H and a-Si becomes shallower, extending further into the gap. This entails a reduction in the Tauc gap (Dunstan 1983) and so progressive severe structural damage at high pressure would increase the apparent pressure coefficient of the band gap. This may account for the change in pressure coefficient observed by Minomura (1981) above 50 kbar; PLE experiments are planned in order to observe whether the same effect occurs in our samples above 90 kbar. However, it is difficult to imagine a mechanism of defect creation at high pressure which allows annealing at ambient pressure to the densities < 10^{17} cm^{-3} required by the recovery of the PL intensity seen in our data. In this connection it is worth while to note, firstly, that the alcohol mixture is not a satisfactory hydrostatic medium, at room temperature, above about 100 kbar (Piermarini, Block and Barnett 1973) so that large axial
strains may be induced in the sample. The effect on the PL is not known. Secondly, that defect related quenching of the intrinsic PL usually results initially in a strong emission at 0.8-0.9 eV (Street 1978, Dunstan and Boulitrop 1984) for which there is little evidence in our data (fig. 8.5).

Finally we consider the significance of the -1.9 meV/kbar pressure coefficient. The application of hydrostatic pressure in the study of the band structure of crystalline semiconductors has been discussed in chapter 2. Since amorphous and crystalline silicon are alike in many ways, for example, in structure (=equal nearest neighbour separation, see section 8.2.1) and in electronic properties, for example refractive index (a-Si n=3.5, c-Si n=3.42 Connell and Paul 1972), it is reasonable to question whether the crystalline band structure can be used to describe the properties of the amorphous material. One such property would be the pressure coefficient of the band gap. Brodsky (1980) suggests that a value of ~-1 meV/kbar is consistent with his quantum well model of a-Si:H, in which the band edge states are derived from those of crystalline Si (X-minima) by quantum confinement between barriers of large gap material, so that a similar pressure coefficient would be expected. However, since k is not a good quantum number in amorphous materials and the optical transition is allowed, one should not discuss the problem in terms of the Brillouin zone of c-Si but rather in terms of the density of states (DOS). In c-Si, the largest density of states is associated with states with X character; the Γ-like states with a large positive pressure coefficient make only small contributions to the DOS. Their contribution to the conduction band DOS in a-Si:H are expected to be in proportion, and so it is not surprising that the pressure coefficient in a-Si:H is similar to that of the X
minimum in c-Si.

8.4 Pressure Coefficients of Related Amorphous Materials

This argument based on the DOS predicts that a similar pressure coefficient would be found in related materials such as a-GaAs despite the fact that c-GaAs has a direct gap with a large positive pressure coefficient associated with the Γ point.

Only a few results on the pressure dependences of amorphous materials exist. In most cases the results are derived from absorption experiments rather than from PL, this should be a more reliable measure of the pressure dependence of the optical gap even though the results may be less accurate. That is to say that the origin of an absorption edge is less controversial than that of PL, but absorption is a more difficult experiment and the determination of a pressure coefficient from absorption spectra is more difficult than from PL spectra. A summary of the available data is given in table 8.1 along with the pressure coefficients of the corresponding crystalline materials for comparison.

C-Si and c-GaP are both indirect semiconductors in which the conduction band X minima are lowest, therefore arguments based on a quantum well model or the DOS would predict that the pressure coefficient of the corresponding amorphous material would be similar to that of the crystalline material i.e. a small negative pressure coefficient characteristic of the X minima, and this is seen to be the case (given the complexity of the experiments, pressure coefficients of absolute value < 1 meV/kbar should be regarded as of uncertain sign). Conversely for GaAs the DOS argument would predict a small, negative
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<tr>
<th>Amorphous material</th>
<th>Pressure coeff. (meV/kbar)</th>
<th>Crystalline pressure coeff. (meV/kbar)</th>
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<td>-1.9 ± 0.1δ (PL)</td>
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<td></td>
<td>+0.25γ (abs)</td>
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<td>-0.7 to -2.0μ (abs)</td>
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<td>GaP</td>
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<tr>
<td>GaAs</td>
<td>0.7γ (abs)</td>
<td>10.7θ</td>
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</table>

α Weinstein (1981)  
β Paul and Pearson (1955)  
δ This work  
γ Connell and Paul (1972)  
ρ Minomura (1981)  
μ Welber and Brodsky (1977)  
τ Paul and Brooks (1954)  
φ Zallen and Paul (1964)  
θ Wolford and Bradley (1985)

Table 8.1 The pressure coefficients of some amorphous semiconductors are given along with the pressure coefficients of the corresponding crystalline material.
pressure coefficient whilst the quantum well model would predict a
pressure coefficient of approximately 11 meV/kbar. The small coefficient
of a-GaAs therefore tends to support the DOS argument.

Also worthy of note are the coefficients of Ge. C-Ge is also an
indirect semiconductor but with the lowest conduction band minima at the
L point and both crystalline and amorphous materials have similar
pressure coefficients, characteristic of the L minima (the L minima is
also associated with a high density of states).

8.5 Concluding remarks

The PL intensity has been shown not to be significantly quenched by
hydrostatic pressure up to ~90 kbar, almost full recovery of the PL
intensity is observed after unloading from 126 kbar, approximately the
c-Si phase transition pressure (125 kbar). Further work is in hand to
study this resilience to structural damage under hydrostatic pressure as
a function of deposition temperature. Figure 8.8 shows PL spectra taken
at 80K and 0 kbar, for samples deposited at 150°C and 90°C (c.f. 300°C
fig. 8.5). Again, interference fringes are seen on the roughly gaussian
spectra. For the film deposited at 150°C there is still no evidence of
the defect band but for the film deposited at 90°C the gaussian form of
the spectrum is lost at low energy and an emission at 0.85 eV is
probably defect related. Experiments on the pressure dependence of the
PL intensity in these samples will be interesting and may yield the
pressure dependence of the defect band.

A pressure coefficient of -1.9 ± 0.1 meV/kbar has been measured
over the pressure range 0–90 kbar, where no significant quenching is
Fig. 8.8 PL spectra from samples of a-Si:H deposited onto a substrate at (a) 90°C and (b) 150°C by g.d. deposition. Spectra were recorded at 80K and ambient pressure. A defect related emission is seen at 0.85eV (1450 nm) in spectrum (a).
observed, this may therefore be identified as the pressure coefficient of the tail states. The pressure coefficient is consistent with a DOS argument which is supported by evidence from the pressure coefficients of other related amorphous materials.
Chapter 9

CONCLUSIONS

High pressure photoluminescence has been used throughout this thesis to study the physics of semiconductor structures. The applications of the technique have been shown to be wide ranging. Special emphasis has been put on the determination of the band offsets in quantum well structures. However, the technique has also been shown to be of utility in the study of as widely different materials as dilute magnetic semiconductors and amorphous materials. Conclusions from each of the specific research projects have been given in the relevant chapters along with proposals for further work, these are not repeated here. Instead a few words will be said about the technique itself. High pressure PL has been shown to be a powerful technique and will continue to be so. The optical work in the DAC may now be considered as quite routine. An understanding of the importance of the gasket geometry and temperature effects, discussed in chapter 4, makes attainment of the appropriate pressure range straight forward. The cells have been taken to a number of laboratories for the performance of specialised experiments. The design of DAC and force transmitting mechanism has been shown to be well suited to this.

The introduction of the use of liquid argon as the pressure medium has meant that low temperature pressure changes can be made. This has greatly enhanced the speed of data acquisition as well as making possible some very detailed work where great control over the pressure
is required (e.g., the data required to plot quenching curves at Γ-X crossover). Whilst the use of argon has improved the homogeneity of the pressure in the gasket hole over that of the previously used methanol:ethanol solution, the use of helium is in fact preferable, and it is hoped to extend the technique to use this in the near future. The extension of the basic PL technique to more sophisticated experiments is the next obvious step. Electrical measurements and have already been mentioned as have high magnetic field measurements. Invaluable optical techniques which should become equally as routine in the DAC as PL are photoluminescence excitation spectroscopy and absorption. PL has the disadvantage of studying only the lowest lying state; these methods would allow, for example, the study of higher lying quantum well states.
Appendix A

The Periodic Table

The letters s, p, d, ... signify electrons having orbital angular momentum 0, 1, 2, ... in units \( \hbar \); the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.

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The letters s, p, d, ... signify electrons having orbital angular momentum 0, 1, 2, ... in units \( \hbar \); the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.
Appendix B

The Theory of the Diamond Anvil Cell Gasket

The essential theory needed to describe the behaviour of the DAC gasket/diamond system was initially worked out by Schroeder and Webster (1949) in connection with press forging and coining. The theory has been successfully applied to the DAC gasket (Dunstan 1989) and some important conclusions are repeated here.

Following the analysis of Schroeder and Webster, who considered a blank disc squeezed between two hard anvils and taking into account the presence of a gasket hole of radius \( r_g \) the following results are obtained; for \( 0 < \mu < 1 / \sqrt{3(n+1)} \)

\[
\sigma_n = (n+1) k \exp \left\{ 2\mu \left[ \frac{r_0}{t} - \frac{r}{t} \right] \right\} \quad R \leq r \leq r_0
\]

\[
\sigma_n = \frac{k}{\sqrt{3} \mu} + \frac{2k}{\sqrt{3}} \left[ \frac{R}{t} - \frac{r}{t} \right] \quad r_g \leq r \leq R
\]

\[
\sigma_n = k \left[ \frac{1}{\sqrt{3} \mu} - 1 \right] + \frac{2k}{\sqrt{3}} \left[ \frac{R - r_g}{t} \right] \quad r < r_g \quad [B.1]
\]

with

\[
R = r_0 - \frac{t}{2\mu} \log \frac{1}{\sqrt{3(n+1)} \mu}
\]
and for $\mu \geq 1/\sqrt{3(n+1)}$

\[
\sigma_n = (n+1)k + \frac{2k}{\sqrt{3}} \left[ \frac{r_0 - r}{t} \right] \quad \text{for } r_g \leq r \leq r_0
\]

\[
\sigma_n = nk + \frac{2k}{\sqrt{3}} \left[ \frac{r_0 - r_g}{t} \right] \quad \text{for } r < r_g \quad \text{[B.2]}
\]

where $\sigma_n$ is the normal stress component, $r_0$ the radius of the gasket between the diamonds and $t$ its thickness, $k$ is the stress for yielding under uniaxial loading and $\mu$ the coefficient of friction. $n$ is a measure of the massive support provided when the gasket material outside of the anvils is thicker than $t$. It transpires that the massive support offered to the material between the anvils is a considerable fraction of the pressure in the gasket hole. These results are plotted in fig. B.1.

Fig. B.1 The normal stress $\sigma_n$ is plotted as a function of radius (eqns. B.1 and B.2), for aspect ratios $r_0/t = 20$ (curves a and b) and $r_0/t = 5$ (curves c, d) and massive support factors $n = 3$ (a, c) and $n = 0$ (b, d). The coefficient of friction $\mu = 0.1$.

Rearranging eqn. B.2, a maximum gasket thickness $t_{max}$ or aspect ratio $a_{max}$ as a function of hydrostatic pressure $P = \sigma_n$, $r < r_g$ can be
defined.

\[ t_{\text{max}} = \frac{2k}{\sqrt{3} (P-nk)} \left( r - r_0 \right) \]

\[ a_{\text{max}} = \frac{r_0}{t_{\text{max}}} \]

this is plotted in fig. B.2. If the gasket is sufficiently thick it will follow this curve as the load is applied. In this case the gasket is thinned by increasing load and this is sufficient to raise the pressure in the gasket hole. This is termed a thick gasket. In the limiting case of an incompressible fluid the hole must expand. A gasket may also be anywhere below this curve in which case it is termed a thin gasket. In this case the pressure is raised in the gasket hole by extrusion of the metal inwards, the thickness remains almost constant. This is the preferred regime in which to operate a DAC. At some pressure the gasket will join the thick gasket curve and the gasket hole will begin to

Fig. B.2 The maximum gasket thickness is plotted from eqn. B.3 for n=0 (solid curve) and n=3 (chain-dotted curve). The regions below the curve correspond to thin gaskets (see text); the dotted curve shows the typical behavior of a gasket in this regime.

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enlarge. This effect is illustrated in fig. B.3.

Fig. B.3 The normal stress $\sigma_n$ is plotted as a function of radius for a thin gasket as the pressure is raised. From (a) to (d) $r_g$ decreases and at (d) the gasket ceases to be 'thin'. The hole now expands as the thickness is decreased; (g) illustrates the region of instability.

It is the force pressure relationship which is usually measured experimentally, the theoretically predicted form of these curves are shown in fig. B.4 for thick and thin gaskets.

Fig. B.4 Normalised force-pressure plots for (a) thick gaskets and (b) thin gaskets. In (a), curve (i) is for a simple disk; for the curves (ii) $n=0$ and $r_g/r_o=1/3$ (solid curve) $r_g/r_o=1/2$ (broken curve). The curves (iii) are the same as (ii) but with $n=3$. The curve (iv) was obtained numerically for a gasket hole of constant volume, with $r_g/r_o$ increasing as the pressure increases and the thickness decreases. In (b), numerical solutions are given for thin gaskets with an initial value (at $P=0$) of $r_g/r_o=1/3$, and thickness (i) $t=r_o/2$, (ii) $t=r_o/6$ and (iii) $t=r_o/10$. A compressible liquid is used, with $B_o=10k$, $B'=10$. The broken curve is the same as (ii) but with an incompressible liquid.
Appendix C

The Pressure Dependence of the Direct Gap in Strained Layers

The following expressions have been derived for the pressure dependence of the direct band gap of strained layers (O'Reilly 1990). These results have been used in chapter 6 in the analysis of the high pressure data from strained InGaAs quantum wells grown pseudomorphically on GaAs.

For the InGaAs/GaAs quantum wells, the net strain in the plane of the well is given by

\[ \varepsilon_{\parallel} = \varepsilon_{xx} = \varepsilon_{yy} = (a_s - a_x) / a_x \]  \[ \text{[C.1]} \]

where \( a_s \) and \( a_x \) are the lattice constants of the GaAs substrate and the unstrained alloy respectively. In response to the biaxial stress the layer relaxes along the growth direction \( z \), the strain \( \varepsilon_{\perp} = \varepsilon_{zz} \) being of opposite sign to \( \varepsilon_{\parallel} \) and given in second order elasticity theory by

\[ \varepsilon_{\perp} = -\frac{2\sigma}{1-\sigma} \varepsilon_{\parallel} \]  \[ \text{[C.2]} \]

where \( \sigma \) is Poisson's ratio. The total strain can be resolved into a purely axial component, \( \varepsilon_{ax} \), and a hydrostatic component, \( \varepsilon_{vol} \),

\[ \varepsilon_{ax} = \varepsilon_{\perp} - \varepsilon_{\parallel} \]
\[ \varepsilon_{vol} = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} = 2 \varepsilon_{\parallel} + \varepsilon_{\perp} \]  \[ \text{[C.3]} \]

This in-built strain modifies the band-gap of the layer from its unstrained value, \( E_{g}^{0} \), to

\[ E_{g} = E_{g}^{0} + a \varepsilon_{vol} - |b \varepsilon_{ax}| \]  \[ \text{[C.4]} \]
where \( a \) is the hydrostatic deformation potential and \( b \) is the axial deformation potential. Substituting from eqn. C.3, eqn. C.4 may be written as

\[
E_g = E_g^0 + 3a\varepsilon_\parallel + (a + b)\varepsilon_{ax} \tag{C.5}
\]

The band gap is then found to vary with pressure according to

\[
\frac{dE_g}{dP} = a \frac{d}{dP} (3\varepsilon_\parallel) + (a + b) \frac{d\varepsilon_{ax}}{dP} \tag{C.6}
\]

Since the in-plane lattice constant of the alloy varies at the same rate as that of the GaAs substrate \((d/dP)(3\varepsilon_\parallel)\) can be replaced by \(-1/ B_s\), where \( B_s \) is the GaAs bulk modulus. For a free standing alloy the band-gap pressure coefficient is given by

\[
\frac{dE_g}{dP} = \frac{a}{B_x} \tag{C.7}
\]

where \( B_x \) is the bulk modulus of the free standing alloy. Substituting eqn. C.7 into C.6 gives an expression for the strained-well pressure coefficient in terms of the unstrained alloy coefficient.

\[
\frac{dE_g}{dP} = \frac{B_x}{B_s} \frac{dE_g^0}{dP} + (a + b) \frac{d\varepsilon_{ax}}{dP} \tag{C.8}
\]

The pressure dependence of the axial strain can be estimated using elasticity theory. The elastic energy density of a (001)-strained crystal is given by

\[
U = \frac{1}{2} C \left( \varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2 \right) + C \left( \varepsilon_{xx} \varepsilon_{yy} + \varepsilon_{yy} \varepsilon_{zz} + \varepsilon_{xx} \varepsilon_{zz} \right) + \frac{1}{6} C \left( \varepsilon_{xx}^3 + \varepsilon_{yy}^3 + \varepsilon_{zz}^3 \right) + C \left( \varepsilon_{xx} \varepsilon_{yy} \varepsilon_{zz} \right)
\]

\[
+ C \left( \varepsilon_{xx}^2 \varepsilon_{yy} + \varepsilon_{xx} \varepsilon_{yy}^2 + \varepsilon_{xx}^2 \varepsilon_{yy} + \varepsilon_{xx} \varepsilon_{yy} \varepsilon_{zz} + \varepsilon_{yy}^2 \varepsilon_{zz} + \varepsilon_{yy} \varepsilon_{zz}^2 \right)
\]

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\[
\varepsilon_{xx}^2 + \varepsilon_{xx}^2 \quad [C.9]
\]

where \( C_{11} \) and \( C_{12} \) are the second order elastic constants, and \( C_{111} \), \( C_{123} \) and \( C_{112} \) are the third order elastic constants. The pressure along the \( i \)th direction is given by

\[
P_i = -\frac{\partial U}{\partial \varepsilon_{11}} \quad [C.10]
\]

An expression for \( \frac{dc^{ax}}{dP} \) is found by noting that \( \varepsilon_{||}(P) \) is determined by the variation in the lattice constant of the GaAs substrate, while \( \varepsilon_{\perp}(P) \) can then be found from eqns. C.9 and C.10 using the previously determined value of \( \varepsilon_{||}(P) \). In second-order elasticity theory \( \frac{dc^{ax}}{dP} \) is then given by

\[
\frac{dc^{ax}}{dP} = \frac{1}{3} (B^{-1} - B^{-1}) \varepsilon_{||}^0 \frac{1 + \sigma_x}{1 - \sigma_x} \quad [C.11]
\]

where \( \sigma_x \) is Poisson's ratio for the alloy. The bulk modulus \( B \) decreases with increasing lattice constant, \( dc^{ax} \) is therefore negative, and the net axial strain decreases in second-order elasticity theory. Combining eqns. C.7, 6.3 and C.11 the following estimate is made.

\[
(a + b) \frac{dc^{ax}}{dP} = -\frac{4}{3} \left( 1 + \frac{b}{a} \right) \varepsilon_{||}^0 \frac{1 + \sigma_x}{1 - \sigma_x} \frac{dE_g}{dP}
\]

\[
\sigma_x = \frac{10}{3} \varepsilon_{||}^0 \frac{dE_g}{dP} \quad [C.12]
\]

where typical values of \( \sigma_x = 1/3 \) and \( b/a = 1/4 \) are taken.
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