



## **Terms and Conditions of Use of Digitised Theses from Trinity College Library Dublin**

### **Copyright statement**

All material supplied by Trinity College Library is protected by copyright (under the Copyright and Related Rights Act, 2000 as amended) and other relevant Intellectual Property Rights. By accessing and using a Digitised Thesis from Trinity College Library you acknowledge that all Intellectual Property Rights in any Works supplied are the sole and exclusive property of the copyright and/or other IPR holder. Specific copyright holders may not be explicitly identified. Use of materials from other sources within a thesis should not be construed as a claim over them.

A non-exclusive, non-transferable licence is hereby granted to those using or reproducing, in whole or in part, the material for valid purposes, providing the copyright owners are acknowledged using the normal conventions. Where specific permission to use material is required, this is identified and such permission must be sought from the copyright holder or agency cited.

### **Liability statement**

By using a Digitised Thesis, I accept that Trinity College Dublin bears no legal responsibility for the accuracy, legality or comprehensiveness of materials contained within the thesis, and that Trinity College Dublin accepts no liability for indirect, consequential, or incidental, damages or losses arising from use of the thesis for whatever reason. Information located in a thesis may be subject to specific use constraints, details of which may not be explicitly described. It is the responsibility of potential and actual users to be aware of such constraints and to abide by them. By making use of material from a digitised thesis, you accept these copyright and disclaimer provisions. Where it is brought to the attention of Trinity College Library that there may be a breach of copyright or other restraint, it is the policy to withdraw or take down access to a thesis while the issue is being resolved.

### **Access Agreement**

By using a Digitised Thesis from Trinity College Library you are bound by the following Terms & Conditions. Please read them carefully.

I have read and I understand the following statement: All material supplied via a Digitised Thesis from Trinity College Library is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of a thesis is not permitted, except that material may be duplicated by you for your research use or for educational purposes in electronic or print form providing the copyright owners are acknowledged using the normal conventions. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone. This copy has been supplied on the understanding that it is copyright material and that no quotation from the thesis may be published without proper acknowledgement.

# The Electronic Structure of Transparent Conducting Oxides

---

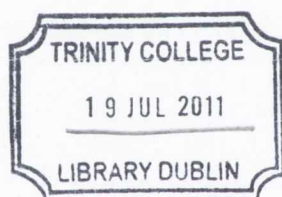
A thesis presented to Trinity College Dublin for  
the degree of Doctor of Philosophy

**Kate Gitanjali Godinho**

**2011**







TH0812

9097

# Declaration

I hereby declare that:

This thesis has not been submitted as an exercise for a degree at this or any other University.

The work contained herein is entirely my own except where otherwise cited, referenced, or acknowledged in the text.

I agree that the library of the University of Dublin may at their discretion lend or copy the thesis upon request

February 2011

Trinity College Dublin

# Thesis Summary

Transparent conducting oxides (TCOs) are a unique class of materials which combine the normally mutually exclusive properties of transparency and conduction. Although their discovery dates back over a century and despite their increasing commercial use since the first applications 70 years ago, the exact mechanism of conduction in TCOs is still not fully understood. Conduction in TCOs occurs due to the presence of defects. These can be either intrinsic defects such as oxygen vacancies, or extrinsic dopants which are deliberately introduced into the material. These defects can either introduce excess electrons into the conduction band to give *n*-type conduction, or excess holes into the valence band, resulting in *p*-type conduction. However, in many TCOs the exact defects which are responsible for conductivity are not known, and the mechanism by which they conduct is poorly understood. The aim of this thesis is thus to provide insight into the mechanism of transparent conductivity in several transparent conductors, through a computational electronic structure approach.

We start by examining the intrinsic conductivity of  $\text{SnO}_2$ , one of the earliest known *n*-type TCOs. Using density functional theory (DFT), we investigate the energetics and electronic structure of the intrinsic defects and find oxygen vacancies to be the lowest energy intrinsic defect under O-poor conditions and therefore the most likely cause of *n*-type conductivity. Although oxygen interstitials are found to have low formation energies under oxygen-rich conditions, their lowest energy geometry is a peroxide ion  $(\text{O}_2)_\text{O}^\times$ , which does not generate the holes required for *p*-type conductivity. Following our DFT analysis, we examine the transition levels and electronic structures of the intrinsic defects using hybrid-DFT methodology. The charge transition levels associated with oxygen vacancies are found to be 0.5 eV below the conduction band minimum, suggesting that they cannot be responsible for the shallow donor levels found experimentally which are thought to be responsible for the intrinsic conductivity of  $\text{SnO}_2$ . While tin interstitials are found to have shallow defect levels, their formation energies are too high for them to be responsible for the majority of intrinsic conductivity. From an analysis of the electronic structure of oxygen vacancies, we conclude that the defect is quite localised, with much of the charge located on the three tin cations, neighbouring the vacancy. We therefore conclude that intrinsic conductivity in  $\text{SnO}_2$  is caused by oxygen vacancies via a polaronic hopping mechanism.

We follow up our study of intrinsic conductivity in  $\text{SnO}_2$  by an examination of several

dopants in tin dioxide. We examine the reasons behind the superior conductivities of Sb and F doped  $\text{SnO}_2$  compared with Bi and Cl doped. Our findings indicate that both Sb and F are more readily incorporated into  $\text{SnO}_2$  than Bi and Cl. In addition, Bi doped  $\text{SnO}_2$  was found to result in more localised defect states than Sb doped, thereby resulting in higher conduction activation energies. In contrast, both Cl and F resulted in similar defect states, but because of the large ionic radius of  $\text{Cl}^-$ , large structural distortions resulted, leading to a very high formation energy for Cl incorporation compared with F. Our investigations of H doping suggest hydrogen to be a plausible cause of conductivity in  $\text{SnO}_2$  and that unintentional H impurities are a possible cause of the shallow donor levels and  $n$ -type conductivity in undoped  $\text{SnO}_2$ .

We also investigate the conductivities of several  $p$ -type TCOs. We start by examining the electronic structures of several copper delafossite TCOs ( $\text{CuMO}_2$ ,  $M = \text{Al, Ga, In, Sc}$ ), using DFT+ $U$  and hybrid-DFT methodology, to gain understanding of their valence band structures. We investigate the reasons for the electronic structure trends across the Group 13 delafossites and compare their valence bands to that of a Group 3 delafossite,  $\text{CuScO}_2$ . To gain further insight into the conduction mechanism in  $p$ -type copper-based materials, we study the intrinsic defects in  $p$ -type  $\text{SrCu}_2\text{O}_2$  using DFT+ $U$  methods. Our findings indicate that copper vacancies are the main cause of  $p$ -type conductivity, though strontium vacancies may form under certain conditions.  $N$ -type defects are found to be unstable under all partial pressure conditions. Both Sr and Cu vacancies are found to result in localised defect states, consistent with a polaronic hopping mechanism of conductivity. The highly localised nature of these states is the most likely reason for the poor conductivity of  $\text{SrCu}_2\text{O}_2$ .

Finally, we consider both intrinsic and extrinsic defects in the  $p$ -type TCO NiO. We find that the most stable intrinsic defect changes from Ni vacancies at O-rich conditions to O vacancies at O-poor conditions, so that  $p$ -type conductivity will only occur under O-rich conditions. Both intrinsic and extrinsic defects in bulk and surface regions are found to result in defect states which are highly localised on O  $2p$  orbitals. This will result in high conduction activation energies, which explains the low  $p$ -type conductivity of NiO. Li dopants were found to be low in energy, though their highly localised nature suggests that they will never introduce high levels of  $p$ -type conductivity into nickel oxide.



# Acknowledgements

I would first like to thank my supervisor, Prof. Graeme Watson for all his help throughout my studies. I would also like to thank Prof. Grayson of the School of Chemistry for allowing me to pursue this PhD and for the use of the facilities of the School of Chemistry.

I acknowledge funding from IRCSET and SFI, without which I would not have been able to carry out this work. I also would like to thank TCHPC and ICHEC for access to their computing facilities.

Thanks to everyone in the group, past and present, for the help, chats and games over the years. I thank Aron for all his help when I first started, Ni Chaoimh for the chocolate, sweets and chats, Natasha, David and Jeremy for proof-reading, and all the other members of the group, Berry, Paddy, Mario, John, Souad and Kalle.

Finally, I would like to thank my parents for their support and encouragement and also to the rest of my family, Anil, Kevin, Liam and Anita for all the support they've given me. And last but not least, I am eternally grateful for Dave, for putting up with me and keeping me sane over the past four years.

# Table of Contents

Declaration..... i

Thesis Summary .....ii

Acknowledgements.....iv

Abbreviations.....ix

Publication List.....x

Chapter 1: Introduction..... 1

1.1 Transparent Conducting Oxides (TCOs) ..... 1

1.2 Requirements for Transparent Conductivity ..... 3

1.2.1 Optical Transparency ..... 3

1.2.2 Conduction Mechanism ..... 5

1.3 N-type TCOs ..... 8

1.3.1 In<sub>2</sub>O<sub>3</sub>..... 9

1.3.2 ZnO ..... 11

1.3.3 SnO<sub>2</sub> ..... 12

1.4 P-type TCOs..... 13

1.5 Applications of Transparent Conductors ..... 17

1.5.1 Flat Panel Displays ..... 17

1.5.2 Functional Window Glass..... 18

1.5.3 Solar Cells..... 20

1.6 Thesis Layout..... 2

Chapter 2: Computational Methods..... 4

2.1 Overview ..... 4

2.2 Quantum Chemistry ..... 4

2.2.1 Schrödinger Equation ..... 4

2.2.2 The Variational Principle..... 5

2.2.3 Born-Oppenheimer Approximation..... 6

2.2.4 Hartree-Fock Method..... 7

2.2.5 Density Functional Theory (DFT) ..... 9

2.2.6 Exchange-Correlation Functional ..... 11

2.2.7 Hybrid-DFT ..... 13

2.2.8 The DFT+*U* approach..... 14

2.3 Simulation details..... 16

|            |                                                                                            |    |
|------------|--------------------------------------------------------------------------------------------|----|
| 2.3.1      | Vienna Ab Initio Simulation Package (VASP).....                                            | 16 |
| 2.3.2      | Electronic and Geometry Optimisation.....                                                  | 16 |
| 2.3.3      | Periodic planewave calculations .....                                                      | 18 |
| 2.3.4      | Pseudopotentials and Planewave Cut-offs .....                                              | 19 |
| 2.3.5      | Band Structures .....                                                                      | 20 |
| 2.3.6      | Electronic Density of States (EDOS).....                                                   | 21 |
| 2.3.7      | Crystal Orbital Overlap Population (COOP) analysis .....                                   | 22 |
| 2.3.8      | Optical Absorption Calculations.....                                                       | 22 |
| 2.3.9      | Bader Charge Analysis.....                                                                 | 23 |
| 2.3.10     | Effective Mass.....                                                                        | 24 |
| 2.4        | Volume Optimisation and Convergence .....                                                  | 24 |
| 2.5        | Defect Calculations .....                                                                  | 25 |
| 2.6        | Experimental Electronic Structure Techniques.....                                          | 30 |
| 2.6.1      | X-ray Photoemission Spectroscopy (XPS) .....                                               | 30 |
| 2.6.2      | X-ray Emission Spectroscopy (XES).....                                                     | 31 |
| Chapter 3: | The Origins of Intrinsic and Extrinsic <i>n</i> -type Conduction in SnO <sub>2</sub> ..... | 33 |
| 3.1        | Summary .....                                                                              | 33 |
| 3.2        | Intrinsic Defects of SnO <sub>2</sub> : GGA Calculations .....                             | 33 |
| 3.2.1      | Introduction.....                                                                          | 33 |
| 3.2.2      | Methodology .....                                                                          | 38 |
| 3.2.3      | GGA Electronic Structure of Bulk SnO <sub>2</sub> .....                                    | 38 |
| 3.2.4      | Supercell Size Convergence.....                                                            | 41 |
| 3.2.5      | Defect Formation Energies .....                                                            | 42 |
| 3.2.6      | Electronic Structure of $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ .....    | 45 |
| 3.2.7      | Electronic Structure of Tin Interstitials.....                                             | 48 |
| 3.2.8      | Electronic Structure of $\text{O}_{\text{i}}'' + 2h^{\bullet}$ .....                       | 53 |
| 3.2.9      | Discussion .....                                                                           | 56 |
| 3.3        | Intrinsic Defects in SnO <sub>2</sub> : HSE06 Calculations .....                           | 57 |
| 3.3.1      | Introduction.....                                                                          | 57 |
| 3.3.2      | Methodology .....                                                                          | 58 |
| 3.3.3      | Bulk Electronic Structure.....                                                             | 59 |
| 3.3.4      | Electronic Structure of Intrinsic Defects.....                                             | 61 |
| 3.3.5      | Charged Defect Transition Levels .....                                                     | 66 |
| 3.3.6      | Discussion .....                                                                           | 68 |
| 3.4        | The Extrinsic Defects of SnO <sub>2</sub> : HSE06 Calculations.....                        | 70 |

|            |                                                                                       |     |
|------------|---------------------------------------------------------------------------------------|-----|
| 3.4.1      | Introduction.....                                                                     | 70  |
| 3.4.2      | Methodology .....                                                                     | 75  |
| 3.4.3      | Defect Formation Energies .....                                                       | 77  |
| 3.4.4      | Electronic Structure of Doped SnO <sub>2</sub> .....                                  | 81  |
| 3.4.5      | Intrinsic-Extrinsic Interactions .....                                                | 91  |
| 3.4.6      | Co-doping with Sb and F .....                                                         | 95  |
| 3.4.7      | Hydrogen Doping .....                                                                 | 96  |
| 3.4.8      | Discussion.....                                                                       | 99  |
| 3.5        | Conclusions.....                                                                      | 101 |
| Chapter 4: | <i>P</i> -type Conduction in Cu-based Transparent Conducting Oxides.....              | 103 |
| 4.1        | Summary .....                                                                         | 103 |
| 4.2        | CuMO <sub>2</sub> (M =Al, Ga, In, Sc): Chemical Bonding and Electronic Structure..... | 103 |
| 4.2.1      | Introduction.....                                                                     | 103 |
| 4.2.2      | Computational Methods.....                                                            | 107 |
| 4.2.3      | Lattice Parameters of CuMO <sub>2</sub> (M=Al, Ga, In, Sc) .....                      | 108 |
| 4.2.4      | Electronic Structure of CuMO <sub>2</sub> (M=Al, Ga, In, Sc).....                     | 109 |
| 4.2.5      | Bader Charges.....                                                                    | 122 |
| 4.2.6      | Effective Mass .....                                                                  | 123 |
| 4.2.7      | Comparison to Experimental XPS.....                                                   | 125 |
| 4.2.8      | Discussion.....                                                                       | 128 |
| 4.3        | The Intrinsic Defects of SrCu <sub>2</sub> O <sub>2</sub> .....                       | 131 |
| 4.3.1      | Introduction.....                                                                     | 131 |
| 4.3.2      | Computational Methods.....                                                            | 133 |
| 4.3.3      | Bulk Electronic Structure.....                                                        | 137 |
| 4.3.4      | X-ray Photoelectron Spectroscopy .....                                                | 140 |
| 4.3.5      | Defect Formation Energies .....                                                       | 141 |
| 4.3.6      | Defect Levels .....                                                                   | 144 |
| 4.3.7      | Electronic Structure of $V'_{\text{Cu}} + h^{\bullet}$ .....                          | 146 |
| 4.3.8      | Electronic Structure of $V''_{\text{Sr}} + 2h^{\bullet}$ .....                        | 148 |
| 4.3.9      | Discussion.....                                                                       | 150 |
| 4.4        | Conclusions.....                                                                      | 152 |
| Chapter 5: | GGA+ <i>U</i> Investigation of Intrinsic and Extrinsic defects in NiO.....            | 154 |
| 5.1        | Summary .....                                                                         | 154 |
| 5.2        | Introduction .....                                                                    | 154 |
| 5.3        | Computational Methods.....                                                            | 160 |



|              |                                                           |     |
|--------------|-----------------------------------------------------------|-----|
| 5.4          | Bulk electronic structure of NiO .....                    | 162 |
| 5.4.1        | Bulk Defect Formation Energies.....                       | 163 |
| 5.4.2        | $V''_{\text{Ni}} + 2h^{\bullet}$ .....                    | 164 |
| 5.4.3        | $V^{\bullet\bullet}_{\text{O}} + 2e'$ .....               | 166 |
| 5.4.4        | $\text{Li}'_{\text{Ni}} + h^{\bullet}$ .....              | 168 |
| 5.4.5        | $\text{N}'_{\text{O}} + h^{\bullet}$ .....                | 170 |
| 5.5          | Electronic Structure of NiO {100} Surface.....            | 172 |
| 5.5.1        | Surface Defect Formation Energies .....                   | 173 |
| 5.5.2        | $V''_{\text{Ni}} + 2h^{\bullet}$ .....                    | 174 |
| 5.5.3        | $V^{\bullet\bullet}_{\text{O}} + 2e'$ .....               | 176 |
| 5.5.4        | $\text{Li}'_{\text{Ni}} + h^{\bullet}$ .....              | 178 |
| 5.5.5        | $\text{N}'_{\text{O}} + h^{\bullet}$ .....                | 181 |
| 5.6          | Discussion .....                                          | 183 |
| 5.7          | Conclusions .....                                         | 185 |
| Chapter 6:   | Conclusions and Future Outlook.....                       | 186 |
| 6.1          | Conclusions .....                                         | 186 |
| 6.1.1        | <i>N</i> -type Conduction in SnO <sub>2</sub> .....       | 186 |
| 6.1.2        | <i>P</i> -type TCOs .....                                 | 189 |
| 6.2          | The Future of Transparent Conductors .....                | 191 |
| 6.2.1        | Mixed Cation <i>n</i> -type TCOs.....                     | 191 |
| 6.2.2        | <i>P</i> -Type Transparent Conducting Chalcogenides ..... | 193 |
| 6.2.3        | Surfaces and Interfaces of TCOs .....                     | 195 |
| Appendix:    | Kröger-Vink Notation .....                                | 197 |
| Bibliography | .....                                                     | 198 |

# Abbreviations

|        |                                               |
|--------|-----------------------------------------------|
| ATO:   | Antimony tin oxide                            |
| CB:    | Conduction band                               |
| CBM:   | Conduction band minimum                       |
| COOP:  | Crystalline orbital overlap population        |
| DFT:   | Density Functional Theory                     |
| EDOS:  | Electronic density of states                  |
| EXAFS: | Extended x-ray absorption fine structure      |
| FTO:   | Fluorine tin oxide                            |
| GGA:   | Generalised gradient approximation            |
| IR:    | Infra-red                                     |
| ITO:   | Indium tin oxide                              |
| HF:    | Hartree-Fock                                  |
| HSE:   | Heyd Scuseria Ernzerhof hybrid-DFT functional |
| LDA:   | Local density approximation                   |
| PAW:   | Projector augmented wave                      |
| PBE:   | Perdew Burke Ernzerhof DFT functional         |
| PEDOS: | Partial electronic density of states          |
| SIE:   | Self-interaction error                        |
| TCO:   | Transparent conducting oxide                  |
| UPS:   | Ultraviolet photoelectron spectroscopy        |
| UV:    | Ultraviolet                                   |
| VASP:  | Vienna Ab-Initio Simulation Package           |
| VB:    | Valence band                                  |
| VBM:   | Valence band maximum                          |
| XANES: | X-ray absorption near edge spectroscopy       |
| XAS:   | X-ray absorption spectroscopy                 |
| XES:   | X-ray emission spectroscopy                   |
| XPS:   | X-ray photoelectron spectroscopy              |

# Publication List

1. A comparative study of the electronic structures of  $\text{SrCu}_2\text{O}_2$  and  $\text{PbCu}_2\text{O}_2$  by density functional theory, high resolution X-ray photoemission and electron paramagnetic resonance spectroscopy.  
K. G. Godinho, G. W. Watson, A. Walsh, A. J. H. Green, D. J. Payne, J. Harmer and R. G. Egdell, *Journal of Materials Chemistry*, 18, 2798 (2008).
2. Energetic and electronic structure analysis of intrinsic defects in  $\text{SnO}_2$ .  
K. G. Godinho, A. Walsh and G. W. Watson, *Journal of Physical Chemistry C*, 113, 439 (2009).
3. Comparative study of band widths in copper delafossites from x-ray emission spectroscopy.  
D. Shin, J. S. Foord, D. J. Payne, T. Arnold, D. J. Aston, R. G. Egdell, K. G. Godinho, D. O. Scanlon, B. J. Morgan, G. W. Watson, E. Mugnier, C. Yaicle, A. Rougier, L. Colakerol, P. A. Glans, L. F. J. Piper and K.E. Smith, *Physical Review B*, 80, 233105 (2009).
4. Understanding conductivity anomalies in Cu(I)-based delafossite transparent conducting oxides: theoretical insights.  
D. O. Scanlon, K. G. Godinho, B. J. Morgan and G. W. Watson, *Journal of Chemical Physics*, 132, 024707 (2010).
5. Understanding conductivity in  $\text{SrCu}_2\text{O}_2$ : stability, geometry and electronic structure of intrinsic defects from first principles.  
K. G. Godinho, J. J. Carey, B. J. Morgan, D. O. Scanlon and G. W. Watson, *Journal of Materials Chemistry*, 20, 1086 (2010).
6. Chemical bonding in copper-based transparent conducting oxides:  $\text{CuMO}_2$  ( $\text{M} = \text{In}, \text{Ga}, \text{Sc}$ )  
K. G. Godinho, B. J. Morgan, J. P. Allen, D. O. Scanlon and G. W. Watson, *Journal of Physics: Condensed Matter*, Accepted (2011)

# Chapter 1: Introduction

## 1.1 Transparent Conducting Oxides (TCOs)

Transparent conducting oxides (TCOs) are compounds which combine the normally mutually exclusive properties of transparency and conductivity. Most highly transparent materials, such as glass, behave as insulators with high electrical resistivities of  $> 10^{10} \Omega \text{ cm}$ , whereas materials with low resistivities ( $10^{-4}$ - $10^{-7} \Omega \text{ cm}$ ), such as metals, do not transmit visible light. The combination of both properties in a single material is thus quite an unusual phenomenon and TCOs have proved indispensable in the development of optoelectronic devices such as solar cells, flat panel displays and light emitting diodes.<sup>1-3</sup>

Transparent conductivity was first discovered just over a century ago in 1907, when transparent CdO thin films were found to possess conductivities of  $\sim 10^3 \text{ S cm}^{-1}$ .<sup>4</sup> This was later followed by the discovery of transparent conductivity in  $\text{SnO}_2$ , leading to the first TCO patent in 1931.<sup>5</sup> This led to the application of  $\text{SnO}_2$  thin films in defrosting aeroplane windows in World War II.<sup>6</sup>  $\text{In}_2\text{O}_3$  was first reported to act as a TCO in 1947, when a patent for its use was first filed,<sup>7</sup> while the transparent conductivity of  $\text{ZnO}$  was not discovered until 1971.<sup>8</sup> Since the 1970s, research into TCOs has steadily increased, and the properties of  $\text{ZnO}$ ,  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$  have been gradually optimised, reducing the electrical resistivities to around  $10^{-4} \Omega \text{ cm}$  with  $>90\%$  transparency in certain films, as illustrated in Fig. 1.1.

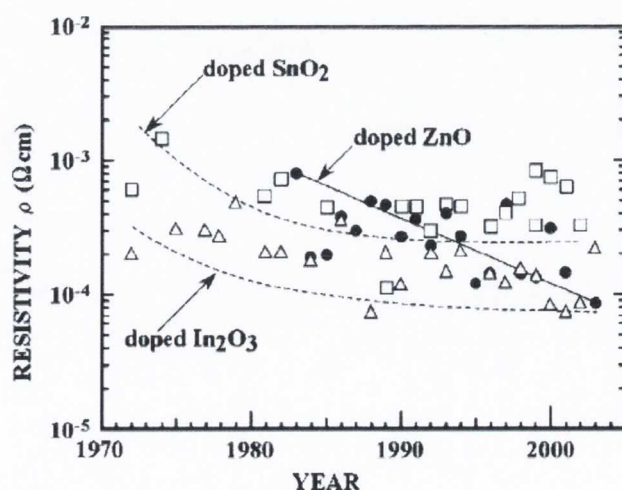


Fig. 1.1 Resistivity for impurity doped TCO films plotted against year of production, between 1972 and 2005. Squares are  $\text{SnO}_2$ , triangles are  $\text{In}_2\text{O}_3$  and circles are  $\text{ZnO}$ .<sup>9</sup>



The most successful TCO so far is tin doped indium oxide (Indium Tin Oxide – ITO), which has become the industrial standard TCO for many optoelectronics applications. Its widespread use stems from the fact that lower resistivities have been achieved in ITO than in any other transparent conductor. Resistivities in ITO have reached as low as  $7.2 \times 10^{-5} \Omega \text{ cm}$ , while retaining >90% visible transparency.<sup>10</sup> In recent years, the demand for ITO has increased considerably, mainly due to the continuing replacement of cathode ray tube technology with flat screen displays. However, indium is quite a rare metal, having an abundance in the Earth’s crust of only 160 ppb by weight, compared with abundances for Zn and Sn of 79000 ppb and 2200 ppb respectively.<sup>11</sup> The overwhelming demand for ITO has led to a huge increase in the cost of indium over the past decade. Fig. 1.2 shows the variation in price of indium since 1991. Between 2002 and 2006 the price of indium rapidly increased from \$97 to \$918 per kg. Although the price has fallen since 2006, its current price is still very high at \$500 per kg. There has thus been a drive in recent years to develop reduced-indium and indium-free materials which can replace ITO as the dominant industrial TCO. Recent research has therefore focused both on developing new TCOs, and improving the conductivities of  $\text{SnO}_2$  and  $\text{ZnO}$  to levels close to those of ITO.

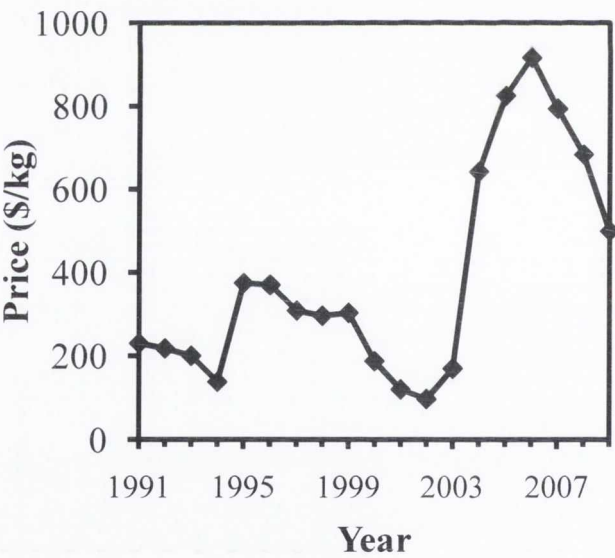


Fig. 1.2 Graph showing the evolution of the price of indium (in \$/kg) between 1991 and 2009, taken from US Geological Survey Data.<sup>12</sup>

Another area of TCO research has been the development of fully transparent electronics in which all components (e.g. wires, transistors, capacitors, etc.) are essentially ‘invisible’ to the naked eye. However, the realisation of transparent circuitry is not possible using the currently available TCOs. The reason for this is that there are two types of semiconductors:

*n*- and *p*-type. *N*-type TCOs conduct by introducing electrons into unoccupied conduction band states, while in *p*-type materials, electrons are removed from the filled valence band, leaving behind positively charged holes as charge carriers. All known highly conductive TCOs (CdO, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, ZnO) are *n*-type semiconductors. However, both *p*- and *n*-type TCOs are needed for the manufacture of the transistors and diodes required for integrated circuits. In the past decade, several *p*-type TCOs have been investigated, including NiO,<sup>13</sup> CuAlO<sub>2</sub><sup>14</sup> and SrCu<sub>2</sub>O<sub>2</sub>.<sup>15</sup> Unfortunately, their conductivities are still quite low ( $\sim 10^2$  S cm<sup>-1</sup>), which has thus far prevented the development of transparent devices.

This thesis has therefore been driven by the two main areas of TCO research – development of indium-free *n*-type materials and enhancement of the conductivity of *p*-type TCOs. Although transparent conducting oxides have been known for over a century, the mechanism by which they conduct is still poorly understood. In the following sections, we will briefly review the requirements for transparent conductivity, as well as discussing several known TCO materials and their applications.

## 1.2 Requirements for Transparent Conductivity

Good TCOs generally have optical transparencies above 80% in the visible range, combined with conductivities of above  $10^3$  S cm<sup>-1</sup>. This imposes certain restrictions on the types of material which can be used. Below, the electronic structure requirements to achieve high levels of transparent conductivity will be outlined.

### 1.2.1 Optical Transparency

For a material to be optically transparent, the lowest energy allowed transition between the filled valence band states and the empty conduction band states (optical band gap), must be greater than the highest frequency of visible light ( $\sim 3.1$  eV).<sup>3</sup> An optical gap lower than this will result in the absorption of photons of visible light and a loss in transparency. It is important to distinguish here between the optical gap of a material and its fundamental direct gap. The fundamental direct gap of a material is defined as the smallest direct gap between the valence band maximum (VBM) and the conduction band minimum (CBM). Although the optical gap obtained through optical measurements and the fundamental gap found in band structure calculations are often compared, they are not always the same thing. When considering the optical gap of a material, the allowed and forbidden



transitions must be taken into account. It is not always the case that a transition at the fundamental band gap is symmetry allowed. For example, the transparent conductor  $\text{In}_2\text{O}_3$  is known to have an optical gap of 3.75 eV.<sup>16</sup> This was widely assumed, up until recently, to arise from the fundamental direct transition between the VBM and CBM. However, recent computational work has demonstrated that the fundamental gap is symmetry forbidden and that the optical gap in fact arises from transitions taking place from  $\sim 0.8$  eV below the VBM to the CBM.<sup>17</sup> This has led to a revision of the value of the fundamental direct gap to  $\sim 2.9$  eV. Thus, a TCO can have a fundamental gap smaller than 3.1 eV, as long as it is symmetry forbidden, and the smallest allowed optical transition is greater than 3.1 eV.

As well as having an optical gap greater than 3.1 eV, ideally for *n*-type TCOs, the CBM should be separated from the next highest band by at least 3.1 eV, while for *p*-type TCOs, the VBM should be separated from the next lowest band by over 3.1 eV, as shown in the schematic of Fig. 1.3. This ensures that when electrons are introduced into the CBM for *n*-type (holes in VBM for *p*-type), the optical transitions remain greater than 3.1 eV and the material retains its visible transparency. In most *n*-type TCOs (e.g.  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{CdO}$ ), the CBM is composed of antibonding metal *s* and O *2p* orbitals. These result in a highly dispersed lowest conduction band which separates the CBM from the next highest conduction band by more than 3.1 eV. However, *p*-type TCOs (e.g.  $\text{CuAlO}_2$ ,  $\text{SrCu}_2\text{O}_2$ ) generally have much lower inter-band separations between the VBM and the next lowest band. This leads to a loss in optical transparency upon the introduction of defects into these materials, which is one of the reasons that they have so far failed to equal the performance of the more highly transparent *n*-type TCOs.

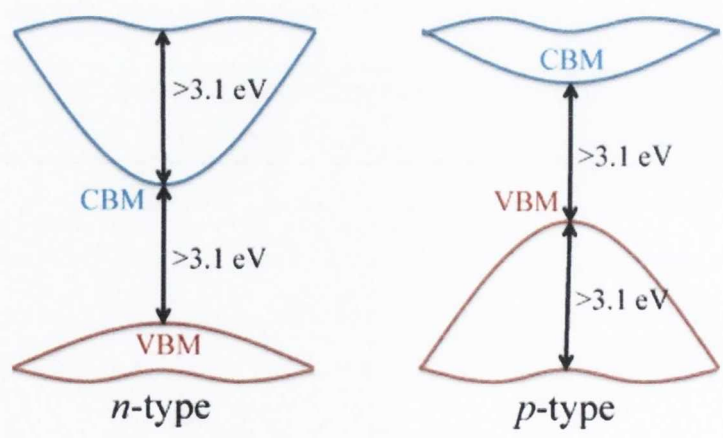


Fig. 1.3 Schematic band structures for *n*- and *p*-type TCOs outlining the requirements for maximum optical transparency. Red lines are occupied valence band states and blue are unoccupied conduction band states.

## 1.2.2 Conduction Mechanism

Usually, materials with the large band gaps required for transparency do not behave as conductors. This is because the excitation of an electron from the valence band to the conduction band would require the absorption of photons with energies greater than 3.1 eV, in the ultraviolet range of the spectrum. Very few electrons get promoted under these circumstances and thus, the conductivity of most wide gap materials remains extremely low (e.g. MgO, Al<sub>2</sub>O<sub>3</sub>). Indeed, in their stoichiometric form, TCOs generally behave as insulators. However, if intrinsic or extrinsic defects are introduced into a material, defect levels can be created in the band gap. For *n*-type conductivity, filled defect levels are introduced near the CBM, resulting in conductivity through the mobility of electrons, while for *p*-type conductivity, empty defect levels result near the VBM which cause conductivity through the movement of holes. For example, in many *n*-type TCOs, conductivity results from oxygen vacancies, which produce two electrons via the defect reaction expressed in Kröger-Vink<sup>18</sup> notation (see Appendix):



Alternatively, *p*-type conduction may be caused by holes produced by oxygen interstitials:



Good TCO materials normally possess a high degree of intrinsic non-stoichiometry due to the presence of defects and are highly susceptible to doping with extrinsic elements to increase the conductivity still further.

Depending on the location of the defect levels and the degree to which the electrons/holes are localised, different conduction mechanisms can result. There are two competing mechanisms for conductivity – band conduction and polaronic conduction – which will be discussed in the following sections.

### 1.2.2.1 Band-type Conduction

Band-type conduction occurs when the defect levels introduced into a material are close enough to the band edges to allow thermal excitation of electrons or holes to the conduction or valence band, respectively, thereby resulting in conductivity (Fig. 1.4). At



room temperature, this requires that the defect levels are within  $k_B T \approx 0.03$  eV of the band edges (shallow defects). *N*-type conductivity arises when filled defect levels are introduced just below the conduction band. The defect electrons are then thermally excited to the conduction band where they can freely move through the solid to cause conduction. *P*-type conduction, on the other hand, occurs when empty defect levels are introduced just above the valence band. Electrons are excited from the valence band into these empty levels, thereby resulting in holes in the valence band, which can easily migrate through the material. Defects which cause conduction via a band mechanism tend to have delocalised defect states, allowing the electrons/holes to be free to move between the various atoms in the system. In certain cases, the defect levels occur within the conduction/valence band, giving rise to high levels of conductivity, without the need for thermal activation. This is known as degenerate conduction.

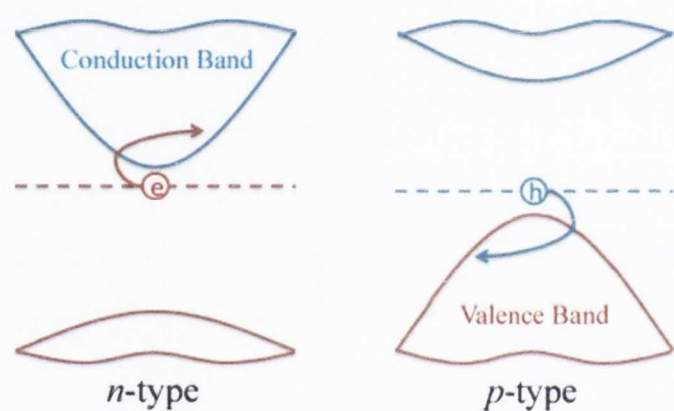


Fig. 1.4 Band structure schematic showing how defect levels introduce band-type conductivity in *n*- and *p*-type TCOs. Dashed red and blue lines are electron donor and acceptor states, respectively.

Conductivity under the band-type mechanism is dependent only on the electron/hole density ( $n$ ) and the mobility ( $\mu$ ), and is governed by:

$$\sigma = \mu n e \tag{1.3}$$

where  $e$  is the electron charge. The mobility can be calculated from:

$$\mu = \frac{e \tau}{m^*} \tag{1.4}$$

where  $\tau$  is the mean time between collisions and  $m^*$  is the effective mass. The effective mass is related to the curvature of the bands. The greater the curvature (dispersion), the lower the effective mass and the greater the mobility will be. Hence, as illustrated in Fig.

1.4, an ideal *n*-type TCO will have a highly dispersed conduction band minimum, while an ideal *p*-type TCO will have a highly dispersed valence band maximum. In *n*-type TCOs, the CBM is often composed of antibonding metal *s* states and O 2*p* states. Because of the diffuse nature of these orbitals, their interaction leads to a highly dispersed CBM,<sup>19-22</sup> resulting in low electron effective masses for ZnO, In<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub> (0.1-0.3 *m<sub>e</sub>*). However, *p*-type TCOs have valence band maxima which are much less dispersed, hence their hole effective masses tend to be higher (0.5-1.0 *m<sub>0</sub>*) than those of *n*-type TCOs. This leads to lower mobilities in *p*-type TCOs, and hence, higher resistivities. The effective mass will be discussed further in Section 2.3.10.

### 1.2.2.2 Polaronic Hopping

In cases where the defect states are located deep in the band gap, a polaronic hopping mechanism of conductivity is likely to dominate. In this case, the levels introduced by defects into the band gap are generally localised on a small number of atoms (small polaron), which leads to an associated lattice distortion and defect levels deep in the band gap. The charge is less free to move than for the band-type mechanism, so that an activation energy (*E<sub>a</sub>*) is required for electrons to hop from one atom to the next. The conductivity is proportional to:

$$\exp\left(-\frac{E_a}{k_B T}\right) \quad (1.5)$$

The lower the activation energy, the higher the conductivity will be. Generally speaking, more localised defects have higher activation energies. Defect levels located deeper in the band gap also tend to be more localised than those closer to the band edges. There are several different mechanisms by which polaronic hopping occurs, such as the variable range hopping (VRH)<sup>23</sup> and correlated barrier hopping (CBH)<sup>24</sup> models. Because of the activation energy required for conduction, the electrons/holes in polaronic systems generally have lower mobilities than materials governed by the band-type mechanism. The *p*-type TCOs CuAlO<sub>2</sub>,<sup>25</sup> NiO<sup>26</sup> and SrCu<sub>2</sub>O<sub>2</sub><sup>27</sup> have all been indicated to conduct via a polaronic hopping mechanism, which is thought to be the reason for their low conductivities compared to *n*-type TCOs, which are assumed to conduct via a band mechanism.<sup>28</sup>

### 1.3 N-type TCOs

The transparent conducting oxides currently used in the optoelectronics industry are all *n*-type conductors. The most commonly used materials are SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub> and ZnO, though Ga<sub>2</sub>O<sub>3</sub> and CdO are also known to act as *n*-type transparent conductors. These oxides have several features in common. In purely formal ionic terms, the cations all have an  $(n - 1)d^{10}ns^0$  electronic configuration (e.g. Sn(IV): [Kr]4d<sup>10</sup>5s<sup>0</sup>5p<sup>0</sup>). The top of the valence band in all of these oxides is dominated by O 2p states, while the bottom of the conduction band is made up of antibonding metal *ns*<sup>0</sup> and O 2p states. These states interact to form a highly dispersed CBM, resulting in a low electron effective mass for conductivity.<sup>22, 29</sup> The highly localised nature of the O 2p orbitals results in little dispersion at the VBM and the hole effective masses in these materials are generally quite large.

Kawazoe *et al.*<sup>20</sup> have proposed that the ideal crystal structure to achieve high levels of *n*-type conductivity is one which consists of linear chains of edge-sharing octahedra, as illustrated in Fig. 1.5. The cations labelled M<sub>B</sub> are *p*-block  $d^{10}s^0$  metal cations. This structure results in short cation-cation distances as there are no oxygen ions directly between two neighbouring M<sub>B</sub> cations. The enhanced overlap between the metal *s* orbitals creates an extended state which can be considered as a ‘highway’ for electrons. Edge-sharing cation octahedra do appear to be a feature of most *n*-type TCOs, with In<sub>2</sub>O<sub>3</sub>, CdO and SnO<sub>2</sub> all possessing chains of octahedral cations.<sup>3, 22, 30</sup> However, the main exception to this is ZnO which is one of the best known TCOs, yet has the wurtzite structure in which each Zn has tetrahedral coordination, while Ga<sub>2</sub>O<sub>3</sub> has a monoclinic structure in which there are both tetrahedral and octahedral cation sites.

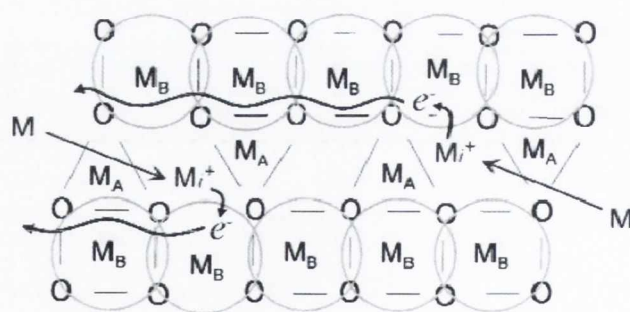


Fig. 1.5 Ideal TCO structure proposed by Kawazoe *et al.*<sup>20</sup> The structure consists of linear chains of edge-sharing M<sub>B</sub>O<sub>6</sub> octahedra with tetrahedral M<sub>A</sub> sites in between. M<sub>i</sub><sup>+</sup> dopants can occupy empty tetrahedral sites and donate electrons for conduction. The linear octahedral chains act as ‘highways’ for electronic conduction.



The model above assumes that the oxygen ions do not play a role in conduction. However, it has been shown that the CBM of *n*-type TCOs derives from O 2*p* interactions with metal *s* orbitals, so that metal-metal interactions alone are not responsible for the CBM dispersion.<sup>22</sup> The coordination of the oxygen ions is thus likely to be important in developing TCOs with high levels of conductivity. Analysis of the bonding and electronic structure of SnO<sub>2</sub> and several mixed cation TCOs has suggested that the oxygen coordination must be highly symmetric in order to obtain a highly dispersed CBM.<sup>22</sup> More recent work has argued that octahedral coordination of oxygen will achieve the greatest overlap between O 2*p* and metal *s* states (Fig. 1.6) and will thus result in a more dispersed CBM.<sup>30</sup> However, octahedral cation coordination does not appear to be essential to achieve good conductivity and thus, the high conductivities of ZnO and Ga<sub>2</sub>O<sub>3</sub> would appear to arise from their highly symmetric oxygen coordination environments, which allow for strong antibonding interactions between metal *s* and O 2*p* orbitals.



Fig. 1.6 Octahedral coordination of oxygen ion by cations showing overlap between metal *s* and O 2*p* states (from Ref. 30).

Intrinsic conduction in *n*-type TCOs occurs through oxygen deficiency which may be introduced either through oxygen vacancies or metal interstitials. Yet, although there have been numerous attempts to clarify the nature of the intrinsic defects and the positions of the electronic donor levels, the origin of conductivity in these materials is still very much a matter of debate. In the following sections, a summary of what is known about the defect structure and conductivity in the *n*-type TCOs, In<sub>2</sub>O<sub>3</sub>, ZnO and SnO<sub>2</sub>, will be given.

### 1.3.1 In<sub>2</sub>O<sub>3</sub>

In<sub>2</sub>O<sub>3</sub> crystallises in the bixbyite structure in space group  $IA\bar{3}$ .<sup>31</sup> As seen in Fig. 1.7, this is

quite a complex unit cell, containing 80 atoms. In this structure, there are two non-equivalent octahedral In sites, In1 and In2. Each In1 lies in a distorted octahedron with six equal In-O bond lengths, while the In2 cations coordinate octahedrally with three different In-O distances.  $\text{In}_2\text{O}_3$  has an optical band gap of 3.75 eV,<sup>16</sup> though it is now known to have a smaller forbidden direct gap of ~2.9 eV.<sup>17</sup>

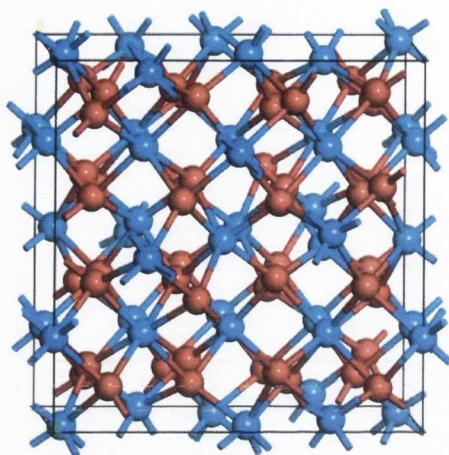


Fig. 1.7 Bixbyite structured unit cell of  $\text{In}_2\text{O}_3$  with In atoms shown in blue and oxygen atoms in red.

To date,  $\text{In}_2\text{O}_3$  has the highest reported conductivity of the TCO family with conductivities reaching  $\sim 10^5 \text{ S cm}^{-1}$  in ITO.<sup>10</sup> ITO is widely used in the electronics industry and is the main TCO used for flat screen displays, touch screens and solar cells. Although the discovery of the transparent conducting properties of ITO dates back to over 60 years ago,<sup>7</sup> its complex structure has made investigations of its defect electronic structure quite difficult. The first density functional theory calculations of pure  $\text{In}_2\text{O}_3$  were not carried out until 1997<sup>32</sup> and calculations of ITO were not performed until 2000.<sup>19</sup> Similar to the other *n*-type TCOs, the valence band of  $\text{In}_2\text{O}_3$  is composed of mainly O 2*p* states while its CBM is made up of mixed In 5*s* and O 2*p* states.<sup>33</sup> Intrinsic oxygen deficiency is thought to be caused by oxygen vacancies,<sup>34-36</sup> which may result in high levels of conductivity through shallow donor levels.<sup>36-38</sup> However, it has recently been proposed that oxygen vacancies form quite deep donor levels and that hydrogen impurities are the cause of *n*-type conductivity.<sup>39-40</sup> In ITO, conductivity arises through the formation of a shallow defect state below the conduction band which is of mixed Sn 5*s*, In 5*s* and O 2*p* character.<sup>19, 35</sup> Charge compensation is achieved in ITO through the formation of oxygen interstitials, which have been found in both theoretical<sup>41</sup> and experimental<sup>42-44</sup> studies to form  $(2\text{Sn}_{\text{In}} + \text{O}_{\text{i}})^{\times}$  defect complexes. These complexes are thought to dissociate and cause conduction via the defect reaction:

$$(2\text{Sn}_{\text{In}} + \text{O}_i)^{\times} \rightarrow 2\text{Sn}_{\text{In}}^{\bullet} + 2e' + \frac{1}{2}\text{O}_2 \quad (1.6)$$

### 1.3.2 ZnO

ZnO has the wurtzite structure in which each Zn(II) is tetrahedrally coordinated to four oxygen ions and each oxygen is also tetrahedrally coordinated (Fig. 1.8). The oxygen anions are hexagonally close packed, with half the tetrahedral holes filled by zinc cations. ZnO has an optical band gap of  $\sim 3.4$  eV and like other *n*-type TCOs, has a valence band made up of mainly O 2*p* states, while its conduction band is dominated by Zn 4*s* states.

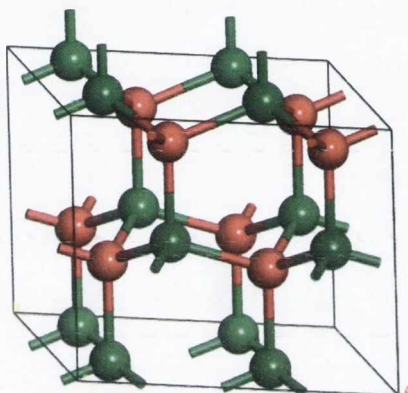


Fig. 1.8 Wurtzite structure of ZnO showing tetrahedral coordination of green Zn and red O atoms.

It is thought that conductivity in ZnO is caused by shallow donor levels, introduced by oxygen deficiency.<sup>45-46</sup> Although the defect structure of ZnO has been investigated computationally by many authors, the mechanism of conductivity in ZnO still remains controversial. Intrinsically, oxygen vacancies appear to have the lowest formation energies but it has been suggested that these possess deep donor levels.<sup>47</sup> However, Zn interstitials are also low in energy and have been found in some studies to act as shallow donors which suggests that they may be the cause of intrinsic conductivity.<sup>45, 48-49</sup> The third possibility is that the ‘intrinsic’ conductivity arises from the presence of hydrogen impurities which have been accidentally incorporated into the ZnO films.<sup>50-52</sup> The most commonly used dopants in zinc oxide are Al and Ga. Calculations on gallium zinc oxide (GZO)<sup>53-54</sup> and aluminium zinc oxide (AZO)<sup>54-56</sup> indicate that doping introduces shallow defect states made up of mixed Ga/Al *s*, Zn 4*s* and O 2*p* states. AZO films have been reported with resistivities as low as  $8.5 \times 10^{-5} \Omega \text{ cm}$ ,<sup>57</sup> which is close to the lowest value reported for ITO. However, AZO films have yet to replace ITO in optoelectronic devices because preparing ZnO films on large area substrates is difficult.<sup>58</sup>



### 1.3.3 SnO<sub>2</sub>

SnO<sub>2</sub> crystallises in the rutile structure in space group  $P4_2/mnm$  (Fig. 1.9).<sup>59</sup> In this structure, each Sn(IV) ion sits at the centre of a slightly distorted octahedron of oxygen anions, with each oxygen being coordinated to two tin cations. Like all TCOs, SnO<sub>2</sub> is non-conductive in its stoichiometric form, having a band gap of 3.6 eV, much too large to allow for thermal excitation of electrons. However, once it becomes non-stoichiometric through the loss of oxygen, SnO<sub>2</sub> is transformed into an excellent transparent conducting oxide with an intrinsic conductivity of  $\sim 10^{-3} \Omega \text{ cm}$ .<sup>60</sup> Antimony tin oxide (ATO) and fluorine tin oxide (FTO) have been widely used in glass coatings since their first use in World War II as windscreen de-icers.<sup>6</sup> Since then, the use of doped SnO<sub>2</sub> films has spread to anti-frost coatings in supermarket fridges, anti-fog coatings on glass oven doors and low emissivity architectural windows.<sup>60-61</sup>

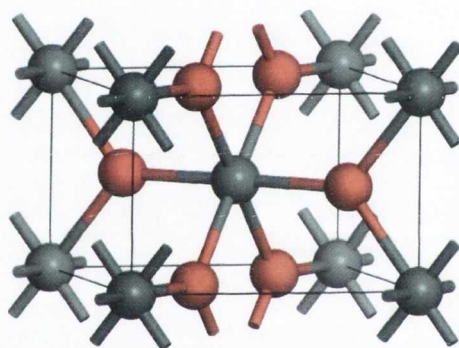


Fig. 1.9 Unit cell of SnO<sub>2</sub> showing octahedrally coordinated tin atoms in grey and trigonally coordinated oxygen in red.

Despite the fact that transparent conducting SnO<sub>2</sub> films have the longest commercial history of any TCO, there have been very few investigations of the underlying defect structure and conduction mechanism. It is generally thought that oxygen deficiency and *n*-type conductivity are caused by oxygen vacancies,<sup>38, 62-64</sup> though tin interstitials were predicted to be more stable in one theoretical study.<sup>65</sup> Intrinsic conductivity is thought to occur through shallow donor levels located 0.15-0.30 eV below the conduction band.<sup>62, 66</sup> However, the defect levels of oxygen vacancies are generally thought to occur deep in the band gap,<sup>38, 65, 67</sup> which has led to the prediction that the shallow levels arise from the presence of hydrogen impurities.<sup>67-68</sup> The electronic structure of doped SnO<sub>2</sub> has not yet been thoroughly investigated and the reasons behind the superior conductivity of Sb and F doped films over other dopants (e.g. Bi, As, Cl, I) have not been fully explored. ATO has

been found to result in band-type conductivity through shallow donor levels, which are thought to be made up of Sb 5s, Sn 5s and O 2p states, <sup>69-70</sup> while FTO films result in degenerate conductivity, but the electronic structure of donor levels in FTO is poorly understood. <sup>71</sup>

## 1.4 *P*-type TCOs

The next major stepping stone in TCO technology is the development of fully transparent electronic circuits. <sup>72</sup> These ‘invisible’ circuits have numerous applications. An apparently ordinary window pane could have a fully transparent liquid crystal display implanted in it, allowing it to become a flat screen display at the touch of a button. Invisible burglar alarms could be manufactured and even simple items such as eyeglasses could be used as display screens. As TCOs have been around for the past 100 years, it would appear at first sight that the production of these devices should be straightforward. Yet, the widespread use of transparent technology is still many years in the future. The reason for this is that a number of the components of complex circuits require both *n*- and *p*-type materials. However, all of the early developed TCOs occur with *n*-type conductivity. The first *p*-type TCO was not discovered until 1993 when transparent conductive NiO films were first prepared. <sup>13</sup>

The difficulty of obtaining *p*-type films arises from the underlying electronic structure of most metal oxides. As outlined above, all *n*-type TCOs have valence band maxima made up of mainly O 2p states. Introduction of a hole into these systems effectively requires the oxidation of oxygen. This is not energetically favourable and because of the localised nature of the O 2p orbitals, the hole will localise on a single oxygen ion, requiring a high activation energy to hop from one site to the next. For this reason, all attempts to *p*-type dope the conventional *n*-type TCOs have resulted in extremely low conductivities. <sup>73-75</sup>

Although NiO was the first *p*-type TCO discovered, it was not until 1997 that the search for *p*-type TCOs began in earnest. <sup>14</sup> Hosono and co-workers developed a strategy to design new *p*-type materials, through a method known as ‘Chemical Modulation of the Valence Band’. <sup>76</sup> Their reasoning was to select cations of the  $d^{10}s^0$  electronic configuration, in which the energy of the  $d^{10}$  orbitals is close to that of the O 2p orbitals – Cu(I), Ag(I) and Au(I). The similarity in energy between the metal *d* orbitals and the O 2p orbitals allows a substantial degree of overlap, resulting in a covalent system in which the valence band is made up of mixed O 2p and metal *d* states, as shown in Fig. 1.10.

However, the oxides  $\text{Cu}_2\text{O}$ ,  $\text{Ag}_2\text{O}$  and  $\text{Au}_2\text{O}$  are not transparent as they have optical gaps of 2.17 eV,<sup>77</sup> 1.3 eV<sup>78</sup> and 0.8 eV respectively.<sup>79</sup> All of these oxides possess the cuprite structure shown in Fig. 1.11, which is made up of two intersecting three-dimensional chains of M-O atoms. The metal ions form linear O-M-O bonds, while the oxygen ions have tetrahedral coordination. It has been shown that in  $\text{Cu}_2\text{O}$ , the three-dimensional Cu-Cu interactions result in an overall decrease in the band gap.<sup>80</sup> By reducing the M-M interactions, an increase in the band gap should be achieved.

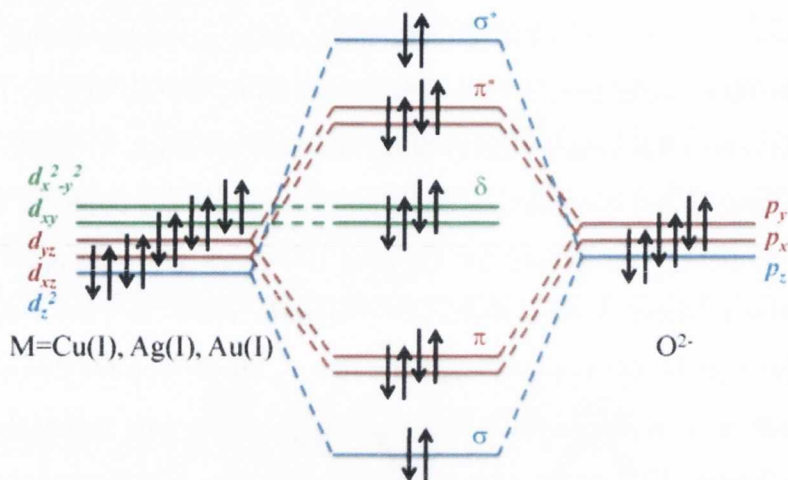


Fig. 1.10 Valence band structure of ideal *p*-type transparent conducting oxide designed by Hosono *et al.*,<sup>14</sup> showing the mixing between metal *d* and O 2*p* states, within an M-O bond directed along the *z*-axis.

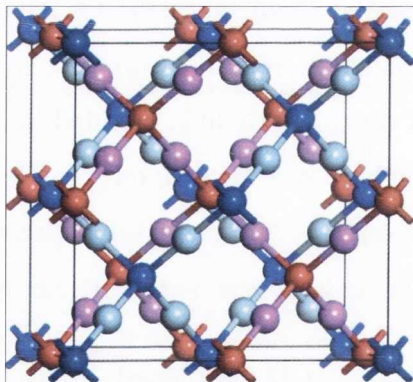


Fig. 1.11 Cuprite structure of  $\text{Cu}_2\text{O}$ ,  $\text{Ag}_2\text{O}$  and  $\text{Au}_2\text{O}$ , showing intersecting M-O networks in blue and red. Dark blue and red atoms are O atoms and light blue and pink atoms are metal ions.

Using these principles, the copper delafossite ( $\text{CuMO}_2$ ) structure shown in Fig. 1.12 was chosen as a *p*-type TCO candidate. In this structure, the Cu ions are linearly coordinated to two oxygen ions, forming O-Cu-O dumb-bells like in  $\text{Cu}_2\text{O}$ . Each oxygen is tetrahedrally coordinated to the Cu and three M(III) ions, so that a layer of  $\text{MO}_6$  octahedra separates the



Cu ions along the  $c$ -axis. The O-Cu-O dumb-bells form close-packed layers which stack with either ABAB symmetry to form a rhombohedral unit cell or with ABCABC symmetry to give a hexagonal unit cell. Interactions between Cu cations are limited to the  $a$ - and  $b$ -directions, thereby reducing the Cu-Cu interactions from three- to two-dimensional. This has been postulated to result in an increase in the band gap compared to  $\text{Cu}_2\text{O}$ .<sup>80-81</sup>

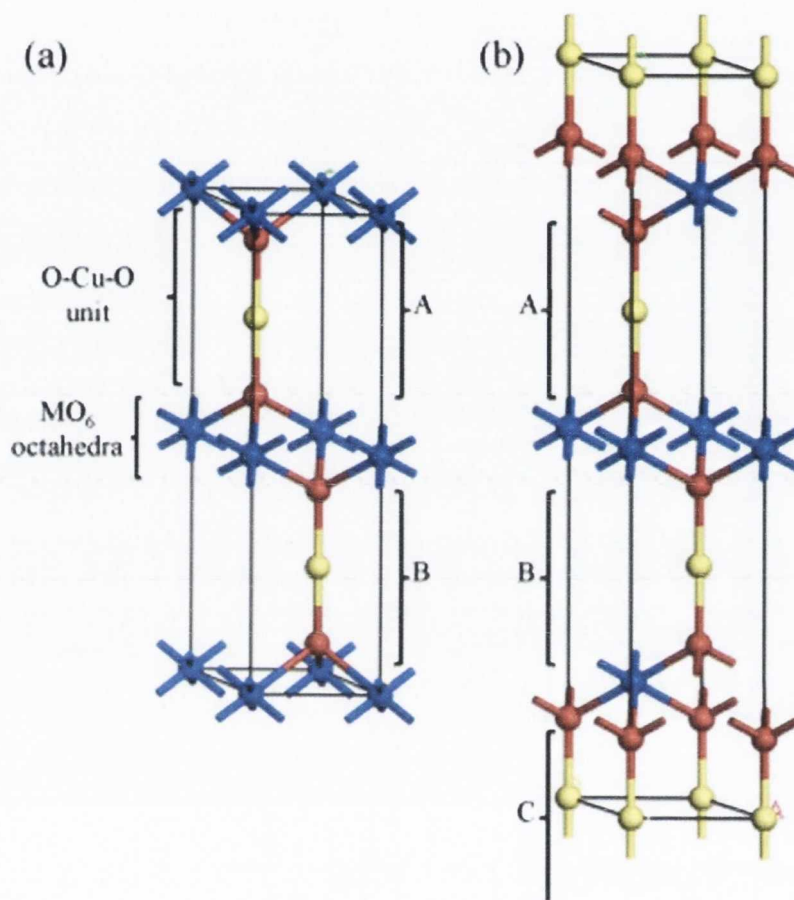


Fig. 1.12 Delafossite  $\text{CuMO}_2$  structure, showing (a) rhombohedral and (b) hexagonal stacking arrangements. Yellow atoms are Cu(I), blue are M(III) and red are  $\text{O}^{2-}$ .

The first  $p$ -type delafossite TCO developed was  $\text{CuAlO}_2$  which was found to have an optical gap of 3.5 eV making it transparent.<sup>14</sup> These novel  $p$ -type films had a conductivity of  $1 \text{ S cm}^{-1}$ , four orders of magnitude lower than the  $10^4 \text{ S cm}^{-1}$  conductivities achieved in  $n$ -type films. Nevertheless, these films offered the first real promise of developing new  $p$ -type TCOs, which could then be manufactured into  $p$ - $n$  diodes for transparent electronics. By changing the M(III) ion, it was hoped that a  $p$ -type TCO with improved conductivity could be developed. In the intervening decade since transparent conducting  $\text{CuAlO}_2$  was first produced, many other delafossite materials have been investigated. The Group 13 delafossites  $\text{CuGaO}_2$ <sup>76</sup> and  $\text{CuInO}_2$ <sup>82</sup> have both been demonstrated to act as  $p$ -type TCOs,

as do the Group 3 delafossites  $\text{CuScO}_2$ <sup>83</sup> and  $\text{CuYO}_2$ .<sup>84</sup> Thus far, the highest conductivity achieved in copper delafossites is  $220 \text{ S cm}^{-1}$  for Mg doped  $\text{CuCrO}_2$ .<sup>84</sup>

Following on from their delafossite work, Hosono *et al.* proposed a second Cu-based TCO in 1998.<sup>15</sup> This new transparent conductor,  $\text{SrCu}_2\text{O}_2$ , was designed to reduce the Cu-Cu interactions even further. In this structure (Fig. 1.13), the Cu ions again form linear O-Cu-O dumb-bells which run through the structure in zigzag chains in both the [100] and [010] directions. These chains are joined together by linearly bonded O-Sr-O dumb-bells. Each Cu atom can now only interact with its nearest neighbour Cu within the Cu-O-Cu chain, thereby reducing the three-dimensional  $\text{Cu}_2\text{O}$  interaction to one-dimensional. This leads to a widening of the optical gap to 3.3 eV.<sup>15</sup> However, the highest conductivity reached in strontium copper oxide films is only  $5.3 \times 10^{-2} \text{ S cm}^{-1}$ ,<sup>85</sup> six orders of magnitude below that of *n*-type materials. Other  $\text{MCu}_2\text{O}_2$  structures such as  $\text{PbCu}_2\text{O}_2$ ,<sup>86</sup>  $\text{BaCu}_2\text{O}_2$ ,<sup>87</sup>  $\text{CaCu}_2\text{O}_2$ <sup>87</sup> and  $\text{MgCu}_2\text{O}_2$ <sup>87</sup> have also been investigated, but strontium copper oxide is the only one to show TCO properties.

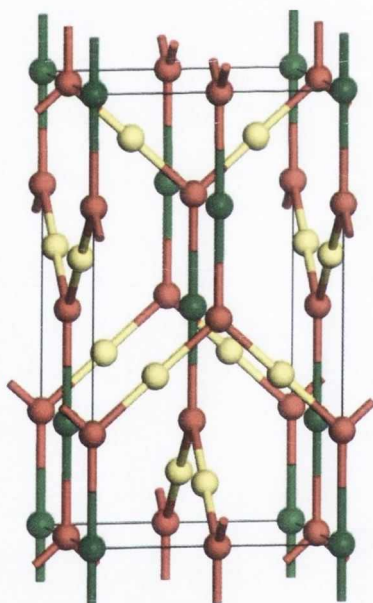


Fig. 1.13 Structure of  $\text{SrCu}_2\text{O}_2$  unit cell with Sr ions in green, Cu in yellow and O in red.

Conductivity in *p*-type TCOs occurs through oxygen excess, which can be introduced by oxygen interstitials or cation vacancies. For example, in NiO, cation deficiency is known to be the cause of conductivity through the defect reaction:<sup>88-89</sup>



In all known *p*-type TCOs, conduction occurs through a polaronic hopping mechanism,<sup>89-92</sup> with the associated defect levels occurring deep in the band gap. The localised nature of the associated defect states is most likely the reason why high levels of conductivity have not been achieved in *p*-type materials. However, as *p*-type TCOs are relatively new materials, with investigations beginning only a decade or so ago, their optimum conductivities may not yet have been reached and further research into these materials may lead to higher conductivities which rival those of *n*-type materials.

## 1.5 Applications of Transparent Conductors

Since the initial use of tin dioxide in defrosting aeroplane windows in World War II, the number of applications of transparent conducting films has steadily expanded so that they are now in wide commercial use in devices such as solar cells, electrochromic windows, touch panel displays, oven windows and flat panel displays.<sup>6</sup> The development of *p*-type TCOs and transparent electronics can only widen the numerous uses of TCOs, making them an integral part of everyday devices and an essential part of the consumer electronics industry.

### 1.5.1 Flat Panel Displays

Since the first appearance of flat screens in laptop computers in the mid-1980s, flat screen technology has become increasingly used so that it has now fully replaced cathode ray tubes as the standard for display monitors. Although initially much of the flat screen television market was based on plasma technology, the cheaper price of liquid crystal displays (LCDs) has meant that LCD technology has overtaken plasma in the flat screen television market.<sup>93</sup>

A schematic showing the structure of an LCD screen is shown in Fig. 1.14. It consists of a sandwich-like structure in which the liquid crystal lies between two glass plates. The outside of each plate is coated with a polarising material, while the inside is coated with a transparent conducting film (ITO), which acts as an electrode. The polarisers at the front and back of the LCD are aligned perpendicularly. Nematic liquid crystals are made up of thread-like molecules which align in a twisted helical structure. In the LCD, the molecules in the liquid crystal are twisted such that the molecules at the front and back are aligned with each of the polarisers. When light passes through the liquid crystal, its polarisation



axis is aligned along the molecular axes so that the light twists and exits the liquid crystal with the same polarisation as the front film. A colour filter in the front glass plate then results in a red, green or blue pixel on the flat screen display. The role of the ITO electrodes is to create an electric field which untwists the liquid crystal molecules, preventing light from passing through and creating a black pixel on the display.

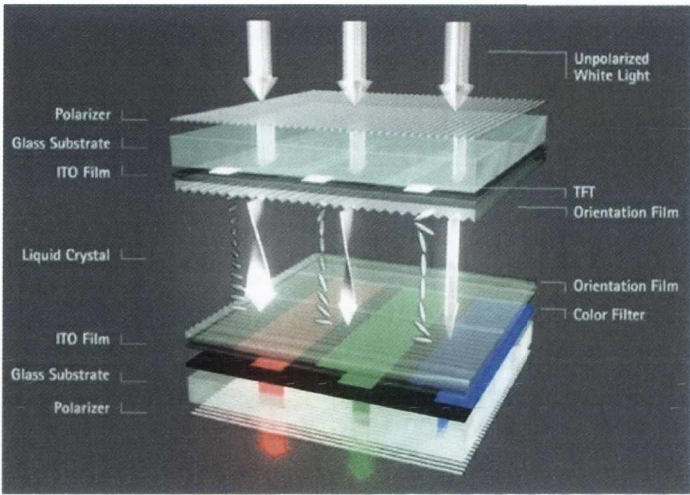


Fig. 1.14 Layered structure of a liquid crystal display (LCD) screen, showing the polarisation of light as it passes through the display. <sup>94</sup>

Currently, ITO is the main TCO used in flat screen displays because of its low resistance and high etchability. <sup>6</sup> Tin dioxide has too high a resistivity and is also difficult to etch, so it has yet to be used commercially in LCDs, despite its lower cost. However, the low resistivity of Al doped zinc oxide films, as well as its high etchability, makes it a prospective candidate for lower cost indium-free flat panel displays.

### 1.5.2 Functional Window Glass

By far the greatest application of TCOs is as functional coatings on windows. Tin dioxide has become the most widely used material for this purpose. In supermarkets, transparent conductors allow a current to be passed through fridge and freezer doors, preventing condensation from obscuring the consumers' view of products. Oven windows are commonly coated with  $\text{SnO}_2$  so that the glass reflects infra-red light back into the oven, keeping the oven hot while the outside glass remains cool. TCOs can also be used as invisible security circuits on glass to protect valuable paintings from thieves while also providing some protection from UV light. <sup>6</sup>

TCO coatings are widely used in low emissivity architectural windows. These types of windows are manufactured simply by coating one side of the glass with a transparent conductor. As well as having high visible transparencies, most TCOs also reflect light in the infrared region of the spectrum. As shown in Fig. 1.15, this means that when solar radiation impinges on the glass, the visible rays pass through, allowing light into the room, while the long range IR heat rays are reflected off the TCO coating. Conversely, heat from inside the house will be reflected back inside. Thus, TCO coatings help to keep a house cool in summer, while also minimising loss of heat through windows in winter.<sup>95</sup>

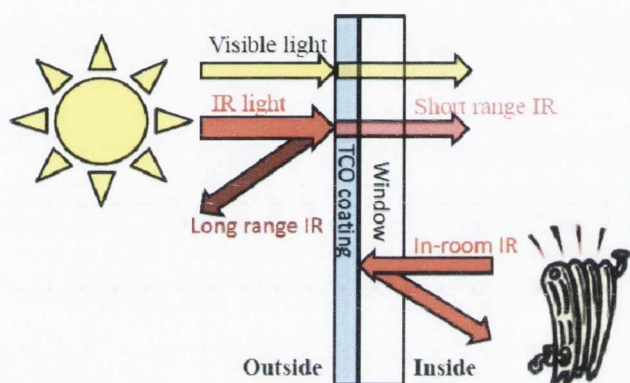


Fig. 1.15 Schematic showing low emissivity window which keeps heat inside in winter and outside in summer while allowing visible light to pass through.

Another major commercial application of TCO coatings is in electrochromic ‘smart’ windows. Electrochromic (EC) materials can change their optical properties upon the application of a voltage. The EC materials used in smart windows darken when a current is passed through and become transparent under zero voltage. This allows the transmittance to be varied, allowing light in or out of a window depending on the solar glare or degree of privacy required. Smart windows consist of five layers as shown in Fig. 1.16. The central layer is an ionic conductor which acts as an electrolyte to carry ions from one side of the device to the other. On one side of the ionic conductor is an EC film which can conduct both electrons and ions (e.g.  $\text{WO}_3$ ). On the other side of the ionic conductor is an ion storage film (e.g.  $\text{NiO}$ ). Both sides of the central three-layer film are coated with a transparent conducting layer (usually ITO or  $\text{SnO}_2$ ). When a voltage is applied between the TCO films, ions are shuttled from the ion storage layer, through the electrolyte, to the EC film, making the glass opaque. Reversal of the voltage results in ion transfer from the EC film to the ion storage layer, restoring transparency to the glass. By adjusting the applied voltage, different levels of transparency can be achieved.

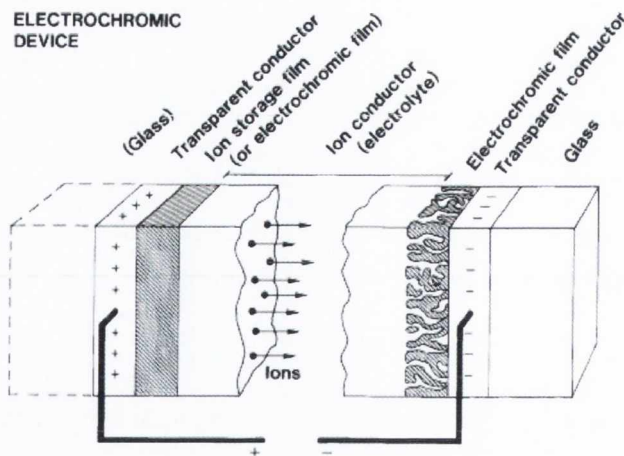


Fig. 1.16 Diagram showing structure of electrochromic device used in smart windows which can alter their optical properties from transparent to opaque upon the application of a voltage.<sup>96</sup>

### 1.5.3 Solar Cells

The third major use of transparent conducting films is in solar cells. Various types of solar cells are available, including thin film solar cells, dye sensitised solar cells and, most commonly, crystalline silicon based solar cells. The basic solar cell structure is shown in Fig. 1.17. The main component of the solar cell to generate electricity is the  $p$ - $n$  junction. This is made up of a layer of  $n$ -type material on top of a  $p$ -type layer. Frequently, a homojunction made up of  $n$ -type P doped silicon and  $p$ -type B doped silicon is used. Thin film solar cells of  $n$ -type CdS combined with  $p$ -type CdTe or CuInGaSe<sub>2</sub> are also available. Incident photons from sunlight result in the excitation of electrons at the  $p$ - $n$  junction, creating unpaired holes and electrons. This results in the flow of holes towards the  $p$ -type

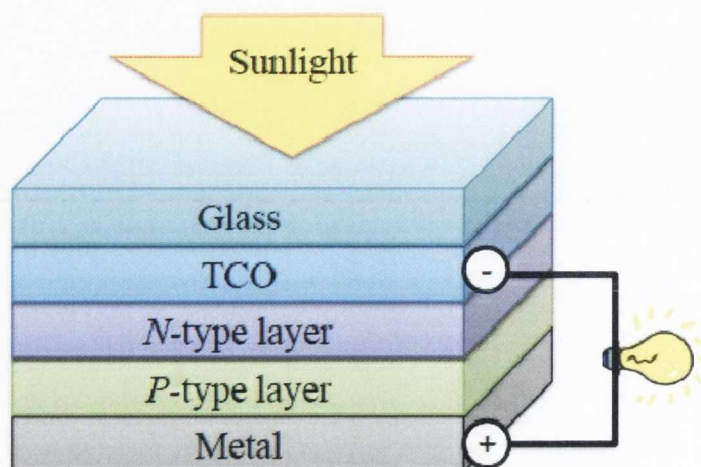


Fig. 1.17 Schematic showing the basic internal layered structure used in solar cell construction.



layer and the flow of electrons towards the  $n$ -type layer, so that an electric current flows across the junction. By placing a metal anode under the  $p$ -type layer and a TCO cathode above the  $n$ -type material, a current can be made to flow in an external circuit. Although the anode does not need to be transparent, as the cathode is located above the  $p$ - $n$  junction, transparency is a necessity for the solar cell to function. The most common TCOs used for this purpose are indium tin oxide and fluorine tin oxide.

## 1.6 Thesis Layout

Despite the ubiquitous use of transparent conducting oxides over the past 60 years, the underlying mechanism by which defects and dopants induce conductivity is still poorly understood. This thesis thus aims to correct some of the deficiencies in the field by performing electronic structure studies of both intrinsic and extrinsic defects in several TCO materials. A brief overview of TCOs was given in Chapter 1, including a summary of some of the materials used and their device applications.

In Chapter 2, the computational methods used in this thesis will be discussed. The quantum theory underlying the electronic structure methods will first be outlined, followed by a brief summary of the implementation of these methods within the Vienna Ab Initio Simulation Package (VASP), used to carry out our computational simulations. The computational tools used to analyse the obtained data will also be summarised, as well as a brief introduction to the experimental electronic structure techniques used in conjunction with this work.

Chapter 3 will examine the electronic structure of defects in the  $n$ -type TCO  $\text{SnO}_2$ . Initially, density functional theory calculations of the intrinsic defects will be discussed, including a complete analysis of the electronic structure of each defect, as well as the overall defect energetics. Following on from this, the results of hybrid-DFT calculations of the intrinsic defects will be introduced, so that a complete picture of the intrinsic defect structure of  $\text{SnO}_2$  is obtained. In the final part of the chapter, hybrid-DFT calculations of dopants in  $\text{SnO}_2$  will be presented, which provide insight into the mechanism by which the conductivity of tin dioxide can be enhanced through doping.

In Chapter 4, the focus will turn to  $p$ -type TCOs, specifically the copper delafossites ( $\text{CuMO}_2$ ) and  $\text{SrCu}_2\text{O}_2$ . The bulk electronic structures of  $\text{CuAlO}_2$ ,  $\text{CuGaO}_2$ ,  $\text{CuInO}_2$  and  $\text{CuScO}_2$  are initially examined, providing some understanding of the conductivity trend in

the delafossite series. In the second half of the chapter, the intrinsic defects of  $\text{SrCu}_2\text{O}_2$  are discussed, with a detailed description of the electronic structure of each defect. The energetics of defect formation are also examined, resulting in a thorough understanding of the mechanism of intrinsic conductivity in  $\text{SrCu}_2\text{O}_2$ .

In Chapter 5, *p*-type intrinsic and extrinsic defects in  $\text{NiO}$  will be explored. The electronic structure of defects in bulk sites will be compared to that of surface defects, in order to gain understanding of the thin film aspects of defect chemistry. Again, both the energetics and electronic structure of each defect will be presented, contributing to an improved comprehension of *p*-type conductivity in this oxide.

Finally, Chapter 6 will give a summary of the conclusions reached in this thesis and the impact of this work on the understanding of transparent conductivity in oxides. A discussion of the mechanisms of *n*-type and *p*-type conductivity in the studied TCOs will be presented, outlining our insights into the defect chemistry of these materials. This will be followed by a brief outline of possible future directions for the field of TCO chemistry.

# Chapter 2: Computational Methods

## 2.2 Overview

Since the advent of the first computers, they have increasingly been used in the physical sciences to provide additional information about the internal geometry and electronic structures of compounds, which cannot be observed by experimental methods. The first simulations were based upon molecular mechanics methods which ignore the internal electronic structure and use force field models to treat the interactions between different atoms. However, as computers have become more powerful, an increasing amount of theoretical work is based upon quantum mechanical principles which can delve into the internal electronic structure of atoms, providing detailed information about the electronic structure of many different types of material.

In this chapter, we outline the origins behind the computational methods used throughout this thesis. We start by discussing quantum chemistry and the mathematical origins behind the various methods – Hartree-Fock (HF), Density Functional Theory (DFT) and hybrid-DFT methods. Following on from this, we discuss how these methods are implemented in the computational code used for this work – the Vienna Ab Initio Simulation Package (VASP).

## 2.3 Quantum Chemistry

### 2.3.1 Schrödinger Equation

The foundation for all quantum chemical calculations is the Schrödinger equation,<sup>97</sup> which in its time independent form is:

$$\hat{H}\Psi = E\Psi \quad (2.1)$$

where  $\hat{H}$  is the Hamiltonian operator,  $\Psi$  is the wavefunction, and  $E$  is the energy. The Hamiltonian is defined as the sum of the kinetic and potential energy operators:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 + \hat{V}(r) \quad (2.2)$$



where  $\hbar = \frac{h}{2\pi}$ ,  $i$  is the index over all particles in the system,  $m_i$  is the mass of particle  $i$ ,  $\nabla_i^2 = \frac{\delta^2}{\delta x_i^2} + \frac{\delta^2}{\delta y_i^2} + \frac{\delta^2}{\delta z_i^2}$  is the kinetic energy operator and  $\hat{V}(r)$  is the potential energy of the system as a function of its coordinates in space,  $r$ . The Hamiltonian can be further split up into the contributions to the kinetic energy from the nuclei ( $\hat{T}_N$ ) and the electrons ( $\hat{T}_e$ ) and the contributions to potential energy from the nuclei-nuclei interactions ( $\hat{V}_{NN}$ ), the nuclei-electron interactions ( $\hat{V}_{Ne}$ ), and the electron-electron interactions ( $\hat{V}_{ee}$ ):

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee} \quad (2.3)$$

Solving the Schrödinger equation allows the calculation of the ground state energy and the wavefunction of the system of interest. However, examining the terms in Eq. 2.3, it becomes apparent that although most of the terms can be calculated exactly, it is very difficult, if not impossible, to determine the electron-electron interactions. Hence, the Schrödinger equation can only be solved exactly for systems with one electron (e.g. H, He<sup>+</sup>) and various approximations are needed to solve it numerically for polyelectronic systems.

## 2.3.2 The Variational Principle

The starting point to an approximate solution of the Schrödinger equation is the variational principle. Given a number of trial wavefunctions, the variational principle provides a method of deciding which of these is the ‘best’ wavefunction. The variational principle states that the expectation value of the Hamiltonian  $\hat{H}$  calculated using a trial wavefunction  $\Psi_T$  will never be lower than the true ground state energy,  $E_0$ , which is the expectation value of  $\hat{H}$  calculated using the true ground state wavefunction  $\Psi_0$ .

$$E_T \geq E_0 \quad (2.4)$$

where  $E_T = \langle \Psi_T | \hat{H} | \Psi_T \rangle$  and  $E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$ .

This means that the lowest energy trial wavefunction will be closest in energy to the true wavefunction. The calculation can thus be systematically improved by varying the wavefunction until the lowest energy solution is obtained.

### 2.3.3 Born-Oppenheimer Approximation

In order to simplify Eq. 2.3, the first step is to separate out the nuclear and electronic contributions i.e.  $\Psi = \Psi_e \Psi_N$ . As nuclei move much more slowly compared to the electrons, the kinetic energy of the nuclei can be ignored and the nuclei can be thought of as fixed in space relative to the electrons. This is known as the Born-Oppenheimer approximation.<sup>98</sup> It works for the majority of cases and will only break down if the atoms are very light in which case the nuclear motion cannot be treated classically. The nuclear-nuclear interaction ( $V_{NN}$ ) is now a constant for any given nuclear coordinates and the electronic Schrödinger equation can be re-written as:

$$V_{NN} + \hat{H}_e \Psi_e = E_e \Psi_e \quad (2.5)$$

where the electronic Hamiltonian  $\hat{H}_e$  is defined as:

$$\hat{H}_e = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} \quad (2.6)$$

and the nuclear-nuclear interactions are defined as:

$$V_{NN} = \sum_{A < B} \frac{e^2 Z_A Z_B}{r_{AB}} \quad (2.7)$$

where  $e$  is the charge of the electron,  $Z_A$  and  $Z_B$  are nuclear charges of atoms  $A$  and  $B$  and  $r_{AB}$  is the distance between the nuclei. We can now solve Eq. 2.5 for the electronic wavefunction and electronic energy and add  $V_{NN}$  afterward to get the total energy. The kinetic energy of the electrons is relatively simple to calculate using the operator:

$$\hat{T}_e = - \sum_i^N \frac{1}{2} \nabla_i^2 \quad (2.8)$$

while the nuclear-electron interaction is also trivial and is calculated using the operator:

$$\hat{V}_{eN} = - \sum_A^M \sum_i^n \frac{Z_A}{r_{iA}} \quad (2.9)$$

However, the difficulty of calculating the electron-electron term still remains and hence, it must be approximated using a variety of different methods.

### 2.3.4 Hartree-Fock Method

The many electron wavefunction can be approximated by the product of one electron wavefunctions,  $\chi_i(x_i)$ , which include both a spatial part  $\Psi_i(x_i)$  and a spin part,  $\alpha(x_i)$  or  $\beta(x_i)$ :

$$\Psi_{HP} = \chi_1(x_1)\chi_2(x_2)\chi_3(x_3) \dots \chi_n(x_n) \quad (2.10)$$

This is known as the Hartree product wavefunction. Using this wavefunction, Hartree developed the self-consistent field (SCF) model in 1928.<sup>99-101</sup> In this method, each electron is assumed to move in the average potential field created by the other electrons in the system so that the potential acting on electron  $i$  is calculated from:

$$V_i[j] = \sum_{j \neq i} \int \frac{\chi_j^2(x_j)}{r_{ij}} \delta\tau \quad (2.11)$$

Solving for the energy and wavefunction requires an iterative procedure. A set of trial wavefunctions is selected for each electron. The electron-electron potential for each electron is then calculated from Eq. 2.11. This allows the Hamiltonian to be constructed and the approximate Schrödinger equation is then solved to give a new wavefunction and energy. This new wavefunction is then used to define a new electron-electron operator. The process is then repeated in an iterative procedure until the total energy difference and wavefunction between subsequent iterations are within a certain tolerance. This is known as the Hartree self-consistent field (SCF) method.

The problem with the Hartree product wavefunction is that it fails to obey the Pauli Exclusion Principle, which states that the wavefunction must be antisymmetric to electron interchange. Interchanging two electrons in Eq. 2.10 gives back exactly the same wavefunction. However, if the wavefunction is instead expressed as a determinant, it becomes antisymmetric. This type of wavefunction has the form:

$$\Psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \dots & \dots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \dots & \dots & \chi_N(x_2) \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \chi_1(x_N) & \chi_2(x_N) & \dots & \dots & \chi_N(x_N) \end{vmatrix} \quad (2.12)$$

This is known as a Slater determinant wavefunction.<sup>102</sup> Exchanging two electrons gives back the same wavefunction with the opposite sign. Using these wavefunctions and



Hartree's SCF procedure, Fock developed the Hartree-Fock (HF) Self-Consistent Field method in 1930.<sup>103</sup>

In order to perform calculations for complex systems, the molecular orbitals (MOs) are first expressed in terms of basis functions using the linear combination of atomic orbitals (LCAO) method:

$$\chi_i = \sum_{\mu} C_{\mu}^i \phi_{\mu} \quad (2.13)$$

where  $\phi_{\mu}$  are the atomic orbital-like basis functions and  $C_{\mu}^i$  are the coefficients of the atomic orbitals  $\mu$  within molecular orbital  $i$ . To calculate the Hartree-Fock energy, Roothaan and Hall independently developed a set of matrix equations known as the Roothaan-Hall equations.<sup>104-105</sup> This approach results in a secular equation in the form:

$$FC = SC\varepsilon \quad (2.14)$$

where  $F$  is the Fock matrix which is made up of single-electron energy operators,  $C$  is the matrix of coefficients  $C_{\mu}^i$ ,  $S$  is the overlap matrix of basis functions with elements  $S_{\mu\nu} = \int \phi_{\mu}(r)\phi_{\nu}(r)d\tau$  and  $\varepsilon$  is the diagonal matrix of eigenvalues  $\varepsilon_i$ . Evaluation of the Hartree-Fock energy requires two-electron integrals of the form:

$$J_{ij} = \iint \chi_i(x_1)\chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_1)\chi_j^*(x_2)d\tau_1d\tau_2 \quad (2.15)$$

$$K_{ij} = \iint \chi_i(x_1)\chi_j^*(x_2) \frac{1}{r_{12}} \chi_j(x_1)\chi_i^*(x_2)d\tau_1d\tau_2 \quad (2.16)$$

where  $J_{ij}$  is known as the Coulomb term as it is the classical interaction between two charge clouds and  $K_{ij}$  is known as the exchange integral and is a quantum mechanical effect arising from the antisymmetric wavefunction. The exchange term is only non-zero for electrons of the same spin, as a result of the Slater determinant wavefunctions, thus preventing two electrons of the same spin occupying the same point in space.  $K_{ij}$  is a negative term which results in an overall lowering of the total energy of the system. The calculation of exchange is the most expensive part of a Hartree-Fock calculation and it formally scales with  $N^4$  where  $N$  is the number of basis functions. Hence, the speed of a calculation will depend on the efficiency of the exchange algorithm.

Although the Hartree-Fock approach is a useful method, it suffers from a number of

problems. From the variational principle, the HF energy will always be greater than the true energy. The difference between the exact total energy and the HF energy is defined as the correlation energy.<sup>106</sup> There are two types of correlation – dynamical and non-dynamical. Dynamical electron correlation describes the effect that for two electrons, the probability of finding one electron at a certain position depends on the position of the second electron. As HF uses a mean field approach, this type of correlation is completely neglected. Non-dynamical correlation occurs in systems which can be described by more than one degenerate determinant, such as molecules where the highest occupied molecular orbital is made up of two or more degenerate states. In this case, HF chooses to populate one of the degenerate states rather than giving both equal weight. In the majority of cases, dynamical correlation is the main contributor to the correlation energy. Although the correlation energy is usually quite small (~0.1% of the total energy), because it is of a similar magnitude to total energy differences, large errors can arise when calculating properties where electrons are redistributed such as binding energies and reaction energies.

Various post-HF methods have been designed to incorporate electron correlation, such as Configuration Interaction (CI) or Moller-Plesset (MP) Perturbation Theory. However, these methods are extremely computationally intensive and are thus not suitable for the large, periodic supercells required for semiconductor defect calculations. Instead, we have chosen to use density functional theory (DFT), described in the following section, which incorporates electron correlation while being computationally tractable.

### 2.3.5 Density Functional Theory (DFT)

Density functional theory (DFT) is derived from the theorems of Hohenberg and Kohn,<sup>107</sup> which proved that in a many electron system the total ground state energy can be written as a unique functional of its electron density, and that the ground state energy is minimised by the ground state electron density. Writing the total energy as a function of the electron density  $\rho(\mathbf{r})$  gives:

$$E[\rho(\mathbf{r})] = \hat{T}[\rho(\mathbf{r})] + \hat{E}_{ee}[\rho(\mathbf{r})] + \hat{E}_{Ne}[\rho(\mathbf{r})] \quad (2.17)$$

where  $\hat{T}$  is the kinetic energy,  $\hat{E}_{ee}$  is the electron-electron interactions and  $\hat{E}_{Ne}$  is the nuclear-electron interaction. This can be rewritten as:

$$E = F + \int \rho(\mathbf{r})V_{ext}(\mathbf{r})d\mathbf{r} \quad (2.18)$$

where  $V_{ext}$  represents the external potential created by the nuclei and  $F$  is known as the Hohenberg and Kohn universal functional and includes the kinetic energy and electron-electron terms. If we knew this functional and the ground state electron density, then the exact ground state energy could be calculated. Unfortunately, the exact form of the functional is unknown. Kohn and Sham<sup>108</sup> introduced a scheme to approximate the functional by considering a fictitious non-interacting system of electrons that has the same exact ground state density as the fully interacting system of electrons. This allows the kinetic energy to be split into that of the non-interacting electrons  $\hat{T}_S$  and a correction term to account for the real interacting electrons ( $\hat{T}_C[\rho(\mathbf{r})]$ ). The  $E_{ee}$  term can similarly be split into the Coulombic interaction  $\hat{J}[\rho(\mathbf{r})]$  and the non-classical part of the electron-electron interaction ( $\hat{E}_{NC}[\rho(\mathbf{r})]$ ). This gives the equation:

$$F = \hat{T}_S + \hat{J}[\rho(\mathbf{r})] + \hat{T}_C[\rho(\mathbf{r})] + \hat{E}_{NC}[\rho(\mathbf{r})] \quad (2.19)$$

The unknown terms ( $\hat{T}_C[\rho(\mathbf{r})]$  and  $\hat{E}_{NC}[\rho(\mathbf{r})]$ ) can be gathered together into a single term,  $E_{XC}[\rho(\mathbf{r})]$ , which is known as the exchange-correlation functional.

The only way to evaluate the kinetic energy term efficiently is to reintroduce the wavefunction by expressing the density as the sum of the square of a set of one-electron orbitals:  $\rho(\mathbf{r}) = \sum_i^N |\chi_i(\mathbf{r})|^2$ . From Eq. 2.8 the kinetic energy term is then:

$$\hat{T}_S = -\frac{1}{2} \sum_i^N \int \chi_i(\mathbf{r}) \nabla^2 \chi_i(\mathbf{r}) d\mathbf{r} \quad (2.20)$$

and the classical Coulombic term can be written in terms of the density as:

$$\hat{J}[\rho(\mathbf{r})] = \frac{1}{2} \int \int \rho(\mathbf{r}_1) \frac{1}{r_{12}} \rho(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.21)$$

Hence,  $E$  can be rewritten as:

$$E = [\hat{T}_S + \hat{J}[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})]] - \int \sum_A^M \frac{Z_A}{r_{1A}} \rho(\mathbf{r}) d\mathbf{r}_1 \quad (2.22)$$

where the term in brackets is  $F$  and the second term is the electron-nuclear interaction. Using this energy expression, the one-electron Kohn-Sham equations can be derived which can be solved for the wavefunction and the total energy using a self-consistent field approach.

DFT is in principle exact and hence, it appears to be superior to HF as it includes both



exchange and correlation. However, as the functional form is unknown,  $E_{XC}$  must be approximated, so that instead of the exact exchange and zero correlation of the Hartree-Fock approach, we end up with *approximate* exchange and *approximate* correlation. The advantage to this is that, since the evaluation of exchange in HF is the most expensive part of the calculation, DFT calculations are generally computationally less expensive. However, approximating exchange and correlation does have some drawbacks which will be discussed later.

### 2.3.6 Exchange-Correlation Functional

The dependence of  $E_{XC}$  on the density can be expressed in terms of  $\rho(\mathbf{r})$  and the exchange-correlation energy per electron  $\varepsilon_{xc}[\rho(\mathbf{r})]$ :

$$E_{XC}[\rho(\mathbf{r})] = \int \rho(\mathbf{r})\varepsilon_{xc}[\rho(\mathbf{r})]d\mathbf{r} \quad (2.23)$$

By integrating  $\varepsilon_{xc}$  over all points in the system, the total exchange-correlation ( $E_{XC}$ ) can be evaluated. The simplest formulation for  $E_{XC}$  is the local density approximation (LDA). This approximation is based on the uniform electron gas, in which the electron density is constant throughout all space. The assumption in LDA is that, at each point  $\mathbf{r}$  in the system,  $\varepsilon_{xc}$  is equal to the exchange-correlation of a homogeneous electron gas with the same density. The exchange part,  $\varepsilon_x$ , can be evaluated from the explicit equation derived by Bloch and Dirac which expresses the exchange as a function of the density.<sup>109-110</sup> Unfortunately, the functional form for the correlation,  $\varepsilon_c$ , is not known. However, using quantum Monte Carlo, Ceperley and Alder<sup>111</sup> successfully computed the total energy for several electron gases of different densities and obtained correlation energies for each by subtracting off the exchange. Vosko, Wilk and Nusair (VWN)<sup>112</sup> later performed fits to this data to give an equation for the LDA correlation energy.

LDA assumes that the exchange-correlation is dependent on the density alone and not how the density is changing. In most real systems, the density varies rapidly, and  $\varepsilon_{xc}$  is dependent on the local environment. Despite its simplicity, LDA still performs relatively well and is widely used in quantum chemistry. However, it is known to suffer from a number of problems, including the overbinding of electrons, which results in the overestimation of atomisation and ionisation energies. For this reason, more sophisticated methods have been developed, which include both the electron density and the gradient of

the density, and are known as generalised gradient approximation (GGA) functionals. Most GGA exchange and correlation functionals are calculated using the LDA exchange and correlation, with correction terms to include the gradient. There are two different classes of GGA functionals which have been developed. The first of these are derived by fitting to experimental data e.g. Becke's exchange and correlation functionals,<sup>113</sup> and the Lee-Yang-Parr (LYP) correlation functional.<sup>114</sup> However, the data used for these fits are generally derived from molecules and compounds of the first few rows of the periodic table and thus care should be taken when applying these functionals to compounds of heavier elements. The second class of GGA functionals does not rely on any empirical parameters and thus should be more applicable to a wide range of chemical compounds (e.g. PW91 exchange-correlation functional developed by Perdew and Wang<sup>115</sup>). The PBE exchange and correlation functionals developed by Perdew, Burke and Ernzerhof in 1996<sup>116</sup> which are used in our VASP calculations belong to this latter class of functionals and are widely used for solid state calculations.

Due to the simplicity of the DFT approach, it has become one of the most popular methods for quantum chemical calculations. However, it does suffer from a number of drawbacks. Many of the problems derive from the use of an approximate exchange-correlation functional. In the formulation of Eq. 2.19, the Coulomb term  $\hat{J}[\rho(\mathbf{r})]$  includes the spurious interaction of an electron with itself. If an exact exchange-correlation functional was known, this interaction could be fully removed from the system. However, because of the approximate nature of  $E_{XC}$ , DFT contains a self-interaction error (SIE) whereby each electron interacts with itself. The SIE destabilises highly localised orbitals due to the close proximity of an electron with itself, causing the electrons to delocalise to minimise the self-interaction. Hence, in cases involving a localised defect state, DFT tends to delocalise the defect electron or hole density rather than localising on a few atoms. This has been previously demonstrated in calculations in the case of  $\text{CeO}_2$ , where the creation of an oxygen vacancy at the surface should result in the formation of two  $\text{Ce}^{3+}$  ions.<sup>117</sup> Instead, DFT calculations show the charge to be completely delocalised over all the cerium atoms, completely at odds with the known experimental results. Another problem in DFT is that band gaps are often much smaller than their experimental values and in extreme cases, DFT can predict a metallic system with zero band gap for a known insulator. This problem is inherent to DFT and occurs due to a discontinuity in the exact exchange-correlation functional.<sup>118</sup>

Several methods have been developed to eliminate or reduce the SIE from DFT



calculations. Some of these such as the self-interaction corrected (SIC) functional derived by Perdew and Zunger<sup>119</sup> explicitly subtract the unphysical self-interaction terms. However, this is quite a complicated approach and is not widely used. In the following sections, two approximate methods of correcting for the deficiencies of DFT will be discussed: the hybrid-DFT approach in Section 2.3.7 and the DFT+ $U$  approach in Section 2.3.8.

## 2.3.7 Hybrid-DFT

Hartree-Fock provides a method which does not suffer from the SIE as it uses the exact exchange. However, the problem with HF is that it omits correlation. Mixing the exact exchange of HF with the approximate DFT exchange-correlation functional should reduce the SIE and result in an improved exchange-correlation functional. Simply combining HF exchange with DFT correlation was not found to work well and an improved approach is to use a linear combination of HF exchange and DFT exchange-correlation within the hybrid-DFT method, first developed by Becke in 1993:<sup>120-121</sup>

$$E_{XC} = a_1 E_X^{HF} + (1 - a_1) E_{XC}^{DFT} \quad (2.24)$$

By changing the value of  $a_1$ , the amount of HF exchange included in the calculation can be varied.  $a_1$  can be fitted to known experimental data such as the electronic structure of the material of interest. Normally, the percentage of HF exchange is between 20% and 40%.

A number of more sophisticated functionals have been developed which include parameters that have been fitted to experimental data. One of the most popular functionals is B3LYP<sup>122</sup> which uses Becke's<sup>120</sup> hybrid exchange functional containing 20% HF exchange along with the Lee-Yang-Parr (LYP<sup>114</sup>) correlation functional:

$$E_{XC}^{B3LYP} = (1 - a) E_X^{LSDA} + a E_X^{HF} + b E_X^{B88} + c E_C^{LYP} + (1 - c) E_C^{LSDA} \quad (2.25)$$

The three parameters  $a$ ,  $b$ ,  $c$  were fitted to the atomisation energies, ionisation potentials and proton affinities of a set of compounds of the first row elements. Although B3LYP is regularly used to perform calculations of metal oxides, this is not best practice since it was not originally fitted to these materials. Recently, it has been suggested that the percentage exchange in many cases is too low and its performance in the case of metals can be quite poor.<sup>123</sup> PBE0 is a much better choice of functional to use for metals as it does not rely on any fitting parameters and has been shown to perform well for a number of



semiconductors.<sup>124</sup> It is composed of 75% PBE exchange and 100% PBE correlation functionals combined with 25% Hartree-Fock exchange, as derived from perturbation theory,<sup>125</sup> and has the form:

$$E_{XC}^{PBE0} = \frac{1}{4}E_X^{HF} + \frac{3}{4}E_X^{PBE} + E_C^{PBE} \quad (2.26)$$

This functional has been shown recently to produce better results in solid state calculations for lattice parameters and atomisation energies compared to B3LYP.<sup>123</sup> A recent variation of PBE0 is the HSE06 functional, which applies a screened Coulomb potential to the exchange interaction.<sup>126-127</sup> This means that at large distances, the exchange term is screened so that at long range the functional has pure-DFT behaviour while it behaves as a hybrid-functional at short range. The advantage of this is that it reduces the computational cost of the calculations since HF exchange only needs to be evaluated at short distances. HSE06 has been shown to perform extremely well for many materials, producing band gaps and lattice parameters in very good agreement with experiment for a set of 21 metallic, semiconducting and insulating solids.<sup>128-129</sup> The extent to which the HSE06 functional is screened is governed by the screening parameter,  $\omega$ . Setting  $\omega = 0$  gives a pure PBE0 functional while for  $\omega = \infty$ , the functional behaves as pure PBE. In our HSE06 calculations  $\omega$  was set to  $0.207 \text{ \AA}^{-1}$  as this was previously suggested to be its optimal value for a range of semiconductors and insulators.<sup>130</sup> The percentage exchange in HSE06 is set to 25% as for PBE0.

### 2.3.8 The DFT+ $U$ approach

One of the drawbacks of implementing hybrid-DFT within planewave codes is that, due to the evaluation of HF exchange, calculations are computationally very expensive, which limits the size of the system which can be dealt with. Defect calculations require the use of large supercells to minimise the interactions between defects in different cells. Unfortunately, because of the high computational cost of hybrid-DFT calculations, smaller cells must be used in which there can be large defect-defect interactions. The DFT+ $U$ <sup>131-132</sup> approach presents a method to correct for self-interaction, while being less computationally expensive than hybrid-DFT. DFT+ $U$  is an approach which was originally developed for strongly-correlated systems, such as transition metal oxides. In these materials, the  $d$  electrons spend more time in regions near the ions where the presence of other electrons leads to strong Coulomb repulsion – hence, their motions are correlated.

The SIE can lead to the delocalisation of the electrons over several states, leading to an incorrect orbital occupation. In the DFT+ $U$  approach, the interactions between electrons at the same atomic centre (on-site interactions) are treated using a parameterised Hamiltonian. Normally, these interactions are included for a specific orbital quantum number,  $l$ . In the Dudarev<sup>131</sup> formulation of GGA+ $U$  used in the VASP code, the energy is given by:

$$E_{GGA+U} = E_{GGA} + \frac{U-J}{2} \sum_{\sigma,m} (n_{l,m,\sigma} - n_{l,m,\sigma}^2) \quad (2.27)$$

Here  $n_{l,m,\sigma}$  is the occupation number for an orbital with quantum number,  $l$ , magnetic quantum number,  $m$  and a spin of  $\sigma$ . The  $U$  and  $J$  parameters correspond to the average Coulomb and exchange interactions between electrons of the same angular momentum on the same atom. The extra term in the energy expression can be thought of as a penalty term which opposes partial occupancy of orbitals. This term is zero when the occupation number is zero or one and non-zero when there is fractional occupation.

One problem which arises in GGA+ $U$  calculations is the choice of  $U$  and  $J$  values. As  $U$  and  $J$  are not used separately in Eq. 2.27, only the difference ( $U - J$ ) is relevant. Hence, the  $J$  value is normally set to zero so that only the  $U$  parameter is required. The optimal value for  $U$  is dependent on the system of interest and the properties which are being examined. Although first principles methods by which to calculate  $U$ -values have been proposed,<sup>133-134</sup> most often the  $U$ -values are obtained by fitting to experimental data. In this procedure, several calculations are carried out using different values of  $U$  so that the optimum  $U$ -value to accurately reproduce the empirical parameter of interest can be selected. This fitting may be performed using a peak in an X-ray photoemission spectrum (XPS) or alternatively, by fitting to a known defect peak so that the position of the peak in the experimental XPS is replicated by the calculated electronic density of states (EDOS). In cases where both approaches have been used, (e.g.  $\text{CeO}_2$ <sup>135-136</sup>), similar values of  $U$  have been obtained.

The GGA+ $U$  approach is particularly useful to deal with atoms with partially filled  $d$  or  $f$  orbitals such as transition metals or rare earth metals. GGA calculations for known semiconductors, such as NiO and  $\text{Cu}_2\text{O}$ , result in the wrong occupations of orbitals so that the electronic structure is incorrect. By introducing a  $U$  parameter to the  $d$  orbitals, an improved description of the electronic structure can be obtained and hence, we use the



GGA+ $U$  approach for Cu-based TCOs and NiO calculations in Chapters 4 and 5.

GGA+ $U$  has also proved an excellent method to improve the description of localised defect states. As mentioned earlier, GGA tends to delocalise charge density over many atoms, even in cases which are known to have localised solutions. By penalising the partial occupancy of atomic orbitals, GGA+ $U$  results in more accurate descriptions of localised defect states, such as the oxygen vacancy induced reduction of a Ce(IV) to Ce(III) in ceria.<sup>117</sup>

## 2.4 Simulation details

### 2.4.1 Vienna Ab Initio Simulation Package (VASP)

All calculations were performed using the Vienna Ab Initio Simulation Package (VASP).<sup>137-139</sup> VASP is a quantum mechanical code which is widely used to perform electronic structure calculations of solid state materials. Within VASP, DFT, DFT+ $U$ , Hartree-Fock and hybrid-DFT methods are implemented, making it a flexible code with which to perform calculations. Once the initial unit cell is specified, periodic boundary conditions are used to repeat the unit cell in three directions to represent an infinite lattice. Full electronic and geometric optimisations are then carried out, which result in a minimum energy structure for the material of interest. Further calculations can then be performed to determine properties such as the band structure, density of states and optical absorption spectrum.

### 2.4.2 Electronic and Geometry Optimisation

The optimised electronic and geometric structures are determined through an iterative procedure as outlined in the schematic of Fig. 2.1. An initial guess at the electron charge density and the wavefunction is supplied. This may be either the wavefunction generated from a previous calculation or alternatively, VASP can generate a trial charge based upon the atomic charge densities with a randomly generated wavefunction. The initial wavefunction and density are used to set up the initial Hamiltonian for the system. Following this, a self-consistent procedure such as the Davidson block iteration scheme<sup>140</sup> is used to obtain the energy and wavefunction for this Hamiltonian. The new wavefunction is then used to calculate the charge density, which is mixed with the charge density from



the previous step using the Broyden/Pulay mixing scheme,<sup>141-142</sup> to give the charge density for the next electronic structure step. Mixing of the old and new charge densities results in better convergence compared with using the new charge density alone. A new Hamiltonian is then set up and the procedure repeats until the energy and wavefunction are self-consistent to within a certain tolerance. Once a self-consistent wavefunction is obtained, the forces on the system are calculated as the derivative of the energy with respect to the ionic positions via the Hellmann-Feynman theorem.<sup>143-144</sup> The positions of the atoms are then updated using a geometry optimisation procedure such as the Quasi-Newton or conjugate gradients methods. The entire cycle is then repeated, optimising the wavefunction and geometry until the forces are self-consistent to within a certain tolerance.

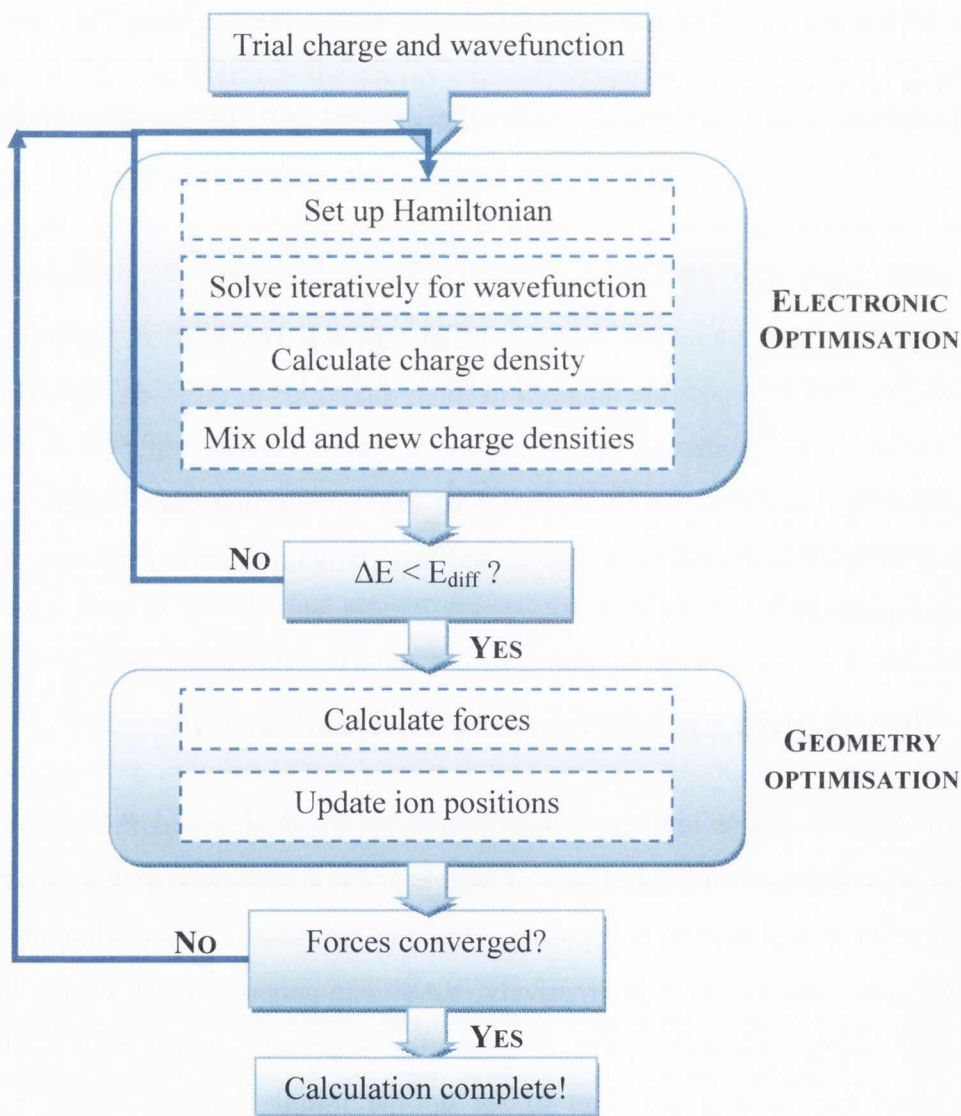


Fig. 2.1 Schematic showing the geometry and electronic optimisation steps within the VASP code.

### 2.4.3 Periodic planewave calculations

VASP uses a planewave basis set as a mathematical representation of the wavefunction. Planewaves take advantage of the fact that rather than having isolated molecular orbitals, solids possess a continuous band of energy levels, which makes planewaves a very efficient approach in representing the wavefunction since they are naturally periodic. The wavefunction is given by the expression:

$$\Psi_j(\mathbf{r}) = \exp[i\mathbf{k} \cdot \mathbf{r}] f_j(\mathbf{r}) \quad (2.28)$$

and  $f_j(\mathbf{r})$  is given by:

$$f_j(\mathbf{r}) = \sum_{\mathbf{G}} c_{j,\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}] \quad (2.29)$$

$f_j(\mathbf{r})$  is a periodic Bloch function<sup>109</sup> which represents the cell periodic part of the wavefunction and is expanded into a finite number of planewaves by summing over the set of reciprocal lattice vectors,  $\mathbf{G}$ .  $c_{j,\mathbf{G}}$  are the planewave coefficients.  $\mathbf{k}$  is a vector which represents the phase of the wavefunction in repeated unit cells, hence, the term  $\exp[i\mathbf{k} \cdot \mathbf{r}]$  is a phase factor which describes the interactions between repeating 3-D unit cells. To understand what this means, consider a 1-dimensional system in which each unit cell of length  $a$ , contains a single  $1s$  orbital (Fig. 2.2). Different combinations of in-phase and out-of-phase interactions between orbitals in unit cells occur at different  $\mathbf{k}$ -vectors. For example, at  $\mathbf{k} = 0$ , all cells are in-phase with each other, while at  $\mathbf{k} = \frac{\pi}{a}$ , the cells are out-of-phase with each other. In between  $0$  and  $\frac{\pi}{a}$ , there are an infinite number of configurations of different phases. Although there are an infinite number of  $\mathbf{k}$  values, because of the periodicity of the wavefunction, it only has unique values in the range  $0 \leq \mathbf{k} \leq \frac{\pi}{a}$ . Outside of this range, the wavefunction repeats so that at  $\mathbf{k} = 0$ , it is the same as at  $-\frac{2\pi}{a}, \frac{2\pi}{a}, \frac{4\pi}{a}$ , etc. This range of unique values of  $\mathbf{k}$  is known as the first Brillouin Zone. Normally, these values are referred to in fractional reciprocal coordinates, so that  $\frac{\pi}{a}$  is 0.5, and  $\frac{\pi}{2a}$  is 0.25. The energy of the system varies with  $\mathbf{k}$  as shown by the graph in Fig. 2.2. The energy is lowest at  $\mathbf{k} = 0$ , in this case, because it is the most in-phase interaction and highest at  $\mathbf{k} = 0.5$ , as this is the most out-of-phase interaction in this system.

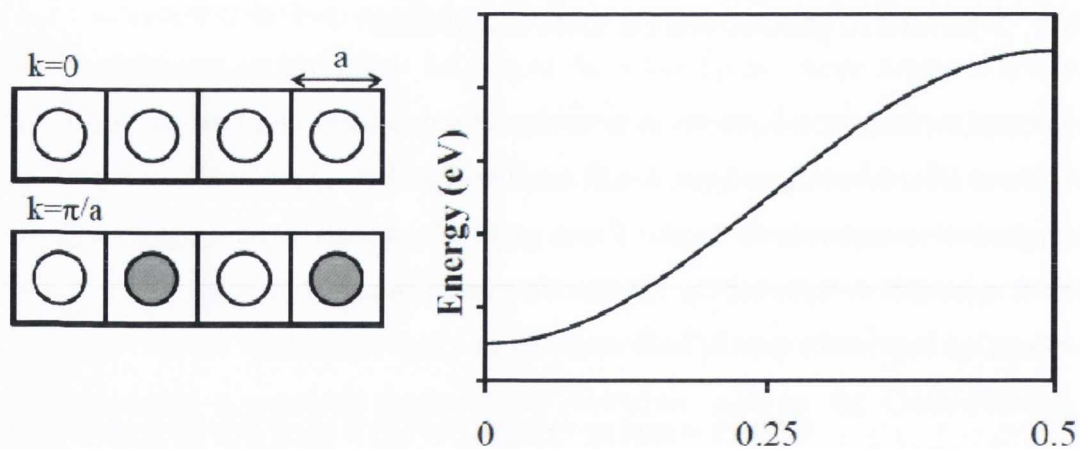


Fig. 2.2 Schematic showing the phases of the wavefunction at different  $k$ -points in a fictional one-dimensional periodic system containing one  $s$ -orbital per unit cell. Graph shows the variation of the energy at different  $k$ -points.

Collectively, the  $k$ -vectors are more commonly referred to as  $k$ -points. As the wavefunction in Eq. 2.28 is a function of the  $k$ -points, calculation of properties such as electron density and total energy require an integration over all  $k$ -points in the system. Since this would require an infinite number of  $k$ -points, the approach taken in calculations is to approximate the integral by a sum over a selected set of  $k$ -points. A regular 3-dimensional grid of points which samples the entire Brillouin Zone is normally used, such as the Monkhorst-Pack<sup>145</sup> mesh. To ensure accuracy in calculations, the size of the  $k$ -point mesh must be rigorously tested. This is performed by carrying out calculations at increasing numbers of  $k$ -points until the total energy converges to within a certain tolerance (0.01 eV/atom in our calculations). As the size of the cell increases, the reciprocal cell reduces in size so that fewer number of  $k$ -points are needed to model a larger cell. Thus, if the unit cell is doubled, the number of  $k$ -points required to sample reciprocal space is halved.

## 2.4.4 Pseudopotentials and Planewave Cut-offs

The wavefunction of Eq. 2.28 produces an infinite number of planewaves, since it contains an infinite sum over reciprocal lattice vectors,  $\mathbf{G}$ . In practice, a cut-off energy is normally used to reduce the planewaves to a finite size. Hence, planewaves of higher kinetic energy than the cut-off are omitted, with the kinetic energy of the planewaves defined as:  $\frac{1}{2}|\mathbf{k} + \mathbf{G}|^2$ . The planewave energy cut-off required varies, depending on the system which is being studied. To maintain high accuracy in calculations, a series of test calculations



with increasing cut-offs should be carried out so that the total energy is consistent to within a certain tolerance (0.01 eV/atom in our calculations).

Normally, in planewave basis sets, only the valence electrons are represented explicitly. The problem of representing valence electrons with planewaves is that their wavefunctions show rapid oscillations near the nuclei due to the requirement that they be orthogonal with the core electrons. A large number of planewaves with high kinetic energy would be required to accurately model the rapidly oscillating wavefunction. To get around this problem, a pseudopotential is normally introduced which describes the interaction between the valence electrons with the combined core electrons and nucleus. The pseudopotential has the same shape as the valence electrons outside the core region but has fewer nodes in the core region, thereby reducing the size of the planewave basis set needed. The VASP calculations presented in this work were performed using the projector augmented wave (PAW) potentials.<sup>146-147</sup> In this method, localised basis sets are used to represent the core electrons and their effect is projected onto the valence electrons. This method retains the physics of all-electron calculations, while having the numerical advantages of pseudopotential methods.

## 2.4.5 Band Structures

One way of gaining information about the electronic structure of a material is to plot the energy eigenvalues as a function of  $k$ -points to give the band structure. By examining the positions of the valence band maximum and the conduction band minimum within the band structure, the magnitude and nature of the band gap can be determined. A more dispersed band occurs when the interacting orbitals are more diffuse so that they can interact with each other, while flat bands occur when the orbitals are more localised so that there is less interaction between them. For example, antibonding interactions between metal  $s$  orbitals and oxygen  $2p$  orbitals tend to result in dispersed bands since  $s$  and  $p$  orbitals are diffuse by their nature. Hence, in many TCOs, such as  $\text{SnO}_2$ , the conduction band minimum shows a high visual dispersion at the  $\Gamma$  point (see Chapter 3). However, for compounds with a localised  $d$ -orbital based conduction band, such as  $\text{CuScO}_2$ , the dispersion is much less (see Chapter 4).

Plotting the energy over all  $k$ -points would require an infinite number of  $k$ -vectors. Hence, the usual approach is to choose special high symmetry points in the Brillouin Zone and plot the evolution of the bands between these points. The Brillouin Zone is specific to the

space group of the particular material being studied. For example, the high symmetry points within the Brillouin Zone of the space group of  $\text{SnO}_2$ ,  $P4_2/mnm$ , are shown in Fig. 2.3. Each of the high symmetry points is given a special label, such as  $\Gamma = (0, 0, 0)$  and  $X = (0, 0.5, 0)$ . Thus, the energy can be plotted over a path which visits each of these points e.g.  $\Gamma \rightarrow Z \rightarrow A \rightarrow R \rightarrow X \rightarrow M \rightarrow \Gamma$  (Fig. 2.3). The high symmetry points for the Brillouin Zone for our calculations were taken from Bradley and Cracknell.<sup>148</sup>

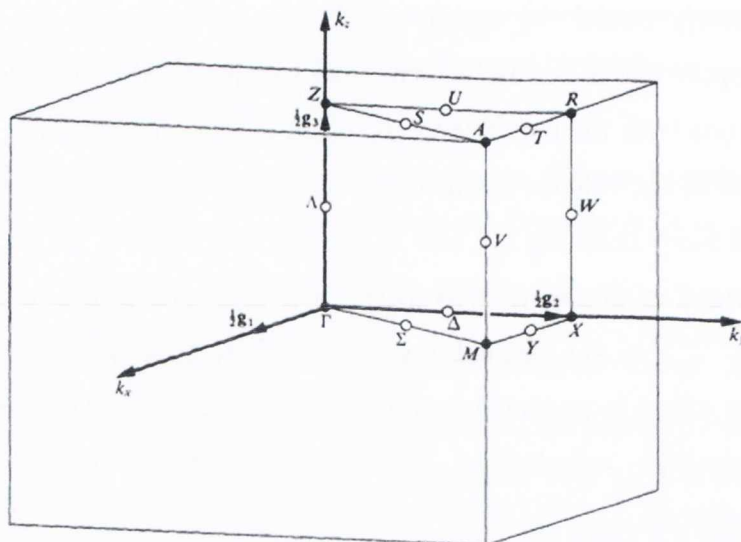


Fig. 2.3 The Brillouin Zone of space group  $P4_2/mnm$  taken from Bradley and Cracknell.<sup>148</sup>  $\Gamma = (0, 0, 0)$ ;  $M = (\frac{1}{2}, \frac{1}{2}, 0)$ ;  $Z = (0, 0, \frac{1}{2})$ ;  $A = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ;  $R = (0, \frac{1}{2}, \frac{1}{2})$ ;  $X = (0, \frac{1}{2}, 0)$ .

To perform a band structure calculation in the VASP code, an initial self-consistent calculation must be carried out using a homogeneous  $k$ -point mesh to generate an accurate charge density and wavefunction. As the band structure calculation is performed using defined pathways between  $k$ -points, the next step is to perform a non self-consistent calculation, in which the charge density is kept constant, to evaluate the energy eigenvalues at each of these  $k$ -points. Following this, the eigenvalues can be plotted against  $k$ -points to give the band structure.

## 2.4.6 Electronic Density of States (EDOS)

The electronic density of states (EDOS) is another way of displaying information about the electronic structure of a material. The total EDOS shows the density of eigenvalues as a function of energy, essentially an integrated band structure. Although the total EDOS does provide information about the total electronic structure, it does not indicate which ion these states belong to. A more useful approach is to calculate the partial electronic density of



states (PEDOS) by projecting the wavefunction onto specific atoms. The wavefunctions are projected onto spherical harmonics within spheres of a certain radius around each ion. In order to reflect the electron density surrounding each ion accurately, this radius should be determined by examining the charge density around each atom. The ratio between projection radii can be worked out by plotting the charge density map and measuring the radius of the charge density sphere surrounding each atom. The ratio between the radii is then calculated and the size of the radii (in Å) is then varied, while keeping the ratio constant, until the correct number of electrons is obtained in the calculation. The projection spheres normally overlap since it is impossible to account for the charge density using non-overlapping spheres.

### 2.4.7 Crystal Orbital Overlap Population (COOP) analysis

Although the PEDOS gives information on which atomic orbitals are interacting, it does not tell us about the bonding or antibonding nature of the interaction. However, by examining the overlap population for a particular bond, we can gain information about the nature of the bonding. Plotting the overlap population of states over a particular energy range gives the overlap population weighted EDOS curve, which is known as a crystal orbital overlap population (COOP).<sup>149</sup> The integral of the COOP up to the Fermi level gives the total overlap population for the bond. The areas where the curve is positive correspond to bonding interactions, while antibonding interactions have a negative COOP curve. The amplitude of the curve is dependent on the number of states in the energy interval, the size of the coupling and the magnitude of the coefficients. To calculate the COOP, two orbitals are specified – one from each atom – and the interactions between these orbitals are calculated. All two-orbital interactions of interest can be plotted to give an understanding of the states in the EDOS which arise from bonding, antibonding and non-bonding interactions.

### 2.4.8 Optical Absorption Calculations

Since we are interested in high transparency in these systems, one parameter of interest is the size of the optical gap. Band structure calculations allow the fundamental band gap to be calculated. However, for many systems, the optical gap obtained from experimental data differs from the direct fundamental band gap as optical transitions at the fundamental gap are symmetry forbidden. This has recently been demonstrated for  $\text{In}_2\text{O}_3$ ,<sup>17</sup> in which



the optical gap was found to be 0.8 eV larger than the fundamental band gap due to the forbidden nature of the direct fundamental transition. The consequence of this is that the fundamental band gap should not be compared directly to the experimentally obtained gap unless accurate optical absorption calculations have been performed. This comparison is regularly performed in theoretical papers, with some authors even using a ‘scissors operator’ to shift the direct fundamental gap artificially so that it equals the experimental optical gap.

In order to compare calculation to experiment accurately, we have computed the optical absorption spectrum so that the magnitude and position of the allowed and forbidden band gaps in  $k$ -space can be gauged. Within the VASP code, the dielectric matrix is calculated using the transversal approximation and the PAW<sup>146-147</sup> method. In this methodology, the absorption spectrum is summed over all possible direct valence to conduction band transitions, ignoring indirect and intraband absorptions.<sup>150</sup> Electron-hole correlations are not treated within the framework of single particle transitions and would require treatment by higher order electronic structure methods.<sup>151-152</sup> These methods have previously been used in a variety of solid state calculations and have been shown to produce reasonable optical absorption spectra.<sup>153-155</sup>

## 2.4.9 Bader Charge Analysis

Bader analysis<sup>156</sup> is used to calculate the charges on the individual atoms which make up the material. Bader charges can be used as an indication of the degree of covalency in a particular system and are also of use to identify changes in atomic charge which occur after the introduction of a defect. The electron density is analysed to identify an atomic volume, which is defined as the region in space including the nucleus that lies within all zero-flux surfaces ( $\nabla\rho \cdot \mathbf{n} = 0$ ,  $\rho$  is density and  $\mathbf{n}$  is a unit vector normal to the surface) surrounding the nucleus. The points where  $\nabla\rho$  is zero are known as bond critical points and define whether or not a bond between two atoms exists. The partial atomic charge  $q_k$  is the difference between the nuclear charge  $Z_k$  and the number of electrons in an atomic basin surrounding each atom:

$$q_k = Z_k - \int_{\Omega_k} \rho(\mathbf{r}) d\mathbf{r} \quad (2.30)$$

where the integral is over the spatial volume  $\Omega_k$  enclosed by the zero-flux surface of atom

*k*. Bader analysis in this work was performed using the program of Henkelman *et al.*<sup>157</sup>

## 2.4.10 Effective Mass

In semiconductor physics, one quantity which is often used to gauge the conductivity of a material is its transport effective mass. This gives an estimate of the conductive ability of the bulk material. A low effective mass translates to a higher mobility and therefore greater conductivity. For a material to have good *n*-type conductivity, it should have a low electron effective mass at the CBM and similarly, a good *p*-type conductor should have a low hole effective mass at the VBM. Bands with low effective masses possess a high degree of curvature and conversely, flat bands have high effective masses. Highly dispersed bands lead to a high degree of electron/hole delocalisation which results in high conductivity. In contrast, flat bands result in localised electrons/holes which are not very mobile. We have calculated the transport effective mass,  $m_T^*(E_k)$ , using the following equation:<sup>158</sup>

$$\frac{1}{m_T^*(E_k)} = \frac{1}{\hbar^2 k} \frac{dE_k}{dk} \quad (2.31)$$

where  $E_k$  is the band edge energy as a function of the wave vector  $k$ , which is obtained directly from the calculations. This assumes that the first derivative of  $E_k$  is the same as that of a parabolic band at the same  $k$ -point. However, in many of these materials, the VBM and CBM are not parabolic. This approach also assumes a band-like conduction mechanism, hence, if a polaronic hopping mechanism dominates, the calculated masses may not be accurate and can only be used to provide a rough estimate of the conductive ability of the material in question.

## 2.5 Volume Optimisation and Convergence

To obtain the minimum energy geometry for a particular material, the unit cell was optimised at a series of volumes (lattice constants) to allow the atomic positions, lattice vectors and angles to relax within a constrained total volume. The resulting energy-volume data was then fitted to the Murnaghan equation of state<sup>159</sup> in order to find the equilibrium cell volume. This approach avoids the problem of Pulay stress which arises in planewave basis set calculations due to the basis set being incomplete with respect to changes in volume. Non-constant volume calculations result in an underestimation of the equilibrium volume unless a very large planewave cut-off is used.



In order to determine the minimum energy structure, convergence with respect to cut-off energy and  $k$ -point density must be achieved. To test for convergence, for each system a series of energy-volume curves were plotted using different planewave cut-off energies and  $k$ -point densities. The minimum energy for each curve was then compared to ensure convergence to within 0.01 eV/atom. For example, Table 2.1 lists the minimum energies and lattice constants for SnO<sub>2</sub>, calculated at three different planewave cut-offs and three different Monkhorst-Pack  $k$ -point meshes. There is very little difference in the minimum energy between the three  $k$ -point meshes. This indicates that the calculation is well converged, even for the smallest  $4 \times 4 \times 6$   $k$ -point mesh. The energy-volume curves plotted at three different planewave cut-offs are shown in Fig. 2.4. This illustrates that the energies at the 400 eV cut-off are not fully converged as they deviate significantly from the energies calculated using 500 eV and 600 eV cut-offs. A small difference in energy of  $< 0.01$  eV is seen between the 500 eV and 600 eV calculations, indicating that the 500 eV calculation is converged. For SnO<sub>2</sub>, we thus used a cut-off of 500 eV combined with a  $6 \times 6 \times 8$   $k$ -point mesh to ensure the greatest degree of accuracy in calculations.

| Energy cut-off | $k$ -points            | Lattice constant (Å) | Min. Energy (eV) |
|----------------|------------------------|----------------------|------------------|
| 400 eV         | $6 \times 6 \times 8$  | 1.0185               | -37.769          |
|                | $4 \times 4 \times 6$  | 1.0192               | -37.697          |
| 500 eV         | $6 \times 6 \times 8$  | 1.0192               | -37.696          |
|                | $8 \times 8 \times 10$ | 1.0192               | -37.696          |
| 600 eV         | $6 \times 6 \times 8$  | 1.0191               | -37.704          |

Table 2.1 Optimised lattice constants and minimum energies for SnO<sub>2</sub> at a number of different  $k$ -point densities and energy cut-offs.

## 2.6 Defect Calculations

In a real crystalline system, defects are generally randomly distributed throughout the structure. However, it is not possible to achieve this situation in calculations involving periodic boundary conditions. Instead, the unit cell is expanded in all directions to form a larger unit known as a supercell. The defect is then placed in the centre of the supercell which is repeated in space using periodic boundary conditions, so that a periodic array of defects is formed. It is preferable to use as large a supercell as possible to minimise defect-defect interactions and so that the defect concentration remains realistic. However, in



practice, the size of the supercell is limited by the computational resources available and significant defect-defect interactions can still be present. Although there have been a number of strategies proposed to correct for this error, none of these have proved completely satisfactory.<sup>160</sup> Hence, we have not attempted to perform any corrections to the defect energies.

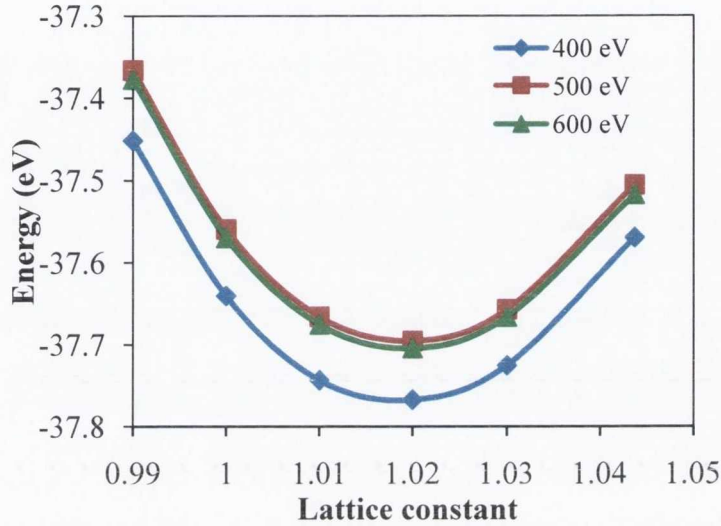


Fig. 2.4 Murnaghan fit of energy versus lattice constant for  $\text{SnO}_2$  using  $6 \times 6 \times 8$  Monkhorst-Pack  $k$ -point grid. Three curves are shown corresponding to fits using 400 eV, 500 eV and 600 eV cut-offs.

For neutral defects, it is trivial to come up with a balanced equation to describe the defect formation. For example, the balanced chemical equation, in Kröger-Vink notation, for the formation of a neutral oxygen vacancy is:



The formation energy of an oxygen vacancy thus has the form:

$$E_f(D) = E_{\text{tot}}(D) - E_{\text{tot}}(\text{stoic}) + \frac{1}{2} E(\text{O}_2) \quad (2.33)$$

where  $E_{\text{tot}}(D)$ ,  $E_{\text{tot}}(\text{stoic})$  and  $E(\text{O}_2)$  are the total energies of the defective cell, stoichiometric cell and an  $\text{O}_2$  molecule, respectively. However, this equation does not take into account the chemical conditions under which the defect forms i.e. whether defect formation occurs in an oxygen-rich or oxygen-poor environment. To take this into account, chemical potential terms must be added to Eq. 2.33. For each element  $A$  in the pure system, a term  $n_A \mu_A$  is added, where  $n_A$  is the number of atoms of  $A$  exchanged with an external

atomic reservoir (positive for vacancy formation and negative for interstitials) and  $\mu_A$  is the chemical potential of atom  $A$ . Hence, the formation energy of an oxygen vacancy is:

$$E_f(D) = E_{tot}(D) - E_{tot}(stoic) + \frac{1}{2}E(O_2) + \mu_O \quad (2.34)$$

At low oxygen partial pressures,  $\mu_O$  is negative and thus, the formation energy of an oxygen vacancy is reduced, favouring an oxygen deficient system. Conversely, higher oxygen partial pressures result in  $\mu_O$  values close to zero, which disfavour oxygen vacancy formation.

When performing calculations of charged defects, a uniform background charge is assumed to keep the overall cell charge neutral. The formula for defect formation energy contains an extra term to take into account the defect charge. For a binary metal oxide (MO), a defect  $D$  in charge state  $q$  has a formation energy given by the formula: <sup>161</sup>

$$E_f(D^q) = E_{tot}(D^q) - E_{tot}(MO) + n_M E(M) + \frac{1}{2}n_O E(O_2) + n_M \mu_M + n_O \mu_O + qE_F + qE_{VBM} \quad (2.35)$$

where:  $n_M$  and  $n_O$  are the number of M and O atoms exchanged with an external atomic reservoir;  $E(MO)$ ,  $E(M)$  and  $E(O_2)$  are the total energies of the metal oxide, the pure metal and an oxygen molecule, respectively;  $\mu_M$  and  $\mu_O$  are the chemical potentials of M and O;  $E_F$  is the Fermi energy and  $E_{VBM}$  is the energy eigenvalue of the valence band maximum.

$E_F$  represents the energy of an electron reservoir with which defect electrons are exchanged. The defect formation energies are plotted as a function of  $E_F$ , which is defined such that the VBM is set to 0 eV in the stoichiometric supercell. When the material is  $n$ -doped, the Fermi energy will lie close to the CBM, whereas  $p$ -doping causes the Fermi energy to shift towards the VBM. The Fermi level of the undoped material should lie somewhere in the middle of the band gap and can be calculated using a self-consistent method for a given temperature and pressure. <sup>162</sup>

The atomic chemical potentials represent the energies of the atomic reservoirs with which atoms are exchanged. A range of values can be found for each atomic chemical potential, so that the overall material remains in chemical equilibrium. There are three conditions for finding the stability range for the chemical potentials:

Condition 1: The sum of the atomic chemical potentials is set to be equal to the formation energy of the pure material. This ensures that the material remains in overall chemical equilibrium. For  $\text{SnO}_2$  this gives:

$$\mu_{\text{Sn}} + 2\mu_{\text{O}} = \Delta H_f(\text{SnO}_2) \quad (2.36)$$

Condition 2: The chemical potentials must ensure that the compound does not decompose into its component elements. This sets the upper limit on the atomic chemical potentials to be less than zero:

$$\mu_{\text{Sn}} < 0 \text{ eV}, \mu_{\text{O}} < 0 \text{ eV} \quad (2.37)$$

Condition 3: The final step is to work out the formation energies of all other phases the elements may have, to ensure that the phase of interest remains stable. For example,  $\text{SnO}_2$  will decompose to  $\text{SnO}$  under sufficiently oxygen-poor conditions. To ensure that we remain in the stability region for  $\text{SnO}_2$ , the limit is:

$$\mu_{\text{Sn}} + \mu_{\text{O}} \leq \Delta H_f(\text{SnO}) \quad (2.38)$$

Through a linear combination of Eq. 2.36 and 2.38, the lower oxygen chemical potential limit is found to be:  $\mu_{\text{O}} \geq \Delta H_f(\text{SnO}_2) - \Delta H_f(\text{SnO})$ . Thus, the full limit for  $\mu_{\text{O}}$  is  $\Delta H_f(\text{SnO}_2) - \Delta H_f(\text{SnO}) \leq \mu_{\text{O}} \leq 0 \text{ eV}$ , while the limits on  $\mu_{\text{Sn}}$  can be found by rearranging Eq. 2.36 to give  $\mu_{\text{Sn}} = \Delta H_f(\text{SnO}_2) - 2\mu_{\text{O}}$ .

For a binary system such as  $\text{SnO}_2$ , once the chemical potential of one element has been set, the other is automatically limited by Eq. 2.36. However, this still results in two independent variables in Eq. 2.35,  $E_F$  and  $\mu_A$ . In order to represent the defect formation energy graphically, the usual approach is to plot the formation energy against  $E_F$  at constant chemical potential as shown in Fig. 2.5. Two plots are presented, one at the upper limit of the chemical potential (e.g. oxygen-rich conditions) and the second at the lower limit of the chemical potential (e.g. oxygen-poor conditions). As each defect has several charge states, only the most stable charge state at each  $E_F$  is plotted. A defect switches between charge states  $q$  and  $q'$  at the electrical donor/acceptor level  $\varepsilon(q/q')$  which is defined as the value of the Fermi energy where  $\Delta H(D^q) = \Delta H(D^{q'})$ . This is marked by solid dots in the Fermi energy plot of Fig. 2.5.



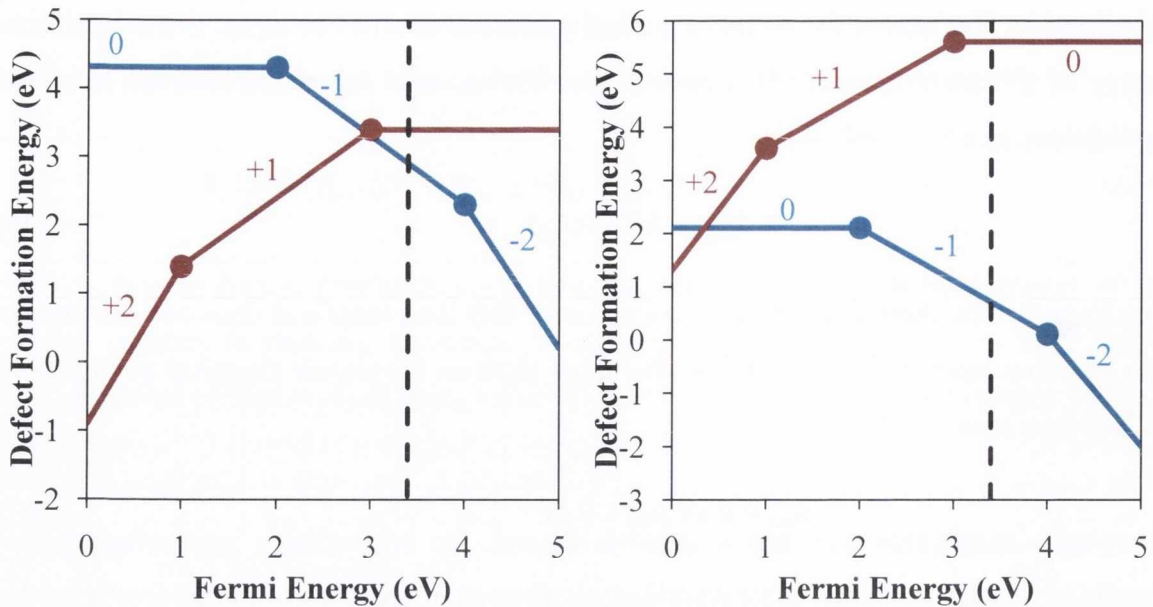


Fig. 2.5 Example plot of defect formation energy against Fermi energy. The red line represents an electron donor defect such as  $V_O$  and the blue line represents an electron acceptor defect such as  $O_i$  while the dashed line marks the band gap. Solid circles mark positions of charge transition levels where defects change charge state. Figure on left represents oxygen-poor conditions while right-hand figure shows oxygen-rich conditions.

For ternary systems, defining a range of chemical potentials becomes more difficult, since there are now three independent variables to work with – two chemical potentials and  $E_F$ . In these cases, the chemical potential range is normally plotted on a two dimensional plot with one chemical potential on the  $x$ -axis and the second on the  $y$ -axis, so that a triangular region can be defined in which Conditions 1 and 2 above hold. Following this, phase boundaries can be drawn which separate out any competing binary or ternary phases from the ternary system of interest. This method will be used in Section 4.2 to define the stability region for  $\text{SrCu}_2\text{O}_2$ .

Eq. 2.35 assumes that the energy of the valence band maximum is the same in the defective cell as in the stoichiometric cell. However, in charged defect calculations, spurious defect-defect interactions can cause large differences between the VBMs in the pure and defective cells. Hence, an alignment procedure must be applied to align the VBMs of the pure and defective supercells. One of the most commonly used methods to perform this alignment is to align the electrostatic potentials between the supercells. This is carried out using average electrostatic potentials in the stoichiometric supercell,  $V_{av}(\text{stoic})$  and in a bulk-like environment in the defective supercell,  $V_{av}(D^q)$  such that:

$$E_{VBM}(D^q) = E_{VBM}(\text{stoic}) + V_{av}(D^q) - V_{av}(\text{stoic}) \quad (2.39)$$

There are many other corrections which have been applied to charged defect calculations to correct for defect-defect interactions. The most common of these is the Makov-Payne correction<sup>163</sup> which corrects the Coulombic interaction due to the long-range interactions of highly charged defects. However, this correction only works for cubic supercells and unrelaxed defects and has been shown to overestimate the correction term for defects in semiconductors.<sup>160, 164-165</sup> Due to these problems we have not applied this correction to our calculations.

## 2.7 Experimental Electronic Structure Techniques

To gauge the accuracy of the electronic structures obtained in calculations, it is necessary to compare these to available experimental electronic structures acquired using a variety of techniques. Our calculated results have thus been compared to the electronic structures obtained by the collaborating experimental groups of Prof. Russ Egdell at Oxford University, and Prof. Kevin Smith at Boston University. The valence band spectra of various materials were examined using the techniques of x-ray photoemission spectroscopy (XPS) and x-ray emission spectroscopy (XES).

### 2.7.1 X-ray Photoemission Spectroscopy (XPS)

Photoemission spectroscopy is a widely used technique to determine information about the electronic structure of solid state materials. It is based upon the photoelectric effect that the interaction of light with a solid results in the emission of electrons. In photoemission spectroscopy, photons from a monochromatic light source are directed at a sample under ultra high vacuum conditions. These photons excite electrons from below the Fermi level of the material, giving them enough kinetic energy to be emitted from the compound (Fig. 2.6). These electrons can then be collected in a detector and their kinetic energies and emission angles measured. The kinetic energies ( $E_k$ ) can be converted to binding energies ( $E_B$ ) by applying the relation formulated by Einstein: <sup>166</sup>  $E_k = h\nu - E_B$  where  $\nu$  is the frequency of the incoming light. The intensity can then be plotted against the binding energy to give the photoemission spectrum of the occupied states of the material.

Depending on the type of source used in the experiment, information about different parts of the electronic structure can be gleaned. High energy x-rays can be used to gain information about the core-level states of the atoms (XPS) while lower energy ultraviolet

photons are used to excite the lower binding energy valence electrons (UPS). Photoemission experiments are generally carried out using a synchrotron source, as its photon energy can be varied over a wide energy range, allowing both the core and valence electrons to be probed.

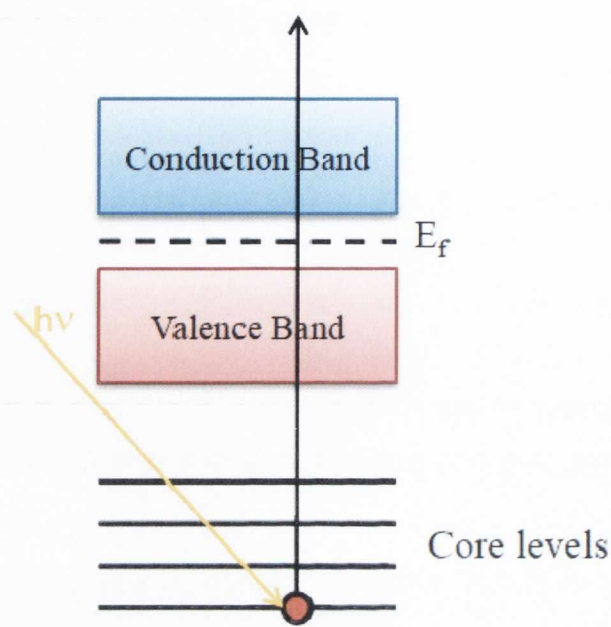


Fig. 2.6 Schematic of X-ray photoemission spectroscopy showing the excitation of an electron by photons with an energy given by  $h\nu$ .

To compare experimental XPS to the calculated total EDOS for a particular material, it is necessary to obtain a cross-section weighted density of states. This is calculated by multiplying the PEDOS contribution for each atom by the electron ionisation cross-section weighting determined by Yeh and Lindau.<sup>167</sup> The ionisation cross-section measures the probability of photoemission when a photon interacts with a particular atomic orbital. This means that some atomic orbitals are easier to ‘see’ in photoemission than others. For example, when dealing with copper oxide based materials such as  $\text{CuAlO}_2$  and  $\text{SrCu}_2\text{O}_2$  (Chapter 4), the ionisation cross-section for Cu  $3d$  states ( $1.2 \times 10^{-3}$  Mb) is a factor of 20 larger than the O  $2p$  cross-section ( $6 \times 10^{-5}$  Mb).<sup>167</sup> As a result, the valence band XPS spectra of  $\text{SrCu}_2\text{O}_2$  and  $\text{CuAlO}_2$  mirror the Cu  $3d$  PEDOS even though the O  $2p$  states have significant contributions to the calculated total EDOS.

### 2.7.2 X-ray Emission Spectroscopy (XES)

X-ray emission spectroscopy (XES) is used to probe the partial density of states of a



material. An x-ray photon is first used to excite a core electron, so that it is either promoted to a state in the conduction band (resonant XES), or ejected from the system entirely (non-resonant XES). This leaves behind a core hole. This hole is refilled by a valence electron, with the decay leading to the emission of an x-ray photon. This process is illustrated in Fig. 2.7. The recombination process can occur via a number of mechanisms, resulting in photons of different energies, corresponding to various valence band electrons. As the core hole is localised on a specific element, this allows the PEDOS of that atom to be obtained. In combination with XPS, an overall picture of the electronic structure of a material can be obtained.

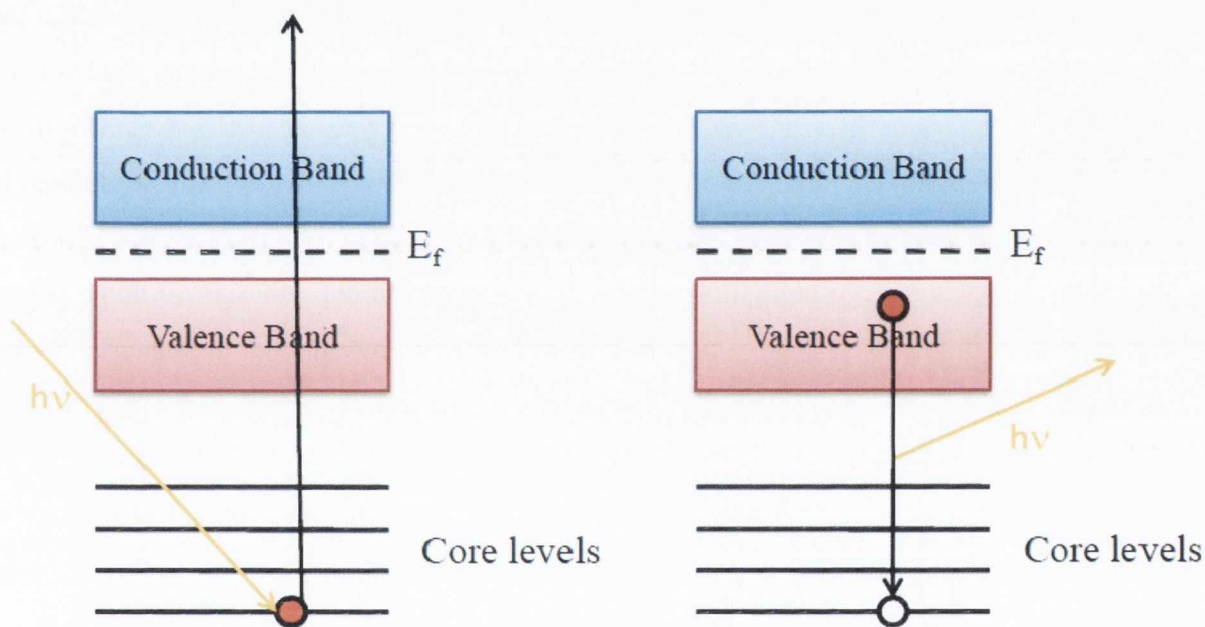


Fig. 2.7 Schematic of x-ray emission spectroscopy showing the excitation of an electron by light (left) and the subsequent relaxation of a valence band electron to the core hole with the emission of radiation.

# Chapter 3: The Origins of Intrinsic and Extrinsic *n*-type Conduction in SnO<sub>2</sub>

## 3.2 Summary

SnO<sub>2</sub> is one of the best known *n*-type TCOs and has gained widespread industrial use as a glass coating over the past 70 years. Despite its long commercial history, the exact mechanism behind its intrinsic and extrinsic conductivity is yet to be fully understood. In this chapter, we explore the intrinsic defects and dopants of SnO<sub>2</sub> which are responsible for *n*-type conductivity. We begin by examining the energetics and electronic structure of intrinsic defects using GGA-DFT. Our findings point to oxygen vacancies as the origin of intrinsic *n*-type conductivity. Further clarification of the nature of the intrinsic defects is provided by detailed charged defect calculations using the HSE06 hybrid functional, which reveal the deep nature of the oxygen vacancy donor states. In the final part of this chapter, HSE06 calculations of doped SnO<sub>2</sub> are carried out to investigate the nature of the electronic states introduced by *n*-type dopants. By comparing Sb with Bi and F with Cl, we can consider the reasons why Sb and F are such successful dopants while Bi and Cl doped SnO<sub>2</sub> have low conductivities. As hydrogen is a known impurity in SnO<sub>2</sub> films, we also consider the effects of H doping on the electronic structure, so that the possibility that ‘intrinsic’ *n*-type conduction is accidentally induced by hydrogen can be explored.

## 3.3 Intrinsic Defects of SnO<sub>2</sub>: GGA Calculations

### 3.3.1 Introduction

SnO<sub>2</sub> crystallises with the rutile structure, space group  $P4_2/mnm$  ( $D_{4h}^{14}$ ), in which each Sn(IV) ion sits at the centre of a slightly distorted oxygen octahedron (Fig. 3.1 (a)).<sup>59</sup> Sn also possesses a lower +2 oxidation state, with Sn(II) adopting distorted fourfold coordination in the corresponding monoxide SnO as illustrated in Fig. 3.1 (b).<sup>168</sup> In this structure, the SnO<sub>4</sub> tetrahedra form layers which are held together by van der Waals interactions. The Sn(II) ions each possess lone pairs which point into the gap between the layers, leading to slight distortion in the tetrahedra.<sup>169</sup> SnO<sub>2</sub> has a band gap of ~3.6 eV and is therefore transparent. It becomes an *n*-type TCO only when made oxygen deficient, with

SnO<sub>2-δ</sub> thin films possessing resistivities of  $\sim 10^{-3} \Omega \text{ cm}$ <sup>170</sup> and carrier concentrations of  $\sim 10^{20} \text{ cm}^{-3}$ .<sup>171</sup> There is currently much debate in the literature over the cause of conductivity in undoped SnO<sub>2</sub>. Although intrinsic defects appear to be the most likely cause, there have been suggestions that accidental extrinsic impurities such as hydrogen may play a role.<sup>68</sup> However, in this section, we will focus on the intrinsic mechanisms of conductivity, without considering the possibility of extrinsic impurities.

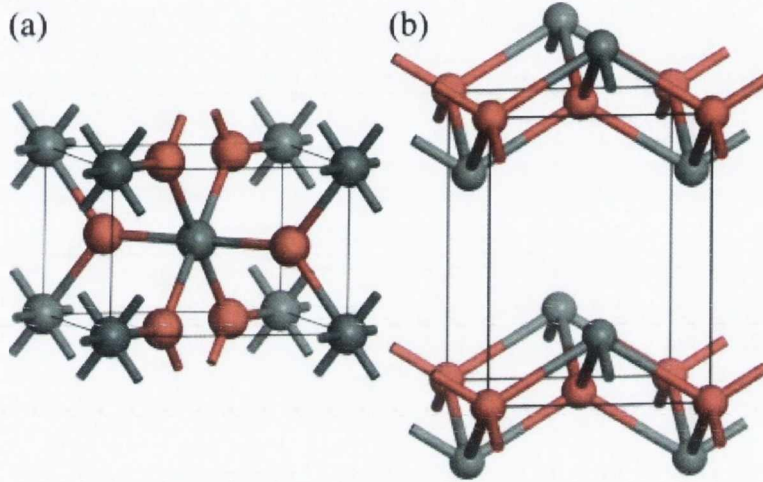


Fig. 3.1 Unit cells of (a) SnO<sub>2</sub> and (b) SnO with tin atoms in grey and oxygen atoms in red.

The primary intrinsic defects which may cause oxygen deficiency are tin interstitials and oxygen vacancies. Oxygen vacancies form via the defect equation:



while Sn(IV) and Sn(II) interstitials can form via the reactions:



The electrons produced in these defect reactions form defect levels which have been experimentally located 0.15-0.30 eV below the conduction band.<sup>62, 66, 172-173</sup> However, it is not clear exactly where the electrons are localised/delocalised and what the charge density of the defect states actually looks like. One proposal is that the ease of formation of oxygen deficient defects is due to the dual valency of Sn.<sup>174-176</sup> The electrons which form via the defect reactions in Eqn. 3.1-3.3, can go on to cause a tin reduction via the mechanism:





Electronic conductivity could then occur due to the mobility of electrons from Sn(II) to Sn(IV) sites.<sup>174-176</sup> It is known that oxygen vacancy formation at the surface of SnO<sub>2</sub> results in the reduction of surface Sn(IV) cations to Sn(II), with photoemission revealing the presence of a defect state 1.4 eV above the valence band maximum, of mixed Sn 5s and 5p character.<sup>173, 177-179</sup> Experimental results have suggested that the intrinsic bulk defect states which arise in SnO<sub>2</sub> are of Sn 5s character, consistent with the formation of Sn(II), while various authors have noted the presence of Sn(II) in *n*-type SnO<sub>2-δ</sub> thin films.<sup>179</sup> The observation of a SnO phase has been made in high-resolution transmission electron microscopy (HRTEM)<sup>180</sup> and fine structure emissions ascribed to Sn(II) have been observed in photoluminescence spectra.<sup>181</sup> However, quantum chemical calculations of the defect electron density surrounding an oxygen vacancy or tin interstitial are sadly lacking, making it uncertain whether this is a valid mechanism, or if the electrons simply delocalise over many tin sites. Bulk Sn(II) may trap two electrons, blocking their mobility, and it is thus unclear whether reduction to Sn(II) can cause conductivity.<sup>182</sup>

It still remains uncertain whether undoped SnO<sub>2</sub> conducts via a polaronic hopping or band-type conduction mechanism. A variable range hopping mechanism has been suggested by a number of authors,<sup>183-187</sup> while thermionic emission<sup>188-189</sup> and band conduction<sup>184</sup> have also been proposed. The conduction mechanism is generally agreed to be thermally activated, with plots of conductivity against temperature revealing two regions with different activation energies. Region I (low temperature region) has almost constant resistivity with temperature, whereas Region II (high temperature region) experiences a large decrease in resistivity with temperature.<sup>171, 190-192</sup> Region I has been found to be dominated by shallow donors with measured activation energies of 0.008-0.08 eV,<sup>171, 190-192</sup> while in Region II, conductivity is caused by deep donors with activation energies of 0.1-0.4 eV.<sup>171, 190-192</sup> The intrinsic shallow donors are responsible for the majority of the room temperature intrinsic conductivity, with the deep donors requiring higher temperatures to conduct.

The widely made assumption across the literature is that oxygen vacancies are the lowest energy intrinsic defect. Evidence for this assumption comes from various fits of oxygen partial pressure against conductivity which have slopes consistent with an oxygen vacancy mechanism.<sup>62, 193-194</sup> Based on these measurements, donor levels identified 0.03 eV and 0.15 eV below the CBM were assigned to  $V_O^\bullet/V_O^\times$  and  $V_O^{\bullet\bullet}/V_O^\bullet$ .<sup>62, 173</sup> Further evidence for the existence of these shallow states comes from cathodoluminescence studies which identified a band at 1.94 eV to result from a transition between a surface oxygen vacancy

level at 1.4 eV above the VBM and a bulk shallow donor level at 0.15 eV below the CBM.<sup>173</sup> Oxygen vacancies have also been observed in electron paramagnetic resonance studies, which have identified a resonance at  $g = 1.89$ , associated with singly ionised oxygen vacancies ( $V_O^\bullet$ ).<sup>195-197</sup> This resonance occurs after CO/Ar treatment of SnO<sub>2</sub>, which results in the formation of  $V_O^\bullet$  through the interaction of CO with surface oxygen to form CO<sub>2</sub> and neutral oxygen vacancies by the defect reaction:  $CO + O_O \rightarrow CO_2 + V_O^\times$ . This forms a paramagnetic defect via the mechanism:  $V_O^\times \rightarrow V_O^\bullet + e'$ , producing an electron in a donor level of Sn 5s character, as evidenced in EPR by a resonance at  $g = 1.99$  assigned to an unpaired electron on tin.<sup>198</sup>  $V_O^\bullet$  is thought to transfer electrons onto tin ions to form  $V_O^{\bullet\bullet}$  through the reaction:  $Sn_{Sn}^\times + 2V_O^\bullet \rightarrow Sn_{Sn}^{\prime\prime} + 2V_O^{\bullet\bullet}$ . Various photoluminescence studies have also observed bands which have been attributed to the presence of oxygen vacancies in SnO<sub>2</sub> films.<sup>199-201</sup>

In contrast, experimental evidence for the presence of tin interstitials in oxygen deficient samples is quite sparse. In the rutile structure, only half of the oxygen octahedra are occupied by Sn(IV), leaving large, empty octahedra which can be occupied by interstitials. One study in 1989<sup>202</sup> suggested tin interstitials to be the cause of conductivity based on a slight increase in the lattice constant, with little other evidence presented to back up these claims. Observation of tin interstitials was, however, made in high resolution transmission electron microscopy (HRTEM), which found evidence for the presence of tin interstitials in thin films of SnO<sub>2</sub>.<sup>203</sup> Peaks in photoluminescence spectra have also been tentatively assigned to Sn interstitials,<sup>204</sup> while the presence of Sn(II) interstitials in SnO<sub>2</sub> microstructures has also been suggested.<sup>205-206</sup>

There have been a limited number of calculations of intrinsic defects in SnO<sub>2</sub>, although many calculations are available qualifying the bulk electronic structure.<sup>207-211</sup> The earliest electronic structure calculations of an oxygen vacancy, using tight binding Green's function calculations, showed the defect to form shallow donor levels, which could be responsible for experimentally observed levels.<sup>212</sup> However, the formation energies of defects in SnO<sub>2</sub> were not calculated until later, when Freeman and Catlow<sup>63</sup> used a force field approach to model Schottky and Frenkel defects. Their findings were that Schottky defects would be the most stable, although a later study using an improved potential model predicted oxygen Frenkel defects to be more stable.<sup>213</sup> In either case, no net non-stoichiometry will result, hence neither can account for conductivity. Attempts to quantify the energetics of non-stoichiometric defects were first made in 2002, when Kilic and Zunger<sup>65</sup> performed a



complete DFT-LDA study of the energetics of charged defects in  $\text{SnO}_2$ . Their calculations suggested that under oxygen-poor conditions  $\text{Sn}_i^{\bullet\bullet\bullet}$  is the most stable defect, rather than  $V_O^{\bullet\bullet}$ . Both defects were found to have shallow defect transition levels, consistent with experimental observations. Since both defects were found to have low formation energies, the authors combined the two to make the defect complex  $(\text{Sn}_i + V_O)^\times$ , concluding that it would be the dominant defect in the system, as this complex was lower in energy than its combined isolated defects. Since both  $\text{Sn}_i^{\bullet\bullet\bullet}$  and  $V_O^{\bullet\bullet}$  are positively charged, combining the two does not appear to make chemical sense, without some charge compensation mechanism. Although the authors suggest that the complex will result in the interstitial being in the +2 charge state, this would still result in a complex with an overall charge of +4, requiring four electrons somewhere unspecified in the system for charge neutrality.

A later DFT study using *a posteriori* corrections to improve the description of the band gap, contradicted these results and found oxygen vacancies to be the most stable intrinsic defect.<sup>67</sup> Yet, as oxygen vacancies were found to produce donor levels located deep in the band gap the study concluded that they could not be responsible for the observed *n*-type conductivity of  $\text{SnO}_2$ . Instead, hydrogen impurities were proposed to be the cause of the shallow experimental donor levels and hence, the ‘intrinsic’ conductivity. Recently, the increases in computational power have allowed for calculations of oxygen vacancies in  $\text{SnO}_2$  using hybrid-DFT to be carried out.<sup>38</sup> These calculations largely invalidate some of the previous DFT work, finding that both GGA and LDA calculations, with and without *U* corrections result in donor levels clustered around 1.4 eV above the VBM, with the band gaps varying between 0.6 eV in GGA and 1.8 eV in GGA+*U* calculations, so that GGA+*U* predicts deep levels while LDA and GGA show shallow donor levels. In contrast, PBE0 hybrid-DFT calculations found  $\text{SnO}_2$  to have a deep donor level located 0.5 eV below the CBM. The authors suggested that hydrogen impurities may be the cause of shallow donors, though no calculations of these were carried out.

Although these previous calculations have carried out studies of the energetics of defect formation, a complete study of the electronic structure of defects in  $\text{SnO}_2$  has yet to be carried out. In the following sections we thus present the results of DFT-GGA calculations of the intrinsic defects of  $\text{SnO}_2$  which represents the first thorough study of energetics and electronic structure of this valuable transparent conducting oxide.



### 3.3.2 Methodology

GGA-DFT (PBE) was used to carry out all of the intrinsic defect calculations within this section. For Sn, the  $5s$ ,  $5p$  and  $4d$  electrons were explicitly included in the valence with the remaining core electrons treated using the PAW potential, while the  $2s$  and  $2p$  electrons were explicitly included for O. Calculations used a planewave cut-off energy of 500 eV and a Monkhorst-Pack<sup>145</sup>  $k$ -point mesh of  $6 \times 6 \times 8$  for the unit cell, while the forces were converged to within 0.01 eV/Å. Defect calculations were performed using a  $3 \times 3 \times 4$  (216 atoms) supercell expansion, with a  $2 \times 2 \times 2$  Monkhorst-Pack  $k$ -point grid. The defects used were all charge neutral overall, hence there is no Fermi level dependence. The defect formation energies  $E_f(D)$  were calculated as outlined in Section 2.5 using the formula:

$$E_f(D) = E_{tot}(D) - E_{tot}(\text{SnO}_2) + \frac{1}{2}n_{\text{O}}E(\text{O}_2) + n_{\text{Sn}}E(\alpha - \text{Sn}) + n_{\text{O}}\mu_{\text{O}} + n_{\text{Sn}}\mu_{\text{Sn}} \quad (3.5)$$

The chemical potential limits are set as in Section 2.5 with the oxygen-rich limit occurring when  $\mu_{\text{O}}$  is equal to the chemical potential of oxygen in  $\text{O}_2$  (0 eV). The oxygen-poor limit is defined when  $\mu_{\text{O}} = \Delta H_f(\text{SnO}_2) - \Delta H_f(\text{SnO})$ , which is calculated as -3.09 eV compared to a value of -3.08 eV experimentally.<sup>214</sup> The full constraint is thus:  $-3.09 \text{ eV} \leq \mu_{\text{O}} \leq 0 \text{ eV}$ .  $\mu_{\text{Sn}}$  can be determined from the formation energy of  $\text{SnO}_2$  ( $\mu_{\text{Sn}} + 2\mu_{\text{O}} = \Delta H_f(\text{SnO}_2)$ ), which is calculated as -6.39 eV compared to -5.98 eV experimentally.<sup>214</sup> Hence  $\mu_{\text{Sn}}$  can be calculated from  $\mu_{\text{Sn}} = \Delta H_{\text{SnO}_2} - 2\mu_{\text{O}}$ , giving a range of:  $-6.39 \text{ eV} \leq \mu_{\text{Sn}} \leq -0.20 \text{ eV}$ .

### 3.3.3 GGA Electronic Structure of Bulk $\text{SnO}_2$

Full geometry and volume optimisations were performed on the initial experimental structure,<sup>59</sup> with the equilibrium volume obtained from a fit to the Murnaghan equation of state.<sup>159</sup> The calculated lattice parameters and bond lengths are increased from their experimental values by about 2%, as expected for GGA calculations (Table 3.1). Bader charge analysis<sup>157</sup> shows the tin atoms to have a charge of  $+2.52e$  and the oxygen atoms to have a charge of  $-1.26e$ . This indicates a high degree of covalent character in the bonding, as seen in previous studies of  $\text{SnO}_2$ <sup>215-216</sup> and the corresponding monoxide  $\text{SnO}$ .<sup>168-169, 217</sup>

The band structure of the bulk material is shown in Fig. 3.2 (a) and is similar in appearance to previous calculations.<sup>207-208, 210, 218-219</sup> The calculated band gap is 0.64 eV and

|              | Experimental         | Calculated (error)   |
|--------------|----------------------|----------------------|
| <i>a</i> (Å) | 4.740                | 4.834 (+2.0%)        |
| <i>c</i> (Å) | 3.188                | 3.244 (+1.8%)        |
| <i>u</i> (Å) | 0.3063               | 0.3066 (+0.1%)       |
| Sn-O(Å)      | 4 × 2.056, 2 × 2.053 | 4 × 2.093, 2 × 2.096 |

Table 3.1 Structural parameters and bond lengths for SnO<sub>2</sub> as calculated using GGA-DFT compared to their experimental values. <sup>59</sup>

direct at  $\Gamma$ , as compared to the experimental optical gap of 2.9-4.3 eV. <sup>170, 191, 220-224</sup> This is not unexpected as DFT is known to greatly underestimate the band gaps of metal oxides, despite the fact that the ground state properties are well described. <sup>225</sup> However, caution is needed when comparing the theoretical and experimental gaps here, as it is well known that the optical gap in SnO<sub>2</sub> is forbidden, and previous calculations have shown the optical transition to come from bands 0.8 eV below the VBM. <sup>226</sup> To quantify the optical gap in our calculations, we have calculated the optical absorption spectrum for SnO<sub>2</sub> as shown in Fig. 3.2 (b). This shows the onset of optical absorption to begin at 1.38 eV, 0.74 eV higher than the fundamental band gap. This corresponds to a transition from the second highest valence band to the conduction band minimum. Fig. 3.2 (b) shows that the initial optical absorption is quite weak and extrapolating the linear portion of the  $\alpha$ -curve to the  $x$ -axis gives a calculated optical band gap of ~1.75 eV. This suggests that measured experimental optical gaps may be 0.7-1.0 eV higher than the forbidden fundamental band gap and the weak tailing of the absorption may explain the reason for the large range of observed optical band gaps ranging from 2.9-4.3 eV. <sup>170, 191, 220-224</sup>

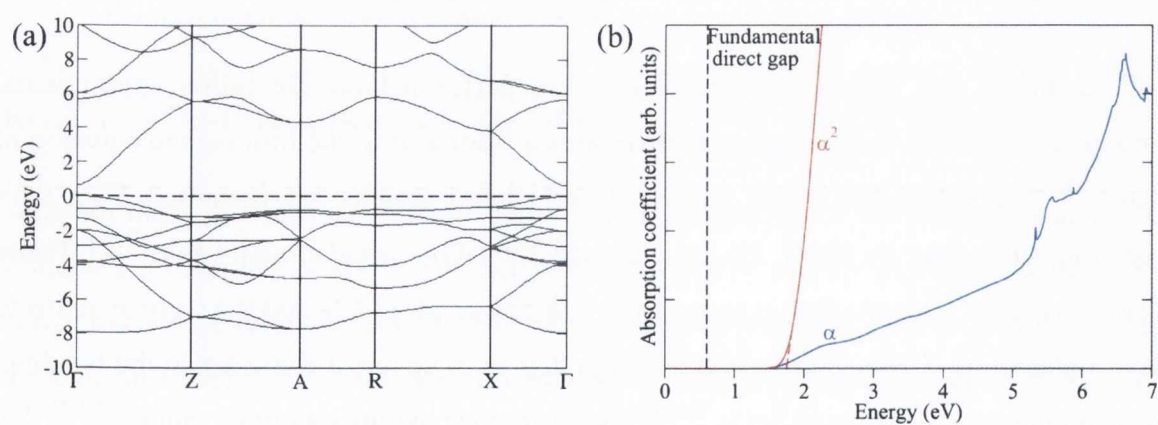


Fig. 3.2 (a) Calculated GGA band structure of SnO<sub>2</sub> with dashed line marking valence band maximum. (b) Calculated GGA optical absorption spectrum of SnO<sub>2</sub>. Black dashed line shows fundamental band gap, blue line shows absorption coefficient ( $\alpha$ ) and red line shows square of absorption coefficient ( $\alpha^2$ ). Red dashed line extrapolates to  $x$ -axis to give calculated optical gap.



Returning to the band structure, a large dispersion in the lowest-lying conduction band at  $\Gamma$  of approximately 5 eV can be observed. This dispersion arises from the interaction between the Sn 5s orbitals with the O 2p orbitals<sup>20, 22</sup> and is an important band structure feature of a good TCO, as it limits optical absorbance in the visible and infrared regions of the spectrum, while providing a light effective electron mass for carrier transport.<sup>19</sup> We have determined the smallest electron effective mass at the CBM of SnO<sub>2</sub> to be 0.16  $m_e$  along the direction  $\Gamma$ -R, while the hole effective mass at the VBM is much larger at 1.29  $m_0$  along the  $\Gamma$ -Z direction. These values compare well to the experimentally-determined electron and hole effective masses of 0.1-0.4  $m_e$ ,<sup>221, 223, 227</sup> and 1.0  $m_0$ <sup>221</sup> respectively.

The electronic density of states (EDOS) of SnO<sub>2</sub> is shown in Fig. 3.3. The atomic projections were calculated with sphere radii of 1.50 Å for Sn and 1.32 Å for O. Our EDOS compare well with previous calculations<sup>207, 209, 216, 219, 228</sup> and photoemission results.<sup>216, 229-230</sup> The valence band (VB) is mainly made up of O 2p states, with small contributions from Sn states. A significant density of Sn 5s states is seen in the valence band between -8 and -6 eV, arising from bonding  $\sigma$  interactions with O 2p states within the Sn-O bonds. Sn 5p states contribute to the VB from -6 to -2 eV resulting from the  $\sigma$ - and  $\pi$  interactions with the O 2p states. In the upper part of the VB from -5 to -1 eV, there is a slight contribution from Sn 4d states due to a small amount of mixing between the Sn 4d states and O 2p states in the lower VB at -21 eV (not shown here). This has been previously reported in other calculations<sup>207, 215</sup> and it was shown by crystal orbital overlap population (COOP) to be due to antibonding Sn 4d - O 2p interactions.<sup>207</sup> The CBM is made up of mainly Sn 5s character, with some Sn 5p, O 2s and O 2p contributions.

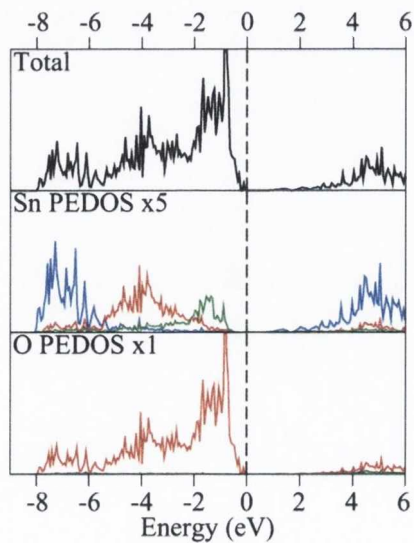


Fig. 3.3 Calculated GGA EDOS/PEDOS of bulk SnO<sub>2</sub>, with dashed line marking valence band maximum. Blue lines represent s states, red are p states and green are d states.



### 3.3.4 Supercell Size Convergence

In order to carry out accurate defect calculations, defect-defect interactions should be minimised. To perform defect calculations, it is thus necessary to test defect energies for convergence with supercell size. Table 3.2 shows the defect formation energies of selected charge neutral defects in  $2 \times 2 \times 2$  (48 atoms),  $3 \times 3 \times 4$  (216 atoms) and  $4 \times 4 \times 5$  (480 atoms) supercells. Due to the high computational cost of performing calculations in the largest 480 atom supercell, calculations were only carried out for the Sn interstitial and Sn vacancy, since Sn is a large cation and is likely to have slow convergence with supercell size.

| Supercell size                                          | $2 \times 2 \times 2$ | $3 \times 3 \times 4$ | $4 \times 4 \times 5$ |
|---------------------------------------------------------|-----------------------|-----------------------|-----------------------|
| No. of atoms                                            | 48                    | 216                   | 480                   |
| $V_O^{\bullet\bullet} + Sn_{Sn}''$                      | 4.53                  | 4.54                  | -                     |
| $Sn_i^{\bullet\bullet\bullet}(\text{oct}) + 2Sn_{Sn}''$ | 6.12                  | 3.73                  | 2.57                  |
| $O_i'' + 2h^\bullet$                                    | 2.51                  | 2.32                  | -                     |
| $V_{Sn}''' + 4h^\bullet$                                | 11.99                 | 12.33                 | 12.54                 |

Table 3.2 Defect formation energies (eV) of selected charge neutral defects in 48, 216 and 480 atom supercells.

Examining the results of the calculations, it is clear that most of the defects in the  $2 \times 2 \times 2$  supercell are not completely converged. The oxygen vacancy is the only one to show good agreement with the  $3 \times 3 \times 4$  supercell, with agreement to within 0.01 eV. The tin interstitial shows the worst energy convergence in going from the 48 atom supercell to the 216 atom supercell with a difference in energy of 2.39 eV between the calculations. This is due to the large amount of lattice strain placed on the system when a large tin ion is placed in an empty interstitial site. Another factor is the highly charged nature of the Sn(IV) cation, which results in a large Coulombic repulsion between it and the surrounding tin ions, extending far from the lattice site. In contrast, the difference in formation energies for the oxygen interstitial is only 0.19 eV, due to the smaller ionic radius and lower charge state of the oxygen anion. Although the Sn(IV) vacancy is highly charged, its energy changes by only 0.34 eV in going from 48 to 216 atom supercells. However, removal of a tin cation causes less lattice strain than the insertion of a tin interstitial, resulting in a smaller supercell needed to model the lattice distortion accurately. Upon placing the tin interstitial into the larger 480 atom supercell, there is still a decrease in energy of 1.16 eV,

indicating that its formation energy in the  $3 \times 3 \times 4$  supercell is still not completely converged. There is also a 0.21 eV difference in energy for the tin vacancy in the 480 and 216 atom supercells, suggesting that large supercells are required to achieve complete convergence for Sn(IV) defects.

Because of the high computational cost of calculations in the 480 atom supercell, we are unable to carry out a complete study of intrinsic defects in this supercell. Although some authors have suggested methods of linearly scaling the energies to the limit of an infinitely-sized supercell, these methods only works for cubic supercells and SnO<sub>2</sub> has a tetragonal unit cell.<sup>160</sup> Another method of correcting for spurious defect-defect interactions is the use of Makov-Payne corrections. These only require calculations to be carried out in a single supercell (preferably the biggest possible) and can then be added to the calculated defect energies as a correction term. However, there are a number of problems with these corrections. Firstly, they were originally designed for use in a cubic cell and secondly they were designed for use in unrelaxed systems. In a recent survey of the corrections available in defect calculations, these came out as one of the worst.<sup>160</sup> The corrected energies were often worse than the raw, uncorrected energies, and frequently went in the wrong direction compared to the answer obtained by linear scaling.<sup>160</sup> Hence, our DFT calculations were carried out in the intermediate  $3 \times 3 \times 4$  supercell with no corrections for defect-defect interactions.

### 3.3.5 Defect Formation Energies

We have considered a series of charge neutral intrinsic defects in SnO<sub>2</sub>. These can be divided into stoichiometric defects, which do not result in a change in stoichiometry and will not therefore generate charge carriers, and non-stoichiometric defects which may contribute to conductivity in SnO<sub>2</sub>. Calculations were performed by placing a number of isolated defects into the supercell in the indicated formal charge states. Tin/oxygen vacancies and interstitials were inserted, with the interstitials being placed in both tetrahedral and octahedral sites. Charge neutral combinations of these defects were then considered, with their formation energies calculated from those of the individual charged defects. Calculations of neutral defect clusters formed by combining the formally charged defects in the same supercell were also performed, so that the binding energy can be obtained from the difference in energy. We include a defect cluster composed of an oxygen vacancy and a tin interstitial ( $\text{Sn}_i + V_{\text{O}}$ )<sup>×</sup>, as this complex was suggested to be the cause of



oxygen deficiency in a previous DFT study.<sup>65</sup> The resulting defect formation energies are listed in Table 3.3, using Kröger-Vink notation to describe the defects. The tabulated defects are those inserted into the system and may relax to give different structures, which will be discussed in more detail later.

| Stoichiometric                            | Isolated | Cluster |          |         |
|-------------------------------------------|----------|---------|----------|---------|
| $V_{Sn}^{''''} + Sn_i^{''''}(\text{oct})$ | 9.59     | -       |          |         |
| $V_{Sn}^{''''} + Sn_i^{''''}(\text{tet})$ | 9.80     | -       |          |         |
| $V_O^{''} + O_i^{''}$                     | 7.00     | 6.48    |          |         |
| $V_{Sn}^{''''} + 2V_O^{''}$               | 11.01    | 6.48    |          |         |
|                                           | O-poor   |         | O-rich   |         |
| Oxygen deficient                          | Isolated | Cluster | Isolated | Cluster |
| $V_O^{''} + Sn_{Sn}^{''}$                 | 2.14     | 1.45    | 5.24     | 4.54    |
| $Sn_i^{''''}(\text{oct}) + 2Sn_{Sn}^{''}$ | 2.85     | 3.93    | 9.04     | 10.12   |
| $Sn_i^{''''}(\text{tet}) + 2Sn_{Sn}^{''}$ | 3.07     | 3.73    | 9.26     | 9.92    |
| $Sn_i^{''}(\text{oct}) + Sn_{Sn}^{''}$    | 2.53     | 3.93    | 8.72     | 10.12   |
| $Sn_i^{''}(\text{tet}) + Sn_{Sn}^{''}$    | 2.84     | 3.73    | 9.03     | 9.92    |
| $(Sn_i(\text{oct}) + V_O)^{\times}$       | -        | 3.70    | -        | 12.98   |
| Oxygen-excess                             | Isolated | Cluster | Isolated | Cluster |
| $V_{Sn}^{''''} + 4h^{\bullet}$            | 14.09    | 12.13   | 7.90     | 5.94    |
| $O_i^{''}(\text{tet}) + 2h^{\bullet}$     | 8.54     | 5.11    | 5.44     | 2.02    |
| $O_i^{''}(\text{oct}) + 2h^{\bullet}$     | 8.54     | 5.41    | 5.44     | 2.32    |

Table 3.3 Defect formation energies of neutral combinations of defects in SnO<sub>2</sub> calculated from isolated defects and defect clusters. O-rich corresponds to a ( $\mu_{Sn}, \mu_O$ ) = (−6.39 eV, 0 eV) and O-poor corresponds to ( $\mu_{Sn}, \mu_O$ ) = (−0.20 eV, −3.09 eV).

The stoichiometric defects all have high formation energies, thus limiting the formation of non-conducting defects. As tin interstitials were inserted into both octahedral and tetrahedral sites, two possible configurations for the cation Frenkel defect ( $V_{Sn}^{''''} + Sn_i^{''''}$ ) resulted, with the octahedral configuration being lower in energy. When the component charged defects are isolated, the anion Frenkel ( $V_O^{''} + O_i^{''}$ ) is the most stable stoichiometric defect. Previous force field calculations performed by Freeman and Catlow<sup>63</sup> resulted in energies of 15.57 eV, 11.08 eV and 19.86 eV for the Schottky ( $V_{Sn}^{''''} + 2V_O^{''}$ ), anion Frenkel



and cation Frenkel defects, respectively. Their calculated energies appear very high compared to our values. However, a later study by Hines *et al.*<sup>213</sup> using an improved potential model calculated energies of 11.32 eV and 7.99 eV for the Schottky and anion Frenkel defects, in better agreement with our results. Clustering the defects reduces their formation energies, with the anion Frenkel and the Schottky defect clusters having identical formation energies. (The formation energy of the  $V_{\text{Sn}}'''' + \text{Sn}_i^{\bullet\bullet\bullet}$  defect cluster is not shown as the interstitial recombined with the vacancy upon relaxation.) However, the formation energies are still high and non-stoichiometric defects are thus likely to dominate the defect structure.

It is found that the most stable non-stoichiometric defect is dependent on the oxygen partial pressure. Under oxygen-poor conditions, defects which cause oxygen excess ( $V_{\text{Sn}}'''' + 4h^\bullet$  and  $\text{O}_i'' + 2h^\bullet$ ) have high formation energies and thus, defects which cause oxygen deficiency will dominate under these conditions. The most stable defect is found to be  $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ . The clustered  $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$  defect is 0.69 eV lower in energy than the equivalent isolated defects, suggesting an enhanced stability when the defects occur in close proximity, arising from attractive Coulomb interactions. This result is in disagreement with the conclusions of Kilic and Zunger,<sup>65</sup> who suggested a tin interstitial dominated mechanism of non-stoichiometry. They concluded that a  $(\text{Sn}_i + V_{\text{O}})^\times$  complex would be responsible for oxygen deficiency in  $\text{SnO}_2$ , due to a high energy of attraction between  $V_{\text{O}}$  and  $\text{Sn}_i$ . However, our results show this defect to be much higher in energy than  $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ . If we examine the other defects involving tin interstitials ( $\text{Sn}_i^{\bullet\bullet\bullet} + 2\text{Sn}_{\text{Sn}}''$  and  $\text{Sn}_i^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ ), it can be seen that they all have higher formation energies than  $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$  and hence, are less likely to form. Although tin interstitial formation may contribute to the overall non-stoichiometry, the dominant mechanism of oxygen deficiency will be oxygen vacancy formation.

Comparing the isolated energies to the clustered calculations shows that for most defects, clustering lowers the energy. However, the tin interstitial combinations show unusual behaviour as the isolated formation energies are lower than the cluster calculations. The geometry of these defects will be examined later to investigate this discrepancy.

Under oxygen-rich conditions, defects which cause oxygen deficiency increase in energy, while defects which cause oxygen excess are lower in energy. The most stable non-stoichiometric defect under these conditions is the  $\text{O}_i'' + 2h^\bullet$  defect cluster. The formation energy of this defect differs, depending on whether the interstitial is inserted into a

tetrahedral or octahedral site, with the tetrahedral defect being lower in energy by 0.30 eV. As the  $O_i''(\text{tet}) + 2h^\bullet$  cluster has a binding energy of -3.43 eV, there is clearly a large stabilisation when the interstitial and the holes are considered together. We will examine the detailed geometry and electronic structure later to investigate the reasons behind this stabilisation. Although the formation energy of  $V_{\text{Sn}}''' + 4h^\bullet$  decreases under oxygen-rich conditions, it is still considerably higher than that of the oxygen interstitial. The reason for this is the high formation energy of the holes. Formation of a hole requires an electron to be removed from the O 2p valence band, which is highly unfavourable energetically due to the high electronegativity of oxygen. As  $V_{\text{Sn}}'''$  is compensated by four oxygen holes in the valence band, its formation energy is high and it is unlikely to form.

### 3.3.6 Electronic Structure of $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$

At low oxygen partial pressure, the most stable defect is  $V_{\text{O}}^{\bullet\bullet}$  charge compensated by the reduction of a Sn(IV) ion to Sn(II) ( $\text{Sn}_{\text{Sn}}''$ ). In the neutral defect cluster ( $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ ), formation of the oxygen vacancy leads to the loss of coordination of three neighbouring tin ions and their relaxation away from the vacancy (two by 0.16 Å and one by 0.19 Å). For the isolated  $V_{\text{O}}^{\bullet\bullet}$ , these tin atoms show a greater relaxation away from the vacancy (two by 0.26 and one by 0.25 Å) due to greater Coulombic repulsion between the tin ions.

The Bader charges for  $V_{\text{O}}^{\bullet\bullet}$ ,  $\text{Sn}_{\text{Sn}}''$  and their defect cluster are shown in Table 3.4.  $\text{Sn}_{\text{Sn}}''$  occurs as a delocalised reduction rather than localising on a single tin atom. This can be seen from the decrease in average tin charge from 2.52e in bulk tin dioxide to 2.50e in the defective supercell. The difference between total Sn charge in bulk  $\text{SnO}_2$  and the defective  $\text{Sn}_{\text{Sn}}''$  system is 1.41e, indicative of a reduction to Sn(II) overall (Bader charge of 1.25e). The average tin charge for  $V_{\text{O}}^{\bullet\bullet}$  is the same as in bulk  $\text{SnO}_2$ , although a slight reduction in charge on the three tin ions neighbouring the vacancy is observed. It is likely that the

|                                                       | <b>Sn<sub>nn</sub></b> | <b>Sn<sub>av</sub></b> | <b>Sn<sub>tot</sub></b> |
|-------------------------------------------------------|------------------------|------------------------|-------------------------|
| <b>bulk</b>                                           | -                      | 2.52                   | 181.49                  |
| <b>Sn<sub>Sn</sub>''</b>                              | -                      | 2.50                   | 180.08                  |
| <b>V<sub>O</sub><sup>••</sup></b>                     | 2 × 2.40, 2.41         | 2.52                   | 181.30                  |
| <b>V<sub>O</sub><sup>••</sup> + Sn<sub>Sn</sub>''</b> | 2 × 2.27, 2.33         | 2.51                   | 180.04                  |

Table 3.4 Bader charges for  $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$  in  $\text{SnO}_2$ .  $\text{Sn}_{\text{nn}}$  are the charges on the nearest neighbour tin ions;  $\text{Sn}_{\text{av}}$  and  $\text{Sn}_{\text{tot}}$  are the average and total Sn charges in each supercell.



change in electron density occurs as a result of the loss in coordination of these tin ions from 6- to 5-fold coordinate. There is a larger loss in charge on these three tin ions for  $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$  compared to the isolated vacancy, accounting for  $0.34e$  of the reduction in total. The remaining excess charge is delocalised over all tin ions in the system, shown by the difference of  $1.26e$  in total tin charge between the isolated vacancy and the combined defect.

The EDOS/PEDOS for both the isolated and clustered defects are shown in Fig. 3.4 with the valence band maximum set to 0 eV. The bottom of the Sn 5s conduction band is occupied by  $2e^-$  for both  $\text{Sn}_{\text{Sn}}''$  and  $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ . The EDOS for  $\text{Sn}_{\text{Sn}}''$  is similar to that of bulk  $\text{SnO}_2$ , except for the occupation of states at the CBM. There are no apparent defect

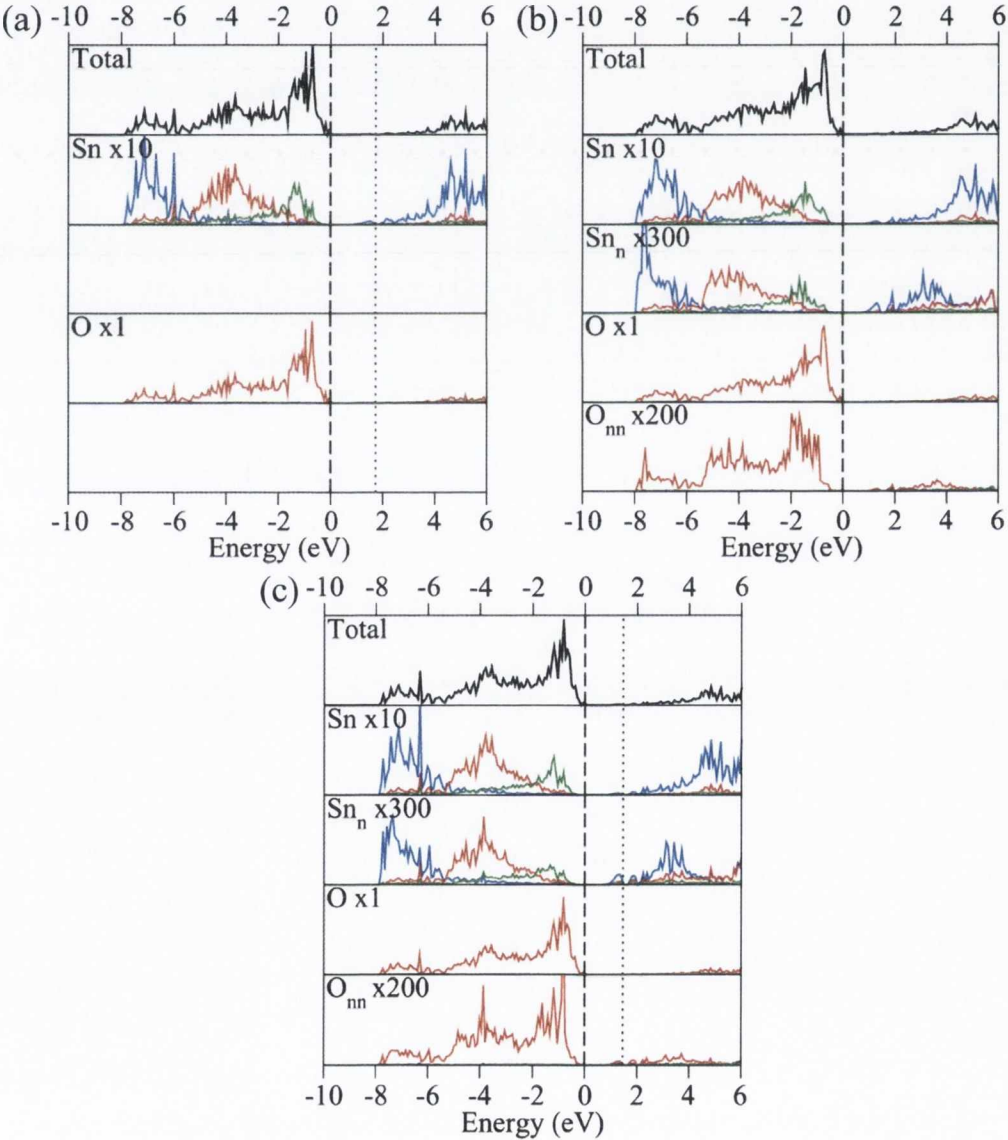


Fig. 3.4 Total and partial EDOS for (a)  $\text{Sn}_{\text{Sn}}''$  (b)  $V_{\text{O}}^{\bullet\bullet}$  (c)  $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$  in  $\text{SnO}_2$ .  $\text{Sn}_n$  and  $\text{O}_{nn}$  are tin and oxygen atoms neighbouring the vacancy. Dashed line indicates VBM and dotted line shows position of highest occupied level. Blue lines are  $s$ , red are  $p$  and green are  $d$  states.



states in its EDOS. However, as the tin reduction is delocalised, this is not unexpected. The EDOS for  $V_O^{\bullet\bullet}$  shows an empty state split off from the CBM by 0.3 eV which is a mixture of Sn 5s character from the tin ions neighbouring the vacancy and of O 2p character from oxygen ions close to the defect. For  $V_O^{\bullet\bullet} + Sn_{Sn}''$ , this state becomes filled by the extra  $2e^-$  from the tin reduction. The location of this defect state agrees qualitatively with experimental evidence, which places donor levels for oxygen vacancies 0.03-0.15 eV below the CBM.<sup>62, 173</sup> Similar states of Sn 5s character have been observed on reduced  $SnO_2$  surfaces by resonant photoemission spectroscopy due to the reduction of Sn(IV) ions neighbouring oxygen vacancies to Sn(II).<sup>230</sup>

Charge density maps for  $V_O^{\bullet\bullet} + Sn_{Sn}''$  are shown in Fig. 3.5. The valence band partial charge density from -10 eV up to the defect state (Fig. 3.5 (a)) shows most of the density to be on the oxygen atoms with some spherical 5s character on Sn atoms, consistent with the low energy s states seen in the EDOS. The Sn atoms surrounding the vacancy show lone pair-like density consistent with the partial reduction indicated by Bader analysis. The charge density difference between the valence band of the defective and non-defective cells (Fig. 3.5 (b)) shows an increase in electron density on the tin ions neighbouring the defect, suggesting a reduction. In addition, a polarisation of the charge on the oxygen ions surrounding the defect can be seen. The charge density for the defect state located 0.3 eV below the CBM in Fig. 3.5 (c) shows the density to be mainly on O ions near the defect with a small amount of lone pair-like density on the neighbouring Sn ions. Similar mixing of Sn 5s with O 2p states has been observed previously for lone pairs in SnO.<sup>169, 217</sup>

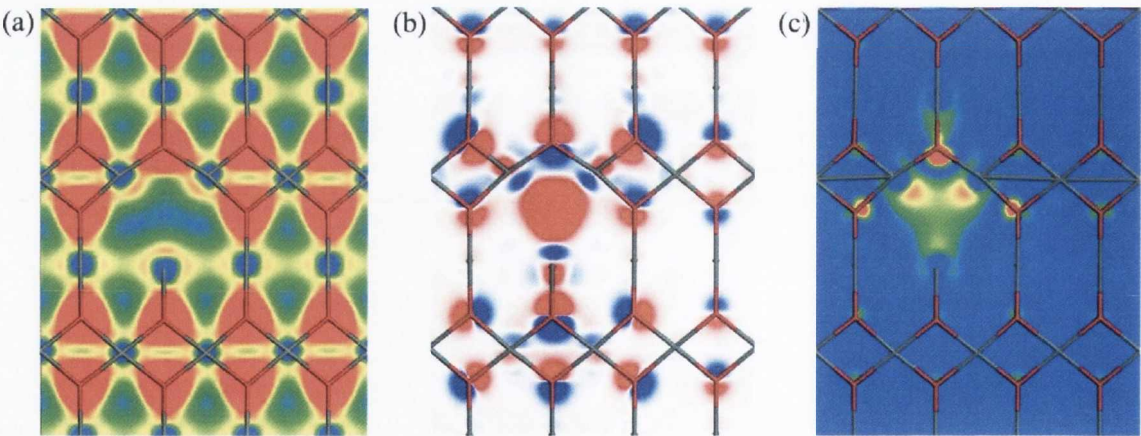


Fig. 3.5 Charge density plots for  $V_O^{\bullet\bullet} + Sn_{Sn}''$  in  $SnO_2$ . (a) Partial charge density between -10 eV and defect state plotted at contour levels from 0 (blue) to 0.3  $e/\text{\AA}^3$  (red). (b) Charge density difference between valence band of bulk and defective cells plotted from -0.1 (red) to 0.1  $e/\text{\AA}^3$  (blue). (c) Partial charge density of defect state at contour levels between 0 (blue) and 0.05  $e/\text{\AA}^3$  (red). Grey atoms are tin and red are oxygen.

### 3.3.7 Electronic Structure of Tin Interstitials

Tin interstitials inserted into both tetrahedral and octahedral sites were found to relax to different equilibrium geometries. Very little deviation in structure was seen between the +2 and +4 charge states. The octahedral interstitials insert into the centre of an oxygen octahedron with two Sn-O bond lengths of 2.00 Å and four of 2.13 Å (Fig. 3.6 (a)). The tin coordination is similar to that of Sn(IV) in bulk SnO<sub>2</sub>, though the bond lengths differ slightly due to the smaller size of the interstitial site compared to the lattice sites. The tetrahedral interstitials both relax to give split interstitial structures, in which the interstitial tin displaces a lattice tin to form two tetrahedral interstitials around a vacant lattice site (Fig. 3.6 (b)). Sn<sub>i</sub><sup>••••</sup>(tet) forms interstitials 3.73 Å apart with Sn-O bond lengths of 2 × 2.02, (O1, O2) 2.05 (O3) and 1.96 Å (O4), whereas Sn<sub>i</sub><sup>••</sup>(tet) forms two tetrahedral interstitials, 3.69 Å apart, with similar Sn-O bond lengths. Although the coordination of the tetrahedral interstitials is similar to that in SnO, the bond lengths are significantly shorter than those calculated for SnO (2.26 Å),<sup>169, 217</sup> suggesting that the interstitials may not be in a +2 charge state.

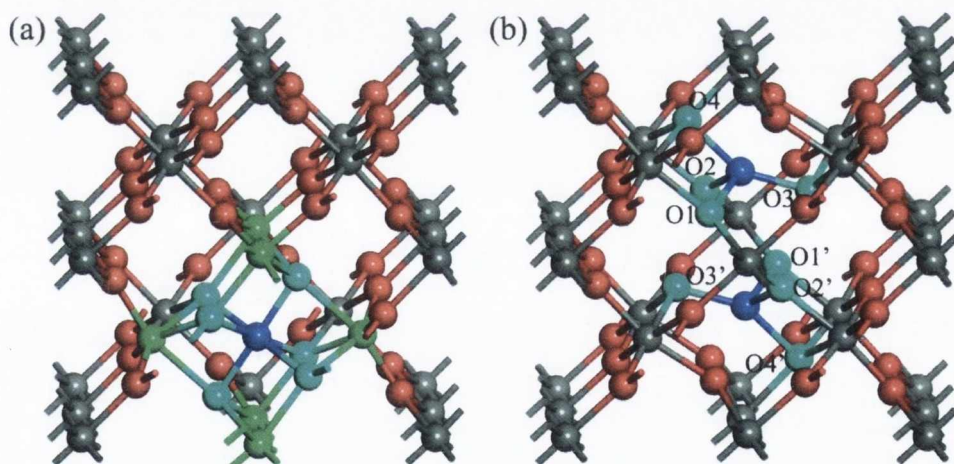


Fig. 3.6 Local structure around tin interstitial defects in SnO<sub>2</sub> showing (a) Sn<sub>i</sub><sup>••••</sup>(oct)/Sn<sub>i</sub><sup>••</sup>(oct) and (b) Sn<sub>i</sub><sup>••••</sup>(tet)/Sn<sub>i</sub><sup>••</sup>(tet). Dark blue atoms are interstitials, light blue are nearest neighbour oxygen and green are nearest neighbour tin.

The Bader charges in Table 3.5 indicate all interstitials to be in the same charge state. Although the charge is lower than that of Sn(IV) in bulk SnO<sub>2</sub>, in no case does it approach that of Sn(II) in SnO (1.25 $e$ ). Given the small change in charge involved, the indication is that these are all Sn(IV) interstitials. This suggests that Sn<sub>i</sub><sup>••••</sup>(oct) is an accurate description of the defect, whereas Sn<sub>i</sub><sup>••••</sup>(tet) in fact relaxes to give 2Sn<sub>i</sub><sup>••••</sup> + V<sub>Sn</sub><sup>••••</sup>. Regarding the inserted Sn(II) interstitials, as the interstitials relax to a +4 charge state, a



charge compensation mechanism must exist so that the overall defect charge is +2. As the average tin charge in the +2 system is lower than that in the +4 system, charge compensation is likely to be achieved by a tin reduction. The difference in total Sn charge between  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{oct})$  and  $\text{Sn}_i^{\bullet\bullet}(\text{oct})$  is  $1.22e$ , indicating an overall reduction of a single tin ion in the +2 system to Sn(II) ( $\text{Sn}_{\text{Sn}}''$ ). Similarly, comparing the total Sn charge for  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{tet})$  and  $\text{Sn}_i^{\bullet\bullet}(\text{tet})$  shows a difference of  $1.16e$ , also suggesting the presence of an overall Sn reduction in the  $\text{Sn}_i^{\bullet\bullet}(\text{tet})$  defect. The octahedral defect shows a slightly greater reduction on the six tin ions neighbouring the interstitial; however, this accounts for a total reduction in charge of only  $0.24e$ . The remaining charge is delocalised over all tin ions in the system.  $\text{Sn}_i^{\bullet\bullet}(\text{tet})$  likewise shows a delocalised reduction. The observed delocalisation is not unexpected as DFT is known to exaggerate the delocalisation of defect states due to the self-interaction error.<sup>135, 231-232</sup> Hence, the inserted  $\text{Sn}_i^{\bullet\bullet}(\text{oct})$  defect relaxes to  $\text{Sn}_i^{\bullet\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ , while the inserted  $\text{Sn}_i^{\bullet\bullet}(\text{tet})$  defect relaxes to  $2\text{Sn}_i^{\bullet\bullet\bullet} + V_{\text{Sn}}''' + \text{Sn}_{\text{Sn}}''$ .

|                                      | Sn <sub>i</sub> | Sn <sub>av</sub> | Sn <sub>tot</sub> |
|--------------------------------------|-----------------|------------------|-------------------|
| SnO <sub>2</sub>                     | -               | 2.52             | 181.49            |
| SnO                                  | -               | 1.25             | -                 |
| Sn <sub>i</sub> <sup>•••</sup> (oct) | 2.35            | 2.52             | 183.74            |
| Sn <sub>i</sub> <sup>••</sup> (oct)  | 2.33            | 2.51             | 182.53            |
| Sn <sub>i</sub> <sup>•••</sup> (tet) | 2.36, 2.34      | 2.52             | 183.81            |
| Sn <sub>i</sub> <sup>••</sup> (tet)  | 2.33, 2.32      | 2.51             | 182.54            |

Table 3.5 Calculated Bader charges (in *e*) for  $\text{Sn}_i^{\bullet\bullet\bullet}$  and  $\text{Sn}_i^{\bullet\bullet}$ , inserted into octahedral and tetrahedral environments in SnO<sub>2</sub>. Sn<sub>av</sub> and Sn<sub>tot</sub> are the average and total Sn charge in each defective supercell.

The structures of the charge neutral defect clusters,  $\text{Sn}_i^{\bullet\bullet\bullet} + 2\text{Sn}_{\text{Sn}}''$  and  $\text{Sn}_i^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ , are shown in Fig. 3.7. As both of these defect clusters have the same number of electrons, both relax to give the same structure; however, different structures are obtained if the interstitial is inserted into an octahedral or tetrahedral site. The octahedral cluster has a similar geometry to that found for the isolated octahedral interstitials above, suggesting it to be in the +4 charge state. The tetrahedral cluster forms two tetrahedrally coordinated tin interstitials with a distance of 2.65 Å between them. This is structurally similar to the tetrahedral interstitials above, except for a shorter Sn-Sn distance, which may be an indication of a change in charge state. The Bader charges for these defect clusters are shown in Table 3.6.  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{oct}) + 2\text{Sn}_{\text{Sn}}''$  has a similar charge to that found for the isolated



interstitials above, indicating that it is most likely  $\text{Sn}_i^{\bullet\bullet\bullet}$  with charge compensation achieved through a four electron delocalised reduction on the tin atoms so that the overall defect is  $\text{Sn}_i^{\bullet\bullet\bullet} + 2\text{Sn}_{\text{Sn}}''$ . However, in the tetrahedral cluster, the two interstitial tin atoms each possess a Bader charge of  $1.87e$ , intermediate between that of Sn(II) ( $1.25e$ ) and that of Sn(IV) ( $2.52e$ ). This indicates that the interstitials may be in an unusual intermediate +3 charge state. Charge compensation is again accomplished through a delocalised tin reduction. This gives rise to the overall defect structure of:  $2\text{Sn}_i^{\bullet\bullet} + V_{\text{Sn}}''' + \text{Sn}_{\text{Sn}}''$  or alternatively treating the two tins as a dimer:  $(\text{Sn}_2)_{\text{Sn}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ .

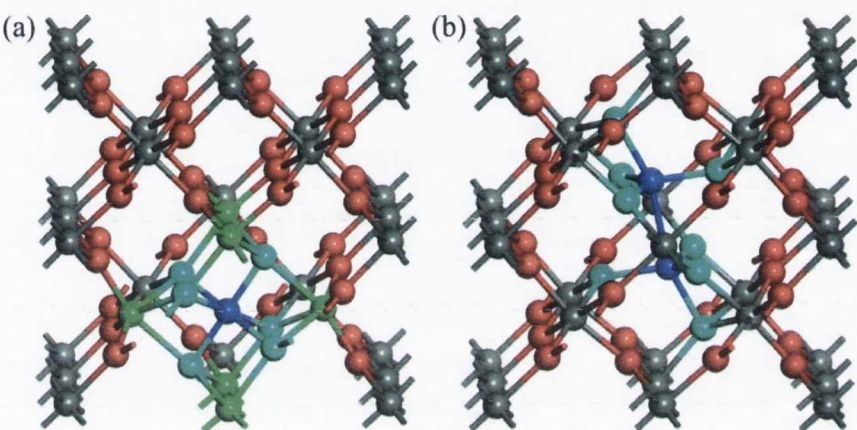


Fig. 3.7 Local structure around tin interstitial defect clusters in  $\text{SnO}_2$  showing (a)  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{oct}) + 2\text{Sn}_{\text{Sn}}'' / \text{Sn}_i^{\bullet\bullet}(\text{oct}) + \text{Sn}_{\text{Sn}}''$  and (b)  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{tet}) + 2\text{Sn}_{\text{Sn}}'' / \text{Sn}_i^{\bullet\bullet}(\text{tet}) + \text{Sn}_{\text{Sn}}''$ . Blue atoms are interstitials, light blue are nearest neighbour oxygen atoms and green are nearest neighbour tin atoms.

|                                                                              | $\text{Sn}_i$   | $\text{Sn}_{\text{av}}$ | $\text{Sn}_{\text{tot}}$ |
|------------------------------------------------------------------------------|-----------------|-------------------------|--------------------------|
| $\text{Sn}_i^{\bullet\bullet\bullet}(\text{oct}) + 2\text{Sn}_{\text{Sn}}''$ | 2.30            | 2.50                    | 181.27                   |
| $\text{Sn}_i^{\bullet\bullet\bullet}(\text{tet}) + 2\text{Sn}_{\text{Sn}}''$ | $2 \times 1.87$ | 2.50                    | 181.46                   |
| $(V_{\text{O}} + \text{Sn}_i)$                                               | 1.75, 1.23      | 2.50                    | 172.67                   |

Table 3.6 Bader charges (in  $e$ ) for tin interstitial clusters in  $\text{SnO}_2$ ;  $\text{Sn}_i$ ,  $\text{Sn}_{\text{av}}$  and  $\text{Sn}_{\text{tot}}$  are the interstitial, average and total tin charges.

The  $(\text{Sn}_i + V_{\text{O}})^{\times}$  cluster suggested by Kilic and Zunger<sup>65</sup> exhibits a geometrically similar structure to that of the isolated tetrahedral interstitials (Fig. 3.8). The interstitial displaces a lattice tin atom to form a split interstitial structure where the inserted tin coordinates to three tin ions, while the displaced tin ion is tetrahedrally coordinated. Two other tin ions have lost coordination due to the creation of an oxygen vacancy. Bader analysis of the  $(\text{Sn}_i + V_{\text{O}})^{\times}$  defect cluster indicates the tetrahedral tin ion to have a charge of  $1.75e$ , while the 3-coordinate tin has a charge of  $1.23e$ . Two other tin ions neighbouring the oxygen

vacancy have lost coordination and have Bader charges of  $2.23e$  each. This suggests that the 3-coordinate tin is in a +2 charge state, while the tetrahedral tin is in a +3 charge state. Charge compensation is achieved through a 3-electron reduction delocalised over the remaining tin atoms, with the 5-fold coordinate tin ions neighbouring the vacancy having a greater tendency to reduce. Hence, the defect is most closely described by:  $\text{Sn}_i^{\bullet\bullet} + \text{Sn}_i^{\bullet\bullet\bullet} + V_{\text{O}}^{\bullet\bullet} + V_{\text{Sn}}^{\bullet\bullet\bullet\bullet} + \text{Sn}_{\text{Sn}}^{\bullet\bullet\bullet}$ .

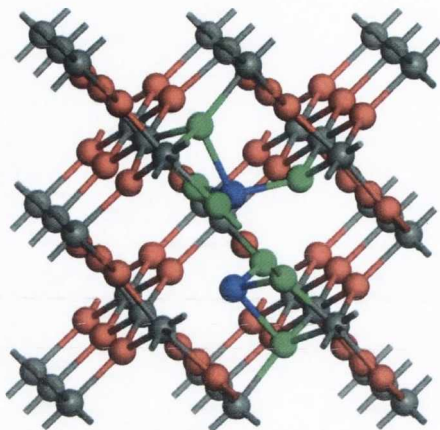


Fig. 3.8 Local structure of the neutral defect cluster of an oxygen vacancy and tin interstitial  $(\text{Sn}_i + V_{\text{O}})^{\times}$  in  $\text{SnO}_2$ . Blue atoms are interstitials and green are nearest neighbour oxygen atoms.

To further clarify the nature of these defects, the EDOS/PEDOS of the defect clusters  $\text{Sn}_i^{\bullet\bullet\bullet\bullet}(\text{oct}) + 2\text{Sn}_{\text{Sn}}^{\bullet\bullet}$ ,  $\text{Sn}_i^{\bullet\bullet\bullet\bullet}(\text{tet}) + \text{Sn}_{\text{Sn}}^{\bullet\bullet}$  and  $(\text{Sn}_i + V_{\text{O}})^{\times}$  are shown in Fig. 3.9. The octahedral defect has a defect state just below the conduction band minimum which is made up of mainly Sn 5s character. The major contributions to this defect state arise from the interstitial itself and the six tin ions surrounding the defect. A larger density of Sn 5s states can be seen at the bottom of the valence band for these tin ions compared to tin ions in the bulk. This is further evidence of the slight reduction of these tin ions seen in the Bader charges. The tetrahedral defect also shows two filled defect states near the bottom of the conduction band. These are more split off from the conduction band than the states of the octahedral interstitial and are a mixture of Sn 5s, 5p and 4d character from the two interstitials. Finally,  $(V_{\text{O}} + \text{Sn}_i)^{\times}$  shows localised defect states bearing similarity to the tetrahedral defect. Sn1, the 3-coordinate tin, has a defect state of mainly Sn 5p character with very little Sn 5s contribution, while Sn2, the 4-coordinate tin, has a state of mixed Sn 5s, 5p and 4d character. The two 5-coordinate tin ions are not shown here but both also contribute Sn 5s density to the defect state.

The charge density of each of the defect states is shown in Fig. 3.10. The octahedral interstitial has a quite delocalised charge density, with slightly greater contributions from



the six tin ions neighbouring the defect. This suggests conduction via a band-like rather than polaronic mechanism. However, the tetrahedral interstitial has a charge density which is very localised, in the region between the two tin interstitials and the octahedra of six oxygens surrounding the defect. Similarly, the defect state for  $(V_O + Sn_i)^\times$  is also very localised between the tin ions and the oxygens surrounding the defect. Thus, both of these defects are likely to be polaronic in nature.

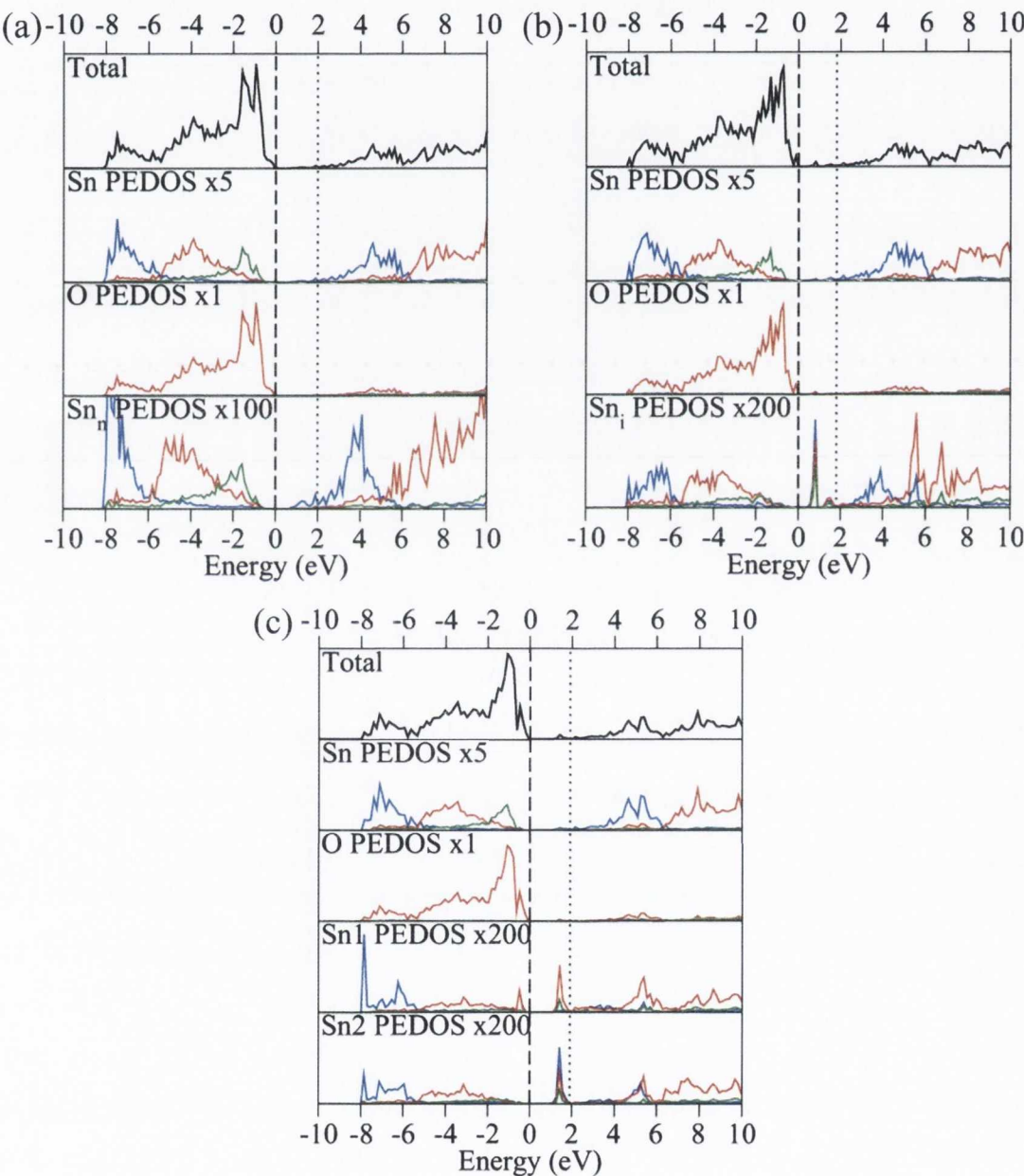


Fig. 3.9 GGA EDOS/PEDOS for tin interstitial defects in  $SnO_2$ . (a)  $Sn_i^{\bullet\bullet\bullet}(\text{oct}) + 2Sn_{Sn}''$  with  $Sn_n$  showing PEDOS of six tin atoms neighbouring the interstitial. (b)  $Sn_i^{\bullet\bullet\bullet}(\text{tet}) + 2Sn_{Sn}''$ . (c)  $(Sn_i + V_O)^\times$  with  $Sn1$  and  $Sn2$  showing PEDOS of 3- and 4-coordinate tin interstitials, respectively. Blue lines are  $s$  states, red are  $p$  states and green are  $d$  states. Dashed line denotes valence band maximum while dotted line illustrates position of highest occupied level.



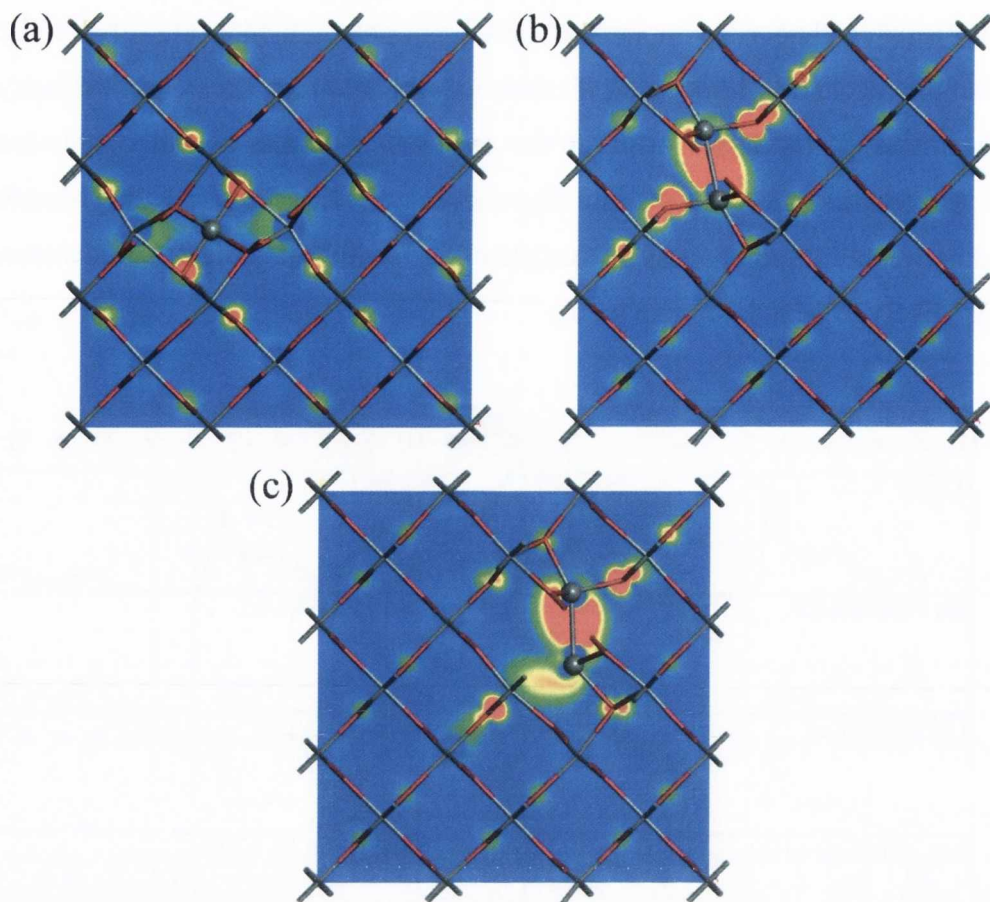


Fig. 3.10 Partial charge densities for defect states of (a)  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{oct}) + 2\text{Sn}_{\text{Sn}}^{''}$ , (b)  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{tet}) + 2\text{Sn}_{\text{Sn}}^{''}$  and (c)  $(V_O + \text{Sn}_i)^{\times}$  in  $\text{SnO}_2$ , all plotted between 0 (blue) and  $0.05 \text{ e}/\text{\AA}^3$  (red). Grey atoms are Sn and red are O.

### 3.3.8 Electronic Structure of $\text{O}_i^{''} + 2h^{\bullet}$

At high oxygen partial pressure, oxygen interstitials have the lowest defect energy and hence, will dominate the defect structure. Isolated  $\text{O}_i^{''}$  defects inserted into tetrahedral and octahedral sites both relaxed to give the same structure, which is the reason for the equal energies observed in Table 3.3. However, instead of the expected  $\text{O}^{2-}$  interstitial ( $\text{O}_i^{''}$ ), the inserted oxygen relaxes towards a lattice oxygen to form a peroxide anion ( $\text{O}_2^{2-}$ ) substituting at a lattice site, similar to that observed in calculations for ZnO.<sup>233</sup> In fact, the peroxide configuration is thought to be the most stable configuration for oxygen interstitials in many different metal oxides.<sup>234</sup> This may also explain the presence of IR and Raman stretching modes associated with Sn-O<sub>2</sub> in thin films.<sup>191</sup> The Bader charges (Table 3.7) show each peroxide oxygen to be in a -1 charge state and the bond length of  $1.51 \text{ \AA}$  is typical of a peroxide ion. The remaining -2 charge results in a tin reduction which is delocalised over all tin atoms, as seen by the  $1.49e$  difference in total Sn charge between the non-defective and defective cells. The inserted  $\text{O}_i^{''}$  thus relaxes to give:  $(\text{O}_2)_O^{\times} + \text{Sn}_{\text{Sn}}^{''}$ .

|                                                      | O-O (Å) | O <sub>i</sub> | Sn <sub>av</sub> | Sn <sub>tot</sub> |
|------------------------------------------------------|---------|----------------|------------------|-------------------|
| O <sub>i</sub> <sup>''</sup>                         | 1.51    | -0.69, -0.70   | 2.50             | 179.99            |
| O <sub>i</sub> <sup>''</sup> (oct) + 2h <sup>•</sup> | 1.49    | -0.71, -0.62   | 2.52             | 181.41            |
| O <sub>i</sub> <sup>''</sup> (tet) + 2h <sup>•</sup> | 1.51    | -0.70, -0.68   | 2.52             | 181.23            |

Table 3.7 Bond lengths and Bader charges for oxygen interstitials in SnO<sub>2</sub>. O<sub>i</sub> is the oxygen interstitial charge, Sn<sub>av</sub> is the average Sn charge and Sn<sub>tot</sub> is the total Sn charge in the defective cell.

The insertion of a O<sub>i</sub><sup>''</sup> + 2h<sup>•</sup> defect cluster also results in the formation of a peroxide ion (O<sub>2</sub>)<sub>O</sub><sup>×</sup>. The apparent high binding energy in Table 3.3 occurs as the isolated formation energy is that of O<sub>i</sub><sup>''</sup> compensated by two oxygen holes. As O<sub>i</sub><sup>''</sup> is actually composed of (O<sub>2</sub>)<sub>O</sub><sup>×</sup> charge compensated by a tin reduction, the tin reduction and the oxygen holes charge annihilate in the defect cluster, resulting in a significantly lower defect energy compared to the isolated defect, with the average Sn charge remaining similar to pure SnO<sub>2</sub>. This illustrates the importance of considering defect structure as well as energetics. Two slightly different structures were obtained, depending on whether the interstitial was inserted into a tetrahedral or octahedral lattice site. The octahedral interstitial relaxed to give the structure shown in Fig. 3.11 (a), in which one peroxide oxygen bonded to two tin atoms with bond lengths of 2.07 Å, while the second bonds to one tin atom with a bond length of 2.03 Å. A lower energy structure was obtained when the interstitial was inserted into a tetrahedral lattice site (Fig. 3.11 (b)). Each peroxide oxygen bonds to two tin atoms with bond lengths of 2.24 Å and 2.06 Å.

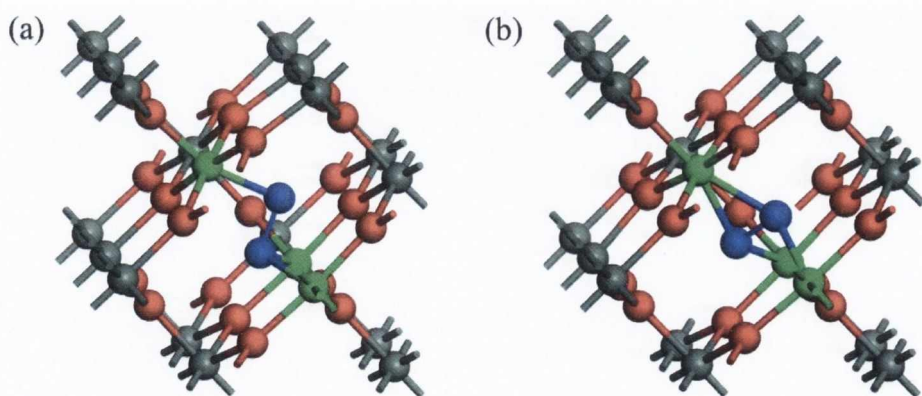


Fig. 3.11 Local structure around O<sub>i</sub><sup>''</sup> + 2h<sup>•</sup> defect clusters in SnO<sub>2</sub>. (a) Structure of interstitial inserted into octahedral site. (b) Structure of interstitial inserted into tetrahedral site. Blue atoms are peroxide ion and green atoms are nearest neighbour Sn atoms.

The EDOS for both O<sub>i</sub><sup>''</sup>(oct) + 2h<sup>•</sup> and O<sub>i</sub><sup>''</sup>(tet) + 2h<sup>•</sup> are shown in Fig. 3.12 with the VBM set to 0 eV. Both structures show an unoccupied state of O 2p character from the



peroxide ion located at 4.9 eV for  $(\text{O}_2)_{\text{O}}^{\times}(\text{oct})$  and 4.4 eV for  $(\text{O}_2)_{\text{O}}^{\times}(\text{tet})$ , which is associated with an empty  $\sigma^*$  level of the peroxide ion. As these states occur deep into the conduction band, *p*-type conductivity through oxygen holes is prohibitive. Both structures show a localised state, occupied by four electrons, at the top of the valence band of O 2*p* character from the peroxide ion. It appears to be more localised in the tetrahedral structure than in the octahedral geometry. The partial charge density for this state (Fig. 3.13) shows it to be associated mainly with the oxygen atoms of the peroxide ion with small contributions from oxygen ions surrounding the defect, suggesting it to be a filled  $\pi^*$  level for the peroxide ion.

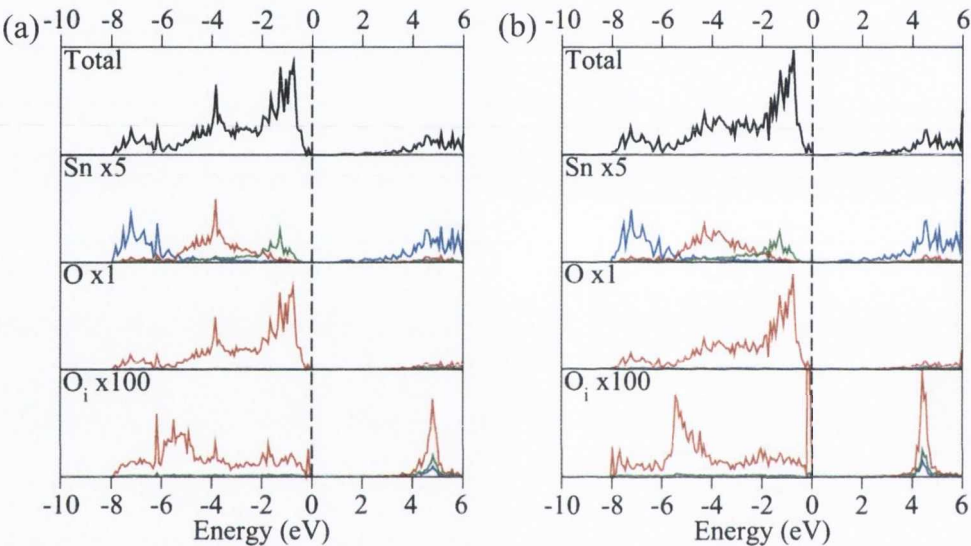


Fig. 3.12 EDOS/PEDOS for (a)  $(\text{O}_2)_{\text{O}}^{\times}(\text{oct})$  and (b)  $(\text{O}_2)_{\text{O}}^{\times}(\text{tet})$  in  $\text{SnO}_2$ . Blue lines are *s* states, red are *p* states and green are *d* states and dashed line marks VBM.

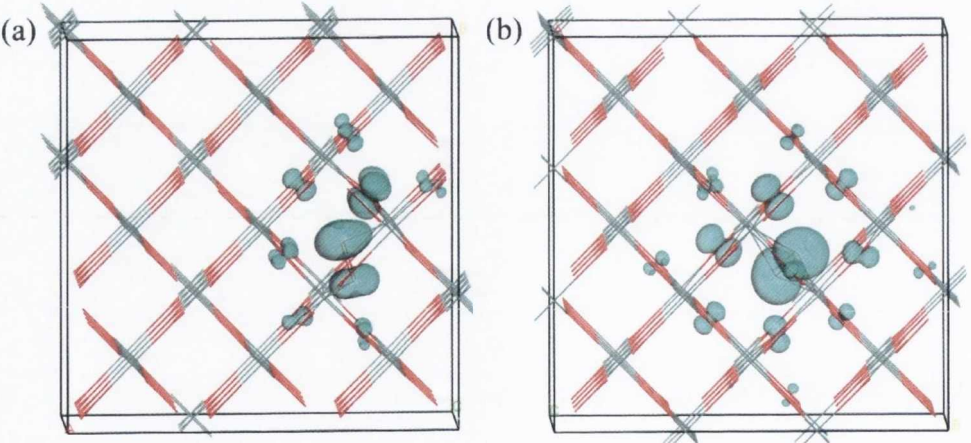


Fig. 3.13 Partial charge density plots of (a) defect state at -0.4 eV for  $(\text{O}_2)_{\text{O}}^{\times}(\text{oct})$  at isosurface level of  $0.05 \text{ e}/\text{\AA}^3$  and (b) defect state at -0.2 eV of  $(\text{O}_2)_{\text{O}}^{\times}(\text{tet})$  at isosurface level of  $0.05 \text{ e}/\text{\AA}^3$ . Grey atoms are tin and red are oxygen.



### 3.3.9 Discussion

Previous DFT studies have focused on defect energetics, with a lack of detailed geometric and electronic structure analysis.<sup>65, 67</sup> From a comprehensive examination of the defect structure we have shown that, in many cases, the inserted defect relaxes to give a completely different defect. For example, tin interstitials inserted into tetrahedral sites relax to give split interstitial structures, while for oxygen interstitials the inserted defect relaxes to give a substitutional peroxide ion. This emphasises the importance of careful consideration of the defect structure as well as the energetics.

Our analysis shows that non-stoichiometric defects are far more likely to occur than stoichiometric defects, which is the reason for the observed non-stoichiometry of  $\text{SnO}_2$ . Oxygen deficiency ( $\text{SnO}_{2-\delta}$ ) occurs due to the presence of  $V_{\text{O}}^{\bullet\bullet}$  with charge compensation via  $\text{Sn}_{\text{Sn}}''$  giving rise to  $n$ -type conductivity. However, varying the oxygen partial pressure will affect the stability of this defect and under extreme oxygen-rich conditions, oxygen-excess ( $\text{SnO}_{2+\delta}$ ) will occur due to the presence of peroxide ions  $(\text{O}_2)_{\text{O}}^{\times}$ . The formation of this defect is unlikely to lead to intrinsic  $p$ -type conductivity as it is charge neutral and does not produce any free hole carriers in the valence band. The existence of peroxide ions has already been proposed in heavily doped  $\text{SnO}_2$  where the introduction of substitutional  $\text{M}^{3+}$  ions leads to the formation of localised oxygen holes.<sup>235</sup> Instead of acting as charge carriers, adjacent holes tend to pair up to form peroxide ions. At high oxygen partial pressure, the only defect that could induce  $p$ -type behaviour is  $V_{\text{Sn}}''' + 4h^{\bullet}$  which has a higher formation energy than  $V_{\text{O}}^{\bullet\bullet}$  so that even under oxygen-rich conditions,  $n$ -type conductivity will dominate. This is the reason why  $p$ -type conductivity in undoped  $\text{SnO}_2$  is difficult to achieve although there have been a few reported instances.<sup>236</sup>

We have shown that the stability of  $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$  is due to the loss in coordination of tin ions neighbouring the vacancy, making them more susceptible to  $\text{Sn(II)}$  reduction. However, we do not observe a highly localised reduction to a single  $\text{Sn(II)}$  species. Instead, we observe a delocalised reduction over all tin ions in the system, with a partial localisation on the three tin ions neighbouring the vacancy. The failure to observe a single  $\text{Sn}^{2+}$  ion may be related to the self-interaction error inherent in DFT.<sup>135</sup> We have observed the existence of single particle levels at the bottom of the conduction band for  $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ . Conductivity is likely to occur through the promotion of electrons from these levels to the conduction band, with the mobility of electrons from  $\text{Sn(II)}$  to  $\text{Sn(IV)}$  sites. We have determined these levels to be

a mixture of Sn 5s and O 2p character from tin and oxygen ions neighbouring the vacancy. The mixing of these states is not unexpected as previous calculations for SnO have observed the mixing of lone pair states for Sn(II).<sup>169, 217</sup>

The severe underestimation of the band gap which is inherent to GGA-DFT calculations can introduce large quantitative errors in the formation energies. Although it is possible to partially correct for these errors through the application of an *a posteriori* correction,<sup>237</sup> we do not follow this route due to the arbitrary nature of the corrections and the serious approximations involved. Instead, we have chosen to carry out further calculations of selected intrinsic defects using hybrid-DFT which should lead to an improved description of the electronic structure.

## 3.4 Intrinsic Defects in SnO<sub>2</sub>: HSE06 Calculations

### 3.4.1 Introduction

Although the DFT calculations outlined above allow us to determine defect stability, the inherent self-interaction error of DFT leads to problems in evaluating the electronic structure. In particular, for  $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ , we cannot be certain if the observed delocalisation of the tin reduction is an artefact of the SIE or an actual delocalised defect. In addition, due to the small size of the calculated band gap (0.6 eV) it is not possible to calculate accurate charge transition levels, which are necessary to determine the deep or shallow nature of the defect states.

The first attempt to study charge transition levels in SnO<sub>2</sub> was the LDA study of Kilic and Zunger.<sup>65</sup> These calculations indicated the donor levels of oxygen vacancies to be located 0.1 eV below the CBM, while tin interstitials were found to have donor levels in the calculated conduction band, suggesting that tin interstitials are fully ionised under all conditions. More recently, attempts have been made to obtain more accurate charge transition levels through DFT+*U* calculations.<sup>238</sup> This approach uses DFT+*U* calculations to partially correct the band gap, following which an extrapolation procedure is used which combines the DFT and DFT+*U* results by fitting to the experimental band gap. This type of *a posteriori* correction has previously been used to examine the positions of charge transition levels for intrinsic defects in SnO<sub>2</sub>.<sup>67</sup> In contrast to the LDA results,<sup>65</sup> oxygen vacancies were found to be the lowest energy defect with tin interstitials having high



formation energies. However, although oxygen vacancies were found to be the dominant cause of oxygen deficiency, their charge transition levels were located deep in the band gap, 1.8 eV below the CBM. This result, combined with the high formation energies of tin interstitials, led the authors to conclude that accidental hydrogen impurities are the origin of shallow donor levels, and the cause of ‘intrinsic’ *n*-type conductivity in SnO<sub>2</sub>.

These DFT and DFT+*U* calculations have, however, been cast into doubt by the most recent work on charge transition levels in SnO<sub>2</sub>.<sup>38</sup> This study investigated oxygen vacancies in SnO<sub>2</sub>, ZnO and In<sub>2</sub>O<sub>3</sub> using the HSE06 and PBE0 hybrid-DFT functionals. These should result in more accurate charge transition levels by producing a more accurate band gap, while also reducing the SIE. The authors found that GGA and LDA calculations, with and without +*U* corrections, resulted in little difference between the position of the charge transition levels for each of the TCOs, with all donor levels occurring deep in the experimental gap. However, when hybrid-DFT calculations were carried out, the oxygen vacancy donor levels shifted towards the conduction band. For SnO<sub>2</sub>, PBE0 placed the donor level 0.5 eV below the CBM, less deep than the 1.8 eV previously calculated.<sup>67</sup> This indicates that despite the many *a posteriori* corrections available, DFT cannot be used to determine charge transition levels in SnO<sub>2</sub> accurately.

### 3.4.2 Methodology

Hybrid-DFT calculations of intrinsic defects in SnO<sub>2</sub> were carried out using the HSE06 functional.<sup>126</sup> Defect calculations employed the 48 atom 2 × 2 × 2 supercell with a 500 eV planewave cut-off and a 2 × 2 × 2 Gamma-centred *k*-point mesh. Hybrid calculations are much more computationally intensive than DFT calculations, and hence the larger 3 × 3 × 4 (216 atoms) supercell used for GGA calculations could not be used.

Calculations of charge transition levels were carried out as outlined in Section 2.5. A defect in charge state *q* has a formation energy given by:

$$E_f(D^q) = E_{tot}(D^q) - E_{tot}(\text{SnO}_2) + \frac{1}{2}n_{\text{O}}E(\text{O}_2) + n_{\text{Sn}}E(\alpha - \text{Sn}) + n_{\text{O}}\mu_{\text{O}} + n_{\text{Sn}}\mu_{\text{Sn}} + qE_F + qE_{VBM} \quad (3.6)$$

The chemical potential limits are set following the procedure outlined in Section 3.3.2. The oxygen-rich limit is set as  $\mu_{\text{O}} \leq 0$  eV and the oxygen-poor limit results from the inequality:  $\mu_{\text{O}} \geq \Delta H_f(\text{SnO}_2) - \Delta H_f(\text{SnO})$ . The formation energy of SnO<sub>2</sub> is calculated to be -5.25 eV



compared to -5.98 eV experimentally,<sup>214</sup> while  $\Delta H_f(\text{SnO})$  is calculated as -2.52 eV, compared to the experimental value of -2.90 eV,<sup>214</sup> resulting in an oxygen-poor limit of  $\mu_{\text{O}} \geq -2.73$  eV. However, at  $\mu_{\text{O}} = -2.73$  eV,  $\mu_{\text{Sn}} = \Delta H_f(\text{SnO}_2) - 2\mu_{\text{O}} = 0.22$  eV which would result in the formation of Sn metal. HSE06 calculations thus suggest that SnO is chemically unstable. Hence, the lower limit on  $\mu_{\text{O}}$  is set by the Sn-rich limit  $\mu_{\text{Sn}} \leq 0$  eV. The overall limit for oxygen-poor conditions is  $(\mu_{\text{Sn}}, \mu_{\text{O}}) = (0 \text{ eV}, -2.63 \text{ eV})$ , while the oxygen-rich limit is defined by  $(\mu_{\text{Sn}}, \mu_{\text{O}}) = (-5.25 \text{ eV}, 0 \text{ eV})$ .

Due to the small size of the supercell and the highly charged nature of the defects, large errors can arise in the calculations due to the interaction between defects in different supercells. For the charged defects, we have thus used the program *sxdefectalign* developed by Freysoldt *et al.*,<sup>239</sup> which includes both a charged defect correction, and a potential correction to align the VBMs between bulk and defective supercells. The evaluation of this correction requires the static dielectric constant of  $\text{SnO}_2$  to be calculated. However, this is not yet possible in VASP using the HSE06 functional and we have thus used the experimentally measured dielectric constants. As the dielectric constants are anisotropic ( $\epsilon_{\parallel} = 9.0$  and  $\epsilon_{\perp} = 14.0$ <sup>240</sup>) we have used an averaged value calculated from  $\frac{1}{3}(\epsilon_{\parallel} + 2\epsilon_{\perp})$ , giving an average dielectric constant of 12.3.

### 3.4.3 Bulk Electronic Structure

The calculated HSE06 bond lengths and lattice parameters are shown in Table 3.8. These show excellent agreement with experiment<sup>59</sup> to within 0.4%. Each Sn is surrounded by four oxygen ions with bond lengths of 2.063 Å and two of 2.062 Å. The calculated HSE06 band structure is shown in Fig. 3.14 (a). It appears very similar to that for the PBE calculations aside from the larger size of the calculated band gap. The HSE06 calculations give a direct band gap at  $\Gamma$  of 2.9 eV. A large dispersion at  $\Gamma$  is again seen, suggesting a low electron effective mass for carrier transport.

To examine the nature of the band gap further, we have calculated the optical absorption spectrum shown in Fig. 3.14 (b). Similar to GGA, the optical transition at the fundamental gap is symmetry forbidden and the lowest energy allowed transition occurs at the  $\Gamma$ -point of the Brillouin Zone, between the second-highest VBM and the CBM. Although absorption begins at 3.6 eV, Fig. 3.14 (b) shows the absorption to be quite weak up until ~4.2 eV. This gives much better agreement with experimental optical gaps of 3.5-4.2 eV

170, 191, 220-224 compared to GGA calculations. We thus conclude that in SnO<sub>2</sub>, the forbidden nature of the fundamental gap results in experimental optical gaps which are 0.7-1.3 eV greater than the direct gap at  $\Gamma$ .

|         | Experimental                     | Calculated (error)               |
|---------|----------------------------------|----------------------------------|
| $a$ (Å) | 4.740                            | 4.761 (+0.4%)                    |
| $c$ (Å) | 3.188                            | 3.195 (+0.2%)                    |
| $u$ (Å) | 0.3063                           | 0.3063 (+0.0%)                   |
| Sn-O(Å) | $4 \times 2.056, 2 \times 2.053$ | $4 \times 2.063, 2 \times 2.061$ |

Table 3.8 Calculated bond lengths and lattice parameters for SnO<sub>2</sub> using HSE06 hybrid-DFT functional compared to their experimental values.<sup>59</sup>

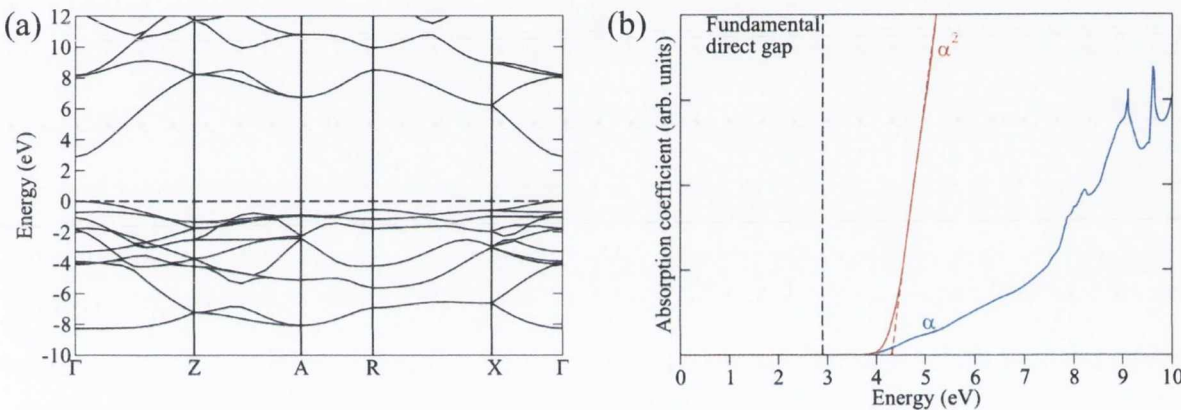


Fig. 3.14 (a) Band structure of SnO<sub>2</sub> as calculated using HSE06 functional with dashed line indicating valence band maximum. (b) Optical absorption spectrum of SnO<sub>2</sub> as calculated using HSE06 with blue line showing absorption coefficient ( $\alpha$ ), red line indicating the square of the optical absorption ( $\alpha^2$ ) and black dashed line denoting position of fundamental band gap. Red dashed line extrapolates  $\alpha^2$  to  $x$ -axis to give optical gap.

The calculated HSE06 density of states is shown in Fig. 3.15 and is similar to that obtained through GGA calculations. The valence band width is slightly wider at 8.3 eV in HSE06 compared with 7.9 eV in GGA. This may be due to the shorter Sn-O bond length in the hybrid-DFT calculations, which results in greater interactions between the Sn  $s/p/d$  and O  $2p$  orbitals giving a wider valence band. The HSE06 calculations result in a CBM made up of mainly Sn  $5s$  states with some mixing of Sn  $5p$ , O  $2s$  and O  $2p$  states. The calculated Bader charges of  $2.63e$  for Sn and  $-1.31e$  for O show greater ionicity than the equivalent GGA charges, showing HSE06 to predict lower covalency compared to GGA. The dominant Sn  $5s$  nature of the conduction band is the origin of the high dispersion, with the delocalised nature of the  $s$  states, likely to result in highly mobile electrons.

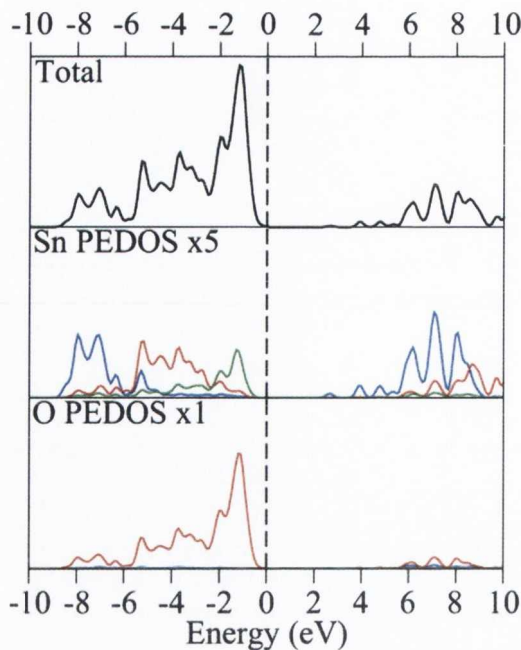


Fig. 3.15 HSE06 EDOS/PEDOS with dashed line marking valence band maximum while blue, red and green lines indicate *s*, *p* and *d* states respectively.

### 3.4.4 Electronic Structure of Intrinsic Defects

To compare the results of the hybrid-DFT calculations directly to those obtained using GGA, we have examined the electronic structure of the intrinsic defects using HSE06. HSE06 results in an improved electronic structure due to the inclusion of a proportion of exact HF exchange. This should result in a better description of defect localisation compared to the GGA calculations. Defect calculations were carried out for oxygen vacancies, oxygen interstitials and tin interstitials. Tin vacancies were not included in the HSE06 calculations since our GGA calculations showed them to be extremely high in energy. The interstitials were again inserted into both tetrahedral and octahedral sites. This resulted in two geometrical configurations for tin interstitials while the oxygen interstitials both relaxed to the same peroxide geometry,  $(\text{O}_2)_\text{O}^\times$ .

#### 3.4.4.1 Oxygen Deficiency: $V_\text{O}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$

Oxygen vacancies are the dominant cause of intrinsic oxygen deficiency in  $\text{SnO}_2$  and the most likely cause of intrinsic *n*-type conductivity. The obtained geometry is similar to that seen in GGA, with the removal of the oxygen resulting in three 5-coordinate tin ions surrounding the vacancy. All three relax inwards, towards the vacancy, with two showing relaxations of 0.05 Å and one of 0.03 Å. These are similar to the observed relaxations in a  $2 \times 2 \times 2$  supercell in GGA calculations.



Fig. 3.16 (a) shows the EDOS/PEDOS for  $V_O^{\bullet\bullet} + Sn_{Sn}''$ . The two extra electrons occupy a defect state in the middle of the band gap, which extends from  $\sim 1$  eV above the VBM to  $\sim 0.5$  eV below the CBM. Thus, while the GGA calculations suggest the state to occur at the bottom of the CBM, the HSE06 calculations result in a state which is deep in the band gap. The defect state has a similar composition to that seen in GGA, resulting from mixed Sn  $5s$ ,  $5p$  and  $5d$  states from the nearest neighbour tin ions combined with a small amount of O  $2p$  character from oxygen ions near the vacancy. In fact, the partial charge density plotted in Fig. 3.16 (b) shows a high degree of similarity with the GGA calculations. The defect electrons localise in the vacancy itself, with the density spreading over the region between the three tin ions.

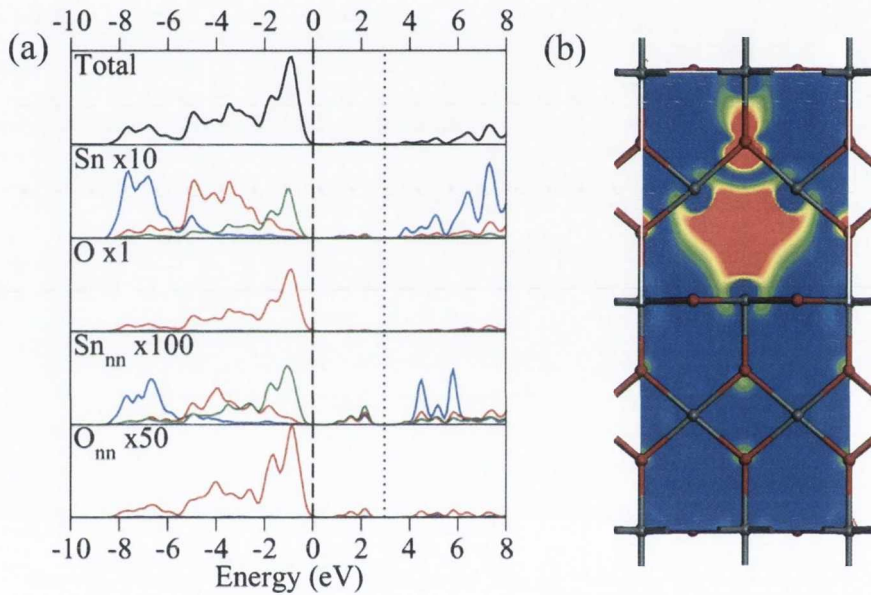


Fig. 3.16 (a) HSE06 EDOS/PEDOS for  $V_O^{\bullet\bullet} + Sn_{Sn}''$  in  $SnO_2$  showing PEDOS for nearest neighbour Sn ( $Sn_{nn}$ ) and nearest neighbour O ( $O_{nn}$ ). Blue lines are  $s$  states, red are  $p$  states and green are  $d$  states. Dashed line indicates VBM and dotted line marks position of highest occupied level. (b) Partial charge density for defect state of  $V_O^{\bullet\bullet} + Sn_{Sn}''$  plotted at between 0 (blue)  $0.05 \text{ e}/\text{\AA}^3$  (red). Grey atoms are Sn and red are O.

To examine the extent of defect localisation, Bader charge analysis of the defective system was performed. For the defect state itself,  $1.00e$  of the charge is distributed over the three nearest neighbour Sn ions, with a further  $0.17e$  on the nearest neighbour oxygen which bridges two of these tin ions. In GGA calculations, only  $0.37e$  was localised on the three tin ions with a further  $0.06e$  on the oxygen. Thus, a much greater defect localisation is observed in the HSE06 calculations compared with GGA. As a measure of the extent to which the three tin ions are reduced, their total Bader charges were calculated, and found to be  $2.19e$ ,  $2.23e$  and  $2.28e$ . This is a greater reduction than that seen for GGA, although, again, none have been reduced to Sn(II) ( $1.35e$ ). If, however, we add up the total electron

gain of these three tin ions compared to the average charge of bulk Sn(IV) ( $2.67e$ ), it sums to  $1.32e$ , which equals the expected change in charge for a tin reduction ( $2.67e - 1.35e = 1.32e$ ). Whereas GGA calculations result in a reduction which is only partially localised near the vacancy, HSE06 results in a tin reduction which is localised on the three nearest neighbour tin ions. This strong localisation suggests that oxygen vacancies in  $\text{SnO}_2$  will conduct via a polaronic hopping mechanism of conductivity.

### 3.4.4.2 Oxygen Excess: $(\text{O}_2)_\text{O}^\times$

Oxygen interstitials, inserted into  $\text{SnO}_2$ , were found to relax to give a peroxide structure  $((\text{O}_2)_\text{O}^\times)$ , similar to that found in GGA calculations. The peroxide bond straddles the lattice oxygen site with a bond length of  $1.45 \text{ \AA}$ . The calculated HSE06 EDOS in Fig. 3.17 (a), shows four distinct peaks at  $-8.8 \text{ eV}$ ,  $-6.1 \text{ eV}$ ,  $-0.5 \text{ eV}$  and  $+7 \text{ eV}$  which arise from the  $\sigma$ ,  $\pi$ ,  $\pi^*$  and  $\sigma^*$  states of the peroxide ion, respectively. The partial charge density of the occupied  $\pi^*$  state is shown in Fig. 3.17 (b) and shows the density to be localised mainly on the peroxide, with a small amount on oxygen ions surrounding the defect. Bader charges indicate 49% of the defect charge to be localised on the peroxide, while the remaining charge is distributed over oxygen ions near the defect. The states introduced by peroxide ions are thus localised and will not be very mobile. The HSE06 calculations thus confirm the results of our GGA calculations, indicating that  $p$ -type conductivity through the introduction of oxygen interstitials is unlikely, due to the formation of charge neutral  $(\text{O}_2)_\text{O}^\times$  defects.

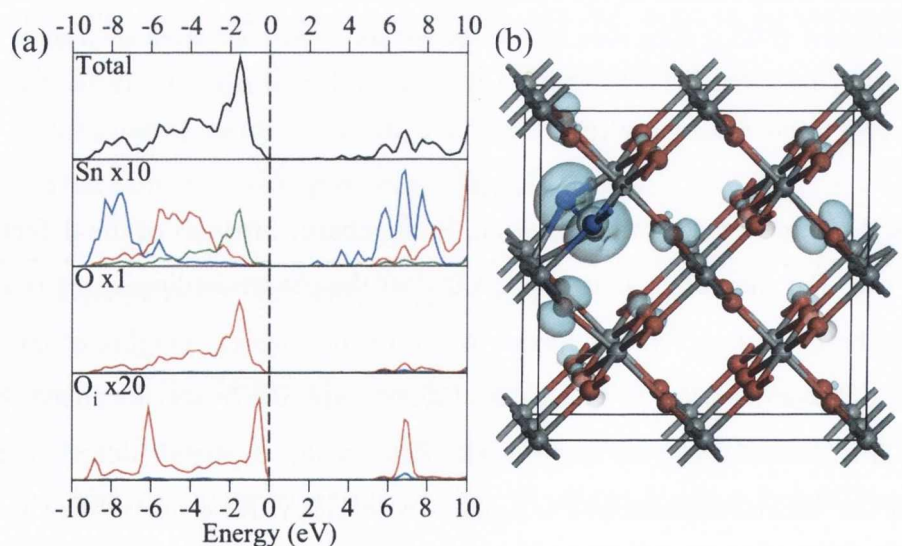


Fig. 3.17 (a) HSE06 EDOS/PEDOS for  $(\text{O}_2)_\text{O}^\times$  in  $\text{SnO}_2$  with dashed line marking VBM, blue lines for  $s$  states, red for  $p$  and green for  $d$  states. (b) Partial charge density of  $\pi^*$  state located  $0.5 \text{ eV}$  below VBM, plotted at isosurface of  $0.05 \text{ e/\AA}^3$ . Grey atoms are Sn and red are O.



### 3.4.4.3 Tin Interstitials

Using HSE06, the tin interstitials relax to the geometries illustrated in Fig. 3.18. At first appearance, both octahedral and tetrahedral interstitials appear to have similar structures to those found in GGA. However, HSE06 results in a greater distortion in the octahedral structure compared to GGA. The interstitial is displaced from the centre of the octahedral site towards O5 and O6, resulting in  $\text{Sn}_i\text{-O}$  bond lengths of 2.10/2.08 Å for O1/O2, 2.69/2.40 Å for O3/O4 and 2.09/2.15 Å for O5/O6. The  $\text{Sn}_i\text{-O3}$  and  $\text{Sn}_i\text{-O4}$  bond lengths are considerably longer than the 2.06 Å bulk  $\text{Sn-O}$  bond length. This differs significantly from the symmetric structure obtained using GGA, and suggests that the interstitial may be in a different charge state. The HSE06 geometry of  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{tet}) + \text{Sn}_{\text{Sn}}''$  is similar to the GGA structure, forming a split interstitial structure  $((\text{Sn}_2)_{\text{Sn}})$ , with the tin ions 2.55 Å apart (Fig. 3.18 (b)). Each tin has distorted tetrahedral coordination with three oxygen ions (O1, O2, O3) in a trigonal planar geometry with bond lengths of 1.95 Å ( $\text{Sn-O1}$ ) and 2.00 Å (O2, O3) while O4 has a longer bond length of 1.10 Å.

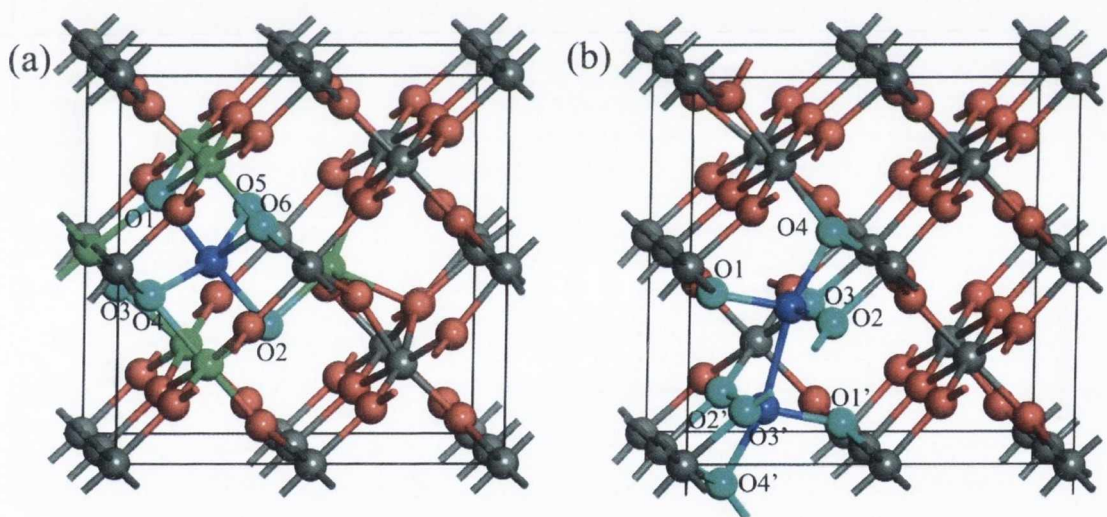


Fig. 3.18 HSE06 geometries of (a)  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{oct}) + 2\text{Sn}_{\text{Sn}}''$  and (b)  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{tet}) + 2\text{Sn}_{\text{Sn}}''$  in  $\text{SnO}_2$ . Dark blue atoms are interstitials, light blue are nearest neighbour oxygen and green are nearest neighbour tin atoms.

Fig. 3.19 displays the EDOS/PEDOS of both  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{oct}) + \text{Sn}_{\text{Sn}}''$  and  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{tet}) + \text{Sn}_{\text{Sn}}''$ . In both cases, two electrons occupy a localised state located 2.0 eV above the VBM, while the remaining two electrons occupy states at the bottom of the conduction band. For  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{oct}) + \text{Sn}_{\text{Sn}}''$ , the 2 eV defect state is of mixed Sn 5s and 5p character from the interstitial, while for  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{tet}) + \text{Sn}_{\text{Sn}}''$  there is a significant contribution from Sn 4d states as well as 5s/5p states. To further probe the nature of the defect states, Fig. 3.20 shows the partial charge density for the defect states of  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{oct}) + \text{Sn}_{\text{Sn}}''$ . The lower energy state is



localised mainly on the interstitial and one neighbouring tin ion, with some density spreading onto nearest neighbour oxygen atoms. The conduction band state is quite delocalised over many of the oxygen and tin atoms in the system. This is suggestive of a more band-like model of conductivity. For  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{tet}) + \text{Sn}_{\text{Sn}}''$ , the lower energy state (Fig. 3.21 (a)) is localised on the tin dimer with some density spreading onto the six oxygen ions closest to the defect, while the higher energy state (Fig. 3.21 (b)) is partially localised on the Sn-Sn bond, with the remainder delocalised over all Sn and O ions in the system. This delocalisation again suggests that tin interstitials will conduct via a band-like mechanism.

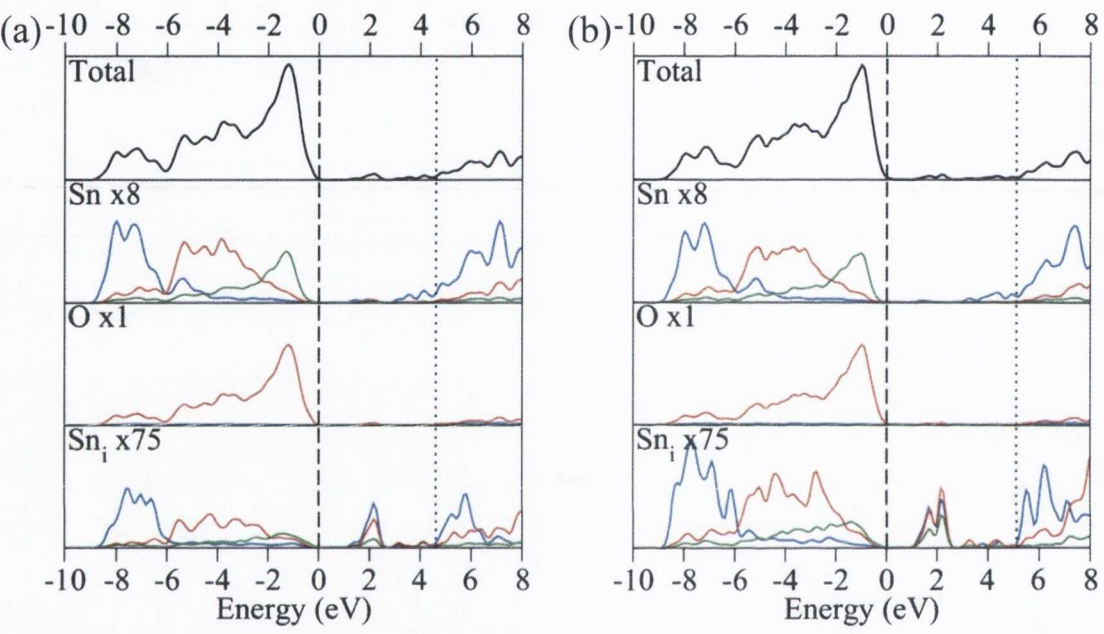


Fig. 3.19 The HSE06 EDOS/PEDOS for (a)  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{oct}) + 2\text{Sn}_{\text{Sn}}''$  and (b)  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{tet}) + 2\text{Sn}_{\text{Sn}}''$  in  $\text{SnO}_2$ . Dashed line marks VBM and dotted line indicates position of highest occupied level. Blue, red and green lines are *s*, *p* and *d* states respectively.

Bader charges for the  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{oct}) + \text{Sn}_{\text{Sn}}''$  defect show the interstitial to have a charge of  $1.78e$ , suggesting a partial reduction from the bulk Sn(IV) charge of  $2.67e$ . The six other tin ions nearest neighbour to the defect have also been slightly reduced to charges between  $2.17e$  and  $2.58e$ . The total Sn reduction for  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{oct}) + 2\text{Sn}_{\text{Sn}}''$  is  $2.70e$ , which is similar to the reduction expected for the formation of two Sn(II) ions of  $2.64e$ .  $2.15e$  of this reduction is localised on the interstitial and its six nearest neighbour tin ions, with the interstitial having a  $0.89e$  reduction. This suggests the interstitial to be close to a +2 charge state, giving a defect structure similar to  $\text{Sn}_i^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ , differing from the GGA electronic structure in which the interstitial is in a +4 charge state. For  $\text{Sn}_i^{\bullet\bullet\bullet}(\text{tet}) + 2\text{Sn}_{\text{Sn}}''$ , Bader charge analysis shows each interstitial to have a charge of  $1.95e$ , intermediate between that of Sn(II) and that of Sn(IV). This confirms the results of GGA, suggesting the interstitials

to be in an intermediate +3 charge state. The structure is thus the same as GGA, and can be described by:  $(\text{Sn}_2)_{\text{Sn}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ .

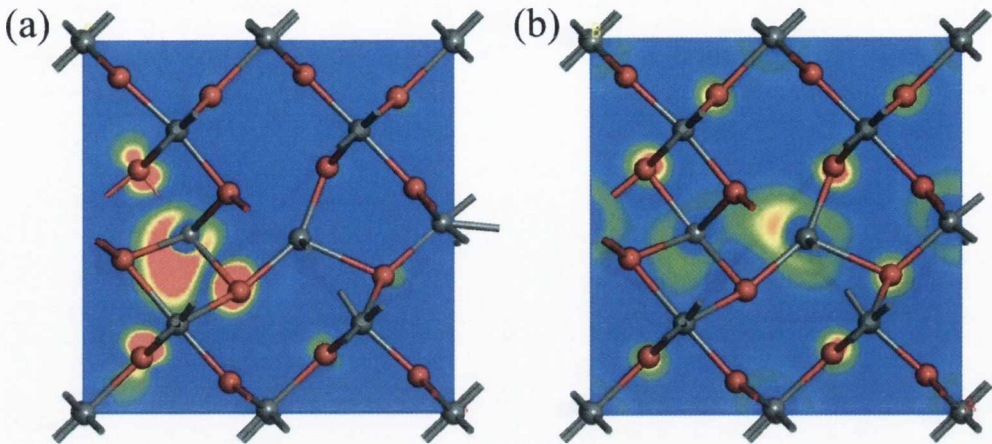


Fig. 3.20 HSE06 partial charge densities for  $\text{Sn}_i^{***}(\text{oct}) + 2\text{Sn}_{\text{Sn}}''$  in  $\text{SnO}_2$ , showing (a) defect state 2 eV above VBM and (b) partial charge density from 2.5 eV to CBM. Both are plotted at between 0 (blue) and  $0.05 \text{ e}/\text{\AA}^3$  (red). Grey atoms are Sn and red are O.

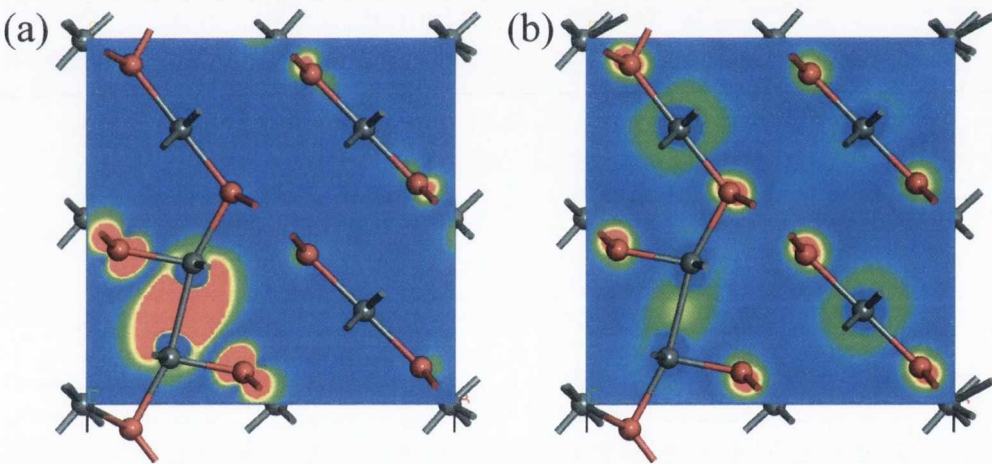


Fig. 3.21 The calculated HSE06 partial charge densities for  $\text{Sn}_i^{***}(\text{tet}) + \text{Sn}_{\text{Sn}}''$  in  $\text{SnO}_2$ . (a) Band gap state located 2 eV above VBM. (b) Partial charge density from 2.5 eV to CBM. Both are plotted between 0 (blue) and  $0.05 \text{ e}/\text{\AA}^3$  (red). Grey atoms are Sn and red are O.

### 3.4.5 Charged Defect Transition Levels

Fig. 3.22 shows the formation energies of charged defects in  $\text{SnO}_2$  plotted against the Fermi energy. The charge transition levels are marked by solid dots. Oxygen-poor conditions favour tin interstitials and oxygen vacancies, while oxygen interstitials are higher in energy. The relative stability of tin interstitials and oxygen vacancies is Fermi-level dependent. Below  $E_F = 1.3 \text{ eV}$ ,  $\text{Sn}_i$  is the most stable defect, while above this energy, oxygen vacancies will dominate the defect structure. As  $n$ -type doping conditions



correspond to Fermi energies close to the CBM, this suggests that oxygen vacancies are the majority *n*-type defect. When the chemical conditions shift to an extreme oxygen-rich environment, both oxygen vacancies and tin interstitials are raised in energy, while the formation energy of oxygen interstitials decreases. Tin interstitials are high in energy over the entire range of  $E_F$ , while oxygen vacancies are the most stable defect below  $E_F = 1.6$  eV. The Fermi level plot thus suggests that  $V_O^{\bullet\bullet}$  will dominate the defect structure at *p*-type conditions (low  $E_F$ ), while  $(O_2)_O^\times$  will dominate above  $E_F = 1.6$  eV (*n*-type conditions). As concluded by the GGA calculations, *p*-type conduction is thus extremely difficult to achieve in undoped  $\text{SnO}_2$ .

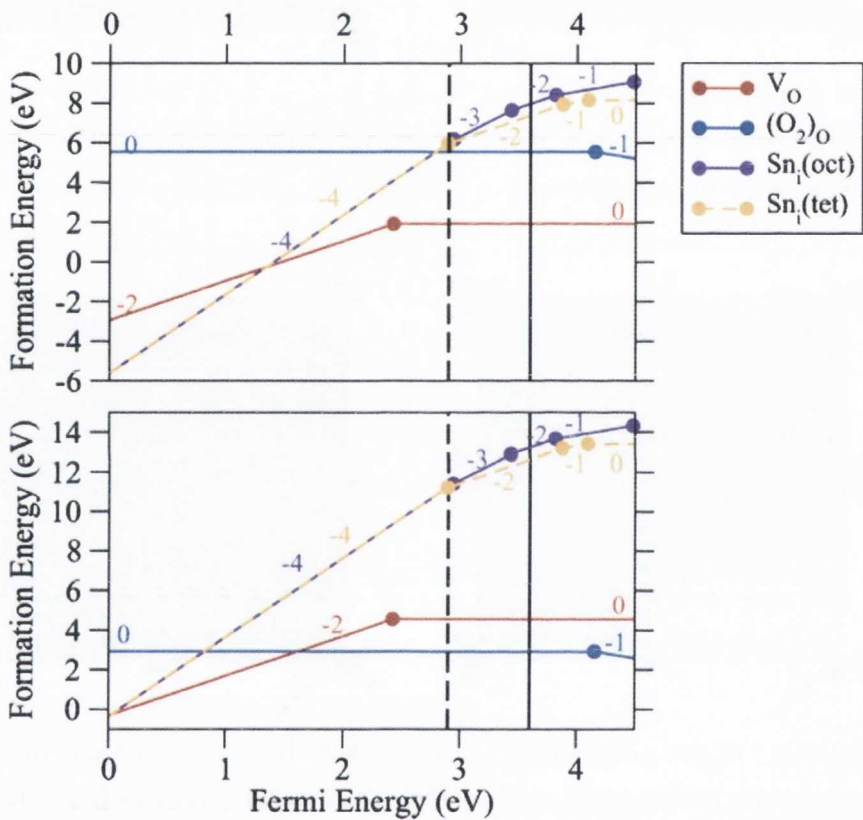


Fig. 3.22 Plot of defect formation energies against Fermi energy for charged defects in  $\text{SnO}_2$ . The top panel shows the formation energies under extreme oxygen-poor conditions ( $\mu_{\text{Sn}} = 0, \mu_{\text{O}} = -2.63$  eV) while the lower panel shows formation energies at oxygen-rich conditions ( $\mu_{\text{Sn}} = -5.25, \mu_{\text{O}} = 0$ ). The calculated band gap is marked by a dashed black line while the experimental band gap of 3.6 eV is indicated by the solid black line. Solid dots indicate the positions of charge transition levels.

Whether a defect results in high levels of conductivity or not is dependent on the position of its charge transition level in the band gap. Table 3.9 lists the positions of the charge transition levels of each defect relative to the CBM. Good *p*-type defects should have transition levels close to the VBM, while high levels of *n*-type conductivity require the levels to be near the CBM.  $V_O$  is found to have a deep (+2/0) transition level, located 0.5



eV below the calculated CBM. This suggests that experimentally observed shallow donor levels 0.03-0.15 eV below the CBM<sup>62, 66, 172</sup> do not result from oxygen vacancy formation. Oxygen vacancies require the temperature to be raised to achieve high levels of *n*-type conductivity and may be responsible for the higher donor activation energies of 0.1-0.4 eV, observed in conductivity studies.<sup>171, 190-192</sup> In comparison, all donor levels for tin interstitials were found to be shallow, indicating that all Sn<sub>i</sub> defects will be fully ionised at room temperature. However, due to the high formation energies of tin interstitials, they are unlikely to be the majority cause of shallow donor levels and *n*-type conduction in tin dioxide. The shallow observed donor levels must result from the presence of impurities such as hydrogen as suggested previously.<sup>67</sup> Hence, we conclude that *intrinsic n*-type conduction in SnO<sub>2</sub> arises from the deep donor levels of oxygen vacancies. *P*-type conductivity in SnO<sub>2</sub> is very unlikely to occur, as the transition levels for (O<sub>2</sub>)<sub>O</sub> are located in the conduction band. It is thus unsurprising that *p*-type SnO<sub>2</sub> is very difficult to obtain.

| V <sub>O</sub> |       | (O <sub>2</sub> ) <sub>O</sub> |       | Sn <sub>i</sub> (oct) |       | Sn <sub>i</sub> (tet) |       |
|----------------|-------|--------------------------------|-------|-----------------------|-------|-----------------------|-------|
| (+/2/0)        | -0.46 | (0/-1)                         | +1.27 | (+4/+3)               | +0.05 | (+4/+2)               | 0.00  |
|                |       | (-1/-2)                        | +2.07 | (+3/+2)               | +0.55 | (+2/+1)               | +0.99 |
|                |       |                                |       | (+2/+1)               | +0.93 | (+1/0)                | +1.21 |
|                |       |                                |       | (+1/0)                | +1.59 |                       |       |

Table 3.9 Location of charge transition levels (*q/q'*) relative to the CBM (in eV) for the intrinsic defects of SnO<sub>2</sub> as calculated using HSE06. The calculated band gap is 2.9 eV.

### 3.4.6 Discussion

We have successfully employed the HSE06 hybrid-DFT functional to model the intrinsic defects of SnO<sub>2</sub>, thereby providing an improved electronic structure compared to that obtained using conventional DFT-GGA methodology. For bulk SnO<sub>2</sub>, hybrid-DFT calculations resulted in lattice parameters which are in excellent agreement with experiment, as well as an optical gap of ~4.2 eV, well within the range of experimental optical gaps between 3.4 eV and 4.3 eV.<sup>191, 220-224</sup>

For most defects, the obtained HSE06 defect electronic structures were similar to those from GGA, except for a higher degree of charge localisation in the hybrid-DFT calculations. The HSE06 defect state of V<sub>O</sub><sup>••</sup> + Sn<sub>Sn</sub><sup>''</sup> had a similar partial charge density to GGA, but with a greater percentage of the density localised on the three Sn atoms nearest

neighbour to the vacancy. While HSE06 calculations localised 50% of the defect charge on these tin ions, only 18% was localised in GGA. The fact that oxygen vacancies do not have completely localised defect states may be the reason for the high conductivity of oxygen deficient  $\text{SnO}_2$ . A previous LDA study of the electronic structure of oxygen vacancies in the TCOs  $\text{In}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\text{Ga}_2\text{O}_3$  <sup>30</sup> found that the material with the greatest charge delocalisation ( $\text{In}_2\text{O}_3$ ) also possessed the highest conductivity. The greater localisation present in HSE06 is also observed when the tin reduction  $\text{Sn}_{\text{Sn}}''$  is considered. While GGA calculations predicted a reduction which was delocalised over all the Sn atoms in the system, with only  $0.34e$  localised over the three neighbouring Sn cations, the results of HSE06 show the reduction to be localised on the three Sn nearest neighbours. This result demonstrates the improved nature of the hybrid-DFT calculations in giving a more accurate description of the defect electronic structure. The localised nature of the oxygen vacancy state suggests that intrinsic *n*-type conduction will occur via a polaronic, rather than a band-like mechanism, thus explaining the experimental observation of variable range hopping conduction in  $\text{SnO}_2$ . <sup>183-187</sup>

While tetrahedral tin interstitials ( $\text{Sn}_{\text{i}}^{\bullet\bullet\bullet\bullet}(\text{tet}) + \text{Sn}_{\text{Sn}}''$ ) possessed defect structures similar to that seen in GGA, the HSE06 calculations predicted an alternative geometry for the octahedral interstitial ( $\text{Sn}_{\text{i}}^{\bullet\bullet\bullet\bullet}(\text{oct}) + \text{Sn}_{\text{Sn}}''$ ). Rather than occurring with symmetric octahedral coordination, similar to  $\text{Sn(IV)}$  in bulk  $\text{SnO}_2$ , the octahedral interstitial was displaced from the centre of the site, resulting in an asymmetric environment with two longer Sn-O bond lengths and four shorter ones. Further analysis indicated the defect structure to be similar to  $\text{Sn}_{\text{i}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ , in contrast to the GGA structure ( $\text{Sn}_{\text{i}}^{\bullet\bullet\bullet\bullet} + 2\text{Sn}_{\text{Sn}}''$ ). Thus, while GGA calculations result in four highly mobile electrons, the HSE06 calculations give two localised electrons trapped on  $\text{Sn(II)}$  and two electrons which delocalise over the system. This difference is likely to arise from the inclusion of a proportion of exact HF exchange in the hybrid-DFT calculations, thereby resulting in increased localisation.

Analysis of the Fermi level plot obtained using HSE06 demonstrated that oxygen vacancies are the lowest energy defect under oxygen-poor conditions, while oxygen interstitials were determined to be lowest in energy in an oxygen-rich environment, in good agreement with the conclusions of our GGA study. *P*-type conductivity through peroxide ions was found to be prohibitive due to the placement of the charge transition levels in the conduction band, confirming that intrinsic *p*-type conduction in  $\text{SnO}_2$  is not favoured. Yet,



the calculations placed the donor levels of oxygen vacancies 0.5 eV below the calculated CBM, rather than resulting in shallow donor levels as previously assumed.<sup>62, 66</sup> A similar placement of the donor levels of oxygen vacancies has been previously seen in PBE0 calculations,<sup>38</sup> while there have also been several experimental reports of levels located 0.30-0.69 eV below the conduction band in deep level transient spectroscopy<sup>241</sup> and admittance spectroscopy.<sup>242-243</sup> Although tin interstitials do act as shallow donors, their formation energies are too high to be the majority cause of conductivity. We can thus conclude from the energetics that oxygen vacancies are the cause of *intrinsic* *n*-type conductivity. It has previously been suggested that hydrogen impurities, accidentally incorporated into thin films, may be responsible for the shallow observed donor levels in tin dioxide.<sup>67</sup> To investigate this possibility, we will investigate their electronic structure in the next section, as well as examining the origins behind extrinsic conductivity in SnO<sub>2</sub>.

## 3.5 The Extrinsic Defects of SnO<sub>2</sub>: HSE06 Calculations

### 3.5.1 Introduction

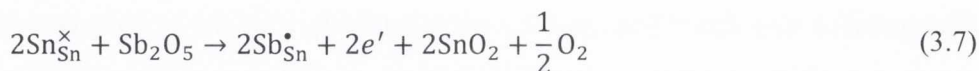
Although SnO<sub>2</sub> has high intrinsic conductivities of  $\sim 10^{-3} \Omega \text{ cm}$ , improvement of the conductivity to  $\sim 10^{-4} \Omega \text{ cm}$  is necessary for its use in optoelectronic applications. These high levels of conduction can be achieved by the addition of dopant ions to tin dioxide. Substitutional doping can take place at either the tin site or the oxygen site. Suitable cation dopants should have an oxidation state of +5, one higher than that of Sn(IV), thereby providing one excess electron for *n*-type conduction. Alternatively, anion doping can be carried out by replacing oxygen with an anion of charge state -1. Most commonly, Sb is used as a cationic dopant,<sup>185, 244-245</sup> while anionic doping is performed using F.<sup>246-248</sup> The reasons why these are the most suitable dopants for SnO<sub>2</sub> are not completely understood. For cationic doping, any of the Group 15 or Group 5 metals would appear to be suitable, while anionic doping could, in theory, be performed with one of the other halogens. In fact, there have been few experimental or theoretical investigations examining the structural and electronic differences between different cationic or anionic dopants.

The first report of transparent conductivity in antimony tin oxide (ATO) was in 1972 when thin films with 98% transparency and resistivities of  $6 \times 10^{-3} \Omega \text{ cm}$  were made.<sup>249</sup> Since

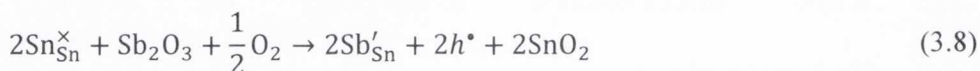


then, the resistivity of ATO has been improved to levels of  $\sim 6 \times 10^{-4} \Omega \text{ cm}$ .<sup>250</sup> ATO is known to conduct via a band mechanism in which the excess electrons introduced by Sb(V) dopants are excited into the bottom of the conduction band.<sup>251-252</sup> Low conduction activation energies of  $\sim 0.01-0.035 \text{ eV}$ <sup>172, 182</sup> indicate that donor levels are very shallow. Thus ATO does not result in band gap peaks in XPS and UPS.<sup>253-254</sup>

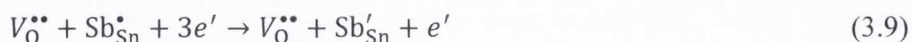
Like all Group 15 cations, Sb has variable valence and can have a charge of either +5 or +3. Substitution of Sb(V) at lattice Sn(IV) sites results in one excess electron for *n*-type conductivity via the defect reaction:



However, substitution of Sb(III) leads to a single excess hole and thus *p*-type conductivity, through the defect reaction:



*N*-type conductivity in ATO will thus only occur when the concentration of Sb(V) exceeds that of Sb(III). Although both oxidation states have been observed in ATO, through Mössbauer spectroscopy<sup>255-257</sup> and X-ray photoemission spectroscopy,<sup>258</sup> it is thought that Sb(III) generally segregates at the surface, while the majority of bulk Sb dopants occur in the +5 oxidation state and act as donors.<sup>254-255, 259</sup> Extended x-ray absorption fine structure (EXAFS) investigations into the doping sites of Sb in SnO<sub>2</sub> have shown that the nearest neighbour distances for Sb-O are generally slightly smaller than Sn-O distances.<sup>259-260</sup> This is consistent with the dominance of Sb(V), which has a smaller ionic radius of 0.74 Å compared to Sn(IV) (0.83 Å) and Sb(III) (0.90 Å).<sup>261</sup> However, it is thought that at higher doping concentrations, Sb(III) cations form, resulting in decreases in conductivity above a dopant concentration of  $\sim 10-15\%$ ,<sup>190, 258, 260, 262-263</sup> and even causing *p*-type conductivity under certain conditions.<sup>264</sup> One possible mechanism for their formation is the clustering of Sb cations with intrinsic oxygen vacancies via the mechanism:



Whereas an isolated oxygen vacancy and an isolated Sb(V) dopant would together produce three conduction electrons, formation of the two next to each other may lead to the formation of Sb(III), which traps two electrons leaving only one electron for conduction.

<sup>265</sup> The formation of Sb dopants neighbouring vacancies has been implied by EXAFS

studies, which found that, on average, Sb is 5-coordinate, consistent with the lower Sb coordination neighbouring vacancies.<sup>259-260</sup> In fact, LDA calculations have suggested that, when both defects are present in SnO<sub>2</sub>, their overall formation energy is lowest when the Sb neighbours the vacancy.<sup>266</sup> Dopant-vacancy clustering is thus highly likely to occur in SnO<sub>2</sub> and we have included this possibility in our calculations.

The electronic structure of ATO has been examined in several studies.<sup>69-70, 266-269</sup> The first such work was carried out using LDA and found the excess electron to occupy an impurity level in the band gap of mixed Sb 5s and O 2p character.<sup>70</sup> Conduction was thought to involve the excitation of electrons from this band to the mainly Sn 5s CBM. However, a later tight binding study found the defect state to contain a significant proportion of Sn 5s states as well as O 2p and Sb 5s states and to occur at the CBM, so that degenerate conduction will result.<sup>69</sup> A similar mixing between the dopant Sb 5s and conduction band states has been seen in GGA<sup>268-269</sup> and LDA<sup>266</sup> calculations.

Several other Group 15 elements have been investigated as alternatives to Sb, yet none have reached the conductivity levels of ATO. N doping has not been successful due to the small ionic radius of N(V) (0.27 Å). This leads to the preferable substitution of N<sup>3-</sup> at oxygen sites, resulting in the formation of N'<sub>O</sub> + h<sup>\*</sup> which causes *p*-type conduction.<sup>75</sup> However, N doped SnO<sub>2</sub> is not a good *p*-type conductor due to the deep, localised nature of its acceptor levels.<sup>267, 270-271</sup> Phosphorous<sup>272-273</sup> and arsenic<sup>274-275</sup> also have small ionic radii of 0.52 Å and 0.60 Å, but both substitute at Sn sites and result in *n*-type conductivity. However, neither shows the high levels of conductivity required for a good TCO and thus neither has been extensively investigated. Bi doping has been examined by several authors in comparison with Sb doping.<sup>244, 265</sup> Although the ionic radius of Bi (0.90 Å) is only slightly larger than Sn (0.83 Å), the resistivity of Bi doped SnO<sub>2</sub> remains high compared with ATO. Group 5 cations also offer possibilities for *n*-type doping of SnO<sub>2</sub>. Of these, V does not significantly affect conductivity,<sup>276-277</sup> Nb(V) introduces only small increases in conductivity,<sup>265, 278-279</sup> while Ta doped SnO<sub>2</sub> shows promise as an *n*-type dopant with resistivities as low as  $1 \times 10^{-4} \Omega \text{ cm}$ .<sup>280-283</sup> This again suggests the role of ionic radius, as Ta has a similar ionic radius (0.78 Å) to Sn(IV) (0.83 Å). V has a much smaller ionic radius of 0.68 Å, but this does not explain why Nb(V), with an ionic radius of 0.78 Å is not a suitable dopant. The origins of conductivity in cation doped SnO<sub>2</sub> must thus lie in the underlying electronic structure. DFT calculations have indicated that Sb, Bi, Ta and Nb doped SnO<sub>2</sub> result in defect states near the CBM whereas the states for As and V doped



SnO<sub>2</sub> are located lower in the band gap<sup>69</sup> but a thorough investigation using HSE06 has yet to be performed.

Fluorine tin oxide (FTO) possesses higher conductivities than ATO<sup>284-285</sup> and has been widely used as a coating on glass since the 1940s.<sup>248</sup> FTO has a low resistivity of  $\sim 4 \times 10^{-4}$   $\Omega$  cm,<sup>286-287</sup> with conduction occurring via an activated mechanism with an extremely low activation energy of 0.22 to 3.12 meV.<sup>288</sup> Fluorine substitutes for oxygen via the mechanism:



At lower fluorine concentrations,  $F_O^\bullet + e'$  dominates the defect structure resulting in high levels of conductivity.<sup>289-290</sup> However, when heavily doped with F, the conductivity of SnO<sub>2</sub> begins to decrease.<sup>291-293</sup> The reason for the increase in resistivity has been proposed to be due to the formation of fluorine interstitials at higher doping concentrations:<sup>294</sup>



LDA calculations have indicated that  $F_i' + h^\bullet$  is higher in energy than  $F_O^\bullet + e'$  and FTO is thus likely to be dominated by substitutional fluorine.<sup>294-295</sup> At higher doping concentrations, however, a greater number of fluorine interstitials are likely to form, which act as compensating acceptors, reducing the conductivity. LDA calculations have suggested that fluorine interstitials and fluorine substitutional defects have a high binding energy and that in highly doped FTO, the complex  $F_i - F_O$  may form, which was calculated to be lower in energy than a combination of isolated  $F_i'$  and  $F_O^\bullet$  defects.<sup>294-295</sup> In this complex, the holes and electrons are completely compensated, resulting in zero net conductivity. Another possible mechanism for the damping of conductivity in highly doped FTO is the substitution of fluorine at oxygen vacancy sites.<sup>296</sup> Each isolated vacancy produces two conduction electrons, while each fluorine substitutional results in one conduction electron, giving three conduction electrons when the two defects are well separated. However, when the fluorine substitutes at a vacancy site, only one conduction electron results via the mechanism:



There have been very few calculations of the electronic structure of fluorine doped tin dioxide. LDA studies on 24-<sup>71</sup> and 216-atom<sup>294-295</sup> supercells of SnO<sub>2</sub> indicated that



fluorine does not result in the formation of band gap states, in agreement with a degenerate semiconductor model of conduction. The fluorine states were not found to significantly perturb the electronic structure and hybridised with states at the bottom of the conduction band, resulting in a slight polarisation of the charge density of the nearest neighbour tin ions.

Several other halogens have been doped into SnO<sub>2</sub> as an alternative to F doping. Cl is often unintentionally incorporated into SnO<sub>2</sub> through the use of SnCl<sub>4</sub> and SnCl<sub>2</sub> precursors and has been detected in nominally undoped films.<sup>191, 289, 292</sup> However, deliberate Cl doping has been found to result in a resistivity of  $\sim 2 \times 10^{-3} \Omega \text{ cm}$ ,<sup>297-298</sup> an order of magnitude higher than that of FTO. Br<sup>299</sup> and I<sup>300</sup> have also been doped into SnO<sub>2</sub> films, with both resulting in low levels of conductivity. One reason for the low resistivity of Cl, Br and I doped SnO<sub>2</sub> compared to FTO, may be the very large ionic radii of these anions compared with O<sup>2-</sup>. Whereas F<sup>-</sup> has an ionic radius of 1.16 Å, comparable to the ionic radius of O<sup>2-</sup>, (1.22 Å) Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> have ionic radii of 1.67, 1.82 and 2.06 Å, respectively. This suggests that doping with Cl, Br and I will be highly unfavourable energetically. Evidence for their unsuitability as dopants comes from the low growth rates of Br- and Cl doped films compared to undoped and F doped films.<sup>286</sup>

Several authors have reported that improvement of the conductivity of SnO<sub>2</sub> beyond that of ATO and FTO can be achieved through co-doping with fluorine and antimony.<sup>246, 285, 287, 301</sup> Since ATO reaches a conductivity limit caused by formation of Sb(III) acceptors ( $\text{Sb}'_{\text{Sn}} + h^*$ ), while FTO is limited by formation of F interstitials as acceptors ( $\text{F}'_{\text{I}} + h^*$ ), combining the two below their individual limits may result in a lower overall conductivity. The results of co-doping studies have shown improvement of the resistivity to levels below those of ATO and FTO with the lowest achieved resistivity of  $3 \times 10^{-4} \Omega \text{ cm}$ .<sup>301</sup> However, as of yet there have been few investigations of co-doping and the origin of the improved conductivities is not understood.

In recent years, it has been postulated that the *n*-type conductivity in undoped TCOs occurs through the presence of hydrogen impurities. Hydrogen has been suggested to be a cause of 'intrinsic' conductivity in In<sub>2</sub>O<sub>3</sub>,<sup>68</sup> ZnO,<sup>50</sup> SnO<sub>2</sub><sup>67</sup> and Ga<sub>2</sub>O<sub>3</sub>.<sup>302</sup> In SnO<sub>2</sub>, hydrogen has been shown in LDA<sup>303</sup> and GGA<sup>67</sup> calculations to possess donor levels which are shallow to the conduction band, suggesting that hydrogen impurities may be responsible for the experimentally observed shallow levels originally attributed to oxygen vacancies<sup>62,</sup>

<sup>66</sup> Recently, the donor levels of muonium ( $\text{Mu} = \mu^+ e^-$ ), which can be considered as a light

isotope of hydrogen, were probed using muon spin rotation and relaxation spectroscopy.<sup>68</sup> This demonstrated the shallow nature of the muonium donor levels, suggesting that hydrogen may be the cause of observed shallow donor levels in SnO<sub>2</sub> and the resultant *n*-type conductivity.

In the following sections, we investigate the effects of cationic doping with Sb and Bi and anionic doping with Cl and F on the electronic structure of SnO<sub>2</sub>. We also examine the possibilities of doubly doping with Sb and F, as well as the effects of clustering of these dopants with intrinsic oxygen vacancies. Finally, we examine hydrogen doping to identify the effect of hydrogen on the electronic structure and the mechanism behind hydrogen-induced *n*-type conductivity in SnO<sub>2</sub>.

### 3.5.2 Methodology

All calculations of extrinsic defects were carried out using the HSE06 hybrid-DFT functional. The 5*s*, 5*p* and 4*d* electrons were explicitly included in the valence for Sn, while for O, Cl, F, Sb and Bi, only the *s* and *p* electrons were treated explicitly. Defect calculations were carried out in a 48 atom 2 × 2 × 2 supercell with a 2 × 2 × 2  $\Gamma$ -centred *k*-point mesh. All calculations used a planewave cut-off of 500 eV and forces were converged to within 0.01 eV/Å.

The energy ( $E_f(D)$ ) for substitution of a dopant X at a lattice tin or oxygen site can be calculated from:

$$E_f(D) = E_{tot}(D) + \frac{1}{2}n_O E(O_2) + n_{Sn} E(\alpha - Sn) - n_X E(X) + n_O \mu_O + n_{Sn} \mu_{Sn} - n_X \mu_X \quad (3.13)$$

where  $E_{tot}(D)$  is the total energy of the defective cell,  $n_O$  and  $n_{Sn}$  are the number of O and Sn atoms which are being replaced by the number  $n_X$  of dopant atoms;  $E(O_2)$ ,  $E(\alpha - Sn)$ , and  $E(X)$  are the total energies of the O<sub>2</sub> molecule, Sn metal and the elemental form of the dopant X and  $\mu_O$ ,  $\mu_{Sn}$  and  $\mu_X$  are the elemental chemical potentials.

The chemical potential limits for SnO<sub>2</sub> formation are defined as in Section 3.4.2 as  $(\mu_{Sn}, \mu_O) = (-5.25 \text{ eV}, 0.00 \text{ eV})$  for oxygen-rich conditions and  $(0.00 \text{ eV}, -2.63 \text{ eV})$  for oxygen-poor conditions. The doping limits are determined by considering the possible binary and ternary compounds for each dopant. For example, Sb doping is limited by the

formation of  $\text{Sb}_2\text{O}_5$  and  $\text{Sb}_2\text{O}_3$  oxides, giving chemical potential limits defined by:

$$2\mu_{\text{Sb}} + 5\mu_{\text{O}} \leq \Delta H_f(\text{Sb}_2\text{O}_5) = -9.40 \text{ eV} \quad (3.14)$$

$$2\mu_{\text{Sb}} + 3\mu_{\text{O}} \leq \Delta H_f(\text{Sb}_2\text{O}_3) = -6.74 \text{ eV} \quad (3.15)$$

Substituting for O-rich conditions ( $\mu_{\text{O}} = 0 \text{ eV}$ ) gives limits of  $(\mu_{\text{Sn}}, \mu_{\text{O}}, \mu_{\text{Sb}}) = (-5.25, 0.00, -4.70)$  to avoid  $\text{Sb}_2\text{O}_5$  formation and  $(-5.25, 0.00, -3.37)$  to avoid  $\text{Sb}_2\text{O}_3$  formation. To ensure that neither phase forms, we must set  $\mu_{\text{Sb}} \leq -4.70 \text{ eV}$ , so that at the O-rich conditions, Sb doping is limited by  $\text{Sb}_2\text{O}_5$  formation. Alternatively, the O-poor limit ( $\mu_{\text{O}} = -2.63 \text{ eV}$ ) can be substituted into Eq. 3.14 and 3.15 which results in  $\mu_{\text{Sb}} > 0 \text{ eV}$  in both cases. We thus set  $\mu_{\text{Sb}} = 0 \text{ eV}$ , giving the O-poor limit  $(0.00, -2.63, 0.00)$  and the  $\text{Sb}_2\text{O}_3$  limit  $(0.00, -2.63, 0.00)$ .

Similarly, the limits for Bi, F and Cl doping are defined by the inequalities:

$$2\mu_{\text{Bi}} + 3\mu_{\text{O}} \leq \Delta H_f(\text{Bi}_2\text{O}_3) = -5.77 \text{ eV} \quad (3.16)$$

$$2\mu_{\text{Bi}} + 2\mu_{\text{Sn}} + 7\mu_{\text{O}} \leq \Delta H_f(\text{Bi}_2\text{Sn}_2\text{O}_7) = -19.09 \text{ eV} \quad (3.17)$$

$$\mu_{\text{Sn}} + 4\mu_{\text{F}} \leq \Delta H_f(\text{SnF}_4) = -12.52 \text{ eV} \quad (3.18)$$

$$\mu_{\text{Sn}} + 2\mu_{\text{F}} \leq \Delta H_f(\text{SnF}_2) = -6.95 \text{ eV} \quad (3.19)$$

$$\mu_{\text{Sn}} + 4\mu_{\text{Cl}} \leq \Delta H_f(\text{SnCl}_4) = -5.15 \text{ eV} \quad (3.20)$$

$$\mu_{\text{Sn}} + 2\mu_{\text{Cl}} \leq \Delta H_f(\text{SnCl}_2) = -3.04 \text{ eV} \quad (3.21)$$

As  $\text{Bi}_2\text{Sn}_2\text{O}_7$  possesses an extremely large 352 atom unit cell,<sup>304</sup> we could not currently perform HSE06 calculations to determine its formation energy. We have thus used the experimental formation enthalpy of  $\text{Bi}_2\text{Sn}_2\text{O}_7$  of  $-19.09 \text{ eV}$ <sup>305</sup> to estimate the defect equilibrium. Using the limits of Eqs. 3.14-3.21, we have calculated the chemical potential limits shown in Table 3.10. Each dopant possesses both an O-rich and O-poor limit which limit the formation of binary phases.



|    | O-rich | O-poor |
|----|--------|--------|
| Sn | -5.25  | 0.00   |
| O  | 0.00   | -2.63  |
| Sb | -4.70  | 0.00   |
| Bi | -4.29  | -0.36  |
| F  | -1.82  | -3.47  |
| Cl | 0.00   | -1.52  |

Table 3.10 Limits of atomic chemical potentials (in eV) of Sn, O, Sb, Bi, F and Cl under O-rich and O-poor conditions.

### 3.5.3 Defect Formation Energies

Cationic doping was carried out by replacing a single atom of Sn with Sb or Bi in the 48 atom supercell, giving a doping concentration of 6.25%. For anionic doping, a single oxygen atom was replaced by F or Cl, resulting in a doping concentration of 3.125%. The formation energies for each of these extrinsic defects are shown in Table 3.11, under the chemical potential limits of Table 3.10. The lowest formation energy is for F doping under O-poor conditions, while Sb doping is also low in energy under O-rich conditions. Bi doping is less energetically favourable than Sb doping, thus explaining the lower observed conductivities of Bi doped SnO<sub>2</sub>. Cl doping is very unfavourable energetically, thereby explaining the low conductivities of Cl doped SnO<sub>2</sub>.

| Dopant                                 | O-rich | O-poor |
|----------------------------------------|--------|--------|
| $\text{Sb}_{\text{Sn}}^{\bullet} + e'$ | 1.46   | 2.01   |
| $\text{Bi}_{\text{Sn}}^{\bullet} + e'$ | 2.63   | 3.94   |
| $\text{F}_{\text{O}}^{\bullet} + e'$   | 2.16   | 1.19   |
| $\text{Cl}_{\text{O}}^{\bullet} + e'$  | 5.46   | 4.35   |

Table 3.11 Doping energies (in eV) for single Sb, Bi, F and Cl dopants in 48 atom supercell of SnO<sub>2</sub> under the chemical potential limits tabulated in Table 3.10.

To understand the effects of higher doping concentrations, supercells containing two atoms of the same dopant were also considered, giving a cationic doping concentration of 12.5% and a 6.25% anionic dopant concentration. There are many different configurations available for doubly doping the supercell. Because of the high computational expense of

performing hybrid-DFT calculations, we were unable to model every possible dopant configuration, and considered only a selection of representative sites.

For cationic doping, we first considered sites in which both dopants are attached to the same oxygen anion. Each oxygen site has trigonal planar coordination as shown in Fig. 3.23 (a), in which the two ‘A’ atoms have longer Sn-O bond lengths of 2.063 Å, while the ‘B’ atom has a shorter Sn-O bond length on 2.061 Å. Thus, two doubly doped configurations are possible – either with both dopants on A sites ( $M_{AA}$ ) or with one A-site and one B-site dopant ( $M_{AB}$ ) – as shown in Fig. 3.24 (b)-(c). We also considered one dopant configuration in which the dopants were far away from each other ( $M_{far}$ ), which is shown in Fig. 3.24 (c).

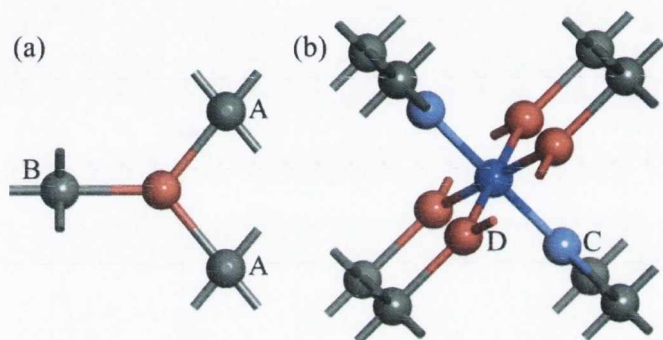


Fig. 3.23 (a) Trigonal planar oxygen site in  $\text{SnO}_2$  with A and B marking equivalent tin atoms. (b) Octahedral tin (blue atom) site in  $\text{SnO}_2$  with equivalent ‘D’ atoms in red and ‘C’ atoms in purple.

Anionic doping is more complex, because of the asymmetric nature of the octahedral tin site shown in Fig. 3.23 (b). As well as possessing two different types of O site - two with bond lengths of 2.061 Å (C) and four with bond lengths of 2.063 Å (D) - there are also three different bond angles. While the C-Sn-D angles are all 90°, the D-Sn-D angles alternate between 79° and 101°. This leads to five different anion doping configurations: two C sites ( $X_{CC}^{180}$ ); a C and a D site ( $X_{CD}^{90}$ ); two D sites at 180° ( $X_{DD}^{180}$ ); two D sites at 79° ( $X_{DD}^{79}$ ), and two D sites at 101° ( $X_{DD}^{101}$ ), as shown in Fig. 3.25 (b)-(e). Finally, one configuration with both dopants far apart was also considered ( $X_{far}$ ), as illustrated in Fig. 3.25 (f).

It must be noted that due to the small size of the  $2 \times 2 \times 2$  supercell, the cationic  $M_{AA}$  and the anionic  $X_{DD}^{101}$  configurations result in periodic rows of dopants along the  $c$ -axis. This type of clustering is unlikely to exist in the real system and may affect the resulting defect energetics. Unfortunately, we cannot currently repeat calculations in a larger supercell due to the limits of computational resources.



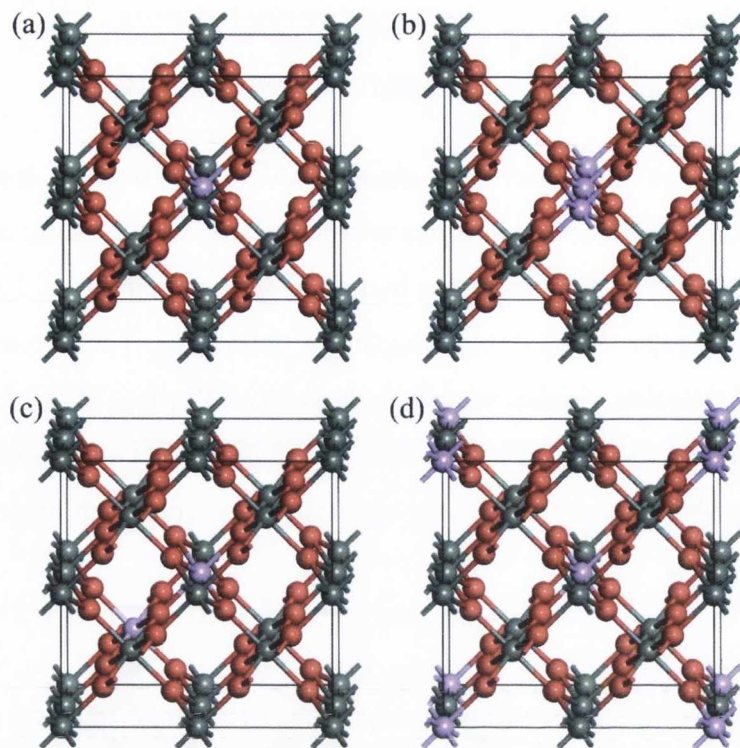


Fig. 3.24 Cationic doping configurations in 48 atom supercell of  $\text{SnO}_2$ , showing (a) single dopant (b)  $M_{AA}$  (c)  $M_{AB}$  and (d)  $M_{\text{far}}$ . Red atoms are oxygen, grey are tin and pink are Sb/Bi.

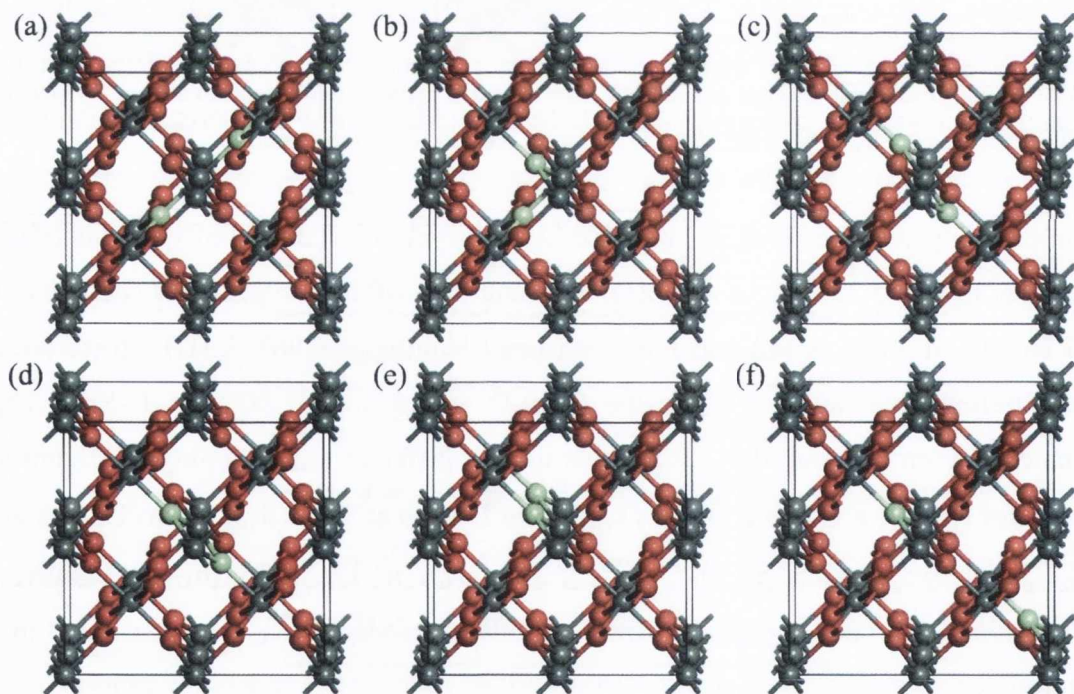


Fig. 3.25 Anionic doping configurations of  $2 \times 2 \times 2$  supercell of  $\text{SnO}_2$ , showing (a)  $X_{CC}^{180}$  (b)  $X_{CD}^{90}$  (c)  $X_{DD}^{180}$  (d)  $X_{DD}^{79}$  (e)  $X_{DD}^{101}$  and (f)  $X_{\text{far}}$ . Grey atoms are tin, red are oxygen and green are F/Cl.

Table 3.12 presents the calculated energies per dopant for Sb and Bi doped  $\text{SnO}_2$ . A higher dopant concentration appears to be more energetically favourable for Sb doping, with all two-dopant configurations lower in energy per dopant than one dopant per supercell. The



most stable configuration is  $\text{Sb}_{\text{far}}$ , while the configurations  $\text{Sb}_{\text{AA}}$  and  $\text{Sb}_{\text{AB}}$  are slightly less energetically favourable. It thus appears that the dopant concentration of 12.5% is energetically favourable over the 6.25% doping level. In contrast, Bi doping is less energetically favourable at 12.5% doping levels compared to 6.25%. However, when the doping concentration is high, a clear preference for clustering of Bi cations is seen, with the  $\text{Bi}_{\text{AA}}$  and  $\text{Bi}_{\text{AB}}$  systems both lower in energy than  $\text{Bi}_{\text{far}}$ . Thus, despite the similarity in electronic structure of these two Group 15 cations, they have completely different doping preferences at high dopant concentrations. The clustering behaviour of Bi may act to dampen conductivity by creating bismuth oxide sub-phases within the doped  $\text{SnO}_2$ . In contrast, the Sb dopants will preferably occur further apart, with very little interaction between each other. This difference may partially explain the lower conductivity of Bi doped  $\text{SnO}_2$  compared with Sb doped  $\text{SnO}_2$ .

|                         | M-M (Å) | O-rich      | O-poor |
|-------------------------|---------|-------------|--------|
| <b>Sb<sub>AA</sub></b>  | 3.20    | 1.39        | 1.94   |
| <b>Sb<sub>AB</sub></b>  | 3.76    | 1.28        | 1.83   |
| <b>Sb<sub>far</sub></b> | 7.45    | <b>1.26</b> | 1.81   |
| <b>Bi<sub>AA</sub></b>  | 3.20    | 2.69        | 4.00   |
| <b>Bi<sub>AB</sub></b>  | 3.83    | <b>2.67</b> | 3.98   |
| <b>Bi<sub>far</sub></b> | 7.45    | 2.75        | 4.06   |

Table 3.12 Formation energy (in eV) per dopant for Sb and Bi in  $\text{SnO}_2$ , presented under both O-rich and O-poor chemical potential limits. The distance M-M between the dopants is also given.

The energies for F and Cl doping are tabulated in Table 3.13. F doping at higher concentrations is less energetically favourable, with all 6.25% configurations having higher energies than that of the 3.125% doped supercell. The lowest energy dopant configuration is  $\text{F}_{\text{CD}}^{90}$  and the highest is  $\text{F}_{\text{DD}}^{180}$ , with no clear correlation occurring between dopant distance and formation energy. F doping is energetically favoured under O-poor conditions, which is due to dopant substitution at oxygen vacancy sites. For Cl doping, most configurations are higher in energy than the singly doped supercell, though both  $\text{Cl}_{\text{CD}}^{90}$  and  $\text{Cl}_{\text{DD}}^{101}$  are lower in energy. Again, little correlation between dopant distance and formation energy is observed. The lowest energy defect is  $\text{Cl}_{\text{DD}}^{101}$  while the highest is  $\text{Cl}_{\text{CD}}^{90}$ . However, all Cl defects are extremely high in energy, and thus Cl doping is unlikely to result in high levels of  $n$ -type conductivity in  $\text{SnO}_2$ .

|                 | X-X (Å) | O-poor | O-rich |
|-----------------|---------|--------|--------|
| $F_{CC}^{180}$  | 4.14    | 1.71   | 2.68   |
| $F_{CD}^{90}$   | 2.85    | 1.56   | 2.53   |
| $F_{DD}^{180}$  | 4.23    | 1.78   | 2.75   |
| $F_{DD}^{79}$   | 2.66    | 1.72   | 2.68   |
| $F_{DD}^{101}$  | 3.20    | 1.57   | 2.54   |
| $F_{far}$       | 7.45    | 1.66   | 2.63   |
| $Cl_{CC}^{180}$ | 4.31    | 5.85   | 6.96   |
| $Cl_{CD}^{90}$  | 2.82    | 4.09   | 5.19   |
| $Cl_{DD}^{180}$ | 4.44    | 5.25   | 6.36   |
| $Cl_{DD}^{79}$  | 2.88    | 4.86   | 5.97   |
| $Cl_{DD}^{101}$ | 3.20    | 4.02   | 5.13   |
| $Cl_{far}$      | 7.45    | 5.44   | 6.55   |

Table 3.13 Formation energy (in eV) per F/Cl dopant, for anion doping of SnO<sub>2</sub> under both O-poor and O/Cl-rich conditions. The shortest distance between the dopants (X-X) is also given.

## 3.5.4 Electronic Structure of Doped SnO<sub>2</sub>

### 3.5.4.1 Antimony

The ionic radius of Sb(V) is 0.74 Å, similar to that of Sn(IV) which has an ionic radius of 0.83 Å.<sup>261</sup> Thus, the insertion of Sb(V) results in very little distortion in bond length compared to SnO<sub>2</sub>. Insertion of a single Sb cation in the 48 atom supercell results in a shortening of the bond lengths by 0.06 and 0.05 Å, to  $2 \times 2.00$  Å and  $4 \times 2.01$  Å. In the Sb<sub>AA</sub> configuration, the Sb-O bond lengths are slightly longer, with two of 2.04 Å and four of 2.05 Å, corresponding to decreases of 0.02 and 0.01 Å. The reason for the smaller change in this case may be a consequence of the small supercell size, as the Sb<sub>AA</sub> configuration results in a row of Sb atoms along the *c*-axis of the crystal. The insertion of two Sb ions in the Sb<sub>AB</sub> configuration results in a distortion of the Sb-O<sub>6</sub> octahedra. Each Sb has four bond lengths of 2.04 Å perpendicular to the Sb-O-Sb plane, one of 2.06 Å to the bridging oxygen and a shorter bond length of 2.02 Å directed away from the bridging oxygen. The longer bond lengths in the Sb-O-Sb plane indicate repulsion between the two Sb ions, which results in their overall relaxation away from each other by 0.03 Å. Finally, in the Sb<sub>far</sub> configuration, each Sb has six Sb-O bond lengths of 2.03 Å, giving a decrease in bond length of 0.03 Å. These findings are in line with experimental EXAFS data for Sb



doped  $\text{SnO}_2$  which measured the Sb-O bond length to be 0.04-0.06 Å smaller than bulk Sn-O bond lengths.<sup>259-260</sup>

Fig. 3.24 shows the EDOS/PEDOS for Sb doped  $\text{SnO}_2$ . In the singly doped supercell (Fig. 3.26 (a)), there are two defect states visible in the EDOS: one at the bottom of the valence band, and a second just below the CBM. The -9 eV valence band state is composed of mainly Sb 5s character with a small amount of mixing between Sn 5s and O 2p states, while the conduction band state is of mixed Sb 5s, Sn 5s and O 2p character and is a one-electron donor level. It is the presence of this CBM state that gives rise to *n*-type conductivity in Sb doped  $\text{SnO}_2$ . To probe the nature of this state further, its partial charge density at the  $\Gamma$ -point of the Brillouin Zone is plotted in Fig. 3.27 (a). It can be seen that a significant portion of the density is localised on the Sb, with the remainder delocalised over Sn and O atoms. Analysis of the Bader charges (Table 3.14) associated with this state indicates that the Sb has 7% of the charge density, while the Sn ions share 64% and the oxygen ions share 29%. This indicates the density to be quite delocalised, suggesting a band-type mechanism, which may be the reason for the high levels of *n*-type conductivity in Sb doped  $\text{SnO}_2$ .

Doping of two Sb ions per supercell likewise results in a Sb 5s state at the bottom of the valence band and occupied donor levels near the CBM. The nature of the conduction band states varies slightly, depending on the doping configuration. For the  $\text{Sb}_{\text{AA}}$  configuration, there are two occupied peaks of mixed Sb 5s and Sn 5s character, while the highest energy peak is of purely Sn 5s character. The partial charge density of the highest occupied state of  $\text{Sb}_{\text{AA}}$  at the  $\Gamma$ -point of the Brillouin Zone is shown in Fig. 3.27 (b) and shows a high degree of localisation on the Sb ions.  $\text{Sb}_{\text{AB}}$  and  $\text{Sb}_{\text{far}}$  configurations, all three peaks are of mixed Sb 5s and Sn 5s character. The partial charge densities associated with these defect states are shown in Fig. 3.27 (c)-(d). Both show some localisation on the Sb, with the remainder of the charge delocalised over Sn 5s and O 2p states.

Table 3.14 shows the Bader charges of the conduction band states. In  $\text{Sb}_{\text{AA}}$ , 21% of the charge is localised on the two Sb ions, with an additional 47% on Sn and 32% on O.  $\text{Sb}_{\text{AB}}$  and  $\text{Sb}_{\text{far}}$  have less charge on the Sb ions (15% and 13%) and a higher amount on Sn (55% and 57%). The lowest energy dopant configuration is thus the one with the least amount of charge localised on Sb, and conversely,  $\text{Sb}_{\text{AA}}$  has the highest Sb localisation and greatest formation energy. By delocalising more of the charge over Sn and O ions, the bulk



electronic structure is less perturbed by the dopant, allowing conduction to occur in a band-like manner.

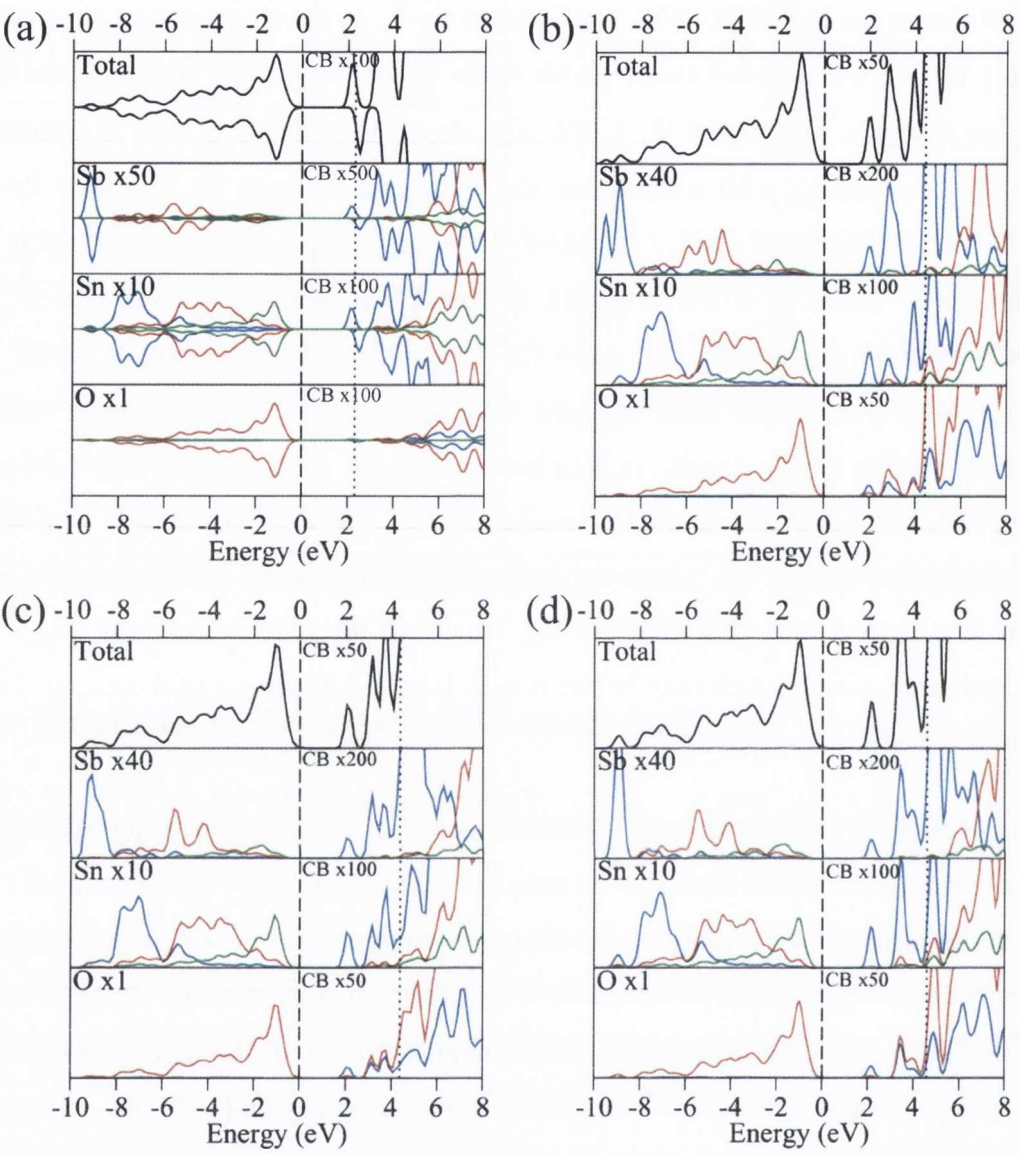


Fig. 3.26 Total and partial EDOS for Sb doped SnO<sub>2</sub> for doping configurations: (a) single Sb (b) Sb<sub>AA</sub> (c) Sb<sub>AB</sub> and (d) Sb<sub>far</sub>. Dashed line indicates VBM and dotted line shows highest occupied state. Blue lines are *s* states, red are *p* states and green are *d* states.

|                   | Single Sb | Sb <sub>AA</sub> | Sb <sub>AB</sub> | Sb <sub>far</sub> |
|-------------------|-----------|------------------|------------------|-------------------|
| Sb <sub>tot</sub> | 0.07      | 0.21             | 0.15             | 0.13              |
| Sn <sub>tot</sub> | 0.64      | 0.47             | 0.55             | 0.57              |
| O <sub>tot</sub>  | 0.29      | 0.32             | 0.30             | 0.30              |

Table 3.14 Bader charges (in%) for doping of SnO<sub>2</sub> with Sb, giving total charge on Sb (Sb<sub>tot</sub>), Sn (Sn<sub>tot</sub>) and O (O<sub>tot</sub>), for each dopant configuration.

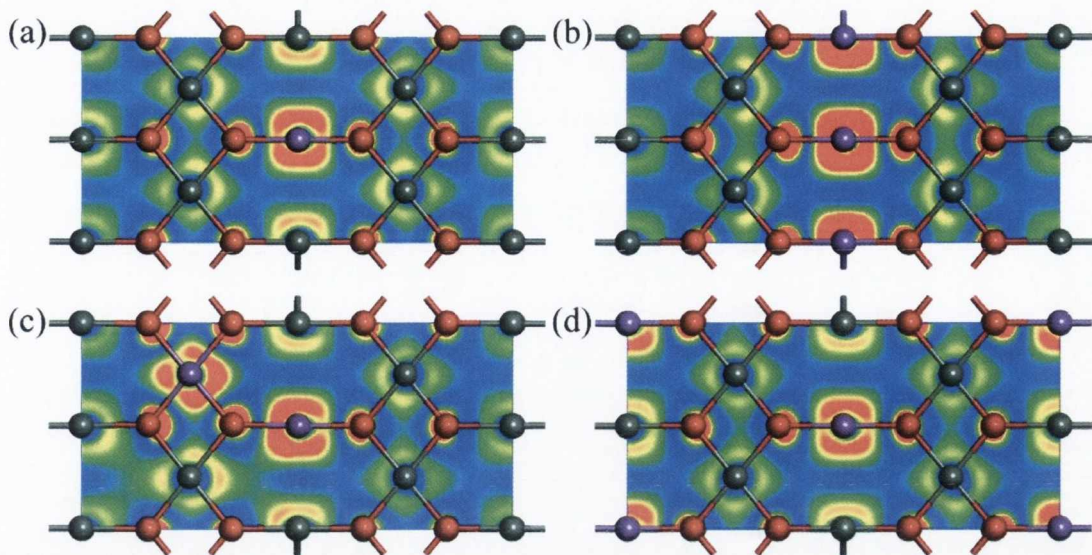


Fig. 3.27 Partial charge density for conduction band states of (a) single Sb dopant (b)  $\text{Sb}_{\text{AA}}$  (c)  $\text{Sb}_{\text{AB}}$  and (d)  $\text{Sb}_{\text{far}}$  at  $\Gamma$ -point of Brillouin Zone. All are plotted at isolevels between 0 (blue) and  $0.02 \text{ e}/\text{\AA}^3$  (red). Grey atoms are Sn, red are O and pink are Sb.

### 3.5.4.2 Bismuth

$\text{Bi(V)}$  has an ionic radius of  $0.90 \text{ \AA}$ , only slightly larger than the  $\text{Sn(IV)}$  radius of  $0.83 \text{ \AA}$ .<sup>261</sup> Doping of Bi thus results in small increases in the Bi-O bond lengths compared to Sn-O. The single Bi dopant possesses four Bi-O bond lengths of  $2.18 \text{ \AA}$  and two of  $2.16 \text{ \AA}$ , longer than bulk Sn-O bond lengths by  $0.11 \text{ \AA}$  and  $0.10 \text{ \AA}$ , respectively. In  $\text{Bi}_{\text{AA}}$ , two Bi-O bond lengths increase by  $0.11 \text{ \AA}$  to  $2.17 \text{ \AA}$  and four increase by  $0.08 \text{ \AA}$  to  $2.14 \text{ \AA}$ . For  $\text{Bi}_{\text{AB}}$ , the  $\text{BiO}_6$  octahedra distort, with the A site having bond lengths of  $3 \times 2.13, 2.12, 2.16$  and  $2.14 \text{ \AA}$ , while the B site has bond lengths of  $4 \times 2.14, 2.11$ , and  $2.09 \text{ \AA}$ . Finally, in the  $\text{Bi}_{\text{far}}$  configuration, each Bi atom has two bond lengths of  $2.13 \text{ \AA}$  and four of  $2.16 \text{ \AA}$ .

The EDOS and PEDOS for Bi doped  $\text{SnO}_2$  are shown in Fig. 3.28. Similar to the Sb case, Bi dopants result in two main defect states – a Bi  $6s$  state at the bottom of the valence band and states of Bi  $6s$  mixed with Sn  $5s$  and O  $2p$  character at the bottom of the conduction band. However, the valence band Bi  $6s$  states occur at a lower energy than the Sb  $5s$  states. Because of this, they cannot mix as much with the Sn  $5s$  states at the bottom of the valence band. Hence, there is less mixing between dopant  $s$  and tin  $5s$  states in Bi doped  $\text{SnO}_2$ , compared with  $\text{Sb}:\text{SnO}_2$ , which results in a lower degree of mixing of these states at the CBM in Bi doped  $\text{SnO}_2$ . This may help to explain the low conductivities of  $\text{Bi}:\text{SnO}_2$  compared to ATO.



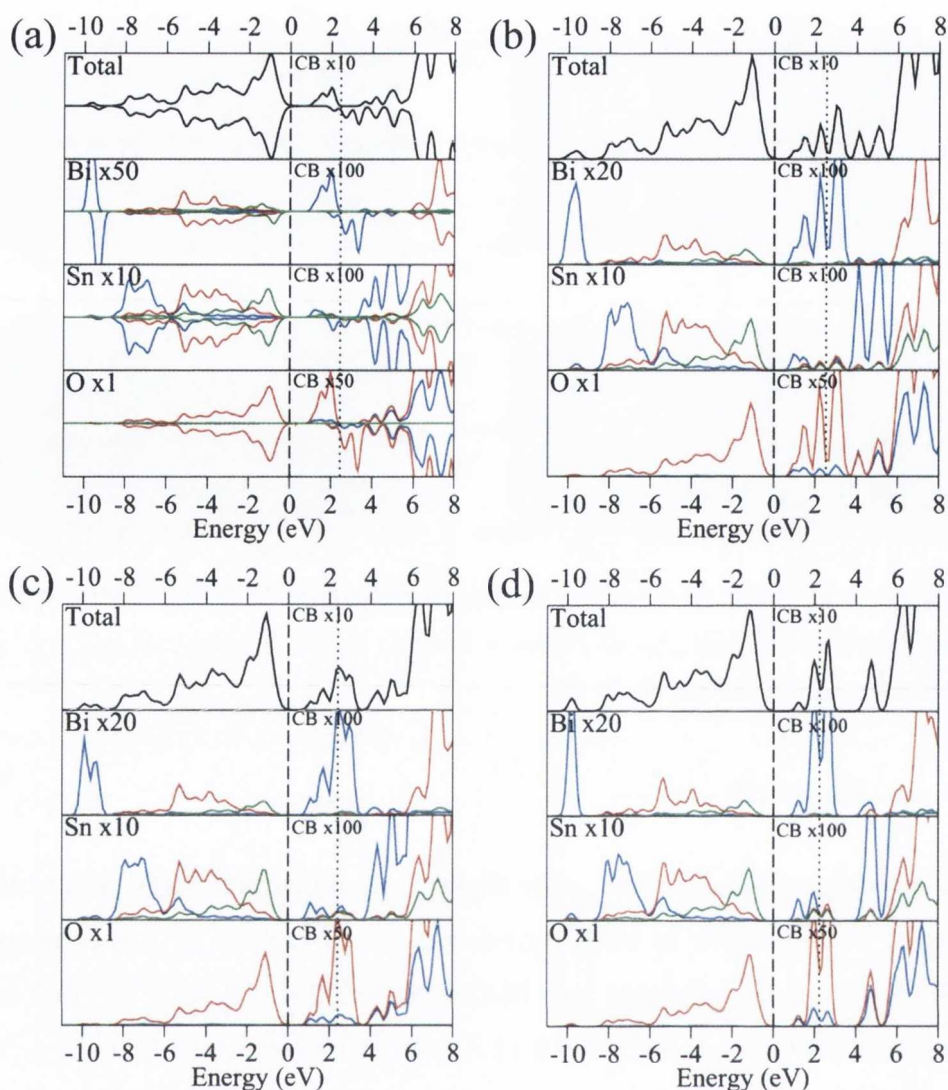


Fig. 3.28 Total and partial EDOS for Bi doped  $\text{SnO}_2$  in the configurations: (a) single Bi (b)  $\text{Bi}_{\text{AA}}$  (c)  $\text{Bi}_{\text{AB}}$  and (d)  $\text{Bi}_{\text{far}}$ . Dashed line marks VBM and dotted line marks highest occupied level. Blue lines are  $s$  states, red are  $p$  states and green are  $d$  states.

When a single Bi is placed in the supercell, one electron is donated to the system for conduction ( $\text{Bi}_{\text{Sn}}^{\bullet} + e'$ ). This electron forms a singly occupied state at the bottom of the conduction band in Fig. 3.28 (a), which is of mainly Bi  $6s$  character mixed with a small amount of Sn  $5s$  and O  $2p$  character. The partial charge density of this state at the  $\Gamma$ -point of the Brillouin Zone is plotted in Fig. 3.29 (a). This shows a high localisation of the electron density on the Bi and its nearest neighbour oxygen atoms, with less electron density further from the defect, in contrast to the high delocalisation seen in ATO. Table 3.15 shows the Bader charges of the conduction band state for  $\text{Bi}:\text{SnO}_2$ . 19% of the charge is localised on the Bi atom and 63% is on O, in contrast to Sb doping where only 7% of the charge localises on the dopant Sb, while 64% of the remaining charge is on Sn. In fact, in the Bi system, 49% of the charge is localised on the six nearest neighbour oxygen ions, so that 68% of the total defect charge is localised on the Bi and its oxygen nearest neighbours.



Bi doping thus results in more localised defect states of mixed Bi 6*s* and O 2*p* character with lower Sn 5*s* contributions than in the Sb system. This suggests that Bi doped SnO<sub>2</sub> will have a higher conduction activation energy than Sb doped, which would explain the lower conductivity of the Bi doped system.

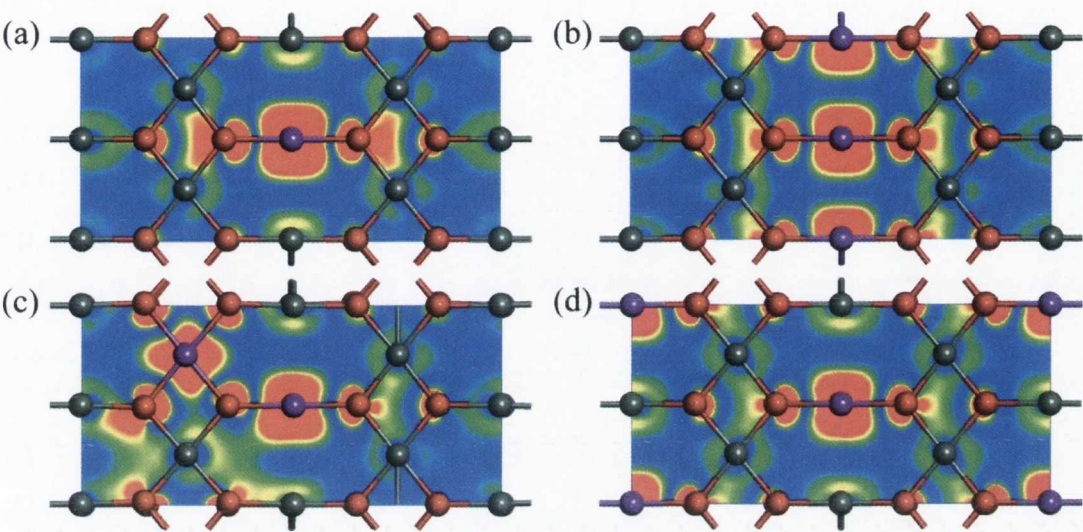


Fig. 3.29 Partial charge density of highest occupied state for Bi doped SnO<sub>2</sub>, plotted at the  $\Gamma$ -point of the Brillouin Zone. (a) single Bi (b) Bi<sub>AA</sub> (c) Bi<sub>AB</sub> and (d) Bi<sub>far</sub>. All are plotted between 0 (blue) and 0.02 e/Å<sup>3</sup> (red). Grey atoms are Sn, red are O and pink are Bi.

|                   | single Bi | Bi <sub>AA</sub> | Bi <sub>AB</sub> | Bi <sub>far</sub> |
|-------------------|-----------|------------------|------------------|-------------------|
| Bi <sub>tot</sub> | 0.19      | 0.23             | 0.22             | 0.20              |
| Sn <sub>tot</sub> | 0.18      | 0.18             | 0.22             | 0.23              |
| O <sub>tot</sub>  | 0.63      | 0.59             | 0.57             | 0.57              |
| O <sub>nn</sub>   | 0.49      | 0.46             | 0.46             | 0.45              |

Table 3.15 Bader charges (in%) for the highest occupied states of single Bi dopant, Bi<sub>AA</sub>, Bi<sub>BB</sub> and Bi<sub>far</sub>. Table shows total (tot) charges for each atom and combined charge on nearest neighbour oxygens (O<sub>nn</sub>).

With two Bi dopants per supercell, there are two electrons available to the system for conduction. In each case, these two electrons occupy a defect state of mainly Bi 6*s* character, mixed with O 2*p* character and a small amount of Sn 5*s* character in the EDOS of Fig. 3.28 (c)-(d). To compare the composition of these states, the partial charge densities of each are plotted in Fig. 3.29 (c)-(d). Each results in a more localised defect state than those for the equivalent Sb configurations, with a large amount of charge localised on the Bi and their nearest neighbour oxygen ions. Table 3.15 shows the percentage Bader charge for each defect. 69% of the charge is localised on the Bi and neighbouring oxygen ions for

$\text{Bi}_{\text{AA}}$ , 68% is localised for  $\text{Bi}_{\text{AB}}$  and 65% is localised for  $\text{Bi}_{\text{far}}$ .  $\text{Bi}_{\text{far}}$  is thus the most delocalised defect and also the highest in energy. This suggests that Bi dopants preferably form localised defect states and are thus likely to have high conduction activation energies.

### 3.5.4.3 Fluorine

Doping with fluorine does not introduce significant structural changes into the system, because of the similarity in ionic radius between  $\text{F}^-$  (1.16 Å) and  $\text{O}^{2-}$  (1.22 Å).<sup>261</sup> Introduction of a single  $\text{F}^-$  ion into the 48 atom supercell results in two longer Sn-F bonds of length 2.19 Å and a shorter bond of length 2.17 Å. This corresponds to increases of 0.13 Å and 0.11 Å from bulk Sn-O bond lengths. Given that  $\text{F}^-$  is a smaller anion than  $\text{O}^{2-}$ , it is surprising that the bond lengths increase upon F doping. If we compare the bond lengths to those in the binary tin fluoride compounds,  $\text{SnF}_2$  and  $\text{SnF}_4$ , it may be noted that in F doped  $\text{SnO}_2$ , Sn-F bond lengths are more similar to those in  $\text{SnF}_2$  (2.06-2.39 Å)<sup>306</sup> than to those of  $\text{SnF}_4$  (1.87 and 2.03 Å).<sup>307</sup> This suggests that the tin charge may have been reduced slightly towards Sn(II). For the doubly doped configurations, Sn-F bond lengths of 2.11-2.21 Å are seen, corresponding to increases in bond lengths of 0.05-0.15 Å.

The density of states for selected dopant configurations are shown in Fig. 3.30. When doping a single F atom per supercell, the effect is to fill the bottom-most states of the conduction band, introducing occupied defect states of mixed Sn 5s, O 2s and O 2p character near the CBM. The fluorine 2p states occur in the lower valence band, between -8.5 eV and -5 eV and mix with the O 2p and Sn 5s states in the same energy range. The extra electron induced by F doping occupies a conduction band state of mainly Sn 5s character with a small amount of O 2s, O 2p and F 2p states. Fig. 3.30 (b)-(d) show the EDOS of selected doubly doped configurations:  $\text{F}_{\text{CD}}^{90}$ ,  $\text{F}_{\text{DD}}^{180}$  and  $\text{F}_{\text{far}}$ . Each of these has a similar composition to the single dopant, with the F 2p states occurring in the lower valence band, while the two dopant electrons occupy states of Sn 5s character at the bottom of the conduction band. Comparing the lowest energy  $\text{F}_{\text{CD}}^{90}$  configuration to the highest energy  $\text{F}_{\text{DD}}^{180}$  defect, the one noticeable difference is the presence of a defect peak of mixed Sn 5s, O 2p and F 2p character at the bottom of the VB of  $\text{F}_{\text{DD}}^{180}$ . This suggests a more localised character, compared to  $\text{F}_{\text{CD}}^{90}$  where no significant perturbation of the host electronic structure is observed. This suggests that lower energy F dopant configurations are the ones which least perturb the host valence/conduction bands, creating quite delocalised defect electronic structures. The EDOS of  $\text{F}_{\text{far}}$  is also shown in Fig. 3.30 (d) to



examine the effect of dopant separation. In this case, a shoulder of Sn 5*s*, O 2*p* and F 2*p* character can be seen at the bottom of the VB, which may be the reason for the higher energy of  $F_{\text{far}}$  compared to  $F_{\text{CD}}^{90}$ . However, this shoulder is less intense than that of  $F_{\text{DD}}^{180}$ , thus providing an explanation for the lower energy of  $F_{\text{far}}$  relative to  $F_{\text{DD}}^{180}$ .

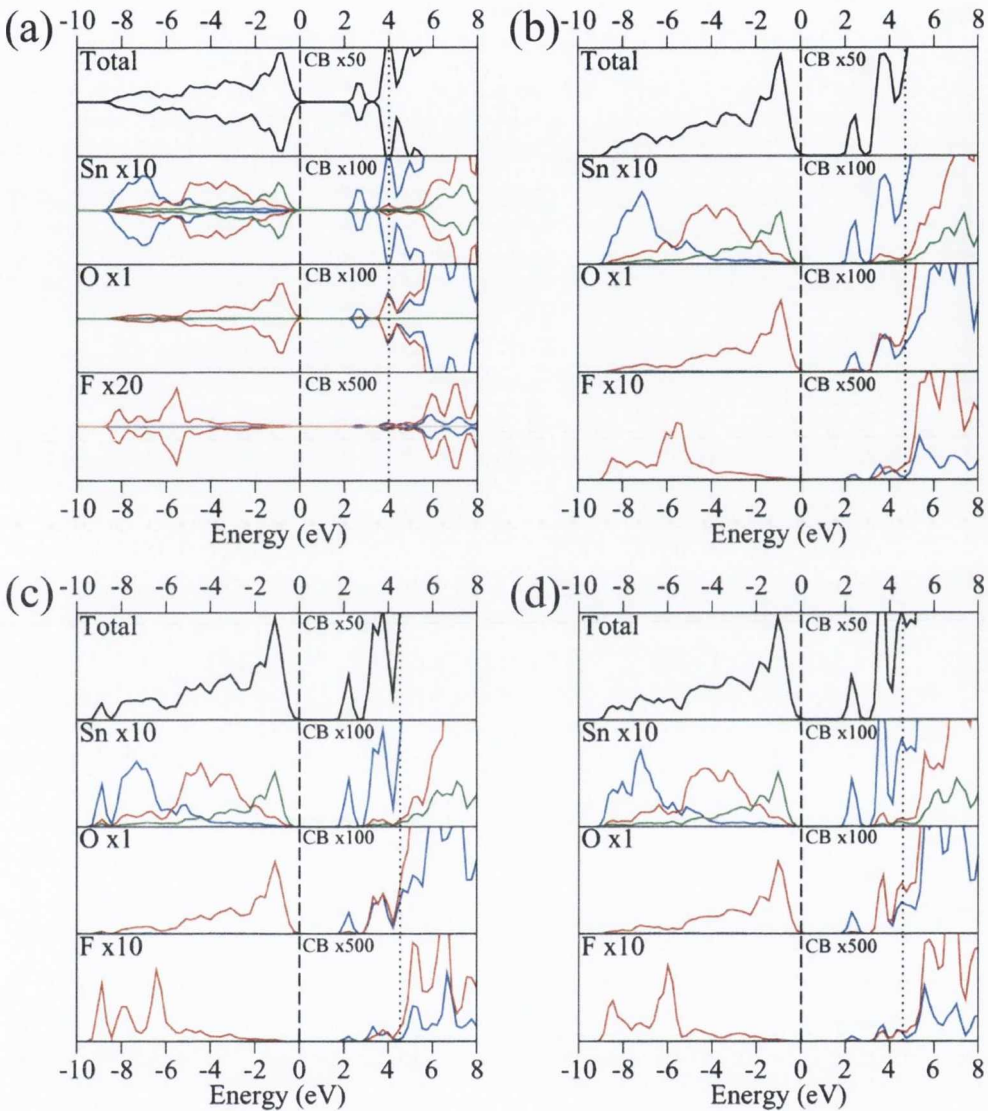


Fig. 3.30 Total and partial EDOS for (a) single F dopant in 48 atom supercell (b)  $F_{\text{CD}}^{90}$  (c)  $F_{\text{DD}}^{180}$  and (d)  $F_{\text{far}}$ . Dashed line marks VBM and dotted line indicates highest occupied state. Blue lines are *s*, red are *p* and green are *d* states.

Further information about the defect localisation can be gleaned from the partial charge densities shown in Fig. 3.31. The partial charge of the highest occupied state at the  $\Gamma$ -point of the Brillouin Zone is plotted for the defects selected above. In each case, the charge is quite delocalised, over O and F 2*p* states and Sn 5*s* states. The tin atoms neighbouring the fluorine dopants possess slightly greater charge density which is oriented in lobes directed towards the dopants. This may be a result of the lower valency of the fluorine, resulting in



a Coulombic attraction of the tin electrons towards the dopants. The fluorine anions appear to have lower charge densities relative to the oxygen ions. To analyse the charge density further, the Bader charges for each defect state are presented in Table 3.16. In all cases 72-73% of the charge is on tin atoms, indicating that the excess electrons delocalise over states of mainly tin character. The tin ions neighbouring the dopants have slightly greater charge density. On average, the tin ions have 4% of the charge each, while the nearest neighbour tin ions can have up to 8% of the charge. The defects in which the charge is more localised on the nearest neighbour tin ions ( $F_{DD}^{180}$ ,  $F_{DD}^{79}$ ,  $F_{DD}^{101}$ ) are higher in energy than the more delocalised defects. The most stable defects are those which least perturb the host electronic structure and have more delocalised defect states.

|                                 | $F_{tot}$ | $Sn_{tot}$ | $O_{tot}$ | $Sn_{nn}$                      |
|---------------------------------|-----------|------------|-----------|--------------------------------|
| <b>single F</b>                 | 0.01      | 0.72       | 0.27      | $2 \times 0.06$                |
| <b><math>F_{CC}(180)</math></b> | 0.01      | 0.72       | 0.26      | $4 \times 0.05$                |
| <b><math>F_{CD}(90)</math></b>  | 0.01      | 0.72       | 0.26      | $2 \times 0.06, 0.07, 0.05$    |
| <b><math>F_{DD}(180)</math></b> | 0.01      | 0.72       | 0.27      | $2 \times 0.07$                |
| <b><math>F_{DD}(79)</math></b>  | 0.02      | 0.72       | 0.26      | $2 \times 0.08$                |
| <b><math>F_{DD}(101)</math></b> | 0.02      | 0.72       | 0.26      | $2 \times 0.07, 2 \times 0.05$ |
| <b><math>F_{far}</math></b>     | 0.01      | 0.73       | 0.26      | $4 \times 0.05$                |

Table 3.16 Bader charges (in%) associated with highest occupied states at the  $\Gamma$ -point of Brillouin Zone for various doping configurations of F doped  $SnO_2$ .  $F_{tot}$ ,  $Sn_{tot}$  and  $O_{tot}$  are total F, Sn and O charges and  $Sn_{nn}$  is charge on nearest neighbour tin cations.

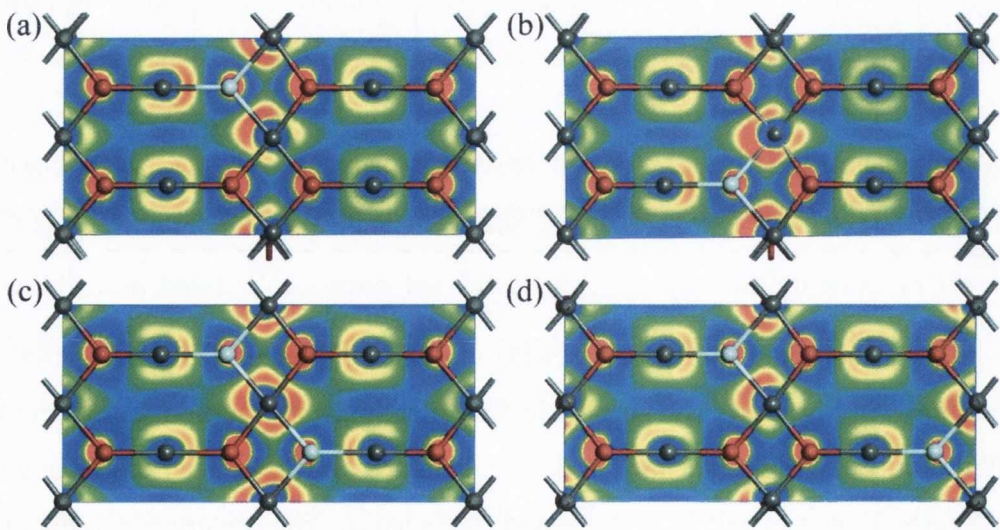


Fig. 3.31 Partial charge density for highest occupied states at  $\Gamma$ -point of Brillouin Zone of (a) single F dopant, (b)  $F_{CD}^{90}$ , (c)  $F_{DD}^{180}$  and (d)  $F_{far}$ , plotted between isolevels of 0 (blue) and  $0.02 \text{ e}/\text{\AA}^3$  (red). Grey atoms are Sn, red are O and green are F.

### 3.5.4.4 Chlorine

Cl<sup>-</sup> has a much larger ionic radius (1.67 Å) than O<sup>2-</sup> (1.22 Å). <sup>261</sup> Cl doping was thus found to introduce large structural changes, with the Sn-Cl bond lengths being much larger than the Sn-O bond lengths of bulk SnO<sub>2</sub>. When a single dopant is substituted in the 48 atom supercell, the Sn-Cl bond lengths relax to 2.31 Å and 2 × 2.37 Å, which are 0.25 Å and 0.31 Å longer than bulk Sn-O bond lengths. These are, by far, the largest structural changes induced by any of the studied dopants. When a second dopant is added to the cell, bond lengths vary between 2.15 Å in Cl<sub>CC</sub><sup>180</sup> and 2.65 Å in Cl<sub>CD</sub><sup>90</sup>. The large structural distortion induced by Cl may partially account for its high formation energies.

The EDOS for Cl doped SnO<sub>2</sub> are shown in Fig. 3.32. Only the single dopant and the lowest energy doubly doped configuration, Cl<sub>DD</sub><sup>101</sup>, are shown, as the results are similar for all other configurations. Singly doping the supercell does not result in any major changes to the electronic structure. The extra electron fills the Sn 5s states at the bottom of the conduction band, resulting in metallic conductivity. The Cl 3p states are spread across the entire valence band and do not contribute significantly to the conduction band states. With the addition of a second Cl to the system, two electrons are now available for conduction. These electrons occupy the Sn 5s states at the bottom of the conduction band. An extra defect state is also visible at the bottom of the valence band, of mixed Sn 5s, Cl 3p and O 2p character. This state is not dissimilar to the defect states seen for F<sub>DD</sub><sup>180</sup> and F<sub>far</sub>, indicating a similarity in electronic structure between F doped and Cl doped SnO<sub>2</sub>.

Fig. 3.33 displays the partial charge densities for the highest occupied state at the  $\Gamma$ -point of the Brillouin Zone. Only selected dopant configurations are shown; as for F doping, we have chosen the lowest and highest energy configurations (Cl<sub>DD</sub><sup>101</sup> and Cl<sub>CC</sub><sup>180</sup>) as well as Cl<sub>far</sub> and the singly doped supercell. In each case, the charge is delocalised over Sn, O and Cl states, with greater charge density present on the Sn atoms neighbouring the Cl dopants. Cl<sub>DD</sub><sup>101</sup> appears to be the most localised defect, which may be the reason that it is lowest in energy. The higher energy Cl<sub>CC</sub><sup>180</sup> shows a high degree of delocalisation. As further evidence of the nature of these defect states, their Bader charges are tabulated in Table 3.17. For each defect, 69-71% of the charge comes from Sn states and only 1-5% is from Cl states.

In all cases, the charges on the nearest neighbour Sn cations are slightly greater than the charges further from the defect, though there is little difference between the nearest neighbour charges of the different configurations. It thus appears that the large geometrical



distortion is the most likely reason for the high formation energies of Cl defects, as the electronic structure bears similarity to that produced upon F doping.

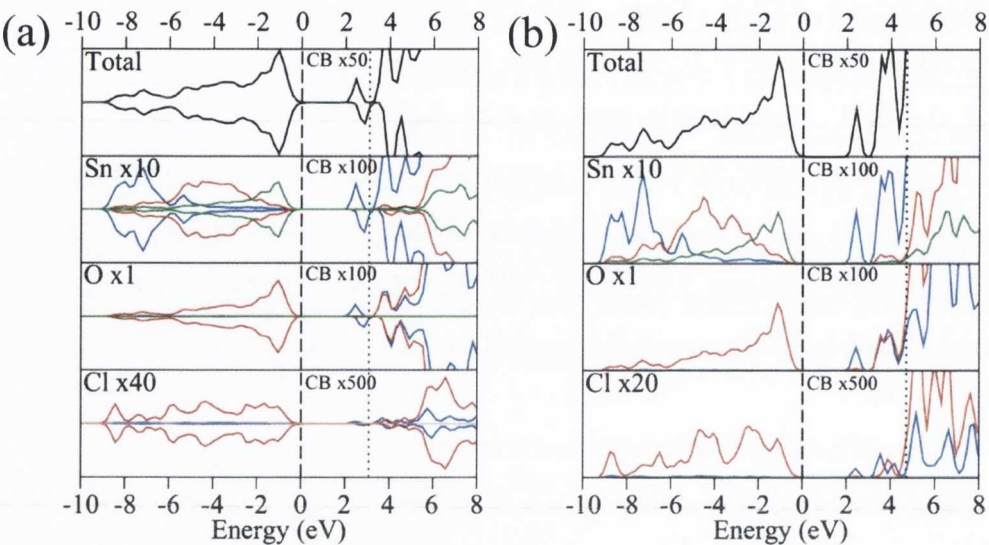


Fig. 3.32 EDOS/PEDOS for (a) single Cl dopant in 48 atom supercell and (b)  $\text{Cl}_{\text{DD}}^{101}$ , with dashed line indicating VBM and dotted line marking highest occupied state. Blue lines are *s* states, red are *p* and green are *d* states.

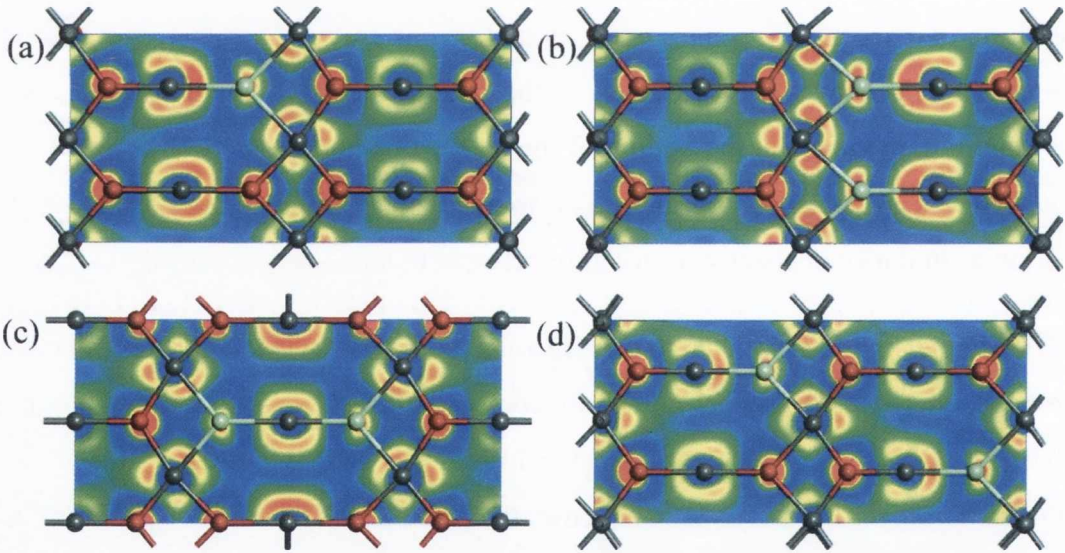


Fig. 3.33 Partial charge density of the highest occupied state at the  $\Gamma$ -point of the Brillouin Zone for (a) single Cl (b)  $\text{Cl}_{\text{DD}}^{101}$  (c)  $\text{Cl}_{\text{CC}}^{180}$  and (d)  $\text{Cl}_{\text{far}}$ , plotted between isolevels of 0 (blue) and  $0.02 \text{ e}/\text{\AA}^3$  (red). Grey atoms are Sn, red are O and green are Cl.

### 3.5.5 Intrinsic-Extrinsic Interactions

One possible mechanism for the lowering of extrinsic defect formation energies is the formation of defect clusters involving both intrinsic and extrinsic defects. In ITO, Sn dopants have previously been found to be stabilised by intrinsic oxygen vacancies and In



|                             | Cl <sub>tot</sub> | Sn <sub>tot</sub> | O <sub>tot</sub> | Sn <sub>nn</sub>   |
|-----------------------------|-------------------|-------------------|------------------|--------------------|
| <b>single Cl</b>            | 0.01              | 0.72              | 0.27             | 3 × 0.05           |
| <b>Cl<sub>CC</sub>(180)</b> | 0.02              | 0.71              | 0.27             | 4 × 0.05           |
| <b>Cl<sub>CD</sub>(90)</b>  | 0.03              | 0.69              | 0.28             | 0.11, 4 × 0.04     |
| <b>Cl<sub>DD</sub>(180)</b> | 0.05              | 0.70              | 0.26             | 2 × 0.05, 2 × 0.04 |
| <b>Cl<sub>DD</sub>(79)</b>  | 0.02              | 0.71              | 0.27             | 2 × 0.05, 2 × 0.04 |
| <b>Cl<sub>DD</sub>(101)</b> | 0.03              | 0.71              | 0.26             | 4 × 0.06           |
| <b>Cl<sub>far</sub></b>     | 0.02              | 0.71              | 0.26             | 6 × 0.04           |

Table 3.17 Bader charges (in%) for Cl doping of SnO<sub>2</sub> showing total charge of Cl, (Cl<sub>tot</sub>) Sn (Sn<sub>tot</sub>) and O (O<sub>tot</sub>) and charge on tin ions nearest neighbour to Cl (Sn<sub>nn</sub>).

interstitials, which have the effect of lowering the dopant energies and creating shallower donor levels.<sup>308</sup> As a test of the effect of this clustering in SnO<sub>2</sub>, we have considered defect clusters made up of Sb and an oxygen vacancy ((Sb<sub>Sn</sub> + V<sub>O</sub>)<sup>×</sup>), and fluorine and an oxygen vacancy ((F<sub>O</sub> + V<sub>O</sub>)<sup>×</sup>).

The formation energies of these two defect clusters are shown in Table 3.18, compared to the formation energies of combined isolated defects. Both defects have lower formation energies when clustered compared to isolated. This suggests a tendency of intrinsic oxygen vacancies to occur neighbouring dopant ions. The clustering of Sb dopants and oxygen vacancies has already been suggested, based on EXAFS findings that Sb had an average coordination number of ~5.<sup>260</sup> The cluster binding energy is lower for (F<sub>O</sub> + V<sub>O</sub>)<sup>×</sup> (0.15 eV), compared to the higher binding energy of 1.01 eV for (Sb<sub>Sn</sub> + V<sub>O</sub>)<sup>×</sup>. This suggests a greater tendency of the defects to cluster in ATO compared to fluorine tin oxide.

To examine the electronic structure of these defects, the electronic densities of states for (Sb<sub>Sn</sub> + V<sub>O</sub>)<sup>×</sup> and (F<sub>O</sub> + V<sub>O</sub>)<sup>×</sup> are shown in Fig. 3.34. For (Sb<sub>Sn</sub> + V<sub>O</sub>)<sup>×</sup>, two defect states are present in the band gap. The first (Band I) is doubly occupied and occurs ~1 eV above the VBM and is made up of mainly Sb 5s states. This state occurs in a similar position to that found for oxygen vacancies. A second singly occupied defect state (Band II) occurs at the CBM and is made up of mainly Sb 5s character mixed with a small amount of Sn 5s character. The position of this state is similar to that found for isolated Sb dopants. For (F<sub>O</sub> + V<sub>O</sub>)<sup>×</sup>, two defect states are also seen in the band gap. The lower energy doubly occupied state (Band I) is of mainly Sn 5s character and occurs ~1 eV above the VBM, suggesting it to be associated with the oxygen vacancy. The higher energy singly occupied

state (Band II) occurs at the CBM and is of mainly Sn 5s character.

|                                                          | Cluster |        | Isolated |        |
|----------------------------------------------------------|---------|--------|----------|--------|
|                                                          | O-rich  | O-poor | O-rich   | O-poor |
| $(\text{Sb}_{\text{Sn}} + \text{V}_{\text{O}})^{\times}$ | 5.00    | 2.55   | 6.01     | 3.56   |
| $(\text{F}_{\text{O}} + \text{V}_{\text{O}})^{\times}$   | 6.57    | 2.98   | 6.72     | 3.12   |

Table 3.18 Formation energies (in eV) for selected defect clusters, compared to the energies calculated from the equivalent isolated defects at both O-rich and O-poor conditions.

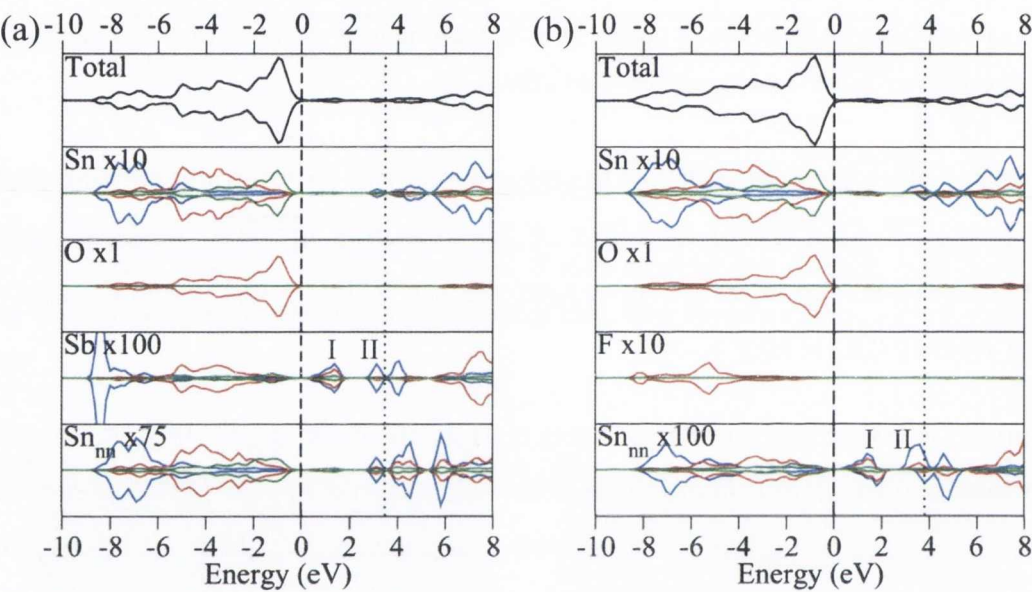


Fig. 3.34 EDOS/EDOS for (a)  $(\text{Sb}_{\text{Sn}} + \text{V}_{\text{O}})^{\times}$  and (b)  $(\text{F}_{\text{O}} + \text{V}_{\text{O}})^{\times}$ , with VBM marked by dashed line and highest occupied state by dotted line. Roman numerals mark the defect states. Blue lines are *s* states, red are *p* states and green are *d* states.

To elucidate the nature of the band gap states further, the partial charge densities for both  $(\text{Sb}_{\text{Sn}} + \text{V}_{\text{O}})^{\times}$  and  $(\text{F}_{\text{O}} + \text{V}_{\text{O}})^{\times}$  are shown in Fig. 3.35. Band I appears similar to the oxygen vacancy partial charge density for both defects. However, rather than the charge being evenly distributed across the vacancy site, the charge partially localises in a lobe on the Sb ion, directed towards the vacancy for  $(\text{Sb}_{\text{Sn}} + \text{V}_{\text{O}})^{\times}$  and on the Sn neighbour to the F for  $(\text{F}_{\text{O}} + \text{V}_{\text{O}})^{\times}$ . Band II localises on the Sb for  $(\text{Sb}_{\text{Sn}} + \text{V}_{\text{O}})^{\times}$  and on one Sn for  $(\text{F}_{\text{O}} + \text{V}_{\text{O}})^{\times}$ . These charge densities are suggestive of trapping of charge at the defect centre. The Bader charges associated with each of the defect states are shown in Table 3.19. For  $(\text{Sb}_{\text{Sn}} + \text{V}_{\text{O}})^{\times}$ , Band I has a significant proportion of the charge localised on the Sb ion, with zero charge on the two other nearest neighbour tin ions. Band II is less localised, with 0.62*e* of the charge split between the Sb and the nearest neighbour tin cations. In  $(\text{F}_{\text{O}} +$



$V_O)^{\times}$ , Band I is quite localised on the nearest neighbour tin ion bonded to the fluorine, with very little charge on the other two nearest neighbour tin ions. Again, Band II is less localised, with only  $0.35e$  on the three nearest neighbour tin ions.

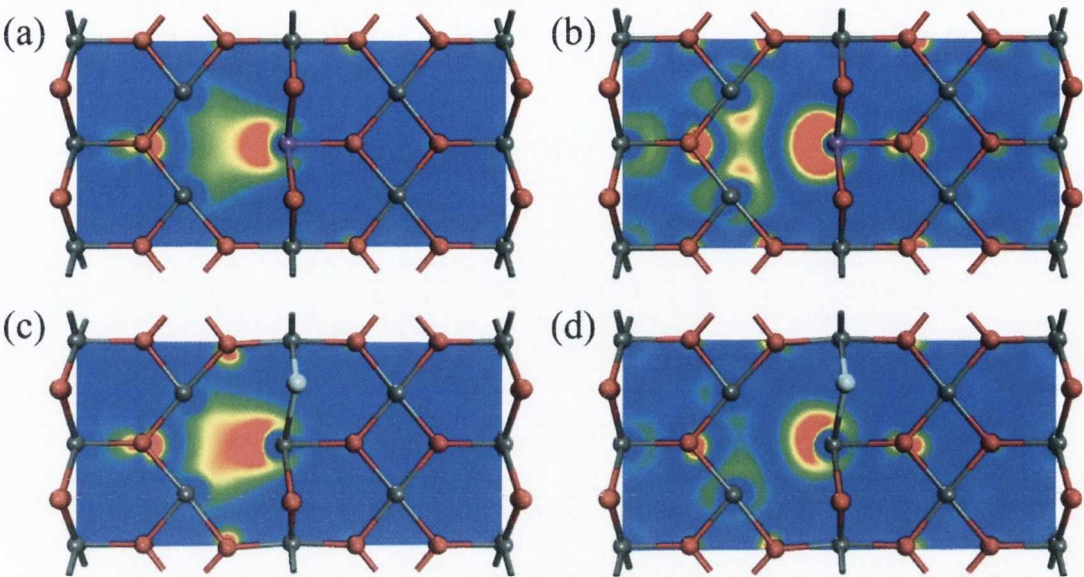


Fig. 3.35 Partial charge densities for defect states of  $(Sb_{Sn} + V_O)^{\times}$  and  $(F_O + V_O)^{\times}$ . (a) shows Band I of  $(Sb_{Sn} + V_O)^{\times}$  plotted from 0 (blue) to  $0.1\text{ e}/\text{\AA}^3$  (red), (b) shows Band II of  $(Sb_{Sn} + V_O)^{\times}$  between 0 (blue) and  $0.05\text{ e}/\text{\AA}^3$  (red), (c) is Band I of  $(F_O + V_O)^{\times}$  from 0 (blue) to  $0.1\text{ e}/\text{\AA}^3$  (red) and (d) shows Band II of  $(F_O + V_O)^{\times}$  from 0 (blue) and  $0.05\text{ e}/\text{\AA}^3$  (red). Grey atoms are Sn, red are O, pink are Sb and green are F.

|                   | $(Sb_{Sn} + V_O)^{\times}$ |                 | $(F_O + V_O)^{\times}$ |                  |
|-------------------|----------------------------|-----------------|------------------------|------------------|
|                   | Band I                     | Band II         | Band I                 | Band II          |
| Sb                | 0.75                       | 0.32            | -                      | -                |
| Sn <sub>nn</sub>  | $2 \times 0.00$            | $2 \times 0.15$ | 0.95, 0.01, 0.00       | 0.23, 0.04, 0.08 |
| Sn <sub>tot</sub> | 0.22                       | 0.91            | 0.98                   | 0.65             |
| O <sub>tot</sub>  | 1.03                       | 0.78            | 0.98                   | 0.34             |
| F                 | -                          | -               | 0.04                   | 0.02             |

Table 3.19 Bader charges (in  $e$ ) for defect states of  $(Sb_{Sn} + V_O)^{\times}$  and  $(F_O + V_O)^{\times}$  in  $SnO_2$  showing charges on nearest neighbour Sn ( $Sn_{nn}$ ), total Sn charge ( $Sn_{tot}$ ) and total O charge ( $O_{tot}$ ).

To investigate whether any of the cations in these clusters have been reduced, the total Bader charges for  $(Sb_{Sn} + V_O)^{\times}$  and  $(F_O + V_O)^{\times}$  are shown in Table 3.20. In the antimony-vacancy cluster, the antimony exhibits a significant reduction from its  $+5.00e$  charge state in  $Sb_2O_5$  to  $3.59e$  in the defect cluster. While this is higher than the Sb(III) charge in  $Sb_2O_3$ , it does suggest that the Sb has been reduced significantly. The nearest neighbour tin ions also experience a slight reduction from bulk Sn(IV), though neither has been reduced



to Sn(II). In the case of  $(F_O + V_O)^\times$ , one nearest neighbour Sn has been reduced to a significant extent ( $1.75e$ ), though it possesses a higher oxidation state than Sn(II). The other two Sn neighbours similarly experience some reduction.

|                                | Sb   | Sn <sub>av</sub> | Sn <sub>nn</sub> |
|--------------------------------|------|------------------|------------------|
| $(Sb_{Sn} + V_O)^\times$       | 3.59 | 2.64             | $2 \times 2.35$  |
| $(F_O + V_O)^\times$           | -    | 2.64             | 1.75, 2.27, 2.38 |
| Sb <sub>2</sub> O <sub>3</sub> | 2.99 | -                | -                |
| SnO                            | -    | 1.34             | -                |
| SnO <sub>2</sub>               | -    | 2.70             | -                |

Table 3.20 Total Bader charges (in  $e$ ) for Sb, average Sn ( $Sn_{av}$ ) and Sn nearest neighbour to vacancy ( $Sn_{nn}$ ) for vacancy-dopant clusters in SnO<sub>2</sub> compared with their average charges in bulk Sb<sub>2</sub>O<sub>3</sub>, SnO and SnO<sub>2</sub>.

The overall picture that emerges from this analysis is that the clustering of a dopant neighbouring an oxygen vacancy will result in the trapping of charge at the defect centre, and the subsequent loss of conductivity. The fact that these types of defect clusters are more stable than their isolated alternatives, suggests that they will readily form in doped SnO<sub>2</sub>, thereby reducing the electron mobility. This may explain the experimental finding of a doping limit in Sb:SnO<sub>2</sub> and F:SnO<sub>2</sub> after which the conductivity begins to decrease with subsequent addition of dopant.<sup>253, 265</sup>

### 3.5.6 Co-doping with Sb and F

One method of increasing the conductivity of doped SnO<sub>2</sub> is co-doping with two or more elements. We have thus tested the effect of the clustering of Sb and F dopants, as this has previously been suggested as a method of enhancing the conductivity compared with the doping of Sb or F alone.<sup>246, 285, 287, 301</sup> A dopant cluster involving Sb and F was found to have a formation energy of 3.23 eV under oxygen-rich conditions, compared to a 3.62 eV value for combined, isolated defects. At oxygen-poor conditions, the energies change to 2.06 eV and 2.45 eV for the clustered and isolated defects, respectively. This indicates that there is a stabilisation effect provided by the clustering of the two dopants.

The EDOS for  $(Sb_{Sn} + F_O)^\times$  is shown in Fig. 3.36 (a). A defect state is present at the bottom of the conduction band, made up of mainly Sb 5s states. The partial charge density of this state is shown in Fig. 3.36 (b) and shows the state to be localised mainly on the Sb,

with a small amount of charge on nearby oxygen ions and on the fluorine. Bader charge analysis indicates a Sb charge of  $4.09e$ , lower than the charge of Sb(V), though the antimony is not fully reduced to Sb(III). The charge is higher than that in the  $(\text{Sb}_{\text{Sn}} + \text{V}_{\text{O}})^{\times}$  system, suggesting a lesser degree of reduction. In the defect state,  $0.46e$  of the charge is on the Sb, while only  $0.03e$  is on F. The five nearest neighbour oxygen ions share  $0.71e$  of the charge. This indicates a high degree of localisation of the defect state, suggesting a high conduction activation energy. This suggests that co-doping with Sb and F in high concentrations is not a suitable way to enhance conductivity, as the resulting defects are too localised and will hence not be very mobile.

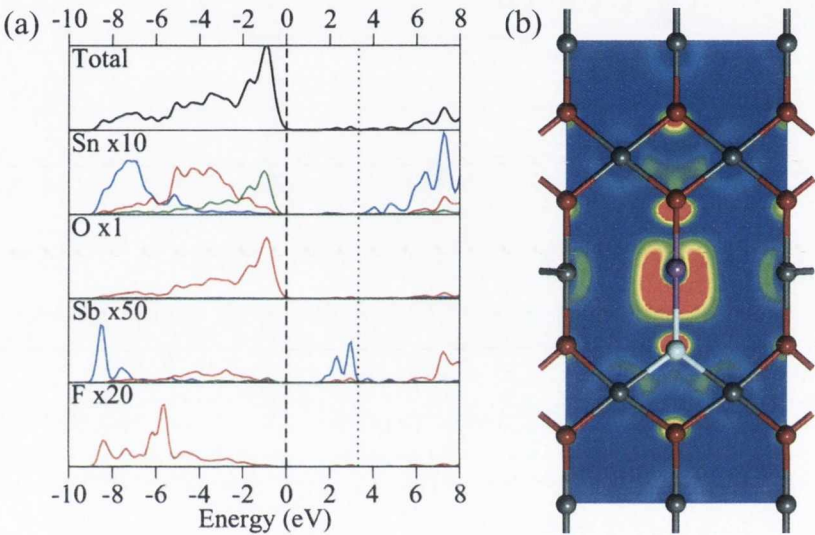


Fig. 3.36 (a) EDOS/PEDOS for  $(\text{Sb}_{\text{Sn}} + \text{F}_{\text{O}})^{\times}$  with dashed line marking VBM and dotted line showing position of highest occupied state. Red lines are  $p$  states, blue are  $s$  states and green are  $d$  states. (b) Partial charge density of highest occupied state at  $\Gamma$ -point of Brillouin Zone for  $(\text{Sb}_{\text{Sn}} + \text{F}_{\text{O}})^{\times}$  plotted between 0 (blue) and  $0.05 \text{ e}/\text{\AA}^3$  (red).

### 3.5.7 Hydrogen Doping

Hydrogen impurities have previously been suggested to be the cause of shallow donor levels seen in undoped  $\text{SnO}_2$ .<sup>67</sup> To investigate this possibility, we have performed calculations of hydrogen in the two doping modes suggested previously: at an interstitial position and substitutionally for oxygen. As a chemical potential limit, we have used the formation energy of water, calculated to be  $-2.64 \text{ eV}$ . This leads to the limits  $(\mu_{\text{Sn}}, \mu_{\text{O}}, \mu_{\text{H}}) = (-5.25 \text{ eV}, 0 \text{ eV}, -1.32 \text{ eV})$  at oxygen-rich conditions and  $(0 \text{ eV}, -2.63 \text{ eV}, -0.01 \text{ eV})$  under oxygen-poor conditions.

The formation energies for these dopants are shown in Table 3.21. Under both chemical



potential limits, hydrogen interstitials are the most stable defect. The formation energy of substitutional hydrogen is lower under O-poor conditions, however, it still has a higher energy than the interstitial formation energy of 1.37 eV. Hydrogen will thus insert preferably as interstitials, in agreement with the calculations of Singh *et al.*<sup>67</sup> The low energy of formation of hydrogen interstitials suggests that they will form easily in SnO<sub>2</sub>, whether introduced accidentally or through doping.

|                    | O-rich | O-poor |
|--------------------|--------|--------|
| $H_i^\bullet + e'$ | 2.68   | 1.37   |
| $H_o^\bullet + e'$ | 6.32   | 2.38   |

Table 3.21 Formation energies (in eV) of hydrogen defects in SnO<sub>2</sub> under oxygen-rich and oxygen-poor chemical potential limits.

The relaxed geometries for both doping modes are shown in Fig. 3.37. The interstitial relaxes towards one oxygen, giving an O-H bond length of 0.99 Å. The three Sn nearest to the hydrogen relax away resulting in longer Sn-O bond lengths of 2.18 Å, and 2 × 2.20 Å. When hydrogen is substituted for oxygen, the three nearest neighbour Sn ions relax away from the defect, giving one long Sn-H bond length of 2.17 Å and two shorter bond lengths of 2.07 Å. Thus, H doping induces only small structural changes, lengthening bond lengths by 0.01-0.14 Å compared to Sn-O.

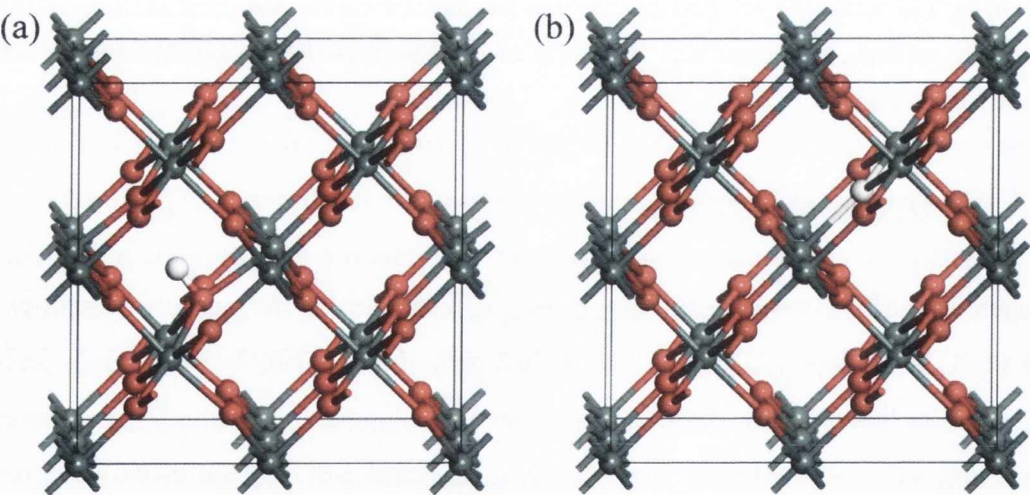


Fig. 3.37 Structure of (a)  $H_i^\bullet + e'$  and (b)  $H_o^\bullet + e'$  in SnO<sub>2</sub> with tin atoms in grey, oxygen in red and hydrogen in white.

Fig. 3.38 shows the EDOS for H doped SnO<sub>2</sub>. Both interstitial and substitutional hydrogen result in defect states which are merged with the bottom of the conduction band. These



states are of mainly Sn 5s character, mixed with a small amount of O 2p states. The partial charge densities of the highest occupied state at the  $\Gamma$ -point of the Brillouin Zone are shown in Fig. 3.39. In both cases, the electron density is quite delocalised.  $H_i^\bullet + e'$  has a partial charge density similar to bulk  $\text{SnO}_2$ , with the charge delocalised over Sn and O states and no charge on the interstitial hydrogen. In the case of  $H_o^\bullet + e'$ , significant electron density is seen on the hydrogen site and the three nearest neighbour tin ions show lone pair like lobes, suggestive of reduction.

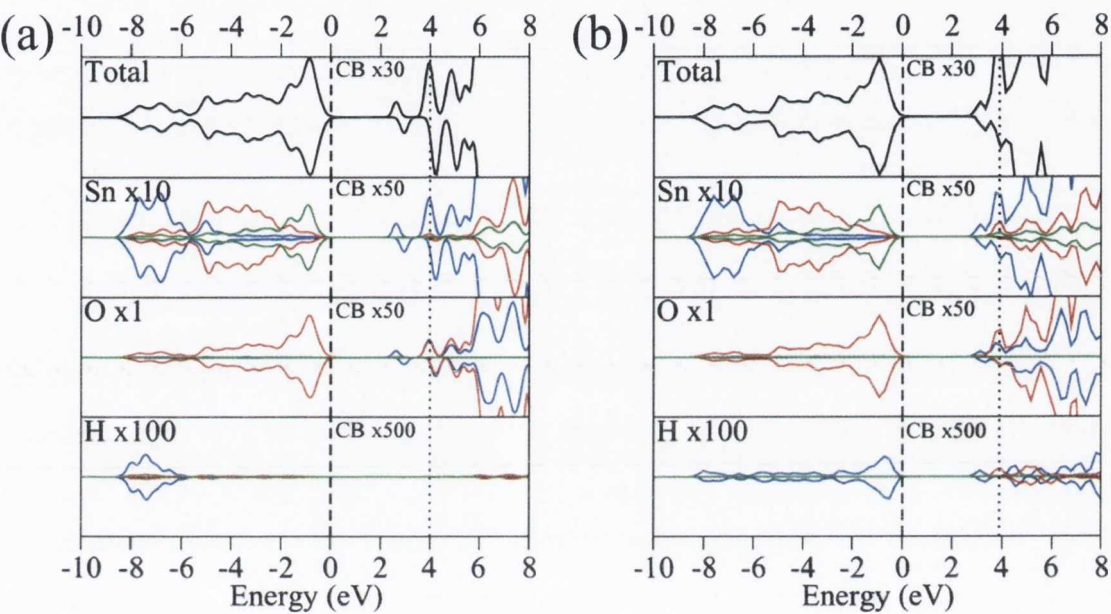


Fig. 3.38 EDOS/PEDOS for (a)  $H_i^\bullet + e'$  and (b)  $H_o^\bullet + e'$ , with dashed line marking VBM and dotted line indicating highest occupied state. Blue lines are *s* states, red are *p* states and green are *d* states.

Bader charge analysis of  $H_i^\bullet + e'$  shows the hydrogen to have a charge of  $+0.63e$ , while a delocalised reduction of the tin ions is suggested by a lower average tin charge of  $2.64e$ , compared to the  $2.67e$  charge in stoichiometric  $\text{SnO}_2$ . The oxygen ion nearest neighbour to the hydrogen experiences an increase in charge density to  $-1.68e$ , compared to  $-1.34e$  in bulk  $\text{SnO}_2$ , suggesting it to have increased ionicity. For  $H_o^\bullet + e'$ , the hydrogen is negatively charged, with a calculated Bader charge of  $-0.49e$ . The three tin ions nearest neighbour to the defect also experience a reduction – two to  $2.43e$  and the third to  $2.49e$ . The total reduction on these three tin ions is  $0.67e$ , which is similar to the charge expected for a single electron reduction of tin ( $0.67e$ ). This indicates that the extra electron provided upon hydrogen substitution delocalises over these three tin ions, giving a defect structure of  $H_o^\bullet + \text{Sn}'_{\text{Sn}}$ . Thus, the substitutional hydrogen has a much more localised defect state than interstitial hydrogen, suggesting that the mobility of electrons for the interstitial may be higher.

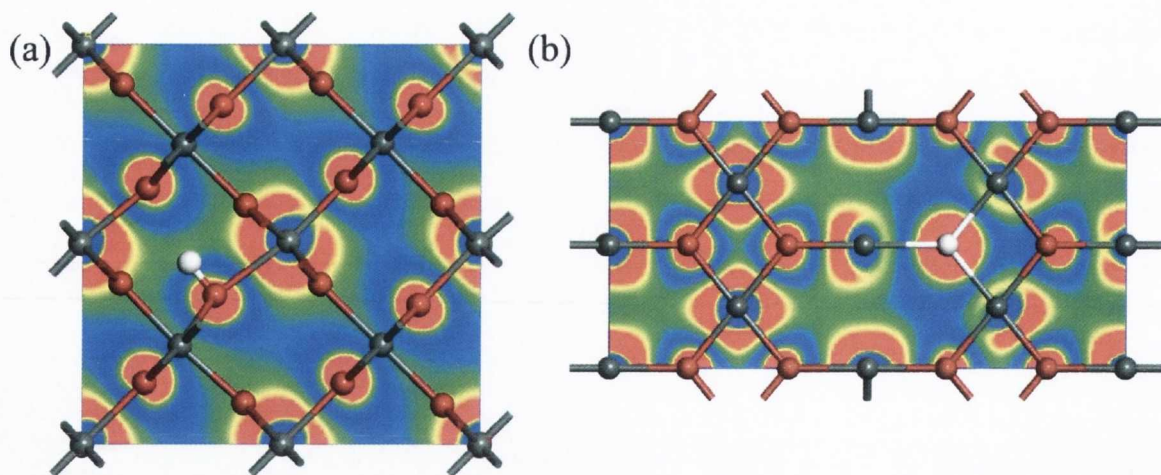


Fig. 3.39 Partial charge densities of highest occupied state at  $\Gamma$ -point of Brillouin Zone for (a)  $H_1^* + e'$  and (b)  $H_0^* + e'$  plotted at isolevels between 0 (blue) and  $0.01 \text{ e}/\text{\AA}^3$  (red). Grey atoms are Sn, red are O and white are H.

### 3.5.8 Discussion

Sb and F dopants in  $\text{SnO}_2$  were both found to be more energetically favourable than either Bi or Cl. This helps to explain why antimony tin oxide and fluorine tin oxide are successful TCOs, while Bi and Cl are poor dopants in tin dioxide. To investigate further the reasons for the relatively poor performance of Bi and Cl doped  $\text{SnO}_2$ , we also examined their electronic structures. While Cl resulted in a similar electronic structure to that of FTO, the electronic structures of Bi and Sb doped  $\text{SnO}_2$  differed significantly. Both Bi and Sb result in a defect state of Bi/Sb  $s$  character at the bottom of the valence band. While the Sb  $5s$  states mix significantly with the Sn  $5s$  and O  $2p$  states, the Bi  $6s$  state occurs at too low an energy to mix to the same extent. The Bi  $6s$  states at the bottom of the CBM similarly show very little mixing with Sn  $5s$  states, while the CBM states for Sb doping are of mixed Sb  $5s$  and Sn  $5s$  character. This results in the Sb defect states being much more delocalised than the Bi states, which are extremely localised on the Bi and its nearest oxygen neighbours. The greater localisation surrounding a Bi dopant is likely to be detrimental to conductivity as it will raise the conduction activation energy, thereby resulting in low electron mobilities in Bi doped  $\text{SnO}_2$ .

The reasons why Cl doping is not viable become clear immediately upon examining the defect formation energies. Cl dopants were found to have very high energies of formation, suggesting that high levels of doping are not achievable. While F, Sb and Bi induce very little structural change into the host lattice, the introduction of Cl was found to result in large deviations from bulk  $\text{SnO}_2$  bond lengths, thereby explaining why the formation



energies are so high. Indeed, comparing the anionic radii of  $F^-$  (1.16 Å),  $Cl^-$  (1.67 Å) and  $O^{2-}$  (1.22 Å), demonstrates that the ionic radius of Cl is too large to comfortably fit into the  $SnO_2$  lattice. As far as electronic structure is concerned, both F and Cl result in defect levels near the conduction band which are very delocalised. In fact, there is little difference between the electronic structures of F and Cl doped  $SnO_2$ . Thus, while electronic structure factors dictate the difference in conductivity between Sb and Bi doped  $SnO_2$ , F and Cl doped  $SnO_2$  are distinguishable purely based on energetic and geometrical constraints.

FTO is well known to be a much better conductor than ATO.<sup>309</sup> Our calculations demonstrate that fluorine has lower doping energies than antimony, which may partially explain the lower conductivities of FTO. Comparing the electronic structures of the two dopant systems, the defect states in ATO partially localise on the antimony cations, thereby perturbing the host electronic structure. In FTO, there is very little contribution from the fluorine anions to the defect state, and the electron density is delocalised over Sn 5s and O 2p states, with little perturbation of the host electronic structure. Thus, while in ATO, there is a partial trapping of the charge at antimony ions which inhibits conductivity, FTO has no charge traps and can result in higher levels of conductivity.

Although the clustering of F and Sb dopants with oxygen vacancies was found to be energetically favourable, the formation of these defect clusters will act to inhibit conductivity. The reason for this is that both clusters trap electrons at the vacancy site. In the case of Sb, a reduction towards Sb(III) is seen, while F doping induces a localised Sn(II) reduction at the vacancy site. In each case, all three electrons provided by the defect are trapped by the vacancy and the surrounding cations, thereby acting to reduce the number of electrons available for conductivity. However, it was found that the binding energy of F dopants with O vacancies was much lower than that of Sb dopants with vacancies. Thus, the lower tendency of dopants to cluster with vacancies in FTO may explain its higher conductivity compared to ATO.

Although there is experimental evidence that co-doping with F and Sb results in higher levels of conductivity, our calculations have shown that there will be a limit on the amount of achievable co-doping, imposed by the formation of F-Sb clusters. These are more energetically favourable than their combined isolated dopants, suggesting that they will form easily in co-doped  $SnO_2$ . Placing a fluorine next to Sb results in a reduction of the Sb, so that the two electrons provided by the defect end up localised at the defect site. Similar to the clustering of dopants with oxygen vacancies, lower mobilities will result due to the



trapping of the available conduction electrons.

We have tested the effect of hydrogen defects on the electronic structure of  $\text{SnO}_2$  by performing calculations of substitutional and interstitial defects. The results indicate that hydrogen interstitials are lower in energy than substitutionals, although both are likely to contribute to conductivity. The introduction of hydrogen results in states at the bottom of the conduction band which possess a high degree of delocalisation, suggestive of a band-like conduction mechanism. Hydrogen has previously been suggested to be the origin of shallow donor levels which are thought to be the cause of conduction in undoped  $\text{SnO}_2$ .<sup>67-68, 303</sup> Our results suggest that hydrogen impurities may be the cause of these intrinsic shallow donor levels, though without an analysis of the charge transition levels, we cannot determine the exact nature of these levels. From our results, we can suggest a second possible origin for these levels. As  $\text{SnCl}_2$  and  $\text{SnCl}_4$  are very often used as precursors for  $\text{SnO}_2$  thin films, it may be that Cl impurities induce shallow levels, thereby resulting in *n*-type conductivity. The location of our defect states at the bottom of the conduction band certainly suggests that Cl may have shallow donor levels, though a complete analysis would require the evaluation of its charge transition levels.

### 3.6 Conclusions

By examining the intrinsic defects of  $\text{SnO}_2$  using both GGA and HSE06 functionals, we conclude that there is no intrinsic mechanism by which shallow donor levels can be introduced into tin dioxide. Oxygen vacancies were found to be the lowest energy defect but have deep donor levels, and although tin interstitials possess shallow levels, their formation energies are too high. We thus conclude that any *intrinsic* conductivity present in  $\text{SnO}_2$  must occur through polaronic hopping over oxygen vacancies, with the electrons located in deep levels, 0.5 eV below the CBM.

The shallow experimental donor levels must arise through the presence of impurities. The results of our extrinsic defect study suggest two possible origins: hydrogen or chlorine. Hydrogen is a ubiquitous impurity which may accidentally be introduced during thin film deposition, while the use of  $\text{SnCl}_2$  and  $\text{SnCl}_4$  as precursors also suggests the accidental incorporation of chlorine may play a role.

By comparing Sb with Bi and F with Cl, we conclude that Sb is a much better *n*-type dopant than Bi because of its lower energy and the more delocalised nature of its defect

states. The defect states induced by Bi doping are much too localised to achieve high levels of conductivity, and a polaronic mechanism is likely to dominate in Bi doped tin dioxide. In contrast, the higher conductivity of F doped SnO<sub>2</sub> over Cl doped SnO<sub>2</sub> is purely based on energetics. The large ionic radius of Cl<sup>-</sup> makes it energetically unfavourable to incorporate into the host lattice and its dopant formation energies are high, whereas F<sup>-</sup> has an ionic radius close to that of O<sup>2-</sup>, thereby resulting in higher dopability and higher conductivities.



# Chapter 4: *P*-type Conduction in Cu-based Transparent Conducting Oxides

## 4.2 Summary

In this chapter, the properties of several *p*-type transparent conducting oxides in the ternary copper oxide family are examined. We start by considering the electronic structure and geometry of several copper delafossites ( $\text{CuMO}_2$ ). These were the first *p*-type copper-based TCO materials discovered and although their conductivities remain low, it is of interest to examine their bulk electronic properties to understand the reasons behind *p*-type conductivity in these materials. We have performed a thorough examination of the electronic structure of  $\text{CuAlO}_2$ ,  $\text{CuGaO}_2$ ,  $\text{CuInO}_2$  and  $\text{CuScO}_2$  using both DFT+*U* and hybrid-DFT methods in order to gain understanding of the trends in their experimental conductivities and the influence of the trivalent cation on the electronic structure. The second part of this chapter is dedicated to a detailed defect study of  $\text{SrCu}_2\text{O}_2$  using GGA+*U* calculations.  $\text{SrCu}_2\text{O}_2$  is currently one of the only known *p*-type TCOs with a direct band gap. However, in order for it to be applicable in transparent electronic devices, its conductivity must be significantly improved. By examining the stability and electronic structure of various intrinsic defects, insight into its conduction mechanism can be provided, which will aid in the design of new *p*-type TCOs with improved conductivity.

## 4.3 $\text{CuMO}_2$ (M = Al, Ga, In, Sc): Chemical Bonding and Electronic Structure

### 4.3.1 Introduction

The first copper-based TCO discovered was  $\text{CuAlO}_2$ , a member of the delafossite family of compounds.<sup>14</sup> The delafossite ( $\text{CuMO}_2$ ) structure consists of close-packed layers of Cu atoms which are linearly coordinated to two oxygen atoms to form O-Cu-O dumb-bells parallel to the crystallographic *c*-axis (Fig. 4.1). Each oxygen also coordinates to three M(III) ions, forming layers of metal-centred  $\text{MO}_6$  octahedra parallel to the *ab*-plane. Depending on the packing of the Cu cations, the delafossite structure can have either an

ABAB packed hexagonal (space group  $P6_3/mmc$ ) unit cell or an ABCABC packed rhombohedral (space group  $R3-mh$ ) unit cell.<sup>310</sup> Various trivalent metal ions have been investigated for delafossite TCOs, with the leading candidates being Group 3 and Group 13 metals. From a recent DFT study, it has been suggested that Group 3 metals prefer to crystallise with the hexagonal structure, whereas Group 13 metals prefer the rhombohedral structure;<sup>311</sup> however, the energy differences were found to be small, with little difference in electronic structure between the two geometries. Hence, we have used the less computationally demanding rhombohedral cell for all calculations presented here.

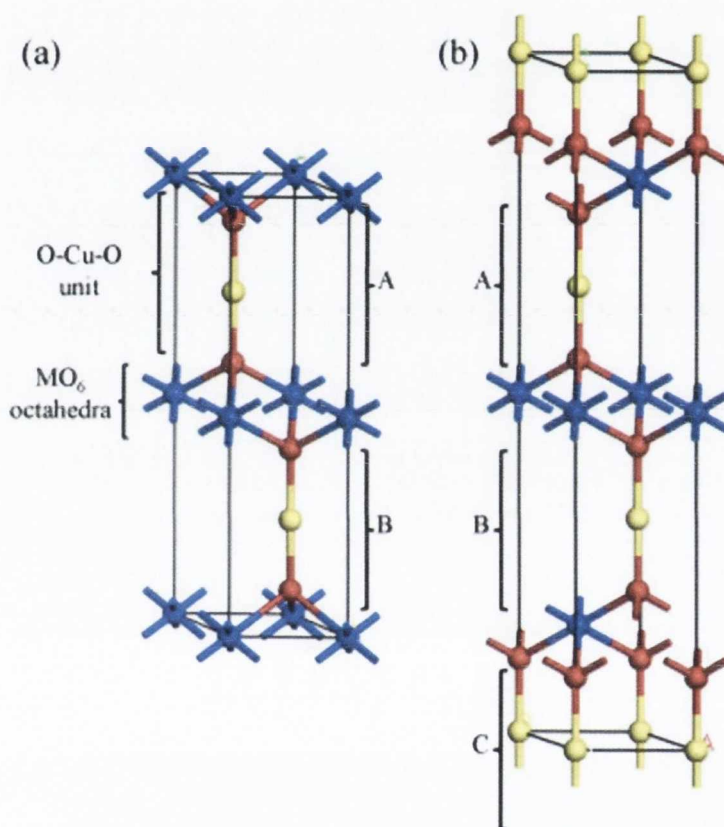


Fig. 4.1 The structure of the (a) hexagonal and (b) rhombohedral delafossite unit cells. The red atoms are O, yellow are Cu and blue are trivalent metal cations (In, Ga, Sc).

The first delafossite TCOs investigated were those containing Group 13 ions (Al, Ga, In). Being the first TCO of this type, CuAlO<sub>2</sub> has been the subject of many studies since its initial discovery in 1997.<sup>14</sup> It possesses an optical band gap of ~3.5 eV and conductivities of up to 2.4 S cm<sup>-1</sup> have been achieved so far.<sup>312</sup> Although the conductivity of CuAlO<sub>2</sub> is quite low, it has already been investigated as a material for *p-n* junctions, in combination with *n*-type ZnO, which show promise for ‘invisible electronics’ applications.<sup>313-314</sup> However, as improved *p*-type materials would be preferable, several investigations of other Group 13 delafossites have been undertaken, focusing mainly on CuGaO<sub>2</sub> and CuInO<sub>2</sub>. *P*-



type conductivity in CuGaO<sub>2</sub> was first discovered in 2000 by Hosono *et al.*<sup>76</sup> A wide optical band gap of ~3.6 eV<sup>315</sup> has been observed, with the highest conductivity being reached in Fe doped films of ~1 S cm<sup>-1</sup>.<sup>316</sup> CuInO<sub>2</sub> has been of great interest as a TCO material due to its ability to be bipolar doped.<sup>317</sup> This was first observed in 2001 and is thought to be of great value for the design of homogeneous *p-n* junctions.<sup>318</sup> However, its conductivity has remained very low with *p*-type conductivities of 0.0028 S cm<sup>-1</sup> reported for Ca doped films and *n*-type conductivities of 0.0038 S cm<sup>-1</sup> for Sn doped films.<sup>317</sup> The remaining Group 13 delafossites (CuBO<sub>2</sub> and CuTlO<sub>2</sub>) have not been fully investigated. CuBO<sub>2</sub> was reported to behave as a *p*-type TCO in 2007 and appears to be a promising TCO candidate, as it possesses a high intrinsic conductivity of 1.65 S cm<sup>-1</sup>.<sup>319</sup> However, a recent HSE06 calculation found significant disagreement between the calculated and experimental lattice parameters.<sup>320</sup> It is thus uncertain whether CuBO<sub>2</sub> crystallises in the delafossite structure and further investigation is needed to confirm the *p*-type capability of CuBO<sub>2</sub>. The final Group 13 cation Tl, has not yet been reported in a copper delafossite structure. Thus its electronic structure and transparent conducting ability are currently unknown.

Since the Group 3 metals are isoelectronic with those of Group 13, it was thought that they would be suitable *p*-type delafossite candidates and investigations of their electronic structure have been ongoing since 2000, when oxygen-intercalated CuScO<sub>2+x</sub> films were found to behave as good *p*-type conductors with conductivities as high as 30 S cm<sup>-1</sup>.<sup>83</sup> However, increasing conductivity came at the expense of transparency with the oxygen-intercalated films having optical transparencies of ~40%, well below the ~80% requirement for a good TCO. Further investigation of CuScO<sub>2</sub> has found that combined Mg doping and O-intercalation of the films gave ~70% transparency for longer wavelengths (>700 nm) and ~50% transparency at 550 nm wavelengths.<sup>321</sup> The major advantage of CuScO<sub>2</sub> is that it possesses a direct band gap, ideal for its use in *p-n* junctions. CuScO<sub>2</sub> is thought to possess a direct band gap at L,<sup>322-324</sup> although from band structure calculations it is known that there is only a small energy difference between the smallest direct gap and the smallest indirect gap (~0.02 eV).<sup>311</sup> One of the major drawbacks of the Group 13 delafossites is that their fundamental band gaps are indirect between the valence band maximum at F and the conduction band minimum at  $\Gamma$ .<sup>76, 90, 153, 324-327</sup> This creates problems for their use in *p-n* diodes as the absorption/emission is more efficient in direct gap materials.<sup>328</sup> The improved conductivity of CuScO<sub>2</sub> compared to Group 13 delafossites, as well as its direct band gap, has led to investigation of the other Group 3



delafossites,  $\text{CuYO}_2$  and  $\text{CuLaO}_2$ , as possible TCO materials. Ca doped  $\text{CuYO}_2$  has been synthesised with a band gap of 3.5 eV and a conductivity of  $1.05 \text{ S cm}^{-1}$ ,<sup>84</sup> suggesting it may be a potential TCO candidate. However,  $\text{CuLaO}_2$  has a band gap of only 2.33 eV and is not therefore transparent, and thus cannot be used as a TCO.<sup>329</sup> Apart from the Group 3 and Group 13 metals,  $\text{CuCrO}_2$  has also been investigated as a TCO material. In fact, Mg doped  $\text{CuCrO}_2$  has been found to have the highest conductivity of all *p*-type TCOs,  $220 \text{ S cm}^{-1}$ ,<sup>84</sup> although this still lags far behind *n*-type TCOs ( $\sim 10^4 \text{ S cm}^{-1}$ ). However, for the current study, we have focused mainly on the Group 13 delafossites, with  $\text{CuScO}_2$  presented to give a comparison with a Group 3 delafossite.

In terms of conductivity, it is known that all of these materials become conductive when an oxygen excess is introduced.<sup>25, 83, 330-331</sup> This may be caused either by oxygen interstitials or by copper vacancies. A number of calculations have been performed to attempt to identify the intrinsic defect which is responsible. Cu vacancies have been suggested to be responsible for conductivity in  $\text{CuScO}_2$ ,<sup>332</sup>  $\text{CuGaO}_2$ <sup>333</sup> and  $\text{CuAlO}_2$ ,<sup>325, 334</sup> whereas both Cu vacancies and O interstitials are thought to be significant in  $\text{CuInO}_2$ .<sup>335</sup> Attempts have also been made to rationalise the bipolar dopability of  $\text{CuInO}_2$  through the calculation of the positions of the valence and conduction bands of these oxides.<sup>153</sup>  $\text{CuAlO}_2$  and  $\text{CuGaO}_2$  were found to have high energy valence band maxima combined with high energy conduction band minima, whereas  $\text{CuInO}_2$  was found to have a high energy VBM combined with a low energy CBM, suggesting this to be the reason for its bipolar dopability. Experimentally, it is known that conduction occurs via a thermally activated mechanism, with activation energies of 0.15 eV,<sup>90</sup> 0.22 eV,<sup>76</sup> 0.19 eV<sup>317</sup> and 0.11 eV<sup>83</sup> for  $\text{CuAlO}_2$ ,  $\text{CuGaO}_2$ ,  $\text{CuInO}_2$  and  $\text{CuScO}_2$ , respectively. The conduction mechanism is thought to be small polaronic hopping,<sup>25, 331</sup> however, recently a band conduction model was also suggested.<sup>336</sup>

The electronic structure of delafossite TCOs has been investigated both experimentally and computationally.  $\text{CuAlO}_2$  has been found to possess an indirect band gap with its VBM at F and CBM at  $\Gamma$  with a valence band is of mainly Cu 3*d* and O 2*p* character and a conduction band of mixed Cu 4*s/p*, Al *s* and O *s/p* character.<sup>80, 322, 324, 326-327, 337-340</sup> Results vary, however, on the positioning of the smallest direct gap, with some authors placing it at L<sup>153, 324, 326</sup> while others place it at  $\Gamma$ .<sup>81, 311, 340</sup>  $\text{CuGaO}_2$  and  $\text{CuInO}_2$  have similar electronic structures to that of  $\text{CuAlO}_2$ , possessing indirect fundamental F- $\Gamma$  band gaps and similar valence and conduction band compositions.<sup>81, 153, 311, 324, 326-327, 335, 338-339, 341</sup>  $\text{CuScO}_2$

possesses a valence band which is similar in composition to those of the Group 13 delafossites, however, its conduction band is made up of mainly Sc 3*d* states.<sup>311, 324, 338</sup> It has been observed experimentally that the Group 13 delafossites do not appear to follow the expected band gap trend, whereby the band gap decreases with increasing ion size. Instead, the band gap increases from 3.5 eV for CuAlO<sub>2</sub> to 3.6 eV for CuGaO<sub>2</sub> to 3.9 eV for CuInO<sub>2</sub>. This anomaly has been explained using LDA calculations.<sup>153</sup> These show that although the fundamental band gap at  $\Gamma$  does in fact follow the expected trend, optical transitions at  $\Gamma$  are symmetry forbidden, and thus, the optical gap in these compounds actually involves a transition at F or L.

It has been suggested that the reason for the larger band gap in the delafossite compounds compared to Cu<sub>2</sub>O (2.17 eV<sup>77</sup>) is due to a reduction in the *d-d* interactions between the copper ions.<sup>80</sup> In Cu<sub>2</sub>O, the Cu ions interact in three dimensions, whereas in the delafossite compounds the interaction is reduced to two-dimensional. Calculations have been carried out to probe the nature of these *d-d* interactions in several delafossite compounds.<sup>338</sup> For CuAlO<sub>2</sub>, a small amount of *d-d* interaction was observed in crystalline orbital overlap population (COOP) analysis, whereas for CuInO<sub>2</sub> the interaction decreased significantly. These results indicated Cu-Cu interactions in copper delafossites to be insignificant compared with the larger Cu-O interactions. We thus only display COOP analysis of Cu-O interactions in this work.

### 4.3.2 Computational Methods

Calculations of the copper delafossites were carried out using both GGA+*U* (PBE) and HSE06 methodologies. For Cu, In, Ga and Sc, the valence *s*, *p* and *d* electrons were treated explicitly, while for O and Al only the *s* and *p* electrons were explicitly included in the valence. GGA+*U* calculations were carried out using  $U = 5.2$  eV, applied to the Cu 3*d* states, as this value has been previously shown to accurately reproduce the valence band photoemission spectra of Cu<sub>2</sub>O, CuAlO<sub>2</sub> and CuCrO<sub>2</sub>.<sup>310, 342-343</sup> Calculations were performed using a  $8 \times 8 \times 8$   $\Gamma$ -centred *k*-point mesh and a 500 eV planewave cut-off and were deemed to be converged when forces on atoms were less than 0.001 eV/Å. Partial electronic density of states (PEDOS) calculations were carried out using spherical projections of 1.4 Å for Cu, Sc and O, 1.5 Å for In and 1.2 Å for Ga. HSE06 calculations were carried out using a reduced planewave cut-off of 400 eV with a  $\Gamma$ -centred  $8 \times 8 \times 8$  mesh and a reduced convergence criteria on the forces of 0.01 eV/Å.



4.3.3 Lattice Parameters of CuMO<sub>2</sub> (M=Al, Ga, In, Sc)

Table 4.1 displays the experimental lattice parameters for the four compounds. The *a* and *c* lattice parameters are seen to increase going down Group 13, with CuAlO<sub>2</sub> having the shortest parameters and CuInO<sub>2</sub> the longest. CuScO<sub>2</sub> has an *a* lattice parameter intermediate between those of CuGaO<sub>2</sub> and CuInO<sub>2</sub>, in line with the intermediate ionic radius of Sc (Sc = 0.745 Å, Ga = 0.620 Å, In = 0.800 Å<sup>261</sup>), while its *c* lattice parameter is intermediate between those of CuAlO<sub>2</sub> and CuGaO<sub>2</sub>. Cu-O bond lengths decrease slightly going down Group 13, while CuScO<sub>2</sub> possesses the smallest Cu-O bond length of the compounds at 1.83 Å. Conversely, M-O distances increase going down Group 13, while the Sc-O distance fits in between Ga-O and In-O, again due to the intermediate ionic radius of Sc.

| Experimental | CuAlO <sub>2</sub> | CuGaO <sub>2</sub> | CuInO <sub>2</sub> | CuScO <sub>2</sub> |
|--------------|--------------------|--------------------|--------------------|--------------------|
| <i>a</i> (Å) | 2.86               | 2.98               | 3.30               | 3.22               |
| <i>c</i> (Å) | 16.95              | 17.17              | 17.45              | 17.10              |
| Cu-O (Å)     | 1.86               | 1.85               | 1.84               | 1.83               |
| M-O (Å)      | 1.91               | 2.00               | 2.19               | 2.12               |

Table 4.1 Experimental bond lengths and lattice parameters<sup>82, 344-346</sup> for CuAlO<sub>2</sub>, CuInO<sub>2</sub>, CuGaO<sub>2</sub> and CuScO<sub>2</sub>.

The optimised GGA+*U* structural parameters are shown in Table 4.2. The calculated lattice parameters are in good agreement with their experimental values<sup>82, 344-345</sup> and the experimental trends outlined above. Overestimates of the *a* parameters of 0.9-1.7% are seen, while the *c* parameter shows a smaller error of 0.1-0.4%. The Cu-O bond distance remains similar to experiment, showing errors of between 0.1 and 0.5% while the M-O distance shows a larger deviation of 0.8-1.4%. Table 4.3 shows the calculated HSE06 lattice parameters which again follow the general trends of the experimental values.<sup>82, 344-345</sup> However, in this case the lattice parameters and bond lengths are slightly underestimated relative to experiment. The *a* lattice parameter is underestimated by 0.8-1.2%, whereas the *c* lattice parameter is underestimated by a lesser amount (0.1-0.5%). Cu-O distances remain within 0.3% of their experimental values, whereas M-O distances are smaller than experiment by 0.6 to 1.2%. Generally, HSE06 calculations tend to predict smaller lattice parameters and bond lengths than GGA+*U* calculations and a slight underestimation is not unexpected.<sup>128</sup>



| GGA+ <i>U</i> | CuAlO <sub>2</sub> | CuGaO <sub>2</sub> | CuInO <sub>2</sub> | CuScO <sub>2</sub> |
|---------------|--------------------|--------------------|--------------------|--------------------|
| <i>a</i> (Å)  | 2.89 (+1.0)        | 3.02 (+1.6)        | 3.36 (+1.7)        | 3.25 (+0.9)        |
| <i>c</i> (Å)  | 17.03 (+0.4)       | 17.25 (+0.4)       | 17.48 (+0.1)       | 17.15 (+0.3)       |
| Cu-O (Å)      | 1.87 (+0.3)        | 1.86 (+0.5)        | 1.84 (+0.0)        | 1.83 (+0.1)        |
| M-O (Å)       | 1.93 (+0.9)        | 2.02 (+1.2)        | 2.22 (+1.4)        | 2.14 (+0.8)        |

Table 4.2 The calculated GGA+*U* structural parameters for CuAlO<sub>2</sub>, CuInO<sub>2</sub>, CuGaO<sub>2</sub> and CuScO<sub>2</sub>, with percentage deviation from experimental values<sup>82, 344-345</sup> given in brackets.

| HSE06        | CuAlO <sub>2</sub> | CuGaO <sub>2</sub> | CuInO <sub>2</sub> | CuScO <sub>2</sub> |
|--------------|--------------------|--------------------|--------------------|--------------------|
| <i>a</i> (Å) | 2.83 (-1.2)        | 2.95 (-1.0)        | 3.28 (-0.8)        | 3.20 (-0.8)        |
| <i>c</i> (Å) | 16.91 (-0.3)       | 17.13 (-0.2)       | 17.36 (-0.5)       | 17.08 (-0.1)       |
| Cu-O (Å)     | 1.86 (-0.3)        | 1.85 (+0.1)        | 1.84 (-0.3)        | 1.83 (-0.1)        |
| M-O (Å)      | 1.89 (-0.9)        | 1.98 (-1.0)        | 2.17 (-0.8)        | 2.11 (-0.6)        |

Table 4.3 Calculated HSE06 structural parameters for CuAlO<sub>2</sub>, CuInO<sub>2</sub>, CuGaO<sub>2</sub> and CuScO<sub>2</sub> with percentage deviation from experimental values<sup>82, 344-345</sup> given in brackets.

## 4.3.4 Electronic Structure of CuMO<sub>2</sub> (M=Al, Ga, In, Sc)

### 4.3.4.1 CuAlO<sub>2</sub>

The band structure of CuAlO<sub>2</sub> is shown in Fig. 4.2, as calculated using both GGA+*U* and HSE06 functionals. Both calculated band structures show similar topographies, with the main differences being the magnitude of the band gap and the valence band width. The calculated GGA+*U* and HSE06 band gaps are listed in Table 4.4. The smallest band gap is indirect between the VBM at F and the CBM at  $\Gamma$  in both cases and is of magnitude 2.28 eV in GGA+*U* and 3.58 eV in HSE06 calculations. However, the position of the smallest direct gap differs between the two methods. GGA + *U* gives a direct gap of 3.63 eV at  $\Gamma$ , whilst for HSE06 the smallest direct gap occurs at L and is 4.05 eV. Previous DFT calculations differ in their positioning of the direct gap with some placing at L<sup>153, 326-327, 347</sup> and others at  $\Gamma$ .<sup>90, 153, 218, 311, 326, 334, 340</sup> Given the small difference of 0.03 eV in the GGA+*U* calculations between the magnitudes of the gaps at  $\Gamma$  and L, it is easy to see why the different positions arise. In the HSE06 calculations, the  $\Gamma$ - $\Gamma$  gap is 1.24 eV larger than the direct L-L gap, thus clarifying the nature of the smallest direct band gap in CuAlO<sub>2</sub>. The valence band widths differ between the two calculations with GGA+*U* calculations

giving a valence band width of 7.33 eV and the HSE06 functional resulting in a larger valence band width of 8.82 eV. The valence band width in CuAlO<sub>2</sub> is primarily controlled by the interactions between Cu 3*d* and O 2*p* states. As the Cu-O bond length is smaller in the HSE06 calculations, the overlap between these orbitals is larger, causing a larger interaction and thus, a greater valence band width.

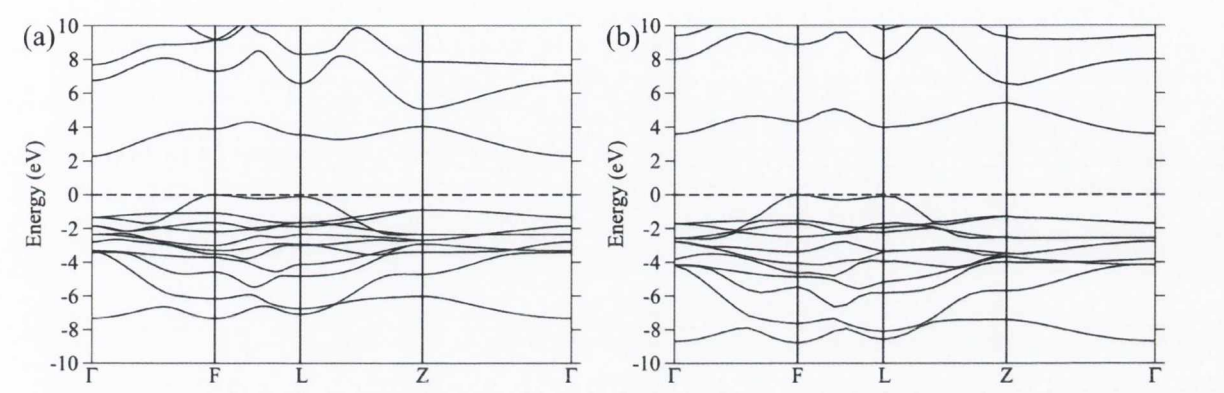


Fig. 4.2 Band structure of CuAlO<sub>2</sub> as calculated using (a) GGA+*U* and (b) HSE06 functionals. The dashed line indicates the valence band maximum.

|            | GGA + <i>U</i> | HSE06       |
|------------|----------------|-------------|
| <b>Γ-Γ</b> | <b>3.63</b>    | 5.29        |
| <b>F-F</b> | 3.89           | 4.31        |
| <b>L-L</b> | 3.66           | <b>4.05</b> |
| <b>Z-Z</b> | 4.94           | 6.72        |
| <b>F-Γ</b> | 2.28           | 3.58        |

Table 4.4 Magnitudes (in eV) of the direct band gaps and smallest indirect gap between VBM at F and CBM at  $\Gamma$  at the high symmetry points of the Brillouin Zone for CuAlO<sub>2</sub>, as calculated using GGA+*U* and HSE06 methodologies.

To allow direct comparison to experiment, we have calculated the optical absorption spectrum, shown in Fig. 4.3. The onset of optical absorption coincides with the fundamental direct gap of 4.05 eV, corresponding to a direct transition between the VBM and CBM at L. As the initial absorption intensities are quite weak, extrapolating  $\alpha^2$  to the *x*-axis gives a slightly larger optical gap of  $\sim$ 4.2 eV. The optical absorption calculations indicate that the direct gaps at  $\Gamma$  and Z are symmetry forbidden, while those at L and F are symmetry allowed, consistent with previous LDA calculations.<sup>153</sup> Given this result, the GGA+*U* optical gap does not correspond to the fundamental band gap at  $\Gamma$  and in fact, corresponds to a direct transition at L. Experimentally, the optical gap is  $\sim$ 3.5 eV,



indicating that both GGA+ $U$  and HSE06 calculations overestimate this gap by  $\sim 0.1$  and  $\sim 0.4$  eV, respectively. It could be expected that GGA+ $U$  would result in an underestimated band gap due to the inherent error of DFT, whilst HSE06 usually results in a band gap close to its experimental value. However, it has recently been found<sup>347-348</sup> that the experimental band gap for CuAlO<sub>2</sub> is overestimated by many different methods (LDA+ $U$ , B3LYP, HSE06 and self-consistent GW). The problem is thought to be due to a non-negligible contribution of lattice polarisation to electronic screening which leads to an overall decrease of the band gap. Inclusion of model polaronic corrections in self-consistent GW calculations resulted in a 1 eV smaller band gap compared to GW results without these corrections.<sup>348</sup>

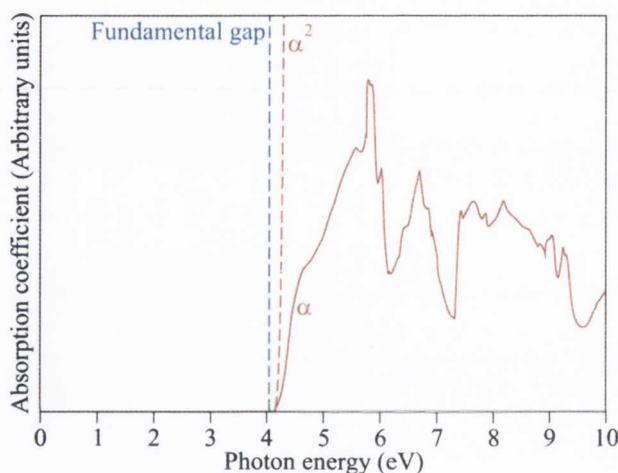


Fig. 4.3 Optical absorption spectrum for CuAlO<sub>2</sub> as calculated using HSE06 functional. Blue dashed line shows magnitude of fundamental direct gap whilst the red dashed line shows the square of the optical absorption coefficient.

Fig. 4.4 shows the EDOS/PEDOS for CuAlO<sub>2</sub>. Both HSE06 and GGA+ $U$  give similar densities of states, with HSE06 having a greater band gap and valence band width. There are four distinct regions in the VB density of states, marked by Roman numerals in Fig. 4.4. In Region I, at the bottom of the VB, a distinct peak is seen, made up of a mixture of mainly O 2 $p$  states with a small amount of Cu 3 $d$  and Al 4 $s$  states. The middle of the VB in Region II is composed of mainly O 2 $p$  states with a small amount of Cu 3 $d$  states. Region III is dominated by Cu 3 $d$  states with only small O 2 $p$  contributions. Finally, at the top of the VB (Region IV), a peak of Cu 3 $d$  states mixed with a small amount of O 2 $p$  states is seen. The valence band maximum at  $\Gamma$  is made up of 71, 18 and 8% Cu 3 $d$ , O 2 $p$  and Cu 4 $s$  in GGA+ $U$ , compared with 81, 12 and 7% in HSE06. The smaller percentage of O 2 $p$  states and increased amount of Cu 3 $d$  in the HSE06 calculation suggests reduced mixing

between the Cu 3*d* and O 2*p* orbitals and hence, a lower covalency. The conduction band is made up of a mixture of Cu 4*s*/3*d*, Al 4*s*/4*p*/3*d* and O 2*p* states.

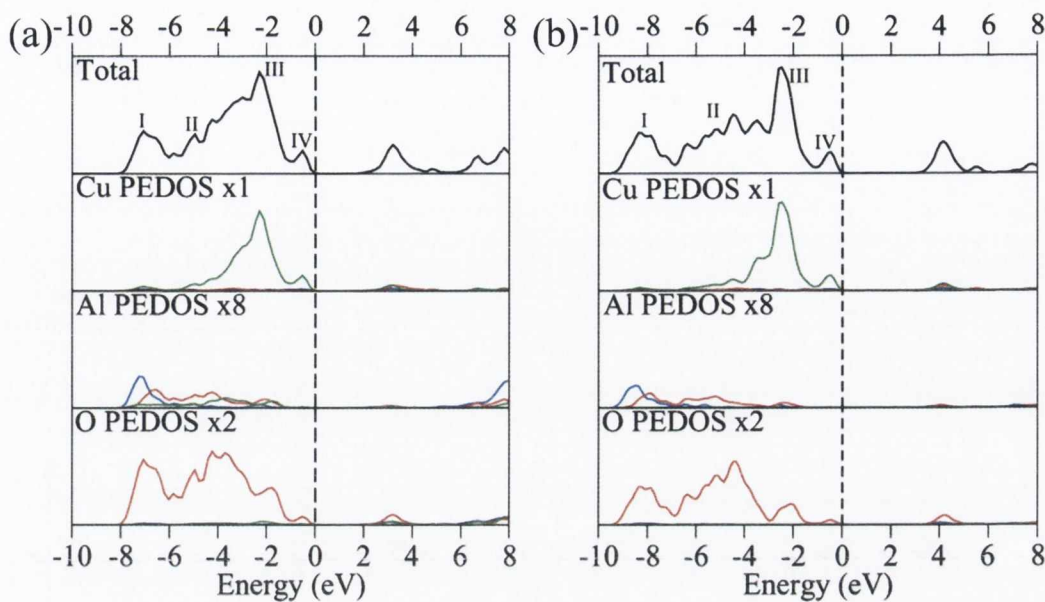


Fig. 4.4 Calculated EDOS and PEDOS for CuAlO<sub>2</sub> using (a) GGA+*U* and (b) HSE06 functionals. Blue lines are *s* states, red are *p* states and green are *d* states and dashed line marks the VBM.

The valence band structure can be understood by decomposing the Cu 3*d* and O 2*p* states into their component orbitals (Fig. 4.5 (a)) and examining their interactions through COOP analysis (Fig. 4.5 (b)). This is shown only for the GGA+*U* calculations as the HSE06 calculations give similar results. If we consider the valence band of CuAlO<sub>2</sub> to be made up of a filled band of O 2*p* states below a filled band of Cu 3*d* states, the bottom of the valence band can be considered as resulting from bonding interactions between these states, while the top is made up of antibonding interactions. This can be clearly seen in the COOP analysis which shows bonding  $\sigma$  and  $\pi$  interactions at the bottom of the valence band between -7.5 and -3 eV and antibonding interactions occurring between -2 and 0 eV. Three major peaks are seen in the Cu 3*d* PEDOS centred around -2.6 eV (*d<sub>xy</sub>* and *d<sub>x<sup>2</sup>-y<sup>2</sup></sub>*), -2.0 eV (*d<sub>yz</sub>* and *d<sub>xz</sub>*) and -0.5 eV(*d<sub>z<sup>2</sup></sub>*), which correspond in the COOP in Fig. 4.5 (b) to  $\delta$ ,  $\pi$  and  $\sigma$  interactions, respectively. The O 2*p* orbitals show a number of peaks across the energy range with the *p<sub>x</sub>* and *p<sub>y</sub>* orbitals possessing similar topography due to their  $\pi$  symmetry, while the O *p<sub>z</sub>* shows a different trend due to its  $\sigma$  symmetry.

The origins of these interactions can be understood by considering a single O-Cu-O dumb-bell lying along the crystallographic *c*-axis. The Cu 3*d<sub>z<sup>2</sup></sub>* orbital lies directly along this bond and can thus interact head-on with the O 2*p<sub>z</sub>* orbitals via strong  $\sigma$  interactions. This gives

rise to a bonding interaction which is mainly O  $2p_z$  with a small amount of Cu  $3d_z^2$  character at -7.2 eV (O  $2p_x/p_y$  contributions occur due to interactions with Al  $5s$  states present at the same energy) and an antibonding interaction which is mainly Cu  $3d_z^2$  with a small amount of O  $2p_z$  character at -0.5 eV.  $\pi$  interactions between the O  $2p_x/p_y$  and Cu  $3d_{yz}/d_{xz}$  orbitals result in significant mixing of these states, with the O  $2p_x/p_y$  states dominating the bonding interaction centred around -4 eV and the Cu  $3d_{yz}/d_{xz}$  dominating the antibonding interaction at -2 eV. Finally, the Cu  $3d_{xy}$  and  $3d_{x^2-y^2}$  states around -2.6 eV are of non-bonding character as they are of  $\delta$ -symmetry and cannot interact strongly with the O  $2p$  states. The COOP shows the  $\delta$  interactions to be extremely weak across the entire valence band region.

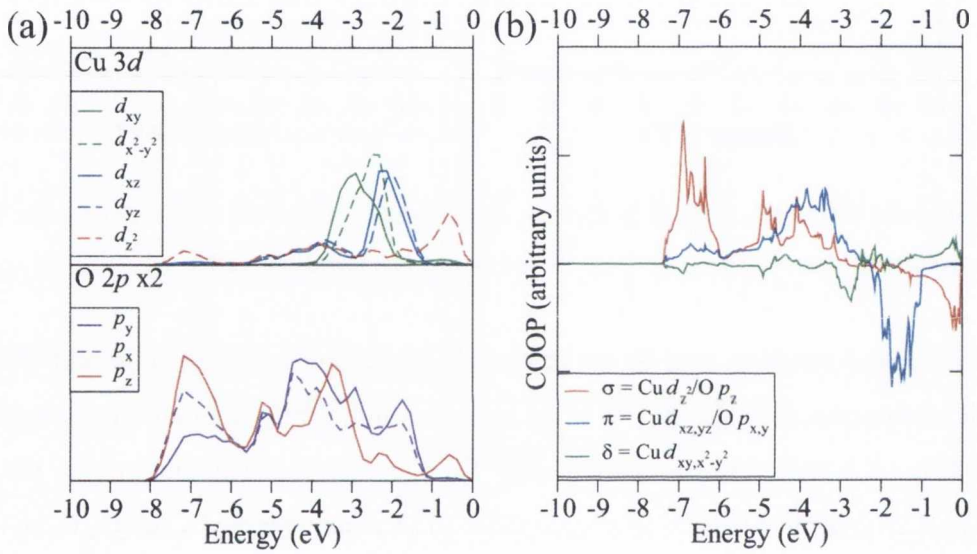


Fig. 4.5 (a) GGA+ $U$  PEDOS of CuAlO<sub>2</sub>, decomposed into individual Cu  $3d$  and O  $2p$  orbital contributions. (b) GGA+ $U$  COOP analysis for CuAlO<sub>2</sub> showing the bonding (positive) and antibonding (negative)  $\sigma$ ,  $\pi$  and  $\delta$  interactions between Cu  $3d$  and O  $2p$  orbitals.

#### 4.3.4.2 CuGaO<sub>2</sub>

Fig. 4.6 shows the GGA+ $U$  and HSE06 band structures of CuGaO<sub>2</sub>. The overall features remain similar with the main difference again being the magnitude of the band gap. The HSE06 results show a larger VB width (8.76 eV) than DFT+ $U$  (7.38 eV), possibly due to the smaller Cu-O distance in the HSE06 calculations. The smallest gap (Table 4.5) is indirect with the VBM at F and the CBM at  $\Gamma$  as previously found<sup>153, 327, 333</sup> and is of magnitude 1.16 eV and 2.58 eV in GGA+ $U$  and HSE06, respectively. The smallest direct gap occurs at  $\Gamma$  and is 2.08 eV in GGA+ $U$  and 3.90 eV in HSE06. However, the calculated HSE06 absorption spectrum in Fig. 4.7 shows that in this case the fundamental direct gap



does not coincide with the optical gap. The optical gap is in fact 4.01 eV, corresponding to a direct transition at L, while the fundamental gap at  $\Gamma$  is symmetry forbidden. GGA+*U* calculations thus underestimate the experimental optical gap (3.6 eV) by 0.1 eV, whereas HSE06 calculations overestimate this gap by 0.4 eV.

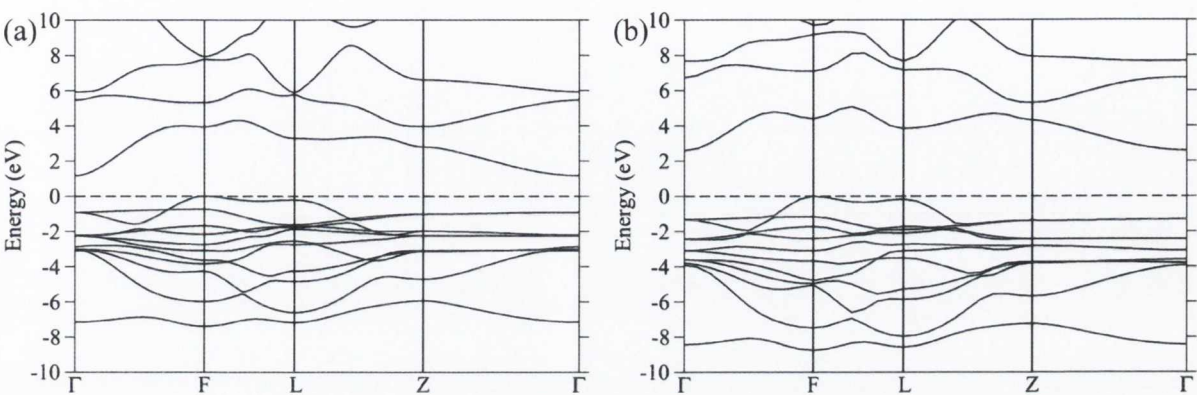


Fig. 4.6 Band structure of CuGaO<sub>2</sub> as calculated using (a) GGA+*U* and (b) HSE06 functionals. The dashed line indicates the valence band maximum.

|                     | GGA + <i>U</i> | HSE06 |
|---------------------|----------------|-------|
| $\Gamma$ - $\Gamma$ | 2.08           | 3.90  |
| F-F                 | 3.94           | 4.39  |
| L-L                 | 3.49           | 4.01  |
| Z-Z                 | 4.93           | 5.85  |
| F- $\Gamma$         | 1.16           | 2.58  |

Table 4.5 Calculated direct band gaps (in eV) at high symmetry points of Brillouin Zone and smallest indirect band gap for CuGaO<sub>2</sub>.

The total and partial EDOS for CuGaO<sub>2</sub> are shown in Fig. 4.8. Similar to CuAlO<sub>2</sub>, the valence band is made up of a mixture of Cu 3*d* and O 2*p* states. The lower part of the valence band in Region I is composed of mainly O 2*p* states with some mixing between Ga 4*s* states. In Region II the valence band is dominated by O 2*p* states with significant Cu 3*d* contributions. Cu 3*d* states dominate in Region III, while in the upper valence band, Region IV, a mixture of O 2*p* and Cu 3*d* states is seen. At the VBM, the compositions for GGA+*U*/HSE06 are 68/78% Cu 3*d*, 19/12% O 2*p* and 11/8% Cu 4*s* states. Similar to CuAlO<sub>2</sub>, HSE06 again predicts a greater proportion of Cu states at the VBM compared to GGA+*U*, suggesting the system to be less covalent in HSE06 calculations. The lower percentage of Cu 3*d* states at the VBM compared to CuAlO<sub>2</sub> suggests a higher degree of

orbital mixing and a greater covalency in Cu-O bonding in copper gallium oxide. The conduction band minimum is made up of a mixture of Cu 3d/4s, Ga 4s, and O 2s/2p states.

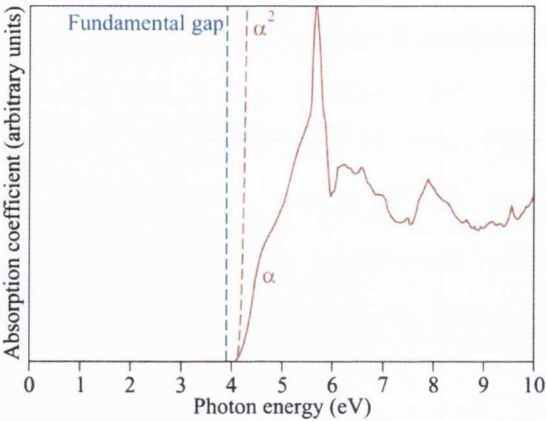


Fig. 4.7 Optical absorption spectrum of CuGaO<sub>2</sub> as calculated using the HSE06 functional. The blue dashed line shows the fundamental direct gap at  $\Gamma$  and the red dashed line shows the square of the absorption coefficient.

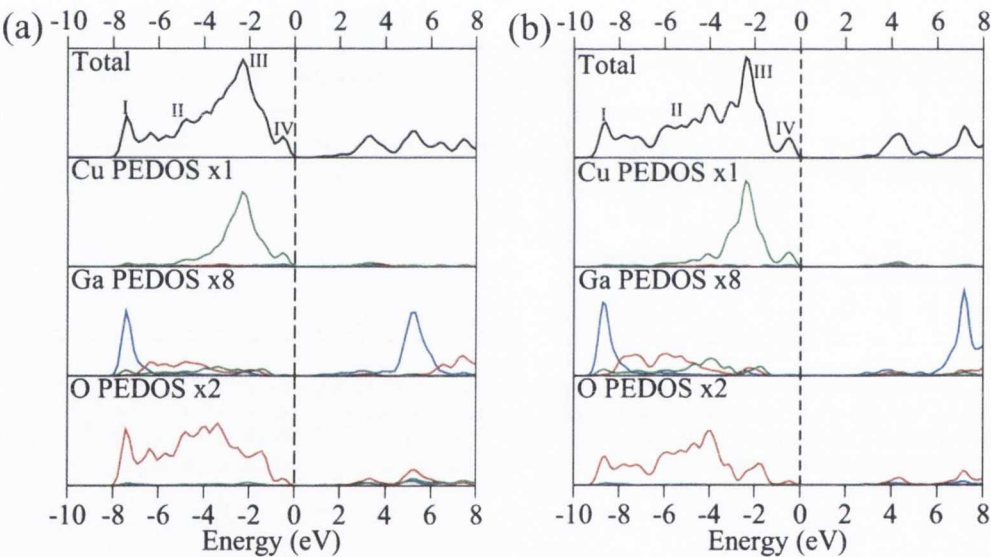


Fig. 4.8 Total EDOS/PEDOS for CuGaO<sub>2</sub> as calculated using (a) GGA+*U* and (b) HSE06. The dashed line indicates the valence band maximum. Blue lines indicate *s* states, red are *p* states and green are *d* states.

Following a similar analysis as for CuAlO<sub>2</sub>, the O 2*p* and Cu 3*d* states can be broken down into their component orbitals as shown in Fig. 4.9 (a). This analysis is presented only for GGA+*U* as HSE06 results are similar. Combining this with the COOP analysis of Fig. 4.9 (b) allows a complete understanding of each peak in the total EDOS.  $\sigma$  interactions between O 2*p<sub>z</sub>* and Cu 3*d<sub>z<sup>2</sup></sub>* states lead to a bonding state at the bottom of the valence band at -7.3 eV of mainly O 2*p<sub>z</sub>* character and an antibonding state at the top of the valence band at -0.5 eV of mainly Cu 3*d<sub>z<sup>2</sup></sub>* character. Significant mixing between O 2*p<sub>x/y</sub>* and Cu

$3d_{xz}/d_{yz}$  states occurs due to  $\pi$  interactions, which lead to a bonding interaction dominated by O  $2p_x/p_y$  states at -3.5 eV and an antibonding interaction dominated by Cu  $3d_{xz}/d_{yz}$  states at -2 eV. The non-bonding Cu  $3d_{xy}$  and  $3d_{x^2-y^2}$  states appear at -2.7 and -2.2 eV and show little interaction with O  $2p$  states. The COOP interactions are stronger than those for CuAlO<sub>2</sub>, consistent with the 0.01 Å shorter Cu-O bond length in CuGaO<sub>2</sub>. However, the overall valence band width of CuGaO<sub>2</sub> is narrower than that of CuAlO<sub>2</sub>, suggesting that there may be another factor controlling valence band width, which will be discussed in Section 4.3.7.

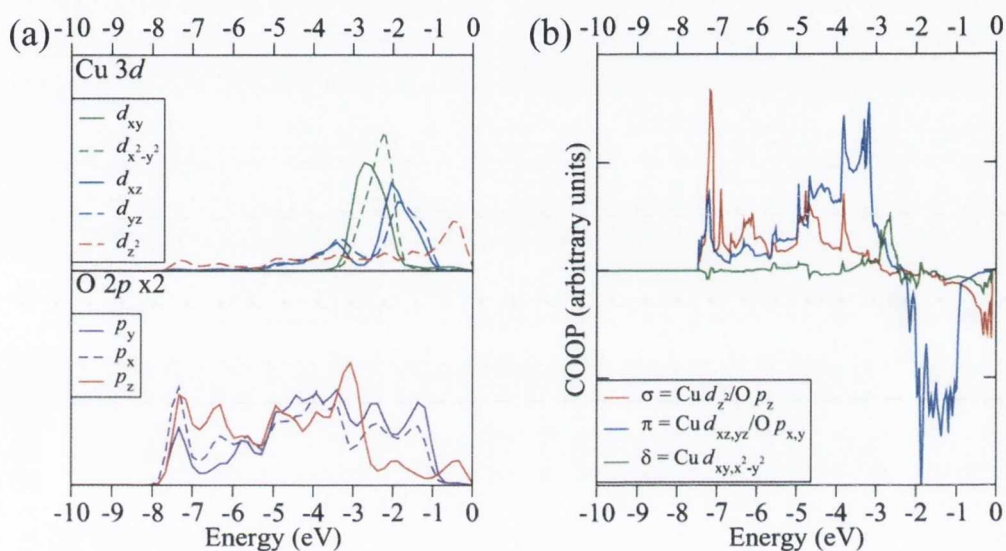


Fig. 4.9 (a) Orbital-decomposed Cu 3d and O 2p PEDOS for CuGaO<sub>2</sub>. (b) GGA+U COOP for CuGaO<sub>2</sub> showing the bonding (positive) and antibonding (negative) interactions between Cu 3d and O 2p orbitals.

#### 4.3.4.3 CuInO<sub>2</sub>

CuInO<sub>2</sub> possesses a similar electronic structure to CuAlO<sub>2</sub> and CuGaO<sub>2</sub>. Its GGA+U and HSE06 band structures are shown in Fig. 4.10, while Table 4.6 summarises the calculated band gaps. The smallest band gap is once again indirect between F and  $\Gamma$ . CuInO<sub>2</sub> possesses the smallest indirect gap of the three delafossites at 0.57 eV for GGA and 1.89 eV for HSE06 calculations. Similar to CuGaO<sub>2</sub>, the fundamental direct gap is at  $\Gamma$  and has a magnitude of 1.10 eV in GGA+U calculations, with a larger value of 2.73 eV obtained for HSE06. However, as for the other delafossites discussed above, the  $\Gamma$ - $\Gamma$  transition is symmetry forbidden so that the HSE06 optical absorption spectrum in Fig. 4.11 shows the optical gap to be 4.52 eV, corresponding to an optical transition at the L point of the Brillouin Zone. As for CuAlO<sub>2</sub> and CuGaO<sub>2</sub>, the hybrid-DFT calculations overestimate the measured experimental optical gap of 3.9 eV,<sup>76, 317</sup> while the GGA+U calculations give an



optical gap of 3.89 eV, in good agreement with experiment. This may again be attributed to the lack of inclusion of polaronic effects in the calculations.<sup>349</sup>

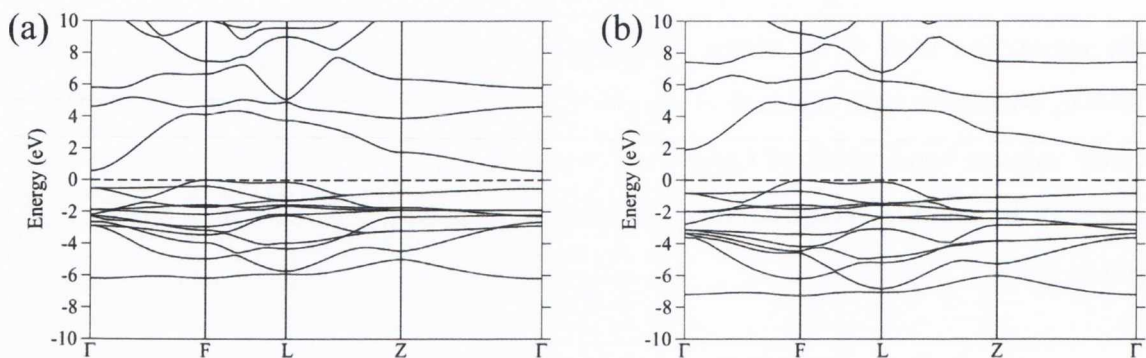


Fig. 4.10 Band structure of CuInO<sub>2</sub> as calculated using (a) GGA+*U* and (b) HSE06. The dashed line shows the valence band maximum.

|            | GGA + <i>U</i> | HSE06       |
|------------|----------------|-------------|
| <b>Γ-Γ</b> | <b>1.10</b>    | <b>2.73</b> |
| <b>F-F</b> | 4.13           | 4.69        |
| <b>L-L</b> | 3.89           | 4.52        |
| <b>Z-Z</b> | 4.19           | 4.93        |
| <b>F-Γ</b> | 0.57           | 1.89        |

Table 4.6 Direct band gaps (in eV) at high symmetry points of the Brillouin Zone and smallest indirect band gap for CuInO<sub>2</sub>.

Fig. 4.12 shows the density of states for CuInO<sub>2</sub>. The valence band width is calculated as 6.21 eV and 7.28 eV for GGA+*U* and HSE06, respectively. This is the smallest valence band width of the three compounds considered so far. It could be expected that the valence band width should decrease with increasing Cu-O distance due to smaller interactions between Cu 3*d* and O 2*p* states. However, in this case, although Cu-O distance increases going down Group 13, the valence band width stays almost the same for CuAlO<sub>2</sub> and CuGaO<sub>2</sub>, while decreasing significantly for CuInO<sub>2</sub>. The reasons the valence band width does not follow the expected trend will be discussed in detail in Section 4.3.7. O 2*p* states dominate the valence band in Regions I and II with a small amount of mixing of In 5*s* states in Region I. In Region III, Cu 3*d* states dominate, while in Region IV, there is a significant admixture of O 2*p* and Cu 3*d* states. At the VBM, for GGA+*U*/HSE06, there are 67/77% Cu 3*d*, 17/10% O 2*p* and 14/12% Cu 4*s* states. The amount of Cu 3*d* states is decreased relative to the Al and Ga delafossites and the O 2*p* states have also decreased,

while there are greater contributions from Cu 4s states. The conduction band is made up of a mixture of Cu 3d states, In 5s and 5p states and O 2p and 2s states.

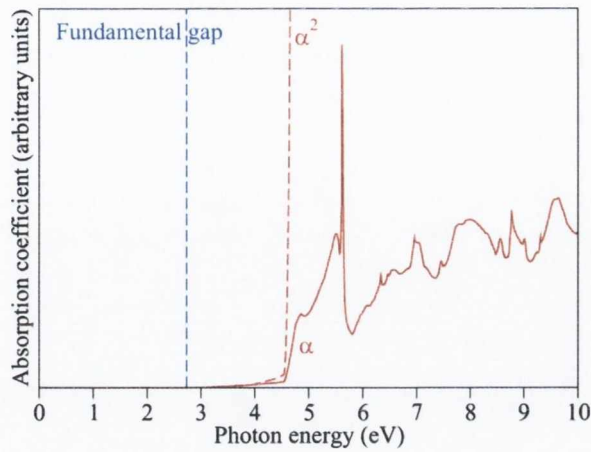


Fig. 4.11 Optical absorption spectrum of CuInO<sub>2</sub> as calculated using HSE06 functional. The blue dashed line indicates the fundamental gap and the red dashed line is the square of the absorption coefficient.

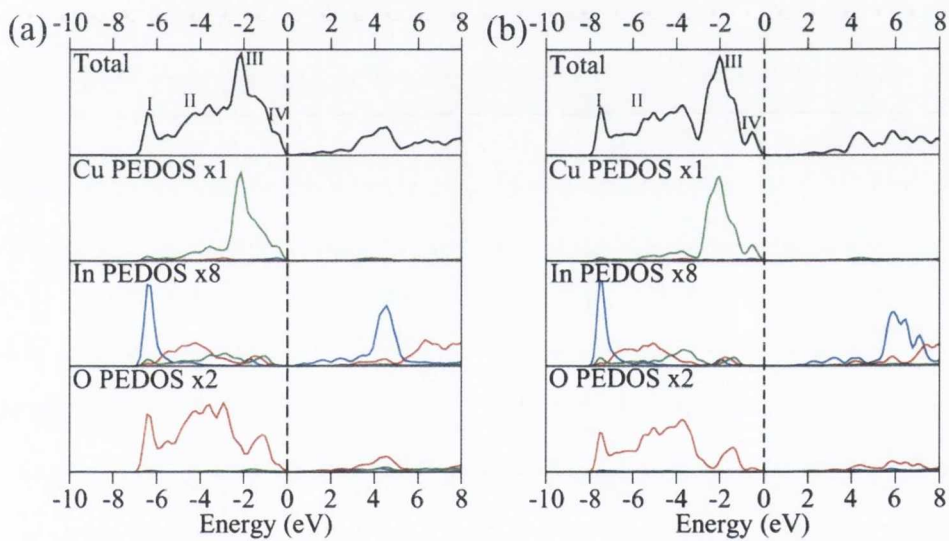


Fig. 4.12 Calculated EDOS and PEDOS for CuInO<sub>2</sub> using (a) GGA+*U* and (b) HSE06. The dashed line indicates the valence band maximum. Blue line indicates *s* states, red are *p* states and green are *d* states.

Fig. 4.13 (a) shows the orbital-decomposed valence band PEDOS, while the  $\sigma$ ,  $\pi$  and  $\delta$  interactions are examined in the COOP in Fig. 4.13 (b). The interactions are similar to those discussed for CuAlO<sub>2</sub> and CuGaO<sub>2</sub> with  $\sigma$  interactions occurring at the top and bottom of the valence band,  $\pi$  interactions in the middle and the  $\delta$  interactions giving rise to the main Cu 3d peak at -2.2 eV. COOP analysis indicates stronger bonding and antibonding interactions in this case than for the other two Group 13 delafossites discussed. This is consistent with the fact that CuInO<sub>2</sub> possesses the shortest Cu-O bond length of the three compounds, which leads to stronger orbital overlap.

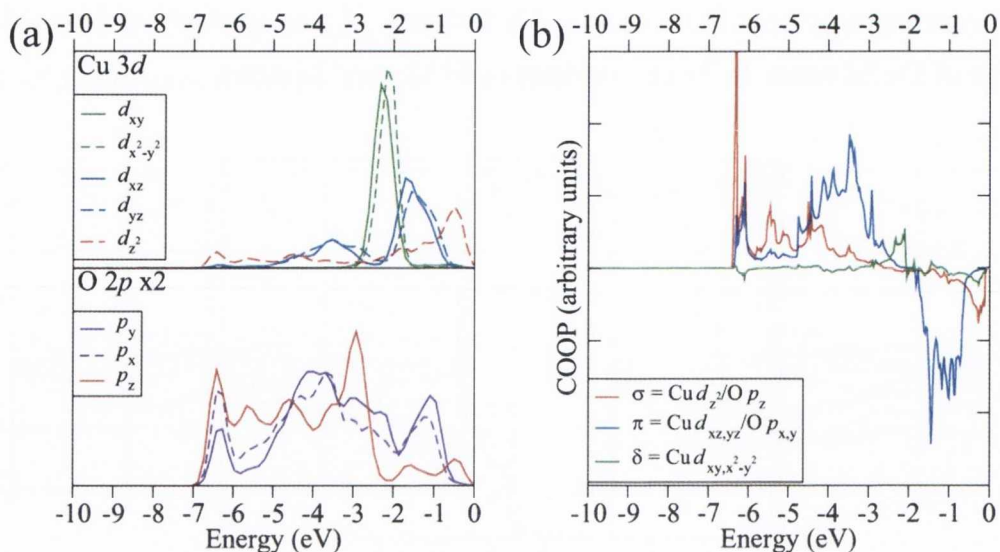


Fig. 4.13 (a) GGA+*U* orbital-decomposed Cu 3d and O 2p PEDOS for CuInO<sub>2</sub>. (b) COOP analysis for CuInO<sub>2</sub> showing bonding (positive) and antibonding (negative) interactions between O 2p and Cu 3d orbitals.

#### 4.3.4.4 CuScO<sub>2</sub>

The band structure of CuScO<sub>2</sub> is shown in Fig. 4.14, as calculated using GGA+*U* and HSE06, while Table 4.7 shows the calculated band gaps at the high symmetry points of the Brillouin Zone. The valence band width is 5.20 eV in GGA+*U* and 6.31 eV in HSE06, the smallest of the compounds considered here. The CBM is visually less dispersed at either the CBM at L or at the  $\Gamma$  point than for the Group 13 delafossites. This is because the conduction band of CuScO<sub>2</sub> is composed of mainly Sc 3d states which, due to their more localised nature, do not interact as strongly. All the Group 13 delafossites have significant M(III) *s* contributions to the conduction band which results in high dispersion.<sup>350</sup>

In contrast to the Group 13 delafossites, the smallest band gap is direct at L and is of magnitude 2.84 eV in GGA+*U* and 3.67 eV for HSE06. However, the GGA+*U* calculations also show a small indirect gap of 2.88 eV between the VBM at L and the CBM at  $\Gamma$ . This small difference between indirect and direct gaps has been previously seen in GGA calculations of CuScO<sub>2</sub>.<sup>311</sup> For HSE06 calculations, the smallest indirect gap is between the VBM at F and CBM at L and there is a larger difference of 0.16 eV between the smallest direct and indirect band gaps. This confirms the direct nature of the CuScO<sub>2</sub> fundamental gap, suggesting that it may be a useful material for *p-n* junctions. The experimentally measured optical gap is 3.3 eV<sup>83</sup> and has been suggested by previous calculations to occur at L.<sup>322, 324</sup> Indeed, the calculated optical absorption spectrum in Fig. 4.15 shows an optical gap of 3.67 eV, corresponding to a direct L-L transition. Again,



GGA+*U* calculations underestimate the experimental optical gap whereas the HSE06 calculations show a ~0.4 eV overestimation.

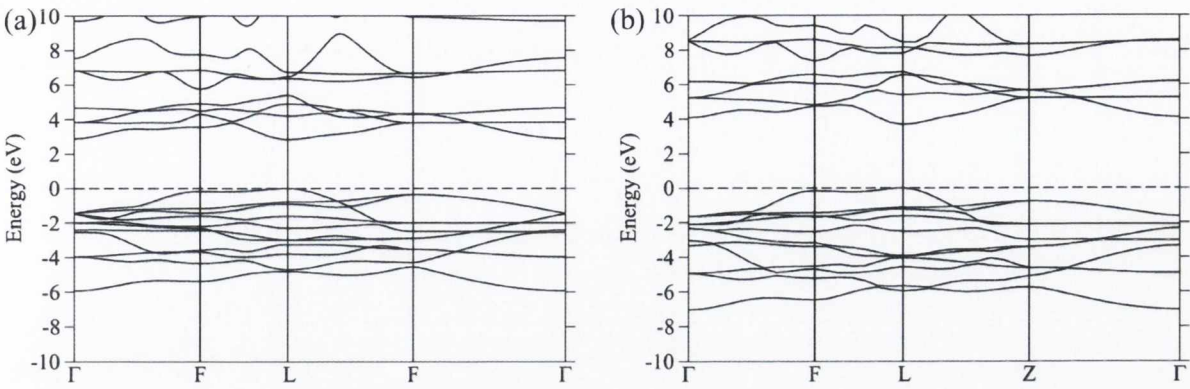


Fig. 4.14 Band structure of CuScO<sub>2</sub> as calculated using (a) GGA+*U* and (b) HSE06. The dashed line indicates the valence band maximum.

|     | GGA + <i>U</i> | HSE06       |
|-----|----------------|-------------|
| Γ-Γ | 4.33           | 5.73        |
| F-F | 3.73           | 4.96        |
| L-L | <b>2.84</b>    | <b>3.67</b> |
| Z-Z | 4.19           | 4.97        |
| F-L | 3.02           | 3.82        |
| L-Γ | 2.88           | 4.08        |

Table 4.7 Direct band gaps (in eV) at high symmetry points of Brillouin Zone and smallest indirect band gaps for CuScO<sub>2</sub>.

The calculated total and partial EDOS for CuScO<sub>2</sub> are shown in Fig. 4.16. Similar to the EDOS for the Group 13 delafossites, the valence band is composed of mainly Cu 3*d* and O 2*p* states. The lower valence band in Regions I and II is dominated by O 2*p* states with only a small contribution from Cu 3*d* states. In Region III, Cu 3*d* states dominate with little contribution from O 2*p* states, while the upper part of the valence band in Region IV is composed of a mixture of Cu 3*d* states and O 2*p* states. The VBM in GGA+*U*/HSE06 is made up of 68/79% Cu 3*d*, 18/10% O 2*p* and 13/11% Cu 4*s* states. This suggests a higher covalency than CuAlO<sub>2</sub> and a lower covalency than the other two delafossites. In contrast to the previous delafossites examined, the conduction band of CuScO<sub>2</sub> is dominated by Sc 3*d* states with a small amount of mixing with O 2*p* states.

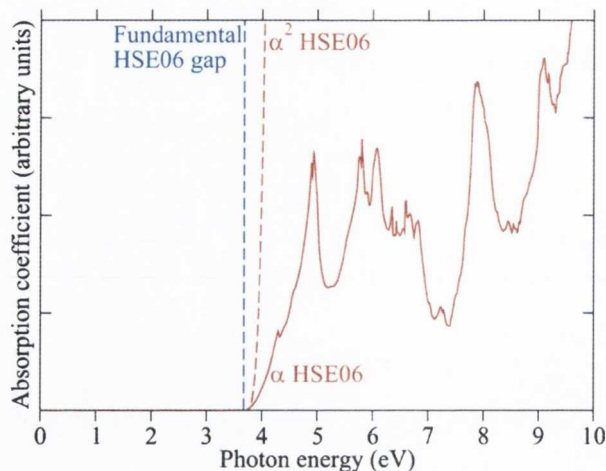


Fig. 4.15 HSE06 optical absorption spectrum of  $\text{CuScO}_2$ . The blue dashed line indicates the fundamental gap and the red dashed line is the square of the absorption coefficient.

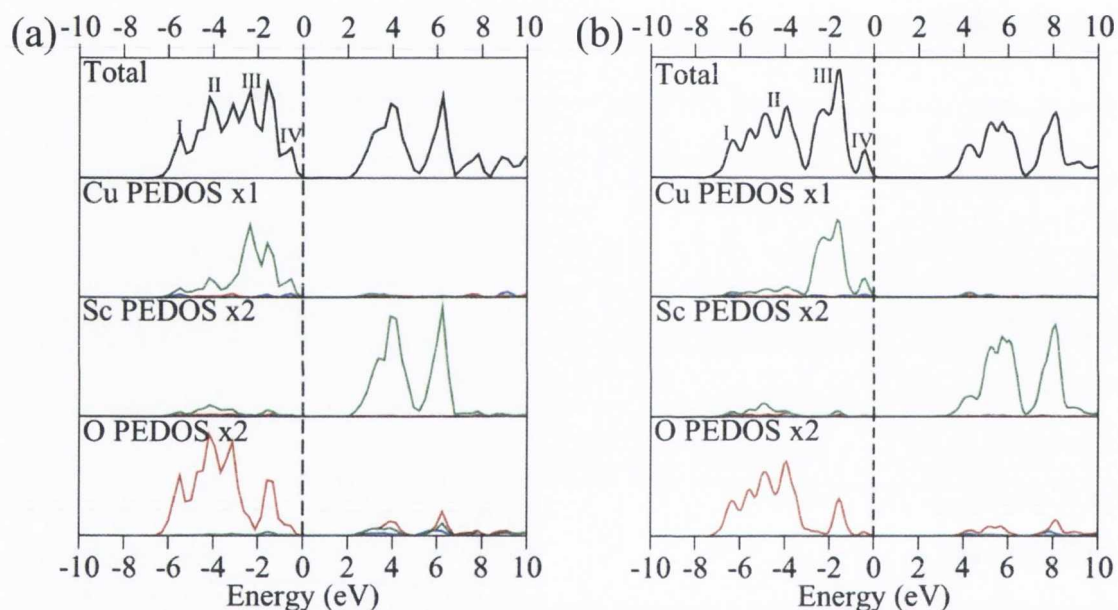


Fig. 4.16 EDOS and PEDOS for  $\text{CuScO}_2$  as calculated using (a) GGA+ $U$  and (b) HSE06. Dashed line indicates valence band maximum. Blue line indicates  $s$  states, red are  $p$  states and green are  $d$  states.

Fig. 4.17 (a) shows the orbital-decomposed Cu  $3d$  and O  $2p$  valence band states along with the COOP in Fig. 4.17 (b). In the O  $2p$  PEDOS, there are four main peaks - three at lower energy and one near the top of the valence band - while for the Cu  $3d$  states, there are three main states, all located towards the top of the valence band. The lowest energy state at -5.5 eV is made up of mainly O  $2p_z$  states due to bonding O-Cu  $\sigma$  interactions. At -4 eV, there is a state of mainly O  $2p_x/p_y$  character from bonding  $\pi$  interactions. The predominantly O  $2p$  state at -3.2 eV is non-bonding in nature and is of mixed  $p_x$ ,  $p_y$  and  $p_z$  character. The non-bonding Cu  $3d_{xy}/d_{x^2-y^2}$  states at -2.1 eV show almost zero mixing with the O  $2p$  states, as seen by the weak nature of the  $\delta$  interaction in the COOP. Strong antibonding  $\pi$

interactions give rise to the state at -1.3 eV of mixed O  $2p_x/p_y$  and Cu  $3d_{xz}/d_{yz}$  character, while the  $\sigma$ -antibonding interactions at the top of the valence band are relatively weak. CuScO<sub>2</sub> possesses the strongest COOP interactions of the four delafossites discussed. This is in line with CuScO<sub>2</sub> having the shortest Cu-O bond length of the compounds, and therefore the strongest overlap between O  $2p$  and Cu  $3d$  orbitals.

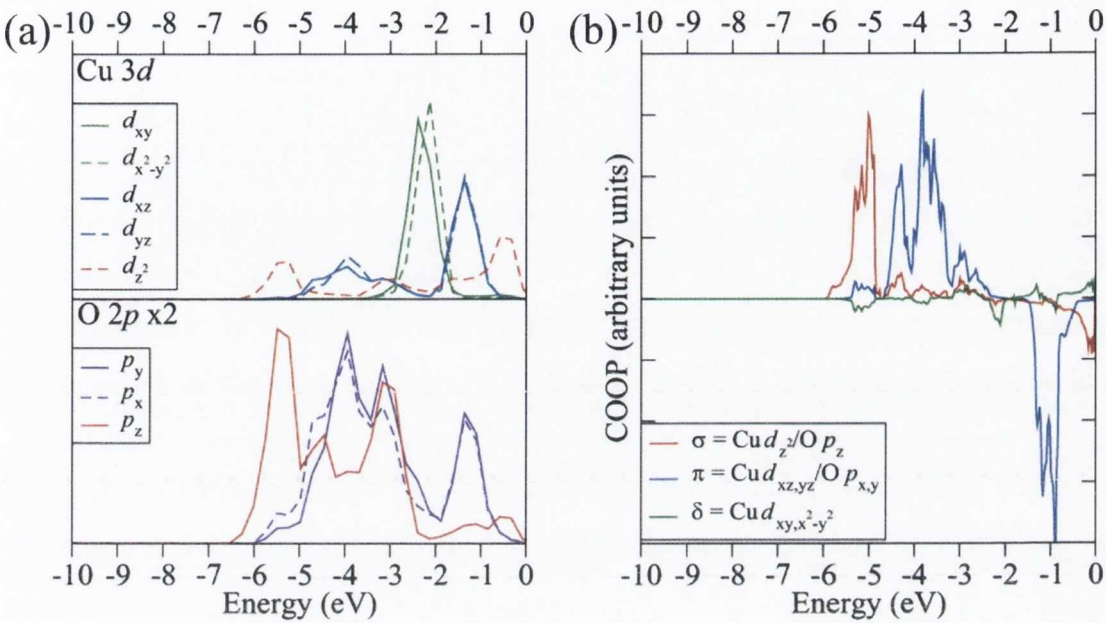


Fig. 4.17 (a) GGA+*U* orbital-decomposed Cu 3*d* and O 2*p* PEDOS for CuScO<sub>2</sub>. (b) GGA+*U* COOP analysis for CuScO<sub>2</sub> showing  $\sigma$ ,  $\pi$  and  $\delta$  bonding (positive) and antibonding (negative) interactions.

### 4.3.5 Bader Charges

Table 4.8 shows the calculated Bader charges for each delafossite considered. In each case, the HSE06 charges are more ionic than the GGA+*U* values. The Cu charges are similar in all compounds using GGA+*U*, with the highest charge of 0.53*e* occurring in CuGaO<sub>2</sub> and the lowest in CuInO<sub>2</sub> of 0.50*e*. HSE06 calculations suggest the Cu charge in CuAlO<sub>2</sub> to be 0.62*e* while CuInO<sub>2</sub> again possesses the lowest Cu charge of 0.56*e*. This compares to a charge of +1 expected in the fully ionic compound, indicating all of these delafossites to possess high covalency in Cu-O bonding. Examining the M(III) charges, the calculations indicate Al to be the most ionic M(III) cation, having a charge of 2.48*e* in GGA+*U*, while HSE06 predicts it to have a charge of 2.50*e*. Indium is the most covalent metal with a charge of 1.83*e* in GGA+*U* and 1.97*e* in HSE06 calculations. The O charges also suggest CuAlO<sub>2</sub> to be the most ionic compound and CuInO<sub>2</sub> to be the most covalent.



|           | CuAlO <sub>2</sub> |       | CuGaO <sub>2</sub> |       | CuInO <sub>2</sub> |       | CuScO <sub>2</sub> |       |
|-----------|--------------------|-------|--------------------|-------|--------------------|-------|--------------------|-------|
|           | GGA+ <i>U</i>      | HSE06 | GGA+ <i>U</i>      | HSE06 | GGA+ <i>U</i>      | HSE06 | GGA+ <i>U</i>      | HSE06 |
| <b>Cu</b> | 0.52               | 0.62  | 0.53               | 0.61  | 0.50               | 0.56  | 0.51               | 0.59  |
| <b>M</b>  | 2.48               | 2.50  | 1.88               | 2.00  | 1.83               | 1.97  | 2.03               | 2.13  |
| <b>O</b>  | -1.50              | -1.56 | -1.20              | -1.30 | -1.17              | -1.26 | -1.27              | -1.36 |

Table 4.8 Calculated Bader charges (in *e*) for CuAlO<sub>2</sub>, CuGaO<sub>2</sub>, CuInO<sub>2</sub> and CuScO<sub>2</sub> as calculated using both GGA+*U* and HSE06 methodologies.

Although all of the delafossites considered possess a high degree of covalency both in Cu-O and M-O bonding, the degree of covalency differs, increasing from CuAlO<sub>2</sub> to CuScO<sub>2</sub> to CuGaO<sub>2</sub> to CuInO<sub>2</sub>. Covalency thus increases going down Group 13, correlating with longer M-O bond distances going down this group. However, CuScO<sub>2</sub> does not appear to fit with the trend as the Sc-O distance is the second longest, yet CuScO<sub>2</sub> is the second-most ionic delafossite. It might be expected that the compound with the highest degree of covalency would show the greatest conductivity as it should possess the greatest mixing between O 2*p* and Cu 3*d* states in the valence band, thus resulting in greater hole delocalisation. In fact, the experimental conductivity trend is opposite to the trend in covalency, with conductivity decreasing going down Group 13 and CuScO<sub>2</sub> showing the highest intrinsic conductivity of the delafossites considered here, while being the second-most ionic compound according to Bader analysis. Thus, covalency alone cannot be used to rationalise the conductivity trend in these delafossites.

### 4.3.6 Effective Mass

As these delafossites are *p*-type conductors they should all have a low effective mass at the valence band maximum, allowing for greater mobility for hole transport. Conversely, *n*-type conductors should have a low effective mass at the conduction band minimum. We have calculated the transport effective mass,  $m_T^*(E)$  at the VBM and CBM of each delafossite, as outlined in Section 2.3.10. It must be noted that there are some reservations about applying effective mass theory to compounds such as delafossites, which do not have perfectly parabolic VBMs and conduct via a polaronic rather than a band-type mechanism.<sup>351</sup> Nevertheless, effective masses are widely used as an indicator of conductive properties and we thus use them to provide insight into the conducting properties of these materials. Table 4.9 shows the calculated GGA+*U* effective masses at the VBM and CBM for each

compound. The effective masses for the VBM and CBM of CuAlO<sub>2</sub>, CuGaO<sub>2</sub> and CuInO<sub>2</sub> were calculated at F and  $\Gamma$ , respectively, while those for CuScO<sub>2</sub> were both calculated at L.

|     |                    | Point                                  | $m_{100}$ | $m_{010}$ | $m_{001}$ |
|-----|--------------------|----------------------------------------|-----------|-----------|-----------|
| VBM | CuAlO <sub>2</sub> | F ( $\frac{1}{2}$ , $\frac{1}{2}$ , 0) | 2.52      | 2.52      | 0.68      |
|     | CuGaO <sub>2</sub> | F ( $\frac{1}{2}$ , $\frac{1}{2}$ , 0) | 2.04      | 2.04      | 0.58      |
|     | CuInO <sub>2</sub> | F ( $\frac{1}{2}$ , $\frac{1}{2}$ , 0) | 3.22      | 3.22      | 0.68      |
|     | CuScO <sub>2</sub> | L (0, $\frac{1}{2}$ , 0)               | 3.12      | 0.45      | 3.12      |
| CBM | CuAlO <sub>2</sub> | $\Gamma$ (0, 0, 0)                     | 0.85      | 0.85      | 0.85      |
|     | CuGaO <sub>2</sub> | $\Gamma$ (0, 0, 0)                     | 0.42      | 0.42      | 0.42      |
|     | CuInO <sub>2</sub> | $\Gamma$ (0, 0, 0)                     | 0.37      | 0.37      | 0.37      |
|     | CuScO <sub>2</sub> | L (0, $\frac{1}{2}$ , 0)               | 1.08      | 0.56      | 1.08      |

Table 4.9 GGA+*U* effective masses (in  $m_0$ ) at VBM and CBM for CuAlO<sub>2</sub>, CuGaO<sub>2</sub>, CuInO<sub>2</sub> and CuScO<sub>2</sub>.

The VBM effective masses for *p*-type conductivity of the Group 13 delafossites were found to be isotropic in the [100] and [010] directions, with the lowest effective masses occurring in the [001] direction of 0.68 $m_0$ , 0.58 $m_0$  and 0.68 $m_0$  for CuAlO<sub>2</sub>, CuGaO<sub>2</sub> and CuInO<sub>2</sub>, respectively. CuScO<sub>2</sub> has a VBM effective mass which is isotropic in the [100] and [001] directions with the lowest effective mass in the [010] direction of 0.45 $m_0$ . The difference in the direction of the lowest effective mass is due to the VBMs of the Group 13 delafossites occurring at F while CuScO<sub>2</sub> has its VBM at L. We have also calculated the effective masses along the high symmetry directions of the Brillouin Zone and found that CuAlO<sub>2</sub>, CuGaO<sub>2</sub> and CuInO<sub>2</sub> possess lower effective masses in the F- $\Gamma$  direction of 0.49 $m_0$ , 0.46 $m_0$  and 0.58 $m_0$ , respectively. The VBM effective mass data thus follows the experimental *p*-type conductivity trend, with CuScO<sub>2</sub> having the lowest calculated effective mass and the highest reported conductivity,<sup>83-84</sup> while CuInO<sub>2</sub> has the lowest reported conductivity<sup>316</sup> of the compounds and the largest effective mass. However, the effective mass data for CuAlO<sub>2</sub> and CuGaO<sub>2</sub> is not in complete agreement, as CuAlO<sub>2</sub> has been reported to have a higher conductivity than CuGaO<sub>2</sub>. However, given that conductivity data for these compounds has only been available in the last ten years, optimum levels of conductivity have yet to be reached and future studies may find CuGaO<sub>2</sub> possesses higher levels of conductivity.

As CuInO<sub>2</sub> can be bipolar doped, it is of interest to examine the conduction band effective mass for each compound to determine its electron effective mass for *n*-type conductivity.



For  $\text{CuAlO}_2$ ,  $\text{CuGaO}_2$  and  $\text{CuInO}_2$ , the effective masses were found to be isotropic in the [100], [010] and [001] directions with values of  $0.85m_0$ ,  $0.42m_0$  and  $0.37m_0$ , respectively. The CBM of  $\text{CuScO}_2$  occurs at L, resulting in an anisotropic effective mass, with the smallest effective mass in the [010] direction of  $0.56m_0$ . The calculated effective masses along the high symmetry directions show  $\text{CuAlO}_2$  and  $\text{CuGaO}_2$  to have lower effective masses of  $0.33m_0$  each along  $\Gamma$ -Z and  $\text{CuInO}_2$  has calculated effective masses of  $0.38m_0$  and  $0.37m_0$  along  $\Gamma$ -Z and  $\Gamma$ -F, respectively. The effective masses of  $\text{CuScO}_2$  are  $1.08m_0$  and  $1.05m_0$  along L-F and L-Z, respectively. The high effective mass found for  $\text{CuScO}_2$  relative to  $\text{CuInO}_2$  and  $\text{CuGaO}_2$  is not unexpected given the lesser dispersion at the CBM visible in its band structure. Although  $\text{CuAlO}_2$ ,  $\text{CuGaO}_2$  and  $\text{CuInO}_2$  have low CB effective masses, only  $\text{CuInO}_2$  has thus far shown *n*-type dopability. This has been suggested previously to be due to the lower energy of the CBM of  $\text{CuInO}_2$  relative to  $\text{CuGaO}_2$  and  $\text{CuAlO}_2$ .<sup>153</sup>

### 4.3.7 Comparison to Experimental XPS

In collaboration with Prof. Egdel at Oxford University, we have performed a comparative study of the experimental X-ray photoemission spectroscopy (XPS) and X-ray emission spectroscopy (XES) with our calculated GGA+*U* electronic density of states.<sup>352</sup> Fig. 4.18 shows the O *K* XES for  $\text{CuGaO}_2$ ,  $\text{CuInO}_2$  and  $\text{CuScO}_2$  compared to the calculated GGA+*U* O 2*p* PEDOS. The XES spectra are dominated by a strong peak, labelled II in Fig. 4.18 with the weaker features I and III at higher and lower photon energies. These features are well reproduced by the calculated O PEDOS. The band width in GGA+*U* is underestimated compared to experiment but this is a well known error in calculations. The trend in band widths correlates well between theory and experiment, with the valence band width narrowing from  $\text{CuGaO}_2$  to  $\text{CuInO}_2$  to  $\text{CuScO}_2$ .

Fig. 4.19 (a) shows the XPS of  $\text{CuInO}_2$  compared to the cross-section weighted total EDOS. The XPS for the other delafossites are similar and are not shown here. The major peak (I') in the XPS occurs at 2.7 eV below the Fermi level which does not coincide with peak I in the XES in Fig. 4.18. Peak I occurs 1.9 eV below the Fermi level and appears as a shoulder in the XPS. This difference occurs because the XPS is determined by the cross-section weighted density of states which is calculated from the sum of the partial density of states for each ion weighted by a one electron ionisation cross-section. Although the total density of states is made up of a mixture of Cu and O states, the ionisation cross-section of



the Cu 3*d* states ( $1.2 \times 10^{-3}$  Mb) is twenty times larger than the O 2*p* cross-section ( $6 \times 10^{-5}$  Mb).<sup>167</sup> Hence, the overall XPS is dominated by Cu 3*d* states, as illustrated in the bottom panel of Fig. 4.19. The correlation between the calculated EDOS and the XPS is excellent with peaks marked I to III being well reproduced in calculations.

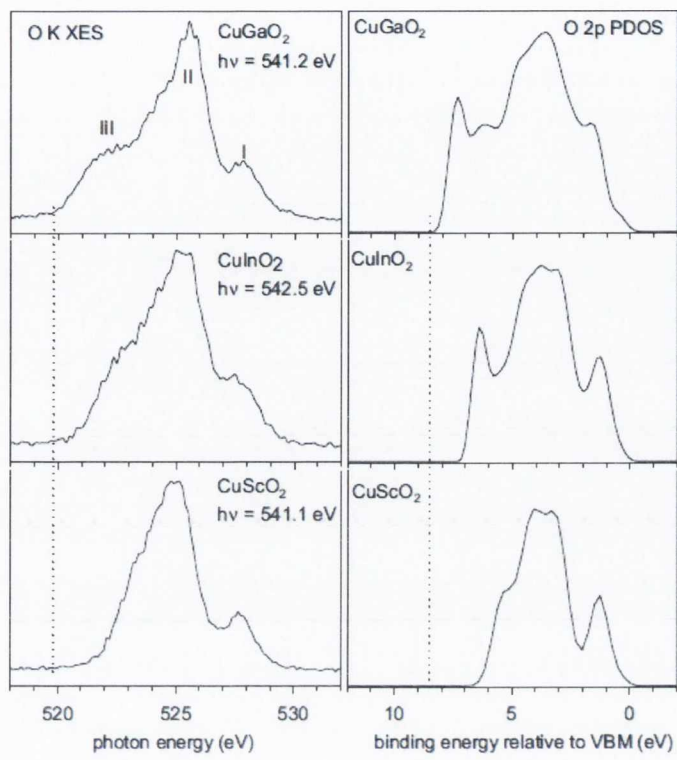


Fig. 4.18 O *K*-shell x-ray emission spectra of CuGaO<sub>2</sub>, CuInO<sub>2</sub> and CuScO<sub>2</sub> (on left) compared with O 2*p* PEDOS for the same three materials (on right).<sup>352</sup>

To demonstrate further the agreement between theory and experiment, Fig. 4.19 (b) shows the orbital decomposed PEDOS for Cu and O compared to the XPS and XES for CuInO<sub>2</sub>. The XPS shows very good agreement with the decomposed Cu 3*d* PEDOS, with the  $\delta$  states corresponding to the main XPS peak at 2.7 eV and the  $\pi$  and  $\sigma$  states corresponding to shoulders in the XPS at higher binding energies. The XES also correlates well with the calculated O PEDOS, with the  $\sigma$  and  $\pi$  states corresponding to shoulders in the XES. This demonstrates the ability of EDOS calculations to not only reproduce the total EDOS accurately but also to predict correctly the partial EDOS for each atomic orbital involved.

The aforementioned calculations show that the valence band widths follow the trend CuAlO<sub>2</sub> > CuGaO<sub>2</sub> > CuInO<sub>2</sub> > CuScO<sub>2</sub>. However, the Cu-O bond lengths increase in the order CuScO<sub>2</sub> < CuInO<sub>2</sub> < CuGaO<sub>2</sub> < CuAlO<sub>2</sub>. Since the top and bottom of the valence band are made up of Cu 3*d* and O 2*p* states, it might be expected that as the Cu-O bond

length increases, the interactions between these orbitals would decrease, resulting in a narrower valence band. However, clearly the trend is the opposite here, with the band width increasing with Cu-O bond length. In order to verify this trend, we have plotted the GGA+*U* calculated band widths against Cu-O bond length for a number of delafossites in Fig. 4.20, along with a comparison to the available experimental valence band widths measured by XES. This shows the calculated trend to be in clear agreement with experiment with both showing an increase in band width with increasing Cu-O bond length.

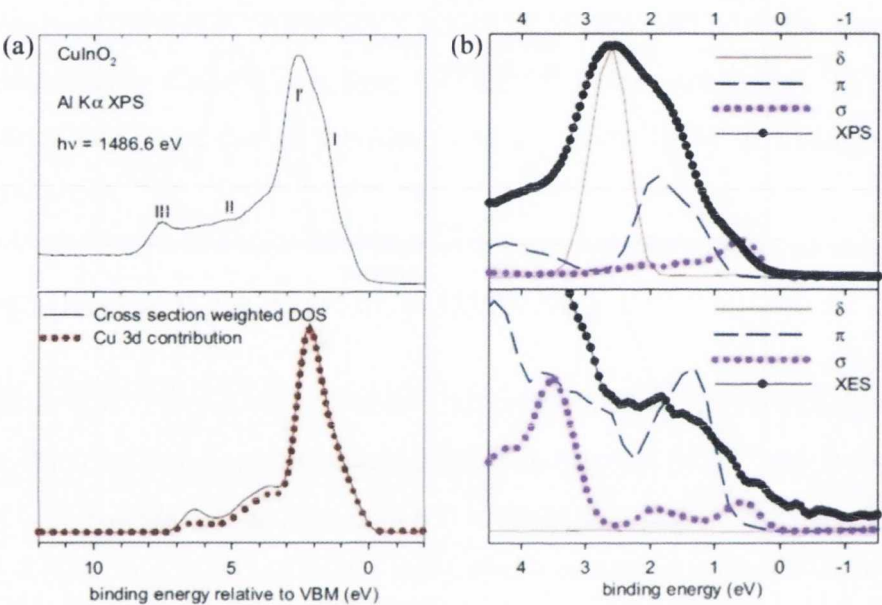


Fig. 4.19 (a) Valence band XPS of 2% Eu doped CuInO<sub>2</sub> (top) compared with calculated cross-section weighted density of states of pure CuInO<sub>2</sub> (bottom). The dotted red line shows the Cu 3d contribution to the cross-section weighted density of states. (b) Top panel: Cu PEDOS for CuInO<sub>2</sub> calculated using GGA+*U* and decomposed into components with  $\delta$ ,  $\pi$ , and  $\sigma$  symmetry compared with Al K $\alpha$  XPS. The energy scale for the calculated EDOS is multiplied by a factor of 1.2 to match the position of the peak in the  $\delta$  component with that observed experimentally. Bottom panel: Comparison between decomposed O PEDOS and O K-edge XES along the same lines as above.<sup>352</sup>

The explanation for the band width trend lies in the electronic structure of the delafossites. Looking first at the Group 13 delafossites, each EDOS possesses a significant contribution from M(III) *s* states at the bottom of the valence band. These result from mixing between the O 2*p* and M(III) *s* orbitals within the M-O bonds. At the same time,  $\sigma$ -bonding interactions within the Cu-O bonds lead to an O 2*p<sub>z</sub>* dominated state at the bottom of the valence band. Going down Group 13, the M-O bond length increases, resulting in weaker M(III) *s*/O 2*p* interactions. It is this interaction which leads to a shrinking of the overall

band width going from  $\text{CuAlO}_2$  to  $\text{CuGaO}_2$  to  $\text{CuInO}_2$ . For  $\text{CuScO}_2$  there are no Sc  $s$  states at the bottom of the valence band and hence its valence band width is narrower. If, instead of looking at the overall band width we examine the  $\pi$  interactions, which are not affected by the M(III)  $s$  states, the effect of the Cu-O bond length can be clearly seen.  $\text{CuAlO}_2$  has the smallest separation between the antibonding O  $2p_x/p_y$  and bonding Cu  $3d_{xz}/d_{yz}$  states (1.5 eV),  $\text{CuGaO}_2$  has a larger separation of 1.6 eV, for  $\text{CuInO}_2$  the separation is 2.0 eV while  $\text{CuScO}_2$  has a separation of 2.7 eV. Thus direct correlation between  $\pi$  interaction and Cu-O bond length can be seen, indicating that the overall band width increase is purely due to the presence of M(III)  $s$  states.

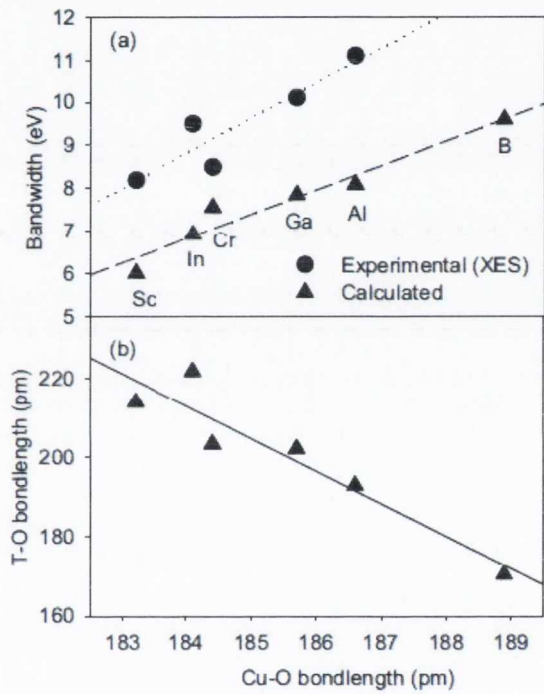


Fig. 4.20 (a) Plot showing experimentally measured (dotted line) and calculated GGA+ $U$  (dashed line) band widths plotted against Cu-O bond lengths, showing data for  $\text{CuAlO}_2$ ,  $\text{CuGaO}_2$ ,  $\text{CuInO}_2$  and  $\text{CuScO}_2$ <sup>352</sup> as well as  $\text{CuCrO}_2$ <sup>310, 337, 342</sup> and  $\text{CuBO}_2$ <sup>320</sup>. (b) Plot of calculated GGA+ $U$  M(III)-O bond lengths against Cu-O bond lengths.

### 4.3.8 Discussion

Comparing the HSE06 results to those of GGA+ $U$ , it appears at first sight that HSE06 is worse at predicting band gap sizes and is not much better than GGA+ $U$  at predicting lattice parameters. Whereas GGA+ $U$  overestimates the lattice parameters, HSE06 underestimates them so that neither method accurately predicts the experimental lattice parameters. For all the delafossites considered, the sizes of the band gaps calculated using HSE06 are



overestimated, and the optical gap calculated using GGA+ $U$  is closer to experiment. However, this problem has been seen in previous DFT calculations and is thought to be due to the lack of consideration of polaronic effects in the calculations.<sup>347-348</sup> The only way to account for this is through a fully self consistent GW calculation, which is beyond the reach of currently available computational resources. Through comparison of the calculated density of states with experimental XPS and XES, the accuracy of our calculations has been demonstrated, and the inaccuracies in the size of the band gap are unlikely to affect the discussion of the valence band electronic structure.

For the Group 13 delafossites, the size of the smallest direct band gap decreases with increasing atomic number, going from Al to Ga to In, in agreement with the conclusions of Nie *et al.*<sup>153</sup> This is the reverse of the trend in experimental optical band gaps, which are 3.5 eV for CuAlO<sub>2</sub>, 3.6 eV for CuGaO<sub>2</sub> and 3.9 eV for CuInO<sub>2</sub>.<sup>14, 83, 315, 317</sup> However, calculations of the optical absorption spectra shows that  $\Gamma$ - $\Gamma$  and Z-Z transitions are symmetry forbidden. The fundamental direct gap occurs at  $\Gamma$  for CuGaO<sub>2</sub> and CuInO<sub>2</sub>, while for CuAlO<sub>2</sub> the fundamental gap occurs at L in HSE06 calculations and at  $\Gamma$  in GGA+ $U$  calculations. Hence, the calculated optical gap is not the same as the fundamental gap for CuGaO<sub>2</sub> and CuInO<sub>2</sub> and the optical gaps for all these compounds occur at L. Thus, in the GGA+ $U$  calculations the optical gaps are 3.66, 3.49 and 3.89 eV, while for HSE06 the optical gaps are 4.05, 4.01 and 4.52 eV, respectively for CuAlO<sub>2</sub>, CuGaO<sub>2</sub> and CuInO<sub>2</sub>. These calculated gaps are in much better agreement with experimental trends. However, transitions from the VBM to the CBM of CuScO<sub>2</sub> are symmetry allowed,<sup>324</sup> meaning that the minimum calculated band gap at L of 2.84 eV in GGA+ $U$  and 3.67 eV in HSE06 corresponds to the optical band gap of 3.3 eV seen experimentally.<sup>83</sup> Although all the Group 13 delafossites were found to be indirect gap semiconductors, with their VBMs at F and CBMs at  $\Gamma$ , CuScO<sub>2</sub> was found to be a direct gap semiconductor which is more favourable for its use in optoelectronic applications due to its greater efficiency in absorption/emission.<sup>328</sup>

For CuScO<sub>2</sub>, the difference between the direct gap at L and the smallest indirect gap is only 0.04 eV in GGA+ $U$  and 0.16 eV in HSE06, compared to differences of 0.5-1.4 eV for the Group 13 delafossites, which is in agreement with the results of Huda *et al.*<sup>311</sup> This is likely to arise from the difference in the electronic structure between Group 3 and Group 13 delafossites. Whereas Group 13 delafossites have significant contributions from M(III)  $s$  states in the valence band and CBM, CuScO<sub>2</sub> has no significant Sc contributions to the valence band and a conduction band of dominant Sc  $3d$  character. The CBMs of the Group

13 delafossites are visually dispersed due to the interactions between M(III) *s* states, while CuScO<sub>2</sub> has a less disperse conduction band which means that there is less difference between the band gaps at different points across the Brillouin Zone.

All of these materials were found to have valence bands made up of a mixture of Cu 3*d* and O 2*p* states, with the bonding interactions resulting in a lower VB of mainly O 2*p* states and antibonding interactions giving rise to an upper VB of mainly Cu 3*d* character. Our calculations are in very good agreement with experimental XPS and XES data with the trends in band width correlating well with experiment. The band width is seen to increase with increasing Cu-O bond length which is opposite to the trend expected, given that the valence band is determined mainly by the overlap between Cu 3*d* and O 2*p* orbitals. Rather than originating solely from Cu 3*d*/O 2*p* interactions, the position of the bottom of the valence band in Group 13 delafossites is determined by the interactions between M(III) *s* and O 2*p* states. As the M-O distance increases going down Group 13, the M(III) *s*/O 2*p* interactions weaken, resulting in a narrower valence band in CuInO<sub>2</sub> than in CuAlO<sub>2</sub>. CuScO<sub>2</sub> has no contribution from Sc *s* states at the bottom of the valence band, giving it the narrowest valence band width of the four delafossites. The effect of Cu-O interactions on the valence band can be seen by considering only the  $\pi$  interactions. This clearly demonstrates that decreasing the Cu-O bond length has the effect of narrowing the  $\pi$ -band width, giving a clear trend going from CuAlO<sub>2</sub> to CuGaO<sub>2</sub> to CuInO<sub>2</sub> to CuScO<sub>2</sub>.

The extent of covalency in bonding has been examined through Bader analysis. The HSE06 calculations generally result in more ionic Bader charges than GGA+*U* but the covalency trends are the same using both methods. Covalency increases going down Group 13 while CuScO<sub>2</sub> has a covalency between those of CuAlO<sub>2</sub> and CuGaO<sub>2</sub>. An analysis of the PEDOS shows decreasing Cu 3*d* character and increasing O 2*p* character going from CuAlO<sub>2</sub> to CuScO<sub>2</sub> to CuGaO<sub>2</sub> to CuInO<sub>2</sub>, indicating a greater amount of mixing between O 2*p* and Cu 3*d* states and hence a greater covalency. Although increased mixing between Cu 3*d* and O 2*p* states could be expected to increase conductivity through greater hole delocalisation, the experimental conductivity follows the trend CuScO<sub>2</sub> > CuAlO<sub>2</sub> > CuGaO<sub>2</sub> > CuInO<sub>2</sub>, clearly suggesting that the more ionic materials have better conductivities. Thus, covalency alone cannot explain the conductivity trend of these materials. In contrast, our calculated effective masses show good correlation with the experimental conductivity trend with the effective masses following the sequence: CuScO<sub>2</sub> < CuGaO<sub>2</sub> < CuAlO<sub>2</sub> < CuInO<sub>2</sub>. According to experiment, CuAlO<sub>2</sub> generally has a higher conductivity than CuGaO<sub>2</sub>. Apart from this inconsistency, our calculations predict CuScO<sub>2</sub>



to be the best conductor while  $\text{CuInO}_2$  should have the highest resistivity of the four compounds, which has indeed been found to be the case experimentally. Effective mass theory, however, is based on classical semiconductors with parabolic bands. Delafossites and Cu(I) based oxides in general have been shown to be polaronic in nature,<sup>3, 25, 90, 92, 331, 343, 351, 353</sup> and therefore will not be well described within effective mass theory. A simple visual analysis of the dispersion at the VBM for all four delafossites reveals the flat nature of the bands, which will not be conducive to high performance *p*-type conductivity. It is thus not surprising that *p*-type Cu(I)-based TCOs based on the delafossite structure have continued to fail to live up to the expectations placed on them by the semiconducting and optoelectronic industries<sup>6, 14, 72</sup>.

## 4.4 The Intrinsic Defects of $\text{SrCu}_2\text{O}_2$

### 4.4.1 Introduction

After the achievement of *p*-type conductivity in copper delafossites, Hosono *et al.* turned their attention to other copper oxide based compounds. This led to the discovery of *p*-type transparent conductivity in  $\text{SrCu}_2\text{O}_2$  in 1998.<sup>15</sup> It was initially thought that strontium copper oxide would be an improvement upon the delafossites through a reduction of Cu-Cu interactions (3-D in  $\text{Cu}_2\text{O}$  and 2-D in  $\text{CuMO}_2$ ) to one-dimensional, thereby increasing the band gap.<sup>81</sup> In fact,  $\text{SrCu}_2\text{O}_2$  was found to have a band gap of 3.3 eV, ideal for transparency, but its conductivity lags four orders of magnitude behind that of the best *p*-type TCOs at only  $5.3 \times 10^{-2} \text{ S cm}^{-1}$ .<sup>85</sup> However, one redeeming feature of  $\text{SrCu}_2\text{O}_2$  is the fact that its band gap is direct, since most *p*-type TCOs, such as the delafossites discussed above, have indirect band gaps. As direct band gaps are more efficient for the absorption/emission of light, TCOs with direct band gaps are more highly sought after for the production of *p-n* junctions.<sup>328</sup> This, along with the fact that  $\text{SrCu}_2\text{O}_2$  requires less harsh synthesis conditions than the delafossites, has made strontium copper oxide one of the most promising *p*-type TCOs for the development of transparent electronics. A successful *p-n* junction of *p*-type  $\text{SrCu}_2\text{O}_2$  in combination with *n*-type ZnO has already been fabricated.<sup>354-355</sup>

$\text{SrCu}_2\text{O}_2$  crystallises in a tetragonal structure of space group  $I4_1/amd$  with a unit cell defined by the lattice constants  $a = 5.480 \text{ \AA}$  and  $c = 9.825 \text{ \AA}$ ,<sup>356</sup> as shown in Fig. 4.21. Each Cu atom coordinates linearly to two oxygen atoms to form zigzag chains of O-Cu-O



bonds in the orthogonal [100] and [010] directions, while each Sr ion is surrounded by a distorted octahedron of oxygen atoms, with the two closest oxygen ions aligned linearly along the *c*-axis.

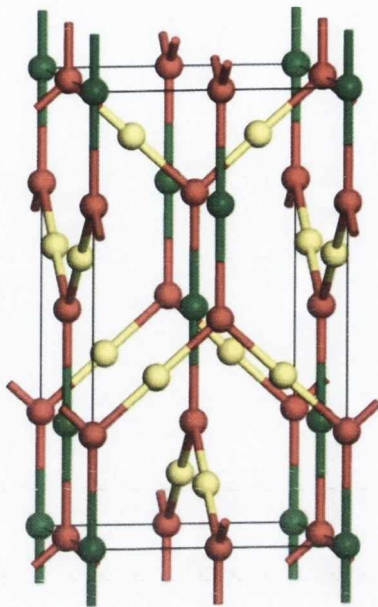


Fig. 4.21 The unit cell of SrCu<sub>2</sub>O<sub>2</sub>. Green atoms are Sr, yellow are Cu and red are O.

Conductivity in undoped SrCu<sub>2</sub>O<sub>2</sub> arises from the presence of holes, introduced by oxygen excess, which is presumed to be due to intrinsic defects, such as Cu vacancies or oxygen interstitials. Conduction is known to occur via a thermally activated mechanism with an activation energy of ~0.2 eV.<sup>15, 27</sup> The conduction mechanism is believed to be small polaron hopping, similar to that found for the copper delafossite TCOs.<sup>90</sup> It is possible to improve the conductivity through the introduction of dopants, such as K,<sup>27, 86, 357</sup> which increases the hole concentration, or Ca which increases the band gap and lowers the effective mass.<sup>87, 358</sup> Both dopants are found to result in lower activation energies for conduction, with K doped films having activation energies of ~0.1 eV<sup>27</sup> and Ca doping resulting in activation energies of ~0.16 eV.<sup>358</sup> However, the exact defects and mechanism responsible for *p*-type conductivity are not well understood.

Although some computational work on SrCu<sub>2</sub>O<sub>2</sub> has been performed, it has tended to focus on the electronic structure of the pure material without any analysis of the defect structure.<sup>86-87, 327, 358-361</sup> Electronic structure calculations have shown a direct gap at  $\Gamma$  and a valence band composed of a mixture of Cu 3*d* and O 2*p* states.<sup>81, 86-87, 327, 359-360</sup> To the best of our knowledge, there is only one previous computational study on intrinsic defects in SrCu<sub>2</sub>O<sub>2</sub>, which was carried out using GGA.<sup>325</sup> The only defects considered were copper and

oxygen vacancies, with no consideration of any other possible intrinsic defects which may occur in the system and no consideration of the electronic structure of any defects. As conductivity in  $\text{SrCu}_2\text{O}_2$  is thought to occur via a polaronic hole-hopping mechanism,<sup>27</sup> the defect structure should be polaronic in nature. However, GGA/LDA methods are well known to have problems in localising defects due to the self-interaction error, and thus it is unlikely to result in even a qualitatively correct defect structure.

The possibility of exchanging  $\text{Sr}^{2+}$  for various other +2 cations has previously been investigated. One proposed material is  $\text{PbCu}_2\text{O}_2$ , which possesses a different structure to  $\text{SrCu}_2\text{O}_2$  based in the space group  $C12/c1$ . However, its band gap is only 1.7 eV and therefore, it is not transparent, preventing its use as a TCO.<sup>86</sup> LDA calculations of  $\text{SrCu}_2\text{O}_2$ ,  $\text{MgCu}_2\text{O}_2$ ,  $\text{CaCu}_2\text{O}_2$  and  $\text{BaCu}_2\text{O}_2$  have been performed previously in order to test the effect of the cation on the electronic structure.<sup>87</sup>  $\text{SrCu}_2\text{O}_2$  was found to have the largest band gap and therefore the best transparency.  $\text{MgCu}_2\text{O}_2$  had the narrowest band gap and is therefore unlikely to be transparent, while  $\text{CaCu}_2\text{O}_2$  and  $\text{BaCu}_2\text{O}_2$  both had similar sized band gaps, 0.3 eV smaller than  $\text{SrCu}_2\text{O}_2$ , suggesting both materials to be transparent. All three proposed compounds had calculated hole effective masses lower than that of  $\text{SrCu}_2\text{O}_2$ , indicating that  $\text{SrCu}_2\text{O}_2$  is the worst *p*-type conductor of this set of materials. It was concluded from the calculations that the largest band gap could be achieved by doping  $\text{SrCu}_2\text{O}_2$  with a small amount of Ca, thereby retaining transparency while resulting in a lower hole effective mass.

The current calculations focus on the electronic structure of  $\text{SrCu}_2\text{O}_2$  and its intrinsic defects. The GGA+*U* methodology is used, thereby correcting for the inherent self-interaction error of DFT and resulting in improved defect localisation. The mechanism of intrinsic conductivity is explored, while attempting to understand the limited conduction in  $\text{SrCu}_2\text{O}_2$  which has so far restricted its use as a commercial transparent conductor.

#### 4.4.2 Computational Methods

Calculations were carried out using GGA+*U* to correct for the SIE. To demonstrate the self-interaction error of DFT in this system, Fig. 4.22 shows the band structure for a Cu vacancy defect as calculated using standard GGA. This shows the absence of any distinct single particle level in the band gap. Instead, GGA predicts a formally metallic system for the Cu vacancy, with the single particle level clearly crossing the Fermi level. This is completely at variance with the known activated conduction mechanism in this material,<sup>15</sup>



<sup>27</sup> and further highlights the unsuitability of LDA/GGA in describing materials with polaronic conduction.<sup>27</sup> The value of  $U$  employed in the GGA+ $U$  calculations was 5.2 eV applied to the Cu 3d states as for the delafossites above. Calculations were fully spin polarised in order to properly describe the unpaired electrons produced upon defect formation. A  $4 \times 4 \times 2$  Monkhorst-Pack<sup>145</sup>  $k$ -point grid was used for the unit cell with a planewave energy cut-off of 500 eV. Intrinsic defect calculations were performed in a  $2 \times 2 \times 1$  supercell containing 80 atoms with a  $2 \times 2 \times 2$   $k$ -point grid. The structural optimizations were deemed to be converged when the force on every ion was less than 0.01 eV Å<sup>-1</sup>.

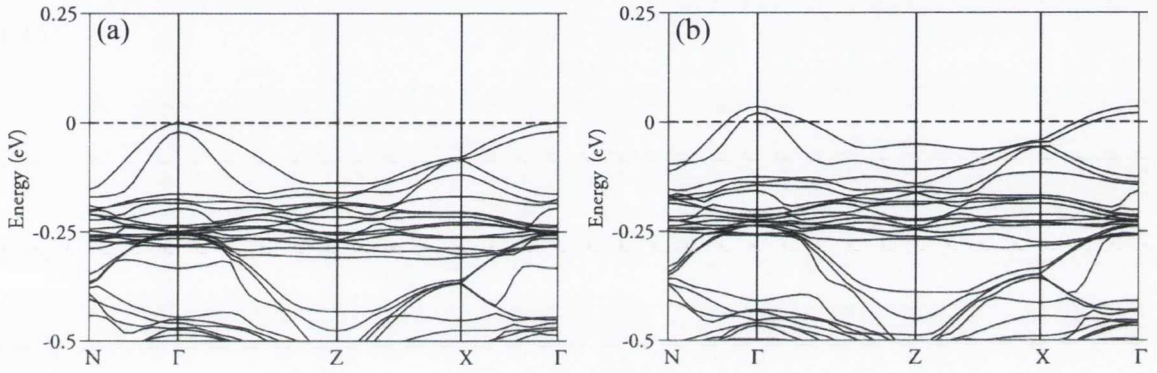


Fig. 4.22 The band structure of a Cu vacancy in SrCu<sub>2</sub>O<sub>2</sub> as calculated using standard GGA calculations. (a) shows the  $\alpha$ -spin bands and (b) shows the  $\beta$ -spin bands. The dashed line indicates the highest occupied level.

Defect calculations were carried out as outlined in Section 2.5. The following equation was used to calculate defect formation energies,  $E_f(D)$ :

$$E_f(D) = E_{tot}(D) - E_{tot}(\text{SrCu}_2\text{O}_2) + n_{\text{Sr}}E(\text{Sr}) + n_{\text{Cu}}E(\text{Cu}) + \frac{1}{2}n_{\text{O}}E(\text{O}_2) + n_{\text{Sr}}\mu_{\text{Sr}} + n_{\text{Cu}}\mu_{\text{Cu}} + n_{\text{O}}\mu_{\text{O}} \quad (4.1)$$

where  $E_{tot}(D)$  and  $E_{tot}(\text{SrCu}_2\text{O}_2)$  are the total energies of the defective and pure supercells;  $E(\text{Sr})$ ,  $E(\text{Cu})$  and  $E(\text{O}_2)$  are the energies of an Sr atom in Sr metal, Cu atom in Cu metal and an O<sub>2</sub> molecule respectively;  $n_A$  is the number of atoms of  $A$  exchanged with the external atomic reservoir and  $\mu_A$  is the chemical potential of element  $A$ .

The chemical potential limits can be set based on the procedure outlined in Section 2.5. The chemical potentials are first limited to a range determined by the formation enthalpy of SrCu<sub>2</sub>O<sub>2</sub>,  $\Delta H_f(\text{SrCu}_2\text{O}_2)$ , in order to maintain a stable compound:



$$\mu_{\text{Sr}} + 2\mu_{\text{Cu}} + 2\mu_{\text{O}} = \Delta H_f(\text{SrCu}_2\text{O}_2) \quad (4.2)$$

We calculated  $\Delta H_f(\text{SrCu}_2\text{O}_2)$  to be -7.27 eV, compared to its experimentally determined value of -8.21 eV.<sup>362</sup> To avoid precipitation into elemental Sr and Cu metals and O<sub>2</sub> gas, we also require:

$$\mu_{\text{Sr}} < 0, \mu_{\text{Cu}} < 0, \mu_{\text{O}} < 0 \quad (4.3)$$

For a ternary compound, the chemical potentials are further constrained by the decomposition of  $\text{SrCu}_2\text{O}_2$  into binary compounds. The atomic chemical potentials thus must obey the inequalities:

$$\mu_{\text{Cu}} + \mu_{\text{O}} \leq \Delta H_f(\text{CuO}) \quad (4.4)$$

$$2\mu_{\text{Cu}} + \mu_{\text{O}} \leq \Delta H_f(\text{Cu}_2\text{O}) \quad (4.5)$$

$$\mu_{\text{Sr}} + \mu_{\text{O}} \leq \Delta H_f(\text{SrO}) \quad (4.6)$$

The calculated formation enthalpies for CuO, Cu<sub>2</sub>O and SrO are -1.36 eV, -1.55 eV and -5.50 eV, compared to experimentally determined values of -1.63 eV,<sup>214</sup> -1.75 eV<sup>214</sup> and -6.14 eV,<sup>363</sup> respectively. Through the linear combination of Eqn. 4.4, 4.5 and 4.6 with Eqn. 4.2, the boundaries between  $\text{SrCu}_2\text{O}_2$  and the binary compounds can be defined. For example, combining Eqn. 4.4 with 4.2 gives the inequality:

$$\mu_{\text{Sr}} \geq \Delta H_f(\text{SrCu}_2\text{O}_2) - 2\Delta H_f(\text{CuO}) \quad (4.7)$$

which results in the limit  $\mu_{\text{Sr}} \geq -4.54$  eV to avoid decomposition to CuO. Similarly, the Cu<sub>2</sub>O limit can be derived as  $\mu_{\text{Sr}} - 2\mu_{\text{Cu}} \geq -4.17$  eV and that for SrO formation is defined as  $\mu_{\text{Sr}} - 2\mu_{\text{Cu}} \leq -3.73$  eV. Using these limits and the approach of Walsh *et al.*<sup>364</sup> and Persson *et al.*,<sup>365</sup> the phase diagram for  $\text{SrCu}_2\text{O}_2$  can be drawn up as in Fig. 4.23 (a), which shows the range of chemical potentials under which  $\text{SrCu}_2\text{O}_2$  forms.

The triangle vertices correspond to Sr/O-rich conditions ( $\mu_{\text{Sr}} = \mu_{\text{O}} = 0.00$  eV,  $\mu_{\text{Cu}} = -3.63$  eV), Cu/O-rich conditions ( $\mu_{\text{Sr}} = -7.27$  eV,  $\mu_{\text{Cu}} = \mu_{\text{O}} = 0.00$  eV) and Cu/Sr-rich conditions ( $\mu_{\text{Sr}} = \mu_{\text{Cu}} = 0.00$  eV,  $\mu_{\text{O}} = -3.63$  eV) and are calculated directly from Eqn. 4.2. The boundaries for binary phase formation result in a narrow range of chemical potentials under which  $\text{SrCu}_2\text{O}_2$  is thermodynamically stable. Our results show good agreement with the stability region found by repeating the above methodology using the experimental

formation enthalpies (experimental values taken from Refs. 214, 363) in Fig. 4.23 (b). This explains the narrow range of oxygen partial pressures under which  $\text{SrCu}_2\text{O}_2$  forms experimentally.<sup>366</sup>

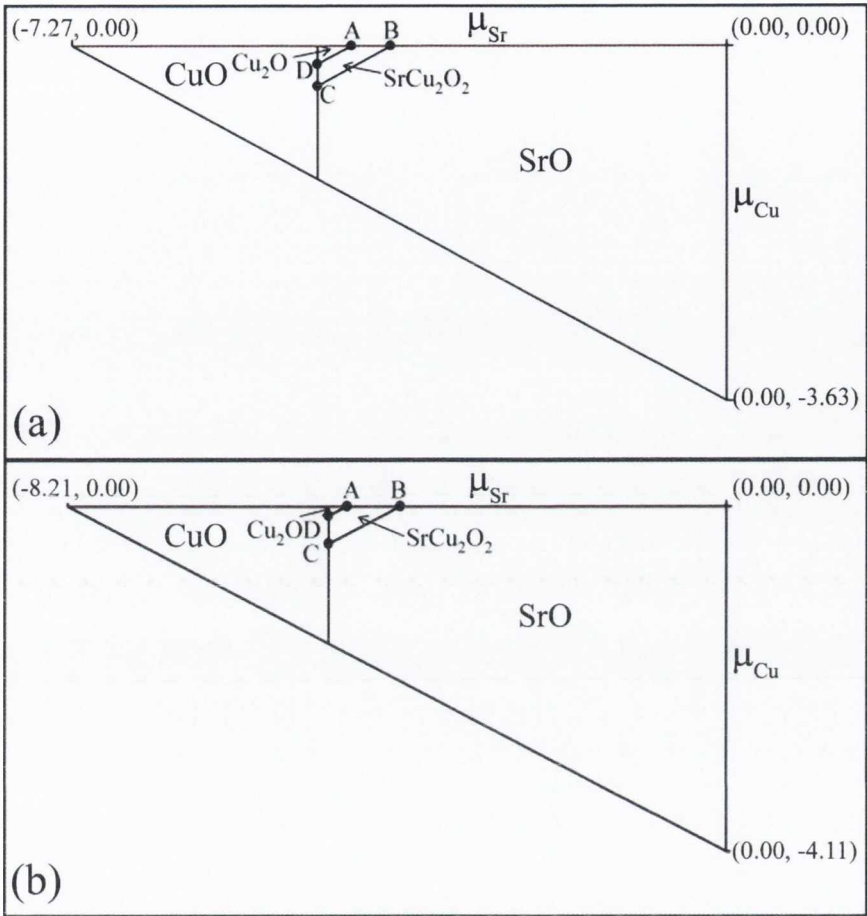


Fig. 4.23 The phase diagram of  $\text{SrCu}_2\text{O}_2$ , indicating the range of chemical potentials (in eV) under which  $\text{SrCu}_2\text{O}_2$  is stable. (a) Calculated phase triangle using formation energies from GGA+ $U$  calculations and (b) phase diagram found using experimental formation energies.<sup>214, 363</sup>

The four sets of chemical potentials marking the boundaries of stability are labelled A, B, C and D in Fig. 4.23 and their values are given in Table 4.10. The region under which  $\text{SrCu}_2\text{O}_2$  forms corresponds to relatively copper-rich, strontium-poor and oxygen-poor conditions. We have calculated defect energies using these four sets of conditions in order to examine the differences in defect equilibrium which result. Condition A is at the copper-rich limit of the stability region combined with a mid-range Sr chemical potential with  $\mu_{\text{O}}$  relatively low. Condition B is at the Sr-rich, O-poor, Cu-rich limits of the stability region and should therefore favour the formation of the oxygen-poor defects (Sr interstitials, O vacancies and Cu interstitials) and is thus the worst condition for  $p$ -type defects to form. Condition C corresponds to the Sr-poor, Cu-poor and O-rich limits of the stability region

and should favour oxygen-excess defects (Sr/Cu vacancies and O interstitials), thus providing optimum conditions for *p*-type conductivity. Finally, D is at the Sr-poor limit with  $\mu_{\text{Cu}}$  and  $\mu_{\text{O}}$  having mid-range values, thus favouring Sr vacancy formation.

|          | $\mu_{\text{Sr}}$ | $\mu_{\text{Cu}}$ | $\mu_{\text{O}}$ |
|----------|-------------------|-------------------|------------------|
| <b>A</b> | -4.16             | 0.00              | -1.55            |
| <b>B</b> | -3.72             | 0.00              | -1.77            |
| <b>C</b> | -4.54             | -0.41             | -0.95            |
| <b>D</b> | -4.54             | -0.19             | -1.17            |

Table 4.10 Values for Sr, Cu and O chemical potential limits marked A, B, C and D in Fig. 4.23.

### 4.4.3 Bulk Electronic Structure

The optimised cell parameters and bond lengths are shown in Table 4.11. The calculated lattice vectors and bond lengths for SrCu<sub>2</sub>O<sub>2</sub> are in excellent agreement with experiment,<sup>356</sup> showing a slight overestimation as expected for GGA+*U* calculations. The *a* and *c* lattice vectors are overestimated by 0.4% and 0.5% compared to experiment, while the Cu-O and Sr-O bond lengths also show 0.4 and 0.5% overestimations. Each Cu ion is coordinated to two O ions with a calculated bond distance of 1.85 Å, similar to the Cu-O bond length in the delafossites, while each Sr ion is coordinates to two oxygen ions with a bond distance of 2.47 Å. Each Sr also has four oxygen ions surrounding it in the *ab* plane at a distance of 2.75 Å.

|              | Calculated (Error) | Experimental |
|--------------|--------------------|--------------|
| <i>a</i> (Å) | 5.50 (+0.4%)       | 5.48         |
| <i>c</i> (Å) | 9.87 (+0.5%)       | 9.83         |
| Cu-O (Å)     | 1.85 (+0.4%)       | 1.84         |
| Sr-O (Å)     | 2.47 (+0.5%)       | 2.46         |

Table 4.11 Calculated lattice parameters and bond lengths for SrCu<sub>2</sub>O<sub>2</sub> compared to their experimental values.<sup>356</sup>

The calculated band structure for SrCu<sub>2</sub>O<sub>2</sub> is shown in Fig. 4.24 (a). The VBM and CBM both occur at  $\Gamma$ , making SrCu<sub>2</sub>O<sub>2</sub> a direct gap material with a calculated band gap of 2.1 eV. As discussed in Section 2.3.8, the optical band gap is not necessarily the same as the



fundamental band gap. In order to quantify the difference between these two parameters in  $\text{SrCu}_2\text{O}_2$ , we have calculated the optical absorption spectrum shown in Fig. 4.24 (b). Optical absorption begins at  $\sim 2.6$  eV, compared to our calculated fundamental direct band gap of  $\sim 2.1$  eV. Band-edge transitions at the  $\Gamma$  point are symmetry forbidden, consistent with the work of Nie *et al.*<sup>87</sup> Analysis of the calculated optical transition matrix indicates that the lowest energy allowed optical transition is from the VBM to the second conduction band at  $\Gamma$ . This corresponds to a difference of  $\sim 0.5$  eV between the optical and fundamental band gaps of this material. The GGA calculations underestimate the experimental optical gap ( $3.3 \text{ eV}$ <sup>15</sup>) by  $0.7$  eV due to the inherent error of DFT.

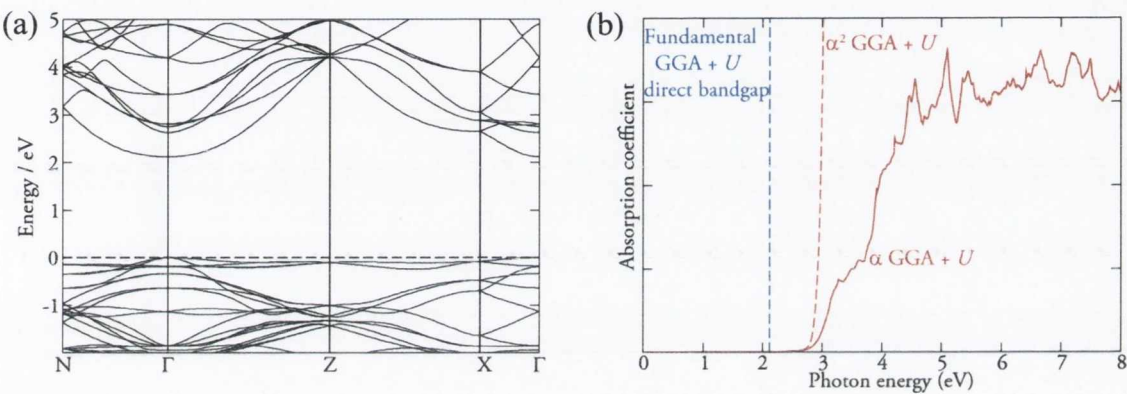


Fig. 4.24 (a) Band structure of pure  $\text{SrCu}_2\text{O}_2$  plotted along the high symmetry directions. The dashed line indicates the highest occupied level. (b) Calculated optical absorption spectrum of  $\text{SrCu}_2\text{O}_2$  summed over all possible direct valence to conduction band transitions. The dashed blue line marks the fundamental band gap and the onset of optical absorption is denoted by the red dashed line.

To estimate carrier mobility in  $\text{SrCu}_2\text{O}_2$ , we have calculated the effective masses at the VBM and CBM using the method outlined in Section 2.3.10. Effective masses are only used as an approximate indicator of conductivity in this case, as the conduction mechanism is polaronic, and the VBM is not perfectly parabolic.<sup>15, 27</sup> Table 4.12 shows the calculated effective masses along the high symmetry directions in  $\text{SrCu}_2\text{O}_2$ . The lowest VBM effective mass occurs along the direction  $\Gamma$ -N and has a value of  $0.79m_0$ , while the lowest CBM effective mass is along  $\Gamma$ -X with a magnitude of  $0.49m_0$ . Thus,  $\text{SrCu}_2\text{O}_2$  possesses better electron mobility for *n*-type conductivity than hole mobility for *p*-type conductivity. Indeed, a visual inspection of the band structure suggests the CBM to have much higher dispersion than the VBM which appears quite flat. This may be one of the reasons why  $\text{SrCu}_2\text{O}_2$  demonstrates such low *p*-type conductivities experimentally, and given that its hole effective mass is  $\sim 0.4m_0$  greater than the delafossites, explains why  $\text{SrCu}_2\text{O}_2$  performs worse than delafossite compounds as a TCO.

The calculated total and partial electronic density of states for  $\text{SrCu}_2\text{O}_2$  are shown in Fig. 4.25. The atomic projections were calculated using sphere radii of 1.55 Å for Sr, 1.45 Å for Cu and 1.45 Å for O. The overall composition of the density of states is similar to those of the delafossites discussed above. Fig. 4.25 shows the valence band to have three distinct regions, marked I, II and III. In Region I, the lower valence band between -5.3 and -2.8 eV, states of O 2*p* character mix with states of Cu 3*d* character, with the Cu 3*d* states dominating. Between -2.8 and -2 eV (Region II) states of Cu 3*d* character dominate with very little contribution from O 2*p* states. Finally, in Region III, the upper part of the valence band, from -2 eV to the VBM, there is significant mixing of O 2*p* and Cu 3*d* states, with the Cu 3*d* dominating. Sr ions provide very little contribution to the valence band. The conduction band is made up of a mixture of Sr *s/d*, Cu *s/d* and O *s/p* states.

|     | $\Gamma$ -Z | $\Gamma$ -N | $\Gamma$ -X |
|-----|-------------|-------------|-------------|
| VBM | 2.87        | 0.79        | 1.54        |
| CBM | 1.24        | 1.65        | 0.49        |

Table 4.12 Calculated effective masses (in  $m_0$ ) at the VBM and CBM of  $\text{SrCu}_2\text{O}_2$  along the high symmetry directions of the Brillouin Zone.

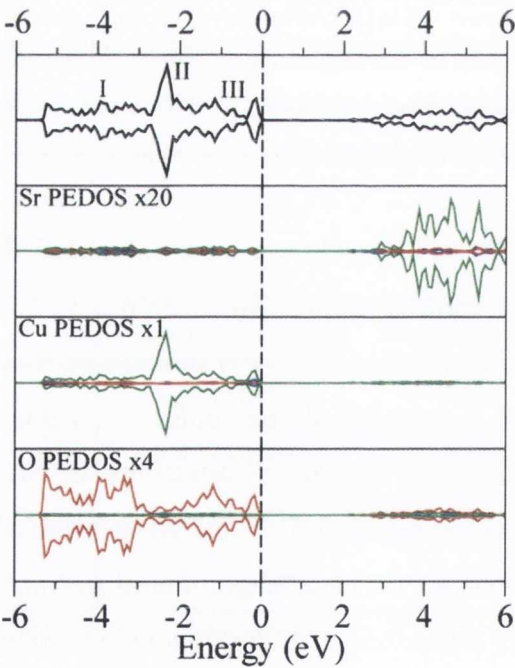


Fig. 4.25 Total and partial EDOS of  $\text{SrCu}_2\text{O}_2$  with blue lines showing *s* states, red lines for *p* states and green for *d* states. The dashed lines indicate the highest occupied state (the VBM).

Following the analysis for the delafossites, the valence band structure can be understood by

considering the orbital symmetry of the O  $2p$  and Cu  $3d$  orbitals involved. The orbital interactions can again be divided into those of  $\sigma$ -character (O  $2p_z$  and Cu  $3d_z^2$ ), those of  $\pi$ -character (O  $2p_x/p_y$  and Cu  $3d_{xz}/d_{yz}$ ) and those of non-bonding  $\delta$ -character (Cu  $3d_{xy}/d_{x^2-y^2}$ ). The bottom of the valence band in Region I corresponds to bonding  $\sigma$  and  $\pi$  interactions while Region III consists of antibonding  $\sigma$  and  $\pi$  interactions. Region II is an area of non-bonding interactions from  $d$ -orbitals of  $\delta$ -symmetry.

At the  $\Gamma$ -point of the Brillouin Zone, the VBM is made up of 59% Cu  $3d$  states, 30% O  $2p$  and 11% Cu  $4s$  states. Compared to the delafossites discussed above, there is a larger proportion of O  $2p$  states contributing to the valence band maximum. This suggests a higher degree of covalency in bonding in this case. Indeed, the Bader charges show the Sr ions to have a charge of  $+1.55e$ , the Cu to have a charge of  $0.45e$  and the O to have a charge of  $-1.23e$ . These charges indicate a higher degree of covalency in Cu-O bonding than for the delafossites, where the Cu charge is higher at  $0.50$ - $0.53e$ .

#### 4.4.4 X-ray Photoelectron Spectroscopy

The valence band X-ray photoemission spectrum of  $\text{SrCu}_2\text{O}_2$ , obtained by our collaborator Prof. Russ Egdel, <sup>86</sup> is shown in Fig. 4.26 along with our calculated cross-section weighted EDOS. The spectrum has been arbitrarily shifted so that the zero of the binding energy scale coincides with the top of the valence band to allow direct comparison between experimental and theoretical results. The cross-section weighted density of states is in excellent agreement with the XPS. The EDOS shows five main features, a strong central peak surrounded by two lower energy features and two higher energy features. Similarly, the XPS possesses a strong central peak with two shoulders at lower energy and two at higher energy. Rather than mirroring the total EDOS, the cross-section weighted EDOS follows the shape of the Cu  $3d$  states. This is because the Cu  $3d$  ionisation cross-section ( $1.2 \times 10^{-3}$  Mb) is a factor of 20 bigger than the cross-section of O  $2p$  states ( $6 \times 10^{-5}$  Mb). The lower energy features in the region of the O  $2p$  states (at  $-4.5$  and  $-5.5$  eV) arise due to covalent mixing between the Cu  $3d$  and O  $2p$  states which further demonstrates the high degree of covalency present within the Cu-O bonding.



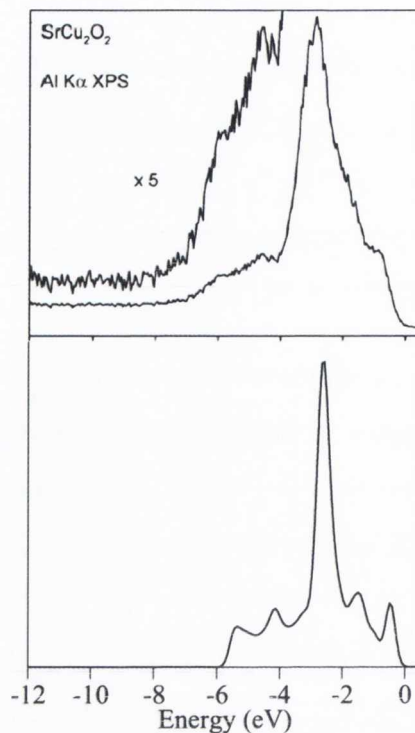


Fig. 4.26 Valence band X-ray photoemission spectrum of  $\text{SrCu}_2\text{O}_2$  (from Ref. 86) compared to the cross-section weighted density of states from GGA+ $U$  calculations.

#### 4.4.5 Defect Formation Energies

There are a number of intrinsic defects which can occur in  $\text{SrCu}_2\text{O}_2$ .  $P$ -type conductivity may be caused by the formation of oxygen-excess defects, such as Cu(I) vacancies ( $V'_{\text{Cu}}$ ),  $\text{O}^{2-}$  interstitials ( $\text{O}''_i$ ) or Sr(II) vacancies ( $V''_{\text{Sr}}$ ), which lead to conductivity through charge-compensating holes ( $h^\bullet$ ). Alternatively, if oxygen deficient defects such as  $\text{O}^{2-}$  vacancies ( $V^{\bullet\bullet}_\text{O}$ ), Cu(I) interstitials ( $\text{Cu}^\bullet_i$ ) or Sr(II) interstitials ( $\text{Sr}^{\bullet\bullet}_i$ ) form, the result would be  $n$ -type conductivity through charge-compensating electrons ( $e'$ ). To achieve good  $p$ -type conductivity in  $\text{SrCu}_2\text{O}_2$ , we thus require that defects which cause  $p$ -type conductivity have low formation energies, while those causing  $n$ -type conductivity should have higher formation energies to avoid the recombination of electrons and holes and subsequent loss in conductivity.

Table 4.13 shows the formation energies of defects in  $\text{SrCu}_2\text{O}_2$ , without taking chemical potentials into account. The defects have been split into two groups - those causing oxygen deficiency and those causing oxygen excess. There are two types of Cu vacancy that can occur in copper oxide based materials.<sup>367</sup> The first is a simple vacancy formed by the removal of a Cu(I) ion ( $V'_{\text{Cu}} + h^\bullet$ ). The second type is known as a split vacancy and results

when a Cu ion near a Cu vacancy is displaced towards the vacancy, effectively resulting in two Cu vacancies with an interstitial Cu in between ( $2V'_{\text{Cu}} + \text{Cu}_i^{\bullet} + h^{\bullet}$ ). As  $\text{SrCu}_2\text{O}_2$  is known to become non-stoichiometric through oxygen excess, it might be expected that the defects causing oxygen excess would be much lower in energy than oxygen deficient defects, which should be energetically unfavourable. The defect with the lowest energy overall is  $\text{O}_i'' + 2h^{\bullet}$ , with a formation energy of 0.68 eV, suggesting oxygen excess in  $\text{SrCu}_2\text{O}_2$  to be caused by oxygen interstitials. The lowest energy oxygen deficient defect is  $\text{Sr}_i^{\bullet\bullet} + 2e'$  with a formation energy of 0.85 eV. Since this is quite a low formation energy, a substantial amount of Sr interstitials could form, destroying any *p*-type conductivity. Conversely,  $V_{\text{Sr}}'' + 2h^{\bullet}$  has a very high formation energy, suggesting that it is unlikely to be a major cause of oxygen excess in the material, while  $V_{\text{O}}^{\bullet\bullet} + 2e'$  will probably not form as a hole-killer defect due to its high formation energy.

| Oxygen Excess                         | Energy (eV) |
|---------------------------------------|-------------|
| $V'_{\text{Cu}} + h^{\bullet}$        | 1.29        |
| Split $V'_{\text{Cu}} + h^{\bullet}$  | 2.12        |
| $\text{O}_i'' + 2h^{\bullet}$         | 0.68        |
| $V_{\text{Sr}}'' + 2h^{\bullet}$      | 5.50        |
| Oxygen Deficient                      | Energy (eV) |
| $V_{\text{O}}^{\bullet\bullet} + 2e'$ | 4.06        |
| $\text{Sr}_i^{\bullet\bullet} + 2e'$  | 0.85        |
| $\text{Cu}_i^{\bullet} + e'$          | 2.54        |

Table 4.13 Defect formation energies (in eV) in  $\text{SrCu}_2\text{O}_2$  without taking chemical potential into account. Split  $V'_{\text{Cu}} + h^{\bullet} = 2V'_{\text{Cu}} + \text{Cu}_i^{\bullet} + h^{\bullet}$ .

The inclusion of chemical potentials leads to a complete change in the trends in Table 4.13, due to the restricted chemical potential range under which  $\text{SrCu}_2\text{O}_2$  forms. This is shown in Table 4.14 under the four conditions marked in Fig. 4.23. As the stability region for  $\text{SrCu}_2\text{O}_2$  corresponds to Sr-poor conditions combined with a low oxygen chemical potential, oxygen and strontium interstitials are destabilised under all conditions while Sr vacancies become lower in energy.  $\mu_{\text{Cu}}$  is close to zero in the  $\text{SrCu}_2\text{O}_2$  stability region and hence, the formation energies of copper vacancies and interstitials are only weakly affected by chemical potential changes.

Under Condition A ( $\mu_{\text{Sr}} = -4.16$  eV,  $\mu_{\text{Cu}} = 0$  eV,  $\mu_{\text{O}} = -1.55$  eV), the lowest energy defect is  $V'_{\text{Cu}} + h^\bullet$ . This corresponds to Cu-rich conditions, under which Cu vacancies will have their highest possible formation energy.  $V''_{\text{Sr}} + 2h^\bullet$  also has a low formation energy of 1.34 eV and may contribute to the overall defect structure.  $\text{Sr}_i^{\bullet\bullet} + 2e'$  is the highest energy defect and hence, is very unlikely to form. In fact, all of the oxygen deficient defects are higher in energy than any of the oxygen-excess defects. Hence, these conditions will result in a net non-stoichiometry due to oxygen-excess.

| Oxygen Excess                        | A           | B           | C           | D           |
|--------------------------------------|-------------|-------------|-------------|-------------|
| $V'_{\text{Cu}} + h^\bullet$         | <b>1.29</b> | <b>1.29</b> | <b>0.88</b> | 1.10        |
| Split $V'_{\text{Cu}} + h^\bullet$   | 2.12        | 2.12        | 1.71        | 1.93        |
| $\text{O}_i'' + 2h^\bullet$          | 2.23        | 2.45        | 1.63        | 1.85        |
| $V''_{\text{Sr}} + 2h^\bullet$       | 1.34        | 1.77        | 0.96        | <b>0.96</b> |
| Oxygen Deficient                     | A           | B           | C           | D           |
| $V^\bullet_0 + 2e'$                  | 2.51        | 2.29        | 3.10        | 2.89        |
| $\text{Sr}_i^{\bullet\bullet} + 2e'$ | 5.02        | 4.58        | 5.40        | 5.40        |
| $\text{Cu}_i^\bullet + e'$           | 2.54        | 2.54        | 2.95        | 2.73        |

Table 4.14 Formation energies (in eV) of intrinsic defects in  $\text{SrCu}_2\text{O}_2$  under the chemical potential limits listed in Table 4.10. The lowest energy defects under each limit are marked in red. Split  $V'_{\text{Cu}} + h^\bullet = 2V'_{\text{Cu}} + \text{Cu}_i^\bullet + h^\bullet$ .

Condition B corresponds to copper-rich conditions, with the strontium chemical potential also having its highest possible value in the stability range (i.e. relatively strontium-rich conditions) and the oxygen chemical potential having its lowest possible value (oxygen-poor conditions). This combination of chemical potentials represents the most favourable conditions in the stability range for oxygen deficiency and indeed, all oxygen deficient defects possess lower formation energies than under conditions A, C or D. However, oxygen deficient defects are still more than 1 eV higher in energy than the lowest energy oxygen excess defect ( $V'_{\text{Cu}} + h^\bullet$ ), hence a net oxygen-excess will result, dominated by copper vacancies.

Under Condition C,  $\mu_{\text{Cu}}$  and  $\mu_{\text{Sr}}$  are at their lowest values in the stability range, while  $\mu_{\text{O}}$  is at the oxygen-rich limit for  $\text{SrCu}_2\text{O}_2$  formation. These are the optimum conditions for oxygen-rich  $\text{SrCu}_2\text{O}_2$  as this set of chemical potentials results in the lowest possible



formation energies for copper vacancies, strontium vacancies and oxygen interstitials. The energies of the oxygen-rich defects are all very low, in the range 0.88-1.71 eV, while the oxygen deficient defects are all higher in energy in the range 2.95-5.40 eV. These conditions should thus result in the greatest possible oxygen excess and hence, *p*-type conductivity. The lowest energy defect is  $V'_{\text{Cu}} + h^{\bullet}$  with a formation energy of 0.88 eV with  $V''_{\text{Sr}} + 2h^{\bullet}$  also having a low formation energy of 0.96 eV. Hence, an overall oxygen-excess will result, with the system dominated by copper vacancies.

Under the chemical potential set D,  $\mu_{\text{Sr}}$  is at the strontium-poor limit of  $\text{SrCu}_2\text{O}_2$  stability, while  $\mu_{\text{Cu}}$  is relatively high (-0.19 eV) and  $\mu_{\text{O}}$  is quite low (-1.17 eV). This lowers the energy of strontium vacancies relative to other defects so that they become the lowest energy defect.  $V'_{\text{Cu}} + h^{\bullet}$  also has a low formation energy of 1.10 eV and thus will contribute to the defect structure. Oxygen deficient defects remain as the highest energy defects and are thus unlikely to form as hole-killer defects. Once again, an oxygen-excess will result favouring *p*-type conductivity.

Having surveyed the various limits of the stability region, we can thus conclude that copper vacancies are likely to dominate the defect structure under most experimental conditions. Given the right combination of chemical potentials, Sr vacancies may become lower in energy but this appears to be over a small area of the stability region. However, under no condition will any of the oxygen deficient defects begin to dominate the defect structure, as their energies are always much higher than the oxygen-rich defects.

#### 4.4.6 Defect Levels

Although energetic analysis allows us to predict the most stable defects, it does not tell us which of these, if any, will result in conductivity. It is therefore of importance to examine the changes in electronic structure that result from defect formation. Defects which result in good *p*-type conductivity should possess single particle levels near the valence band maximum, which cause *p*-type conductivity through hole-hopping. On the other hand, successful *n*-type conductivity requires the relevant defects to have electron donor levels near the conduction band minimum. Fig. 4.27 illustrates the positions of the single particle levels (SPL) within the band gap of  $\text{SrCu}_2\text{O}_2$ .

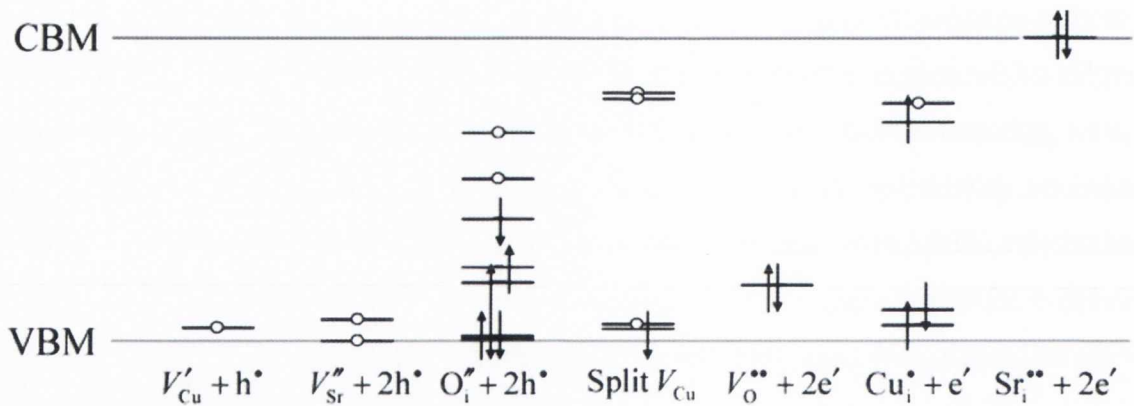


Fig. 4.27 Positions of single particle levels of intrinsic defects in the band gap of SrCu<sub>2</sub>O<sub>2</sub> at the  $\Gamma$  point of the Brillouin Zone. Empty circles indicate holes and arrows indicate electrons in up/down spins.

The two lowest energy *p*-type defects, copper and strontium vacancies, both have single particle levels located just above the VBM. For  $V'_{Cu} + h^\bullet$ , one hole state is produced 0.09 eV above the VBM, while for  $V''_{Sr} + 2h^\bullet$  two hole states occur - the lowest at the VBM and the second located 0.15 eV above the VBM.  $O'_i + 2h^\bullet$  produces a number of SPL inside the band gap. Six of these are occupied by the electrons of the inserted oxygen while two hole states are located 1.13 and 1.45 eV above the valence band. As these are very deep in the band gap, oxygen interstitials can be expected to have a high activation energy for conduction. The position of the SPL, combined with their high formation energies, suggests that oxygen interstitials are an unlikely contributor to *p*-type conductivity in SrCu<sub>2</sub>O<sub>2</sub>. Split vacancies result in two SPL above the VBM and two unoccupied SPL below the CBM. The two SPL above the VBM consist of a filled state and an empty hole state. As the split vacancy consists of a combination of two copper vacancies with a copper ion in an interstitial site, the two SPL near the VBM can be considered as acceptor levels resulting from the two vacancies while the SPL near the CBM are donor levels from the interstitial.

Electron donor defects can introduce *n*-type conductivity if their SPL occur close to the CBM. Fig. 4.27 suggests that  $Sr''_i + 2e'$  could induce *n*-type conductivity as it introduces two electrons into the bottom of the conduction band. However,  $Sr''_i + 2e'$  is the highest energy defect under all conditions, hence the electrons produced will always be charge-compensated by holes from the acceptor defects and it will not cause *n*-type conductivity.  $Cu'_i + e'$  results in two filled SPL just above the VBM, one filled SPL 0.59 eV below the CBM and one empty SPL 0.46 eV below the CBM. These levels are quite deep, suggesting that copper interstitials will not result in *n*-type conduction. The existence of SPL near the



VBM is unexpected for this defect. The explanation for these levels lies in the underlying defect structure. Fig. 4.28 illustrates the relaxed geometry of the Cu interstitial defect. The inserted Cu atom relaxes towards a lattice Cu to form a Cu-Cu dimer. The defect can therefore be described in Kröger-Vink notation as  $V'_{Cu} + 2Cu_i^\bullet$ . The SPLs above the VBM thus result from the formation of  $V'_{Cu}$  and those near the CBM result from the Cu-dimer.  $V_{O}^{\bullet\bullet} + 2e'$  cannot cause *n*-type conductivity in  $SrCu_2O_2$  as its donor SPL occurs deep in the band gap, 0.22 eV above the VBM.

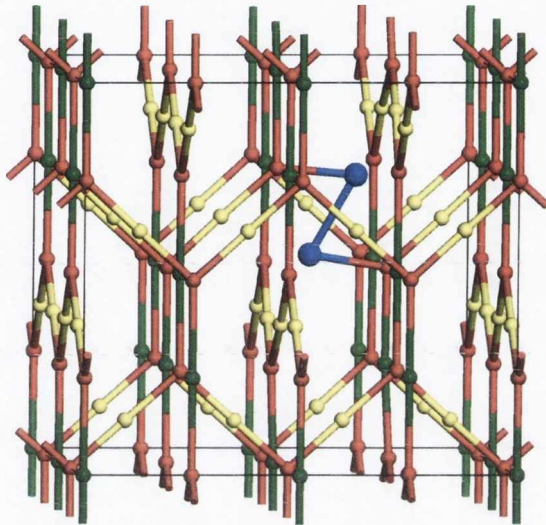


Fig. 4.28 Relaxed geometry of the inserted  $Cu_i^\bullet + e'$  defect in  $SrCu_2O_2$ , with Cu ions in yellow, Sr in green and O in red. The defect relaxes to form Cu dimer shown as two blue Cu atoms.

#### 4.4.7 Electronic Structure of $V'_{Cu} + h^\bullet$

To understand the reasons behind the stability of  $V'_{Cu} + h^\bullet$ , we present a detailed analysis of its geometry and electronic structure. The local geometry surrounding a copper vacancy is shown in Fig. 4.29. The oxygen ions neighbouring the vacancy have lost coordination from 3- to 2-fold coordinate and relax away from the vacancy by 0.24 Å due to Coulombic repulsion. The two copper ions nearest to the vacancy also relax away by 0.11 Å, while the four nearest-neighbour strontium ions relax towards the vacancy by 0.13 Å.

The band structure of  $V'_{Cu} + h^\bullet$  is plotted in Fig. 4.30. The removal of a Cu atom leads to a system with one unpaired electron, resulting in a singly unoccupied level in the band gap of the material. This level is located 0.09 eV above the VBM at the  $\Gamma$ -point in the  $\beta$ -spin component of the band structure and is quite flat, suggesting a localised nature and a high effective mass. The level is too deep for thermal excitation of electrons from the valence



band ( $<0.03$  eV). The defect state is composed of mixed Cu  $3d$  and O  $2p$  states, mainly from atoms near the defect. To clarify the nature of this state, we have plotted the electron density of this band as a light blue isosurface in Fig. 4.29. Here, we can see that the hole state is spread across a small number of atoms surrounding the defect – six Cu and two O ions. This appears to be a relatively localised defect state and examination of the Bader charges (Table 4.15) associated with the defect shows a total of 67% of the charge to be on the Cu ions while 33% is located over the O ions. The Cu and O ions neighbouring the defect hold 60% of the charge altogether, indicating a high degree of localisation near the defect. This suggests that conduction for this defect will occur via a polaronic hopping mechanism rather than a band conduction mechanism.

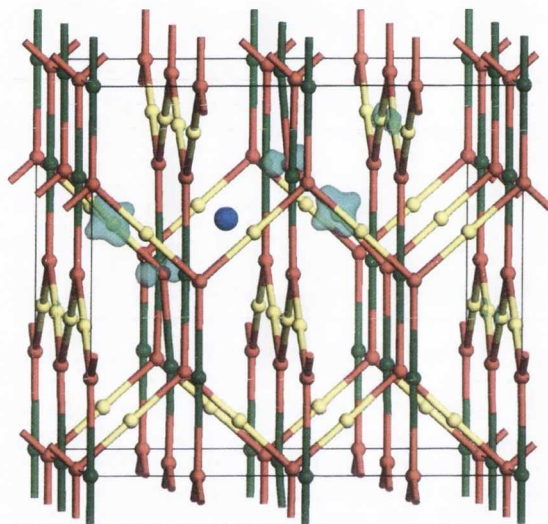


Fig. 4.29 Relaxed geometry of  $V'_{Cu} + h^*$  in  $SrCu_2O_2$ , with blue atom indicating the vacancy, Sr in green, Cu in yellow and O in red. Light blue isosurface illustrates the electron density of the defect band located 0.09 eV above the VBM at an isosurface level of  $0.05 \text{ e}/\text{\AA}^3$

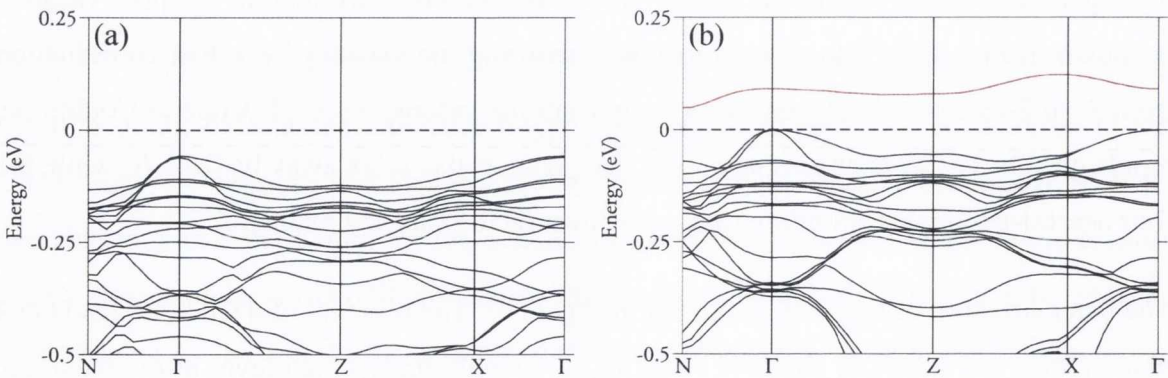


Fig. 4.30 Band structure for  $V'_{Cu} + h^*$  defect in  $SrCu_2O_2$ , showing (a)  $\alpha$ -spin and (b)  $\beta$ -spin bands. The dashed line indicates the highest occupied level. The red line indicates the defect acceptor band.

| Atom                     | Bader Charge ( <i>e</i> ) |
|--------------------------|---------------------------|
| <b>Sr<sub>tot</sub></b>  | 0.00                      |
| <b>Cu<sub>tot</sub></b>  | 0.67                      |
| <b>O<sub>tot</sub></b>   | 0.33                      |
| <b>6 Cu<sub>nn</sub></b> | 2×0.13, 4×0.05            |
| <b>2 O<sub>nn</sub></b>  | 2×0.08                    |

Table 4.15 Bader charges (in *e*) for acceptor state located 0.09 eV above the VBM for the  $V'_{\text{Cu}} + h^{\bullet}$  defect in  $\text{SrCu}_2\text{O}_2$ , showing total Sr, Cu and O charges and charges on Cu and O ions neighbouring defect (Cu<sub>nn</sub> and O<sub>nn</sub>).

### 4.4.8 Electronic Structure of $V''_{\text{Sr}} + 2h^{\bullet}$

As Sr vacancies may also contribute to the defect structure, we have performed a thorough investigation of their electronic structure to investigate the reasons behind their stability. The relaxed geometry surrounding the  $V''_{\text{Sr}} + 2h^{\bullet}$  defect is shown in Fig. 4.31. Removal of an Sr ion results in the loss of coordination of two oxygen atoms from 3- to 2-coordinate and their relaxation away from the vacancy by 0.33 Å, caused by the Coulombic repulsion between the effective negative charge of the vacancy and the negatively charged oxygens. The four Sr ions nearest to the vacancy relax towards the vacancy by 0.28 Å each, due to the attraction of the positively charged  $\text{Sr}^{2+}$  and the vacancy.

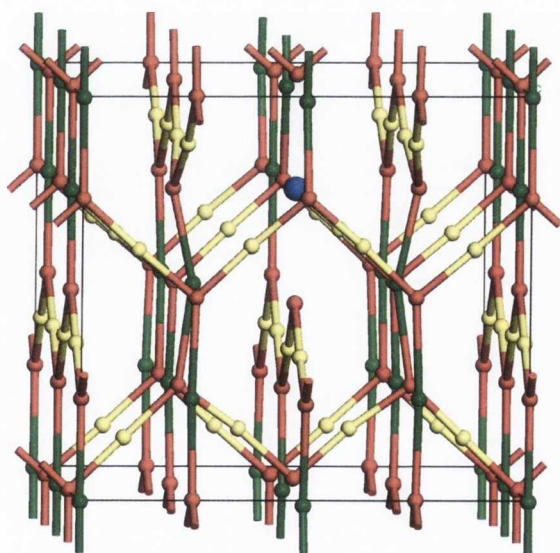


Fig. 4.31 Structure of  $V''_{\text{Sr}} + 2h^{\bullet}$  in  $\text{SrCu}_2\text{O}_2$  with the blue atom marking Sr vacancy, Cu atoms in yellow, Sr in green and O in red.

To examine the nature of the holes created upon vacancy formation, we have plotted the band structure of  $V_{\text{Sr}}'' + 2h^\bullet$  in Fig. 4.32. Two singly occupied bands are seen in the  $\beta$ -spin component of the band structure. Both bands are quite flat, indicating that they will have a high hole effective mass for carrier transport. The lower acceptor band (Band I) lies across the top of the valence band and crosses the Fermi level which would result in metallic conduction, in contrast to the known activated conduction model. However, the flat nature of this band suggests it to be highly localised, giving rise to conductivity via polaronic hopping. The upper SPL (Band II) is split off from the valence band by 0.15 eV. Both of these levels are composed of a mixture of Cu 3*d* and O 2*p* states from atoms surrounding the vacancy.

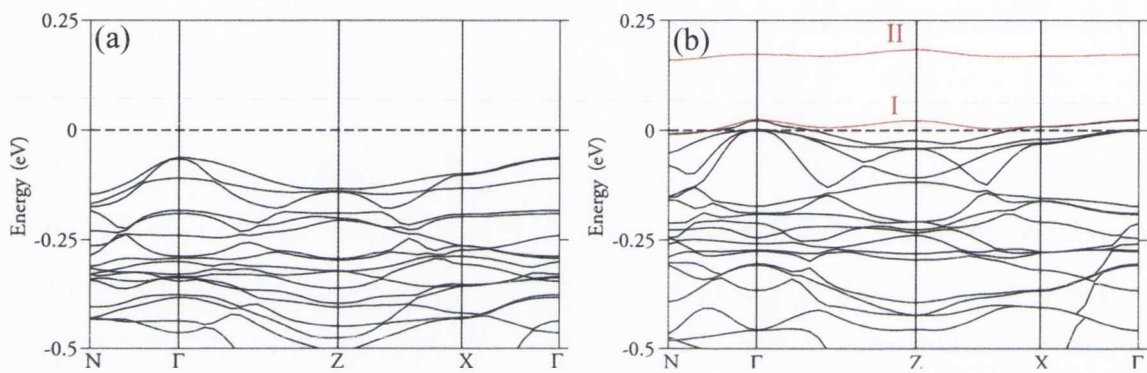


Fig. 4.32 Band structure for  $V_{\text{Sr}}'' + 2h^\bullet$  in  $\text{SrCu}_2\text{O}_2$  showing (a)  $\alpha$ -spin and (b)  $\beta$ -spin bands. The dashed line indicates the highest occupied level and the red lines are unoccupied acceptor bands.

To investigate the exact nature of the defect bands, we have plotted the partial charge density of both bands in Fig. 4.33 and show a breakdown of their composition in terms of Bader charges in Table 4.16. Band I is the more delocalised of the two bands (Fig. 4.33 (a)), with the charge density spread mainly over 8 Cu ions. 36% of the total charge is localised over these eight ions with the remaining charge delocalised over Cu and O ions further from the vacancy, so that a total of 73% of the charge is on Cu while 27% is on O ions. Band II shows a much higher degree of localisation, with the partial charge density in Fig. 4.33 (b), localised over four Cu ions in a tetrahedral arrangement, with very little charge density elsewhere in the system. The Bader charges show 52% of the total charge for this state to be localised on these four atoms, though the overall band composition is similar to Band I with 72% of the charge on Cu and 28% on O ions. The localisation of both defect states is suggestive of a polaronic hopping mechanism of conductivity.



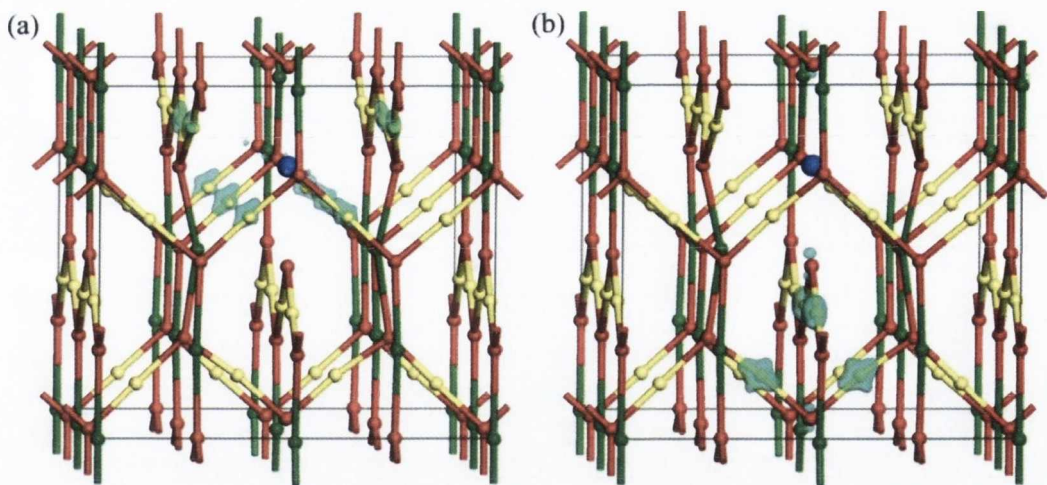


Fig. 4.33 Partial charge density for defect states of  $V_{\text{Sr}}'' + 2h^*$  in  $\text{SrCu}_2\text{O}_2$  located (a) at VBM and (b) 0.15 eV above VBM plotted on a blue isosurface of  $0.08 \text{ e}/\text{\AA}^3$ . The blue atom is the Sr vacancy, red atoms are O, green are Sr and yellow are Cu.

| Atom                     | Band I          | Band II         |
|--------------------------|-----------------|-----------------|
| $\text{Sr}_{\text{tot}}$ | 0.00            | 0.00            |
| $\text{Cu}_{\text{tot}}$ | 0.73            | 0.72            |
| $\text{O}_{\text{tot}}$  | 0.27            | 0.28            |
| $\text{Cu}_n$            | $8 \times 0.05$ | $4 \times 0.13$ |

Table 4.16 Bader charges (in  $e$ ) for acceptor bands (Band I at VBM and Band II 0.15 eV above VBM) induced by  $V_{\text{Sr}}'' + 2h^*$  in  $\text{SrCu}_2\text{O}_2$ , indicating total Sr, Cu and O charges and charges on Cu ions near the vacancy ( $\text{Cu}_n$ ).

### 4.4.9 Discussion

When performing electronic structure calculations, it is extremely useful to be able to compare the obtained data to experiment, to determine the accuracy of the calculations. By calculating a cross-section weighted density of states for  $\text{SrCu}_2\text{O}_2$ , we have directly compared our GGA+ $U$  valence band structure to the experimental electronic structure derived using X-ray photoemission spectroscopy. This shows our calculations to be highly accurate in not only reproducing the main XPS peak but also the shoulders at higher and lower binding energies. This demonstrates the ability to use DFT calculations in conjunction with experiment, in order to fully understand the valence band electronic structure of a material.

The 0.5 eV difference between the calculated values for the optical and fundamental band gaps of  $\text{SrCu}_2\text{O}_2$  has implications for future theoretical studies of this material. Currently,

many computational studies rely on a fitting procedure to align the calculated fundamental gap with the known experimental optical gap. This has become a regular occurrence in GGA+ $U$  calculations, where  $U$  values are often chosen based on their ability to reproduce the band gap,<sup>35, 368</sup> despite the fact that this procedure is only warranted for Mott insulators where the gap originates from the splitting of states of the same nature. In fact, some researchers still employ *a posteriori* corrections such as the ‘scissors operators’ to correct the problems GGA/LDA functionals have in predicting defect levels relative to ‘correct positioning’ of the band edges.<sup>368</sup> Given that the current study leads to the conclusion that the known experimental optical gap of  $\sim 3.3$  eV does not correspond to the fundamental gap, this casts into doubt any studies which use the experimental gap of  $\text{SrCu}_2\text{O}_2$  as a fitting parameter. If a fitting procedure is applied (which is a highly questionable practice), the calculated gap should be fitted to an experimental gap of  $\sim 2.8$  eV.

Analysis of the bulk electronic structure suggests that one explanation for the poor conductivity in  $\text{SrCu}_2\text{O}_2$  is the relatively high effective mass of the VBM. It is clear from the flat nature of the bands at the VBM (Fig. 4.24), that  $\text{SrCu}_2\text{O}_2$  does not possess the necessary dispersion for good  $p$ -type conduction, therefore it is not surprising that the effective masses of the VBM are so high. Conductivity in  $\text{SrCu}_2\text{O}_2$  occurs via a polaronic-hopping conduction mechanism rather than a band conduction mechanism so the effective mass may not be as important in this case. In order to improve conductivity it is necessary to change the nature of the VBM, perhaps through the introduction of dopants such as Ca.<sup>87</sup> This may result in lower effective masses at the VBM and may alter the conduction mechanism so that it is more band-like in nature similar to conduction mechanisms in  $n$ -type TCOs. Further experimental and theoretical work on dopants is thus of importance to attempt to optimise conductivity in this material.

This study represents the first comprehensive analysis of the intrinsic defects of  $\text{SrCu}_2\text{O}_2$ . We demonstrate that GGA is unsuitable to treat defects in this material as it results in the complete delocalisation of hole states, incorrectly predicting metallic conduction. Previous GGA/LDA studies of  $p$ -type defects in various copper delafossite TCOs and  $\text{SrCu}_2\text{O}_2$ <sup>325, 333, 369</sup> are thus questionable, given that they are unlikely to result in the correct localisation of defects required for a polaronic hopping conduction mechanism.<sup>3, 25, 331, 353</sup> GGA+ $U$  calculations show distinct acceptor levels in the band gap for most of the defects, consistent with the activated conductivity observed experimentally.<sup>15, 27</sup> The flatness of these defect bands is indicative of a highly localised nature with a high hole effective mass, indicating that  $p$ -type intrinsic defects in  $\text{SrCu}_2\text{O}_2$  will conduct via a polaronic hopping



mechanism. However, although  $V_{\text{Sr}}'' + 2h^*$  possesses two very flat bands, the lower energy state for this defect crosses the Fermi level, which should give rise to metallic conduction. Nonetheless, this defect band shows a high degree of localisation with most of the charge residing on 8 Cu ions neighbouring the defect, suggestive of polaronic conduction. This indicates that GGA+ $U$  places the defect state too low in energy and that the band should instead reside deep in the band gap, resulting in an activated conduction mechanism. Thus, a further investigation of this defect using more sophisticated methods such as hybrid-DFT may be needed to confirm the nature of its electronic structure.

Examination of the defect formation energies in  $\text{SrCu}_2\text{O}_2$  shows the importance of consideration of chemical potentials in this material. Omission of these leads to the mistaken conclusion that oxygen interstitials are the most stable defect, with Sr interstitials also having low formation energies and Sr vacancies appearing to be very high in energy. Due to the narrow range of chemical potentials under which  $\text{SrCu}_2\text{O}_2$  is stable, which correspond to relatively Sr-poor, Cu-rich and O-poor conditions, we have shown that the most stable defects are Cu vacancies and Sr vacancies, which will form in different concentrations, depending on the chemical conditions. Oxygen-excess is favoured under all conditions within the stability range of  $\text{SrCu}_2\text{O}_2$ , with oxygen deficient defects unlikely to form. Combining the energetics with the positions of the SPL indicates that both  $V_{\text{Cu}}' + h^*$  and  $V_{\text{Sr}}'' + 2h^*$  are likely to lead to  $p$ -type conductivity through acceptor states located above the valence band maximum. These were shown to be localised on several Cu and O ions in agreement with an activated hole-hopping mechanism of conductivity. This is consistent with the activation energy of 0.236 eV seen experimentally.<sup>27</sup> While strontium interstitials do introduce defect levels suitable for  $n$ -type conductivity, they are highly unlikely to occur in  $\text{SrCu}_2\text{O}_2$  due to the high formation energies of these defects.

## 4.5 Conclusions

GGA+ $U$  calculations of Cu(I)-based TCOs have been demonstrated to be extremely effective not only for modelling the bulk electronic structure but also for performing defect studies. The calculated valence band densities of states for all compounds are in excellent agreement with experimental X-ray photoemission spectra, demonstrating the ability of electronic structure calculations to be used as a tool to interpret experimental data. Through a detailed analysis of the EDOS, we have fully explained the bonding and antibonding interactions between Cu 3*d* and O 2*p* states which give rise to the valence band features of



the Group 3 and 13 delafossites and extended this analysis to explain the valence band features of  $\text{SrCu}_2\text{O}_2$ .

We have found that most of these compounds ( $\text{CuInO}_2$ ,  $\text{CuGaO}_2$ ,  $\text{SrCu}_2\text{O}_2$ ) have an optically-forbidden transition at the fundamental band gap. The result of this is that the experimentally-measured optical gap may be as much as 0.5 eV larger than the fundamental band gap. Hence, extreme caution must be taken for these compounds when comparing calculated and experimental band gaps. Although HSE06 calculations normally result in a reasonable estimate of the band gap, we have shown that in the case of copper delafossites, HSE06 consistently overestimates the band gap which may be due to the lack of polaronic corrections in the calculations.

Effective masses have been successfully used to explain the conductivity trends for these compounds.  $\text{CuScO}_2$  was found to have the lowest effective mass, corresponding to the highest experimental conductivity, while the effective mass for  $\text{SrCu}_2\text{O}_2$  was calculated to be very high ( $0.79m_0$ ), thus explaining why its conductivity remains very low. Analysis of the formation of intrinsic defects in  $\text{SrCu}_2\text{O}_2$  tell us that *n*-type (oxygen deficient) defects are unlikely to form, and that *p*-type (oxygen excess) defects are favoured under all growth conditions. Our results indicate that both  $V'_{\text{Cu}} + h^\bullet$  and  $V''_{\text{Sr}} + 2h^{\bullet\bullet}$  can cause distinct acceptor levels above the VBM, consistent with the activated conductivity reported experimentally, and are the probable cause of *p*-type conductivity in this material.

# Chapter 5: GGA+*U* Investigation of Intrinsic and Extrinsic defects in NiO

## 5.2 Summary

In this chapter, we investigate the intrinsic and extrinsic defects of the *p*-type TCO NiO using the GGA+*U* methodology. We examine the changes in electronic structure resulting from oxygen and nickel vacancies, as well as Li and N dopants, at bulk sites and at sites on the {100} surface. Previous calculations of defects in NiO, including those using hybrid-DFT methods, have suggested that the two oxygen holes produced upon Ni vacancy formation are delocalised over all six oxygen ions surrounding the vacancy. We demonstrate that by applying *U* to the O 2*p* states as well as the Ni 3*d* states, the defect states become localised on two oxygen ions (O<sub>0</sub><sup>•</sup>). In fact, all calculated defects in NiO appear to possess a high degree of charge localisation. We discuss the implications of this work for the future use of NiO as a *p*-type TCO.

## 5.3 Introduction

Nickel oxide has been intensely studied for many years due to its diverse applications in spintronics,<sup>370-371</sup> smart windows,<sup>96, 372</sup> solar cells<sup>373-374</sup> and, more recently, as a material for resistance random access memory (RRAM).<sup>375-378</sup> Interest in NiO as a TCO began in 1993 when NiO became the first known *p*-type transparent conductor.<sup>13</sup> These first *p*-type transparent films had a resistivity of  $1.4 \times 10^{-1} \Omega \text{ cm}$  and only 40% transmittance, much higher than the resistivities of  $\sim 10^{-4} \Omega \text{ cm}$  and >80% transmittance obtained for *n*-type TCOs.<sup>3</sup> Nevertheless, the promise of developing fully transparent electronics has led to the investigation of NiO in several possible TCO applications, including *p-n* junctions,<sup>379-381</sup> thin film transistors<sup>382-383</sup> and organic light emitting diodes (OLEDs), using NiO as an electrode.<sup>384</sup> However, further enhancement of its transparent conductive properties are necessary before NiO can be used as a TCO in commercial applications.

NiO has the rocksalt structure in which both anions and cations are arrayed in intersecting face centred cubic lattices (Fig. 5.1). Since Ni(II) is a *d*<sup>8</sup> ion, the electrons have a high spin arrangement as illustrated in Fig. 5.2, with six paired electrons in the lower *t*<sub>2g</sub> levels and

two unpaired electrons in the upper  $e_g^*$  levels. The two electrons in the  $e_g^*$  levels can be arranged in two ways – either both  $\alpha$ -spin or both  $\beta$ -spin. Hence, the NiO structure can have different magnetic arrangements of cations. In the ferromagnetic arrangement, all Ni(II) ions have their electrons aligned in the same spin orientation, so that there is an overall magnetic moment on the material. In the antiferromagnetic arrangement, half of the ions are arranged with  $\alpha$ -spin and half with  $\beta$ -spin, giving zero magnetic moment overall. Various different antiferromagnetic arrangements are possible, with the most stable one having the spins aligned within  $\{111\}$  planes of the crystal, with alternating planes having opposite spin, which is known as the  $AF_2$  configuration.<sup>385</sup> This is illustrated in Fig. 5.1 with the yellow and blue Ni atoms indicating the different spin.

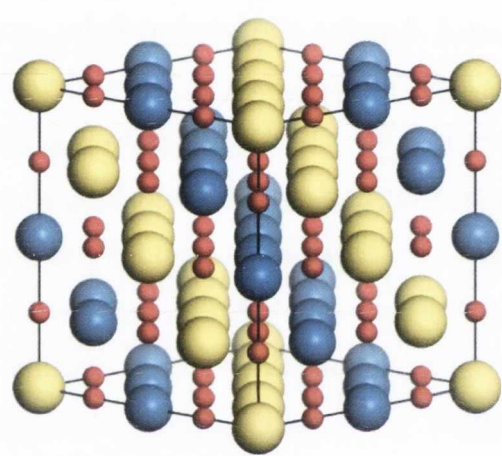


Fig. 5.1 Structure of NiO, showing the antiferromagnetic spin arrangement of the Ni atoms within the  $[111]$  crystal planes. Yellow atoms are  $\alpha$ -spin Ni, blue atoms are  $\beta$ -spin Ni, while the small red atoms are O.

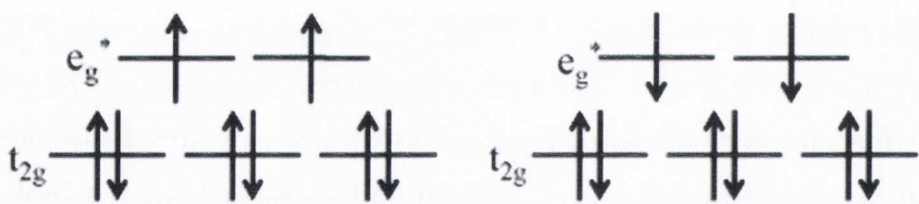


Fig. 5.2 Electronic arrangement for Ni(II) ( $d^8$ ) ion showing two possible spin configurations. On the left, the unpaired  $e_g^*$  electrons are spin up ( $\alpha$ -spin) and on the right, both electrons are spin down ( $\beta$ -spin).

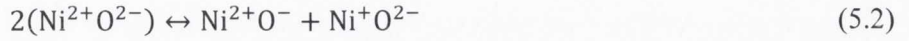
Stoichiometric NiO is an insulator with an optical band gap of 3.5-4.3 eV.<sup>386-390</sup> Initially, it was thought that NiO was a Mott-Hubbard insulator<sup>391-392</sup> where charge density fluctuates according to the model:



Here, the electron configuration fluctuates between:  $d^8, d^8 \leftrightarrow d^7, d^9$ . The band gap in this



type of system is caused solely by Ni  $d$ - $d$  interactions, with little contribution from the oxygen ions. Conduction in Mott-Hubbard NiO would occur through the localisation of holes on Ni to form  $\text{Ni}^{3+}$  ions.<sup>393-394</sup> However, experimental evidence suggested it was not quite this simple as significant O  $2p$  contributions were observed near the band edges in photoemission experiments.<sup>386-387, 389, 395</sup> This indicated that NiO was better described by a charge transfer model<sup>396</sup> in which the charge fluctuates in accordance with:



In this type of system,  $p$ -type conduction occurs through holes localised on oxygen ( $\text{O}^{\cdot}$ ) and the electron configuration fluctuates between:  $d^8, d^8 \leftrightarrow d^8 \underline{L}, d^9$ , where  $\underline{L}$  refers to the oxygen hole. This results in a mainly O  $2p$  VBM, while the conduction band is of dominant Ni  $3d$  character and conduction arises through oxygen holes. It is generally now thought that neither the Mott-Hubbard nor charge-transfer model fully describe NiO. Thus, the electronic structure of NiO can be thought of as a mixture between both models.<sup>397</sup>

Because of the localised nature of the Ni  $3d$  orbitals, calculation of the electronic structure is not straightforward. Density functional theory calculations fail to account for the strong on-site interaction between metal  $3d$  electrons, resulting in a grossly underestimated band gap of  $\sim 0.3$  eV and wrongly predicting purely Mott-Hubbard behaviour.<sup>398-400</sup> The main reasons for these failures is that NiO is a strongly correlated system which possesses highly localised Ni  $3d$  electrons. DFT calculations are unsuitable to describe this type of system and NiO has, for many years, been used as a model system to design methods to deal with strongly correlated materials. The bulk electronic structure of NiO has thus been calculated using a wide variety of methods, including Hartree-Fock,<sup>401-404</sup> GW,<sup>405-410</sup> self interaction corrected DFT,<sup>398, 411-415</sup> hybrid-DFT,<sup>402, 416-420</sup> dynamical mean field theory (DMFT)<sup>421-423</sup> and DFT+ $U$ .<sup>131-132, 134, 424-430</sup>

For the purposes of this work, we have used the GGA+ $U$  methodology as this provides a correction for the on-site Coulombic interactions, while remaining computationally inexpensive compared with HF, GW and hybrid-DFT methods using a planewave basis set. Previous GGA+ $U$  calculations differ in their choice of  $U$  values to apply to the Ni  $3d$  states, with its magnitude varying between 5 and 8 eV.<sup>131-132, 134, 424-430</sup> From a survey of the literature, it appears that the preferred choice in GGA calculations to reproduce experimental results accurately is between 5 and 6 eV. We have based our value of  $U$  upon the work of by Rohrbach *et al.*<sup>427</sup> who carried out a comprehensive evaluation of the

effects of  $U$  values varying between 0 and 9 eV on the GGA electronic structure, magnetic moments and lattice parameters of NiO. The authors concluded that the values for Ni 3d  $U$  and  $J$  should be set as 6.3 eV and 1.0 eV, giving an effective  $U$  ( $U_{eff} = U - J$ ) of 5.3 eV. Following this study, these values have been widely used in GGA+ $U$  calculations<sup>425, 430-433</sup> and have been demonstrated to produce results which are in good agreement with experimental data. There are no previous calculations which have applied a  $U$  term to the O 2p states.

$P$ -type conduction in NiO occurs through the presence of holes, introduced either by intrinsic Ni deficiency, or by extrinsic dopants such as Li. Because of the charge transfer nature of NiO, conduction occurs via a polaronic hopping mechanism,<sup>26, 88, 91, 393, 434</sup> in which the holes hop between oxygen sites,<sup>435</sup> with activation energies of  $\sim 0.4$ - $0.9$  eV.<sup>91, 436-437</sup> It was thought for many years that holes would localise on nickel atoms with the oxidation of Ni(II) to Ni(III).<sup>394, 438-439</sup> Indeed, many recent papers still assume that the holes localise on Ni<sup>3+</sup> ions.<sup>437, 440-442</sup> However, this model of conduction was largely negated when holes in Li doped NiO were found to be of primarily O 2p character in X-ray absorption spectroscopy.<sup>443-444</sup> Hartree-Fock and hybrid-DFT investigations of Li doped NiO have similarly shown the holes to localise on oxygen ions rather than on Ni.<sup>404, 418</sup>

Intrinsic  $p$ -type conductivity in NiO is known to occur through metal deficiency, which may be caused either by oxygen interstitials or Ni vacancies. As the rocksalt structure has a high density, the interstitial sites are quite small and an interstitial dominated defect chemistry is quite unlikely. Experimental results suggest a vacancy dominated mechanism, with various investigations of the conductivity versus oxygen partial pressure trend indicating slopes in agreement with an Ni vacancy dominated model of non-stoichiometry.<sup>436, 445-450</sup> Thermodynamic measurements also suggest that Ni vacancies are the most stable defect and have estimated formation energies of  $\sim 0.66$ - $0.78$  eV.<sup>436, 451</sup> Further evidence is provided by extended x-ray absorption fine structure (EXAFS) analysis, in which the obtained coordination numbers and bond lengths are consistent with Ni vacancy formation.<sup>442</sup> The experimental conclusions have been verified by GGA+ $U$  (Ni 3d) calculations, which demonstrate Ni vacancies to be low in energy, with oxygen interstitials having high formation energies.<sup>89, 430, 452</sup> The electronic structure of intrinsic defects in NiO has been investigated by several authors using LDA+ $U$ ,<sup>431, 453</sup> GGA+ $U$ <sup>425, 452</sup> and SIC-LDA<sup>415, 454</sup> methods. Formation of an Ni(II) vacancy ( $V''_{Ni}$ ) is accompanied by the creation of two holes in the valence band ( $h^*$ ), which the calculations indicate to occupy an empty defect state



$\sim 0.2$ - $0.4$  eV above the VBM. Band structure calculations suggest these single particle levels to cross the VBM which would result in metallic conductivity.<sup>453</sup> Rather than being localised to form two  $O^-$  ions ( $O_O^\bullet$ ), GGA+ $U$  (Ni  $3d$ ) calculations suggest both holes to be delocalised over the oxygen and nickel atoms neighbouring the vacancy.<sup>425, 453</sup> This type of electronic structure is inconsistent with polaronic conduction and suggests a need to investigate the nature of these defect states further.

In NiO, O vacancies and  $n$ -type conduction have been evidenced when sputtered under extreme oxygen-poor conditions.<sup>13, 382, 455</sup> However, films deposited at a higher oxygen partial pressure result in  $p$ -type conduction, indicating that the type of intrinsic defect which forms is highly dependent on chemical conditions. Indeed, calculations of the energetics of several intrinsic defects in NiO have shown that under oxygen-poor conditions, oxygen vacancies dominate the system, while nickel vacancies form under metal-deficient conditions.<sup>89, 430, 452</sup> However, intrinsic  $n$ -type conductivity in NiO is quite poor as the transition levels of O vacancies are very deep, occurring  $\sim 3$  eV below the conduction band.<sup>89, 431, 452</sup> Formation of oxygen vacancies ( $V_O^{\bullet\bullet}$ ) results in two extra electrons in the system which, in calculations, produce a filled state  $\sim 2.5$  eV below the CBM.<sup>425, 431, 452-453</sup> These electrons are delocalised mainly over the Ni atoms neighbouring the vacancy.<sup>425, 453</sup> The highly localised nature of these defect states suggests that  $n$ -type conduction through oxygen vacancies will be quite poor.

To improve the conductivity of NiO, several dopants have been suggested including Na,<sup>456</sup> Al,<sup>441</sup> and most frequently Li.<sup>394, 440, 457-459</sup> Li doping has been found to significantly improve the  $p$ -type conductivity of NiO<sup>440, 460</sup> with Li doped films generally have lower activation energies than undoped films of  $\sim 0.2$ - $0.5$  eV.<sup>394, 461</sup> Li dopants substitute at Ni sites to form the defect,  $Li'_{Ni}$ , with charge compensation through a hole on a nearest neighbour oxygen ( $O_O^\bullet$ ). LDA calculations indicate Li to have a very low doping energy, suggesting it to be more energetically favourable than Ni vacancies.<sup>89, 430</sup> The O  $2p$  hole has been observed directly in X-ray absorption spectroscopy<sup>443-444, 462</sup> and X-ray photoemission spectroscopy.<sup>463</sup> Bremsstrahlung isochromat spectroscopy (BIS), which probes empty conduction band states, indicates an impurity state to occur  $\sim 1.6$  eV above the valence band as a result of Li substitution.<sup>463-464</sup> The nature of this state has also been investigated using HF and hybrid-DFT calculations which predict a single unoccupied level in the middle of the band gap.<sup>404, 418</sup> This state is almost entirely localised on a single oxygen neighbouring the Li.<sup>404, 418, 422</sup> In contrast, LDA+ $U$  calculations indicate only a



slight shoulder at the very top of the valence band, with its electron density delocalised over all six O atoms surrounding the dopant.<sup>453</sup> This predicts a metallic conduction mechanism, inconsistent with the experimental polaronic hopping mechanism of conductivity. Further work is thus needed to provide a proper description of the calculated electronic structure upon Li doping.

As TCO applications involve thin films, the electronic structure of the defective surface is also of importance. The most stable surface of NiO is the {100} surface illustrated in Fig. 5.3. On the surface, the Ni atoms are arranged in alternating rows of  $\alpha$  and  $\beta$ -spin separated by rows of oxygen atoms. The surface oxygen atoms co-ordinate to two  $\alpha$ - and two  $\beta$ -spin Ni in the surface layer and one subsurface Ni atom which may be of either  $\alpha$ - or  $\beta$ -spin, as illustrated in Fig. 5.3 (b). Hence, there are two types of oxygen at the surface, depending on the spin of their subsurface Ni. Photoemission of the surface shows it to possess two surface states in the band gap – one of O 2*p* character near the VBM and a second of Ni 3*d* character just below the CBM.<sup>465-467</sup> Several electronic structure calculations of the pure {100} surface have also been carried out and have also identified these surface states.<sup>413, 427, 433, 468-469</sup>

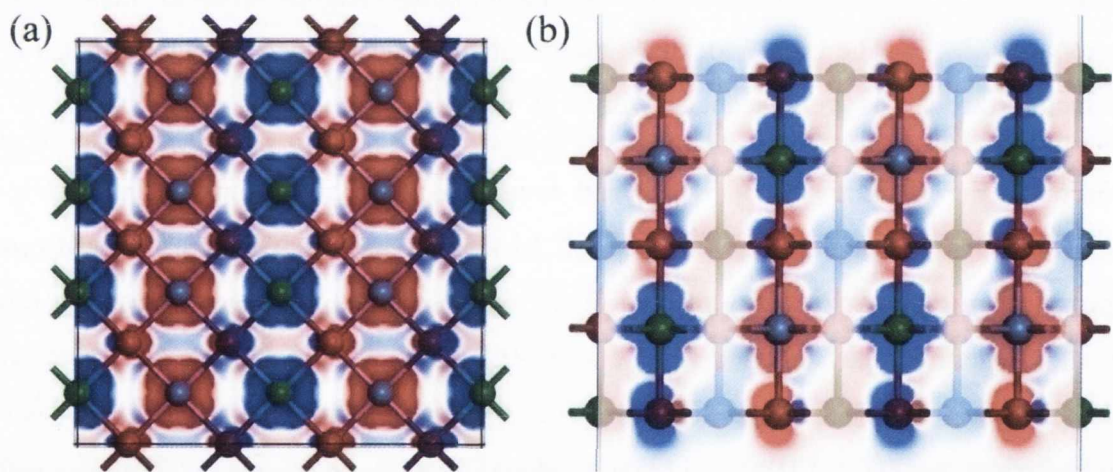


Fig. 5.3 Structure of NiO {100} surface with spin density plotted between  $-0.02 \text{ e}/\text{\AA}^3$  (red) and  $0.02 \text{ e}/\text{\AA}^3$  (blue). (a) shows top view of surface and (b) shows side view. Green atoms are  $\alpha$ -spin Ni and grey are  $\beta$ -spin Ni. Red oxygen atoms are above subsurface  $\beta$ -Ni and dark red are above  $\alpha$ -Ni.

There are very few studies of the electronic structure of defects at the NiO {100} surface. O vacancies are indicated by ultraviolet photoemission spectroscopy (UPS) to introduce a filled defect state  $\sim 1 \text{ eV}$  above the VBM.<sup>470-472</sup> The two trapped electrons are shared between the cations surrounding the defect, rather than being at the vacancy centre.<sup>470</sup> Point defects interpreted to be Ni vacancies have been directly imaged on the {100}

surface using scanning tunnelling microscopy (STM).<sup>473</sup> Very few electronic structure calculations have been carried out to investigate the exact nature of these defects. Oxygen vacancies have been studied using an embedded cluster model involving five Ni and five O ions, within the complete active space self consistent field (CASSCF) approach.<sup>474</sup> Similar to the bulk case, the two electrons associated with the vacancy were calculated to delocalise over the five Ni ions surrounding the vacancy, with little charge on the vacancy itself. Both GGA+ $U$  (Ni 3d) and hybrid-DFT methods were later shown to give similar results,<sup>432</sup> suggesting the two electrons to be trapped near the vacancy site. The defect states of oxygen vacancies were located deep in the band gap, 1.2 eV above the VBM. This study also included calculations of Ni vacancies at the {100} surface, again comparing the results of GGA+ $U$  and hybrid-DFT methods. In this case, the two holes introduced by the removal of Ni were delocalised mainly over the five nearest neighbour oxygen ions using hybrid-DFT, while GGA+ $U$  suggested the holes to be delocalised over a wider region. However, neither method localised the charge on two oxygen ions.

It is a well known problem that uncorrected DFT fails to produce the correct localisation of oxygen hole states.<sup>475-477</sup> It has been shown in previous calculations of oxygen holes in various oxides that DFT+ $U$  produces improved localisation if a  $U$  value is applied to the oxygen 2p states.<sup>232, 478-480</sup> However, all previous calculations of NiO applied a  $U$  to the Ni 3d states alone.<sup>425, 430, 432, 453-454</sup> In this work, we thus apply a  $U$  value to both Ni 3d and O 2p states which results in hole states which are localised on oxygen ions, in agreement with the experimentally observed polaronic hopping conduction mechanism.

## 5.4 Computational Methods

Calculations were carried out using GGA+ $U$  as implemented in the VASP code. The PBE exchange correlation functional<sup>116</sup> was employed along with the PAW pseudopotentials used to represent the interaction between core (Ni: [Ar], O [He]) and valence electrons. In the calculations a  $U_{eff} = U - J = 5.3$  eV was applied to the Ni 3d states, as this was previously found to give a good fit to experimental data, such as lattice parameters, magnetic moments and electronic structure.<sup>427</sup> To achieve the correct hole localisation, we apply a  $U$  value of 7 eV to the O 2p states. This value is based on calculations for Li doped MgO which also has the rocksalt structure.<sup>232, 478</sup>



All calculations were carried out using a planewave cut-off energy of 500 eV, with the forces converged to within 0.01 eV/Å. Bulk defect calculations were carried out using a 128 atom supercell of NiO from a  $4 \times 4 \times 4$  expansion of the primitive face centred cubic unit cell, combined with a  $2 \times 2 \times 2$  Monkhorst-Pack  $k$ -point mesh. For surface calculations, a 5-layer slab of the  $\{100\}$  surface was used with a 17 Å vacuum gap. A  $4 \times 4$  (11.82 Å  $\times$  11.82 Å) surface expansion was used to minimise defect-defect interactions between neighbouring cells with a  $2 \times 2 \times 1$  Monkhorst-Pack  $k$ -point mesh. The partial electronic densities of states were plotted using sphere radii of 1.3 Å for Ni and Li, while a radius of 1.4 Å was used for O and N.

For defect calculations, the chemical potentials were restricted as outlined in Section 2.5. To ensure overall stability of NiO the following limit was set:

$$\mu_{\text{Ni}} + \mu_{\text{O}} = \Delta H_f(\text{NiO}) \quad (5.3)$$

We calculated  $\Delta H_f(\text{NiO})$  as -2.52 eV compared to the experimental value of -2.49 eV from Ref. 481. The elemental chemical potentials were restricted to  $\mu_{\text{Ni}}, \mu_{\text{O}} \leq 0$  eV to avoid precipitation of metallic Ni and O<sub>2</sub> gas. Because of the variable valency of Ni, Ni<sub>2</sub>O<sub>3</sub> can also form. However, its exact crystal structure has not been properly characterised, making it difficult to carry out calculations of its energetics. We have thus used the experimental formation enthalpy of -5.07 eV for Ni<sub>2</sub>O<sub>3</sub>.<sup>214</sup> Combining the limit  $2\mu_{\text{Ni}} + 3\mu_{\text{O}} \leq \Delta H_f(\text{Ni}_2\text{O}_3)$  with Eqn. 5.3 results in a limit of:  $\mu_{\text{O}} \leq \Delta H_f(\text{Ni}_2\text{O}_3) - 2\Delta H_f(\text{NiO})$ . The upper limit on the oxygen chemical potential is thus given by:  $\mu_{\text{O}} \leq -0.10$  eV. This gives an O-poor limit of  $(\mu_{\text{Ni}}, \mu_{\text{O}}) = (0 \text{ eV}, -2.52 \text{ eV})$  and an O-rich limit of  $(-2.42 \text{ eV}, -0.10 \text{ eV})$ .

Doping with Li results in a ternary system limited by  $2\mu_{\text{Li}} + \mu_{\text{O}} \leq \Delta H_f(\text{Li}_2\text{O})$ , to avoid formation of Li<sub>2</sub>O. Using a calculated Li<sub>2</sub>O formation energy of -5.08 eV, this restricts  $\mu_{\text{Li}}$  to be less than -1.28 eV under Ni-poor conditions ( $\mu_{\text{Ni}} = 0$  eV) while under Ni-rich conditions ( $\mu_{\text{Ni}} = -2.52$  eV),  $\mu_{\text{Li}} \leq -2.49$  eV. For N doping, the chemical potentials are restricted by the formation energy of Ni<sub>3</sub>N:  $3\mu_{\text{Ni}} + \mu_{\text{N}} \leq \Delta H_f(\text{Ni}_3\text{N}) = -0.17$  eV. Under O-poor conditions ( $\mu_{\text{O}} \leq -2.52$  eV), the nitrogen chemical potential is restricted to be less than -0.17 eV while oxygen-rich conditions result in the limit  $\mu_{\text{N}} = 0$  eV. The chemical potential limits under O-rich and Ni-rich conditions are summarised in Table 5.1.



|                | $\mu_{\text{Ni}}$ | $\mu_{\text{O}}$ | $\mu_{\text{Li}}$ | $\mu_{\text{N}}$ |
|----------------|-------------------|------------------|-------------------|------------------|
| <b>O-rich</b>  | -2.42             | -0.10            | -2.49             | 0.00             |
| <b>Ni-rich</b> | 0.00              | -2.52            | -1.28             | -0.17            |

Table 5.1 Summary of atomic chemical potentials (in eV) for NiO, at O-rich and Ni-rich limits.

## 5.5 Bulk electronic structure of NiO

Table 5.2 shows the calculated lattice parameters for the NiO unit cell compared to their experimental values. The calculated parameters are in excellent agreement with the experimental values, showing only a very slight overestimation of 0.02%. In the rocksalt structure, each Ni sits at the centre of a regular oxygen octahedron with bond lengths of 2.09 Å. Each Ni was calculated to have a magnetic moment of  $\pm 1.69 \mu_{\text{B}}$ , in good agreement with experimentally measured values of 1.7-1.9  $\mu_{\text{B}}$ .<sup>385, 482-483</sup>

|              | Experiment <sup>484</sup> | Calculated (error) |
|--------------|---------------------------|--------------------|
| <i>a</i> (Å) | 4.178                     | 4.179 (+0.02%)     |
| Ni-O (Å)     | 2.089                     | 2.089 (+0.00%)     |

Table 5.2 Experimental and calculated GGA+*U* lattice parameters for NiO unit cell showing the percentage deviation from experiment in brackets.

The band structure for NiO is shown in Fig. 5.4. The band structure was calculated using the  $2 \times 2 \times 2$  expansion of the cubic unit cell, which contains 64 atoms to obtain the correct antiferromagnetism. The VBM occurs at L while the CBM occurs between L and  $\Gamma$  giving NiO an indirect gap of 3.25 eV. The smallest direct gap occurs at X and is of magnitude 3.68 eV. This compares well to the measured experimental optical gap for NiO of 3.5-4.3 eV.<sup>386-390</sup> Both the VBM and CBM are made up of quite flat bands, due to the strongly localised nature of the Ni 3*d* orbitals. Fig. 5.5 shows the electronic density of states (EDOS) for NiO. This shows the valence band to be made up of a mixture of Ni 3*d* states and O 2*p* states, while the conduction band is dominated by Ni 3*d* states. The bottom of the valence band between -7 and -5 eV contains a mixture of O 2*p* and Ni 3*d* states; between -5 and -3 eV, Ni 3*d* states dominate, and finally, from -3 eV to the VBM, the valence band is made up of a mixture of Ni 3*d* and O 2*p* states. At L, the VBM is made up of a mixture of 20% Ni 3*d* states and 79% O 2*p* states, indicating that it is O 2*p* states that dominate the band edge. This is similar to the proportions of O 2*p* states found in hybrid-DFT

calculations with 30-50% exchange.<sup>418</sup> This confirms the charge transfer nature of the band gap and the  $d^8\bar{L}$  nature of the VBM.

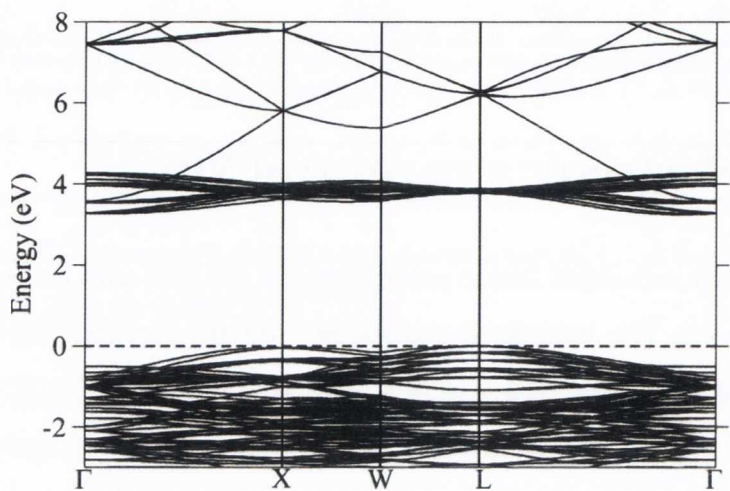


Fig. 5.4 Band structure for NiO as calculated using GGA+*U* methodology. Dashed line indicates valence band maximum.

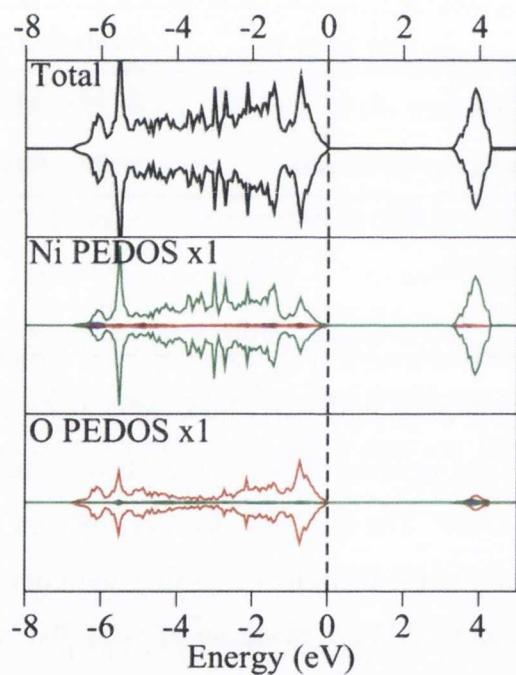


Fig. 5.5 Calculated total and partial EDOS for NiO. Blue lines indicate *s* states, red are *p* states and green are *d* states. Dashed line marks the valence band maximum.

### 5.5.1 Bulk Defect Formation Energies

In examining intrinsic defects, we have limited our study to nickel and oxygen vacancies as these have been previously found to have low formation energies.<sup>89</sup> Extrinsically, Li substitution for Ni ( $\text{Li}'_{\text{Ni}}$ ) is a frequently used method of *p*-doping NiO. However, anionic



doping at the O site has not been examined. Nitrogen is a possible candidate as it has one fewer electron than oxygen and may result in hole formation via the mechanism:



For each defect, all possible geometrical and spin configurations were considered. However, we only show the energetics and electronic structure for the lowest energy configuration of each intrinsic or extrinsic defect.

The formation energies for the bulk intrinsic and extrinsic defects are shown in Table 5.3 under the chemical potential limits of Table 5.1. As expected, the intrinsic non-stoichiometry changes with chemical potential. O-rich conditions result in a majority of Ni vacancies, while Ni-rich conditions give an oxygen vacancy dominated system. This conclusion is in good agreement with previous theoretical work.<sup>89, 452</sup> The formation energy of Ni vacancies is relatively high at 2.00 eV under O-rich conditions, compared with the lower energy of formation of 1.12 eV for oxygen vacancies under O-poor conditions. The high formation energy of Ni vacancies may explain the low experimental conductivity of *p*-type NiO. Li doping is favoured under O-rich conditions where the Ni chemical potential is at its minimum.  $Li'_{Ni} + h^{\bullet}$  has the lowest formation energy of all the bulk defects of 0.39 eV. However, doping with nitrogen is unlikely to result in improved *p*-type conductivity as the formation energy of  $N'_O + h^{\bullet}$  is higher than that of oxygen vacancies. It thus appears that substitutional doping by nitrogen at the oxygen site will not result in excess hole formation.

| Defect                       | O-rich | Ni-rich |
|------------------------------|--------|---------|
| $V''_{Ni} + 2h^{\bullet}$    | 2.00   | 4.42    |
| $V^{\bullet\bullet}_O + 2e'$ | 3.54   | 1.12    |
| $Li'_{Ni} + h^{\bullet}$     | 0.39   | 1.60    |
| $N'_O + h^{\bullet}$         | 4.02   | 1.77    |

Table 5.3 Formation energies (in eV) of intrinsic and extrinsic defects in bulk NiO under the chemical potentials outlined in Table 5.1.

### 5.5.2 $V''_{Ni} + 2h^{\bullet}$

The formation of a Ni(II) vacancy in NiO results in the relaxation of the six surrounding oxygen ions away from the vacancy by 0.12 eV due to Coulombic repulsion between the

negative vacancy and the oxygen ions. This has the effect of shortening the bond lengths between nearest neighbour oxygen ( $O_{nn}$ ) and next nearest neighbour Ni ( $Ni_{nnn}$ ), thus explaining the shortening of Ni-O bond lengths in  $Ni_{1-\delta}O$  in EXAFS.<sup>442</sup> The removal of a single  $\beta$ -spin Ni(II) ion results in a breaking of the spin neutrality of the system. The resulting spin density plot of the region surrounding the vacancy is shown in Fig. 5.6 (a). The most stable spin configuration was found to be that which maintains an overall spin of zero. As shown in Fig. 5.6 (a), two oxygen ions neighbouring the vacancy have each lost a single  $\alpha$ -spin electron so that each possesses a magnetic moment of  $-0.58 \mu_B$ .

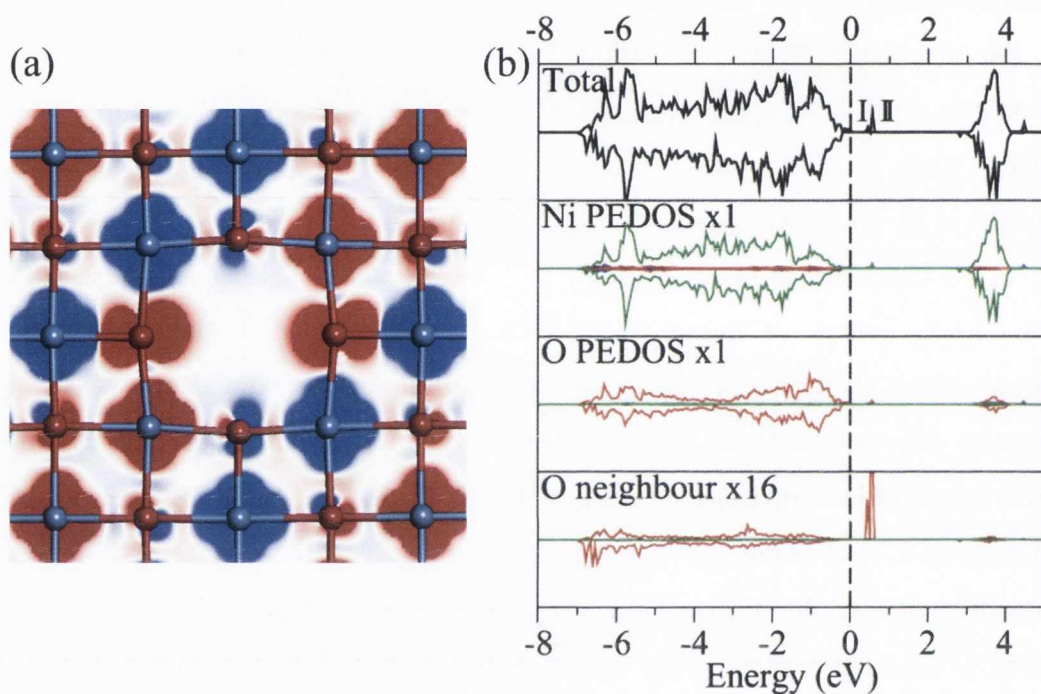


Fig. 5.6 (a) Spin density for  $V''_{Ni} + h^*$  in NiO, plotted between isolevels of  $-0.05$  (red) and  $0.05 \text{ e}/\text{\AA}^3$  (blue). Grey atoms are Ni and red are O. (b) Total and partial EDOS for  $V''_{Ni} + 2h^*$  in NiO. Dashed line highlights position of VBM, while blue, red and green lines are  $s$ ,  $p$  and  $d$  states respectively. Roman numerals mark positions of defect levels. PEDOS is plotted for two O neighbours bearing the holes.

The calculated EDOS/PEDOS for  $V''_{Ni} + 2h^*$  is shown in Fig. 5.6 (b). Two unoccupied defect states (I and II) are seen  $0.5 \text{ eV}$  above the VBM in the  $\alpha$ -spin component of the EDOS, which are of mainly O  $2p$  character from two oxygen ions directly beside the vacancy. Minor contributions from  $Ni_{nnn}$  ions can also be seen. To examine the exact composition of the two defect states, we have plotted their partial charge density which is shown in Fig. 5.7. Both states have similar compositions with the majority of the density localised on two oxygen  $p$ -orbitals. A small amount of density is also spread onto the  $Ni_{nnn}$  ions bonded to these oxygen ions which may be due to superexchange interactions as found previously.<sup>485</sup> These two  $Ni_{nnn}$  also experience a loss in magnetic moment compared



to bulk Ni, showing moments of  $1.50 \mu_B$  in the defective system. Bader charge analysis indicates that each band is made up of 24% Ni and 76% O states (Table 5.4). Each oxygen holds 27% of the charge, while each Ni has 6%, so that a total of 66% of the charge is localised on these four atoms. This degree of localisation, together with the location of the defect state deep in the band gap, suggests that Ni vacancies will cause conduction via a polaronic hopping mechanism, consistent with experimental observations.<sup>26, 88</sup>

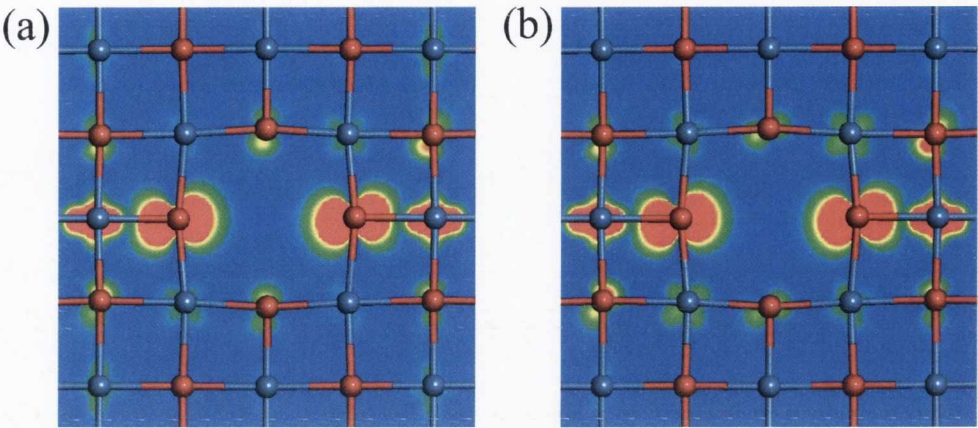


Fig. 5.7 Partial charge density of (a) Band I, lower energy band gap state and (b) Band II, higher energy band gap state, for  $V''_{Ni} + 2h^*$  in NiO, plotted between isolevels of 0 (blue) and  $0.05 \text{ e}/\text{\AA}^3$  (red). Grey atoms are Ni and red are oxygen.

|            | Band I          | Band II         |
|------------|-----------------|-----------------|
| $Ni_{tot}$ | 0.24            | 0.24            |
| $O_{tot}$  | 0.76            | 0.76            |
| $O_{nn}$   | $2 \times 0.27$ | $2 \times 0.27$ |
| $Ni_{nnn}$ | $2 \times 0.06$ | $2 \times 0.06$ |

Table 5.4 Bader charges for  $V''_{Ni} + 2h^*$  in NiO, showing total Ni ( $Ni_{tot}$ ) and O ( $O_{tot}$ ) charges for the two band gap states, Band I and Band II, as well as charges on nearest neighbour  $O_{nn}$  and next nearest neighbour  $Ni_{nnn}$  ions.

### 5.5.3 $V^{\bullet}_O + 2e'$

Removal of an O atom from the lattice leaves behind six under-coordinated Ni neighbours, each of which relaxes towards the vacancy by  $0.07 \text{ \AA}$ . The total spin density for this defect is shown in Fig. 5.8 (a). As an oxygen atom does not have unpaired electrons, the effect on the spin density is not as great as for the Ni vacancy discussed above. However, it can be seen from the spin density that oxygen vacancy formation results in a quenching of the spin of the nearest neighbour Ni atoms. The  $\alpha$ -spin component for the vacancy is directed



towards the  $\beta$ -spin Ni ions, while the vacancy's  $\beta$ -spin points towards the  $\alpha$ -spin Ni ions. Thus, each of the six Ni cations surrounding the vacancy has a magnetic moment of  $\pm 1.60 \mu_B$ , reduced from their bulk value of  $\pm 1.69 \mu_B$ .

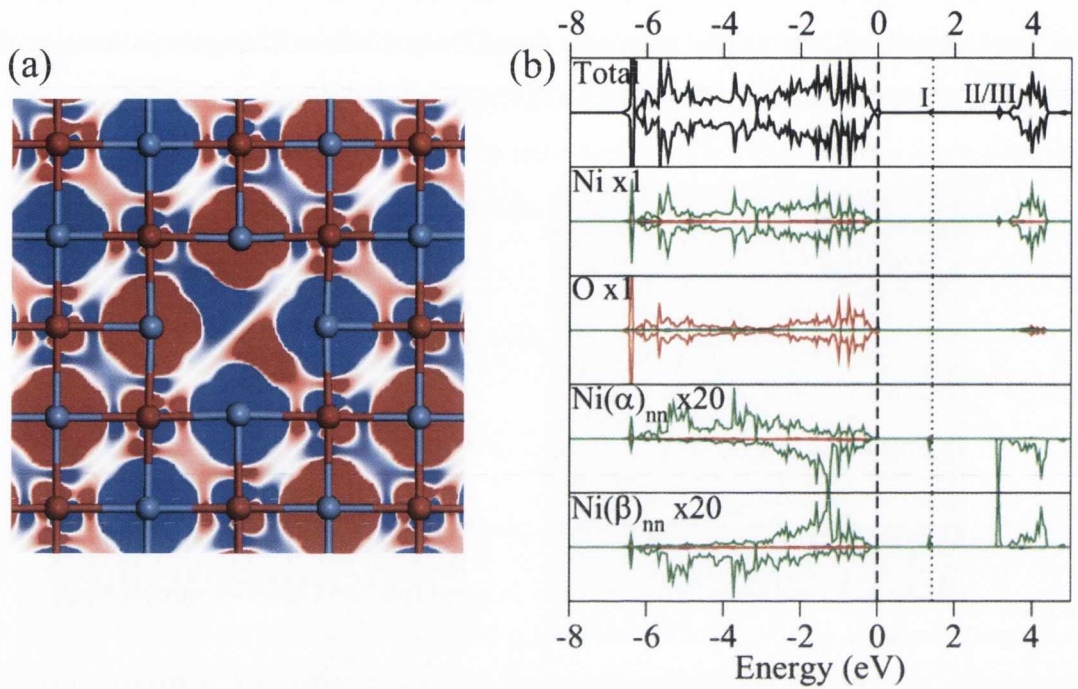


Fig. 5.8 (a) Spin density for  $V_O^{2+} + 2e'$  in NiO plotted between isolevels of  $-0.01$  (red) and  $0.01 \text{ e/\AA}^3$  (blue). Blue atoms are Ni and red are oxygen. (b) Total EDOS/PEDOS for  $V_O^{2+} + 2e'$  in NiO, with the defect levels marked by Roman numerals.  $Ni(\alpha)_{nn}$  and  $Ni(\beta)_{nn}$  are  $\alpha$  and  $\beta$  spin nearest neighbour Ni cations, respectively. Dashed line indicates VBM and dotted line shows highest occupied level. Red lines are  $p$  states and green are  $d$  states.

The creation of an oxygen vacancy leads to the formation of several defect states within the band gap, which can be seen in the EDOS in Fig. 5.8 (b). When an O atom is removed, it leaves behind two electrons, which occupy a defect state  $1.4 \text{ eV}$  above the VBM (labelled I). The lower panels of Fig. 5.8 (b) show the PEDOS for the six Ni ions surrounding the vacancy, which have been split into the three  $\alpha$ -spin and three  $\beta$ -spin Ni(II) ions. Band I is of  $\beta$ -spin Ni  $3d$  character from the  $\alpha$ -Ni, while its  $\alpha$ -spin component arises from the  $\beta$ -Ni. The two electrons of the vacancy act to counteract the excess spin on the neighbouring Ni cations, decreasing their magnetic moments. Another feature of the EDOS is the appearance of two degenerate empty defect states  $0.2 \text{ eV}$  below the CBM (labelled II and III in Fig. 5.8 (b)). Once again, these states are of Ni  $3d$  character, mainly from the six nearest neighbour Ni ions.

The partial charge density for Bands I, II and III is shown in Fig. 5.9. Band I possesses a significant amount of charge density within the vacancy itself, as well as on the

surrounding Ni atoms. Bader charge analysis (Table 5.5) indicates that  $0.43e$  is localised at the vacancy centre, while a further  $1.00e$  is localised on the nearest neighbour Ni ions. The remaining  $0.57e$  is delocalised over Ni and O atoms further from the defect. Band II and III are also highly localised, with the charge density for these bands located mainly on the Ni ions with no electron density within the vacancy itself. Bader analysis (Table 5.5) indicates that  $1.58e$  and  $1.66e$  of the total charge resides on the nearest neighbour Ni ions for Bands II and III, respectively. This suggests that Band I is a state arising from an in-phase interaction between the six Ni ions while Bands II/III arise from out-of-phase interactions. The high degree of localisation, combined with the position of the defect state deep in the band gap, indicates that oxygen vacancies are unlikely to cause high levels of  $n$ -type conductivity and will merely act as electron traps.

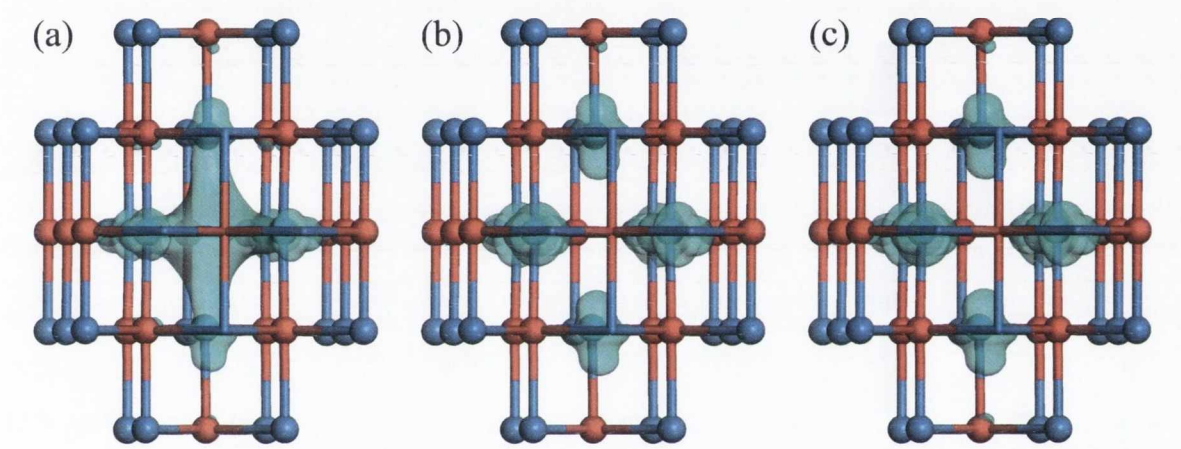


Fig. 5.9 Partial charge density for defect states of  $V_O^{\bullet\bullet} + 2e'$  in NiO, showing (a) Band I, 1.4 eV above VBM, (b) and (c) Band II and III, 0.2 eV below CBM. All are shown at isosurface level of  $0.05\text{ e}/\text{\AA}^3$ .

|            | Band I          | Band II         | Band III        |
|------------|-----------------|-----------------|-----------------|
| $Ni_{tot}$ | 1.11            | 1.78            | 1.77            |
| $O_{tot}$  | 0.46            | 0.22            | 0.23            |
| $Ni_{nn}$  | $6 \times 0.17$ | $6 \times 0.26$ | $6 \times 0.28$ |
| $V_O$      | 0.43            | 0.00            | 0.00            |

Table 5.5 Bader charges (in  $e$ ) for defect states (Band I, II and III) of  $V_O^{\bullet\bullet} + 2e'$  in NiO, giving total Ni ( $Ni_{tot}$ ), total O ( $O_{tot}$ ), nearest neighbour Ni ( $Ni_{nn}$ ) and charge within the oxygen vacancy ( $V_O$ ).

### 5.5.4 $Li'_{Ni} + h^{\bullet}$

Substitution of Li for Ni in the lattice results in the formation of a single hole, which is localised on a single oxygen ion neighbouring the defect. The spin density for our GGA+ $U$  calculations is shown in Fig. 5.10 (a). A single oxygen neighbouring the lithium ion has



lost one electron and has an excess  $\beta$ -spin and a magnetisation of  $-0.36 \mu_B$ . The spin is polarised in the same direction as the removed nickel so that the system has an overall spin of  $+1.00 \mu_B$ . The lithium and hole-bearing oxygen relax away from each other by  $0.33 \text{ \AA}$ , resulting in a Li-O distance of  $2.42 \text{ \AA}$ .

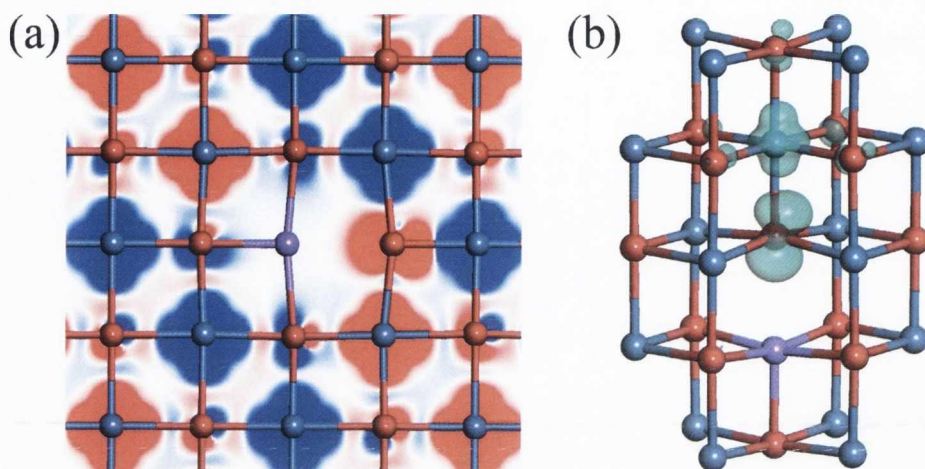


Fig. 5.10 (a) Spin density for  $\text{Li}'_{\text{Ni}} + h^*$  in NiO, plotted at between isolevels of  $-0.05 \text{ e/\AA}^3$  (red) and  $0.05 \text{ e/\AA}^3$  (blue). (b) Partial charge density of defect state of  $\text{Li}'_{\text{Ni}} + h^*$  in NiO,  $0.4 \text{ eV}$  above VBM, plotted on light blue isosurface of  $0.05 \text{ e/\AA}^3$ . Grey atoms are Ni, red are oxygen and pink are Li.

The total and partial EDOS for Li doped NiO are shown in Fig. 5.11. The Li atom shows very little contribution to the EDOS as its  $s$  and  $p$  orbitals are much lower in energy than the O  $2p$  and Ni  $3d$  orbitals. The hole-bearing oxygen shows a peak  $0.4 \text{ eV}$  above the VBM of mainly O  $2p$  character, in the  $\alpha$ -spin component of the PEDOS. The partial charge density associated with this state is shown in Fig. 5.10 (b). The charge is localised mainly on the oxygen ion, with a small amount spreading onto the next nearest neighbour Ni. Bader charges (Table 5.6) indicate that  $0.37e$  resides on the nearest neighbour oxygen, with  $0.18e$  on the next nearest neighbour Ni, so that 55% of the charge density is localised on these two atoms. The remaining  $0.45e$  is distributed over the five other nearest neighbour oxygen ions and on Ni and O atoms further from the defect. The next nearest neighbour Ni shows a loss in magnetic moment to  $1.41 \mu_B$  compared to its bulk magnetisation of  $1.69 \mu_B$ , indicative of a small gain in electron density. The high degree of localisation of the defect state is consistent with the polaronic hopping mechanism of conductivity seen experimentally.<sup>394</sup>

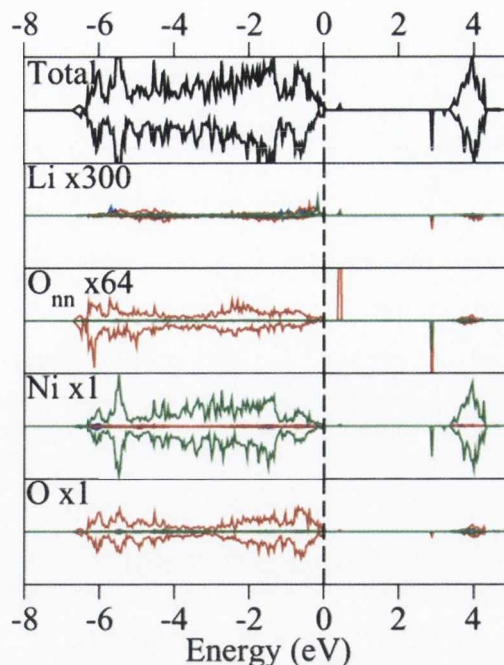


Fig. 5.11 EDOS/PEDOS for  $\text{Li}'_{\text{Ni}} + h^*$  in NiO, with dashed line indicating VBM. Red lines are  $p$  states and green lines are  $d$  states.  $\text{O}_{\text{nn}}$  is hole-bearing nearest neighbour oxygen atom.

|                          | Bader charge |
|--------------------------|--------------|
| $\text{Ni}_{\text{tot}}$ | 0.30         |
| $\text{O}_{\text{tot}}$  | 0.65         |
| <b>Li</b>                | 0.00         |
| $\text{O}_{\text{nn}}$   | 0.37         |
| $\text{Ni}_{\text{nnn}}$ | 0.18         |

Table 5.6 Bader charges for defect state of  $\text{Li}'_{\text{Ni}} + h^*$  in bulk NiO showing total Ni and O charges ( $\text{Ni}_{\text{tot}}$ ,  $\text{O}_{\text{tot}}$ ), charge on Li and charge on hole-bearing nearest neighbour oxygen ion ( $\text{O}_{\text{nn}}$ ) and next nearest neighbour Ni ( $\text{Ni}_{\text{nnn}}$ ).

### 5.5.5 $\text{N}'_0 + h^*$

As nitrogen has one fewer electron than oxygen, the substitution of N for O results in the creation of a single hole state. The spin density shown in Fig. 5.12 (a) indicates that the hole is localised on a  $2p$  orbital of the nitrogen atom, so that the N has excess  $\beta$ -spin and a calculated magnetic moment of  $-0.41 \mu_{\text{B}}$ . The six nearest neighbour Ni ions surrounding the N relax towards the dopant by  $0.07 \text{ \AA}$ .

The density of states for the  $\text{N}'_0 + h^*$  defect is shown in Fig. 5.12 (b). There are significant contributions of the N  $2p$  states across the valence band, with several states introduced into the band gap region. Three filled defect states (I-III) are seen just above the VBM – one of



$\alpha$ -spin and two of  $\beta$ -spin character. These states are of mainly N  $2p$  character with a small amount of Ni  $3d$  character from Ni ions surrounding the dopant. The empty hole state (IV) occurs 0.5 eV above these states and is of mainly N  $2p$  character with a significant contribution from one Ni ion neighbouring the defect (labelled Ni1). Ni1 experiences a loss in magnetic moment, possessing a magnetisation of  $1.42 \mu_B$ . The deep nature of this defect state suggests that N doping is unlikely to result in high levels of  $p$ -type conductivity. An additional defect state (V) occurs 0.1 eV below the CBM which is composed of mainly Ni  $3d$  character from Ni1 with some mixing with N  $2p$  states, which appears to be the antibonding component of Band IV.

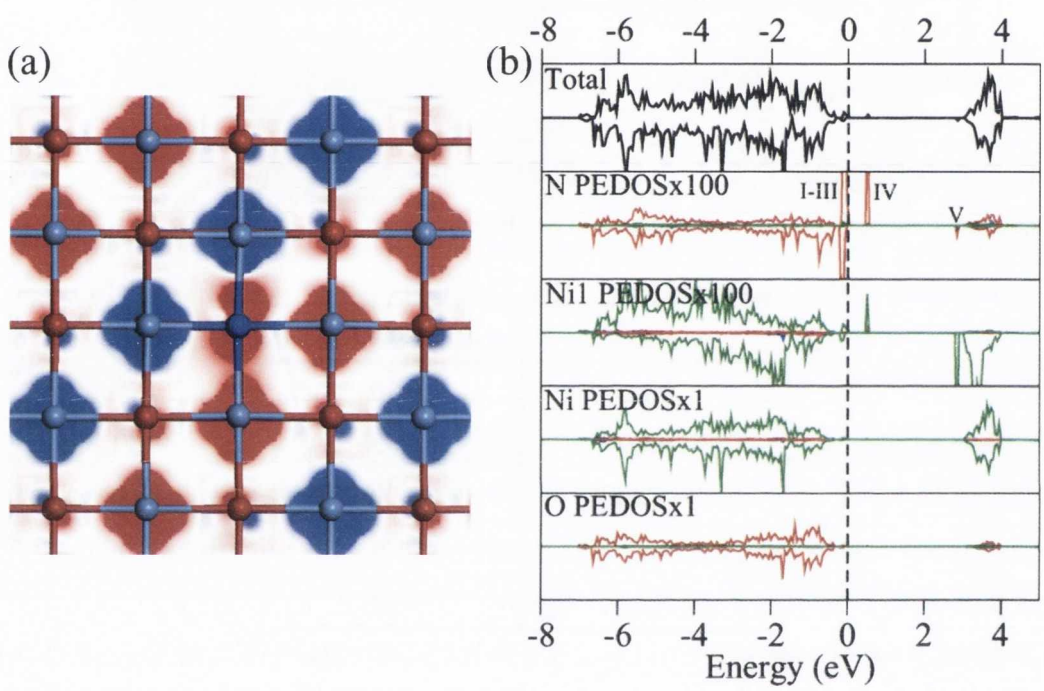


Fig. 5.12 (a) Spin density for  $N_O' + h^*$  in NiO, plotted from  $-0.1 \text{ e}/\text{\AA}^3$  (red) to  $0.1 \text{ e}/\text{\AA}^3$  (blue). Grey atoms are Ni, red are O and dark blue are nitrogen. (b) EDOS/PEDOS for  $N_O' + h^*$  in NiO, with dashed line indicating highest occupied level. Red lines are  $p$  states and green are  $d$  states and Roman numerals mark defect states. Ni1 is nickel atom neighbouring nitrogen which contributes to states IV and V.

The partial charge density of each of these states is plotted in Fig. 5.13. The three valence band states (Band I-III) have been plotted together as they are too close in energy to plot separately. Bands I-III are made up of mainly N and Ni character from the ions surrounding the dopant. 36% of the charge resides on the nitrogen, with a further 24% on the surrounding Ni ions (Table 5.12). The remaining 40% of the charge is delocalised over Ni and O ions further from the defect. Band IV, the empty hole state, is localised mainly on the nitrogen, with a small amount of charge spreading onto two of the Ni atoms. 41% of the charge is on the N with 13% on Ni1 and 6% on a second Ni. Finally, the conduction

band state, Band V, is localised on Ni1 with a small amount of electron density on the nitrogen. In this case, 58% of the charge localises on Ni1 while only 8% is on N.

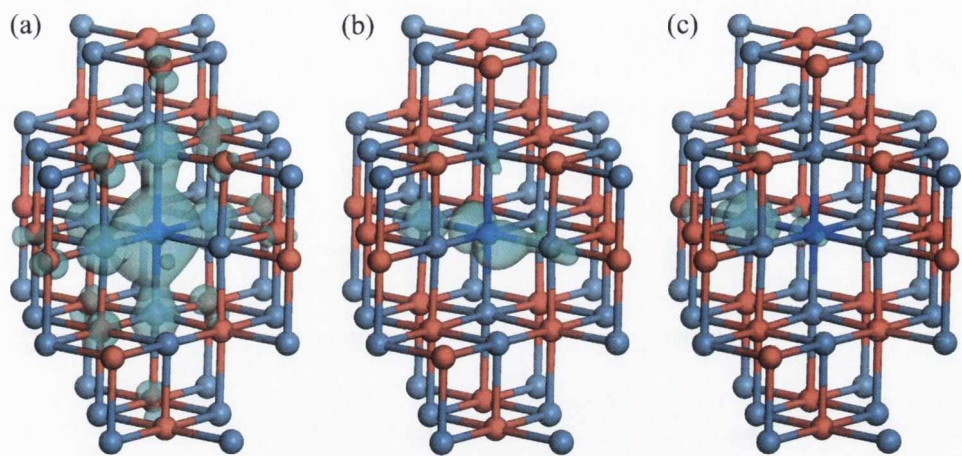


Fig. 5.13 Partial charge density of defect states for  $N'_O + h^*$  in NiO, showing (a) Band I-III, occupied states above VBM, (b) Band IV, hole state 0.5 eV above VBM and (c) Band V, 0.2 eV below CBM. All are plotted on isosurface of  $0.05 \text{ e}/\text{\AA}^3$ .

|                   | Band I-III (%)          | Band IV (%)             | Band V (%)              |
|-------------------|-------------------------|-------------------------|-------------------------|
| N                 | 0.36                    | 0.41                    | 0.08                    |
| Ni <sub>tot</sub> | 0.32                    | 0.35                    | 0.77                    |
| O <sub>tot</sub>  | 0.32                    | 0.24                    | 0.15                    |
| Ni1               | 0.03                    | 0.13                    | 0.58                    |
| Ni <sub>nn</sub>  | 2×0.05, 2×0.06,<br>0.01 | 2×0.02, 2×0.04,<br>0.06 | 2×0.01, 2×0.00,<br>0.01 |

Table 5.7 Bader charge analysis for  $N'_O + h^*$  in NiO, showing the composition (in%) of Bands I-V. Ni<sub>tot</sub> and O<sub>tot</sub> give total Ni and O charges and Ni<sub>nn</sub> gives nearest neighbour Ni charges. Ni1 is nearest neighbour Ni which contributes to Band IV and V.

This analysis indicates that the hole state produced upon nitrogen doping resides mainly on the nitrogen itself, with some delocalisation onto a single neighbouring Ni. The extent of localisation would not be conducive towards conduction, so it is unlikely that this defect would be very mobile. This localisation combined with the high formation energy of  $N'_O + h^*$  suggests that nitrogen doping is not an effective way of increasing the  $p$ -type conductivity of NiO.

## 5.6 Electronic Structure of NiO {100} Surface

Full relaxations of the NiO {100} surface were carried out. This resulted in a relaxed



surface with Ni-O bond lengths of 2.09 Å, similar to those in the bulk. The surface Ni atoms relax slightly inwards by 0.03 Å, while the O ions relax inwards by 0.01 Å. Fig. 5.14 shows the density of states for the {100} surface which appears similar to that of the bulk. The valence band is made up of mixed Ni 3*d* and O 2*p* states, while the conduction band is made up of mainly Ni 3*d* states. A surface state is present below the CBM which is of mainly Ni 3*d* character. This state has been previously seen in several other calculations<sup>413, 427, 433, 468-469</sup> and photoemission experiments.<sup>465-467</sup>

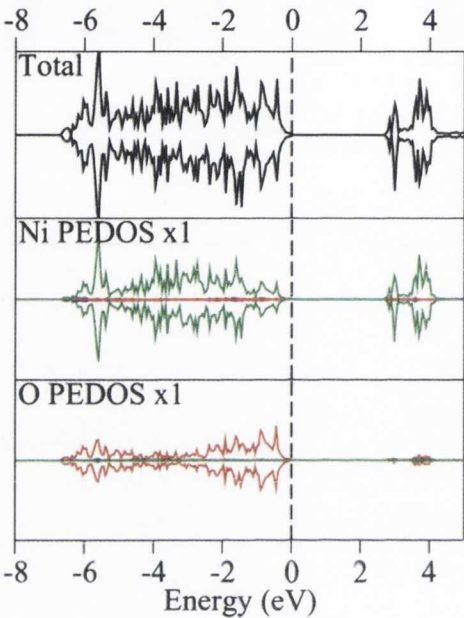


Fig. 5.14 EDOS/PEDOS for NiO {100} surface with VBM indicated by dashed line. Green lines are *d* states and red are *p* states.

### 5.6.1 Surface Defect Formation Energies

At the surface, we again considered Ni and O vacancies in surface sites as well as Li and N dopants in both surface and subsurface sites. The formation energies for all of these defects are shown in Table 5.8, at the chemical potentials outlined in Section 5.4. Similar to the bulk case, the type of non-stoichiometry at the NiO surface varies depending on chemical potential, with O-rich conditions resulting in a Ni-deficient system, while an O-deficient system results from Ni-rich conditions. Ni vacancies have lower formation energies at the surface than in the bulk, indicating that nickel vacancies are likely to form preferentially at surface sites. In contrast, O vacancies are more stable in bulk NiO than at the surface.

Li dopants have very low formation energies at the surface of 0.05 eV under O-rich conditions, much lower than the bulk formation energy of 0.39 eV. Subsurface  $\text{Li}'_{\text{Ni}} + h^\bullet$

has a formation energy of 0.23 eV, intermediate between the formation energies of bulk and surface defects. It is thus likely that Li ions introduced into films will migrate to the surface and subsurface regions because of the lower formation energy.  $N'_O + h^\bullet$  is also lower in energy at the surface than in the bulk. However, its formation energy is still higher than that of oxygen vacancies so that N-doping will not result in *p*-type conductivity. The formation energy of subsurface  $N'_O + h^\bullet$  is intermediate between bulk and surface energies, suggesting that nitrogen prefers to reside in the surface and subsurface regions.

| Surface                 | O-rich | Ni-rich |
|-------------------------|--------|---------|
| $V''_{Ni} + 2h^\bullet$ | 1.44   | 3.85    |
| $V^\bullet_O + 2e'$     | 3.67   | 1.25    |
| $Li'_{Ni} + h^\bullet$  | 0.05   | 1.25    |
| $N'_O + h^\bullet$      | 3.64   | 1.40    |
| Subsurface              | O-rich | Ni-rich |
| $Li'_{Ni} + h^\bullet$  | 0.23   | 1.44    |
| $N'_O + h^\bullet$      | 3.94   | 1.69    |

Table 5.8 Defect formation energies (in eV) of surface and subsurface defects at NiO {100} surface under the chemical potentials listed in Table 5.1.

### 5.6.2 $V''_{Ni} + 2h^\bullet$

Removal of a Ni atom at the surface leads to the formation of two holes. These holes localise on two oxygen atoms neighbouring the vacancy ( $O^\bullet_O$ ). As there are five oxygen atoms available, there are a number of different localisation geometries possible. One hole can localise on the subsurface oxygen below the vacancy while the second localises on one surface oxygen, or alternatively, both holes can localise on surface oxygen ions at either 180° or 90° to each other. We tested each configuration and found that the lowest energy configuration is one in which the holes localise at 180°, as shown in the spin density plots of Fig. 5.15 (a). The lowest energy spin configuration resulted when the oxygen spin is of the same orientation as the removed Ni, resulting in zero net magnetisation of the surface. As we have removed an  $\alpha$ -spin Ni, each oxygen has an excess  $\alpha$ -spin electron. One  $O^\bullet_O$  is directly above a subsurface  $\alpha$ -Ni (O1), while the second is above a  $\beta$ -Ni (O2). Antiferromagnetic coupling between O2 and the  $\beta$ -spin Ni results in a lower magnetic moment of 0.62  $\mu_B$ , while ferromagnetic coupling between O1 and the subsurface  $\alpha$ -Ni



results in a higher oxygen magnetic moment of  $0.70 \mu_B$ . The oxygen ions surrounding the vacancy all relax away from the defect, repelled by the negative charge of the vacancy. O1 and O2 relax away by  $0.15 \text{ \AA}$ , while the remaining two surface O atoms relax away by  $0.20 \text{ \AA}$  and the subsurface O relaxes away by  $0.13 \text{ \AA}$ .

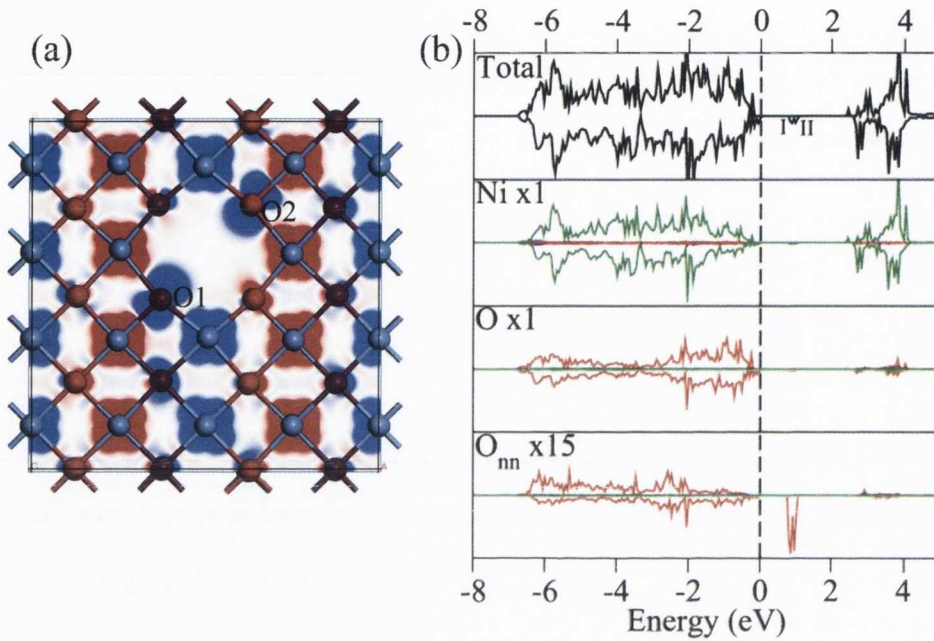


Fig. 5.15 (a) Spin density for  $V''_{Ni} + 2h^*$  at NiO {100} surface, plotted between  $-0.05 \text{ e/\AA}^3$  (red) and  $0.05 \text{ e/\AA}^3$  (blue). Grey atoms are Ni, light red O atoms are above  $\beta$ -Ni and dark red O atoms are above  $\alpha$ -Ni. (b) EDOS/PEDOS for  $V''_{Ni} + 2h^*$  on NiO {100} surface, with dashed line marking VBM. Red lines are  $p$  and green are  $d$  states.  $O_{nn}$  are hole-bearing nearest neighbour oxygen anions.

Fig. 5.15 (b) shows the total and partial EDOS for  $V''_{Ni} + 2h^*$ . Two empty defect levels are present in the band gap, marked I and II, which are made up of mainly O  $2p$  states from O1 and O2. These states appear in the  $\beta$ -spin component of the EDOS and are located 0.8 and 1.0 eV above the VBM. The partial charge densities for both states are shown in Fig. 5.16. The bands are localised mainly on the two nearest neighbour O  $2p$  orbitals, with some density spreading onto the next nearest neighbour Ni beside each oxygen. For Band I, greater electron density is seen on O2, while in Band II, more of the density is on O1, with Bader analysis (Table 5.9) showing Band I to be composed of  $0.21e$  from O1 and  $0.39e$  from O2, while Band II is made up of  $0.38e$  from O1 and  $0.22e$  from O2. This is due to magnetic coupling of the  $\beta$ -spin defect states with the subsurface Ni atoms, which results in the lower energy state (Band I) arising mainly from O2 (above  $\beta$ -Ni), while the higher energy state (Band II) arises from O1 (above  $\alpha$ -Ni). This may suggest that the lowest energy configuration for this defect would be one in which the spin of O2 is reversed to  $\alpha$ -spin. However, this results in a net spin on the system of  $+2.00 \mu_B$  and our calculations

show that the Ni vacancy configurations with zero net magnetic moments are always more stable.

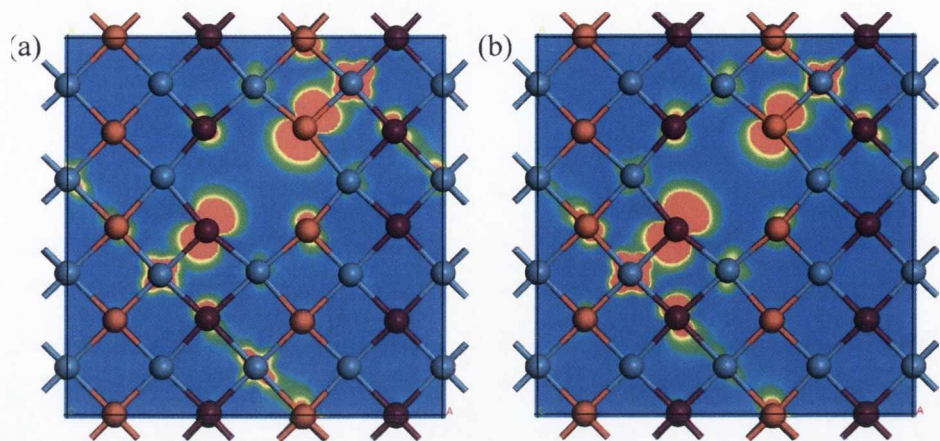


Fig. 5.16 Partial charge density plots for (a) Band I and (b) Band II of  $V''_{Ni} + 2h^*$  on NiO {100} surface, plotted between  $0\text{ e}/\text{\AA}^3$  (blue) and  $0.03\text{ e}/\text{\AA}^3$  (red). Grey atoms are Ni and dark red and light red are  $\alpha$ - and  $\beta$ -O atoms respectively.

|            | Band I     | Band II    |
|------------|------------|------------|
| $Ni_{tot}$ | 0.22       | 0.19       |
| $O_{tot}$  | 0.78       | 0.81       |
| O1 , O2    | 0.21, 0.39 | 0.38, 0.22 |
| Ni1, Ni2   | 0.03, 0.06 | 0.06, 0.04 |

Table 5.9 Bader charge analysis for  $V''_{Ni} + 2h^*$  at NiO {100} surface showing total Ni charge ( $Ni_{tot}$ ), total O charge ( $O_{tot}$ ), charges on hole-bearing O ions (O1 and O2) and charges on next nearest neighbour Ni ions (Ni1, Ni2).

### 5.6.3 $V^{\bullet\bullet}_O + 2e'$

The formation of an oxygen vacancy results in two excess electrons in the system. All five Ni atoms relax towards the vacancy by 0.05 Å, 0.04 Å and 0.01 Å for the subsurface  $\alpha$ -Ni, surface  $\alpha$ -Ni and surface  $\beta$ -Ni atoms, respectively. The spin density plot shown in Fig. 5.17 (a) indicates that the spin of the vacancy itself is polarised, so that the  $\alpha$ -spin component points towards the two  $\beta$ -Ni atoms, while its  $\beta$ -spin component is directed towards the two surface  $\alpha$ -Ni and the subsurface  $\alpha$ -Ni atom. Thus, the five Ni ions surrounding the vacancy have smaller magnetic moments compared to bulk Ni. The three  $\alpha$ -Ni cations have magnetisations of  $1.61\text{ }\mu_B$ , while the two  $\beta$ -Ni atoms have magnetisations of  $-1.57\text{ }\mu_B$ , compared to the bulk value of  $\pm 1.69\text{ }\mu_B$ .



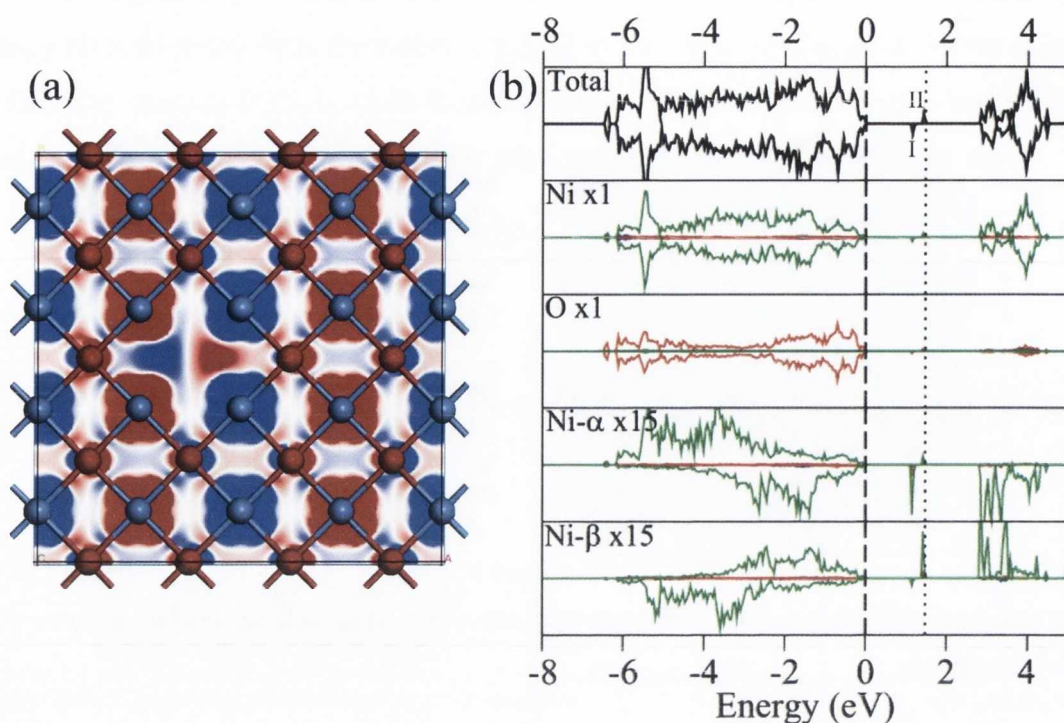


Fig. 5.17 (a) Spin density of  $V_O^{2+} + 2e'$  on NiO {100} surface, plotted between  $-0.05 \text{ e}/\text{\AA}^3$  (red) and  $0.05 \text{ e}/\text{\AA}^3$  (blue). Grey atoms are Ni and red are oxygen. (b) EDOS/PEDOS for  $V_O^{2+} + 2e'$  on NiO {100} surface. PEDOS are plotted separately for Ni ions of  $\alpha$ -spin neighbouring vacancy (Ni- $\alpha$ ) and  $\beta$ -spin Ni neighbours (Ni- $\beta$ ). Dashed line indicates VBM and dotted line is highest occupied level. Green lines are  $d$  states and red are  $p$  states. Roman numerals mark defect states.

The density of states for the surface oxygen vacancy is shown in Fig. 5.17 (b). This shows two defect states in the band gap which are both of mainly Ni  $3d$  character. The lower energy state (Band I) occurs 1.1 eV above the VBM in the  $\beta$ -spin component of the EDOS and is made up mainly of states from the three  $\alpha$ -spin Ni atoms. The higher energy peak (Band II) is in the  $\alpha$ -spin component of the EDOS located 1.4 eV above the VBM, and derives mainly from the two  $\beta$ -spin Ni ions. The lower energy of Band I occurs as it is spread over three Ni atoms compared to only two atoms for Band II. The partial charge density for both of these states is shown in Fig. 5.18 and bears resemblance to that of the bulk vacancy. Band I is localised mainly on the three  $\alpha$ -Ni cations neighbouring the vacancy – two at the surface, and the subsurface Ni, with 65% of the charge localised on these Ni atoms. Band II has 64% of its charge density localised on the remaining two  $\beta$ -Ni cations. Thus, similar to the bulk, surface oxygen vacancies produce defect states in which the charge is localised on the nearest neighbour nickel cations.

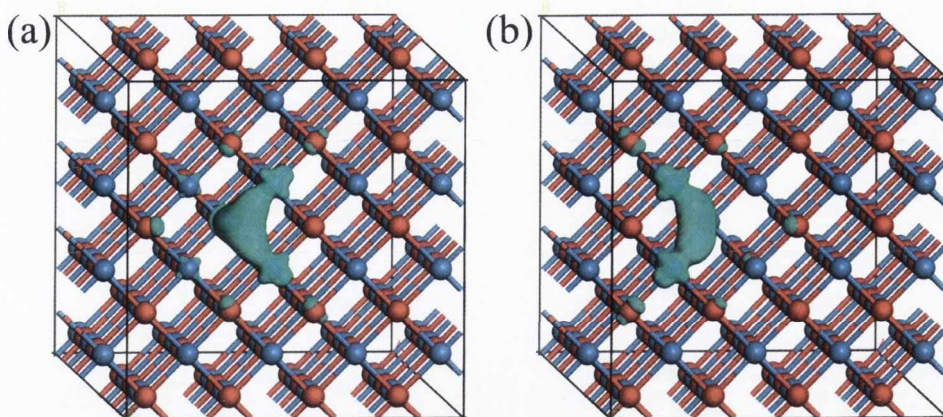


Fig. 5.18 Partial charge density for  $V_O^{2+} + 2e'$  on NiO {100} surface, plotted on light blue isosurface of  $0.03 \text{ e}/\text{\AA}^3$  (red). Band I, the  $\beta$ -spin state is shown in (a) and Band II, the  $\alpha$ -spin state is shown in (b).

|                   | Band I                | Band II    |
|-------------------|-----------------------|------------|
| $Ni_{tot}$        | 0.75                  | 0.76       |
| $O_{tot}$         | 0.25                  | 0.24       |
| $Ni_{nn}(\alpha)$ | $2 \times 0.20, 0.25$ | -          |
| $Ni_{nn}(\beta)$  | -                     | 0.33, 0.31 |

Table 5.10 Bader charges (in  $e$ ) for defect states of  $V_O^{2+} + 2e'$  at NiO {100} surface showing total Ni ( $Ni_{tot}$ ), total O charge ( $O_{tot}$ ) and charge on nearest neighbour Ni atoms ( $Ni_{nn}$ ).

### 5.6.4 $Li'_{Ni} + h^{\bullet}$

The replacement of a Ni(II) by Li(I) at the surface leads to the formation of an oxygen hole on one of the neighbouring oxygen atoms which relaxes away from the Li by  $0.39 \text{ \AA}$ . The spin density for this defect is shown in Fig. 5.19 (a) and shows one oxygen neighbouring the Li to have an excess  $\alpha$ -spin, while its calculated magnetisation is  $0.45 \mu_B$ , compared to a spin of  $+1.69 \mu_B$  on the bulk Ni. Substitution of Li at a subsurface site has a similar effect, with the spin density map in Fig. 5.19 (b) showing that the hole localises on the surface oxygen vertically above the dopant, with a calculated magnetisation of  $0.87 \mu_B$ .

Fig. 5.20 shows the density of states for Li substitutional dopants at surface and subsurface sites. In both, a distinct defect state is seen above the VBM, which is made up of mainly O  $2p$  character from the  $O_O^{\bullet}$ . This state is located  $0.7 \text{ eV}$  above the VBM for the surface defect and  $0.8 \text{ eV}$  above the VBM for the subsurface Li, both occurring further from the VBM than the bulk defect level at  $0.4 \text{ eV}$ . To examine further the nature of the defect states, their partial charge densities are plotted in Fig. 5.21. For the surface  $Li'_{Ni} + h^{\bullet}$ , the



hole is localised on the O 2*p* orbital neighbouring the Li, with some charge density spreading onto the next nearest neighbour Ni and its surrounding oxygens. The next nearest neighbour Ni has a reduced magnetic moment of -1.45  $\mu_B$  compared to its -1.69  $\mu_B$  bulk value. Similarly, the subsurface  $\text{Li}'_{\text{Ni}} + h^*$  has most of the density localised on the surface oxygen vertically above the dopant. This oxygen does not possess a next nearest neighbour Ni at 180° to the Li, upon which some of the charge can localise.

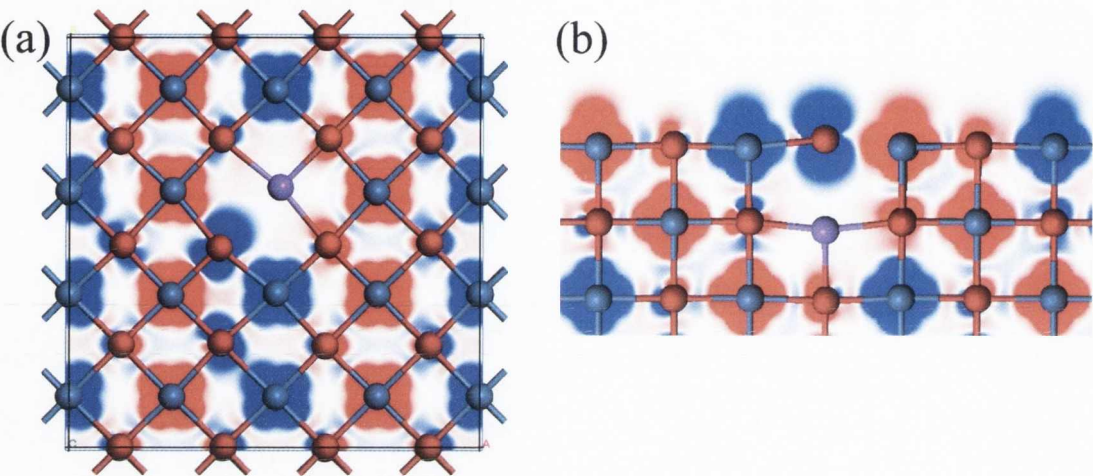


Fig. 5.19 (a) Spin density for  $\text{Li}'_{\text{Ni}} + h^*$  on NiO {100} surface plotted between  $-0.05 \text{ e}/\text{\AA}^3$  (blue) and  $0.05 \text{ e}/\text{\AA}^3$  (red). (b) Spin density for  $\text{Li}'_{\text{Ni}} + h^*$  subsurface to NiO {100} surface plotted between  $-0.05 \text{ e}/\text{\AA}^3$  (red) and  $0.05 \text{ e}/\text{\AA}^3$  (blue). Grey atoms are Ni, red are O and pink are Li.

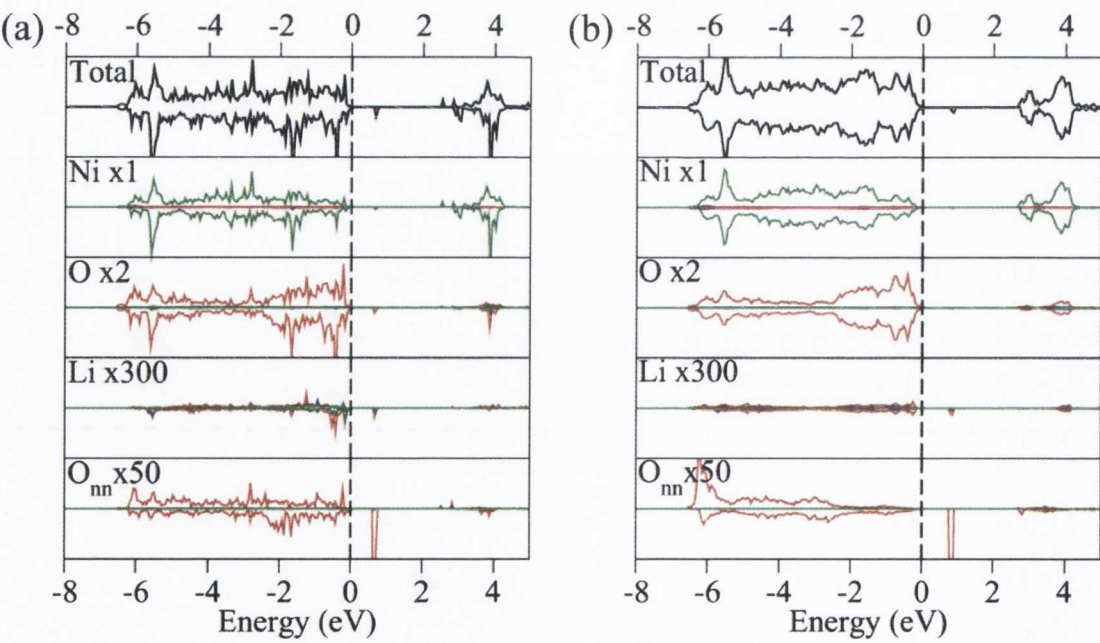


Fig. 5.20 Total and partial EDOS for  $\text{Li}'_{\text{Ni}} + h^*$  at NiO {100} surface substituted at (a) surface and (b) subsurface sites. Dashed line indicates VBM, green lines are *d* states and red are *p* states.  $\text{O}_{\text{nn}}$  is hole-bearing oxygen.

The results of Bader charge analysis for the defect states of surface and subsurface Li are shown in Table 5.11. For the surface dopant,  $0.39e$  is localised on the oxygen, with a further  $0.16e$  on the Ni, while  $0.22e$  is localised over the three other O atoms surrounding the Ni. In contrast,  $0.80e$  for the subsurface defect is localised on a single oxygen ion, indicating it to be almost completely localised. However, the difference in energy between the surface and subsurface Li indicates that some stabilisation is gained by the sharing of charge between  $O_O^\bullet$  and the next nearest neighbour Ni. This sharing of the charge between the O and the Ni may explain why many studies have attributed the holes in NiO to  $Ni^{3+}$  states. In fact, the holes are mainly  $O_O^\bullet$  but do possess a small amount of  $Ni^{3+}$  character, suggesting that they are intermediate between  $O_O^\bullet$  and  $Ni^{3+}$ .

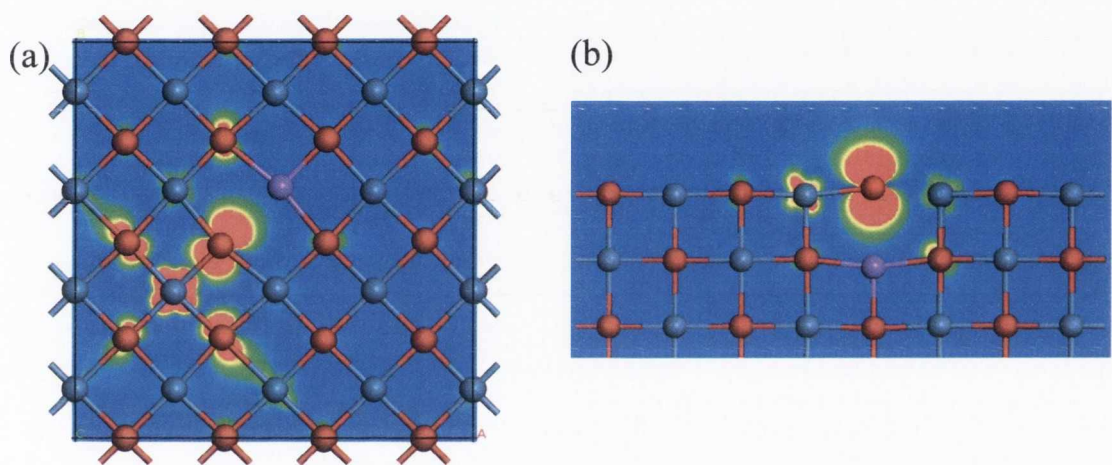


Fig. 5.21 (a) Partial charge density of defect state of  $Li'_{Ni} + h^*$  on NiO {100} surface, at isosurface plotted from 0 (blue) to  $0.05\text{ e}/\text{\AA}^3$  (red). (b) Partial charge density for defect state of subsurface  $Li'_{Ni} + h^*$  plotted from isolevel of  $0\text{ e}/\text{\AA}^3$  (blue) to  $0.05\text{ e}/\text{\AA}^3$  (red). Grey atoms are Ni, red are O and pink is Li.

|            | Surface | Subsurface |
|------------|---------|------------|
| $Ni_{tot}$ | 0.26    | 0.13       |
| $O_{tot}$  | 0.74    | 0.87       |
| $O_{nn}$   | 0.39    | 0.80       |
| $Ni1$      | 0.16    | -          |

Table 5.11 Bader charges (in  $e$ ) for defect state of surface and subsurface  $Li'_{Ni} + h^*$  defect at NiO {100} surface.  $Ni_{tot}$  and  $O_{tot}$  give total Ni and O charges,  $O_{nn}$  gives charge on hole-bearing oxygen and  $Ni1$  gives charge on next nearest neighbour Ni beside oxygen hole.



### 5.6.5 $N'_O + h^\bullet$

Nitrogen substitution at a surface oxygen site results in a hole localised on the nitrogen ( $N'_O$ ), oriented in a  $p$  orbital perpendicular to the surface, as shown in Fig. 5.22 (a). The spin on the nitrogen is in the direction opposite to that of the subsurface Ni and the N has a magnetisation of  $0.55 \mu_B$ . The EDOS for this defect (Fig. 5.23) shows an empty defect state of mainly N  $2p$  character located  $0.8 \text{ eV}$  above the VBM. The lowest energy spin configuration results when the nitrogen atoms on both sides of the slab are of different spin, so that there is zero net spin on the system. In the lowest panel of Fig. 5.23, we show the PEDOS for the  $\alpha$ -spin N which shows an empty single particle level of  $\beta$ -spin. The PEDOS for the  $\beta$ -spin N is similar but has a single particle level of  $\alpha$ -spin.

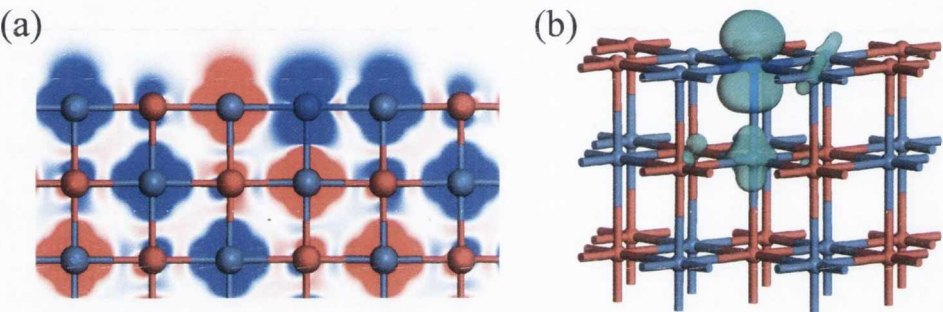


Fig. 5.22 Charge and spin density maps for  $N'_O + h^\bullet$  at  $\text{NiO } \{100\}$  surface, showing (a) spin density plotted between  $-0.05 \text{ e}/\text{\AA}^3$  (red) and  $0.05 \text{ e}/\text{\AA}^3$  (blue) and (b) partial charge density of defect state  $0.8 \text{ eV}$  above VBM, plotted on isosurface of  $0.05 \text{ e}/\text{\AA}^3$ . Grey atoms are Ni, red are O and blue are N.

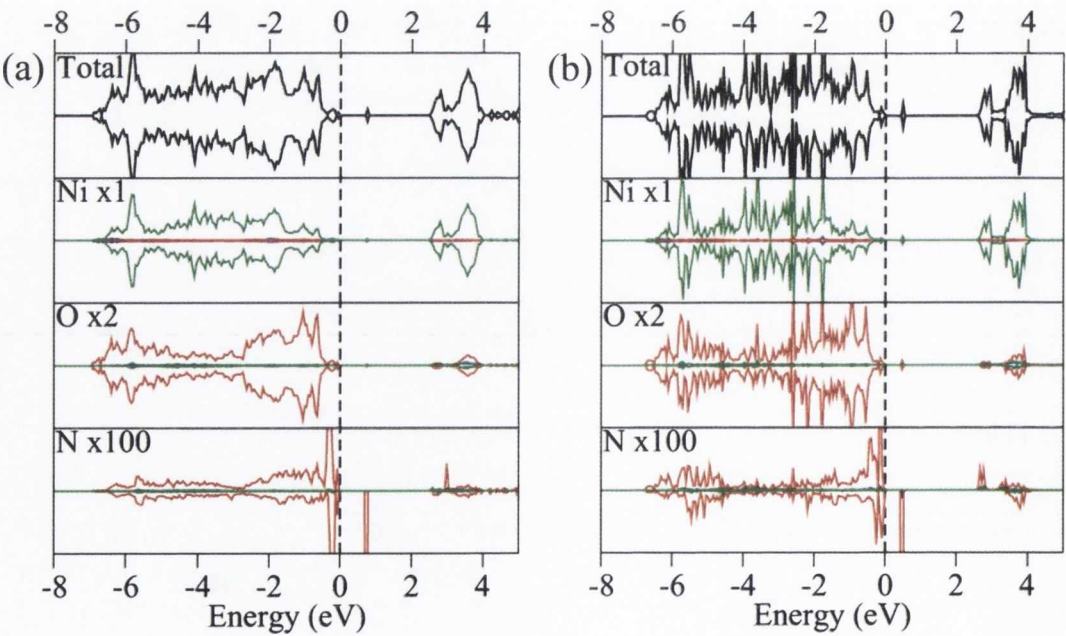


Fig. 5.23 Total and partial EDOS for  $N'_O + h^\bullet$  at (a)  $\{100\}$  surface and (b) at subsurface site. Dashed line indicates highest occupied level, red lines are  $p$  states, and green lines are  $d$  states.

The partial charge density associated with the defect state of  $N'_O + h^*$  at the  $\{100\}$  surface is shown in Fig. 5.22 (b). The majority of the charge is localised on the nitrogen in a  $2p$  orbital perpendicular to the surface. A small amount of charge is also present on the subsurface Ni below the dopant. Bader charge analysis shows  $0.60e$  of the charge to be localised at the nitrogen with a further  $0.11e$  at the Ni (Table 5.12). This indicates the hole state to be very localised, suggesting that any conduction will occur via a polaronic hopping mechanism. However, given the deep nature of the defect state, doping with N is unlikely to result in high levels of conductivity.

|            | Surface | Subsurface |
|------------|---------|------------|
| $Ni_{tot}$ | 0.26    | 0.34       |
| $O_{tot}$  | 0.14    | 0.22       |
| <b>N</b>   | 0.60    | 0.44       |

Table 5.12 Bader charges (in  $e$ ) for defect states of surface and subsurface  $N'_O + h^*$  at NiO  $\{100\}$  surface.  $Ni_{tot}$  is total Ni charge,  $O_{tot}$  is total O charge and N is charge on nitrogen.

Substitution of nitrogen at a subsurface site again results in a hole localised on the nitrogen, which possesses a magnetisation of  $0.44 \mu_B$  (Fig. 5.24 (a)). However, in this case, the lobes of the N  $2p$  orbital are orientated between the Ni ions, rather than being directed towards the atoms as seen for the bulk  $N'_O + h^*$  defect. The  $2p$  orbital is positioned so that one lobe is directed between the three  $\alpha$ -spin Ni atoms while the second is directed towards the three  $\beta$ -spin Ni atoms. The EDOS shows a defect state located  $0.5 \text{ eV}$  above the VBM, which is composed of mainly N  $2p$  states (Fig. 5.23 (b)). Similar to the surface N dopant, the lowest energy spin configuration is one in which the nitrogen on one side of the slab

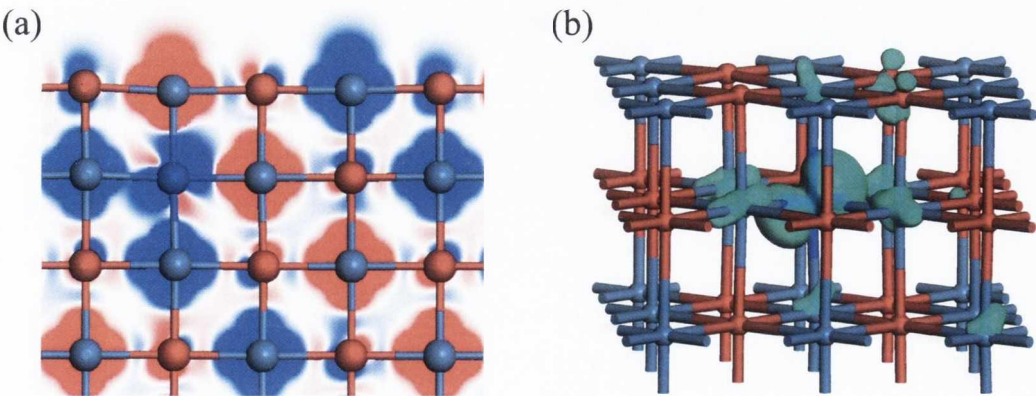


Fig. 5.24 Charge and spin density maps for  $N'_O + h^*$  at  $\{100\}$  subsurface in NiO. (a) shows spin density plotted from  $-0.05 \text{ e}/\text{\AA}^3$  (red) to  $0.05 \text{ e}/\text{\AA}^3$  (red) and (b) shows partial charge density of defect state plotted on isosurface of  $0.05 \text{ e}/\text{\AA}^3$ .



has an excess  $\alpha$ -spin, while the second nitrogen has a  $\beta$ -spin. Fig. 5.23 (b) shows the PEDOS for the  $\alpha$ -spin N which has an empty  $\beta$ -spin state in the band gap. The partial charge density for this defect state is shown in Fig. 5.24 (b). The charge is localised mainly on the nitrogen, with a small amount spread over the six Ni atoms surrounding the dopant. Bader charge analysis of this state (Table 5.12) shows that  $0.44e$  is localised on the nitrogen, while  $0.30e$  is spread over the six Ni atoms.

## 5.7 Discussion

Our calculated GGA+ $U$  formation energies indicate that Ni vacancies and O vacancies can form as intrinsic defects depending on chemical conditions. It is thus necessary to carefully control the chemical conditions to ensure  $p$ -type films form, as charge-compensating oxygen vacancies may form under oxygen-poor conditions. The extrinsic defect formation energies demonstrated that  $\text{Li}'_{\text{Ni}} + h^\bullet$  has a very low formation energy but will form preferentially at surface and subsurface sites. The clustering of Li at the surface is likely to limit the levels of conductivity reached. Calculations of  $\text{N}'_{\text{O}} + h^\bullet$  indicated that the hole localises on the nitrogen itself and the defect has a high energy of formation. This suggests that nitrogen is not a suitable dopant to produce high levels of conductivities in NiO films.

We demonstrate that Ni vacancies located at both bulk and  $\{100\}$  surface sites result in hole states localised on two oxygen ions ( $\text{O}^\bullet_{\text{O}}$ ). This result is in contrast to previous studies using GGA+ $U$  (Ni  $3d$ ),<sup>425, 432, 452</sup> SIC-LDA<sup>454</sup> and hybrid-DFT,<sup>432</sup> which suggested the charge density associated with these defect states to delocalise over all oxygen ions surrounding the vacancy. Previous GGA+ $U$  calculations have demonstrated the necessity of applying a  $U$  to the O  $2p$  states when attempting to localise oxygen holes in several oxides.<sup>232, 478-479</sup> Without a  $U$  value, the hole tends to delocalise over all oxygen states neighbouring the vacancy, as has been seen previously in NiO.<sup>425, 432, 452</sup> By application of an appropriate  $U$  value of 7 eV to the O  $2p$  states, we have demonstrated that rather than being delocalised,  $V''_{\text{Ni}} + 2h^\bullet$  forms a defect state localised on two oxygens and located  $\sim 0.5$  eV and  $\sim 0.9$  eV above the valence band for bulk and surface sites respectively. This high degree of localisation suggests a polaronic mechanism of conductivity as indicated experimentally,<sup>26, 88, 91</sup> which may be the reason that intrinsic  $p$ -type conductivity in NiO remains low.

We show that both bulk and surface oxygen vacancies result in defect states of Ni  $3d$

character from the nickel ions surrounding the vacancy, rather than forming F-centres like in the similarly rocksalt structured MgO.<sup>486</sup> Although some density spreads into the vacancy itself, most of the charge is located on the Ni atoms. The two electrons arising from oxygen vacancy formation occupy a defect state located  $\sim 1.0$  eV above the VBM ( $\sim 2$  eV below CBM). The deep nature of this defect state suggests that oxygen vacancies will not introduce high levels of *n*-type conductivity. It is thus not surprising that NiO is not a good *n*-type conductor, even though oxygen deficiency can be introduced.

Calculations of Li dopants at bulk and surface sites resulted in defect states which were localised on one nearest neighbour oxygen with some mixing with the next nearest Ni bonded to this oxygen. This is in agreement with the results of previous HF and hybrid-DFT calculations which found doping with Li to result in a highly localised oxygen hole.<sup>404, 418</sup> Our calculated defect state for bulk Li was located 0.4 eV above the VBM, indicating a deep acceptor state. The deep nature of the defect state combined with its high degree of localisation indicates that Li doped NiO will conduct via a polaronic hopping mechanism, consistent with experimental evidence.<sup>434</sup>

These GGA+*U* calculations demonstrate conclusively that *p*-type conductivity in NiO is caused by oxygen holes ( $O_O^\bullet$ ) and not by  $Ni^{3+}$  as often cited in the literature.<sup>437, 440-442</sup> Both Ni vacancies and Li dopants result in oxygen holes, and even when the dopant is surrounded by Ni nearest neighbours as in N doped NiO, the charge localises on the nitrogen itself, rather than the Ni atoms. The localised oxygen holes do, however, share some charge density with the Ni atom next nearest neighbour to the defect. This may induce some Ni character to the defect state which may be the reason why so many previous studies have attributed holes to be of Ni(III) character. In no case did we observe the oxidation of a Ni(II) ion to Ni(III) and analysis of Bader charges associated with the defects indicates that the hole state resides mainly on the oxygen ions rather than the Ni ions.

The degree of localisation observed for all defects is in agreement with a polaronic hopping mechanism. This is likely to be the reason why NiO is such a poor *p*-type conductor. Doping with Li produces defect states nearer to the VBM, resulting in Li doped NiO having a lower activation energy for conduction than undoped NiO. However, the defect states are too far above the VBM for a band conduction mechanism to dominate. Given these results, high levels of *p*-type conductivity can never be achieved using Li



doped NiO and unless a more suitable dopant is found, NiO will never reach the high levels of *p*-type conductivity required for commercial transparent electronics applications.

## 5.8 Conclusions

Through a detailed study of the electronic structure of NiO using GGA+*U* methodology, we have demonstrated that holes induced through the presence of Ni vacancies and Li dopants are localised on oxygen sites. Although formation energies of Ni vacancies and Li dopants are found to be low, the deep nature of the defect state combined with the high degree of localisation is not conducive towards high levels of conductivity. NiO does not therefore offer much promise as a *p*-type TCO for future commercial applications.

# Chapter 6: Conclusions and Future Outlook

## 6.2 Conclusions

Despite the wide application of transparent conducting oxides across the electronics industry over the past 60 years, the underlying electronic structure and defects, which give rise to conductivity are still not fully understood. The aim of this thesis was thus to examine the electronic structures of several TCOs using first principles methodology, thereby providing insight into their defect structures and conduction mechanisms.

There are currently two main areas of TCO research: (1) development of new *n*-type materials as cheaper alternatives to indium tin oxide and (2) designing *p*-type TCOs. The first of these problems was addressed in this work by performing a thorough investigation of the intrinsic and extrinsic defects of SnO<sub>2</sub>. The second issue was examined through calculations of the electronic structure of several known *p*-type materials.

### 6.2.1 *N*-type Conduction in SnO<sub>2</sub>

Although SnO<sub>2</sub> is one of the most prominent *n*-type TCOs, up until now its bulk defect structure has not been studied in detail. A complete understanding of the electronic structure of its defects is vital to comprehend fully its mechanism of transparent conductivity.

Our combined GGA and HSE06 approach initially focused solely on the intrinsic defects of SnO<sub>2</sub>. Through this work, we can say conclusively that oxygen vacancies and not tin interstitials are the cause of intrinsic oxygen deficiency. Oxygen vacancies were found to be much lower in energy than tin interstitials in both GGA and HSE06 calculations, indicating their dominance of the defect structure. As well as exploring energetics, we have performed the first detailed calculations of the electronic structure of each of these intrinsic defects. Our examination of oxygen vacancies indicates that the two electrons produced upon defect formation partially localise on the three Sn ions surrounding the vacancy, with the remaining charge delocalised over tin ions further from the defect. The defect structure is thus best described as  $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ . Although the reducibility of the Sn(IV) cations may play a role in the ease of formation of this defect, no single tin ion is reduced to Sn(II) in either GGA or HSE06 calculations. The delocalised nature of the reduction may play a role



as the defect is likely to be more mobile than it would be if it were localised.

HSE06 calculations of the intrinsic defect transition levels in  $\text{SnO}_2$  demonstrated the deep nature of charge transition levels for oxygen vacancies, 0.5 eV below the CBM, showing that they cannot be responsible for the shallow experimental donor levels located 0.15-0.30 eV below the CBM.<sup>62, 66</sup> The only intrinsic defect which could induce shallow levels is the tin interstitial. Unfortunately, both octahedral and tetrahedral tin interstitials are much higher in energy than oxygen vacancies and could not therefore dominate the defect structure. The explanation for the shallow donor levels must thus lie in unintentional impurities, which are accidentally introduced during the production of thin films. Although we cannot say for certain what these impurities are, our HSE06 calculations of extrinsic defects have suggested two possible origins. As hydrogen is a ubiquitous oxide impurity, the first possibility is that hydrogen interstitial or substitutional defects are the cause of the shallow donor levels. The second possibility is that Cl substitutional defects ( $\text{Cl}_\text{O}^\bullet + e'$ ) are accidentally introduced through the use of  $\text{SnCl}_2$  and  $\text{SnCl}_4$  precursors. To test these hypotheses we carried out HSE06 calculations of hydrogen interstitials ( $\text{H}_\text{i}^\bullet + e'$ ) and H substituting at an oxygen site ( $\text{H}_\text{O}^\bullet + e'$ ) and of Cl substitutional dopants. These calculations showed that hydrogen interstitials were very low in energy and much more energetically favourable than H substitutional defects, suggesting that most hydrogen impurities will occupy interstitial sites. The calculated EDOS for both defects indicated that the extra electron will occupy states near the conduction band, suggesting the presence of shallow donor levels. Insertion of Cl is highly unfavourable energetically due to the much greater ionic radius of  $\text{Cl}^-$  (1.67 Å) compared to  $\text{O}^{2-}$  (1.22 Å).<sup>261</sup> Nevertheless, the use of  $\text{SnCl}_4$  and  $\text{SnCl}_2$  as precursors for  $\text{SnO}_2$ , may result in small amounts of Cl being incorporated into the films. The calculated EDOS of Cl doped  $\text{SnO}_2$  suggests that  $\text{Cl}_\text{O}^\bullet + e'$  will induce donor levels near the conduction band minimum. Cl dopants are thus a second candidate as the cause of shallow donor levels in tin dioxide.

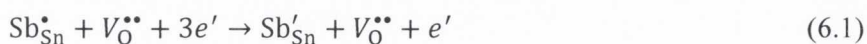
Given the deep nature of the oxygen vacancy donor level, which results in quite a localised defect state, it is likely that any conductivity which results from oxygen vacancies will occur through a polaronic hopping mechanism. In contrast, the shallow nature of the Cl and H states, indicates that they will result in band-type conduction. This may explain the experimental finding that  $\text{SnO}_2$  has two distinct donor activation energies, one of which is shallow with an extremely low activation energy, with the second being a deep level.<sup>171, 190, 192</sup> Both variable range hopping<sup>183, 186, 487</sup> and band-type conduction<sup>184</sup> have been

observed in SnO<sub>2</sub>, which is also in agreement with our hypothesis.

Extrinsically, Sb and F are known to act as excellent *n*-type donors in SnO<sub>2</sub>, though the reason for their preference over other dopants such as Bi and Cl has not previously been determined. Both Bi(V) (0.90 Å) and Sb(V) (0.74 Å) have similar ionic radii to Sn(IV) (0.83 Å)<sup>261</sup> and thus the preference of Sb over Bi cannot be explained by simple geometric considerations. However, the calculations demonstrate that Sb doping is more energetically favourable than the insertion of Bi, thus explaining the lower conductivities of Bi doped films. A comparison of the electronic structure of both dopants in SnO<sub>2</sub> suggests that Bi dopants form more localised defect states than Sb. Sb results in defect states which are of mixed Sb 5*s* and Sn 5*s* character, so that antimony doping does not significantly perturb the electronic structure at the conduction band minimum, allowing conduction to occur via a band conduction mechanism. Bi dopants, however, result in states at the bottom of the conduction band of mixed Bi 6*s* and O 2*p* character from the oxygen ions nearest neighbour to the dopant. The high degree of localisation of these states suggests a more polaronic mechanism of conductivity, with a higher conduction activation energy than for Sb doping and therefore a lower electron mobility. The lower conductivity of Bi doped films can thus be explained both by energetic and electronic structure considerations.

The major reason that fluorine is favoured over chlorine as an anionic dopant is the large ionic radius of chlorine. While F<sup>-</sup> has an ionic radius of 1.16 Å, slightly smaller than the 1.22 Å O<sup>2-</sup> radius, Cl<sup>-</sup> possesses a much larger ionic radius of 1.67 Å. This results in huge structural distortions when chlorine is introduced into the lattice, giving rise to high doping energies. In contrast, F doping results in only small deviations from the bulk Sn-O bond lengths. The electronic structures of F and Cl doped SnO<sub>2</sub> are similar, with both resulting in defect states near the CBM, which are made up of mixed Sn 5*s*, O 2*p* and F/Cl *p* states, similar to the bulk electronic structure. Thus, although both F and Cl will result in band conduction, only fluorine can result in high levels of conductivity due to the high formation energies of Cl substitutionals.

The clustering of oxygen vacancies with Sb or F dopants will inhibit conductivity at high doping levels. Sb dopants neighbouring oxygen vacancies are reduced to Sb(III) which acts as an electron trap. This effectively results in the defect structure:



thereby reducing the number of conduction electrons from three to one. The defect states



associated with the  $(\text{Sb}_{\text{Sn}} + V_{\text{O}})^{\times}$  defect cluster are extremely localised on the Sb and the two nearest neighbour Sn to the vacancy, trapping the electrons and the mobility will be quite low. Similarly, the defect states from the  $(\text{F}_{\text{O}} + V_{\text{O}})^{\times}$  defect cluster are localised mainly on the bridging Sn between the vacancy and fluorine and on the two other Sn ions surrounding the vacancy site. Thus, the clustering of dopant ions with intrinsic oxygen vacancies will result in reduced electron mobility. At higher dopant concentrations, more of the dopant ions may end up clustered with vacancies, which may explain the experimental finding that conductivity in doped  $\text{SnO}_2$  tends to reach a maximum after which it begins to decrease with increased dopant concentration.<sup>260, 263, 488</sup> The much lower binding energy of the fluorine cluster compared to  $(\text{Sb}_{\text{Sn}} + V_{\text{O}})^{\times}$  also provides an explanation for the higher doping concentrations and higher conductivities which are possible in FTO.<sup>294</sup> The interaction of fluorine and oxygen vacancies has a lower tendency to trap the electrons, thereby allowing the system to tolerate higher fluorine concentrations before the charge becomes trapped.

### 6.2.2 *P*-type TCOs

Chapter 4 and 5 of this thesis were dedicated to a thorough investigation of the electronic structure and defects in *p*-type TCOs. As the field of *p*-type TCOs is relatively recent, dating back to the discovery of transparent conductivity in NiO in 1993,<sup>13</sup> as of yet, their properties have not been fully explored.

Through HSE06 and GGA+*U* calculations, we have demonstrated that both the Cu(I)-based TCOs and NiO have valence bands made up of mixed Cu/Ni 3*d* and O 2*p* states. This type of VB should result in higher levels of *p*-type conductivity than conventional *n*-type metal oxides by delocalising the holes over metal *d* and O 2*p* states, rather than having localised O 2*p* holes with poor mobility. Ideally, these *p*-type materials should have a high dispersion at their valence band maxima, thereby resulting in a low hole effective mass for conduction. However, none of these materials possess significant dispersion at the VBM and consequently all have high hole effective masses (0.45-0.79*m*<sub>0</sub>) compared to the low electron effective masses of ~0.1*m*<sub>e</sub> for *n*-type TCOs. As a result, hole states which form at the top of the valence band are quite localised so that the defect calculations for both  $\text{SrCu}_2\text{O}_2$  and NiO indicate that conduction will occur via a polaronic hopping mechanism with low hole mobilities.

Although analysis of the bulk electronic structure can tell us certain aspects about a

material's conductive properties, a complete investigation of its defects is necessary to fully comprehend its conduction mechanism. Thus, for  $\text{SrCu}_2\text{O}_2$  and  $\text{NiO}$ , we have carried out in-depth studies of defect electronic structures. While Ni vacancies have been known for many years to be the cause of  $p$ -type conductivity in  $\text{NiO}$ ,<sup>88, 91, 448</sup> the precise defects responsible for  $p$ -type conductivity in  $\text{SrCu}_2\text{O}_2$  have not been thoroughly examined. Thus, for  $\text{SrCu}_2\text{O}_2$ , a complete study of intrinsic defects was performed to determine the stability of both  $n$ - and  $p$ -type defects whereas in  $\text{NiO}$ , the intrinsic defects were limited to Ni and O vacancies, the known causes of  $p$ - and  $n$ -type conductivity respectively, with the focus on determination of the electronic structure of these defects.

$\text{SrCu}_2\text{O}_2$  was found to have a Cu vacancy dominated defect structure with Sr vacancies also occurring under certain chemical potential conditions.  $N$ -type defects are less stable under all chemical potentials, indicating that intrinsic  $n$ -type  $\text{SrCu}_2\text{O}_2$  will not easily form. Both Sr and Cu vacancies were found to have highly localised defect structures, indicating that conduction will occur in  $\text{SrCu}_2\text{O}_2$  via a polaronic hopping mechanism. The localised nature of these defects is likely to be the reason for the low observed conductivities of strontium copper oxide and suggests that this material does not hold much promise as a commercial  $p$ -type TCO.

In  $\text{NiO}$ , the energetic analysis resulted in the conclusion that undoped nickel oxide can be either  $n$ -type at O-poor conditions through the formation of O vacancies, or  $p$ -type at O-rich conditions through Ni vacancies. This intrinsic bipolarity may be one of the contributing factors to the low conductivities of  $p$ -type  $\text{NiO}$ . Both intrinsic and extrinsic defects in  $\text{NiO}$  resulted in defect states which were highly localised on O  $2p$  orbitals, with lesser contributions from Ni  $3d$  states. Thus, despite the oxidisability of  $\text{Ni(II)}$  to  $\text{Ni(III)}$ , the holes are mainly oxygen-based and are therefore quite immobile. Although conduction can occur via polaronic hopping, it is never likely to reach the same levels as the band-type conduction seen in most  $n$ -type TCOs.

Extrinsically, the most commonly used  $p$ -type dopant to enhance the conductivity of  $\text{NiO}$  is Li. Although the hole states for Li dopants were found to be closer to the VBM than the hole states of Ni vacancies, they were still extremely localised on a single oxygen anion neighbouring the dopant, suggesting a high activation energy for polaronic conductivity. It was also found that the formation energies of Li dopants at the  $\{100\}$  surface and subsurface regions were lower than the bulk formation energies, suggesting a tendency of lithium to migrate towards the surface and subsurface regions, where they will not cause



conductivity. Hence, although Li can enhance the *p*-type conductivity of NiO, Li doped NiO is unlikely to reach conductivities that compete with those of the best *n*-type materials.

To investigate the possibility of anionic doping of NiO, we also examined the substitution of nitrogen at an oxygen site. This defect was found to be very high in energy both in the bulk and at surface and sub-surface sites, indicating that it is unlikely to form in large concentrations. As well as its high formation energy, nitrogen substitution was found to result in hole states which were highly localised on N 2*p* states. These holes are unlikely to have high mobilities and nitrogen is therefore not a suitable dopant to induce high levels of *p*-type conductivity in NiO.

From these results we can conclude that none of the studied *p*-type TCOs have suitable bulk electronic structures to result in high levels of *p*-type conductivity, while the localised defect states of SrCu<sub>2</sub>O<sub>2</sub> and NiO are not conducive to high hole mobilities. It is therefore unlikely that any of these *p*-type oxides will be produced with *p*-type conductivities that are high enough for commercial applications and the search for *p*-type transparent conductors must focus elsewhere.

## 6.3 The Future of Transparent Conductors

### 6.3.1 Mixed Cation *n*-type TCOs

In recent years, transparent conducting oxide research has increasingly moved away from the conventional binary *n*-type TCOs (e.g. In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>), towards multicomponent oxides which include two or more of the  $(n-1)d^{10}ns^0$  cations Ga, In, Sn, Zn and Cd. This has led to the development of a range of amorphous and crystalline mixed cation TCOs including InGaZnO<sub>4</sub>,<sup>489</sup> GaInO<sub>3</sub>,<sup>490</sup> and ZnSnO<sub>3</sub>.<sup>491</sup> These mixed cation oxides have several advantages over the conventional binary *n*-type TCOs. Firstly, they allow for reduced-indium and indium-free materials to be designed, thereby reducing the cost of TCO applications such as flat screen displays. The second advantage is that mixing of two or three different cations allows for a tuning of the material properties, so that the benefits of each binary oxide can be achieved in the one compound. For example, ZnO is very stable in a hydrogen environment, but unstable under acidic or basic conditions. In contrast, SnO<sub>2</sub> has a high stability in acidic or basic environments but is not stable under

hydrogen. However, if  $\text{SnO}_2$  and  $\text{ZnO}$  are mixed to form the ternary oxide,  $\text{ZnSnO}_3$ , the resulting films have high stabilities in both hydrogen and acid/base environments.<sup>491</sup> Thus, by varying the cation types and their ratio, a range of new ternary and quaternary compounds can be designed, with the specific properties required for a particular application. One of the most promising applications for multicomponent oxides is in thin film transistors and as such,  $\text{InGaO}_3(\text{ZnO})_5$ <sup>492</sup> and amorphous  $\text{Zn-In-O}$  films<sup>493</sup> have been used as electron channels in thin film transistors. Flexible thin film transistors using amorphous  $\text{In-Ga-Zn-O}$  films have been developed.<sup>494</sup>

The most common method of obtaining new ternary and quaternary oxides is the use of a combinatorial approach.<sup>495-496</sup> In this method, the ratios of the binary oxides are varied so that a phase diagram can be drawn up, showing the diverse materials which are available at different cation ratios. Following this, specific properties of each phase can be investigated, so that the most suitable materials for particular applications can be found. This approach is, by its nature, slow and arduous, and it would be therefore better if the design of these mixed cation TCOs could be somehow rationalised. This requires a complete understanding of the electronic and structural aspects which give rise to the desired properties of these materials. Currently, it is thought that good overlap between the cation  $s$  orbitals and the O  $2p$  orbitals is essential to achieve a highly dispersed CBM, with a low electron effective mass and high carrier mobility.<sup>30, 497</sup> Many of the crystalline mixed cation TCOs have layered structures which maintain the cation symmetry of the parent binary oxides, thereby preserving the metal-oxygen overlap of the parent oxides. For example, the crystal structure of the  $\text{InGaO}_3(\text{ZnO})_m$  set of compounds consists of alternating layers of wurtzite-structured  $\text{Ga/Zn-O}$  and  $\text{In-O}_6$  octahedra.<sup>498</sup> As with the conventional binary TCOs, the CBM of mixed cation TCOs is made up of mainly metal  $s$  states, while O  $2p$  states make up the VBM. It is thought that intrinsic oxygen vacancies are responsible for  $n$ -type conductivity,<sup>30</sup> though as for the binary oxides, hydrogen interstitials have also been implicated.<sup>499</sup>

As research into these mixed cation TCOs is relatively recent, there have been few computational investigations into their bulk electronic structure,<sup>498, 500-502</sup> and the defect structure of these oxides has not yet been fully explored.<sup>30, 499</sup> It is thus essential that future computational investigations of TCOs focus on understanding the conduction mechanisms within both crystalline and amorphous mixed cation TCOs. These studies should focus on using hybrid-DFT methods to understand fully the bulk geometry and electronic structure of these oxides which gives rise to the properties of interest. It is also



necessary to understand the types of defects which cause conductivity in these oxides and how modifying the structure may affect the defect equilibrium. It is of particular interest in layered systems such as  $\text{InGaO}_3(\text{ZnO})_m$  to examine whether intrinsic oxygen vacancies occur preferentially in the Ga/Zn-O layer or the In-O<sub>6</sub> layer. The electronic structure of dopants in these materials should also be extensively investigated. The complex nature of these materials may cause difficulty in choosing a suitable dopant because of the different cation substitution sites which are available. For example, in a system containing both Sn(IV) and Zn(II) dopants, placing an M(III) cation on a Zn(II) site would result in excess electrons, but if the M(III) substitutes at an Sn(IV) site, it will result in charge-compensating holes. It is thus necessary to carry out extensive calculations of dopant energetics to understand the substitution preferences, and thereby choose dopants which will result in optimum levels of *n*-type conductivity. Through an understanding of the intrinsic and extrinsic defects which lead to *n*-type conductivity, and by investigating different structures, the properties of these mixed cation oxides can be tuned for a particular commercial application.

### 6.3.2 *P*-Type Transparent Conducting Chalcogenides

With the lack of available *p*-type transparent conducting oxides, the search for materials with high *p*-type conductivity has been extended to oxychalcogenide and chalcogenide-based materials containing one of the chalcogens (Ch), S, Se or Te. These include the lanthanide-based oxychalcogenides  $\text{LnCuOCh}$  (Ln = La, Pr, Nd),<sup>503-504</sup> and the chalcogenide-fluoride group of compounds,  $\text{BaCuChF}$ .<sup>505-506</sup>

The  $\text{LnCuOCh}$  family of compounds have layered structures, composed of alternating layers of insulating  $[\text{Ln}_2\text{O}_2]^{2+}$  and semiconducting  $[\text{Cu}_2\text{Ch}_2]^{2-}$ .<sup>503</sup> The *p*-type conducting properties are controlled by the copper chalcogenide layer, while the band gap is controlled by the lanthanide-oxygen interactions. This unique structure allows the properties of these oxychalcogenides to be tuned both by changing the lanthanide cation and by changing the chalcogen anion. The size of the band gap can be tuned by varying Ln between La, Pr, Nd and Ce<sup>507-508</sup> while the conductive properties vary depending on the anion used. *P*-type conductivity in the lanthanum oxychalcogenides ranges from 20 S cm<sup>-1</sup> in  $\text{LaCuOS}$ <sup>509</sup> to 140 S cm<sup>-1</sup> in  $\text{LaCuOSe}$ .<sup>510</sup> All of these compounds exhibit degenerate rather than polaronic conduction and hence, possess higher hole mobilities than the Cu(I) oxide TCOs.<sup>508, 510-511</sup> The higher hole mobilities are thought to result from the higher energy *p* orbitals

of the chalcogenide anions compared to oxygen. This results in greater mixing between Cu  $3d$  and Ch  $p$  states at the VBM, which gives rise to greater hole delocalisation than in Cu(I) oxides.<sup>505, 512</sup> However, the conductivities of these materials are still much lower than  $n$ -type TCOs and further investigation is thus required to improve their  $p$ -type conductivities.

It is also possible to have  $p$ -type transparent conductors which do not contain oxygen. One example of this type of material is the BaCuChF family of compounds.<sup>505-506</sup> Similar to LnCuOCh, these materials are composed of alternating layers of  $[\text{Ba}_2\text{F}_2]^{2+}$  and  $[\text{Cu}_2\text{Ch}_2]^{2-}$ , with conduction occurring in the copper chalcogenide layers. BaCuSF has been found to have conductivities as high as  $1 \times 10^2 \text{ S cm}^{-1}$ ,<sup>513</sup> while conductivities in BaCuTeF have reached  $167 \text{ S cm}^{-1}$ .<sup>514</sup> Again, replacement of the Ba cation with various other 2+ cations allows for the tuning of the band gap, while altering the chalcogen changes the conductive properties.

Because of their high hole mobilities and low resistivities, these layered oxychalcogenide and chalcogenide-fluoride compounds are leading candidates for applications in  $p$ - $n$  junctions. As such, a  $p$ - $n$  junction made up of  $p$ -type LaCuOSe and  $n$ -type InGaZn<sub>5</sub>O<sub>8</sub> has already been fabricated, and shows promise as a light emitting diode.<sup>515</sup> To improve the optoelectronic properties of these materials still further, a complete understanding of their electronic structure and defects is essential. Due to the relatively recent discovery of these compounds, there have been few studies of their bulk electronic structures,<sup>505, 508, 512, 516-518</sup> and their defect electronic structure has yet to be investigated. Future computational investigations of  $p$ -type materials should thus focus initially on understanding their bulk electronic structures using hybrid-DFT methods. The layered nature of these materials allows for various types of compounds to be constructed by varying the cation and the chalcogenide. By comparing the effect of different cations and chalcogenides on the electronic structure, it may be possible to design a material for optimised  $p$ -type conductivity. Further understanding of  $p$ -type conductivity in chalcogenide-based transparent conductors could be gleaned by examining the intrinsic defects responsible for conductivity so that the intrinsic  $p$ -type conduction mechanism can be understood. The relative stability of different intrinsic defects should be thoroughly investigated to ensure that the  $p$ -type conductivity of the chalcogenide is maximised. To enhance the conductivity further, the effects of different dopants on the electronic structure should be studied, so that suitable cationic or anionic dopants can be found which may significantly increase the  $p$ -type conductivity. Electronic structure methods can thus be used to design materials whose properties have been specifically engineered to optimise  $p$ -type conductivity.



### 6.3.3 Surfaces and Interfaces of TCOs

As TCOs are generally deposited as thin films, a large proportion of the atoms lie in surface and sub-surface regions and the surface properties can be important. It is necessary to determine the stability of different surfaces so that the lowest energy surface termination can be understood. Conduction in TCOs generally occurs in the bulk system rather than in the surface region. However, defects may migrate to the surface where they can act as charge traps. For example, it is known that at the  $\text{SnO}_2$  {110} surface, oxygen vacancies form and are charge-compensated by a localised tin reduction ( $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}''$ ).<sup>173</sup> Thus, at the surface two electrons become trapped and are unavailable for *n*-type conduction. It is thus of importance to understand the electronic structure and stability of intrinsic defects at TCO surfaces. Although  $\text{SnO}_2$ <sup>173, 519</sup> and  $\text{ZnO}$ <sup>520-521</sup> surfaces have previously been studied in detail, very few authors have investigated the defect electronic structure of the  $\text{In}_2\text{O}_3$  surface<sup>522</sup> and the surfaces of *p*-type TCOs have yet to be studied. As well as examining intrinsic surface defects, the substitution of dopants at surface sites should also be examined. For  $\text{SnO}_2$ , for example, it is well known that Sb dopants substitute at surface sites as Sb(III) rather than acting as *n*-type Sb(V) dopants as in the bulk.<sup>523</sup> Sb(III) acts as a charge trap and therefore will act to inhibit *n*-type conductivity. It is hence important to examine the electronic structures of doped TCO surfaces so that the effects that surface dopants may have on the overall conductivity can be considered.

Another important area for TCO research is the electronic structure of interfaces. The defects which form at the interface between the TCO film and its substrate or at interfaces between two TCOs in *p-n* junctions, can be quite important in determining the conductive properties. It is thus of importance to perform calculations to determine the stability of these interfaces so that the most stable geometry can be understood. As the VBM and CBM of the two materials at either side of the interface will differ, it is necessary to examine the electronic structure to investigate the band alignment at the interface. The defects that form at substrate-TCO interfaces can act to decrease the conductivity and must be understood in order to fully comprehend the conduction mechanism in TCOs. In *p-n* heterojunctions, the electronic structure at the interface between the *p*- and *n*-type materials controls the conductivity and it is therefore of great importance to investigate fully combinations of different *p*- and *n*-type materials to determine their suitability for *p-n* heterojunctions. The migration of intrinsic and extrinsic defects across the junction must be examined as if *n*-type defects migrate to the *p*-type material, they can act to destroy *p*-type

conductivity and similarly  $p$ -type defects will inhibit conductivity in the  $n$ -type TCO. There have been few previous calculations of either  $p$ - $n$  junction interfaces or substrate-TCO interfaces.<sup>524</sup> Future theoretical studies should thus examine the electronic structure and defects which occur at these interfaces, so that a complete picture of conductivity in TCOs can be obtained.



## Appendix: Kröger-Vink Notation

Defects are normally described using the notation devised by Kröger and Vink.<sup>18</sup> This notation has the general format  $A_S^C$  where  $A$  is the defect species,  $S$  indicates the defect site that  $A$  occupies and  $C$  is the effective charge on the defect.

The defect species  $A$  can be an atom, denoted by its chemical symbol, e.g. Na, Sn, Zn, a vacancy, with symbol  $V$ , or an electron,  $e$  or hole,  $h$ . Note that a vacancy,  $V$ , is always written using italics to distinguish it from the chemical symbol for vanadium, V.

The defect site,  $S$ , may be an interstitial lattice site (symbol  $i$ ) or an existing atomic site within the lattice. For example, when doping  $\text{SnO}_2$  with Sb, a Sb ion is placed on an existing Sn site.

The defect charge indicates the electronic charge on the species relative to the site it occupies. For example, a Sb(V) cation occupying a Sn(IV) site in  $\text{SnO}_2$  has a relative charge of +1. It is denoted using the symbols  $\bullet$  for positive charge,  $'$  for negative charge and  $\times$  for neutral defects.

### Examples

$V_{\text{O}}^{\bullet\bullet}$  indicates a vacancy on an oxygen site with effective charge of +2, i.e. an  $\text{O}^{2-}$  anion has been removed.

$\text{O}_i''$  is an interstitial with an effective charge of -2, i.e.  $\text{O}^{2-}$  interstitial.

$\text{Sn}_{\text{Sn}}^{\times}$  is a tin atom sitting on a tin site with an effective neutral charge e.g. a Sn(IV) ion sitting on its own lattice site in  $\text{SnO}_2$ .

$\text{Sb}_{\text{Sn}}^{\bullet}$  is a Sb ion sitting on a tin site with a relative charge of +1. This may be either a Sb(III) on a Sn(II) site or a Sb(V) on a Sn(IV) site.

$V_i^{\times}$  indicates an empty interstitial site.

$e'$  and  $h^{\bullet}$  are an electron and hole, respectively. A site is not normally specified for these.

# Bibliography

1. T. Minami, *Thin Solid Films*, 2008, **516**, 1314.
2. H. Hosono, *Thin Solid Films*, 2007, **515**, 6000.
3. B. J. Ingram, G. B. Gonzalez, D. R. Kammler, M. I. Bertoni and T. O. Mason, *J. Electroceram.*, 2004, **13**, 167.
4. K. Bädcker, *Ann. Phys.-Berlin*, 1907, **327**, 749.
5. J. T. Littleton, *U.S. Patent*, 2118795, 1938.
6. R. G. Gordon, *MRS Bull.*, 2000, **25**, 52.
7. M. J. Zunick, *U.S. Patent*, 2516663, 1950.
8. K. Wasa, S. Hayakawa and T. Hada, *Jpn. J. Appl. Phys.*, 1971, **10**, 1732.
9. T. Minami, *Semicond. Sci. Technol.*, 2005, **20**, S35.
10. A. Suzuki, T. Matsushita, T. Aoki, Y. Yoneyama and M. Okuda, *Jpn. J. Appl. Phys.*, 2001, **40**, L401.
11. [http://www.webelements.com/periodicity/abundance\\_crust/](http://www.webelements.com/periodicity/abundance_crust/).
12. <http://minerals.usgs.gov/minerals/pubs/commodity/indium/>.
13. H. Sato, T. Minami, S. Takata and T. Yamada, *Thin Solid Films*, 1993, **236**, 27.
14. H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi and H. Hosono, *Nature*, 1997, **389**, 939.
15. A. Kudo, H. Yanagi, H. Hosono and H. Kawazoe, *Appl. Phys. Lett.*, 1998, **73**, 220.
16. R. L. Weiher and R. P. Ley, *J. Appl. Phys.*, 1966, **37**, 299.
17. A. Walsh, J. L. F. Da Silva, S. H. Wei, C. Korber, A. Klein, L. F. J. Piper, A. DeMasi, K. E. Smith, G. Panaccione, P. Torelli, D. J. Payne, A. Bourlange and R. G. Egdell, *Phys. Rev. Lett.*, 2008, **100**, 167402.
18. F. A. Kröger and H. J. Vink, in *Solid State Physics*, eds. F. Seitz and D. Turnbull, 1956, vol. 3, pp. 273-301.
19. O. N. Mryasov and A. J. Freeman, *Phys. Rev. B*, 2001, **64**, 233111.
20. H. Kawazoe and K. Ueda, *J. Am. Ceram. Soc.*, 1999, **82**, 3330.
21. Y. Yang, S. Jin, J. E. Medvedeva, J. R. Ireland, A. W. Metz, J. Ni, M. C. Hersam, A. J. Freeman and T. J. Marks, *J. Am. Chem. Soc.*, 2005, **127**, 8796.
22. H. Mizoguchi and P. M. Woodward, *Chem. Mater.*, 2004, **16**, 5233.
23. N. F. Mott, *Philos. Mag.*, 1969, **19**, 835.
24. G. E. Pike, *Phys. Rev. B*, 1972, **6**, 1572.
25. B. J. Ingram, G. B. Gonzalez, T. O. Mason, D. Y. Shahriari, A. Barnabe, D. Ko and K. R. Poeppelmeier, *Chem. Mater.*, 2004, **16**, 5616.
26. P. Lunkenheimer, A. Loidl, C. R. Ottermann and K. Bange, *Phys. Rev. B*, 1991, **44**, 5927.
27. C. C. B. Lynch, R. G. Egdell and D. S. L. Law, *Chem. Phys. Lett.*, 2005, **401**, 223.
28. P. P. Edwards, A. Porch, M. O. Jones, D. V. Morgan and R. M. Perks, *Dalton Trans.*, 2004, 2995.
29. J. E. Medvedeva, *Europhys. Lett.*, 2007, **78**, 57004.
30. J. E. Medvedeva and C. L. Hettiarachchi, *Phys. Rev. B*, 2010, **81**, 125116.
31. A. Bartos, K. P. Lieb, M. Uhrmacher and D. Wiarda, *Acta Crystallogr. B*, 1993, **49**, 165.
32. H. Odaka, S. Iwata, N. Taga, S. Ohnishi, Y. Kaneta and Y. Shigesato, *Jpn. J. Appl. Phys.*, 1997, **36**, 5551.
33. C. Körber, V. Krishnakumar, A. Klein, G. Panaccione, P. Torelli, A. Walsh, J. L. F. Da Silva, S. H. Wei, R. G. Egdell and D. J. Payne, *Phys. Rev. B*, 2010, **81**, 165207.
34. J. H. W. De Wit, *J. Solid State Chem.*, 1977, **20**, 143.
35. S. Lany and A. Zunger, *Phys. Rev. Lett.*, 2007, **98**, 045501.



36. P. Ágoston and et al., *J. Phys. Condens. Matter*, 2009, **21**, 455801.
37. J. H. W. De Wit, G. Van Unen and M. Lahey, *J. Phys. Chem. Solids*, 1977, **38**, 819.
38. P. Ágoston, K. Albe, R. M. Nieminen and M. J. Puska, *Phys. Rev. Lett.*, 2009, **103**, 245501.
39. T. Koida, M. Kondo, K. Tsutsumi, A. Sakaguchi, M. Suzuki and H. Fujiwara, *J. Appl. Phys.*, 2010, **107**, 033514.
40. S. Limpijumnong, P. Reunchan, A. Janotti and C. G. Van de Walle, *Phys. Rev. B*, 2009, **80**, 193202.
41. O. Warschkow, D. E. Ellis, G. B. González and T. O. Mason, *J. Am. Ceram. Soc.*, 2003, **86**, 1700.
42. G. B. Gonzalez, J. B. Cohen, J.-H. Hwang, T. O. Mason, J. P. Hodges and J. D. Jorgensen, *J. Appl. Phys.*, 2001, **89**, 2550.
43. J. H. Hwang, D. D. Edwards, D. R. Kammler and T. O. Mason, *Solid State Ionics*, 2000, **129**, 135.
44. T. O. Mason, G. B. Gonzalez, J.-H. Hwang and D. R. Kammler, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2183.
45. D. C. Look, J. W. Hemsky and J. R. Sizelove, *Phys. Rev. Lett.*, 1999, **82**, 2552.
46. P. H. Kasai, *Phys. Rev.*, 1963, **130**, 989.
47. A. F. Kohan, G. Ceder, D. Morgan and C. G. Van de Walle, *Phys. Rev. B*, 2000, **61**, 15019.
48. S. J. Clark, J. Robertson, S. Lany and A. Zunger, *Phys. Rev. B*, 2010, **81**, 115311.
49. D. C. Look, G. C. Farlow, P. Reunchan, S. Limpijumnong, S. B. Zhang and K. Nordlund, *Phys. Rev. Lett.*, 2005, **95**, 225502.
50. C. G. Van de Walle, *Phys. Rev. Lett.*, 2000, **85**, 1012.
51. S. F. J. Cox, E. A. Davis, S. P. Cottrell, P. J. C. King, J. S. Lord, J. M. Gil, H. V. Alberto, R. C. Vilão, J. Piroto Duarte, N. Ayres de Campos, A. Weidinger, R. L. Lichti and S. J. C. Irvine, *Phys. Rev. Lett.*, 2001, **86**, 2601.
52. D. M. Hofmann, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B. K. Meyer, S. B. Orlinskii, J. Schmidt and P. G. Baranov, *Phys. Rev. Lett.*, 2002, **88**, 045504.
53. Y. Imai, A. Watanabe and I. Shimono, *J. Mater. Sci.: Mater. Electron.*, 2003, **14**, 149.
54. W. Körner and C. Elsässer, *Phys. Rev. B*, 2010, **81**, 085324.
55. P. Palacios, K. Sánchez and P. Wahnón, *Thin Solid Films*, 2009, **517**, 2448.
56. D. Iuşan, R. Knut, B. Sanyal, O. Karis, O. Eriksson, V. A. Coleman, G. Westin, J. M. Wikberg and P. Svedlindh, *Phys. Rev. B*, 2008, **78**, 085319.
57. H. Agura, A. Suzuki, T. Matsushita, T. Aoki and M. Okuda, *Thin Solid Films*, 2003, **445**, 263.
58. T. Minami, *MRS Bull.*, 2000, **25**, 38.
59. T. Yamanaka, R. Kurashima and J. Mimaki, *Z. Kristallogr.*, 2000, **215**, 424.
60. M. Batzill and U. Diebold, *Prog. Surf. Sci.*, 2005, **79**, 47.
61. G. Frank, E. Kauer and H. Köstlin, *Thin Solid Films*, 1981, **77**, 107.
62. S. Samson and C. G. Fonstad, *J. Appl. Phys.*, 1973, **44**, 4618.
63. C. M. Freeman and C. R. A. Catlow, *J. Solid State Chem.*, 1990, **85**, 65.
64. K. G. Godinho, A. Walsh and G. W. Watson, *J. Phys. Chem. C*, 2009, **113**, 439.
65. C. Kilic and A. Zunger, *Phys. Rev. Lett.*, 2002, **88**, 095501.
66. J. A. Marley and R. C. Dockerty, *Phys. Rev.*, 1965, **140**, A304.
67. A. K. Singh, A. Janotti, M. Scheffler and C. G. Van de Walle, *Phys. Rev. Lett.*, 2008, **101**, 055502.
68. P. D. C. King, R. L. Lichti, Y. G. Celebi, J. M. Gil, R. C. Vilão, H. V. Alberto, J. Piroto Duarte, D. J. Payne, R. G. Egdell, I. McKenzie, C. F. McConville, S. F. J. Cox and T. D. Veal, *Phys. Rev. B*, 2009, **80**, 081201.
69. V. M. Zainullina, *Physica B*, 2007, **391**, 280.

70. K. C. Mishra, K. H. Johnson and P. C. Schmidt, *Phys. Rev. B*, 1995, **51**, 13972.
71. J. Xu, S. Huang and Z. Wang, *Solid State Commun.*, 2009, **149**, 527.
72. G. Thomas, *Nature*, 1997, **389**, 907.
73. Y. Cui and F. Bruneval, *Appl. Phys. Lett.*, 2010, **97**, 042108.
74. S. Majumdar and P. Banerji, *J. Appl. Phys.*, 2010, **107**, 063702.
75. S. S. Pan, G. H. Li, L. B. Wang, Y. D. Shen, Y. Wang, T. Mei and X. Hu, *Appl. Phys. Lett.*, 2009, **95**, 222112.
76. H. Yanagi, H. Kawazoe, A. Kudo, M. Yasukawa and H. Hosono, *J. Electroceram.*, 2000, **4**, 407.
77. S. Nikitine, J. B. Grun and M. Sieskind, *J. Phys. Chem. Solids*, 1961, **17**, 292.
78. L. H. Tjeng, M. B. J. Meinders, J. van Elp, J. Ghijsen, G. A. Sawatzky and R. L. Johnson, *Phys. Rev. B*, 1990, **41**, 3190.
79. H. Shi, R. Asahi and C. Stampfl, *Phys. Rev. B*, 2007, **75**, 205125.
80. A. Buljan, M. Llunell, E. Ruiz and P. Alemany, *Chem. Mater.*, 2001, **13**, 338.
81. S. Boudin, C. Felser and F. Studer, *Solid State Sci.*, 2003, **5**, 741.
82. M. Shimode, M. Sasaki and K. Mukaida, *J. Solid State Chem.*, 2000, **151**, 16.
83. N. Duan, A. W. Sleight, M. K. Jayaraj and J. Tate, *Appl. Phys. Lett.*, 2000, **77**, 1325.
84. R. Nagarajan, N. Duan, M. K. Jayaraj, J. Li, K. A. Vanaja, A. Yokochi, A. Draeseke, J. Tate and A. W. Sleight, *Int. J. Inorg. Mater.*, 2001, **3**, 265.
85. E. Bobeico, E. Varsano, C. Minarini and F. Roca, *Thin Solid Films*, 2003, **444**, 70.
86. K. G. Godinho, G. W. Watson, A. Walsh, A. J. H. Green, D. J. Payne, J. Harmer and R. G. Egdell, *J. Mater. Chem.*, 2008, **18**, 2798.
87. X. L. Nie, S. H. Wei and S. B. Zhang, *Phys. Rev. B*, 2002, **65**, 075111.
88. D. P. Snowden and H. Saltsburg, *Phys. Rev. Lett.*, 1965, **14**, 497.
89. S. Lany, J. Osorio-Guillén and A. Zunger, *Phys. Rev. B*, 2007, **75**, 241203.
90. B. J. Ingram, T. O. Mason, R. Asahi, K. T. Park and A. J. Freeman, *Phys. Rev. B*, 2001, **64**, 155114.
91. M. A. Kolber and R. K. MacCrone, *Phys. Rev. Lett.*, 1972, **29**, 1457.
92. D. O. Scanlon, B. J. Morgan, G. W. Watson and A. Walsh, *Phys. Rev. Lett.*, 2009, **103**, 096405.
93. Y. Ishii, *J. Display Technol.*, 2007, **3**, 351.
94. [http://www.fokus-technologies.de/technology\\_en.phtml](http://www.fokus-technologies.de/technology_en.phtml).
95. C. G. Granqvist, *Sol. Energy Mater. Sol. Cells*, 2007, **91**, 1529.
96. G. A. Niklasson and C. G. Granqvist, *J. Mater. Chem.*, 2007, **17**, 127.
97. E. Schrödinger, *Ann. Phys.-Berlin*, 1926, **384**, 361.
98. M. Born and R. Oppenheimer, *Ann. Phys.-Berlin*, 1927, **389**, 457.
99. D. R. Hartree, *Math. Proc. Camb. Phil. Soc.*, 1928, **24**, 89.
100. D. R. Hartree, *Math. Proc. Camb. Phil. Soc.*, 1928, **24**, 111.
101. D. R. Hartree, *Math. Proc. Camb. Phil. Soc.*, 1928, **24**, 426.
102. J. C. Slater, *Phys. Rev.*, 1929, **34**, 1293.
103. V. Fock, *Z. Phys. A*, 1930, **62**, 795.
104. G. G. Hall, *Proc. R. Soc. London, A*, 1951, **205**, 541.
105. C. C. J. Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.
106. P.-O. Löwdin, *Phys. Rev.*, 1955, **97**, 1509.
107. P. Hohenberg and W. Kohn, *Phys. Rev. B*, 1964, **136**, B864.
108. W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, 1133.
109. F. Bloch, *Z. Phys. A*, 1929, **57**, 545.
110. P. A. M. Dirac, *Math. Proc. Camb. Phil. Soc.*, 1930, **26**, 376.
111. D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.*, 1980, **45**, 566.
112. S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.
113. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.



114. C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
115. J. P. Perdew, *Electronic Structure of Solids*, Akademie Verlag, Berlin, 1991.
116. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
117. M. Nolan, S. C. Parker and G. W. Watson, *Surf. Sci.*, 2005, **595**, 223.
118. L. J. Sham and M. Schluter, *Phys. Rev. B*, 1985, **32**, 3883.
119. J. P. Perdew and A. Zunger, *Phys. Rev. B*, 1981, **23**, 5048.
120. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372.
121. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
122. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
123. J. Paier, M. Marsman and G. Kresse, *J. Chem. Phys.*, 2007, **127**, 024103.
124. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.
125. J. P. Perdew, M. Ernzerhof and K. Burke, *J. Chem. Phys.*, 1996, **105**, 9982.
126. J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2006, **124**, 219906.
127. J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207.
128. J. Heyd, J. E. Peralta, G. E. Scuseria and R. L. Martin, *J. Chem. Phys.*, 2005, **123**, 174101.
129. J. Heyd and G. E. Scuseria, *J. Chem. Phys.*, 2004, **121**, 1187.
130. A. V. Krukau, O. A. Vydrov, A. F. Izmaylov and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 224106.
131. S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys and A. P. Sutton, *Phys. Rev. B*, 1998, **57**, 1505.
132. V. I. Anisimov, J. Zaanen and O. K. Andersen, *Phys. Rev. B*, 1991, **44**, 943.
133. A. Janotti, D. Segev and C. G. Van de Walle, *Phys. Rev. B*, 2006, **74**, 045202.
134. K. Karlsson, F. Aryasetiawan and O. Jepsen, *Phys. Rev. B*, 2010, **81**, 245113.
135. M. Nolan, S. Grigoleit, D. C. Sayle, S. C. Parker and G. W. Watson, *Surf. Sci.*, 2005, **576**, 217.
136. C. Loschen, J. Carrasco, K. M. Neyman and F. Illas, *Phys. Rev. B*, 2007, **75**, 035115.
137. G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251.
138. G. Kresse and J. Furthmuller, *Comp. Mater. Sci.*, 1996, **6**, 15.
139. G. Kresse and J. Furthmuller, *Phys. Rev. B*, 1996, **54**, 11169.
140. E. R. Davidson, *Methods in Computational Molecular Physics*, NATO Advanced Study Institute, Plenum, New York, 1983.
141. D. D. Johnson, *Phys. Rev. B*, 1988, **38**, 12807.
142. P. Pulay, *Chem. Phys. Lett.*, 1980, **73**, 393.
143. H. Hellmann, *Einführung in die Quantenchemie*, F. Deuticke, Leipzig und Wien, 1937.
144. R. P. Feynman, *Phys. Rev.*, 1939, **56**, 340.
145. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188.
146. P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953.
147. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.
148. C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids*, Clarendon, Oxford, 1972.
149. T. Hughbanks and R. Hoffmann, *J. Am. Chem. Soc.*, 1983, **105**, 3528.
150. B. Adolph, J. Furthmuller and F. Bechstedt, *Phys. Rev. B*, 2001, **63**, 125108.
151. J. Paier, M. Marsman and G. Kresse, *Phys. Rev. B*, 2008, **78**, 121201.
152. L. E. Ramos, J. Paier, G. Kresse and F. Bechstedt, *Phys. Rev. B*, 2008, **78**, 195423.
153. X. L. Nie, S. H. Wei and S. B. Zhang, *Phys. Rev. Lett.*, 2002, **88**, 066405.
154. A. Walsh, J. L. F. Da Silva, Y. F. Yan, M. M. Al-Jassim and S. H. Wei, *Phys. Rev. B*, 2009, **79**, 073105.

155. A. Walsh, Y. Yan, M. N. Huda, M. M. Al-Jassim and S. H. Wei, *Chem. Mater.*, 2009, **21**, 547.
156. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, 1990.
157. G. Henkelman, A. Arnaldsson and H. Jonsson, *Comp. Mater. Sci.*, 2006, **36**, 354.
158. D. D. Wagman, *J. Phys. Chem. Ref. Data*, 1982, **11** (Suppl. 2) 116.
159. F. D. Murnaghan, *Proc. Natl. Acad. Sci. U. S. A.*, 1944, **30**, 244.
160. C. W. M. Castleton, A. Hoglund and S. Mirbt, *Phys. Rev. B*, 2006, **73**, 035215.
161. S. B. Zhang and J. E. Northrup, *Phys. Rev. Lett.*, 1991, **67**, 2339.
162. G. Roma and Y. Limoge, *Nucl. Instrum. Meth. B*, 2003, **202**, 120.
163. G. Makov and M. C. Payne, *Phys. Rev. B*, 1995, **51**, 4014.
164. C. G. Van de Walle and J. Neugebauer, *J. Appl. Phys.*, 2004, **95**, 3851.
165. U. Gerstmann, P. Deak, R. Rurali, B. Aradi, T. Frauenheim and H. Overhof, *Physica B*, 2003, **340**, 190.
166. A. Einstein, *Ann. Phys.-Berlin*, 1905, **322**, 132.
167. J. J. Yeh and I. Lindau, *Atom. Data Nucl. Data*, 1985, **32**, 1.
168. G. W. Watson, *J. Chem. Phys.*, 2001, **114**, 758.
169. A. Walsh and G. W. Watson, *Phys. Rev. B*, 2004, **70**, 235114.
170. A. E. Rakhshani, Y. Makdisi and H. A. Ramazaniyan, *J. Appl. Phys.*, 1998, **83**, 1049.
171. K. B. Sundaram and G. K. Bhagavat, *J. Phys. D*, 1981, **14**, 333.
172. C. G. Fonstad and R. H. Rediker, *J. Appl. Phys.*, 1971, **42**, 2911.
173. J. D. Prades, J. Arbiol, A. Cirera, J. R. Morante, M. Avella, L. Zanotti, E. Comini, G. Faglia and G. Sberveglieri, *Sens. Actuat. B*, 2007, **126**, 6.
174. B. Alterkop, N. Parkansky, S. Goldsmith and R. L. Boxman, *J. Phys. D*, 2003, **36**, 552.
175. C. A. Vincent, *J. Electrochem. Soc.*, 1972, **119**, 515.
176. A. Derbal, S. Omeiri, A. Bouguelia and M. Trari, *Int. J. Hydrogen Energy*, 2008, **33**, 4274.
177. R. G. Egdell, S. Eriksen and W. R. Flavell, *Solid State Commun.*, 1986, **60**, 835.
178. D. F. Cox, T. B. Fryberger and S. Semancik, *Phys. Rev. B*, 1988, **38**, 2072.
179. P. DePadova, R. Larciprete, C. Ottaviani, C. Quaresima, P. Perfetti, E. Borsella, C. Astaldi, C. Comicioli, C. Crotti, M. Matteucci, M. Zacchigna and K. Prince, *Appl. Surf. Sci.*, 1996, **104**, 349.
180. D. Maestre, J. Ramirez-Castellanos, P. Hidalgo, A. Cremades, J. M. Gonzalez-Calbet and J. Piqueras, *Eur. J. Inorg. Chem.*, 2007, 1544.
181. M. Fang and et al., *J. Phys. D*, 2007, **40**, 7648.
182. D. Belanger, J. P. Dodelet, B. A. Lombos and J. I. Dickson, *J. Electrochem. Soc.*, 1985, **132**, 1398.
183. A. J. C. Lanfredi, R. R. Geraldles, O. M. Berengue, E. R. Leite and A. J. Chiquito, *J. Appl. Phys.*, 2009, **105**, 023708.
184. K. Subba Ramaiah and V. Sundara Raja, *Appl. Surf. Sci.*, 2006, **253**, 1451.
185. T. R. Giralidi, A. J. C. Lanfredi, E. R. Leite, M. T. Escote, E. Longo, J. A. Varela, C. Ribeiro and A. J. Chiquito, *J. Appl. Phys.*, 2007, **102**, 034312.
186. Y.-J. Ma, F. Zhou, L. Lu and Z. Zhang, *Solid State Commun.*, 2004, **130**, 313.
187. F. Yakuphanoglu, *J. Alloys Compd.*, 2009, **470**, 55.
188. S. A. Pianaro, P. R. Bueno, P. Olivi, E. Longo and J. A. Varela, *J. Mater. Sci.: Mater. Electron.*, 1998, **9**, 159.
189. A. B. Glot, A. V. Gaponov and A. P. Sandoval-García, *Physica B*, 2010, **405**, 705.
190. E. K. Shokr, M. M. Wakkad, H. A. Abd El-Ghanny and H. M. Ali, *J. Phys. Chem. Solids*, 2000, **61**, 75.



191. P. S. Patil, R. K. Kaware, T. Seth, D. P. Amalnerkar and P. S. Chigare, *Ceram. Int.*, 2003, **29**, 725.
192. E. R. Leite, A. M. Nascimento, P. R. Bueno, E. Longo and J. A. Varela, *J. Mater. Sci.: Mater. Electron.*, 1999, **10**, 321.
193. J. Maier and W. Gopel, *J. Solid State Chem.*, 1988, **72**, 293.
194. L. Z. Yang, Z. T. Sui and C. Z. Wang, *J. Solid State Chem.*, 1994, **113**, 221.
195. P. Dinola, F. Morazzoni, R. Scotti and D. Narducci, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3711.
196. F. Morazzoni, C. Canevali, N. Chiodini, C. Mari, R. Ruffo, R. Scotti, L. Armelao, E. Tondello, L. Depero and E. Bontempi, *Mat. Sci. Eng. C*, 2001, **15**, 167.
197. S. H. Sun, G. W. Meng, G. X. Zhang, T. Gao, B. Y. Geng, L. D. Zhang and J. Zuo, *Chem. Phys. Lett.*, 2003, **376**, 103.
198. R. S. Ningthoujam, D. Lahiri, V. Sudarsan, H. K. Poswal, S. K. Kulshreshtha, S. M. Sharma, B. Bhushan and M. D. Sastry, *Mater. Res. Bull.*, 2007, **42**, 1293.
199. H. Chen, X. Wu, S. Xiong, W. Zhang and J. Zhu, *Appl. Phys. A*, 2009, **97**, 365.
200. D. Maestre, A. Cremades and J. Piqueras, *J. Appl. Phys.*, 2004, **95**, 3027.
201. A. Kar, M. A. Stroschio, M. Dutta, J. Kumari and M. Meyyappan, *Appl. Phys. Lett.*, 2009, **94**, 101905.
202. A. Czapla, E. Kusior and M. Bucko, *Thin Solid Films*, 1989, **182**, 15.
203. J. G. Zheng, X. Pan, M. Schweizer, F. Zhou, U. Weimar, W. Gopel and M. Ruhle, *J. Appl. Phys.*, 1996, **79**, 7688.
204. G. Zhou, S. Ni, X. Sun, X. Wang, Q. Wang and D. He, *J. Mater. Sci.: Mater. Electron.*, 2010, **DOI: 10.1007/s10854-010-0109-8**.
205. M. Fang, X. Tan, B. Cheng and L. Zhang, *J. Mater. Chem.*, 2009, **19**, 1320.
206. M. Fang, L. Zhang, X. Tan, X. Hu, W. Yan and P. Liu, *J. Phys. Chem. C*, 2009, **113**, 9676.
207. P. Barbarat, S. F. Matar and G. LeBlevenec, *J. Mater. Chem.*, 1997, **7**, 2547.
208. M. Calatayud, J. Andres and A. Beltran, *Surf. Sci.*, 1999, **430**, 213.
209. L. A. Errico, *Physica B*, 2007, **389**, 140.
210. M. A. Maki-Jaskari and T. T. Rantala, *Phys. Rev. B*, 2001, **64**, 075407.
211. J. Robertson, K. Xiong and S. J. Clark, *Thin Solid Films*, 2006, **496**, 1.
212. J. Robertson, *Phys. Rev. B*, 1984, **30**, 3520.
213. R. I. Hines, N. L. Allan and W. R. Flavell, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 2057.
214. *CRC Handbook of Chemistry and Physics*, 88 edn., CRC Press, Boca Raton, Florida, 2008.
215. J. Mimaki, T. Tsuchiya and T. Yamanaka, *Z. Kristallogr.*, 2000, **215**, 419.
216. M. S. Moreno, R. F. Egerton, J. J. Rehr and P. A. Midgley, *Phys. Rev. B*, 2005, **71**, 035103.
217. A. Walsh and G. W. Watson, *J. Phys. Chem. B*, 2005, **109**, 18868.
218. J. Robertson, K. Xiong and S. J. Clark, *Phys. Status Solidi B*, 2006, **243**, 2054.
219. Q.-J. Liu, Z.-T. Liu and L.-P. Feng, *Comp. Mater. Sci.*, 2010, **47**, 1016.
220. A. Ferreira da Silva, I. Pepe, C. Persson, J. Souza de Almeida, C. Moyses Araujo, R. Ahuja, B. Johansson, C. Y. An and J.-H. Guo, *Phys. Scr.*, 2004, **2004**, 180.
221. G. Sanon, R. Rup and A. Mansingh, *Phys. Rev. B*, 1991, **44**, 5672.
222. K. B. Sundaram and G. K. Bhagavat, *J. Phys. D*, 1981, **14**, 921.
223. E. Shanthi, V. Dutta, A. Banerjee and K. L. Chopra, *J. Appl. Phys.*, 1980, **51**, 6243.
224. R. Summitt, J. A. Marley and N. F. Borrelli, *J. Phys. Chem. Solids*, 1964, **25**, 1465.
225. Y. Z. Zhu, G. D. Chen, H. G. Ye, A. Walsh, C. Y. Moon and S. H. Wei, *Phys. Rev. B*, 2008, **77**, 245209.
226. F. Thomazi, L. S. Roman, A. F. d. Silva and C. Persson, *Phys. Status Solidi C*, 2009, **6**, 2740.

227. K. J. Button, C. G. Fonstad and W. Dreybrodt, *Phys. Rev. B*, 1971, **4**, 4539.
228. F. R. Sensato, O. T. Filho, E. Longo, J. R. Sambrano and J. Andres, *J. Mol. Struct.*, 2001, **541**, 69.
229. C. McGuinness, C. B. Stagarescu, P. J. Ryan, J. E. Downes, D. Fu, K. E. Smith and R. G. Egdell, *Phys. Rev. B*, 2003, **68**, 165104.
230. J. M. Themlin, R. Sporken, J. Darville, R. Caudano, J. M. Gilles and R. L. Johnson, *Phys. Rev. B*, 1990, **42**, 11914.
231. B. J. Morgan and G. W. Watson, *Surf. Sci.*, 2007, **601**, 5034.
232. D. O. Scanlon, A. Walsh, B. J. Morgan, M. Nolan, J. Fearon and G. W. Watson, *J. Phys. Chem. C*, 2007, **111**, 7971.
233. A. A. Sokol, S. A. French, S. T. Bromley, C. R. A. Catlow, H. J. J. van Dam and P. Sherwood, *Faraday Discuss.*, 2007, **134**, 267.
234. A. A. Sokol, A. Walsh and C. R. A. Catlow, *Chem. Phys. Lett.*, 2010, **492**, 44.
235. C. B. Fitzgerald, M. Venkatesan, L. S. Dorneles, R. Gunning, P. Stamenov, J. M. D. Coey, P. A. Stampe, R. J. Kennedy, E. C. Moreira and U. S. Sias, *Phys. Rev. B*, 2006, **74**, 115307.
236. X. Liu, D. Zhang, Y. Zhang and X. Dai, *J. Appl. Phys.*, 2010, **107**, 064309.
237. S. B. Zhang, S. H. Wei and A. Zunger, *Phys. Rev. B*, 2001, **63**, 075205.
238. A. Janotti and C. G. V. d. Walle, *Appl. Phys. Lett.*, 2005, **87**, 122102.
239. C. Freysoldt, J. Neugebauer and C. G. Van de Walle, *Phys. Rev. Lett.*, 2009, **102**, 016402.
240. H. J. Van Daal, *J. Appl. Phys.*, 1968, **39**, 4467.
241. J. Fan and R. Freer, *Appl. Phys. Lett.*, 2007, **90**, 093511.
242. P. R. Bueno, M. M. Oliveira, W. K. Bacelar-Junior, E. R. Leite, E. Longo, G. Garcia-Belmonte and J. Bisquert, *J. Appl. Phys.*, 2002, **91**, 6007.
243. M. O. Orlandi, M. R. D. Bomio, E. Longo and P. R. Bueno, *J. Appl. Phys.*, 2004, **96**, 3811.
244. R. S. Dale, C. S. Rastomjee, F. H. Potter, R. G. Egdell and T. J. Tate, *Appl. Surf. Sci.*, 1993, **70-71**, 359.
245. Y. S. He, J. C. Campbell, R. C. Murphy, M. F. Arendt and J. S. Swinnea, *J. Mater. Res.*, 1993, **8**, 3131.
246. E. Shanthi, A. Banerjee, V. Dutta and K. L. Chopra, *J. Appl. Phys.*, 1982, **53**, 1615.
247. C. Agashe and S. S. Major, *J. Mater. Sci.*, 1996, **31**, 2965.
248. P. Gerhardinger and D. Strickler, *Key Eng. Mater.*, 2008, **380**, 169.
249. J. L. Vossen and E. S. Poliniak, *Thin Solid Films*, 1972, **13**, 281.
250. K. Y. Rajpure, M. N. Kusumade, M. N. Neumann-Spallart and C. H. Bhosale, *Mater. Chem. Phys.*, 2000, **64**, 184.
251. L. D. Loch, *J. Electrochem. Soc.*, 1963, **110**, 1081.
252. P. A. Cox, R. G. Egdell, C. Harding, A. F. Orchard, W. R. Patterson and P. J. Tavener, *Solid State Commun.*, 1982, **44**, 837.
253. R. G. Egdell, J. Rebane, T. J. Walker and D. S. L. Law, *Phys. Rev. B*, 1999, **59**, 1792.
254. R. G. Egdell, W. R. Flavell and P. Tavener, *J. Solid State Chem.*, 1984, **51**, 345.
255. F. J. Berry, P. E. Holbourn and F. W. D. Woodhams, *J. Chem. Soc., Dalton Trans.*, 1980, 2241.
256. F. J. Berry, *J. Chem. Soc., Dalton Trans.*, 1981, 1442.
257. B. Grzeta, E. Tkalcec, C. Goebbert, M. Takeda, M. Takahashi, K. Nomura and M. Jaksic, *J. Phys. Chem. Solids*, 2002, **63**, 765.
258. C. Terrier, J. P. Chatelon, J. A. Roger, R. Berjoan and C. Dubois, *J. Sol-Gel Sci. Technol.*, 1997, **10**, 75.
259. J. Rockenberger, U. zum Felde, M. Tischer, L. Troger, M. Haase and H. Weller, *J. Chem. Phys.*, 2000, **112**, 4296.



260. V. Geraldo, V. Briois, L. V. A. Scalvi and C. V. Santilli, *J. Eur. Ceram. Soc.*, 2007, **27**, 4265.
261. R. Shannon, *Acta Crystallogr. A*, 1976, **32**, 751.
262. C. Terrier, J. P. Chatelon and J. A. Roger, *Thin Solid Films*, 1997, **295**, 95.
263. A. F. Carroll and L. H. Slack, *J. Electrochem. Soc.*, 1976, **123**, 1889.
264. J. Ni, X. Zhao, X. Zheng, J. Zhao and B. Liu, *Acta Mater.*, 2009, **57**, 278.
265. C. S. Rastomjee, R. S. Dale, R. J. Schaffer, F. H. Jones, R. G. Egdell, G. C. Georgiadis, M. J. Lee, T. J. Tate and L. L. Cao, *Thin Solid Films*, 1996, **279**, 98.
266. Z. Q. Li, Y. L. Yin, X. D. Liu, L. Y. Li, H. Liu and Q. G. Song, *J. Appl. Phys.*, 2009, **106**, 083701.
267. J. B. Varley, A. Janotti and C. G. Van de Walle, *Phys. Rev. B*, 2010, **81**, 245216.
268. H. Yahla, A. Boukra, M. Belhakem and P. E. Lippens, *Solid State Commun.*, 2009, **149**, 2202.
269. G. Qin, D. Li, Z. Chen, Y. Hou, Z. Feng and S. Liu, *Comp. Mater. Sci.*, 2009, **46**, 418.
270. R. Long and N. J. English, *Phys. Lett. A*, 2009, **374**, 319.
271. W.-Z. Xiao, L.-L. Wang, L. Xu, Q. Wan and B. S. Zou, *Solid State Commun.*, 2009, **149**, 1304.
272. J. P. Upadhyay, S. R. Vishwakarma and H. C. Prasad, *Thin Solid Films*, 1989, **169**, 195.
273. Y.-S. Hsu and S. K. Ghandhi, *J. Electrochem. Soc.*, 1980, **127**, 1595.
274. S. R. Vishwakarma, J. P. Upadhyay and H. C. Prasad, *Thin Solid Films*, 1989, **176**, 99.
275. Y.-S. Hsu and S. K. Ghandhi, *J. Electrochem. Soc.*, 1979, **126**, 1434.
276. A. E. Taverner, C. Rayden, S. Warren, A. Gulino, P. A. Cox and R. G. Egdell, *Phys. Rev. B*, 1995, **51**, 6833.
277. R. G. Egdell, A. Gulino, C. Rayden, G. Peacock and P. A. Cox, *J. Mater. Chem.*, 1995, **5**, 499.
278. D. Szczuko, J. Werner, S. Oswald, G. Behr and K. Wetzig, *Appl. Surf. Sci.*, 2001, **179**, 301.
279. D. Leite, I. Mazali, E. Aguiar, W. Las and M. Cilense, *J. Mater. Sci.*, 2006, **41**, 6256.
280. S. Nakao, N. Yamada, T. Hitosugi, Y. Hirose, T. Shimada and T. Hasegawa, *Thin Solid Films*, 2010, **518**, 3093.
281. H. Toyosaki, M. Kawasaki and Y. Tokura, *Appl. Phys. Lett.*, 2008, **93**, 132109.
282. Y.-W. Kim, S. W. Lee and H. Chen, *Thin Solid Films*, 2002, **405**, 256.
283. S. W. Lee, Y.-W. Kim and H. Chen, *Appl. Phys. Lett.*, 2001, **78**, 350.
284. T. Karlsson, A. Roos and C. G. Ribbing, *Sol. Energ. Mater.*, 1985, **11**, 469.
285. B. Stjerna, E. Olsson and C. G. Granqvist, *J. Appl. Phys.*, 1994, **76**, 3797.
286. C. Agashe and S. S. Major, *J. Phys. D*, 1996, **29**, 2988.
287. B. Thangaraju, *Thin Solid Films*, 2002, **402**, 71.
288. V. Bilgin, I. Akyuz, E. Ketenci, S. Kose and F. Atay, *Appl. Surf. Sci.*, 2010, **256**, 6586.
289. M. Fantini and I. Torriani, *Thin Solid Films*, 1986, **138**, 255.
290. D. Zaouk, R. al Asmar, J. Podlecki, Y. Zaatar, A. Khoury and A. Foucaran, *Microelectr. J.*, 2007, **38**, 884.
291. B. Gottlieb, R. Koropecski, R. Arce, R. Crisalle and J. Ferron, *Thin Solid Films*, 1991, **199**, 13.
292. H. Haitjema, J. J. P. Elich and C. J. Hoogendoorn, *Sol. Energ. Mater.*, 1989, **18**, 283.
293. D. R. Acosta, E. P. Zironi, E. Montoya and W. Estrada, *Thin Solid Films*, 1996, **288**, 1.

294. C. D. Canestraro, M. M. Oliveira, R. Valaski, M. V. S. da Silva, D. G. F. David, I. Pepe, A. F. d. Silva, L. S. Roman and C. Persson, *Appl. Surf. Sci.*, 2008, **255**, 1874.
295. C. D. Canestraro, L. S. Roman and C. Persson, *Thin Solid Films*, 2009, **517**, 6301.
296. H. De Waal and F. Simons, *Thin Solid Films*, 1981, **77**, 253.
297. J. A. Aboaf, V. C. Marcotte and N. J. Chou, *J. Electrochem. Soc.*, 1973, **120**, 701.
298. A. K. Abass, *Solid State Commun.*, 1987, **61**, 507.
299. A. K. Abass, N. A. Al-Liabi and W. A. Taha, *Phys. Status Solidi A*, 1988, **106**, 613.
300. A. K. Abass, H. Bakr, S. A. Jassim and T. A. Fahad, *Sol. Energ. Mater.*, 1988, **17**, 425.
301. K. Ravichandran, G. Muruganantham and B. Sakthivel, *Physica B*, 2009, **404**, 4299.
302. P. D. C. King, I. McKenzie and T. D. Veal, *Appl. Phys. Lett.*, 2010, **96**, 062110.
303. C. Kilic and A. Zunger, *Appl. Phys. Lett.*, 2002, **81**, 73.
304. A. Walsh, G. W. Watson, D. J. Payne, G. Atkinson and R. G. Egdell, *J. Mater. Chem.*, 2006, **16**, 3452.
305. N. A. Asryan, T. N. Kol'tsova, A. S. Alikhanyan and G. D. Nipan, *Inorg. Mater.*, 2002, **38**, 1141.
306. R. C. McDonald, H. H. K. Hau and K. Eriks, *Inorg. Chem.*, 1976, **15**, 762.
307. M. Bork and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1996, **622**, 1557.
308. L.-M. Tang, L.-L. Wang, D. Wang, J.-Z. Liu and K.-Q. Chen, *J. Appl. Phys.*, 2010, **107**, 083704.
309. I. Saadeddin, B. Pecquenard, J. P. Manaud, R. Decourt, C. Labrugere, T. Buffeteau and G. Campet, *Appl. Surf. Sci.*, 2007, **253**, 5240.
310. D. O. Scanlon, A. Walsh, B. J. Morgan, G. W. Watson, D. J. Payne and R. G. Egdell, *Phys. Rev. B*, 2009, **79**, 035101.
311. M. N. Huda, Y. F. Yan, A. Walsh, S. H. Wei and M. M. Al-Jassim, *Phys. Rev. B*, 2009, **80**, 035205.
312. S. M. Gao, Y. Zhao, P. P. Gou, N. Chen and Y. Xie, *Nanotechnology*, 2003, **14**, 538.
313. A. N. Banerjee, S. Nandy, C. K. Ghosh and K. K. Chattopadhyay, *Thin Solid Films*, 2007, **515**, 7324.
314. D. S. Kim, T. J. Park, D. H. Kim and S. Y. Choi, *Phys. Status Solidi A*, 2006, **203**, R51.
315. K. Ueda, T. Hase, H. Yanagi, H. Kawazoe, H. Hosono, H. Ohta, M. Orita and M. Hirano, *J. Appl. Phys.*, 2001, **89**, 1790.
316. J. Tate, M. K. Jayaraj, A. D. Draeseke, T. Ulbrich, A. W. Sleight, K. A. Vanaja, R. Nagarajan, J. F. Wager and R. L. Hoffman, *Thin Solid Films*, 2002, **411**, 119.
317. H. Yanagi, T. Hase, S. Ibuki, K. Ueda and H. Hosono, *Appl. Phys. Lett.*, 2001, **78**, 1583.
318. H. Yanagi, K. Ueda, H. Ohta, M. Orita, M. Hirano and H. Hosono, *Solid State Commun.*, 2002, **121**, 15.
319. M. Snure and A. Tiwari, *Appl. Phys. Lett.*, 2007, **91**, 092123.
320. D. O. Scanlon, A. Walsh and G. W. Watson, *Chem. Mater.*, 2009, **21**, 4568.
321. R. Kykyneshi, B. C. Nielsen, J. Tate, J. Li and A. W. Sleight, *J. Appl. Phys.*, 2004, **96**, 6188.
322. S. Gilliland, J. Pellicer-Porres, A. Segura, A. Munoz, P. Rodriguez-Hernandez, D. Kim, M. S. Lee and T. Y. Kim, *Phys. Status Solidi B*, 2007, **244**, 309.
323. S. Gilliland, J. F. Sanchez-Royo, J. Pellicer-Porres, A. Segura, A. Munoz, P. Rodriguez-Hernandez and J. Lopez-Solano, *Thin Solid Films*, 2008, **516**, 1431.
324. L. J. Shi, Z. J. Fang and J. B. Li, *J. Appl. Phys.*, 2008, **104**, 073527.
325. M. Nolan, *Thin Solid Films*, 2008, **516**, 8130.
326. B. Falabrettia and J. Robertson, *J. Appl. Phys.*, 2007, **102**, 123703.



327. J. Robertson, P. W. Peacock, M. D. Towler and R. Needs, *Thin Solid Films*, 2002, **411**, 96.
328. R. W. Brander, *Rev. Phys. Tech.*, 1972, **3**, 145.
329. N. Koriche, A. Bouguelia and M. Trari, *Int. J. Hydrogen Energy*, 2006, **31**, 1196.
330. A. N. Banerjee, C. K. Ghosh and K. K. Chattopadhyay, *Sol. Energy Mater. Sol. Cells*, 2005, **89**, 75.
331. B. J. Ingram, B. J. Harder, N. W. Hrabec, T. A. Mason and K. R. Poeppelmeier, *Chem. Mater.*, 2004, **16**, 5623.
332. Z. J. Fang, L. J. Shi and Y. H. Liu, *Chin. Phys. B*, 2008, **17**, 4279.
333. Z. J. Fang, C. Fang, L. J. Shi, Y. H. Liu and M. C. He, *Chin. Phys. Lett.*, 2008, **25**, 2997.
334. T. Koyanagi, H. Harima, A. Yanase and H. Katayama-yoshida, *J. Phys. Chem. Solids*, 2003, **64**, 1443.
335. L. Liu, K. W. Bai, H. Gong and P. Wu, *Chem. Mater.*, 2005, **17**, 5529.
336. J. Tate, H. L. Ju, J. C. Moon, A. Zakutayev, A. P. Richard, J. Russell and D. H. McIntyre, *Phys. Rev. B*, 2009, **80**, 165206.
337. D. J. Aston, D. J. Payne, A. J. H. Green, R. G. Egdell, D. S. L. Law, J. Guo, P. A. Glans, T. Learmonth and K. E. Smith, *Phys. Rev. B*, 2005, **72**, 195115.
338. H. C. Kandpal and R. Seshadri, *Solid State Sci.*, 2002, **4**, 1045.
339. H. Katayama-Yoshida, K. Sato, H. Kizaki, H. Funashima, I. Hamada, T. Fukushima, V. A. Dinh and M. Toyoda, *Appl. Phys. A*, 2007, **89**, 19.
340. H. Yanagi, S. Inoue, K. Ueda, H. Kawazoe, H. Hosono and N. Hamada, *J. Appl. Phys.*, 2000, **88**, 4159.
341. O. Sipr, F. Rocca and P. Fornasini, *J. Phys. Condens. Matter*, 2009, **21**, 255401.
342. T. Arnold, D. J. Payne, A. Bourlange, J. P. Hu, R. G. Egdell, L. F. J. Piper, L. Colakerol, A. Masi, P. A. Glans, T. Learmonth, K. E. Smith, J. Guo, D. O. Scanlon, A. Walsh, B. J. Morgan and G. W. Watson, *Phys. Rev. B*, 2009, **79**, 075102.
343. D. O. Scanlon, B. J. Morgan and G. W. Watson, *J. Chem. Phys.*, 2009, **131**, 124703.
344. J. Li, A. F. T. Yokochi and A. W. Sleight, *Solid State Sci.*, 2004, **6**, 831.
345. B. U. Koehler and M. Jansen, *Z. Anorg. Allg. Chem.*, 1986, **543**, 73.
346. T. Ishiguro, A. Kitazawa, N. Mizutani and M. Kato, *J. Solid State Chem.*, 1981, **40**, 170.
347. N. E. Christensen, A. Svane, R. Laskowski, B. Palanivel, P. Modak, A. N. Chantis, M. van Schilfgaarde and T. Kotani, *Phys. Rev. B*, 2010, **81**, 045203.
348. J. Vidal, F. Trani, F. Bruneval, M. A. L. Marques and S. Botti, *Phys. Rev. Lett.*, 2010, **104**, 136401.
349. J. Vidal, F. Trani, F. Bruneval, M. A. L. Marques and S. Botti, *arXiv.org: cond-mat.mtrl-sci*, 2009, **0912.0618v1**.
350. A. Walsh, J. L. F. Da Silva and S. H. Wei, *Phys. Rev. B*, 2008, **78**, 075211.
351. B. J. Ingram, M. I. Bertoni, K. R. Poeppelmeier and T. O. Mason, *Thin Solid Films*, 2005, **486**, 86.
352. D. Shin, J. S. Foord, D. J. Payne, T. Arnold, D. J. Aston, R. G. Egdell, K. G. Godinho, D. O. Scanlon, B. J. Morgan, G. W. Watson, E. Mugnier, C. Yaicle, A. Rougier, L. Colakerol, P. A. Glans, L. F. J. Piper and K. E. Smith, *Phys. Rev. B*, 2009, **80**, 233105.
353. F. A. Benko and F. P. Koffyberg, *J. Phys. Chem. Solids*, 1987, **48**, 431.
354. H. Ohta, M. Orita, M. Hirano and H. Hosono, *J. Appl. Phys.*, 2001, **89**, 5720.
355. H. Hosono, H. Ohta, K. Hayashi, M. Orita and M. Hirano, *J. Cryst. Growth*, 2002, **237**, 496.
356. C. L. Teske and H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.*, 1970, **379**, 113.

357. B. Roy, J. D. Perkins, T. Kaydanova, D. L. Young, M. Taylor, A. Miedaner, C. Curtis, H. J. Kleebe, D. W. Readey and D. S. Ginley, *Thin Solid Films*, 2008, **516**, 4093.
358. S. Sheng, G. J. Fang, C. Li, Z. Q. Chen, S. Ma, L. G. Fang and X. Z. Zhao, *Semicond. Sci. Technol.*, 2006, **21**, 586.
359. M. Modreanu, M. Nolan, S. D. Elliott, O. Durand, B. Servet, G. Garry, H. Gehan, G. Huyberechts, E. L. Papadopoulou, M. Androulidaki and E. Aperathitis, *Thin Solid Films*, 2007, **515**, 8624.
360. H. Ohta, M. Orita, M. Hirano, I. Yagi, K. Ueda and H. Hosono, *J. Appl. Phys.*, 2002, **91**, 3074.
361. J. P. Hu, D. J. Payne, R. G. Egdell, N. M. Harrison and V. R. Dhanak, *Chem. Phys. Lett.*, 2007, **450**, 39.
362. G. Moiseev, J. Sestak, V. Jzukovski, I. Garipova and N. Ilynych, *Thermochim. Acta*, 1998, **318**, 201.
363. M. W. Chase, Jr., *J. Phys. Chem. Ref. Data, Monograph 9*, 1998, 1.
364. A. Walsh, Y. F. Yan, M. M. Al-Jassim and S. H. Wei, *J. Phys. Chem. C*, 2008, **112**, 12044.
365. C. Persson, Y. J. Zhao, S. Lany and A. Zunger, *Phys. Rev. B*, 2005, **72**, 035211.
366. V. Varadarajan, D. P. Norton and J. D. Budai, *Thin Solid Films*, 2005, **488**, 173.
367. A. F. Wright and J. S. Nelson, *J. Appl. Phys.*, 2002, **92**, 5849.
368. H. Raebiger, S. Lany and A. Zunger, *Phys. Rev. B*, 2007, **76**, 045209.
369. I. Hamada and H. Katayama-Yoshida, *Physica B*, 2006, **376**, 808.
370. S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova and D. M. Treger, *Science*, 2001, **294**, 1488.
371. I. Žutić, J. Fabian and S. Das Sarma, *Rev. Mod. Phys.*, 2004, **76**, 323.
372. J. S. E. M. Svensson and C. G. Granqvist, *Appl. Phys. Lett.*, 1986, **49**, 1566.
373. J. He, H. Lindstrom, A. Hagfeldt and S.-E. Lindquist, *J. Phys. Chem. B*, 1999, **103**, 8940.
374. D. Paul Joseph, M. Saravanan, B. Muthuraaman, P. Renugamal, S. Sambasivam, S. Philip Raja, P. Maruthamuthu and C. Venkateswaran, *Nanotechnology*, 2008, **19**, 485707.
375. S. Seo, M. J. Lee, D. H. Seo, E. J. Jeoung, D.-S. Suh, Y. S. Joung, I. K. Yoo, I. R. Hwang, S. H. Kim, I. S. Byun, J.-S. Kim, J. S. Choi and B. H. Park, *Appl. Phys. Lett.*, 2004, **85**, 5655.
376. J. F. Gibbons and W. E. Beadle, *Solid-State Electron.*, 1964, **7**, 785.
377. K. Jung, J. Choi, Y. Kim, H. Im, S. Seo, R. Jung, D. Kim, J.-S. Kim, B. H. Park and J. P. Hong, *J. Appl. Phys.*, 2008, **103**, 034504.
378. K. Jung, H. Seo, Y. Kim, H. Im, J. Hong, J.-W. Park and J.-K. Lee, *Appl. Phys. Lett.*, 2007, **90**, 052104.
379. Y. Vygranenko, K. Wang and A. Nathan, *Appl. Phys. Lett.*, 2006, **89**, 172105.
380. H. Ohta, M. Hirano, K. Nakahara, H. Maruta, T. Tanabe, M. Kamiya, T. Kamiya and H. Hosono, *Appl. Phys. Lett.*, 2003, **83**, 1029.
381. Y.-M. Lee and C.-H. Lai, *Solid-State Electron.*, 2009, **53**, 1116.
382. H. S. Bae, C. M. Choi, J. H. Kim and S. Im, *J. Appl. Phys.*, 2005, **97**, 076104.
383. S. Takami, R. Hayakawa, Y. Wakayama and T. Chikyow, *Nanotechnology*, 2010, **21**, 134009.
384. S.-W. Park, J.-M. Choi, E. Kim and S. Im, *Appl. Surf. Sci.*, 2005, **244**, 439.
385. W. L. Roth, *Phys. Rev.*, 1958, **110**, 1333.
386. G. A. Sawatzky and J. W. Allen, *Phys. Rev. Lett.*, 1984, **53**, 2339.
387. R. J. Powell and W. E. Spicer, *Phys. Rev. B*, 1970, **2**, 2182.
388. R. Newman and R. M. Chrenko, *Phys. Rev.*, 1959, **114**, 1507.



389. S. Hüfner, J. Osterwalder, T. Riesterer and F. Hulliger, *Solid State Commun.*, 1984, **52**, 793.
390. B. Sasi, K. G. Gopchandran, P. K. Manoj, P. Koshy, P. Prabhakara Rao and V. K. Vaidyan, *Vacuum*, 2002, **68**, 149.
391. N. F. Mott, *Proc. Phys. Soc. A*, 1949, **62**, 416.
392. J. Hubbard, *Proc. R. Soc. A*, 1964, **277**, 237.
393. D. Adler and J. Feinleib, *Phys. Rev. B*, 1970, **2**, 3112.
394. S. Van Houten, *J. Phys. Chem. Solids*, 1960, **17**, 7.
395. S. J. Oh, J. W. Allen, I. Lindau and J. C. Mikkelsen, *Phys. Rev. B*, 1982, **26**, 4845.
396. J. Zaanen, G. A. Sawatzky and J. W. Allen, *Phys. Rev. Lett.*, 1985, **55**, 418.
397. T. M. Schuler, D. L. Ederer, S. Itza-Ortiz, G. T. Woods, T. A. Callcott and J. C. Woicik, *Phys. Rev. B*, 2005, **71**, 115113.
398. N. E. Brener and J. Callaway, *Phys. Rev. B*, 1987, **35**, 4001.
399. K. Terakura, A. R. Williams, T. Oguchi and J. Kübler, *Phys. Rev. Lett.*, 1984, **52**, 1830.
400. Z. X. Shen, R. S. List, D. S. Dessau, B. O. Wells, O. Jepsen, A. J. Arko, R. Bartlett, C. K. Shih, F. Parmigiani, J. C. Huang and P. A. P. Lindberg, *Phys. Rev. B*, 1991, **44**, 3604.
401. M. D. Towler, N. L. Allan, N. M. Harrison, V. R. Saunders, W. C. Mackrodt and E. Apra, *Phys. Rev. B*, 1994, **50**, 5041.
402. C. H. Patterson, *Int. J. Quantum Chem.*, 2006, **106**, 3383.
403. W. C. Mackrodt and C. Noguera, *Surf. Sci.*, 2000, **457**, L386.
404. W. C. Mackrodt, N. M. Harrison, V. R. Saunders, N. L. Allan and M. D. Towler, *Chem. Phys. Lett.*, 1996, **250**, 66.
405. S. V. Faleev, M. van Schilfgaarde and T. Kotani, *Phys. Rev. Lett.*, 2004, **93**, 126406.
406. F. Aryasetiawan and O. Gunnarsson, *Phys. Rev. Lett.*, 1995, **74**, 3221.
407. S. Massidda, A. Continenza, M. Posternak and A. Baldereschi, *Phys. Rev. B*, 1997, **55**, 13494.
408. J.-L. Li, G. M. Rignanese and S. G. Louie, *Phys. Rev. B*, 2005, **71**, 193102.
409. S. Kobayashi, Y. Nohara, S. Yamamoto and T. Fujiwara, *Phys. Rev. B*, 2008, **78**, 155112.
410. C. Rödl, F. Fuchs, J. Furthmüller and F. Bechstedt, *Phys. Rev. B*, 2009, **79**, 235114.
411. Z. Szotek, W. M. Temmerman and H. Winter, *Phys. Rev. B*, 1993, **47**, 4029.
412. A. Svane and O. Gunnarsson, *Phys. Rev. Lett.*, 1990, **65**, 1148.
413. D. Ködderitzsch, W. Hergert, W. M. Temmerman, Z. Szotek, A. Ernst and H. Winter, *Phys. Rev. B*, 2002, **66**, 064434.
414. G. Fischer, M. Däne, A. Ernst, P. Bruno, M. Lüders, Z. Szotek, W. Temmerman and W. Hergert, *Phys. Rev. B*, 2009, **80**, 014408.
415. M. Däne and et al., *J. Phys. Condens. Matter*, 2009, **21**, 045604.
416. F. Tran, P. Blaha, K. Schwarz and P. Novák, *Phys. Rev. B*, 2006, **74**, 155108.
417. I. de P. R. Moreira, F. Illas and R. L. Martin, *Phys. Rev. B*, 2002, **65**, 155102.
418. W. C. Mackrodt and D. S. Middlemiss, *J. Phys. Condens. Matter*, 2004, **16**, S2811.
419. D. S. Middlemiss and W. C. Mackrodt, *Mol. Phys.*, 2005, **103**, 2513.
420. T. Bredow and A. R. Gerson, *Phys. Rev. B*, 2000, **61**, 5194.
421. J. Kuneš, V. I. Anisimov, S. L. Skornyakov, A. V. Lukoyanov and D. Vollhardt, *Phys. Rev. Lett.*, 2007, **99**, 156404.
422. J. Kuneš, V. I. Anisimov, A. V. Lukoyanov and D. Vollhardt, *Phys. Rev. B*, 2007, **75**, 165115.
423. X. Ren, I. Leonov, G. Keller, M. Kollar, I. Nekrasov and D. Vollhardt, *Phys. Rev. B*, 2006, **74**, 195114.
424. A. I. Liechtenstein, V. I. Anisimov and J. Zaanen, *Phys. Rev. B*, 1995, **52**, R5467.

425. S. Park, H.-S. Ahn, C.-K. Lee, H. Kim, H. Jin, H.-S. Lee, S. Seo, J. Yu and S. Han, *Phys. Rev. B*, 2008, **77**, 134103.
426. O. Bengone, M. Alouani, P. Blöchl and J. Hugel, *Phys. Rev. B*, 2000, **62**, 16392.
427. A. Rohrbach, J. Hafner and G. Kresse, *Phys. Rev. B*, 2004, **69**, 075413.
428. V. I. Anisimov, P. Kuiper and J. Nordgren, *Phys. Rev. B*, 1994, **50**, 8257.
429. V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyżyk and G. A. Sawatzky, *Phys. Rev. B*, 1993, **48**, 16929.
430. P. Wu, V. Ligatchev, Z. G. Yu, J. Zheng, M. B. Sullivan and Y. Zeng, *Phys. Rev. B*, 2009, **79**, 235122.
431. H. D. Lee, B. Magyari-Köpe and Y. Nishi, *Phys. Rev. B*, 2010, **81**, 193202.
432. A. M. Ferrari, C. Pisani, F. Cinquini, L. Giordano and G. Pacchioni, *J. Chem. Phys.*, 2007, **127**, 174711.
433. F. Cinquini, L. Giordano, G. Pacchioni, A. M. Ferrari, C. Pisani and C. Roetti, *Phys. Rev. B*, 2006, **74**, 165403.
434. M. Corti, S. Marini, A. Rigamonti, F. Tedoldi, D. Capsoni and V. Massarotti, *Phys. Rev. B*, 1997, **56**, 11056.
435. J. Feinleib and D. Adler, *Phys. Rev. Lett.*, 1968, **21**, 1010.
436. I. Bransky and N. M. Tallan, *J. Chem. Phys.*, 1968, **49**, 1243.
437. S. A. Makhlof, *Thin Solid Films*, 2008, **516**, 3112.
438. J. H. d. Boer and E. J. W. Verwey, *Proc. Phys. Soc.*, 1937, **49**, 59.
439. B. H. Brandow, *Adv. Phys.*, 1977, **26**, 651.
440. P. Puspharajah, S. Radhakrishna and A. Arof, *J. Mater. Sci.*, 1997, **32**, 3001.
441. S. Nandy and et al., *J. Phys. Condens. Matter*, 2009, **21**, 115804.
442. W.-L. Jang, Y.-M. Lu, W.-S. Hwang, T.-L. Hsiung and H. P. Wang, *Appl. Phys. Lett.*, 2009, **94**, 062103.
443. P. Kuiper, G. Kruizinga, J. Ghijsen, G. A. Sawatzky and H. Verweij, *Phys. Rev. Lett.*, 1989, **62**, 221.
444. J. van Elp, B. G. Searle, G. A. Sawatzky and M. Sacchi, *Solid State Commun.*, 1991, **80**, 67.
445. S. P. Mitoff, *J. Chem. Phys.*, 1961, **35**, 882.
446. R. Farhi and G. Petot-Ervas, *J. Phys. Chem. Solids*, 1978, **39**, 1169.
447. I. Rom, W. Jantscher and W. Sitte, *Solid State Ionics*, 2000, **135**, 731.
448. C. M. Osburn and R. W. Vest, *J. Phys. Chem. Solids*, 1971, **32**, 1331.
449. W. C. Tripp and N. M. Tallan, *J. Am. Ceram. Soc.*, 1970, **53**, 531.
450. N. L. Peterson and C. L. Wiley, *J. Phys. Chem. Solids*, 1985, **46**, 43.
451. R. Haugsrud and T. Norby, *Solid State Ionics*, 1998, **111**, 323.
452. W. Zhang, N. Yu, W. Yu and B. Tang, *Eur. Phys. J. B*, 2008, **64**, 153.
453. V. M. Zainullina, M. A. Korotin, Y. P. Zaikov and N. I. Shurov, *Solid State Sci.*, 2004, **6**, 1139.
454. D. Ködderitzsch, W. Hergert, Z. Szotek and W. M. Temmerman, *Phys. Rev. B*, 2003, **68**, 125114.
455. X. Wang, Y. Li, G. Wang, R. Xiang, D. Jiang, S. Fu, K. Wu, X. Yang, Q. DuanMu, J. Tian and L. Fu, *Physica B*, 2009, **404**, 1058.
456. S. Manna and et al., *J. Phys. D*, 2008, **41**, 155416.
457. J. Wu, C.-W. Nan, Y. Lin and Y. Deng, *Phys. Rev. Lett.*, 2002, **89**, 217601.
458. U. S. Joshi, Y. Matsumoto, K. Itaka, M. Sumiya and H. Koinuma, *Appl. Surf. Sci.*, 2006, **252**, 2524.
459. W.-L. Jang, Y.-M. Lu, W.-S. Hwang and W.-C. Chen, *J. Eur. Ceram. Soc.*, 2010, **30**, 503.
460. E. Antolini, *Mater. Chem. Phys.*, 2003, **82**, 937.
461. A. J. Bosman and C. Crevecoeur, *Phys. Rev.*, 1966, **144**, 763.



462. C. Gougoussis, M. Calandra, A. Seitsonen, C. Brouder, A. Shukla and F. Mauri, *Phys. Rev. B*, 2009, **79**, 045118.
463. J. van Elp, H. Eskes, P. Kuiper and G. A. Sawatzky, *Phys. Rev. B*, 1992, **45**, 1612.
464. S. Hufner, P. Steiner, I. Sander, F. Reinert, H. Schmitt, M. Neumann and S. Witzel, *Solid State Commun.*, 1991, **80**, 869.
465. D. Alders, F. C. Voogt, T. Hibma and G. A. Sawatzky, *Phys. Rev. B*, 1996, **54**, 7716.
466. A. Gorschlüter and H. Merz, *Phys. Rev. B*, 1994, **49**, 17293.
467. A. Freitag, V. Staemmler, D. Cappus, C. A. Ventrice, K. Al Shamery, H. Kühlenbeck and H. J. Freund, *Chem. Phys. Lett.*, 1993, **210**, 10.
468. S. L. Dudarev, A. I. Liechtenstein, M. R. Castell, G. A. D. Briggs and A. P. Sutton, *Phys. Rev. B*, 1997, **56**, 4900.
469. O. Bengone, M. Alouani, J. Hugel and P. Blöchl, *Comp. Mater. Sci.*, 2002, **24**, 192.
470. J. M. McKay and V. E. Henrich, *Phys. Rev. B*, 1985, **32**, 6764.
471. N. Nakajima, H. Kato and Y. Sakisaka, *J. Electron Spectrosc. Relat. Phenom.*, 2005, **144-147**, 873.
472. L. Soriano, M. Abbate, A. Fernández, A. R. González-Elípe, F. Sirotti, G. Rossi and J. M. Sanz, *Chem. Phys. Lett.*, 1997, **266**, 184.
473. M. R. Castell, P. L. Wincott, N. G. Condon, C. Muggelberg, G. Thornton, S. L. Dudarev, A. P. Sutton and G. A. D. Briggs, *Phys. Rev. B*, 1997, **55**, 7859.
474. L. G. M. Pettersson and G. Pacchioni, *Chem. Phys. Lett.*, 1994, **219**, 107.
475. A. K. McMahan, R. M. Martin and S. Satpathy, *Phys. Rev. B*, 1988, **38**, 6650.
476. R. H. Potze, G. A. Sawatzky and M. Abbate, *Phys. Rev. B*, 1995, **51**, 11501.
477. M. d'Avezac, M. Calandra and F. Mauri, *Phys. Rev. B*, 2005, **71**, 205210.
478. M. Nolan and G. W. Watson, *Surf. Sci.*, 2005, **586**, 25.
479. M. Nolan and G. W. Watson, *J. Chem. Phys.*, 2006, **125**, 144701.
480. I. Yeriskin and M. Nolan, *J. Chem. Phys.*, 2009, **131**, 244702.
481. R. D. Holmes, H. S. C. O'Neill and R. J. Arculus, *Geochim. Cosmochim. Acta*, 1986, **50**, 2439.
482. A. K. Cheetham and D. A. O. Hope, *Phys. Rev. B*, 1983, **27**, 6964.
483. B. E. F. Fender, A. J. Jacobson and F. A. Wedgwood, *J. Chem. Phys.*, 1968, **48**, 990.
484. S. Sasaki, K. Fujino and Y. Takeuchi, *Proc. Jpn. Acad. B*, 1979, **55**, 43.
485. P. W. Anderson, *Phys. Rev.*, 1950, **79**, 350.
486. E. Scorza, U. Birkenheuer and C. Pisani, *J. Chem. Phys.*, 1997, **107**, 9645-9658.
487. T. Serin, A. Yildiz, N. Serin, N. Yildirim, F. Özyurt and M. Kasap, *J. Electron. Mater.*, 2010, **39**, 1152.
488. C. Terrier, J. P. Chatelon, R. Berjoan and J. A. Roger, *Thin Solid Films*, 1995, **263**, 37.
489. M. Orita, M. Takeuchi, H. Sakai and H. Tanji, *Jpn. J. Appl. Phys.*, 1995, **34**, L1550.
490. R. J. Cava, J. M. Phillips, J. Kwo, G. A. Thomas, R. B. v. Dover, S. A. Carter, J. J. Krajewski, J. W. F. Peck, J. H. Marshall and D. H. Rapkine, *Appl. Phys. Lett.*, 1994, **64**, 2071.
491. T. Minami, H. Sonohara, S. Takata and H. Sato, *Jpn. J. Appl. Phys.*, 1994, **33**, L1693.
492. K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano and H. Hosono, *Science*, 2003, **300**, 1269.
493. N. L. Dehuff, E. S. Kettenring, D. Hong, H. Q. Chiang, J. F. Wager, R. L. Hoffman, C.-H. Park and D. A. Keszler, *J. Appl. Phys.*, 2005, **97**, 064505.
494. K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano and H. Hosono, *Nature*, 2004, **432**, 488.

495. M. P. Taylor, D. W. Readey, M. F. A. M. van Hest, C. W. Teplin, J. L. Alleman, M. S. Dabney, L. M. Gedvilas, B. M. Keyes, B. To, J. D. Perkins and D. S. Ginley, *Adv. Funct. Mater.*, 2008, **18**, 3169.
496. T. Iwasaki, N. Itagaki, T. Den, H. Kumomi, K. Nomura, T. Kamiya and H. Hosono, *Appl. Phys. Lett.*, 2007, **90**, 242114.
497. H. Hosono, N. Kikuchi, N. Ueda and H. Kawazoe, *J. Non-Cryst. Solids*, 1996, **198**, 165.
498. W.-J. Lee, E.-A. Choi, J. Bang, B. Ryu and K. J. Chang, *Appl. Phys. Lett.*, 2008, **93**, 111901.
499. H. Omura, H. Kumomi, K. Nomura, T. Kamiya, M. Hirano and H. Hosono, *J. Appl. Phys.*, 2009, **105**, 093712.
500. M. Orita, H. Tanji, M. Mizuno, H. Adachi and I. Tanaka, *Phys. Rev. B*, 2000, **61**, 1811.
501. A. Walsh, J. L. F. Da Silva and S.-H. Wei, *Chem. Mater.*, 2009, **21**, 5119.
502. J. L. F. Da Silva, Y. Yan and S.-H. Wei, *Phys. Rev. Lett.*, 2008, **100**, 255501.
503. K. Ueda, S. Inoue, S. Hirose, H. Kawazoe and H. Hosono, *Appl. Phys. Lett.*, 2000, **77**, 2701.
504. K. Ueda and H. Hosono, *J. Appl. Phys.*, 2002, **91**, 4768.
505. A. Zakutayev, R. Kykyneshi, G. Schneider, D. H. McIntyre and J. Tate, *Phys. Rev. B*, 2010, **81**, 155103.
506. H. Yanagi, J. Tate, S. Park, C.-H. Park and D. A. Keszler, *Appl. Phys. Lett.*, 2003, **82**, 2814.
507. H. Hiramatsu, K. Ueda, K. Takafuji, H. Ohta, M. Hirano, T. Kamiya and H. Hosono, *J. Appl. Phys.*, 2003, **94**, 5805.
508. K. Ueda, K. Takafuji, H. Hiramatsu, H. Ohta, T. Kamiya, M. Hirano and H. Hosono, *Chem. Mater.*, 2003, **15**, 3692.
509. H. Hiramatsu, M. Orita, M. Hirano, K. Ueda and H. Hosono, *J. Appl. Phys.*, 2002, **91**, 9177.
510. H. Hiramatsu, K. Ueda, H. Ohta, M. Hirano, T. Kamiya and H. Hosono, *Thin Solid Films*, 2003, **445**, 304.
511. H. Hiramatsu, K. Ueda, H. Ohta, M. Hirano, T. Kamiya and H. Hosono, *Appl. Phys. Lett.*, 2003, **82**, 1048.
512. H. Yanagi, J. Tate, S. Park, C.-H. Park, D. A. Keszler, M. Hirano and H. Hosono, *J. Appl. Phys.*, 2006, **100**, 083705.
513. H. Yanagi, S. Park, A. D. Draeseke, D. A. Keszler and J. Tate, *J. Solid State Chem.*, 2003, **175**, 34.
514. J. Tate, P. F. Newhouse, R. Kykyneshi, P. A. Hersh, J. Kinney, D. H. McIntyre and D. A. Keszler, *Thin Solid Films*, 2008, **516**, 5795.
515. H. Hiramatsu, K. Ueda, H. Ohta, T. Kamiya, M. Hirano and H. Hosono, *Appl. Phys. Lett.*, 2005, **87**, 211107.
516. C.-H. Park, R. Kykyneshi, A. Yokochi, J. Tate and D. A. Keszler, *J. Solid State Chem.*, 2007, **180**, 1672.
517. S.-i. Inoue, K. Ueda, H. Hosono and N. Hamada, *Phys. Rev. B*, 2001, **64**, 245211.
518. K. Ueda, H. Hosono and N. Hamada, *J. Appl. Phys.*, 2005, **98**, 043506.
519. T. T. Rantala, T. S. Rantala and V. Lantto, *Mater. Sci. Semicond. Process.*, 2000, **3**, 103.
520. G. Barcaro, I. O. Thomas and A. Fortunelli, *J. Chem. Phys.*, 2010, **132**, 124703.
521. F. Labat, I. Ciofini and C. Adamo, *J. Chem. Phys.*, 2009, **131**, 044708.
522. E. H. Morales and et al., *New Journal of Physics*, 2008, **10**, 125030.
523. P. A. Cox, R. G. Egdell, C. Harding, W. R. Patterson and P. J. Tavener, *Surf. Sci.*, 1982, **123**, 179.



524. B. Hoffling, A. Schleife, F. Fuchs, C. Rodl and F. Bechstedt, Appl. Phys. Lett., 2010, 97, 032116.