# Title goes here

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of the degree of Doctor of Philosophy

at the
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# Declaration

I, XXX (student no. YYY) hereby declare that, unless otherwise stated, this work is my own, and that it has not been submitted for another degree, either at University College Cork or elsewhere.

Signed: Christopher Broderick

Dedication goes here.

# Acknowledgements

Acknowledgements go here.

# Abstract

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# Publications

The following is a list of published work in which aspects of the research presented in this thesis have featured.

## 1. Refereed journal articles

- "Anisotropic electron g factor as a probe of the electronic structure of $GaBi_xAs_{1-x}$/GaAs epilayers", Christopher A. Broderick, Simone Mazzucato, Hélène Carrère, Thierry Amand, Hejer Makhloufi, Alexandre Arnoult, Chantal Fontaine, Omer Donmez, Ayşe Erol, Muhammad Usman, Eoin P. O'Reilly, and Xavier Marie, *Phys. Rev. B* **90**, 195301 (2014).

## 2. Conference proceedings

- "Theory of the electronic structure of dilute bismide and bismide-nitride alloys of GaAs: Tight-binding and **k**·**p** models", Muhammad Usman, Christopher A. Broderick, and Eoin P. O'Reilly, in *Proceedings of the 31$^{st}$ International Conference on the Physics of Semiconductors* (ICPS), Zurich, Switzerland (2012).

## 3. Conference talks

During the course of my doctoral research I have personally presented the following conference talks:

- "Theory of the electronic structure of the dilute bismide alloy $GaBi_xAs_{1-x}$", Christopher A. Broderick, Muhammad Usman, and Eoin P. O'Reilly, *32$^{nd}$ International Conference on the Physics of Semiconductors* (ICPS), Austin, Texas (2014).

## 4. Conference posters

During the course of my doctoral research I have personally presented the following conference posters:

- "Theory of the enhancement of the electron effective g factor in $GaBi_xAs_{1-x}$/GaAs epilayers", Christopher A. Broderick, Muhammad Usman, and Eoin P. O'Reilly, *5$^{th}$ International Workshop on Bismuth-Containing Semiconductors*, Cork, Ireland (2014).

# Chapter 1

# Introduction and overview

In this introductory chapter we begin in Section 1.1 by describing the background of and motivation for our research on dilute bismide alloys. Following this we describe the structure of the remainder of the thesis in Section 1.2, where we give a description of the content of the remaining chapters, as well as an overview of the primary results that have been achieved during the course of this work.

## 1.1 Background and motivation

Goes here.

## 1.2 Structure of the thesis and overview of primary results

The remainder of this thesis is organised as follows...

# Chapter 2

# Theoretical background: density functional theory and k·p method

## 2.1 Introduction

In this chapter we...

## 2.2 The electronic structure of semiconductors

Insert subsections after thesis skeleton is agreed. Citing a reference here just to generate a bibliography [1].

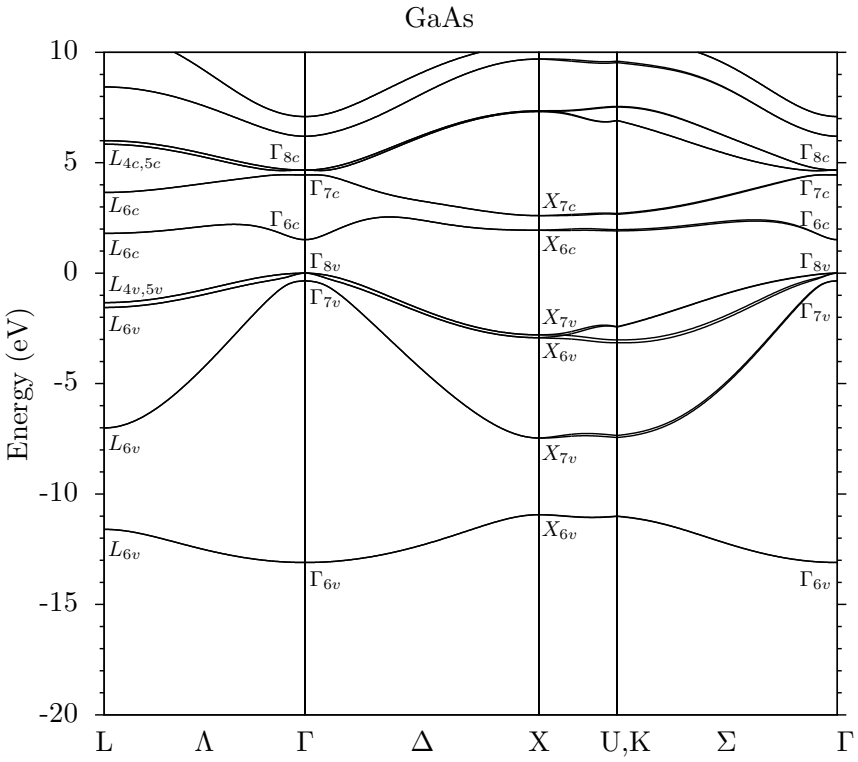


FIGURE 2.1: Band structure of a two-atom GaAs primitive unit cell, calculated using the $sp^3s^*$ tight-binding Hamiltonian described in the text, including spin-orbit coupling and parametrised according to Appendix A. The zero of energy has been taken at the valence band edge, i.e. $E(\Gamma_{8v}) = 0$.

# Chapter 3

# Electronic structure of dilute bismide alloys: the tight-binding method

## 3.1 Introduction

Goes here.

# Chapter 4

# Electronic structure of dilute bismide alloys: the k·p method

## 4.1 Introduction

Goes here.

# Appendix A

# Material parameters for tight-binding and k·p calculations

In this appendix we tabulate the material parameters that were used throughout this thesis to carry out electronic structure calculations using the tight-binding and **k·p** methods.

Our tight-binding parameters are listed in Table A.1 for the zinc blende III-V compounds of interest and include (i) lattice constants, (ii) valence band offsets (relative to the GaAs valence band edge, which we take as our zero of energy), (iii) orbital energies, (iv) the matrix elements of the spin-orbit coupling, (v) the inter-atomic interaction matrix elements, and (vi) the scaling exponents $\eta$ (which are used to scale the inter-atomic matrix elements as $\left(\frac{d_0}{d}\right)^{\eta}$ in strained crystals, where $d_0$ and $d$ are the unstrained and strained nearest-neighbour bond lengths, respectively). These tight-binding parameters were compiled primarily from previous work on the electronic structure of III-V compounds and alloys undertaken at Tyndall National Institute by Dr. Andrew Lindsay.

Our **k·p** parameters are listed in Table A.2 for the zinc blende III-V compounds of interest and include (i) the direct band gaps at the Γ-point (at $T = 0$ K and at room temperature), (ii) spin-orbit-splitting energies, (iii) average valence band energies (for band offset calculations using the model solid theory [2, 3]), (iv) electron effective masses at the Γ-point in the lowest conduction band, (v) Kane parameters, (vi) valence band Luttinger parameters, (vii) lattice constants, (viii) elastic constants, and (ix) Γ-point deformation potentials. These parameters were compiled from a number of sources, including from previous work undertaken at Tyndall National Institute by Dr. Sorcha Healy and from the `Param2002` code developed at the University of Surrey by Dr. Mark Silver. Additional parameters were compiled from Refs. [4], [5] and [6].

TABLE A.1: Material parameters for zinc blende III-V compounds used in $sp^3s^*$ tight-binding calculations.

| Parameter | GaAs | InAs | GaP | GaN | InN | GaBi | InBi |
|---|---|---|---|---|---|---|---|
| $a$ (Å) | 5.6532 | 6.0583 | 5.4505 | 4.4900 | 4.9850 | 6.3280 | 6.6860 |
| $\Delta E_v$ (eV) | 0.00 | 0.21 | −0.47 | −2.28 | −2.00 | 1.10 | 1.10 |
| $E_{s^*_\mathrm{a}}$ (eV) | 7.0914 | 7.2730 | 8.4796 | 12.2000 | 12.2000 | 6.1262 | 6.1262 |
| $E_{s^*_\mathrm{c}}$ (eV) | 6.2000 | 6.6095 | 7.1563 | 12.2000 | 12.2000 | 5.8164 | 5.8164 |
| $E_{s_\mathrm{a}}$ (eV) | −8.6336 | −9.5381 | −8.1124 | −12.3306 | −12.8406 | −8.3774 | −8.3774 |
| $E_{s_\mathrm{c}}$ (eV) | −2.9474 | −2.7219 | −2.1976 | −0.9994 | −0.3794 | −5.6126 | −5.9126 |
| $E_{p_\mathrm{a}}$ (eV) | 0.9252 | 0.7733 | 4.0851 | 2.7120 | 2.2260 | −0.1256 | −0.1256 |
| $E_{p_\mathrm{c}}$ (eV) | 3.5523 | 3.5834 | 1.0952 | 8.5803 | 8.2718 | 1.6940 | 1.7740 |
| $\Delta_\mathrm{a}$ (eV) | 0.4050 | 0.3870 | 0.0666 | 0.0210 | 0.0060 | 2.0142 | 2.0142 |
| $\Delta_\mathrm{c}$ (eV) | 0.1650 | 0.4155 | 0.1734 | 0.0060 | 0.0030 | 0.1152 | 0.1152 |
| $V_{ss\sigma}$ (eV) | −1.6835 | −1.4013 | −1.8727 | −2.0700 | −1.5501 | −1.3425 | −1.3425 |
| $V_{s^*_\mathrm{a}p_\mathrm{c}\sigma}$ (eV) | 2.0400 | 1.3939 | 1.9998 | 1.5442 | 0.4898 | 1.8051 | 1.8051 |
| $V_{s^*_\mathrm{c}p_\mathrm{a}\sigma}$ (eV) | 1.7700 | 1.6123 | 2.1882 | 2.8375 | 2.3295 | 0.5100 | 0.5100 |
| $V_{s_\mathrm{a}p_\mathrm{c}\sigma}$ (eV) | 2.3920 | 1.3079 | 1.8500 | 2.0717 | 0.7974 | 2.3567 | 2.4817 |
| $V_{s_\mathrm{c}p_\mathrm{a}\sigma}$ (eV) | 2.4200 | 2.3337 | 2.7312 | 3.0593 | 2.5956 | 1.2025 | 1.2025 |
| $V_{pp\sigma}$ (eV) | 2.9500 | 2.6588 | 3.0986 | 5.0530 | 4.5382 | 2.0003 | 1.9903 |
| $V_{pp\pi}$ (eV) | −0.7420 | −0.6390 | −0.7424 | −0.7150 | −0.6592 | −0.6354 | −0.7220 |
| $\eta_{ss\sigma}$ | 3.512 | 3.512 | 3.512 | 2.910 | 2.810 | 3.660 | 3.660 |
| $\eta_{s^*_\mathrm{a}p_\mathrm{c}\sigma}$ | 4.200 | 4.200 | 4.200 | 4.000 | 3.000 | 4.200 | 4.200 |
| $\eta_{s^*_\mathrm{c}p_\mathrm{a}\sigma}$ | 7.200 | 7.200 | 7.200 | 6.200 | 6.200 | 7.200 | 7.200 |
| $\eta_{s_\mathrm{a}p_\mathrm{c}\sigma}$ | 4.100 | 4.100 | 4.100 | 3.000 | 3.000 | 4.080 | 4.080 |
| $\eta_{s_\mathrm{c}p_\mathrm{a}\sigma}$ | 4.500 | 4.500 | 4.500 | 4.580 | 4.580 | 4.090 | 4.090 |
| $\eta_{pp\sigma}$ | 3.204 | 3.204 | 3.204 | 2.091 | 2.091 | 2.200 | 2.200 |
| $\eta_{pp\pi}$ | 4.236 | 4.236 | 4.236 | 3.724 | 3.724 | 3.240 | 3.240 |

TABLE A.2: Material parameters for zinc blende III-V compounds used in $\mathbf{k}\cdot\mathbf{p}$ calculations. Since incorporation of Bi and/or N is treated perturbatively (cf. Chapter 4), we do not require or provide band structure parameters for Bi- and N-containing III-V binary compounds. The band gaps are given at $T = 0$ K; the room temperature band gaps are given in parentheses and were calculated using the Varshni parameters of Ref. [4].

| Parameter | GaAs | InAs | AlAs | GaP | InP | AlP | GaN | InN | GaBi | InBi |
|---|---|---|---|---|---|---|---|---|---|---|
| $E_g$ (eV) | 1.519 | 0.418 | 3.099 | 2.886 | 1.424 | 3.630 | — | — | — | — |
| | (1.422) | (0.355) | (2.966) | (2.777) | (1.353) | (3.553) | | | | |
| $\Delta_{\mathrm{SO}}$ (eV) | 0.341 | 0.380 | 0.281 | 0.080 | 0.114 | 0.070 | — | — | — | — |
| $E_{v,\mathrm{av}}$ (eV) | −6.84 | −6.67 | −7.38 | −7.31 | −7.04 | −8.09 | — | — | — | — |
| $m_c^*$ ($m_0$) | 0.0670 | 0.0223 | 0.1500 | 0.1700 | 0.0800 | 0.2200 | — | — | — | — |
| $E_P$ (eV) | 28.8 | 21.5 | 21.1 | 31.4 | 20.7 | 17.7 | — | — | — | — |
| $\gamma_1^{\mathrm{L}}$ | 6.98 | 20.00 | 3.76 | 4.05 | 5.08 | 3.35 | — | — | — | — |
| $\gamma_2^{\mathrm{L}}$ | 2.06 | 8.50 | 0.82 | 0.49 | 1.60 | 0.71 | — | — | — | — |
| $\gamma_3^{\mathrm{L}}$ | 2.93 | 9.20 | 1.42 | 2.93 | 2.10 | 1.23 | — | — | — | — |
| $a$ (Å) | 5.6532 | 6.0583 | 5.6611 | 5.4505 | 5.8687 | 5.4672 | 4.4900 | 4.9850 | 6.3280 | 6.6860 |
| $C_{11}$ (GPa) | 118.0 | 83.0 | 125.0 | 141.0 | 102.0 | 133.0 | 291.0 | 183.4 | 81.6 | 58.5 |
| $C_{12}$ (GPa) | 53.8 | 48.0 | 53.4 | 62.5 | 57.6 | 63.0 | 155.5 | 122.6 | 28.1 | 30.4 |
| $a_c$ (eV) | −7.17 | −5.88 | −5.64 | −9.45 | −6.18 | −5.44 | −2.20 | −2.20 | $-7.17^{\dagger}$ | $-5.88^{\dagger}$ |
| $a_v$ (eV) | 1.16 | 1.00 | 2.47 | 1.70 | 1.27 | 3.15 | 5.20 | 5.20 | $1.16^{\dagger}$ | $1.00^{\dagger}$ |
| $b$ (eV) | −1.70 | −1.80 | −1.60 | −1.50 | −1.50 | −1.60 | −2.20 | −2.20 | $-1.70^{\dagger}$ | $-1.80^{\dagger}$ |

$^{\dagger}$ Due to a lack of information in the literature, the deformation potentials for GaBi (InBi) are taken as equal to those of GaAs (InAs).

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