Imperial College London
Department of Earth Science and Engineering

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ab initio Modeling of Yttria Stabilised Zirconia for Solid Oxide Fuel Cells

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Declaration

This thesis has been written by myself and it has not been submitted in any previous application for a degree. The work reported within was executed by me, unless otherwise stated - Michael Alan Parkes, January 2015
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Abstract

Fuel cells are electrochemical devices that convert chemical fuels directly into electricity, heat, and waste products with higher efficiencies than many conventional combustion technologies. Fuel cells have already found applications in automotive and domestic applications, where their high efficiencies offer potential reductions in CO$_2$ emissions as well as energy savings. A promising technology is the solid oxide fuel cell (SOFC), which typically runs at temperatures between 500 - 1000°C, and can convert hydrogen rich gases, such as methane, directly into heat and electricity.

This thesis presents work on developing improved atomistic models of yttria stabilised zirconia (YSZ), which is used as a catalyst support and electrolyte material in a solid oxide fuel cell. The catalyst, YSZ, and a gas phase containing fuel molecules, meet at the anode to form the anode triple phase boundary (TPB) in an SOFC. The anode TPB is the site at which fuel molecules undergo electrochemical oxidation, a process that releases electrons and waste products. Unfortunately the anode is susceptible to poisoning and damage through detrimental chemical reactions which can lead to carbon deposition and sulphur poisoning. A long term aim for the field of SOFC catalysis is to understand these reactions and design improved catalysts which are resistant to contamination processes. However, to date, the detailed mechanisms involved in these reactions have not been established; even the mechanism for the oxidation of hydrogen at the anode TPB is fiercely debated. For these reasons, there is interest in developing atomistic models of the anode TPB to investigate the thermodynamics of possible reaction paths.

Modeling the anode TPB is dependant on many factors including: materials, surface structure, interfaces, distribution of local defects. A detailed knowledge of the YSZ surface chemistry is currently inhibited by a poor understanding of the distribution and local
atomistic structure of the dopant $Y^{3+}$ ions and oxygen vacancies ($V_\text{o}$ in Kröger-Vink notation) in the bulk crystal and at the surfaces. In this thesis, a comprehensive search for low energy defect structures using a combined classical modeling and density functional theory (DFT) approach is used to identify the low energy defect structures of 3.2mol% YSZ. 3.2mol% YSZ is chosen as the limit of low dopant concentration and as a simple system to investigate, avoiding the combinatorial complexity of higher dopant concentrations and defect-defect interactions. Through analysis of energetics computed using the best available empirical potential model, point charges, DFT, and local strain energy estimated in the harmonic approximation, we examine the main chemical and physical interactions that determine the low energy structures. It is found that the empirical potential model reproduces a general trend of increasing DFT energetics across a series of locally strain relaxed structures, but is unreliable both as it predicts some incorrect low energy structures, and because it finds some meta-stable structures to be unstable. A better predictor of low energy defect structures is the total electrostatic energy of a simple point charge model calculated at the unrelaxed geometries of the defects. In addition, the strain relaxation energy is substantial, and is estimated effectively in the harmonic approximation to the imaginary phonon modes of cubic zirconia (c-ZrO2), but it is not a determining factor for the relative stabilities of low energy defect structures. These results allow us to propose a simple method for identifying low energy YSZ defect structures.

The findings from the studies of bulk 3.2mol% YSZ are used to establish the low energy structures of a 3.2mol% YSZ (111) surface model. After initially demonstrating that a slab model, much larger than that used in previous DFT studies is required to obtain a converged surface energy, the energetic preference for yttrium to segregate to the (111) surface is investigated. After establishing that yttrium indeed segregates to the (111) surface, we compute the DFT energies of 20 low energy symmetry inequivalent surface structures, and identify the preferential defect configurations and surface chemistry sites. In addition, the DFT energy of the low energy NN structure proposed by Reaxff mod-
eling is computed. It is shown that this structures is significantly higher in energy than our minimum energy structure, which has NNN geometry. This highlights the need for large scale DFT calculations in understanding the YSZ (111) surface structure. Having obtained atomistic structures for the surface reaction sites, water dissociation onto the lowest energy YSZ (111) surface is investigated. It is shown that it is preferable for water to associatively adsorb to the YSZ surface, and this is optimal when water adsorbs to the yttrium site. Dissociative adsorption of water is only possible over zirconium sites with the process generally being endothermic. Some exothermic paths for dissociative adsorption exist, however there are large energy barriers to the process. Associative adsorption to the surface yttrium site is the global minimum of the system, and yttrium sites appear to act as a trap for water molecules.

Finally, the methodology developed in previous sections is used to investigate the 6.7mol% YSZ system, which is closer to the $Y_2O_3$ dopant concentration used in most commercial SOFCs (8 - 10 mol%). It is found that, whereas the electrostatic energy of the unrelaxed structures calculated using a point charge model was a good predictor of the likely low energy 3.2mol% defect structures, it is a poor predictor of the likely low energy 6.7mol% defect structures. In addition, while it was found that the best available Born-Mayer-Huggins potential model recreated general trends in DFT energies at 3.2mol%, it completely fails to reproduce DFT energy differences at 6.7mol%. In the absence of an easy to calculate, reliable predictor of the likely low energy DFT defect structures, we correlate the formation energies of the structures to simple geometric parameters. We perform an exhaustive search on 2857 symmetry inequivalent structures, characterising every structure in terms of intuitive quantities, such as: $V_o - V_o$ separation, the average $V_o - Y^{3+}$ interatomic separation, the average $Y^{3+} - Y^{3+}$ interatomic separation, the surface area occupied by the defect cluster, and the volume of the defect cluster. It is possible to explain the electrostatic formation energies of the defects in terms of intuitive attractive and repulsive forces and to find weak trends between the geometric descriptors and
the final relaxed DFT energies, however, without an extensive database of fully relaxed DFT energies, it is hard to determine the statistical meaning of these results. This result highlights the combinatorial complexity of the 6.7mol% system and establishes the need for further large scale DFT calculations on the 6.7 mol% system.
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friend Tim for being a fantastic house mate and friend through primary, secondary, and university education, and dedicate this thesis to my late grandfather Horace “George” Parkes, who sadly passed away while it was being written.

Figure 1: The hydrogen fuel cell generator at the BBC energy day September 2013. Left: Sam Cooper, Centre: Billy Wu, Right: Michael Parkes.
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<tbody>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>ASR</td>
<td>acoustic sum rule</td>
</tr>
<tr>
<td>B3LYP</td>
<td>Becke, three-parameter, Lee-Yang-Parr</td>
</tr>
<tr>
<td>BCC</td>
<td>body centered cubic</td>
</tr>
<tr>
<td>BFGS</td>
<td>Broyden-Fletcher-Goldfarb-Shanno</td>
</tr>
<tr>
<td>BMH</td>
<td>Born-Mayer-Huggins</td>
</tr>
<tr>
<td>c</td>
<td>cubic</td>
</tr>
<tr>
<td>CASTEP</td>
<td>Cambridge serial total energy package</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>ceria</td>
</tr>
<tr>
<td>CGO</td>
<td>ceria gadolinium oxide</td>
</tr>
<tr>
<td>CHP</td>
<td>combined heat and power</td>
</tr>
<tr>
<td>DFPT</td>
<td>density function perturbation theory</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EPR</td>
<td>electron paramagnetic resonance</td>
</tr>
<tr>
<td>EXAFS</td>
<td>x-ray absorption fine spectra</td>
</tr>
<tr>
<td>FCC</td>
<td>face centered cubic</td>
</tr>
<tr>
<td>FFT</td>
<td>fast Fourier transform</td>
</tr>
<tr>
<td>FP-LAPW</td>
<td>full potential-linearized augmented planewave</td>
</tr>
<tr>
<td>GDC</td>
<td>gadolinium doped ceria</td>
</tr>
<tr>
<td>GGA</td>
<td>generalised gradient approximation</td>
</tr>
<tr>
<td>GULP</td>
<td>general utility lattice program</td>
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H₂S hydrogen sulphide
H-spillover hydrogen spillover
HF Hartree-Fock
HO Hydrogen Oxidation
HT-SOFC high temperature solid oxide fuel cell
ICL Imperial College London
IR infra-red
IT-SOFC intermediate temperature solid oxide fuel cell
ITCA international tables of crystallography A
k-space reciprocal-space
LAMMPS Large-scale Atomic/Molecular Massively Parallel Simulator
LDA local density approximation
LEIS low energy ion scattering
LO/TO longitudinal optical-transverse optical
LSCF lanthanum strontium cobalt ferrite
LSM lanthanum strontium manganate
LST/QST linear synchronous transit and quadratic synchronous transit
m monoclinic
m-ZrO₂ monoclinic zirconia
MAS-NMR magic angle spinning nuclear magnetic resonance
MCC Materials Chemistry Consortium
MCFC molten carbonate fuel cell
MD molecular dynamics
MEIS medium energy ion scattering
MP Monkhurst-Pack
NCP normconserving pseudopotentials
NN nearest neighbour
NNN  next nearest neighbour
NNNN  next next nearest neighbour
O-spillover  oxygen anion spillover
OH-spillover  hydroxyl anion spillover
OLCAO  orthogonalised linear combination of atomic orbitals
OR  oxygen reduction
OTF  on the fly
PBE  Perdew-Burke-Ernzerhof
PEMFC  polymer electrolyte membrane fuel cell
PES  potential energy surface
PP  pseudopotential
PW  planewave
PW91  Perdew-Wang 91
PWP-DFT  pseudopotential plane wave density functional theory
R$^2$  coefficient of determination
r-space  real-space
RDF  radial distribution function
ReaxFF  reactive force field
RLS  rate limiting step
RMM-DIIS  residual minimisation direct inversion in the iterative subspace
rPBE  revised Perdew-Burke-Ernzerhof
SCF  self consistent field
ScSZ  scandia stabilised zirconia
SEM  scanning electron microscope
SOFC  solid oxide fuel cell
STM  scanning tunneling microscope
SXRD  anomalous x-ray diffraction
t tetragonal

\textit{t-ZrO}_2 \textit{tetragonal zirconia}

TPB triple phase boundary

TPD temperature programmed desorption

TS transition state

UCP ultrasoft pseudopotentials

UK United Kingdom

UKCP United Kingdom Car-Parinello

V_o oxygen vacancy

XC exchange-correlation

XPS x-ray photoelectron spectroscopy

Y_2O_3 yttria

YSZ yttria stabilised zirconia

ZrO_2 zirconia
Chapter 1

Introduction

This chapter outlines the motivation for the research carried out within this thesis and establishes the main research questions addressed in later sections. The aim of the thesis is to develop improved atomistic models of yttria stabilised zirconia, which is used as a catalyst support material and electrolyte in solid oxide fuel cells (SOFCs). The catalyst, YSZ, and a gas phase containing fuel molecules, meet at the anode to form the anode triple phase boundary (TPB), in an SOFC.

The anode TPB is the site at which fuel molecules undergo electrochemical oxidation, a process that releases electrons and waste products. Unfortunately the anode is susceptible to poisoning and damage through detrimental chemical reactions, which can lead to carbon deposition and sulphur poisoning. A long term aim for the field of SOFC catalysis is to understand these reactions and design improved catalysts which are resistant to contamination processes. However, to date, the detailed mechanisms involved in these reactions have not been established; even the mechanism for the oxidation of hydrogen at the anode TPB is still fiercely debated. For these reasons, there is interest in developing atomistic models of the SOFC anode TPB to be used in modeling the thermodynamics of possible reaction paths.

Modeling the anode TPB is dependant on many factors including: materials, surface structure, interfaces, distribution of local defects etc. Literature relevant to these topics is introduced at the beginning of each chapter in order to establish the context for the specific research reported in each. In the current chapter, we introduce SOFC technologies, their importance, and the current state of the art SOFC anode TPB models. Finally
we outline the main research questions to be addressed in this thesis.

1.1 Background

The generation and storage of energy is currently a hot topic of research, with concerns over energy security, limited reserves of fossil fuels, and the environmental impacts of burning such fuels [15]. These concerns have lead to the exploration of renewable energy sources such as wind and solar, as well as the development of technologies that allow for the efficient conversion and storage of energy. Fuel cells offer an efficient way to convert chemical fuels into electrical energy, while electrolysis cells can convert electrical energy, water, and carbon dioxide, back into fuels [16].

Fuel cells are electrochemical devices that convert chemical fuels directly into electricity, heat, and waste products with higher efficiencies than many conventional combustion technologies[16]. For this reason, they could become part of a future hydrogen economy, where hydrogen is used as a fuel and generated through renewable electrolysis, or made through solar water splitting. Hydrogen is converted back into electricity and water in a fuel cell, as illustrated in Figure 1.1. This could have several advantages including a reduction in CO₂ emissions, as well improvements in air quality[16].

![Figure 1.1: Chemistry of the hydrogen economy.](image)

Fuel cells have found applications in the automotive industry, where polymer electrolyte membrane fuel cells (PEMFCs) have been used to replace internal combustion engines in
cars and buses. The PEMFC is a low temperature fuel cell (65 - 100°C) and converts hydrogen into electricity and water[17]. Low temperature operation is achieved through the use of a platinum catalyst which reduces the activation energy of the hydrogen oxidation (HO) and oxygen reduction (OR) reactions. The electrically insulating proton conducting membrane, is made from a polymer called nafion which is derived from Teflon. While PEMFCs are commercially available, the cost of the platinum catalyst and nafion membranes are an obstacle to the large scale roll out of the technology[18]. Figure 1.2 shows a schematic of a PEMFC.

![Figure 1.2: Schematic of a PEMFC[1].](image)

In addition to the PEMFC, there are several other technologies that offer fuel flexibility and the opportunity to use cheaper catalyst materials. Technologies include; solid oxide fuel cells (SOFCs), and molten carbonate fuel cells (MCFCs). Each type of fuel cell offers different cell chemistry, and different materials used in its construction. The focus of this thesis is SOFCs, which run at high temperatures, typically 500 - 1000°C. High temperatures reduce the activation energies of the electrochemical reactions allowing the use of cheaper catalysts, and enabling the SOFC to run on hydrogen rich gases such as methane, ethane, syn-gas, and even alcohols such as ethanol[19].

SOFCs already have commercial applications in combined heat and power (CHP), which
is the decentralised generation of electricity at a consumers property. By delivering the primary source of energy e.g. gas, to a building, CHP units can generate electricity for appliances and lighting, while the waste heat can be recycled to heat the building and produce hot water [2]. This maximises energy usage of the primary energy source. Figure 1.3 illustrates how CHP may be implemented in a typical home[2].

![CHP in a domestic home](image)

**Figure 1.3: mCHP in a domestic home [2].**

The total efficiency of CHP technologies can be as great as 85% reducing CO$_2$ emissions and the need for fossil fuels [2]. The potential fuel savings of CHP are shown by the Sanky diagram in Figure 1.4. Companies such as; eBay, and google, have already adopted the technology for use at their data centres [18], while there is a growing interest in using SOFCs in transport applications, both for maritime vessels, and automotive.

Fuel is supplied to the SOFC anode where it reacts with oxide ions releasing electrons[19]. The electrons flow around an external circuit to the cathode, performing useful electrical work in the process. At the cathode the electrons reduce oxygen from the air into oxide ions, which are conducted through the electrolyte to complete the circuit. This is illustrated by Figure 1.5.

An SOFC is made from three layers of materials, these are the electrolyte, anode, and
Figure 1.4: diagram showing the advantage of generating heat and power through CHP. Note: efficiencies are illustrative and will vary depending on systems [2].

Figure 1.5: Cartoon of an SOFC cross section[1].

cathode. A typical micro-structure is shown in Figure 1.6, which shows a scanning electron microscope (SEM) image of an SOFC cross section. The electrolyte must be an oxide ion conductor, and an electrical insulator. Yttria stabilised zirconia (YSZ) and scandia stabilised zirconia (ScSZ) are typically used for high temperature SOFCs (HT-SOFCs), which operate at temperatures between 750-1000°C. Gadolinium doped ceria GDC, also referred to as ceria gadolinium oxide (CGO), is used for intermediate temperature SOFCs (IT-SOFCs), which operate between 550 and 750°C [19].
Doping zirconia (ZrO$_2$) and ceria (CeO$_2$) gives the electrolyte materials their oxide ion conductivity. The (Y$_2$O$_3$)$_{0.1}$(ZrO$_2$)$_{0.9}$ composition of YSZ (also referred to as 10mol% Y$_2$O$_3$) has a conductivity of approximately 0.03Scm$^{-1}$ at 1000°C, while the (Gd$_2$O$_3$)$_{0.1}$(CeO$_2$)$_{0.9}$ composition of GDC (also referred to as 10mol% Gd$_2$O$_3$) has a conductivity of approximately 0.025Scm$^{-1}$ at 600°C [19].

Doping ZrO$_2$ with Y$_2$O$_3$ is isoelectronic, with Y$^{3+}$ ions replacing Zr$^{4+}$ ions and forming charge compensating oxygen vacancies ($V_\text{o}^-$ in Kröger-Vink notation). The $V_\text{o}^-$ facilitates the conduction of O$^{2-}$ ions in the lattice and therefore the conductivity is dependent on the Y$_2$O$_3$ concentration. For low concentrations the conductivity rises rapidly with the number of defects but reaches a maximum at 8mol%[20]. It has been argued that for higher concentrations inter-defect interactions reduce the conductivity with the increasing electrostatic interaction between dopant cations and vacancies being the dominant factor[19][21].

ZrO$_2$ exhibits three main crystal structures under standard pressure [22]. At room temperature it adopts a monoclinic (m) structure and upon heating undergoes phase transitions to tetragonal (t) and cubic (c) phases, which occur at 1170°C and 2370°C respectively. The cubic phase exhibits the highest oxide ion (O$^{2-}$) conductivity, making it the most...
technologically relevant for SOFCs. Doping with $\text{Y}_2\text{O}_3$ and other oxides stabilises the cubic phase and thus reduces the temperature at which the $t \rightarrow c$ phase transition occurs. Typical doping compositions include 3, 8, 10 and 12mol% $\text{Y}_2\text{O}_3$. The exact location of the phase boundary between cubic and tetragonal ZrO$_2$ as a function of $\text{Y}_2\text{O}_3$ concentration is still debated [23], however x-ray diffraction data suggests that 8mol% is the minimum concentration at which the cubic phase is stable at room temperature [24][25][26]. At 40mol%, YSZ forms the ordered compound Zr$_3$Y$_4$O$_{12}$ [27].

The cathode is made of a mixed electrical and anionic conductor that serves as an oxygen reduction (OR) catalyst. Typical materials include lanthanum strontium manganate (LSM) or lanthanum strontium cobalt ferrite (LSCF). The choice of cathode material depends on the operating temperature of the device, and its reactivity towards the electrolyte. LSCF is reactive towards YSZ, and is hence used with GDC electrolytes, or with YSZ and a GDC interlayer[19]. Hence, LSM is commonly used for HT-SOFCs while LSCF is used for IT-SOFCs. The anode is a cermet of catalytic metal and electrolyte, with nickel being the most common catalyst[19]. The anode cermet has a complex microstructure consisting of metallic, oxide, and gas phases. The connection between SOFC device performance and anode micro-structure is often explored through x-ray computed tomography (CT) and focussed ion beam - scanning electron microscopy (FIB-SEM) techniques [28]. The anode electrochemistry occurs at the interface between the three phases, in a region known as the triple phase boundary (TPB)[29].

While solid oxide fuel cells can directly operate on gasses such as methane and ethane etc. the anode is susceptible to damage through carbon deposition and sulphur poisoning [30][31][32][33]. Carbon deposition starts to occur at temperatures around 500°C, when an SOFC is operating on humidified methane. Carbon deposition leads to a significant increase in the volume of the anode, leading to eventual cell fracture and delamination[31]. In addition, many fuels contain sulphur impurities such as; mercaptans, tetrahydrothio-
phene, and disulphides, which rapidly decompose to $\text{H}_2\text{S}$ at SOFC operating temperatures. $\text{H}_2\text{S}$ reacts with nickel catalysts reducing cell voltage and performance over time $[34]$. To mitigate the effects of sulphur, additional reformers and chemical filters are used to create syn-gas and remove sulphur impurities, the addition of which, reduce the overall efficiency and versatility of the technology. Extensive efforts are currently devoted to developing anodes that can oxidise hydrocarbons directly, and eliminate the need for these additional components $[35]$.

The search for improved anode materials is dependent on a better understanding of the chemical reactions occurring at the TPB. Despite extensive experimental investigations and kinetic modeling, the detailed mechanism of the simple $\text{H}_2$ oxidation at the anode TPB is still debated $[4][36][37][38][39][40][41][42]$. The overall reaction for hydrogen oxidation is given in equation 1.1, where $\text{O}^{2-}_{\text{YSZ}}$ represents an oxide ion from YSZ, $2e^{-}_{\text{Ni}}$ represents two electrons being accepted by nickel, and $V_{o}$ represents an oxygen vacancy formed in YSZ.

$$H_2(g) + O^{2-}_{\text{YSZ}} \rightarrow H_2O(g) + 2e^{-}_{\text{Ni}} + V_{o}.$$  \hspace{1cm} (1.1)

$\text{H}_2$ has been reported to dissociatively adsorb onto nickel $[43][44]$, but several subsequent steps can be proposed for its final oxidation into water $[38]$, these are illustrated by Figure 1.7.

Water can be formed by one of three types of reaction:

1. Water is formed on nickel due to the “spillover” of oxygen anions from YSZ (O-spillover).

2. Water is formed on nickel following the preliminary spillover of a hydrogen onto YSZ,
Figure 1.7: Cartoon of the proposed hydrogen oxidation mechanisms at the SOFC anode TPB. The three main reaction mechanisms are H-spillover, O-spillover and OH-spillover. Adapted from work by Ammal and Hayden [4].

this forms a hydroxyl ion which can then back-transfer onto the nickel (H-spillover followed by OH-spillover).

3. Water is formed by the consecutive transfer of two hydrogens from the nickel surface (H-spillover).

Electrochemical impedance spectroscopy (EIS) has established the rate limiting step (RLS) for hydrogen oxidation to be a charge transfer process with an activation barrier of 1.04 - 1.68 eV [45]. Kinetic modeling of impedance spectra has provided three different assignments of the RLS. H-spillover, in references [36][37][38][39][4], O-spillover, in references [40][41], and OH-spillover in reference [42]. In addition, it has been shown that the polarisation resistance to hydrogen oxidation is reduced at high water partial pressures [38]. This has been attributed to an increase in the effective TPB due to hydroxylation of the YSZ surface [39].
1.2 Computational

*Ab initio* (Latin for “from the beginning”) simulations, based on quantum mechanical density functional theory (DFT) and empirical atomistic potentials, can provide thermo-dynamic information on the RLS, and the role of water adsorbed onto the surface of YSZ. A detailed description of these methods can be found in the *Methodology* chapter. The importance of developing atomistic TPB models has been established by several review papers [46][47][48][49]. While the case has also been made for designing patterned electrodes, with well defined microstructures and TPBs, to validate atomistic models [50][51].

To this purpose, one of the first atomistic models of hydrogen oxidation at the anode TPB was developed by Anderson and Vayner, who used a rather crude structural model consisting of a YSZ cluster, modeled as 15 atoms, with a single nickel atom placed on-top [52]. More recently, Linic and co-workers [53][54] investigated the energetics of several intermediate products absorbed onto the surfaces of nickel and YSZ. Activation barriers were calculated using the Brønsted-Evans-Polany relationship without thoroughly modeling the TPB, while Gorski and co-workers have also investigated intermediates on the surface of YSZ [55]. A large model of the anode TPB was proposed in a string of papers by Shiskin and Ziegler [56][5][57]. The model is pictured below in Figure 1.8.

The Shishkin - Ziegler model consisted of 70 atoms of 9 mol% YSZ + O, modeled as a nine atomic layer thick slab, with a nickel nano-wire of 18 atoms placed on-top. The YSZ + O slab was exposed to the vacuum space by (111) surface termination, and generated from the bulk crystal with the fewest number of bonds broken, when compared to the (110) and (100) surfaces. The YSZ + O (111) surface comprises of a YSZ (111) surface where the $V_o^-$ has been replaced by an additional neutral O atom, the origin of which, has been questioned by some authors [29]. The nickel nanowire is periodic in one direction and consists a nickel cluster with two (111) surfaces and (100) surface. An interface is
Figure 1.8: Shishkin and Ziegler’s atomistic model of the anode TPB. Nickel is modeled as a nanowire, shown in blue. YSZ is modeled as a slab, shown by the red oxygen, grey zirconium and green yttrium ions [5].

constructed between the (111) surface of YSZ, and one of the (111) surfaces of the nickel nanowire. After a relaxation of the atomic positions using DFT, the nickel (100) surface reconstructs to a surface “resembling” a (111) surface. Shishkin & Ziegler concluded that H-spillover was the RLS, and suggested that hydrogen oxidation was only possible on YSZ in the presence of an additional neutral oxygen atom [5]. In a later paper [57], it was proposed that the additional oxygen atom was not really necessary as hydrogen oxidation was possible through involving oxygen atoms at the interface between nickel and YSZ.

The work by Shishkin & Ziegler came under heavy criticism from Cucinotta et al. [29], who highlighted a number of flaws in the model. The addition of an extra neutral oxygen atom to the YSZ surface was questioned, while Cucinotta et al. highlighted that the mechanism for direct hydrogen oxidation at the interface between YSZ and nickel, proposed by Shishkin & Ziegler, was calculated to be endothermic and contrary to the very behavior of hydrogen oxidation. In addition, criticism was made of the use of a nickel
nanowire and modeling hydrogen catalysis on the unstable (100) surface of nickel, instead of the energetically favorable (111) surface.

Cucinotta et al. proceeded to publish a revised TPB model as pictured in Figure 1.9. The model consisted of a large 219 atom 8.7 mol% YSZ slab, which was 9 atomic layers thick. A 46 atom nickel cluster was placed on-top of the slab so that both nickel and YSZ had low energy (111) surfaces exposed to the vacuum space. Cucinotta et al. concluded that the RLS was determined by the spillover of hydrogen from nickel onto YSZ, and dismissed OH and O-spillover as being energetically unfavorable. In addition, it was established that the process was only exothermic if oxygen ions at the interface between YSZ and nickel were involved in the reaction. The model was then used to investigate the effect of water in hydrogen oxidation. It was concluded that hydrogen oxidation could occur away from the TPB provided additional water was dissociatively adsorbed to the YSZ surface. This enabled the mobility of $\cdot OH$ ions across the surface through a pseudo-Grotthus mechanism [29][58].

In a recent review [49], Shishkin & Ziegler responded to the criticism of Cucinotta et al. by suggesting that the use of a nickel nanowire was valid given that the energetics of hydrogen oxidation on the nanowire were similar to that of a pure nickel surface [5]. This argument was used to validate the model for studying the oxidation of small molecules such as hydrogen. However, a recent DFT study by An and Turner [59] established that nickel nonorods, modeled on YSZ substrates, showed a significant increase in reactivity to binding oxygen, carbon and sulphur species, while Zeng et al. used the Shishkin-Ziegler model to study sulphur adsorption onto the nickel nanowire, and reported that the addition of sulphur caused the “reconstructed” (100 / 111) surface to revert to its previous (100) facets [60]. These results suggest that the Shishkin-Ziegler model is inappropriate for studying the chemistry of larger molecules such as H$_2$S and CH$_4$. A larger TPB model is required [49].
Models of alternative anode cermets have also been proposed by Shiskin & Ziegler, including nickel/GDC [61][62] and Ni/BaCe$_{1-x}$Y$_x$O$_{3-\delta}$ [63]. In all these publications the same model has been used, with the electrolyte simply being changed to create the different anode cermets.

In general, other authors have adapted either the Shiskin - Ziegler or Cucinotta models to investigate the chemistry of the TPB. Ammal and Hayden [4] adapted the Cucinotta model to investigate hydrogen oxidation mechanisms and agreed with Cucinotta et al. that H-spillover is the RLS. Ammal and Hayden also showed that vacancy formation at the Ni/YSZ interface is more favorable than vacancy formation in the bulk crystal, and used half-cell micro-kinetic modeling to establish the temperature at which H-spillover became the RLS. They concluded that the RLS below 1300 K was the conductivity of O$_{2^-}$ ions through the electrolyte, while at temperatures above 1300 K, H-spillover was
the RLS. These results are in agreement with kinetic Monte Carlo simulations performed on a full cell model, which included; oxygen reduction at the cathode, $O^{2-}$ ion migration through the electrolyte, and hydrogen oxidation[64].

Zhang et al. adapted the Shiskin - Ziegler model to investigate a mechanism of carbon deposition [65] and sulphur poisoning [66][67]. It was concluded that $V_o$ created at the Ni/YSZ interface induced carbon deposition and sulphur poisoning, through trapping C-H fragments and sulphur ions. Both proposed poisoning mechanisms blocked $V_o$ sites and prevented the conduction of $O^{2-}$ ions. However, as highlighted by other studies [49][59][60], the Shishkin - Ziegler model may be inappropriate for studying the chemistry of contamination processes.

Beyond the work outlined above, Yang et al. have modeled nanoparticles of barium oxide and YSZ on nickel (111) surfaces, as a potential cermet for water-mediated carbon removal [68], while hydrogen oxidation has been modeled on the (100) surfaces of nickel and YSZ respectively [69]. Within this model, diffusion of protons through bulk nickel into YSZ was considered as a reaction mechanism. It was concluded that migration mechanisms involving bulk diffusion were unfavorable, and oxidation reactions would take place on the surfaces.

All of the atomistic models discussed above have used DFT as the primary method of choice. The most recent anode TPB model (published November 2014) used a reactive force field (ReaxFF) empirical atomistic potential [70], fitted to a database of DFT energies, as developed by van Duin and co-workers [71][72][73][74]. The potential model was used to model hydrogen and butane oxidation at a large TPB model consisting of 240 nickel atoms and 222 atoms of $\sim$14 mol% YSZ, using NVT molecular dynamics (MD) at 1250 and 2000 K. ReaxFF MD of hydrogen oxidation at 1250 K revealed that hydrogen dissociates onto the nickel surface, and two consecutive H-spillover reactions occur at the
Ni/YSZ interface forming water. If water forms on nickel, the molecule dissociates and moves to the YSZ surface, if water forms on YSZ, the molecule stays on the surface for the duration of the simulation. The ReaxFF MD results appear to match the mechanisms reported in previous DFT studies [57][4][29].

ReaxFF MD at 2000K YSZ was used to investigate butane oxidation at the TPB and the mechanism for the chemical reaction listed in equation 1.2 (the last term represents the carbon deposits that cause coking of the anode). It was established that the reaction of butane at the TPB was similar to the pyrolysis butane [75], with the exception that CO and CO$_2$ formation was not observed due to the lack of available oxygen in the YSZ electrolyte, due to oxygen also being needed for the competing water formation reaction.

\[
mC_4H_{10} + 7mO^{2-} \rightarrow 5mH_2O + mCO_2 + 14me^- + \Sigma C_n
\]  

(1.2)

There appears to be a general consensus within the atomistic modeling community that the RLS to hydrogen oxidation at the anode TPB is the spillover of hydrogen from nickel onto the YSZ surface. However, there remains a debate about which is the best model to use given the constraints imposed by the computational cost of the DFT.

From a materials perspective, modeling the anode TPB of an SOFC is a complicated task with many variables. To begin with, the low energy surfaces of the materials, nickel and YSZ, need to be identified and studied. Nickel is an elemental solid and it is well established that the (111) surface is the low energy surface [29]. However, little is known about the surfaces of YSZ, with only theoretical studies suggesting that the (111) surface is energetically favorable [76][22]. In addition, the surface composition of YSZ is still debated and the role of yttrium segregation is unclear [77]. Therefore the atomistic structure of the surface reaction sites is not known. The role of potential yttrium surface
dopants in determining the surface chemistry of the material has not been established. Finally, YSZ is formed from doping the mechanically unstable cubic phase of zirconia with Y₂O₃, a process that both stabilises the cubic phase and affords the material its oxide ion conductivity. The local distribution of the dopant Y³⁺ ions and charge compensation Vₒ within the bulk crystal is still debated, with x-ray and neutron diffraction showing that the defect structure of YSZ is highly disordered with multiple distinct defect clusters. Establishing the relative positions of Y³⁺ ions and Vₒ has not been possible due to the low contrast in the x-ray and neutron scattering powers of Zr⁴⁺ and Y³⁺ ions[78]. The mechanism by which doping stabilises the mechanical instability of the cubic phase is also unclear.

These factors combine to make it very challenging to develop an atomistic model of the reaction mechanisms occurring at the anode TPB, and it is unclear how existing models have been parameterised with respect to these variables. As highlighted by a recent review, the models in the published literature to date have been constructed without any attempt to validate their atomic structures through experimentation or other methods [49]. Indeed, the pathway for fuel oxidation will depend on the structure and composition of the YSZ surface, and bond topology at the Ni/YSZ interface. In addition, recent experimental findings on dopant segregation in YSZ have yet to be incorporated into the construction of current models [79].

The aim of this thesis is to address these challenges and establish the low energy defect structures of YSZ surfaces and bulk, using a combined DFT and empirical atomistic approach. The results of this thesis establish a method for generating sensible structures of YSZ at low dopant concentration, and can be used as a method to validate the local geometry of future TPB models. The key research questions we address are:

- How accurate is the best available empirical atomistic Born-Mayer-Huggins (BMH)
potential in reproducing the DFT energy differences of YSZ defect structures? A BMH potential developed and implemented by previous authors [22][80] to study bulk and surface structures of YSZ is used in preference to ReaxFF for its simplicity and well established and benchmarked computer implementation. State of the art valence bond order ReaxFF potentials, primarily developed and implemented within the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [81], are complex and have many variables. ReaxFF potentials have only recently started to be tested and benchmarked within other computer codes such as the general utility lattice programme (GULP) [82][83].

• In the limit of low dopant concentration (3.2 mol% Y$_2$O$_3$) what are the low energy structures of the Y$_2$O$_3$ defect?

• How do defects interact with the mechanical instability of the cubic phase of zirconia, in order to stabilise its structure?

• What are the major interactions that determine the energetic ordering of the defect clusters at 3.2 mol%?

• Does yttrium segregate to the (111) surface of YSZ?

• What are the low energy 3.2 mol% YSZ (111) surface structures?

• What is the water surface chemistry of the low energy YSZ (111) surface?

• What is the nature of the Y$_2$O$_3$ - Y$_2$O$_3$ defect interactions when studying a 6.7 mol% YSZ system?

• Is there an energetic preference for V$_o$ to align in certain crystallographic orientations?

• What are the low energy defect structures at 6.7 mol%?

The results of the thesis are split into three sections:
1. **Chemical Descriptors of Yttria Stabilised Zirconia at Low Defect Concentration** - This chapter establishes the low energy defect structures of 3.2 mol% YSZ, and evaluates the accuracy of the best available Born-Mayer-Huggins polarisable shell model [22][84] in reproducing the PBE-DFT energy differences of a complete set of symmetry inequivalent defect structures. The chapter establishes the major chemical interactions that determine the PBE-DFT energetic ordering of the 3.2 mol% YSZ defect structures.

3.2 mol% YSZ is chosen as a simple system to investigate, and as discussed in later sections, the combinatorial complexity of 6.7 mol% and higher dopant concentration systems challenges the evaluation the Born-Mayer-Huggins and DFT energies due to additional defect-defect interactions. By studying the 3.2 mol% system first, we can consider these interactions as negligible.

2. **Surface Chemistry Sites of 3.2 mol% Yttria Stabilised Zirconia** - This chapter uses large scale DFT and Born-Mayer-Huggins polarisable shell model calculations to establish the low energy (111) surface structures of 3.2 mol% YSZ. The chapter also establishes the energetic preference for defects to segregate to the (111) surface and determines the interactions between the 3.2 mol% (111) surface chemistry sites and water molecules.

3. **6.7 mol% Yttria Stabilised Zirconia System, and Defect - Defect Interactions** - This chapter uses large scale DFT and Born-Mayer-Huggins polarisable shell model calculations to investigate the low energy structures of 6.7 mol% YSZ defect clusters. We establish that the best available Born-Mayer-Huggins polarisable shell model completely fails to reproduce the DFT energy differences at 6.7 mol%. We establish the nature of defect-defect interactions at 6.7 mol% YSZ and analyse a large set of geometric descriptors in predicting the energetic ordering of relaxed DFT structures. We also investigate the energetic preference for $V_o$ to align in certain
crystallographic orientations.

Each chapter includes a detailed literature review of the research that is relevant to that section. The overall conclusions of the thesis are summarised in the Chapter entitled *Thesis Conclusions*, while the scope for future projects is outlined in *Suggestions for Future Work*. 
Chapter 2

Methodology

This chapter presents an overview of the theoretical aspects of physics and chemistry studied within this thesis, and establishes the fundamental principles from which the results are based. Thorough reviews of the topics discussed within can be found in the published literature[85][86][87][88] and are cited where relevant.

Important material properties including; structure and thermal vibrations, are determined by the interactions between atomic nuclei and electrons. These interactions can be modeled by theories including: classical electrostatic interactions, and quantum mechanics, both of which are implemented in this study.

The forces between atoms are ultimately electrostatic in origin, and can be described through both classical and quantum mechanical theories. Classical theories based on empirical atomistic potentials model the interactions between positive and negatively charged ions. Simulations based on classical methods are computational inexpensive and fast, allowing the quick determination of properties. A downside to the approach is that the empirical atomistic potentials often rely on material dependent parameterisations. These are often derived from experimental results such as x-ray crystal structures and elastic, vibrational, and dielectric properties determined from neutron diffraction. For this reason, a potential that recreates one set of experimental quantities e.g. the lattice parameters of a material, may fail to accurately reproduce another e.g. elastic constants[85], while a potential fitted for one composition and structure may not be transferable to other systems.
In principle, all material properties are determined by the many-body wavefunction of the electrons and atomic nuclei which satisfies the many-body Schrödinger equation. This cannot be solved for the enormous number of atoms that are found within a solid. Hence quantum mechanical ab initio methods that implement a number of approximations to the Schrödinger equation are used to determine the wavefunction and material properties.

2.1 Interatomic Forces and Classical Simulations of Materials

For ionic crystals such as NaCl, empirical atomistic potentials based on the Born model can be effective in predicting material properties as the material is made of a lattice of positively and negatively charged ions. Metallic and covalent systems can be harder to describe with empirical atomistic potentials as electrons are not completely localised around the atomic nuclei. This means it is difficult to calculate the forces between atoms without taking into account the way that the electron density localises or delocalises around the nuclei. The advantage of empirical potential methods over quantum mechanical simulations is that they are computationally inexpensive, meaning very large systems containing $10^3$ - $10^6$ atoms can be simulated.

2.1.1 Electrostatics

Electrostatic interactions are long range and have a simple mathematical form through the Coulomb potential, which has a $r^{-1}$ relationship. A second interaction that can complicate matters is the polarisation of the ions caused by broken symmetry. For instance; if one considers an ion on a high symmetry site within a crystal, at equilibrium all electric fields at the high symmetry point cancel out. However, if the neighbouring ions or ion in question move, a residual electric field is induced at the symmetry site. This will polarise the ion leading to a dipole moment. The dipole moment can then interact with
the charges of neighbouring ions, adding an extra contribution to the total energy of the crystal. Such inductive effects are important, and are commonly approximated through the shell model[90][91][92]. Ions are assumed to comprise of a rigid core consisting of the nucleus and core electrons, surrounded by shell of loosely bound valence electrons. It is then assumed that the core and shell are held together by a elastic potential where the force constant determines the degree of achievable polarisation. The energy between two ions is hence the sum of six interactions: core(1) - core(2), shell(1) - shell(2), core(1) - shell(1), core(2) - shell(2), core(1) - shell(2) and core(2) - shell(1) as illustrated in Figure 2.1:

![Ionic interactions in the shell model](image)

Figure 2.1: Ionic interactions in the shell model

2.1.2 Van der Walls Interactions

Van der Waals forces, known historically as dispersive forces, are second order forces that occur in addition to electrostatic forces. van der Waals forces are the primary bonding force in materials where the atoms or molecules are charge neutral e.g. argon or nitrogen. The most import term is a force that varies by $r^{-6}$, where $r$ is the inter-atomic/intermolecular distance. The force arises from the fact that the electron density of an ion or molecule is constantly fluctuating. Over time this averages to zero, however when a dipole moment occurs on one ion, it induces a moment on a neighbouring ion,
causing a temporary non-zero force to occur.

2.1.3 Repulsive Forces

When two atoms become sufficiently close their respective electron distributions start to overlap. This causes the electrons to interact through electrostatic repulsion, and the Pauli exclusion principle. The Pauli exclusion principle prevents electrons with the same spin state existing in the same space, and leads to electrons to occupying higher energy states. Combined, these two effects cause the energy of the system to increase rapidly as a function of decreasing interatomic distance, r.

While it is possible to calculate the repulsive forces from first principles, it is common to use a functional form with adjustable parameters. One such example is \( Br^{-n} \), where n is commonly equal to 12. A high order polynomial function is commonly chosen, simply for its computational convenience and cost compared to an exponential function, and has little physical meaning. When combined with van der Waals forces, the Lennard-Jones potential is formed which is given in equation 2.1:

\[
\varphi(r) = -4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^6 - \left( \frac{\sigma}{r} \right)^{12} \right] \tag{2.1}
\]

\( \epsilon \) is equal to the potential energy at the equilibrium position, and \( \sigma \) is equal to the distance between atoms at which the energy equals zero. Another common functional form is the Born-Mayer interaction, which is the exponential form of the repulsive forces. This is given in equation 2.2:

\[
\varphi(r) = B \exp(-r/\rho) \tag{2.2}
\]

The parameters B and \( \rho \) are usually determined empirically by fitting the model to a data
set such as the experimental lattice or dielectric constants of a material. The parameters can also be determined through quantum mechanical calculations, where $\rho$ is related to the size of the atoms, and $B$ is a measure of the hardness of the interaction. When combined with the van der Waals forces, the Buckingham potential is formed. This is given by equation 2.3, where $C$ is an additional fitted parameter[85]. Buckingham potentials are commonly used to model many systems with, and without an additional Coulomb interaction. When combined with the Coulomb interaction, the Born-Mayer-Huggins (BMH) potential is formed.

$$\varphi(r) = B \exp(-r/\rho) - \frac{C}{r^6}$$

(2.3)

It is extremely difficult to calculate the parameters $B$, $C$, and $\rho$ in equation 2.3 from first principles. It is nearly always more accurate to fit them empirically than derive them. The limitations of the fitting procedures mean that even when good agreement is obtained with one experimental parameter e.g. lattice constants, the model may not reproduce another data set e.g. elastic constants. It should also be mentioned that very few materials fit neatly into the categories of ionic, covalent or metallic[85].

2.1.4 Total Lattice Energy

The total energy of a crystal is the sum over all the individual atom-atom interactions within the assumption of pairwise additivity. Thus, if $\varphi_{ij}$ is the energy between any two atoms, $i$ and $j$ as a function of interatomic distance, then the full energy of the crystal lattice $E$, is given by equation 2.4:

$$E = \frac{1}{2} \sum_{i,j} \varphi_{ij}(r_{ij})$$

(2.4)

A factor of a half is included to account for the fact that each interaction is counted twice. Such a sum is computationally impossible unless the functional form of $\varphi_{ij}(r_{ij})$
can be restricted to some pre-determined interatomic limit. Examples include interactions that fall off rapidly with distance, such as Lennard-Jones or Buckingham potentials. The cut-off limit of these functions is typically set to 5 - 10 Å, as energies at greater distances are considered negligible. Cut-off limits cannot be used for Coulomb interactions as the summation does not converge on increasing the interaction distance. For these interactions, more complex mathematical techniques are required in order to evaluate the lattice sums correctly. One technique is the Ewald summation.

### 2.1.5 Ewald Summation

The Ewald summation\[93\] is used to evaluate the contribution of the Coulomb energy to the total energy of a crystal lattice, which is composed of two divergent sums. Ewald developed a solution by splitting the sum into two convergent series, one that converges in real-space (r-space) and the other that converges in reciprocal-space (k-space). The first step is to rewrite the function \(r^{-1}\) as a Gaussian function:

\[
\frac{1}{r} = \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} \exp\left(-\rho^2 \right) d\rho
\]  

(2.5)

The Coulomb interaction \((E_c)\) can then be rewritten as:

\[
E_c = \frac{1}{2} \sum_{(l=0)}^{\infty} \sum_{i,j} \frac{q_i q_j}{4\pi \epsilon_0 r_{ij}(l)} = \frac{1}{2} \sum_{(l=0)}^{\infty} \sum_{i,j} \frac{q_i q_j}{2\pi^2 \epsilon_0} \int_{0}^{\infty} \exp\left( -\rho^2 \right) d\rho
\]  

(2.6)

where \(r_{ij}(l)\) is the distance between the \(i\)-th atom in the reference unit cell labelled 0, and the \(j\)-th atom in the \(l\)-th unit cell. \(q_j\) is the charge on the atom. As the long range Coulomb interactions can be expressed as the interaction of the charges of a central unit cell and the surrounding lattice, the Gaussian integral in equation 2.6 can be split into two, one representing the unit cell and, one representing the crystal lattice:
\[
\int_0^\infty \exp\left(-r^2 \rho^2\right) d\rho = \int_0^g \exp\left(-r^2 \rho^2\right) d\rho + \int_g^\infty \exp\left(-r^2 \rho^2\right) d\rho = \int_0^g \exp\left(-r^2 \rho^2\right) d\rho + \frac{2 \text{erfc}(gr)}{r}
\]  
(2.7)

where \( g \) is a free parameter, and \( \text{erfc} \) is a complementary error function:

\[
\text{erfc}(x) = 1 - \text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \exp\left(-y^2\right) dy
\]  
(2.8)

The complementary error function falls to zero quickly with increasing \( r \) and needs no further treatment. The integral between 0 and \( g \) is still a slow function to converge in real space and is Fourier transformed into reciprocal space where it rapidly converges. This completes the evaluation of the Coulomb interactions.

### 2.2 Quantum Mechanical Simulations of Materials

The properties of a material are determined by the wavefunction of the electrons and atomic nuclei. The wavefunction contains all the information about the system, considered in isolation, and satisfies the many-body Schrödinger equation. By solving the equation one can determine the wavefunction of the electrons and hence all the electronic and structural properties of a material. In reality, it is impossible to analytically solve the many-body Schrödinger equation for all but the simplest of case of the hydrogen atom. The many body Schrödinger equation, which describes the wavefunction on \( n \) electrons interacting with \( N \) atomic nuclei is given in equation 2.9

\[
H\psi_{MB}(r_1, r_2, \ldots, r_n, R_1, R_2, \ldots R_N) = E\psi_{MB}(r_1, r_2, \ldots, r_n, R_1, R_2, \ldots R_N)
\]  
(2.9)

E is the total energy of the system, \( H \) is the Hamiltonian operator, \( \psi_{MB} \) is the many-body wavefunction, \( r \) represents the spacial co-ordinates of the electrons \((x,y,z,\sigma)\), and \( R \)
represents the spatial co-ordinates of the nuclei \((x,y,z,\sigma)\). Sigma is the additional spin coordinate of the electrons.

As the system cannot be solved analytically for complex systems, a number of approximations are made to simplify the many-body Schrödinger equation. The first is the Born-Oppenheimer approximation which is used to separate the electronic and nuclear interactions of the wavefunction. The approximation assumes that the electronic wavefunction depends on the position of the nuclei but not their velocities. This is due to the nuclear motion of the nuclei being much slower than that of the electrons. This allows the nuclei to be considered as fixed charged particles. The problem is simplified to the electrons moving in a fixed external potential, leading to the many electron Schrödinger equation\([94]\).

\[
H \psi_{\text{elec}}(r_1, r_2, \ldots, r_n) = E \psi_{\text{elec}}(r_1, r_2, \ldots, r_n)
\] (2.10)

The Hamiltonian operator is given in equation 2.11 and consists of three terms. The first corresponds to the kinetic energy, the second corresponds to the external potential, and the third corresponds to the electron-electron potential. The external potential is simply the Coulombic interaction between the electrons and the atomic nuclei.

\[
H = -\frac{1}{2} \sum_i \nabla_i^2 + V_{\text{ext}} + \sum_{i<j}^{N} \frac{1}{|r_i - r_j|}
\] (2.11)

The variational principle is then used to approximate the solution to the Schrödinger equation by analysing the expectation value of the Hamiltonian. The total energy of a system with a given wavefunction \(\psi\) can be evaluated as:
\[ E[\psi] = \int \psi^* H \psi dx = \langle \psi | H | \psi \rangle \]  \hspace{1cm} (2.12)

where \( E[\psi] \) indicates that the energy is a functional of the wavefunction and depends on the form of the function. The variational principle means that the energy of a trial wavefunction \( \psi \) can never be lower than the energy of the true ground state \( (E_0) \). Hence, by analysing the expectation value of all the possible wavefunctions, the ground state wavefunction can be determined as it minimises the total energy. This gives the ground state wavefunction \( (\psi_0) \).

\[ E[\psi_1] \geq E_0 \]  \hspace{1cm} (2.13)

Even with the approximations outlined above, the many electron Schrödinger equation can only be solved for the simplest of systems due to the number of variables scaling exponentially with the number of electrons. This means it is not practical for performing electronic structure simulations. Further approximations and new methods are introduced to simplify the many electron Schrödinger equation and reduce the number of variables. One such method is density functional theory (DFT).

### 2.2.1 Density Functional Theory

Density Functional Theory (DFT) is derived from the many electron Schrödinger equation and is currently the most widely used method for studying the electronic structure of solids and molecules. This is largely due to the approach proposed by Hohenberg and Kohn [95] in 1964, and Kohn and Sham [96] in 1965. The fundamental statement of DFT is that any property of a system can be viewed as a functional of the ground state electron density. This in turn determines all the information in the many-body wavefunctions for the ground state and all excited states.
The two main theorems of DFT are:

- **Theorem 1**: The external potential $V_{\text{ext}}$ is uniquely determined by the electron density $\rho(r)$. Hence the total energy is a unique functional of the density $E[\rho]$.

- **Theorem 2**: The density which minimises the energy is the ground state density.

The theorems also imply that the charge density uniquely determines the Hamiltonian. The Hamiltonian operator is calculated from the external potential, the total number of electrons, and their positions. The electron-charge density is sufficient to provide all of this information, as explained through spectroscopic observations made by E B Wilson, given below [94]:

- The integral of the electron density over space gives the total number of electrons.
- There is a sharp peak in the electron density at the nuclei, thus providing their positions.
- The intensity of a peak determines the charge of the nucleus.

Hence, the total energy of the system can be re-written as three functionals of the electron-density, $\rho$:

$$
E[\rho] = T[\rho] + V_{\text{ext}}[\rho] + V_{\text{ee}}[\rho] \quad (2.14)
$$

where $T$ is the kinetic energy, $V_{\text{ext}}$ is the external potential and $V_{\text{ee}}$ is the electron-electron potential. $V_{\text{ext}}$ can be easily calculated, however the kinetic energy and electron-electron potential are difficult to formulate as there are no known analytical forms of the functionals. To simplify the problem, the Kohn-Sham approach is applied. This transforms
the problem from a system of $n$ interacting electrons, to a system of $n$ non-interacting electrons, which interact within an effective mean field potential. This allows the kinetic energy and electron-electron potential to be re-written as independent particle equations $T_s$ and $V_H$. The difficult to treat many-body terms are incorporated into an exchange-correlation (XC) functional of the density, known as the exchange-correlation energy ($E_{xc}$). By solving the equations, one finds the ground state density and energy of the original interacting system with the accuracy limited only by the approximations made in the exchange and correlation.

$$E[\rho] = T_s[\rho] + V_{\text{ext}}[\rho] + V_H[\rho] + E_{xc}[\rho]$$

(2.15)

where $V_H[\rho]$ is the Hartree energy, and $E_{xc}[\rho]$ is the exchange-correlation functional. The exchange-correlation functional can be seen as the error introduced to the calculation through making the Kohn-Sham approximation.

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - V_H[\rho])$$

(2.16)

The form of $E_{xc}[\rho]$ is the only unknown in the DFT calculation. If the form of the XC functional was known, then the exact ground state energy and density could be calculated. How accurately $E_{xc}$ is approximated determines the accuracy of the DFT calculation. This means that DFT calculations are characterised by the method used to estimate the exchange and correlation.

### 2.2.2 Exchange-Correlation Functionals

Describing the exact form of the XC functional is crucial for accurately describing a system in terms of DFT. However this is very difficult with the exact form only being known
for the uniform electron gas. Hence, the uniform electron is often used as a guide to approximate the XC energy of other systems. This has given rise to functionals such as the local density approximation (LDA)[96] and the generalised gradient approximation (GGA). One of the most important properties that these approximations should have is that the exchange energy and the Coulomb potential should cancel in a one electron system[97][98]. This should mean that there are no self-interactions in the total energy, however, none of the commonly used approximations have this property. This means that the calculated properties of materials, such as electronic band gaps, have an energy error associated with an electron interacting with itself.

The LDA takes the local electron-density of a material at a given point and compares the value of the electron-density of the uniform electron gas. From this an exchange-correlation energy is extrapolated. This is illustrated in Figure 2.2. An additional source of error in the LDA is that it does not take into account the spatial variation of the electron-density in a material i.e. the electron-density of different chemical environments. Relative improvements can be made by using approximations that take this into account. This has lead to the development of GGAs, where the functional not only depends on the electron-density, but also on its gradient. There are several implementations of GGA functionals. One of the most common is the Perdew-Burke-Ernzerhof (PBE)[99], other examples include: Perdew-Wang 91 (PW91)[99], and rPBE, a revised version of PBE designed to improve the description of metallic surfaces [100]. Exchange energies are perfectly described by Hartree-Fock (HF) theory, and hybrid functionals that use non-local exchange from HF theory have been developed. These include the well known Becke, three-parameter, Lee-Yang-Parr (B3LYP) functional[101], which has been shown to reproduce accurately the experimental band-gaps of a wide range of materials [102]. Hybrid functionals can correct for the electronic self-interaction term in LDA and GGA, but are computationally expensive to implement with planewave DFT.
2.3 Electronic Structure in Periodic Systems

The methods used to simplify the many-body Schrödinger equation, and compute the electronic structure of a material have been outlined. There remains the challenge of applying the DFT methodology to the near infinite number of electrons in a solid. Next, the application of DFT to the solid state is described.

2.3.1 Bloch’s Theorem

The largest challenge when considering the solid state is the number of electrons involved. In a solid, the translational periodicity and symmetry of the crystal reduces the problem so that the electronic structure is only calculated for one unit cell. Hence; the higher the symmetry of the system, the fewer degrees of freedom are needed to accurately describe it. This is shown through Bloch’s theorem[103], which shows that the wavefunction of an electron, in an external periodic potential, can be written as the product of a function with the same periodicity of the potential and an imaginary phase factor arising from the translational symmetry:
\[ \psi_k(r) = \exp^{ik \cdot r} u_k(r) = \cos(k \cdot r) u_k(r) + i \sin(k \cdot r) u_k(r) \]  

where \( e^{ik \cdot r} \) is the phase factor, \( r \) is the position, and \( k \) is the wave vector. For any lattice vector \( a_i \) of a simulation cell the equation is written as:

\[ \psi_k(r + a_i) = \exp^{ik \cdot a_i} \psi_k(r) \]  

Through Bloch’s theorem, the original problem of an infinite number of electrons in a solid is reformulated into an equation which is solved for the electrons in one unit cell, with infinite k-points. In order to construct \( u_k(r) \), which has lattice periodicity of \( u_k(r) = u(r+a_i) \), it is convenient to use a linear combination of periodic basis functions. One such functional form is the planewave.

### 2.3.2 Planewaves

The planewave is a mathematical expression of the condensed phase basis set which represents waves propagating with a constant frequency and amplitude. The periodic function \( u_k(r) \) in Bloch’s theorem can be expanded as a Fourier series in the form:

\[ u_i(r) = \sum_G c_{i,G} \exp^{iG \cdot r} \]  

where \( G \) is the set of reciprocal lattice vectors defined by the condition \( e^{iG \cdot a_i} = 1 \) (i=1,2,3). Hence the electronic wavefunction can be written as:

\[ \psi_{i,k}(r) = \sum_G c_{i,k+G} \exp^{i(k+G) \cdot r} \]  

Through these equations it is shown that any wavefunction with index \( k+G \) is identical
to a wavefunction with index $k$. Hence $k$ can be restricted to the first Brillouin zone in reciprocal space. In practice $k$-points on a grid are used for 3D integration of the wavefunctions, with the grid size being a convergence requirement of the DFT calculation. The number of $k$-points required to converge one unit cell varies inversely with simulation volume i.e. a large unit cell requires fewer $k$-points than a small unit cell. The symmetry of the first Brillouin zone can then be applied to further reduce the number of $k$-points required. The number of $k$-points can also vary with the type of system being simulated. Systems such as insulators and semiconductors, where all occupied electronic states are below the Fermi level of the electrons, require fewer $k$-points relative to metallic systems. This is due to electronic states in a metal bisecting the Fermi level. The Monkhurst-Pack method[104] for $k$-point grid sampling is commonly used to sample the wavefunctions in reciprocal space. In addition to the grid of $k$-points, a finer grid is used to store products of the wavefunctions, such as the charge density [105].

The basis set cut-off (energy-cut-off of planewaves) is another convergence requirement of the planewave DFT method. According to equation 2.20, the periodic wavefunction can be expanded to an infinite summation over all possible values of $G$. However the Fourier coefficients $C_{i,K+G}$ for planewaves decreases with increasing values of $|k + G|$. Since low energy kinetic energy terms make a larger contribution to the to the total kinetic energy than high energy terms, the planewave basis set can be stopped at a certain point to only include planewaves that have kinetic energies less than a certain cut-off-energy. The point at which to stop the summation is decided by the kinetic energy cut-off, defined as:

$$\frac{\hbar}{2m} |k + G|^2 < E_{cut} \quad (2.21)$$

A high energy-cut-off means that more planewaves are included in the summation and this leads to a better representation of the wavefunction. In planewave DFT, this value has
to be sufficiently high to ensure that the physics of the system is described to reasonable degree of accuracy. It is found that very high energy-cut-offs are required to reproduce the wavefunctions of electrons close to the atomic nucleus, which adds a large computational cost to the simulation. As the chemistry and physical properties of the system arises from the valence electrons, a solution is to model the core electrons within the frozen core approximation, replacing the nucleus and core electrons with a pseudopotential (PP). The problem can then be solved for the valence electrons alone.

2.4 Pseudopotentials

To a reasonable degree of accuracy, core electrons are not affected by the chemical environment of the atom. Conversely, the chemical environment is not affected by the core. Hence the atom can be modelled as a frozen core, consisting of the nucleus and core electrons, and the remaining valence electrons. Hence the nucleus and core electrons are considered fixed, and a pseudopotential created by replacing the Coulomb potential of the nucleus, with an effective potential of the nucleus screened by the tightly bound core electrons[106]. Pseudopotentials are derived from all-electron calculations in order to keep the same energy of the all-electron wavefunctions. Through this approach the number of basis functions needed in the calculation can be dramatically reduced without substantial loss of accuracy. The schematic in Figure 2.3 shows how the planewave basis is reduced through the pseudopotential approximation. All-electron wavefunctions have nodes close to the atomic nucleus, which require a large number of basis functions to describe. By stating that the all-electron and pseudo-wavefunctions should be the same beyond a certain radial cut-off, \( r_c \), the wavefunctions of the valence electrons are preserved while the wavefunctions close to the atomic core can be made smooth, and node-less.

2.4.1 Normconserving Pseudopotentials

Hamann et al. introduced the concept of normconserving pseudopotentials (NCP) in 1979[107]. Through NCP approach, the all-electron wave function is replaced by a soft
Figure 2.3: Schematic illustration of all-electron and pseudopotentials and their corresponding wavefunctions. The radius at which all-electron wavefunction and potential match the pseudo-wavefunction and potential is $r_c$ [8][9].

node-less pseudo-wavefunction inside the core radius $r_c$, with the restriction that the pseudo-wavefunction must have the same electronic charge (norm) as the all-electron wavefunction. For $r > r_c$ the pseudo and all-electron wavefunction are identical. The procedure for generating a normconserving pseudopotentials is to initially perform an all electron calculation on an isolated atom, in a chosen electronic configuration (not necessarily the ground state). This provides the valence electron eigenvalues and valence electron wavefunctions. A parameterised form of the ionic pseudopotential or pseudo-wavefunction is chosen, the parameters are then adjusted so that the pseudo-atom calculation gives the same valence electron eigenvalues as the all-electron atom beyond the specified $r_c$.

The use of the NCP approach allows the wavefunctions to be expanded using fewer
planewaves. Despite this, the NCP method still requires a large number of planewaves to describe atoms with highly localised electrons such as 2p elements, and 3d transition metals. For elements with highly localised electrons, the planewave energy-cut-off can be decreased by increasing the radius of $r_c$. This leads to a loss in accuracy. Hence it is generally not possible to create a pseudo-wavefunction that is significantly smoother than the all-electron wave function for these elements. A solution was developed by Vanderbilt[108] who developed the ultrasoft pseudopotential (USP)

### 2.4.2 Ultrasoft Pseudopotentials

By violating the normconservation constraint, softer pseudopotentials with a lower planewave basis energy-cut-off can be created. Pseudopotentials created through this method are called ultrasoft pseudopotentials (USPs). Softness is achieved by removing some of the charge associated with the core electrons and introducing localised atom centred augmentation charges, which in turn compensates for the resulting charge deficit. The electron density can thus be subdivided into a soft part, extending through the unit cell, and a hard part localized in the core regions. USPs are more computationally demanding due to the additional fast Fourier transform (FFT) grids needed to store the augmentation charges. Hence, some types of DFT calculations, including density function perturbation theory (DFPT) [109] (which require products of the augmentation charges) cannot currently be performed using USPs.

### 2.5 Determining Equilibrium Lattice Parameters

The simplest example of how the total energy of a system varies with structure is a cubic crystal with a single lattice parameter e.g. cubic zirconia (c-ZrO$_2$) or nickel. Changing the lattice parameter changes the volume of the unit cell, and the volume that minimises the total energy gives the equilibrium volume, and by proxy, the lattice parameter. When the crystal is not at equilibrium, a pressure is exerted on the cell which can lead to ex-
pansions or compressions. The bulk modulus \( B_0 \) is a measure of a substance’s resistance to uniform compression, and is defined as the ratio of the infinitesimal pressure increase to the resulting decrease in volume. The bulk modulus can be calculated from fitting the Birch-Murnaghan equation of state (equation 2.22 [110]) to a volume vs energy curve calculated from \textit{ab initio} simulations. The results can then be compared to experiments and all-electron full potential-linearized augmented planewave (FP-LAPW) calculations, allowing the accuracy of the planewave-pseudopotential method to be determined.

\[
E(v) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^3 B_0' + \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^2 \left[ 6 - 4 \left( \frac{V_0}{V} \right)^{2/3} \right] \right\} \quad (2.22)
\]

2.5.1 Optimal Atomic Positions - Geometry Optimisation

In addition to the lattice parameters of a crystal, the equilibrium structure is dependant on the positions of the atomic nuclei in a given cell. At the equilibrium position there are no net forces acting on any of the atomic nuclei. If the forces acting on the atoms at a given atomic configuration are calculated, then the atoms may be relaxed towards their equilibrium positions. The force acting on an atom is given by the gradient of the potential energy surface (PES). To minimise the total energy and the forces, each atom is moved in the direction of the force. The charge density and forces are then recalculated after each set of atomic movements, and the process iterated until the atomic positions have converged with respect to the forces and the gradient of the PES. Calculations of this type are commonly referred to as geometry optimisations.

Geometry optimisations can be computationally intensive. The complexity of the task is reduced if a the user has a good initial guess for the optimal geometry. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm is commonly used to minimise the forces.
and the gradient of the PES. Other methods include damped molecular dynamics. Forces are typically minimised to a user defined force convergence tolerance. Finding the optimal geometry of a structure is not a trivial task. For all but the simplest systems, the large number of degrees of freedom prevents a complete investigation of the PES. Many local minima exist and characterising the global minimum can be challenging. In addition, the forces acting on the ions are zero at the saddle points (maxima) of the PES. This means that unstable structures can be calculated as equilibrium structures. The mechanical stability of structures can be assessed by calculating the normal modes of vibration, outlined below.

2.6 Vibrational Properties and Lattice Dynamics

The vibrational properties of a crystal determine a wide range of properties including: thermal conductivity, infra-red (IR), Raman and Neutron scattering. Vibrational properties are closely linked to the forces acting on atoms. Hence, theory is often used to compliment experimental investigations and used to assign spectral peaks[111]. Low vibrational frequencies can indicate phase transition mechanisms, while ab initio methods can predict the presence of imaginary vibrational modes which imply a structure is mechanically unstable with respect to a set of atomic motions. Following the eigenvector of an imaginary vibrational mode can lead to more stable structure.

2.6.1 Lattice Dynamics and Phonons

The vibrational properties of an equilibrium structure may be determined by finding the variation of the energy with respect to ionic displacements[112]. For small atomic displacements, the harmonic approximation applies. This assumes that the PES is quadratic and described by a simple Hookian potential. This is given by the third term in equation 2.23, which shows the total energy of the system as an expansion around the equilibrium positions of the atoms.
\begin{equation}
E = E_0 + \sum_{\kappa,\alpha} \frac{\delta E}{\delta U_{\kappa,\alpha}} + \frac{1}{2} \sum_{\kappa,\alpha,\kappa',\alpha'} U_{\kappa,\alpha} H^{\kappa,\kappa'}_{\alpha,\alpha'} U_{\kappa',\alpha'} + \ldots \ldots \tag{2.23}
\end{equation}

where \( U_{\kappa,\alpha} \) is the vector of atomic displacements, and \( H^{\kappa,\kappa'}_{\alpha,\alpha'} \) is a Hessian matrix of force constants. The force constants matrix contains all of the force constants (k) for the movement of one atom relative to another. The force constants matrix is 3N dimensional, where N corresponds to the number of atoms. At the maxima and minima of the PES, the forces, \( \frac{\delta E}{\delta U_{\kappa,\alpha}} \) are equal to zero and higher order anharmonic terms are neglected within the harmonic approximation. The equation is hence simplified to:

\begin{equation}
E = E_0 + \frac{1}{2} \sum_{\kappa,\alpha,\kappa',\alpha'} U_{\kappa,\alpha} H^{\kappa,\kappa'}_{\alpha,\alpha'} U_{\kappa',\alpha'} \tag{2.24}
\end{equation}

The normal modes of vibration are simply the frequencies of the simple harmonic oscillator and are calculated from the force constants matrix using equation 2.25. The force constants matrix, \( H^{\kappa,\kappa'}_{\alpha,\alpha'} \), is converted into a dynamical matrix, \( D^{\kappa,\kappa'}_{\alpha,\alpha'} \) by dividing by the masses of the atoms (equation 2.26), this is then diagonalised using the eigen equation. The eigenvectors give the atomic motions of the normal modes of vibration, while the square-roots of the eigenvalues give the vibrational frequencies. As the dynamical matrix is 3N dimensional, it follows that there are 3N normal modes of vibration.

\begin{equation}
\omega^2 = \frac{1}{4 \pi^2} \frac{k}{m} \tag{2.25}
\end{equation}

\begin{equation}
D^{\kappa,\kappa'}_{\alpha,\alpha'} = \frac{H^{\kappa,\kappa'}_{\alpha,\alpha'}}{\sqrt{M_{\kappa} M'_{\kappa}}} \tag{2.26}
\end{equation}

Normal modes of vibration refer to the classical treatment of vibrational frequencies, and can be calculated using simple empirical atomistic potential models. Assuming Born von Karman periodic boundary conditions and substituting \( U_{\kappa,\alpha} \) for a planewave representa-
tion, \( U_{\kappa,\alpha} = \epsilon_{m\kappa,\alpha} \exp(igR_{\kappa,\alpha} - \omega t) \), the classical energy expression can be transformed into a quantum mechanical Hamiltonian for nuclei, where the dynamical matrix is calculated for each q-point (q-points are similar to a k-points but for nuclei and forces rather than electronic wavefunctions). q-points are sampled for the first Brillouin zone in the same way that the electronic wavefunction is sampled. Under the harmonic approximation, the nuclear wavefunction is separable by mode transformation, where each mode satisfies the quantum harmonic oscillator for the Schrödinger equation, with energy levels \( E_{m,n} = (n + \frac{1}{2})\hbar\omega_m \). In crystals, the quantum excitations of modes are known as phonons.

For a mechanically stable equilibrium structure, all atomic motions lead to an increase in the total energy. The phonon modes of a mechanically stable structure are real, and the frequency determines the stiffness of the atomic motions. Low frequency modes are commonly referred to as “soft”, and imply that atomic motions along a phonon eigenvector are low in energy. However, soft phonons can also imply that a phonon mode is imaginary. Imaginary phonons correspond to atomic motions that decrease in the total energy of the system, and come from the fact that the eigenvalue of the imaginary vibrational mode is negative. Imaginary phonons imply that a structure is unstable and not at equilibrium. An example is c-ZrO\(_2\). The perfect fluorite structure of c-ZrO\(_2\) is a saddle point on the PES, and the forces acting on the atoms sum to zero. However a set of atomic motions can decrease the energy of a system. Hence c-ZrO\(_2\) has a well documented imaginary phonon mode, discussed in the next chapter. Imaginary phonons are represented on a phonon dispersion as phonons with a negative frequency.

In addition to the basic theory of lattice dynamics, a couple of physical effects need to be taken into account to accurately calculate the vibrational modes of a crystal. These include the acoustic sum rule and longitudinal optical - transverse optical splitting effects, discussed in more detail below. Finally, the symmetry of the phonon eigenvector determines if a mode is IR or Raman active. This allows the computed vibrational modes
to be linked to experiments. Symmetric modes cause no change in the polarisation of the crystal. These modes are Raman active. Asymmetric modes cause a change in the polarisation of the crystal and are IR active.

### 2.6.2 Acoustic Sum Rule

The vibrational Hamiltonian is invariant to a uniform translation in space. This symmetry is the origin of the well-known result that any crystal has three acoustic vibrational modes at q = 0 (Γ-point) with a frequency of zero. This is referred to as the acoustic sum rule (ASR), which for the Γ-point dynamical matrix is expressed by equation 2.27.

\[
\sum_{\kappa} D^{\kappa,\kappa'}_{\alpha,\alpha'}(q = 0) = 0 \quad (2.27)
\]

In planewave calculations the translational invariance is broken as atoms translate with respect to a fixed FFT grid, so the sum rule is never exactly satisfied. One solution is to increase the FFT grid parameters in order to store a more accurate electronic charge density and reduce the translational variance. This can be computationally expensive. An alternative solution is to apply a transformation to the force constants matrix so that it exactly satisfies the ASR. This is achieved by adjusting the frequency of the acoustic modes to zero, without effecting the optical modes.

### 2.6.3 Longitudinal Optical - Transverse Optical Splitting

For crystals with cubic symmetry, the DFT phonon Hamiltonian predicts the presence of a triply degenerate optical mode at the Γ-point. Two modes correspond to a transverse motion of the atoms, and one corresponds to a longitudinal motion, as pictured in Figure 2.4. However, the Hamiltonian is incomplete as it fails to capture a physical phenomenon known as longitudinal optical-transverse optical (LO/TO) splitting, which breaks the de-
generacy of the optical modes, caused by a dipole moment induced by atoms vibrating along the LO mode. Vibrations along the LO mode induce an electric field which adds an additional restoring force causing the LO mode to have a higher frequency than the TO modes.

![Figure 2.4: Illustration of the atomic motions associated with longitudinal and transverse waves in a crystal](image)

The Lyddane-Sachs-Teller relation\[113\] may be used to relate the LO and TO frequencies for simple cubic crystals. The frequencies are linked via the static dielectric constant $\epsilon_0$ and the index of refraction $\epsilon_\infty$, as given in equation 2.28.

$$\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\epsilon_0}{\epsilon_\infty}$$ (2.28)

LO-TO splitting at $q = 0$ is accounted for by calculating dielectric permittivity tensor and the Born effective charge tensor. This allows for the optical frequencies to be corrected at the $\Gamma$. 

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2.7 Computational Implementation

The general utility lattice program (GULP)[114] and Cambridge serial total energy package (CASTEP)[115][116] software packages are used to implement empirical atomistic potential models and DFT methods respectively. Thorough reviews of both software packages can be found in "First principles methods using CASTEP" and "GULP: A computer program for the symmetry adapted simulation of solids". Both codes are widely used by members of the United Kingdom (UK) Car-Parinello consortium (UKCP) and Materials Chemistry Consortium (MCC) and implemented on a number of high power parallel computers including the UK super computer; ARCHER (preceded by HECTOR). The codes are also run locally on the Imperial College London (ICL) high performance computing facility computers: cx1 and cx2.
Chapter 3

Parent Materials and Computational Details

This chapter outlines the convergence requirements of; the DFT calculations, the parameters of the empirical atomistic potential models, density functional perturbation theory (DFPT) phonon calculations, and the equations used to normalise the formation energies of the YSZ defect structures to the energies of the parent materials. The DFT method is initially used to reproduce the bulk crystal properties of: monoclinic zirconia (m-ZrO$_2$), tetragonal zirconia (t-ZrO$_2$), cubic zirconia (c-ZrO$_2$), and bixbyite yttria (Y$_2$O$_3$). These materials are studied as they are used to synthesize yttria stabilised zirconia (YSZ), the main focus of this thesis. Through calculating the energetics of the three low pressure phases of ZrO$_2$, the formation energies of the YSZ defects (studied in later chapters) can be compared to these bulk crystals allowing large amounts of energetic data to be collected. Within this chapter, a brief description of the parent materials and their crystal structures and properties is given, followed by the convergence requirements of the DFT calculations.

Within the planewave pseudopotential density functional theory (PWP-DFT) formalism, the material systems are converged to a suitable degree of accuracy with respect to planewave cut-off-energy (basis-set) and k-points. All DFT calculations are performed with the the Perdew-Burke-Ernzerhof (PBE) implementation of the generalised gradient approximation (GGA) exchange-correlation functional[99]. Ultrasoft pseudopotentials (USPs) are used for all calculations apart from DFPT, which is implemented with norm-conserving pseudopotentials (NCPs). As DFPT phonon calculations are only performed on the c-ZrO$_2$ phase, the convergence criteria of the NCPs are only tested in the c-ZrO$_2$
cell. The accuracy of the PWP-DFT method is tested against equivalent all-electron full-potential linearised augmented planewave (FP-LAPW) DFT calculations. Details of the pseudopotentials are listed in the Appendix. Self-consistent field (SCF) iterations were considered converged when the energy changed by less than $5 \times 10^{-9}$ eV per cell for total energy calculations and $1 \times 10^{-10}$ eV per cell for phonon calculations. Strain relaxed defect structures of YSZ were obtained through Broyden-Fletcher-Goldfarb-Shanno (BFGS) geometry optimisations converged to 0.05 eVÅ$^{-1}$ under constant lattice constant and no symmetry constraints. Broyden density mixing, which mixes the output density of a number of previous SCF iterations using the quasi-Newton relaxation method, was used to produce a new estimate of the charge density for each SCF iteration. Pulay mixing, which mixes the output density with densities from a number of previous SCF iterations using the residual minimisation direct inversion in the iterative subspace (RMM-DIIS) method, was used instead of Broyden mixing when structures had poor SCF convergence. A density mixing cut-off-energy, that was twice the value of the planewave cut-off-energy, was used to improve SCF convergence. Symmetry was used to reduce the number of k-points used in reciprocal space.

3.1 Convergence of ZrO$_2$ DFT Calculations

ZrO$_2$ exhibits three main crystal structures under standard pressure [22]. At room temperature it adopts a monoclinic (m), structure and upon heating under goes phase transitions to tetragonal (t), and , cubic (c) phases. The conventional cells of the m, t and c-ZrO$_2$ phases are pictured in Figure 3.1. In this thesis m, t and c-ZrO$_2$ are studied in order to obtain the total energy of a single ZrO$_2$ formula unit within each crystal phase.

c-ZrO$_2$ has the highest symmetry of the three zirconia phases discussed above, and has one ZrO$_2$ formula unit within a primitive cell. Within the crystal structure, Zr$^{4+}$ ions have 8-fold O-coordination. The crystal has a face centered cubic (FCC) fluorite structure
belonging to the space group Fm3M, (international tables of crystallography A (ITCA) no. 225 [117]). At low temperatures the lattice constant can only be determined for stabilised forms of c-ZrO$_2$. Neutron diffraction at 22°C has established the lattice constant of the conventional cell to be 5.086 Å at the composition Zr$_{0.875}$Mg$_{0.125}$O$_{1.875}$ [118]. Room temperature x-ray diffraction of YSZ single crystals prepared at; 8.1, 11.1, 12.1, 15.5, and 17.9 mol% Y$_2$O$_3$, show a range of lattice constants increasing from 5.132 to 5.162 Å with increasing Y$_2$O$_3$ concentration [119]. The same study established the bulk modulus of YSZ single crystals to be in the range of 194 - 254 GPa. High temperature neutron scattering results give a much larger lattice constant due to the thermal expansion of the crystal[120]. GGA FP-LAPW calculations have computed a lattice constant of 5.11 Å and the bulk modulus to be 236 GPa [121].

t-ZrO$_2$ has lower symmetry than c-ZrO$_2$ and has two ZrO$_2$ formula units within its primitive cell. Within this cell, Zr$^{4+}$ ions have 8-fold O-coordination. The crystal has symmetry operations belonging to the space group P42/nmc (ITCA no. 137). t-ZrO$_2$ can be related to c-ZrO$_2$ through considering the mechanical instability of the cubic phase (discussed below in section 3.4). The mechanical instability of c-ZrO$_2$ leads to a distortion of the oxygen anions along a ⟨1 0 0⟩ crystallographic direction, which breaks the cubic symmetry to produce the tetragonal phase[122] (pictured in Figure 3.9). x-ray diffraction at 1357°C has measured the lattice constants, a=b≠c, as a$_0$ = 3.57 Å , and c$_0$ = 5.18 Å [120][123].

The bulk modulus of yttria-stabilised t-ZrO$_2$ polycrystals (YTZP) have been measured over the temperature range 22 - 1500°C, establishing a bulk modulus of approximately 190 GPa [124]. GGA FP-LAPW calculations have computed lattice constants of; a$_0$ = 3.61 Å , and c$_0$ = 5.25 Å , and the bulk modulus to be 226 GPa [121].

m-ZrO$_2$ has the lowest symmetry of the three ZrO$_2$ phases discussed above. The primitive cell of m-ZrO$_2$ has four ZrO$_2$ formula units, where Zr$^{4+}$ ions have 7-fold O-coordination. The crystal is named after the mineral baddeleyite which has symmetry belonging to
the space group $P2_1/c$ (ITCA no. 14). X-ray diffraction at $27^\circ$C has established lattice constants, $a \neq b \neq c$, as $a_0 = 5.145$ Å, $b_0 = 5.2075$ Å, and $c_0 = 5.3107$ Å [120]. The bulk modulus has been measured as 95 - 189 GPa, while GGA FP-LAPW calculations have computed lattice constants of; $a_0 = 5.19$ Å, $b_0 = 5.25$ Å, and $c_0 = 5.35$ Å and a bulk modulus of 218 GPa [121].

![Figure 3.1: Conventional cells of the m (left), t (middle) and c-ZrO₂ (right) crystal phases. Teal = Zr⁴⁺ ions, red = O²⁻ ions. Ions are not drawn to scale.](image)

### 3.1.1 Planewave Cut-off-energy

The planewave cut-off energy is dictated by the hardness of the pseudopotential rather than the chemical environment of the system. This means that once a planewave cut-off-energy (that converges the total energy of the system to a reasonable degree of accuracy) has been determined, it is transferable from one chemical environment to another. Oxygen and zirconium USPs and NCPs were tested within the primitive cell of c-ZrO₂ at the experimental lattice constant. USPs were generated using the CASTEP “on the fly” (OTF) pseudopotential generator [115][125]. Normconserving pseudopotentials (NCPs) from the Bennett-Rappe pseudopotential library [126][127][128] were used. Figure 3.2 shows how the total energy of the system converges as a function of planewave cut-off-energy. Convergence of the c-ZrO₂ system is dependant on the oxygen pseudopotential which has core like 2s and 2p orbitals and require a higher number of basis functions to

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describe. The USPs converge to 0.3 meV per formula unit at an energy-cut-off of 500 eV, while calculations involving the NCPs converge to 0.8 meV at at an energy-cut-off of 800 eV.

Figure 3.2: Convergence of the total energy of c-ZrO$_2$ as a function of planewave cut-off-energy. Blue: USPs, red: NCPs

3.1.2 k-point Convergence

k-point convergence was analysed in the primitive cells of m, t and c-ZrO$_2$ by varying the Monkhorst-Pack (MP) grid [104]. Convergence of the total energy with respect to k-points is independent of the pseudopotentials used. The convergence of the total energy (to 5 significant figures (s.f) as a function of MP grid is recorded in Table 3.1. The total energy of c-ZrO$_2$ converges to 0.03 meV per unit cell with a MP grid of 6x6x6. Similar convergence is achieved for 2x2x2 supercells of the conventional c-ZrO$_2$ cell, m-ZrO$_2$, and t-ZrO$_2$, with MP grids of 3x3x3, 4x4x4 and 8x8x6, respectively. The supercell contains four primitive cells, hence the reciprocal of the supercell is four times smaller than the
reciprocal of the primitive cell, meaning fewer k-points are needed.

Table 3.1: Total energy convergence of c-ZrO$_2$ as a function of k-point MP grid.

<table>
<thead>
<tr>
<th>MP Grid Size</th>
<th>2x2x2</th>
<th>4x4x4</th>
<th>6x6x6</th>
<th>8x8x8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computed Total Energy / eV</td>
<td>-2357.97905</td>
<td>-2357.90879</td>
<td>-2357.90813</td>
<td>-2357.90816</td>
</tr>
</tbody>
</table>

3.2 Determination of ZrO$_2$ Equilibrium Lattice Parameters

The equilibrium lattice parameters and bulk moduli for the three ZrO$_2$ phases were determined by fitting the Birch-Murnaghan equation of state to a total energy vs unit cell volume curves. The equilibrium lattice constants and bulk moduli were then calculated and compared to results of previous GGA FP-LAPW and experimental studies to determine the error in the PWP-PBE-DFT method.

The unit cell volume of c-ZrO$_2$ was varied by changing lattice constant of the primitive cell, increasing from 2.35 Å to 2.7 Å, in increments of 0.05 Å. The t-ZrO$_2$ and m-ZrO$_2$ phases have lower symmetry than the c-ZrO$_2$ phase and have multiple lattice constants. While it is possible to vary the unit cell volume by increasing or decreasing the lattice constants, such a method will yield inaccurate results as it is not possible to predict the ratios between the lattice constants c/a, or even c/b/a. Instead, a set of variable cell geometry optimisations are performed at different external isotropic pressures. This leads to compressions or expansions of the unit cell that change its volume. The results are plotted in Figures 3.3, 3.4 and 3.5 and recorded in Tables 3.2, 3.3, and 3.4, which show the calculated lattice constants and bulk moduli compared to existing literature results.

The computed lattice constants and bulk moduli of c-ZrO$_2$ compare very well to published GGA FP-LAPW results, and fall within the range of experimental values for YSZ.
Figure 3.3: Birch-Murnaghan equation of state fitted to the total energy curves vs cell volume curves of c-ZrO₂. Blue: USPs, red: NCPs

Figure 3.4: Birch-Murnaghan equation of state fitted to the total energy curves vs cell volume curve of t-ZrO₂.

Table 3.2: Lattice constants and bulk moduli of c-ZrO₂

<table>
<thead>
<tr>
<th>Method</th>
<th>Lattice Constants / Å</th>
<th>Bulk Modulus / GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE USPs</td>
<td>5.11</td>
<td>234</td>
</tr>
<tr>
<td>PBE NCPs</td>
<td>5.12</td>
<td>231</td>
</tr>
<tr>
<td>PW91 FP-LAPW[121]</td>
<td>5.11</td>
<td>236</td>
</tr>
<tr>
<td>Experimental (MgSZ)[119][118]</td>
<td>5.086</td>
<td>194 - 254</td>
</tr>
</tbody>
</table>
Figure 3.5: Birch-Murnaghan equation of state fitted to the total energy curves vs cell volume curve of m-ZrO$_2$.

Table 3.3: Lattice constants and bulk moduli of t-ZrO$_2$

<table>
<thead>
<tr>
<th></th>
<th>Lattice Constants / Å</th>
<th>Bulk Modulus / GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE UCPs</td>
<td>3.61, 5.27</td>
<td>150</td>
</tr>
<tr>
<td>PW91 FP-LAPW[121]</td>
<td>3.61, 5.25</td>
<td>226</td>
</tr>
<tr>
<td>Experimental[120][123]</td>
<td>3.57, 5.18</td>
<td>190</td>
</tr>
</tbody>
</table>

Table 3.4: Lattice constants and bulk moduli of m-ZrO$_2$

<table>
<thead>
<tr>
<th></th>
<th>Lattice Constants / Å</th>
<th>Cell angles $\alpha$, $\beta$, $\gamma$ / degrees</th>
<th>Bulk Modulus / GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE UCPs</td>
<td>5.17, 5.24, 5.36</td>
<td>90.0, 99.6, 90.0</td>
<td>178</td>
</tr>
<tr>
<td>PW91 FP-LAPW[121]</td>
<td>5.19, 5.25, 5.35</td>
<td>N/a</td>
<td>218</td>
</tr>
<tr>
<td>Experimental[120]</td>
<td>5.145, 5.2075, 5.3107</td>
<td>90.0, 99.2, 90.0</td>
<td>95 - 189</td>
</tr>
</tbody>
</table>

The PBE-USP and GGA FP-LAPW lattice constants are within numerical error of one another, while the difference between the PBE-USP lattice constant and the experimental lattice constant is 0.024 Å. The difference between the PBE-USP bulk modulus and GGA FP-LAPW bulk moduli is 2 GPa.

The difference between the PBE-NCP lattice constant and the GGA FP-LAPW lattice
constant is 0.01 Å, while it is 0.034 Å compared to the experimental value. The error in the bulk modulus result is 5 GPa compared to the GGA FP-LAPW result and falls within the range of the experimental values.

Interestingly, it appears that there are inaccurate GGA FP-LAPW results for the t-ZrO$_2$ and m-ZrO$_2$ phases in the literature [121]. In the literature study, which used the PW91 XC functional, a set of single point calculations were performed at fixed unit cell volumes to determine the bulk moduli and lattice constants of the m and t phases. While there is a good agreement between the USP PWP-DFT lattice constants and the all-electron lattice constants, the bulk moduli results are in serious disagreement. There is an error of 23% in the bulk modulus of m-ZrO$_2$ and a 34% error in the bulk modulus of t-ZrO$_2$. To determine the reason for this apparent error, the calculations were re-performed using the LDA XC functional and compared to previous LDA FP-LAPW results [123]. These results were in excellent agreement.

This suggests an error in the published GGA work. In particular, the predicted bulk moduli are unusual for GGA calculations. Furthermore, the description of the work is incomplete, as there is no description of how the two and three dimensional parameter space of the tetragonal and monoclinic crystals were explored. This suggests that perhaps a fixed c/a or fixed c/b/a ratio was used, giving rise to inaccurate results.

3.2.1 Relative Energetics of Monoclinic, Tetragonal, and Cubic ZrO$_2$

The energy per ZrO$_2$ formula unit was computed within the monoclinic, tetragonal, and cubic phase and recorded in Table 3.5 (to 2 s.f). The energies are normalised to that of monoclinic zirconia, and compared to previous theory [129]. The PWP-DFT method accurately reproduces the stability of the three phases, showing that the monoclinic phase
is the lowest in energy while the cubic is the highest.

<table>
<thead>
<tr>
<th>Crystal Phase</th>
<th>Monoclinic</th>
<th>Tetragonal</th>
<th>Cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computed Total Energy per ZrO$_2$ unit / eV</td>
<td>0</td>
<td>0.11</td>
<td>0.21</td>
</tr>
<tr>
<td>PW91 Cohesive Energy per ZrO$_2$ unit [129] / eV</td>
<td>0</td>
<td>0.09</td>
<td>0.08</td>
</tr>
</tbody>
</table>

### 3.3 Convergence of Bixbyite Y$_2$O$_3$ DFT Calculations

Bixbyite Y$_2$O$_3$ is studied in order to obtain the total energy of a single Y$_2$O$_3$ formula unit. The energy of a single formula unit is needed as a reference for the formation energies of various YSZ defect structures, including bulk crystals and surfaces, to the energies of the parent materials. This section outlines the convergence requirements of the Y$_2$O$_3$ system using a set of USPs.

Y$_2$O$_3$ has a body centered cubic (BCC) crystal structure with symmetry operations belonging to the space group Ia3-(T$_d^7$) (no. 206). The low temperature crystal structure of Y$_2$O$_3$ is complex and contains two symmetry inequivalent cation sites, within a 40 atom primitive cell. The structure resembles a fluorite structure and is named after the mineral bixbyite. There have been relatively few ab initio studies of Y$_2$O$_3$ [130] with the results of GGA FP-LAPW calculations only recently being published[131]. The lattice constant of Y$_2$O$_3$ has been measured through room temperature x-ray diffraction as 10.603 Å [132] and 10.604 Å [133], while orthogonalised linear combination of atomic orbitals (OLCAO) calculations within the LDA approximation to DFT, have calculated a lattice constant of 10.39 Å . GGA FP-LAPW calculations have calculated a lattice constant of 10.63 Å . Figure 3.6 shows the conventional cell of Y$_2$O$_3$. 
3.3.1 Planewave Cut-off-energy

The planewave cut-off-energy of the oxygen and yttrium USPs were tested within the 40 atom primitive cell of Y$_2$O$_3$ at the experimental lattice constant. USPs were generated using the CASTEP OTF pseudopotential generator [115][125]. As the energy cut-off depends on the core like 2s and 2p states of the oxygen pseudopotential, the cut-off-energy it is expected to converge at the same value as c-ZrO$_2$ (500 eV). Figure 3.7 shows the convergence of the total energy as a function of planewave cut-off-energy. The total energy of Y$_2$O$_3$ converges to 3 meV per formula unit at a planewave cut-off-energy of 500 eV.

3.3.2 k-point Convergence

k-point convergence of Y$_2$O$_3$ was analysed in the primitive cell by varying the Monkhorst-Pack (MP) grid between 2x2x2 and 8x8x8 increasing in increments of 2x2x2. The convergence of the total energy (to 5 s.f) as a function of MP grid is recorded in Table 3.6.
Figure 3.7: Total energy convergence of $Y_2O_3$ as a function of planewave cut-off-energy.

The total energy of the primitive cell of $Y_2O_3$ cell converges to 0.0026 meV per formula unit with a Monkhorst-Pack (MP) grid of 6x6x6.

<table>
<thead>
<tr>
<th>MP Grid Size</th>
<th>2x2x2</th>
<th>4x4x4</th>
<th>6x6x6</th>
<th>8x8x8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computed Total Energy / eV</td>
<td>-27520.98109</td>
<td>-27520.98250</td>
<td>-27520.98164</td>
<td>-27520.98185</td>
</tr>
</tbody>
</table>

3.3.3 Determination of Equilibrium Lattice Parameters

The $Y_2O_3$ convergence criteria were tested by fitting the Birch-Murnaghan equation of state to the total energy energy vs unit cell volume curve. The equilibrium lattice constant and bulk modulus was calculated and compared to the result of previous GGA FP-LAPW and experimental calculations.

The lattice constant of the primitive $Y_2O_3$ cell was varied around the experimental lattice constant. The results are plotted in Figure 3.8 and recorded in Table 3.7. The computed lattice constant and bulk modulus compare very well to published PBE FP-LAPW results and fall in the range of experimental values. The difference between the PBE-USP lattice
constant and the PBE FP-LAPW lattice constant is 0.016 Å, while it is 0.042 Å compared to the experimental value. The difference in the PBE-USP and PBE FP-LAPW bulk modulus is 8 GPa.

![Figure 3.8: Birch-Murnaghan equation of state fitted to the total energy curves vs cell volume curve of Y$_2$O$_3$.](image)

### Table 3.7: Lattice constants and bulk modulus results for Y$_2$O$_3$

<table>
<thead>
<tr>
<th></th>
<th>Lattice Constant / Å</th>
<th>Bulk Modulus / GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE USPs</td>
<td>10.646</td>
<td>144</td>
</tr>
<tr>
<td>PBE FP-LAPW</td>
<td>10.630</td>
<td>136</td>
</tr>
<tr>
<td>Experimental</td>
<td>10.603 - 10.604</td>
<td>144 - 149.5</td>
</tr>
</tbody>
</table>

### 3.4 Convergence of c-ZrO$_2$ Vibrational Frequencies

The convergence of the total energy, lattice constants, and bulk moduli of the ZrO$_2$ polymorphs with respect to planewave cut-off-energy and k-point MP grids have been established. In addition, the convergence of properties such as phonon frequencies can be dependent on numerical parameters such as the self consistent field (SCF) energy convergence criteria, geometry optimisation force convergence tolerance, and the secondary fine grid of points used to store the electronic charge densities and pseudopotentials (FFT
c-ZrO$_2$ has interesting vibrational properties with the low temperature mechanical instability indicated by an imaginary phonon mode at the X-point of the first Brillouin zone. The imaginary X-point phonon mode has been calculated and reported by several authors [134][10][135][136]. Using the PBE approximation to DFT, the frequency of the imaginary mode is calculated as -195 cm$^{-1}$ [135]. Atomic displacements along this imaginary phonon mode lead to the movement of the oxygen anions along a $\langle 1 0 0 \rangle$ crystallographic direction, producing a distortion of the crystal which breaks the cubic symmetry to produce the tetragonal phase [122]. This is illustrated in Figure 3.9, while Figure 3.10 shows the phonon dispersion of c-ZrO$_2$ calculated by Parlinski et al.[10] using the LDA approximation to DFT. The phonon dispersion clearly shows the imaginary phonon at the X-point.

![Figure 3.9](image)

**Figure 3.9:** Cartoons of the cubic and tetragonal cells of ZrO$_2$. The dotted lines show the tetragonal cell within the cubic cell, while arrows indicate the oxygen ion distortion of the X-point imaginary phonon mode and the distortion adopted by the tetragonal phase.

To test the convergence of the phonon frequencies with respect to the FFT grids, the phonon frequencies of c-ZrO$_2$ were calculated within the primitive cell, and a number of different supercells at the experimental lattice constant. Changing from a primitive cell to a supercell changes the FFT and MP grid scales due to the change in reciprocal space.
lattice vectors. For well converged calculations, the small change in grid scales should have no effect on the total energy or the computed properties of the system.

The electron densities and pseudopotential charges were initially stored on a FFT grid, 1.5x finer than that of the MP grid used to represent the Kohn-Sham orbitals. Longitudinal optical - transverse optical (LO/TO) splitting and acoustic sum rule (ASR) transformations were applied to the force constants matrix to correct the phonon frequencies at the Γ point. Phonon frequencies were calculated in 2x1x1 and 2x2x2 supercells of the conventional c-ZrO$_2$ cell. The high symmetry reciprocal space points of the first Brillouin zone X, W and L fold back onto Γ in the 2x2x2 supercell, while X and W fold back onto Γ in the 2x1x1 supercell. Table 3.8 shows how the vibrational frequencies, rounded to the zero decimal places, vary with respect to periodicity of the cell. Note; degenerate modes have been counted once.

Table 3.6 shows that the phonon frequencies significantly change between the primitive and supercells, implying that the calculations are poorly converged with respect to the FFT grid. Interestingly, the supercells are converged with respect to each other but not with the primitive cell. In addition to the lack of convergence, an additional imaginary
Table 3.8: Phonon frequencies of c-ZrO$_2$ under varying periodic boundary conditions

<table>
<thead>
<tr>
<th>Symmetry Point</th>
<th>Primitive Cell</th>
<th>2x2x2 Supercell</th>
<th>2x1x1 Supercell</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma )</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>236</td>
<td>236</td>
</tr>
<tr>
<td></td>
<td>560</td>
<td>565</td>
<td>565</td>
</tr>
<tr>
<td></td>
<td>640</td>
<td>652</td>
<td>652</td>
</tr>
<tr>
<td>( X )</td>
<td>1212</td>
<td>1199</td>
<td>1199</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>126</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>299</td>
<td>308</td>
<td>308</td>
</tr>
<tr>
<td></td>
<td>349</td>
<td>349</td>
<td>349</td>
</tr>
<tr>
<td></td>
<td>543</td>
<td>543</td>
<td>548</td>
</tr>
<tr>
<td></td>
<td>674</td>
<td>678</td>
<td>678</td>
</tr>
<tr>
<td>( W )</td>
<td>140</td>
<td>63</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>126</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>234</td>
<td>236</td>
<td>236</td>
</tr>
<tr>
<td></td>
<td>252</td>
<td>253</td>
<td>253</td>
</tr>
<tr>
<td></td>
<td>447</td>
<td>453</td>
<td>453</td>
</tr>
<tr>
<td></td>
<td>583</td>
<td>588</td>
<td>588</td>
</tr>
<tr>
<td></td>
<td>648</td>
<td>652</td>
<td>652</td>
</tr>
</tbody>
</table>

phonon mode is computed at the W-point of the first Brillouin zone. This is the first time an imaginary phonon mode at the W-point has been calculated, and is discussed in more depth in chapter *Chemical Descriptors of Yttria Stabilised Zirconia at Low Defect Concentration*. To test the effect of the FFT grid on the calculated phonon frequencies, the atoms were translated across the primitive unit cell using a small displacement vector. The magnitude of the vector was 0.01 Å. Moving the atoms across the cell changes the position of the atomic cores relative to the MP and FFT grids, enabling small changes in the potential energy surface to be detected. In addition, the phonon frequencies were re-calculated for each new position of the atoms in the primitive cell. It is found that the imaginary phonons are the most significantly affected by the displacement of the atoms across the cell. Figure 3.11 shows how the total energy, and the vibrational frequencies of the imaginary phonons modes change as a function atomic displacement relative to the grid scales.
While the total energy changes by as little as 0.15 meV, the small dip in the total energy surface has a drastic effect on the vibrational frequency of the W-point imaginary phonon. The phonon frequency changes from approximately \(-50 \text{ cm}^{-1}\) to \(50 \text{ cm}^{-1}\). It is clear that the grid scales used in the phonon calculation have a significant effect on the computed imaginary frequencies. In addition, a new set of NCPs and different XC-functionals, including LDA and rPBE, were tested to confirm this result. Changing the NCPs has no effect on this result, while using the LDA XC functional smooths the potential energy surface and converges the vibrational frequencies in the primitive cell and supercells. Using LDA, the W-point imaginary phonon is calculated as real, which matches the result reported by Parlinski et al. [10]. rPBE reproduces the PBE results.

The FFT grid was increased to a grid that was 2.5x denser than the k-point MP grid. The phonon frequencies were re-calculated in the primitive, 2x1x1, and 2x2x2 supercells at the experimental lattice constant. The frequencies of the imaginary modes are recorded in Table 3.9. By increasing the FFT grid to a grid of points that is 2.5x finer than the
k-point MP grid, the frequencies of the imaginary phonon modes converge to a reasonable degree of accuracy. There is only a small difference between the frequencies computed in the primitive and supercells.

Table 3.9: Imaginary phonon frequencies of c-ZrO$_2$ calculated with different periodic boundary conditions, and a FFT grid scale five 2.5x finer than the k-point MP grid.

<table>
<thead>
<tr>
<th>Symmetry Point</th>
<th>Primitive Cell</th>
<th>2x2x2 Supercell</th>
<th>2x1x1 Supercell</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>i211</td>
<td>i209</td>
<td>i209</td>
</tr>
<tr>
<td>W</td>
<td>i29</td>
<td>i18</td>
<td>i18</td>
</tr>
</tbody>
</table>

In addition to the error introduced by the fine grid of points, errors in the computed phonon frequencies are introduced when switching between the experimental lattice constant, USP PBE-DFT minimum energy lattice constant, and NCP PBE-DFT minimum energy lattice constant. As the intention is to establish the defect structures of YSZ at the dilute limit and to provide the basis for surface studies, all defect structure calculations were performed at the minimum energy DFT lattice constant of the parent materials. The lattice constant of c-ZrO$_2$ increases by 0.2% when switching to NCPs from USPs. Table 3.10 shows how the vibrational frequencies of the imaginary phonon modes change with changing lattice constant.

Table 3.10: Imaginary phonon frequencies of c-ZrO$_2$ calculated at the experimental, USP PBE-DFT and NCP-DFT lattice constant.

<table>
<thead>
<tr>
<th>Lattice constant of 2x2x2 supercell / Å</th>
<th>Imaginary Frequency X-point / cm$^{-1}$</th>
<th>Imaginary Frequency W-point / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>i209</td>
<td>i18</td>
</tr>
<tr>
<td>USPs</td>
<td>i217</td>
<td>i65</td>
</tr>
<tr>
<td>NCPs</td>
<td>i220</td>
<td>i78</td>
</tr>
</tbody>
</table>

Changing from the USP PBE-DFT lattice constant to the NCP PBE-DFT lattice constant causes a small change in the computed vibrational frequencies of the W and X-point
imaginary phonons. The difference in energy between the computed X-point imaginary
phonon using USPs and NCPs is approximately 0.4 meV. This is not significant to affect
the quantitative results determined from the USP PBE-DFT force constants matrix, com-
puted in later sections. In contrast, switching from the minimum energy USP PBE-DFT
lattice constant to the experimental lattice constant causes a large shift in the frequency
of the W-point imaginary phonon mode.

3.5 Yttria, Zirconia and Oxygen Empirical Atomistic
Potentials

In addition to DFT, the total energy of YSZ is modeled using a Born-Mayer-Huggins
(BMH) (equation 3.1) polarisable shell model based on formal ionic charges which has
been used by several authors [22][137][138][139] to model defects in zirconia. The Zr$^{4+}$ -
O$^{2-}$ interaction parameters were determined by Dwivedi and Cormack [80] by fitting a
potential to the experimental lattice and dielectric constants of t-ZrO$_2$. Those for Y$^{3+}$ -
O$^{2-}$ and O$^{2-}$ - O$^{2-}$ were determined by Lewis and Catlow [140]. In addition to t-ZrO$_2$,
the Zr$^{4+}$ - O$^{2-}$ potentials were shown to reproduce accurately the experimental lattice
constants of stabilised c-ZrO$_2$, but not m-ZrO$_2$, which is unstable with respect to an
orthorhombic phase. The Y$^{3+}$ - O$^{2-}$ potential has been shown to reproduce accurately
the experimental lattice constants of bixbyite Y$_2$O$_3$ [22]. The O$^{2-}$ - O$^{2-}$ interaction has no
Coulomb attraction and is described by a Buckingham potential alone. Calculations using
these potentials reproduce the fact that NNN type YSZ defect structures are more stable
than NN type structures [139][22]. Calculations involving the potentials are performed at
the experimental lattice constant of c-ZrO$_2$. The parameters of the potentials are given
in Tables 3.11 and 3.12 [22].

$$\varphi(r) = \frac{q_a q_b}{r} + A \exp(-r/\rho) - \frac{B}{r^6}$$

(3.1)
An interesting feature of the Zr$^{4+}$ - O$^{2-}$ shell model is the presence of a polarsable Zr$^{4+}$ ion. This enables the charge of the Zr$^{4+}$ ion to change upon a relaxation of the atomic shells. The degree of achievable polarisation for Zr$^{4+}$ is small, which is reflective of the small core like nature of Zr$^{4+}$ ions which have a Pauling radius of 80pm[141]. The spring constant (k) for Zr$^{4+}$ polarisablity is 169.617 eV/Å$^{-2}$. This is in contrast to the large O$^{2-}$ ion which has a Pauling radius of 140pm[141]. The spring constant for the polarisability of the O$^{2-}$ ion is 27.29eV/Å$^{-2}$.

The potential energy curves of the Born-Mayer-Huggins and Buckingham potentials are plotted in Figure 3.12 and 3.13. Figure 3.12 shows that the attraction between Zr$^{4+}$ and O$^{2-}$ ions is greater than the attraction between the Y$^{3+}$ and O$^{2-}$ ions, but the Y$^{3+}$ - O$^{2-}$ potential has a larger repulsive energy term. The potentials predict equilibrium bond lengths of 1.46 Å and 1.69 Å for Zr$^{4+}$ - O$^{2-}$ and Y$^{3+}$ - O$^{2-}$ respectively. The Buckingham potential for the O$^{2-}$ interactions predicts an equilibrium interatomic distance of 1.24 Å.
3.6 Definition of Formation Energies

The defect formation energy is the energy associated with introducing one Y$_2$O$_3$ defect into a ZrO$_2$ system, and can be defined intuitively from chemical and physical concepts. In this thesis, the defect formation energies are calculated for a number of systems, including; bulk crystals at 3.2 and 6.7 mol% Y$_2$O$_3$, and 3.2 mol% Y$_2$O$_3$ YSZ surfaces. By
comparing the defect formation energies in different systems, research questions such as; “are Y\textsubscript{2}O\textsubscript{3} defects attractive or repulsive?” , and “does Y\textsubscript{2}O\textsubscript{3} segregate to the surface of YSZ?” can be addressed.

### 3.6.1 Defect Formation Energy in a Bulk Crystal

For defects modeled in bulk crystals, the formation energy per Y\textsubscript{2}O\textsubscript{3} defect is defined by equation 3.2, where \( E_{\text{defect}} \) is the total energy of the supercell with Y\textsubscript{2}O\textsubscript{3} defects, \( n_0 \) the number of ZrO\textsubscript{2} formula units, and \( n_1 \) the number of Y\textsubscript{2}O\textsubscript{3} defects in the supercell. \( E_{ZrO_2} \) is defined as the energy of a bulk formula unit of ZrO\textsubscript{2} calculated at the USP PBE-DFT equilibrium lattice constants of m, t, or c-ZrO\textsubscript{2}, while \( E_{Y_2O_3} \) is the energy of a bulk formula unit of Y\textsubscript{2}O\textsubscript{3} calculated at the USP PBE-DFT equilibrium lattice constant of bixbyite Y\textsubscript{2}O\textsubscript{3}.

\[
\Delta E_{f\text{defect}} = \frac{1}{n_1} \left( E_{\text{defect}} - n_0 E_{ZrO_2} - n_1 E_{Y_2O_3} \right) \quad (3.2)
\]

### 3.6.2 Defect Formation Energy in a Surface

The formation energy of a YSZ surface is dependent on an additional surface energy. Surfaces are modeled within a slab model, where the crystal is infinite in two dimensions and has periodic images in the third. Additional convergence requirements are required for slab models, and these are discussed in later sections. It is not possible to directly calculate the surface energy of a YSZ surface, as the surface energy depends on the distribution of the defects. It is however possible to calculate the surface energy of a pure ZrO\textsubscript{2} surface and define the defect formation energy relative to this. The formation energy of any surface is the total energy of the slab model, minus the energy of \( n \) formula units calculated within the equivalent bulk crystal. This is defined for ZrO\textsubscript{2} in equation 3.3, where \( E_{ZrO_2\text{slab}} \) is the total energy of the ZrO\textsubscript{2} slab, \( n_0 \) is the number of ZrO\textsubscript{2} formula...
units, and \( E_{ZrO_2} \) the energy of a bulk \( ZrO_2 \) formula unit. The surface energy is commonly normalised to the surface area of the slab \( (A_s) \), allowing slab models with different periodic boundary conditions to be compared. A factor of a half is included to account for the fact that there are two identical surfaces in a slab model.

\[
\Delta E_{fZrO_2-surface} = \frac{1}{2A_s} (E_{c-ZrO_2\text{slab}} - n_0E_{ZrO_2})
\] (3.3)

The formation energy of defect a \( Y_2O_3 \) defect in a YSZ slab model is given by equation 3.3. \( E_{YSZ\text{slab}} \) is the total energy of the defective YSZ slab, \( E_{ZrO_2\text{slab}} \) is the total energy the equivalent undoped \( ZrO_2 \) slab, \( n_0 \) is the number of \( ZrO_2 \) units in the slab, and \( n_1 \) is the number of \( Y_2O_3 \) defects in the YSZ slab.

\[
\Delta E_{fYSZ-surface-defect} = \frac{1}{n_1} (E_{YSZ\text{slab}} - E_{ZrO_2\text{slab}} - n_1E_{Y_2O_3})
\] (3.4)

Binding energies are calculated in accordance with equation 3.5, where \( E_{\text{water-on-YSZ-surface}} \) is the total energy of a water molecule adsorbed to the YSZ surface, \( E_{YSZ-surface} \) is the total energy of the YSZ surface, and \( E_{H_2O} \) is the total energy of an isolated water molecule.

\[
E_{binding} = E_{YSZ-surface} + E_{H_2O} - E_{\text{water-on-YSZ-surface}}
\] (3.5)

### 3.7 Statistical Analysis

Correlations between data sets were analysed using regression analysis. Correlations are described by the coefficient of determination \( (R^2) \) which is the square of the Pearson correlation coefficient. The coefficient of determination has a value between 0 and 1, where 0 is no correlation and 1 is a perfect correlation.
Chapter 4

Chemical Descriptors of Yttria Stabilised Zirconia at Low Defect Concentration

This chapter outlines the methodology used to generate a database of symmetry inequivalent 3.2mol% YSZ defect structures, and the chemical descriptors determined from studying them. 3.2 mol% YSZ is chosen as a simple system to investigate, as the combinatorial complexity of 6.7 mol% and higher dopant concentration systems challenges the evaluation the Born-Mayer-Huggins and DFT energies due to additional defect-defect interactions. The chemical descriptors, based on electrostatics and strain effects, facilitate the creation of structures needed for more complicated models including: multiple defects, and surfaces. The methodology developed in this chapter is applied in later chapters.

Doping c-ZrO$_2$ with Y$_2$O$_3$ is isoelectronic as two Zr$^{4+}$ ions are replaced by two Y$^{3+}$ ions, with charge neutrality maintained by the formation of an oxygen vacancy (V$_{o}$). In Kröger-Vink notation this is:

$$Y_2O_3 \xrightarrow{ZrO_2} 2Y'_Zr + V'_o + 3O'_o$$

(4.1)

Where $Y'_Zr$ indicates a yttrium ion on a zirconium lattice site with a negative charge, $V'_o$ indicates a vacancy on an oxygen lattice site with +2 charge, and $O'_o$ indicates lattice oxygen ions. The $V'_o$ facilitates the conduction of $O^{2-}$ ions in the lattice and therefore the conductivity is dependent on the $Y_2O_3$ concentration. For low concentrations the ionic conductivity rises rapidly with the number of defects but reaches a maximum at
8mol%[20]. It has been argued that for higher concentrations inter-defect interactions reduce the conductivity with the increasing electrostatic interaction between dopant cations and vacancies being the dominant factor[19][21]. The local atomistic structure and distribution of the dopants in YSZ has been the topic of much theoretical and experimental research. Based on diffuse neutron scattering results it has been reported that $V_\circ$ preferentially associate in pairs along $\langle 1\ 1\ 1 \rangle$ directions at dopant concentrations between 10 and 24 mol% without forming a phase with long range order[20][78][142]. Theoretical support for the short range ordering of vacancies in $\langle 1\ 1\ 1 \rangle$ directions has also been provided by DFT calculations[143][144][12][138]. In addition the electron paramagnetic resonance (EPR) spectrum of YSZ contains a prominent trigonal (T centre) peak in samples that have been chemically reduced or exposed to ionizing radiation[145][146][147][148]. This peak has been assigned to a vacancy-vacancy pair lying in a $\langle 1\ 1\ 1 \rangle$ direction neighbouring a Ti$^{3+}$ impurity[149][150][151].

The O-coordination of metal ions within YSZ has also been studied. Early work suggested that a nearest neighbour (NN) type defect structures, with $V_\circ$ in the first coordination shell of Y$^{3+}$ was prevalent on the basis of neutron diffraction, x-ray absorption fine spectra (EXAFS) and a simple point charge model[152][153][154][155]. In the simple point charge model, $V_\circ$ and Y$^{3+}$ ions have effective charges relative to the lattice ions of +2 and -1 respectively and thus have an effective attractive interaction, leading to the prediction that low energy structures with the $V_\circ$ in the first O-coordination sphere of yttrium[152][153][154][155]. More recently it has been established through EXAFS[156][157][158], solid state $^{89}$Y-MAS-NMR[159], and theoretical models based on DFT[160] and cluster expansion thermodynamics[161], that in general, Y$^{3+}$ ions have an 8-fold O-coordination while Zr$^{4+}$ ions have 7-fold O-coordination. This tendency is also apparent in the low temperature monoclinic ground state of zirconia[160]. These results are consistent with next nearest neighbour (NNN) type defect structures, where the $V_\circ$ is found in the first O-coordination sphere of Zr$^{4+}$ and the second O-coordination sphere of Y$^{3+}$. 

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The $^{89}$Y-MAS-NMR data is particularly clear, as the observation of an intense 8-fold O-coordination $^{89}$Y peak establishes that the V$_o$ avoids the first coordination shell of Y$^{3+}$ up to concentrations of around 12.5 mol%. This observation is inconsistent with a simple point charge model of the ionic interactions.

While the preference for Zr$^{4+}$ to have 7-fold and Y$^{3+}$ 8-fold O-coordination is now established, this does not define the relative positions of the Y$^{3+}$ and V$_o$ species. Many possible defect arrangements and orientations are consistent with these requirements. Through x-ray and neutron diffraction it is possible to deduce that the defect structure of YSZ is highly disordered with multiple distinct defect clusters. Establishing the relative positions of Y$^{3+}$ ions and V$_o$ has not been possible due to the low contrast in the x-ray and neutron scattering powers of Zr$^{4+}$ and Y$^{3+}$ ions[78].

It has recently been shown that when dopant V$_o$ and cations are introduced onto the ideal fluorite lattice sites of c-ZrO$_2$ without relaxation of the local geometry, the trend in DFT formation energies is described well by the simple point charge model, and NN type defect structures are favored[144][12]. Upon relaxation of the atomic positions within DFT, however, the NNN type defect structures are favored at low defect concentrations. For 6.7 and 10.4 mol% systems, this is accompanied with an instability in the atomic position of the V$_o$, which can undergo barrier-less migrations (reconstructions) away from its starting location on the ideal c-ZrO$_2$ lattice[138]. This preference for NNN type structures is not reproduced in a point charge model. The instability of V$_o$ upon relaxation is also not reproduced faithfully by more sophisticated force-fields which take into account short range repulsions, van der Waals forces, and ionic polarization, even when the force field parameters have been fitted carefully to diffuse neutron scattering data[138][80][140][137]. The atomic positions and orientation of NNN type defect clusters at low dopant concentrations appear to be governed by a combination of electrostatics and many-body strain elastic terms that have yet to be reduced to an analytic form[144][138]. For high dopant
concentrations (>17mol%) and for the ordered compound Zr$_3$Y$_4$O$_{12}$ (40 mol%), the relative importance of these effects have been established[143][144], however at the low dopant concentrations of 6.7 and 10.4 mol%, which are more relevant to oxide ion conductivity, the relative importance of these interactions is not clear, and it is not been possible to link the instability of structures to simple energetic or geometric parameters[138].

This chapter combines calculations using the empirical atomistic YSZ potentials [80] [140] [137] [22] [139], with large scale PBE-DFT calculations to establish the low energy structures at 3.2 mol%. Initially the accuracy of the empirical force field in reproducing the trend in DFT relaxation energies is evaluated. In the absence of a reliable simple model, we discuss the use of a combination of electrostatic interactions, computed using formal charges and the local strain energy estimated in the harmonic approximation, to provide reliable descriptors of the likely low energy DFT structures, and major interactions at low defect concentrations. We then go on to show that the relative formation energies of the relaxed DFT defect structures can be separated into an electrostatic and strain contribution using a method similar to that used to describe clustering and relaxation in metallic alloys[162]. Finally, we evaluate why the best available empirical potential is unreliable, and study the phonon density of states (DOS) of a number of YSZ defect structures.

4.1 Generating Symmetry Inequivalent 3.2 mol% YSZ Defect Structures

3.2mol% YSZ is modelled by introducing one isolated Y$_2$O$_3$ unit into a 96 atom 2x2x2 supercell of the conventional c-ZrO2 cell. In this supercell, the high symmetry points of the first Brillouin zone, X, W and L fold back onto Γ. This facilitates analysis of the imaginary phonon modes at the X-point of c-ZrO2 in terms of intra-cell atomic displace-
ments, discussed in later sections. The supercell contains 32 Zr$^{4+}$ sites and 64 O$^{2-}$ sites. Given that each defect structure is created by introducing two substitutional Y$^{3+}$ onto the Zr$^{4+}$ sites, and one V$_o$ onto an oxygen site, there are 64 x 32 x 31 possible defect structures, equal to 63488, this is far too many to study with DFT.

Many of these structures are symmetrically equivalent through translation or other space-group symmetry operations[163]. For example, a factor of a half can be introduced to account for the fact that ions of the same species are indistinguishable i.e replacing the first and second Zr$^{4+}$ ions with Y$^{3+}$ ions, is the same as replacing second and first Zr$^{4+}$ ions. This means that there are 31,744 possible defect configurations. Another obvious symmetry operation is the equivalence of every O$^{2-}$ atomic site. This makes the introduction of an V$_o$ independent of its atomic position, removing a factor of 64 from from the total number of defect structures. This leaves 496 remaining structures. Many of the remaining structures are symmetrically equivalent through more complex space group symmetry operations. To identify symmetry inequivalent structures, we perform a symmetry analysis using as proxy, the total energy of the structure calculated using a simple point charge model. We have also tested models that include three and four body interactions and have found that a simple point charge model is sufficient. By generating all the possible defect structures and calculating their total energy with the point charge model, symmetry equivalent structures can be identified as they have the same total energy. This enables a fast screening of symmetry inequivalent structures, with each energy calculation taking approximately 0.1 seconds. This is in contrast to the equivalent SCF calculation using DFT, which can take thousands to tens of thousands of seconds on 96 computer processors. Hence, the energetics of 496 structures can be calculated in approximately half a minute instead of 35 days.

The procedure to generate and compute the energies of all the possible defect structures was fully automated using the python programming language. The systematic process
for introducing one V$_{o}^{-}$ and two Y$^{3+}$ ions is outlined below:

1. Delete the atomic position of the first O$^{2-}$ ion in the GULP cell file and label this atomic position O$_1$. This introduces one V$_{o}^{-}$.

2. Loop over all possible Zr$^{4+}$ ion sites changing any two Zr$^{4+}$ ions into Y$^{3+}$ ions. Label the new Y$^{3+}$ sites according to their original Zr$^{4+}$ site i.e. Y$_1$ and Y$_{32}$ would equate to the 1st and 32nd Zr$^{4+}$ sites.

3. Compute the total energy of the structure using GULP and the simple point charge model.

4. Start a list of structure number vs total energy.

5. Iterate over every possible structure.

6. Sort the list of structure number vs total energies numerically.

7. Remove symmetry equivalents based on identical total energies.

8. Return a list of unique structure numbers and total energies.

The energetics of the 496 structures were calculated and normalised to the total energies of c-ZrO$_2$ and Y$_2$O$_3$ (calculated using the point charge model) using equation 1.2 in the computational details. Figure 4.1 shows the formation energies of 496 structures on the ideal lattice sites of c-ZrO$_2$.

From visual inspection of Figure 4.1, 26 plateau regions can be seen. The plateau’s represent the symmetry in-equivalent structures. An additional two structures are found which cannot be visualised on the graph due to the small difference in their total energies. This gives a total of 28 symmetry inequivalent structures.
The atomic positions of the structures were then allowed to locally strain relax under constant volume within the Born-Mayer-Huggins potential and DFT energy expressions. The structures where all atoms and vacancies reside on the ideal fluorite sites of c-ZrO$_2$ are referred to as the “unrelaxed” structures. The structures that are locally strain relaxed are referred to as the “relaxed” structures. In addition, structures are split into two categories:

1. Short-range, where the V$_o$ resides in the first O-coordination sphere of Y$^{3+}$ (the NN structures).

2. Long-range, where the V$_o$ resides in the first O-coordination sphere of Zr$^{4+}$ and second or greater O-coordination sphere of Y$^{3+}$ (the NNN, NNNN or greater structures).

The lowest energy structure computed by DFT was labelled 1 while the highest energy was labelled 28. The 28 ideal structures, where the dopants and vacancies reside on the lattice sites of c-ZrO$_2$, are pictured below in Figures 4.2, 4.3, 4.4 and 4.5.
Figure 4.2: Unrelaxed 3.2 mol% YSZ structures 1 - 8
Figure 4.3: Unrelaxed 3.2 mol% YSZ structures 9 - 16
Figure 4.4: Unrelaxed 3.2 mol% YSZ structures 17 - 24
We initially attempt to discover the low-energy defect structures, by gathering energetic data sets associated with the 28 symmetry inequivalent structures. All data sets are given as formation energies of calculated relative to c-ZrO$_2$ and Y$_2$O$_3$. The data sets include:

- The electrostatic potential of the ideal structures computed using formal point charges.
- The total energy of the ideal structures computed using DFT.
- The energetics of the relaxed structures using the Born-Mayer-Huggins polarisable shell model.
- The energetics of the relaxed structures using DFT.
By comparing the relative energetics of these data sets, the accuracy of the empirical potential can be assessed. If the empirical potential accurately reproduces the same energetic trends as DFT, it avoids the need for the more computationally intensive method.

Initially the trend between the electrostatic potential and the total DFT energy at the ideal geometries was assessed. A simple predictor was found by showing that the electrostatic potential of the simple point charge model reproduced the energetic trend in the unrelaxed DFT structures (as plotted in Figure 4.6). The energetics can then simply be described as the inverse relationship between the minimum Y$^{3+}$ - V$^{o}$ distance, as plotted in Figure 4.7. This leads to short-range structures being the low energy structures where the V$^{o}$ neighbours a Y$^{3+}$ ion, and matches previous literature findings[144][12].

![Figure 4.6: Scatter of ideal DFT defect formation energetics plotted against the ideal Coulomb formation energies of the equivalent structures. The near perfect R$^2$ of 0.99 suggests that the energetics can be described by Coulomb potentials alone, when the atomic positions of the dopants reside on the perfect lattice sites of c-ZrO$_2$.](image)

Next, the internal coordinates of the 28 symmetry inequivalent defect structures were fully relaxed using both the Born-Mayer-Huggins polarisable shell model, and DFT energy expressions. In Figure 4.8 the resulting relative defect formation energies are compared by
Figure 4.7: Scatter plot of the ideal DFT formation energies plotted against the reciprocal interatomic distance between $Y^{3+}$ and $V_o$. The strong correlation shows that the DFT energetics at the ideal geometries are largely described by Coulomb interactions. The anomalous data point in the NN coordination sphere corresponds to structure two in Figure 4.2. This is the only structure where the vacancy resides in the first coordination sphere of both $Y^{3+}$ ions. This is the lowest energy structure predicted by the point charge model.

plotting against a structure number (which corresponds to the number of the structures given Figures 4.2, 4.3, 4.4 and 4.5) that increases with increasing DFT defect formation energy. The model energies correlate poorly with the DFT energies, yielding an $R^2$ of 0.35.

The potential is unreliable in two respects. It fails to predict the same minimum energy defect structure as predicted by DFT, and predicts many structures to be significantly higher or lower in energy than their DFT equivalents. It also predicts many meta-stable structures to be unstable with respect to local reconstructions. These differences will be analysed in terms of the local geometries and the barriers to $V_o$ migration in the section titled: Analysis of Born-Mayer-Huggins Potential Model below.

The potential and DFT calculations agree in predicting long-range NNN structures to be the lowest energy structures. The defect formation energy of the lowest energy structure
Figure 4.8: Energy relative to the lowest energy DFT structure of the 28 relaxed structures calculated using the empirical potential (red) and DFT (blue). The correlation between the two sets is low ($R^2 = 0.35$), indicating that the empirical potential poorly reproduces DFT energy differences.

Computed by DFT (structure 1 in Figure 4.2 and pictured again in Figure 4.11 with the defect cluster centred) is -1.55 eV. In this structure the $Y'_{Zr} - V_{o} - Y'_{Zr}$ defect cluster has an equilateral triangle topology which is a common feature of all low energy structures.

Remarkably, a better predictor of the relaxed low energy structures is the simple electrostatic energy of a point charge model, calculated at the unrelaxed geometries. Figure 4.9 shows the correlation between the total electrostatic formation energies of the 28 unrelaxed structures, plotted against the DFT formation energies of the equivalent relaxed structures.

Clearly the structures can be split into two subsets; short-range structures, and long-range structures. The first set corresponds to structures with fairly high formation energies, whose relative energetics are not predicted by the electrostatic potential of the equivalent unrelaxed structures. The second set covers a wide range of formation energies, whose energetics correlate strongly to the total electrostatic formation energies of the equivalent
unrelaxed structures, giving a $R^2$ value of 0.75. The limitations of a point charge model are also apparent, as it is found that short-range structures are unfavorable and high in energy when relaxed in DFT. The point charge model predicts them to be the most stable, suggesting that there is a short-range interaction energy that is not captured by the simple model.

### 4.3 Distortion Along Imaginary Phonon Modes as a Predictor of DFT Relaxation Energies

It is plausible that variation in structural relaxation around defects of different geometries is partly responsible for the variation in ordering energies. We investigate the relaxation energetics of the 28 DFT relaxed structures using a quantitative model of *ab initio* force constants based on the unstable phonon mode of perfect, stoichiometric c-ZrO$_2$. As can
be seen in Figure 4.10, c-ZrO$_2$ possesses two imaginary phonon modes at the X and W-point of the first Brillouin zone. The mechanical instabilities at the X and W-point are calculated to be $i217$ cm$^{-1}$ and $i65$ cm$^{-1}$ respectively. The computed imaginary frequency at the X-point is similar to that reported in previous calculations using LDA and PBE functionals with projector augmented wave (PAW) and NCP pseudopotentials. The frequency of the phonon at the W-point is more sensitive to numerical approximations and for instance, varies from 50 cm$^{-1}$ to $i65$ cm$^{-1}$ as the FFT grid scale is increased from x1.5 to x2.5 and was reported as approximately 45 cm$^{-1}$ in previous PAW-PBE calculations using the Quantum ESPRESSO (see Computational Details for more information).

Figure 4.10: The computed phonon dispersion curves of c-ZrO$_2$ showing the negative frequency modes in the region of the X and W-points highlighted in red and blue.

Relaxation along the imaginary X-point phonon mode leads to a distortion of the oxygen anions in a $\langle 1 \ 0 \ 0 \rangle$ direction. Figure 4.14 shows half of the double well potential for the relaxation of the oxygen anions along the eigenvector of the X-point phonon mode. Displacing oxygen anions along the eigen vector of this mode in the 2x2x2 supercell leads to
a reduction in total energy of approximately 2 eV/cell. The displacement pattern is illustrated in Figure 4.11 which shows the pure relaxation of the imaginary X-point phonon mode (left) compared to the relaxation pattern observed in the lowest energy NNN type defect structure (right). It can be seen that the defect structure exhibits a very similar relaxation of the oxygen anions.

Figure 4.11: Left: relaxation of the oxygen anions along the imaginary X-point phonon mode in the 2x2x2 supercell. Right: The relaxation pattern of the oxygen anions observed in the lowest energy defect structure. Note: the similarity of the relaxation patterns (ions not drawn to scale).

Relaxing the ideal bulk crystal along the imaginary W-point phonon mode leads to displacement of the oxygen anions along a \((2 1 0)\) direction. This is pictured in a 2x1x1 supercell (the smallest supercell in which all W-point vibrations fold back onto \(\Gamma\)) in Figure 4.12. As seen in Figure 4.15, the relaxation energy of the anions along the W-point phonon eigen vector is negligible compared to relaxation along the X-point phonon.

To determine the extent that each defect structure \(i\) exploits the imaginary phonon modes of c-ZrO$_2$, and indeed any other phonon modes, the relaxation energy of the ions was cal-
Figure 4.12: 2x1x1 supercells of c-ZrO$_2$ with increasing amplitude of the W-point imaginary phonon eigen vector. Left: Perfect fluorite structure. Amplitudes equate to the values on the x axis in Figure 4.15.

calculated within the harmonic approximation. As discussed in the Methodology, the total energy of the system within the harmonic approximation is given by an expansion of the energy around the equilibrium position:

$$E = E_0 + \frac{1}{2} \sum_{\kappa,\alpha,\kappa',\alpha'} U_{\kappa,\alpha} H_{\alpha,\alpha'}^{\kappa,\kappa'} U_{\kappa',\alpha'}$$  \hspace{1cm} (4.2)

Where the force constants matrix $H_{\alpha,\alpha'}^{\kappa,\kappa'}$ is converted into a dynamical matrix, $D_{\alpha,\alpha'}^{\kappa,\kappa'}$ in Hz$^2$, by dividing by the masses of the atoms:

$$D_{\alpha,\alpha'}^{\kappa,\kappa'} = \frac{H_{\alpha,\alpha'}^{\kappa,\kappa'}}{\sqrt{m_k m_{k'}}}$$  \hspace{1cm} (4.3)

In addition, the dynamical matrix is commonly converted into cm$^{-2}$ by dividing by the speed of light in centimeters per second squared ($c^2 = 8.987551787e+20$ cm$^2$s$^{-2}$). This gives a spherical frequency, which is converted into a non-angular frequency by dividing by the numerical factor of $4\pi^2$. 

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The CASTEP DFPT calculation output contains the dynamical matrix in THz$^2$. The matrix can then be converted back into the force constants matrix given the simple matrix manipulation below:

\[
\begin{pmatrix}
\sqrt{M_\kappa} & 0 & \cdots & 0 \\
0 & \sqrt{M_\kappa} & 0 & \vdots \\
\vdots & 0 & \ddots & 0 \\
0 & \cdots & 0 & \sqrt{M_{\kappa'}}
\end{pmatrix}
\begin{pmatrix}
H^{\kappa,\kappa'}_{\alpha,\alpha'} \\
\frac{H^{\kappa,\kappa'}_{\alpha,\alpha'}}{\sqrt{M_\kappa M_{\kappa'}}} & \cdots & \cdots & \frac{H^{\kappa,\kappa'}_{\alpha,\alpha'}}{\sqrt{M_\kappa M_{\kappa'}}} \\
\frac{H^{\kappa,\kappa'}_{\alpha,\alpha'}}{\sqrt{M_{\kappa'} M_{\kappa}}} & \ddots & \vdots & \vdots \\
\vdots & \ddots & \ddots & \ddots \\
0 & \cdots & 0 & \sqrt{M_{\kappa'}}
\end{pmatrix}
\begin{pmatrix}
\sqrt{M_\kappa} & 0 & \cdots & 0 \\
0 & \sqrt{M_\kappa} & 0 & \vdots \\
\vdots & 0 & \ddots & 0 \\
0 & \cdots & 0 & \sqrt{M_{\kappa'}}
\end{pmatrix}
\]

where the left and right matrices contain the square roots of the masses of the atoms, and the central matrix is the dynamical matrix. The matrix is then multiplied by $4\pi^2$, to give the force constants matrix.

The displacement vector of the atoms $U_{\kappa,\alpha}$ can then be written as the difference between their starting positions in the ideal structure ($r_0$), and their final positions in the relaxed structure ($r$), such that:

\[U_{\kappa,\alpha} = (r - r_0)\]  \hspace{1cm} (4.4)

In addition, the position of the V\textsubscript{o} in the output structure is determined by taking the centre of mass of the 7-fold O-coordinated metal ions. Atomic displacements of the V\textsubscript{o} are set to zero to remove any energetic contributions from this atomic site. Through this method, the total harmonic relaxation energy for all of the ions in the unit cell can be determined. To validate the approach, the potential double well of the X-point imaginary phonon mode was calculated. A set of unit cells were generated with varying amplitude of X-point imaginary phonon eigenvector, where 0 corresponds to the perfect c-ZrO\textsubscript{2} fluorite structure. A selection of the structures are pictured in Figure 4.13, where the amplitude of the phonon eigenvector corresponds to the amplitudes on the x axis of Figure 4.14. The total energy of each cell was calculated using DFT, while the displacement vector
$U_{\kappa,\alpha}$ was calculated for each cell using the method described above. In addition, a fourth power polynomial was fitted to the harmonic region of the DFT potential energy surface in order to determine an estimate for the potential energy surface of the harmonic approximation. As the quadratic term in the polynomial expansion equates to a Hookian potential, the second derivative of the quadratic term gives the force constant ($k$) for the phonon eigenvector. The results are plotted in Figure 4.14, while Figure 4.15 shows the potential energy surface of the W-point imaginary phonon.

The harmonic approximation using the DFPT force constants matrix reproduces the harmonic region of the X-point DFT-PES, with negative curvature, exceptionally accurately. The method using the force constant matrix is even more accurate than fitting a polynomial function. As expected, the harmonic approximation will overestimate the relaxation energy, particularly when the amplitude of the phonon vector is in the an-harmonic region of the DFT-PES. This is due to the approximation not accounting for a restoring force which causes the observed potential well.

The DFT-PES of the W-point imaginary phonon eigenvector shows that the PES of the phonon is very flat. It should be noted that the eigenvector amplitudes are very small in comparison to the X-point imaginary phonon eigenvector, and there is almost no change in the total energy between the phonon eigenvector amplitudes of 0 $\rightarrow$ 0.01.

This method was used to determine the total harmonic relaxation energy of the 28 defect structures. In Figure 4.16 the total harmonic relaxation energy of the 28 defect structures is plotted against the formation energies of the relaxed structures computed using DFT. To be consistent with the analysis of the electrostatic interactions, the data set is split into two sub-categories: short-range structures, and long-range structures. It is clear that there is no trend between the total harmonic relaxation energy of the structures and the DFT formation energies.
Figure 4.13: 2x2x2 supercells of $c$-ZrO$_2$ with increasing amplitude of the X-point imaginary phonon eigen vector. Top left: perfect fluorite structure. Amplitudes equate to the values on the x axis in Figure 4.14.

The results in Figure 4.16 show the relaxation energy for every atomic displacement in the unit cell. It is possible to decompose this energy and analyse the relaxation along each individual phonon eigenvector. The atomic displacement vector $U_{\kappa,\alpha}$ is re-written as a linear combination of the phonon eigenvectors such that:
Figure 4.14: Blue points show the DFT potential energy surface for the displacement of the oxygen anions along the X-point imaginary phonon eigen vector of c-ZrO$_2$. Red points show the quadratic fit to the harmonic region of the DFT PES, with negative curvature. Green points show the harmonic approximation using the DFPT computed force constants matrix.

Figure 4.15: DFT potential energy surface for the displacement of the oxygen anions along the W-point imaginary phonon eigen vector of c-ZrO$_2$.

\[ U_{\kappa,\alpha} = (r - r_0) = \sum \alpha_1\epsilon_1 + \alpha_2\epsilon_2 + \alpha_3\epsilon_3 \ldots \ldots \alpha_n\epsilon_n \quad (4.5) \]

Where $\alpha_1\epsilon_1$ represent the first eigen vector and corresponding scalar etc. The eigen vector
amplitudes \((\alpha_1, \alpha_2, \alpha_3, \ldots, \alpha_n)\) are determined by the dot product of the transpose of the eigenvectors with the displacements in the unit cell \((i)\). As non-corresponding eigenvectors are orthogonal and \(\epsilon_n \epsilon_i^t = 1\), hence the problem simplifies to:

\[
U_{\kappa, \alpha_i} = \alpha_i \epsilon_i
\]  \hspace{1cm} (4.6)

Given the harmonic energy of the system above, the individual contribution for each individual phonon eigenvector \((x)\) can be written as:

\[
E_x = \frac{1}{2} \alpha_i \epsilon_i H_{\alpha_i \alpha_i}^\kappa \alpha_i \epsilon_i
\]  \hspace{1cm} (4.7)

Given the eigen vector equation:
\[
\epsilon_i H^{\kappa,\kappa'}_{\alpha, \alpha'} = \lambda_{\kappa} \epsilon_i 
\]

The equation is re-written as:

\[
E_x = \frac{1}{2} \alpha_i \epsilon_i \lambda_x \alpha_i \epsilon_i 
\]

As \( \epsilon_i \) is a vector in fractional form, it is multiplied by the lattice constant (a) of the supercell to give a Cartesian displacement:

\[
E_x = \frac{1}{2} a \alpha_i \epsilon_i \lambda_x a \alpha_i \epsilon_i 
\]

Given that \( \epsilon_i \times \epsilon_i \) is equal to one, the phonon energy is recovered as:

\[
E_x = \frac{1}{2} a^2 \alpha_i^2 \lambda_x 
\]

Where \( \lambda_x \) is the eigenvalue of the phonon mode. In Figure 4.17 the harmonic relaxation energy of the bulk X-point phonon is plotted against the formation energies of the relaxed structures computed using DFT.

In Figure 4.17 the short-range (red) and long-range (blue) structures are indicated. For low energy structures and all long-range structures, the elastic relaxation along imaginary phonon modes is not a major factor in determining the energetic ordering of the DFT relaxed structures. Although the relaxation energy along the imaginary phonon modes is significant it does not discriminate effectively between different structures: the correlation between the final relaxed DFT energies and the harmonic relaxation energy is poor with
Figure 4.17: Relationship between the DFT formation energies of the relaxed structures and harmonic relaxation along imaginary X-point phonon modes. Blue points show the energetics of long-range structures, red points show the energetics of short-range structures.

an R\(^2\) value of 0.38. In comparison, the relative stability of high energy, short-range structures is described well by the harmonic relaxation energy along imaginary phonon modes, with an R\(^2\) of 0.62.

4.4 Relative Importance of Electrostatic and Relaxation Energies

The formation of 3.2mol% YSZ isolated defect structures can be usefully viewed as a two-step process: firstly, the isolated Y\(_2\)O\(_3\) unit is placed within the unrelaxed c-ZrO\(_2\) structure and secondly, the structure is allowed to relax. For low energy and all long-range structures, the electrostatic energy of the first step reproduces very accurately the trend in DFT energy. The second step can be described using the relaxation along X-point imaginary phonons with W-point phonons making a negligible contribution. The relative
formation energy can be predicted using an artificial synthesis model consisting of the unrelaxed electrostatic formation energies of the point charge model, and the harmonic relaxation along imaginary phonons, given by equation 4.12[164].

\[ E_{\text{fYSZ}}(i, R) \approx A \Delta E_{\text{elec}}(i, R) + B \Delta E_{\text{strain}}(\alpha, R) + C \]  

(4.12)

A, B and C are fitted constants, \( E_{\text{elec}} \) is the electrostatic formation energy of an unrelaxed defect structure in configuration i, and \( E_{\text{strain}} \) is the energy change from atomic relaxation along X-point imaginary phonons. Through the synthesis model, the relative importance of electrostatics and imaginary phonons in determining the final energetic ordering of the relaxed DFT defect structures can be assessed. Figures 4.18 and 4.19 show the synthesis model energy plotted against the DFT formation energies of the relaxed long-range and short-range structures respectively. For long-range structures, almost all of the variance is accounted for by the electrostatic interaction of the defects. The coefficient of determination does not increase significantly when accounting for the X-point phonon strain energy on top of the ionic energy (from 0.75 to 0.79). In contrast, the variance in short-range structures is described exceptionally well by a combination of point charge electrostatics and relaxation along imaginary phonon modes. The coefficient of determination increases from 0.62, with pure relaxation along imaginary X-point phonon modes, to 0.79 when taking into account electrostatics. To incorporate the two sub-categories of structures into a single model, an understanding of a further destabilising force for short-range structures needs to be established. We do not currently have such an understanding.

4.5 Analysis of Born-Mayer-Huggins Potential Model

As discussed in the introduction, the empirical potential model and DFT have been shown to predict the instability of many defect structures at 6.7 and 10.4 mol%. Unstable structures undergo barrier-less reconstructions of the \( \text{V}_\text{O}^{\text{\_}} \), where reconstructions predicted by
Figure 4.18: Synthesis model long-range defect formation energies plotted against DFT formation energies of the relaxed long-range structures. The majority of the variance is accounted for by electrostatic interactions.

DFT are often not predicted by the potential and *vice versa*. Radial distribution functions (RDFs) were used to analyse the relaxed geometries predicted by the potential. Through RDFs, the final atomic positions of the relaxed structures are mapped back onto their unrelaxed geometries by identifying the ideal fluorite O and Zr sites closest to the location of the relaxed Zr, O, Y, and V\textsubscript{o} sites. It was found that seven structures were unstable and underwent barrier-less reconstructions of the V\textsubscript{o} away from its initial stating position on the ideal crystal lattice. In contrast, DFT predicted one unstable structure with a flat energy surface with respect to V\textsubscript{o} reconstruction (pictured in Figure 4.20). Using DFT and a linear synchronous transit (LST) and quadratic synchronous transit (QST) maximisation transition state (TS) search, the energy barrier to reconstruction for the structure in Figure 4.20 was computed as 10meV. This is close to the numerical accuracy of the total energy and so the reconstruction can be spontaneous depending on the geometry optimisation path, method, and tolerances.
Figure 4.19: Synthesis model of short-range defect formation energies plotted against DFT formation energies of the relaxed short-range structures. The majority of the variance is accounted for by relaxation along soft phonon modes.

Through reconstructions, the majority of unstable structures predicted by the potential relax to a geometry that can easily be mapped back to one of the unrelaxed 28 symmetry inequivalent structures. An example, with reference to Figure 4.8, is structure 1, and structure 16. These structures have different unrelaxed geometries, and are meta-stable upon relaxation with DFT. Within the potential, structure 16 is unstable and $V_{o}^-$ reconstruction leads to structure 16 relaxing to a geometry that can be mapped back to the unrelaxed geometry of structure 1. The exception to this is structure 6. When relaxed in the potential, structure 6 takes on a “new” geometry that cannot easily be mapped back onto one of the unrelaxed structures, with an $O^{2-}$ ion residing in an interstitial site between two ideal $O^{2-}$ sublattice sites. Structure 6 is the lowest energy structure predicted by the potential model. When the “new” structure is relaxed in DFT, it is unstable and the $V_{o}^-$ relaxes back to its original starting position on the $O^{2-}$ sublattice.
Figure 4.20: $V_\circ$ reconstruction observed upon strain relaxation in DFT Left: unrelaxed NN defect structure with two 7-fold O-coordinated $Y_{Zr}$ ions. Right: final strain relaxed NNN structure. An $O^{2-}$ ion can be seen migrating between two metal tetrahedral sites. The energy barrier to reconstruction is calculated as 10meV using a DFT LST/QST TS search. (Ions are not drawn to scale).

The instability of structures within the potential can be linked to geometric considerations. Five of the unstable structures have an $V_\circ$ location such that a single $V_\circ$ migration leads to the $Y'_{Zr} - V_\circ - Y'_{Zr}$ cluster taking on an NNN defect structure in equilateral triangle geometry. It is clear that the energy barriers to $V_\circ$ migration predicted by DFT are not reproduced by the potential. To estimate the DFT energy barriers to $V_\circ$ migration, LST/QST - TS searches were performed on two structures that the potential predicts as unstable. Both structures are meta-stable in DFT, but can reconstruct to a more stable NNN structure through the single migration of an $V_\circ$. One structure starts as a short-range NN structure (structure 6), while the second starts as a long-range NNNN structure (structure 16). Specifically, the energies of the transition states between structures 6 and 4, and structures 16 and 1 (pictured in Figures 4.2, 4.3, 4.21, and 4.22), are calculated.
Table 4.1: DFT calculated energy barriers to \( V_o \) migration.

<table>
<thead>
<tr>
<th>Reconstruction path</th>
<th>Forward energy barrier to TS / eV</th>
<th>Reverse energy barrier to TS / eV</th>
<th>Total energy of reconstruction / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure 6 → 4</td>
<td>0.28</td>
<td>0.45</td>
<td>-0.17</td>
</tr>
<tr>
<td>Structure 16 → 1</td>
<td>0.41</td>
<td>0.92</td>
<td>-0.51</td>
</tr>
</tbody>
</table>

Figure 4.21: LST/QST \( V_o \) migration path, structure 6 to structure 4.

Figure 4.22: LST/QST \( V_o \) migration path, structure 16 to structure 1.

The defect structure starting with NN geometry has a lower energy barrier to \( V_o \) migration than the structure in NNNN geometry. The NNNN structure reconstructs to a significantly more stable energy minimum. The existence of energy barriers within DFT but not the potential can be understood by considering the local strain effect between
O$^{2-}$ ions and the metal sublattice. When an O$^{2-}$ migrates, the ion must pass between two Zr$^{4+}$ ions. The migration causes a distortion to the metal sublattice as the interatomic distance between the two Zr$^{4+}$ ions increases to accommodate the movement. The size of the energy barrier appears to be linked to the distance the Zr$^{4+}$ ions have to move from their ideal atomic sites. In the case of the NNNN to NNN migration, the interatomic distance of the Zr$^{4+}$ ions increases from 3.98 Å to 4.02 Å in the TS state, before contracting 3.98 Å in the final NNN structure. In the case of the NN to NNN migration, the interatomic distance increases from 3.97 Å to 3.98 Å in the TS state, and increases again to 4.0 Å in the final NNN structure. This is pictured in Figure 4.23

Figure 4.23: Distortion caused to the metal sublattice upon the $V_o$ migrating.

It is concluded that the connectivity between local minima on the potential energy surface is poorly described by the potential, suggesting that finite temperature and dynamics will be poorly reproduced.
4.6 Symmetry Assignment of Low Energy Defect Structures

Finally we assign the point group of the low energy NNN defects on the ideal lattice sites of c-ZrO$_2$. It should be noted that upon strain relaxation the symmetry of the defects is broken. The $Y'_{Zr} - V_{O} - Y'_{Zr}$ cluster preferentially takes an equilateral triangle geometry with the most favorable structure having Cs symmetry. This occurs when the $Y^{3+} - Y^{3+}$ ions lie on the metal sub-lattice along the line $\langle 2 \ 2 \ 0 \rangle$ (structure 1). The next most favorable structures have $C_{2v}$ and $C_{2}$ symmetries, with the $Y^{3+} - Y^{3+}$ ions lying on the lines $\langle 1 \ 1 \ 0 \rangle$ and $\langle 2 \ 1 \ 1 \rangle$ respectively (structures 2 and 3). These structures are lower in energy than NNN type structures that have symmetries such as $C_{1}$. This can occur when the $Y^{3+} - Y^{3+}$ ions lie on the line $\langle 3 \ 1 \ 1 \rangle$ (structure 4).

4.7 Chapter Conclusions

In this chapter we have established the relative accuracy and importance of empirical potentials, electrostatics and strain relaxation effects in predicting the DFT formation energetics of 3.2mol% YSZ structures. In turn, the chemical descriptors that can identify likely low energy defect structures of YSZ have been determined. It was found that the best available empirical potential poorly recreates the general trend of increasing DFT formation energies across a series of 28 symmetry inequivalent structures. The unreliability of the empirical potential can be analysed in terms of geometric considerations and the energy barriers associated with $V_{O}$ reconstruction. The energy barriers predicted by DFT are not faithfully reproduced by the potential model and in addition, the connectivity between defect structures topologies on the potential energy surface is poorly described.

Low energy defect structures have NNN type geometries where the $V_{O}$ resides in the sec-
ond coordination sphere of a $\text{Y}^{3+}$ ion and the first coordination sphere of a $\text{Zr}^{4+}$ ion. This is optimal when the $\text{Y}^{3+} - \text{V}_o - \text{Y}^{3+}$ defect cluster has equilateral triangle geometry. A very good predictor of the likely low energy NNN structures and indeed of all long-range NNNN and NNNNN type structures is the total electrostatic energy of a simple point charge model calculated at the unrelaxed geometries of the structures. In comparison, the total electrostatic potential calculated at the unrelaxed geometries is a poor descriptor of short-range NN structures, where the $\text{V}_o$ resides in the first coordination shell of a $\text{Y}^{3+}$ ion.

Strain effects are important and can be mapped in terms of relaxation along the imaginary X-point phonons of c-ZrO$_2$. Strain is only significant in determining the energetic ordering of high energy structures with short-range interactions. All long-range structures exploit relaxation along imaginary phonon modes to a similar extent. The results suggest that defects can be characterised by two regimes: long-range structures, whose relative energetics correlate to, or can be predicted by point charge electrostatics; and short-range structures, whose relative energetics correlate to, or can be predicted by a model containing point charge electrostatics plus a harmonic relaxation energy along the imaginary X-point phonon modes of c-ZrO$_2$. Establishing an analytical description of a destabilising force at short-range will allow both regimes to be incorporated into a single model.
Chapter 5

Surface Chemistry Sites of 3.2 mol% Yttria Stabilised Zirconia

In this chapter we apply the findings of the chapter titled *Chemical Descriptors of Yttria Stabilised Zirconia at Low Defect Concentration* to investigate yttria segregation, local defect structure, and surface chemistry sites of a 3.2 mol% YSZ surface model.

c-ZrO$_2$ has three low energy, low index surfaces: (111), (110) and (100). The (110) surface is a Tasker [165] type I surface, where individual layers of atoms are charge neutral and there is no net dipole. The (111) surface is a Tasker type II surface, where the repeating unit, perpendicular to the surface is charged, but groups of layers are charge neutral and non-polar, while the (100) is a Tasker type III surface, in which the repeating unit has a net dipole. LDA-DFT and empirical atomistic potential calculations have shown that the (111) surface of c-ZrO$_2$ is the most stable, with (110), and the stabilised (100) surface, being less energetically favorable [76][166]. As the ideal (100) is polar it has infinite surface energy, however charge neutrality can be enforced by removing half of the oxygen ions in the outermost atomic layer. This surface structure emerged from the analysis of MEIS data [76] [167]. It has been suggested that the (310) surface of c-ZrO$_2$ has a similar surface energy to that of the (100) surface [168], however atomistic potential models have predicted that the (310) surface is less stable than the (100) surface [166]. The same theoretical trend in surface stability is reproduced for the (111), (110), and (100) surfaces of YSZ [76][166]. The three main surfaces of c-ZrO$_2$ are pictured below in Figure 5.1.

The energetic stability of c-ZrO$_2$ surfaces has been rationalised [76][166][49] through the
Figure 5.1: The three main surfaces of c-ZrO$_2$. Left (100), Centre (110) and Right (111).

The number of Zr - O bonds broken through forming the surface. In the bulk crystal, Zr$^{4+}$ ions have 8-fold O-coordination while O$^{2-}$ ions have 4-fold Zr-coordination. The coordination of the Zr$^{4+}$ and O$^{2-}$ ions on the (111) surface is 7 and 3 respectively, while it is 6 and 3 on the (110) surface, and 6 and 2 on the (100) surface. The decreasing coordination of Zr$^{4+}$ and O$^{2-}$ ions leads to a decrease in the stability of the surfaces.

The topic of yttria segregation to the surfaces of YSZ has been the subject of much experimental research. Early x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) suggested that yttrium preferentially segregated to the surfaces of both c and t-ZrO$_2$ polycrystals [169][170][171]. More recent angle resolved XPS studies, with estimated depth penetrations of 2 - 7 nm, depending on the angle of the Al-K$_\alpha$ radiation beam, have suggest that yttrium segregation is not significant in c-ZrO$_2$ [172][173]. Low energy ion scattering (LEIS) using 3 keV $^4$He$^+$ ions at an an intensity of $1 \times 10^{14}$ $^4$He$^+$ ions/cm$^2$, and 5 keV $^{40}$Ar$^+$ ions at an intensity of $5 \times 10^{13}$ $^4$He$^+$ ions/cm$^2$, has also been used to probe the surface and sub-surface composition of $^{94}$ZrO$_2$ enriched 3 mol% and 10 mol% YSZ polycrystals[174] [175] [176] [177]. The LEIS results revealed that the surfaces of the YSZ polycrystals were in fact covered with impurities of sodium, silicon, and calcium , which segregate to the outer most layer of YSZ, even after thorough cleaning. While these results could be a quirk of the samples studied, the findings have been supported by angle resolved XPS results [172], that have also suggested silica impurities
segregate to the surface of YSZ with the attraction between silica and yttria leading to the formation of a yttria rich silica over layer. LEIS results suggest that yttrium segregates to the subsurface layer of YSZ. At 3 mol%, the yttria enrichment factor, determined through sputter profiles, is 18% for 3 mol% YSZ polycrystals, while it is 30% in 10 mol% YSZ polycrystals [176].

There are few single crystal studies regarding the specific surface compositions of the YSZ surfaces. Most previous studies have investigated the surfaces of polycrystals. Until recently, only medium energy ion scattering (MEIS) results were available for the (100) surface [167]. MEIS revealed that the (100) surface enforces charge neutrality by losing half of the oxygen ions in the outermost atomic layer. The remaining oxygen ions then undergo a reconstruction. On this reconstructed surface, surface oxygen ions have 4-fold metal ion coordination, while on the ideal (100) surface they have 2-fold metal ion coordination [76][167]. LDA-DFT calculations have since suggested that the reconstruction of the (100) surface is only possible in the presence of yttrium, suggesting a mechanism for yttrium segregation to this surface [76].

Despite the (111) surface being the theoretical low energy surface of c-ZrO₂, and indeed of YSZ, scanning tunneling microscope (STM), XPS, anomalous x-ray diffraction (SXRD), and temperature programmed desorption (TPD) data for this surface has only recently been published[77][79]. SXRD and XPS measurements show a strong yttrium enrichment factor on the (111) surface, while STM images and X-ray diffraction reveal the formation of stepped surfaces in samples that have been prepared under vacuum. Through the use of calculations using an empirical reactive force field (ReaxFF) potential model, it has been shown that yttrium preferentially segregates to the (111) surface and occupies low coordination step edges. These findings have been supported by TPD measurements which recorded the dehydration/dehydrogenation of formic acid on Y₂O₃, YSZ, and c-ZrO₂ thin films grown on a YSZ substrate. On a pure c-ZrO₂ sample, formic acid undergoes a
dehydrogenation, while on $\text{Y}_2\text{O}_3$ and YSZ, it is found to undergo a dehydration. The observation that formic acid undergoes dehydration on YSZ instead of dehydrogenation establishes that the chemically active sites of YSZ are yttria like. In addition, after sputtering and annealing of the YSZ thin film, the reactivity increases, suggesting that yttrium preferentially segregates to the step edges of YSZ, with under coordinated yttrium ions causing an increase in reactivity\[77].

Theory has been used to give an insight into the thermodynamics of YSZ surfaces. Xia et al. used Born-Mayer-Huggins potentials to develop slab models of 9 - 12 mol\% YSZ with (111) and (110) surfaces respectively. Yttrium segregation to the (111) surface was found to be exothermic while there was no energetic preference for yttrium to segregate to the (110) surface\[166]. Ballabio et al. used DFT to establish the relative stability of YSZ surfaces, while Wang et al. used DFT to show that it is thermodynamically favorable for yttrium ions to segregate to the (111) subsurface layer of YSZ. It appears there is a general consensus that yttria segregates to the surface of YSZ, however the computational cost and intensity of DFT calculations has made it challenging to evaluate the local distribution of $\text{Y}^{3+}$ and $\text{V}_\text{O}^{-}$ species on the YSZ surface. Few computational studies have attempted to analyse the potential low energy surface structures, while establishing the relative positions of defect species is not possible through the use of electron microscopy techniques due to the insulating properties of YSZ.

One of the few studies that attempted to establish the low energy surface defect structures is the work by Mayernick et al. [72] who used a ReaxFF potential model parameterised with DFT calculations, [71] to study the the local geometry of defects on both flat, and stepped (111) YSZ surfaces. Yttrium segregation was found to be energetically favorable for both flat and stepped surfaces, however stepped surfaces were found to be energetically unfavorable compared to flat surfaces. Despite the potential reproducing the fact that $\text{Y}^{3+}$ ions take on a 8-fold O-coordination in the bulk crystal, giving rise to NNN
type defect structures, it was found that a higher fraction of vacancies occupied positions NN to $Y^{3+}$ ions at the surface. In addition, the $V_o$ was found to occupy positions in the sub-surface layer of $O^{2-}$ ions. The preference for yttrium to segregate to the surface and occupy NN type defect structures, with low O-coordination, appears contradictory to its bulk behavior where low energy structures have $Y^{3+}$ ions with 8-fold O-coordination, and $Zr^{4+}$ ions have 7-fold O-coordination.

DFT has been used to investigate the catalysis of YSZ (111) surfaces[55][56]. These studies have not focused on yttria segregation nor the local atomistic structure of the surface. The oxidation of small fuel molecules has been modeled using small unit cells, consisting of a 9 atomic layer thick slab models of the YSZ + O (111) surface. The YSZ + O (111) surface comprises of a YSZ (111) surface where by the $V_o$ has been replaced by an additional neutral O atom, the origin of which, has been questioned by some authors [29]. A recent review highlighted the fact that there had been no attempt to validate the atomic structures of these models, and indeed, the oxidation pathway of fuel molecules on the YSZ surface will depend on structural properties such as; dopant concentration at the surface, bond topology, and interface structure formed with a catalytic metal [49].

This chapter combines calculations using the empirical atomistic YSZ potential[22][140][137][139][80], with large scale PBE-DFT calculations to establish the low energy structures of a 3.2 mol% YSZ (111) surface model. We initially demonstrate that a slab model, much larger than that used in previous DFT studies, is required to obtain a converged surface energy. We then investigate the energetic preference for yttrium to segregate to the (111) surface. After establishing that yttrium indeed segregates to the (111) surface, we compute the DFT energies of 20 low energy symmetry inequivalent surface structures and identify the preferential defect configurations and surface chemistry sites. In addition, we compute the DFT energy of the low energy NN structure proposed by ReaxFF modeling and find that this is significantly higher in energy than our minimum energy structure which has
NNN geometry. This highlights the need for large scale DFT calculations in understanding the YSZ (111) surface structure. Having obtained atomistic structures for the surface reaction sites we investigate the dissociation of water over the lowest energy YSZ defect structure in order to establish the chemically active sites for this reaction.

5.1 c-ZrO$_2$ Slab Convergence

In addition to k-point and planewave basis set cut-off, the convergence of a surface, modeled as an infinite 2D slab with periodic images in the third, depends on the thickness of the slab and its separation from periodic images (vacuum space). The vacuum space needs to be large enough minimise the the interaction between periodic images, while the slab must have enough atomic layers to minimise surface-surface interactions and converge the surface energy. We examine the convergence of the (111) c-ZrO$_2$ and YSZ surfaces with respect to k-point MP grid. We find an MP grid of 3 x 3 x 1 converges the total energy of the slab to 0.7 meV per unit cell. All slab calculations were performed at the minimum energy USP PBE-DFT lattice constants of c-ZrO$_2$ as calculated in previous sections. This allows the formation energy of defect computed in the slab to be directly compared to the those calculated in the bulk crystal. The planewave cut-off-energy was increased to 700 eV for calculations involving water molecules. This accounts cut-off energy converges the total energy of the hydrogen USP to 0.025 meV per unit cell.

5.1.1 Vacuum Space Convergence

To evaluate the convergence of the surface energy with respect to the vacuum spacing, vacuum space convergence of a c-ZrO$_2$ slab, a three atomic layer slab with (111) surfaces was modeled with varying vacuum space. Vacuum space was increased from 6 Å to 12 Å, and the total SCF energy calculated for each structure. The total energy of the system as a function of reciprocal vacuum space is recorded in Figure 5.2. It can be seen that
the total energy of the system converges to 0.5 meV with 10 Å of vacuum space. 10 Å of vacuum space is used in all further slab calculations.

Figure 5.2: Vacuum space convergence of a three atomic layer c-ZrO$_2$ slab with $\langle 1\ 1\ 1 \rangle$ surfaces.

5.1.2 c-ZrO$_2$ Surface Energy Convergence

The surface energy of the (111) c-ZrO$_2$ surface was calculated for a set of geometry optimized slabs with 3, 6, 9, 12, 15, 18, 21, and 24 atomic layers. Figure 5.3 plots the surface energy per unit area against the reciprocal number of atomic layers. The surface energy of the (111) c-ZrO$_2$ surface converges to 0.012 meV/Å$^2$ with a slab thickness of 15 atomic layers.

Upon relaxation of the atomic positions, the sub-surface layer of Zr$^{4+}$ ions contracts and moves into the slab by 0.05 Å. In comparison, the terminating surface O$^{2-}$ ions relax away from the surface of the slab with the Zr - O bond length increasing by 0.02 Å.
5.2 YSZ (111) Surface Energy Convergence

The convergence requirements of a (111) c-ZrO$_2$ surface have been established. In order to accurately investigate yttrium segregation to the (111) surface of YSZ, the slab model must be thick enough to ensure the formation energy of a defect, modeled in the centre of the slab, has the same formation energy as the equivalent defect modeled in the bulk crystal. Hence, the convergence of the defect surface interaction energy is a function of slab thickness and the number of atomic layers.

In addition, adding a defect to the c-ZrO$_2$ slab breaks symmetry and introduces a non-vanishing surface-dipole density. The electrostatic potential of the two sides of the slab will then be different at the cell boundary. Planewave DFT methods impose periodic boundary conditions to this electrostatic potential and introduce an artificial uniform electric field across the slab. To circumvent this problem, it is common to mirror the defect so that there are defects on both sides of the slab. This leads to a net dipole moment of zero, however this approach can lead to unwanted defect-defect interactions across the slab and vacuum region. To counteract this, the number of atomic layers and the size of
the vacuum region must be increased, leading to very large unit cells.

Another solution is the dipole correction method first proposed by Neugebauer and Scheffler [178] and developed by Bengtsson [179]. By treating the resulting electric field as external, it is possible to use a ramp-shaped potential to cancel out the electric field and derive a energy correction term. The use of a dipole correction and energy correction term can give rise to poor SCF convergence. In the sub-sections that follow, we test both methods to determine the best method, and the minimum number of atomic layers, needed to converge the formation energy of a $\text{Y}_2\text{O}_3$ defect cluster introduced into the c-ZrO$_2$ slab.

5.2.1 Mirrored Defect Method

Having previously identified the minimum energy defect structure in the 3.2 mol% bulk crystal, we model the same defect cluster, mirrored onto both surfaces of the (111) c-ZrO$_2$ slab model. The slab thickness was then varied in order to converge the formation energy of the defects.

The previously identified low energy defect cluster has an NNN configuration, where by two $\text{Y}^{3+}$ ions lie along the line $\langle 2 2 0 \rangle$. In the (111) c-ZrO$_2$ slab model, the $\langle 2 2 0 \rangle$ line bisects the (1 1 1) surface at 45°. In addition, each defect cluster occupies three atomic layers. In order to mirror the defect the slab must have a C$_2$ rotational axis or a mirror plane running parallel to the surface. Due to the periodicity of the (111) c-ZrO$_2$ slab, and the structure of the defect cluster, the smallest slab which accommodates these geometric requirements is 15 atomic layers thick. In addition the periodicity of the slab means the slab thickness must increase in increments of 9 atomic layers in order to maintain symmetry. 15, 24, 33, and 42 atomic layer slabs were modeled. The unrelaxed geometry of the 33 atomic layer slab is pictured in Figure 5.4. The interatomic separation of the defects from their periodic images in the x and y directions is 7.23 Å in the slab model.
Figure 5.4: Unrelaxed geometry of a 33 atomic layer c-ZrO$_2$ slab with the lowest energy bulk defect modeled on both surfaces. The slab has C$_{2h}$ symmetry meaning the defects are mirror images of each other.

This is 2.99 Å smaller than the interatomic separation of the defects modeled in the bulk crystal, and it follows that there is an unwanted corresponding defect - defect interaction
which is difficult to avoid without using very large supercells. Defect-defect interactions are explored in more depth in the chapter titled 6.7 mol% Yttria Stabilised Zirconia, and Defect-Defect Interactions.

Figure 5.5: Formation energy per defect of the lowest energy defect cluster identified in bulk 3.2 mol% YSZ, with respect to increasing slab thickness.

Poor SCF convergence was found for the 15 layer slab. The formation energy per defect of the remaining slabs is plotted in Figure 5.5. The defect formation energy does not appear to converge with increasing slab thickness. The next slab in the series is 51 atomic layers thick and consists of 204 atoms, we deem this too expensive to calculate with DFT, with an estimated completion time of 40 hours on 896 processors (estimate produced from doubling the time taken for the 33 layer slab calculation). We move on to investigate the convergence of a single defect modeled in a slab using the dipole correction method.
5.2.2 Dipole Correction Method

The lowest energy defect cluster in the bulk crystal was modeled in the (111) \( \text{c-ZrO}_2 \) slab using the dipole correction method. The number of atomic layers was increased until the formation energy of the defect cluster converged. A selection of unrelaxed geometries are pictured in Figure 5.6, while the defect formation energies are recorded in Figure 5.7. Defect formation energies are calculated in accordance with equation 3.4 in the chapter titled *Parent Materials and Computational Details*. SCF convergence was not achieved for three structures, the 12 atomic layer, 27 atomic layer, and the 30 atomic layer slab. As seen in Figure 5.7, the energy change between the defect modeled in a 24 atomic layer slab and a 33 atomic layer slab is 0.44 eV. The formation energy of the defect appears to converge at 33 atomic layers. As the formation energy per defect in the 24 layer slab is similar to that of the 33 layer slab, we perform all further slab calculations with a 24 atomic layer slab. The 24 layer slab contains 96 atoms which is the same as the 2x2x2 c-ZrO\(_2\) supercell used to model the bulk defects at 3.2 mol\%. This means that all defects modeled in the 24 atomic layer slab are directly comparable to the defects previously studied.

We note that the formation energy per defect is different between the defects modeled using the mirrored defect method and the dipole correction. It would appear that there is an unwanted defect - defect interaction across the slab and vacuum region with the mirrored defect method. It appears that this requires a very large unit cell to minimise.

5.3 Yttria Segregation

To investigate yttria segregation at the (111) surface of YSZ, the low energy defect cluster identified in the bulk crystal was modeled on the surface of the 24 layer slab and moved layer-by-layer into the centre of the slab. The unrelaxed geometries of the slabs
Figure 5.6: A selection of unrelaxed YSZ slabs modeled with the dipole correction method and increasing slab thickness.
Figure 5.7: Formation energy of the lowest energy defect cluster identified for bulk 3.2mol% YSZ, modeled at the (111) surface of c-ZrO$_2$ slabs with increasing thickness.

are pictured in Figure 5.8, while the defect formation energies, along with the formation energy of the equivalent defect in the bulk, are recorded in Figure 5.9. It can be seen that there is a very large energetic preference, approximately -2.05 eV, for the defect to segregate from the bulk to the (111) surface. In addition, the formation energy of the defect converges rapidly towards the formation energy of the defect in the bulk crystal as it is moved into the centre of the slab. The small difference in energy between the defect in the slab and the bulk crystal can be attributed to changes in periodicity and other numerical approximations.
Figure 5.8: Left: the unrelaxed geometry of the lowest energy bulk defect modeled on the (111) surface of YSZ, Centre: the unrelaxed geometry of the defect modeled in the second sub-surface layer, and Right: the unrelaxed geometry of the defect modeled in the third sub-surface layer, or centre of the slab.
Figure 5.9: Formation energy of the lowest energy defect in bulk 3.2 mol% plotted against the formation energy of the defect at the surface, sub-surface, and centre of the 24 atomic layer 3.2 mol% YSZ slab.
5.4 Nearest Neighbour Defect on the (111) YSZ Surface

Few studies have investigated the local distribution of $Y^{3+}$ ions and $V_o^-$ on the surface of YSZ, however ReaxFF empirical atomistic potential modeling [72] has suggested that nearest neighbour type defect structures are favorable on the (111) YSZ surface. The results of ReaxFF modeling suggest that $V_o^-$ are preferentially located in the sub-surface layer of $O^{2-}$ ions, while preferentially occupying the first O-coordination sphere of the dopant $Y^{3+}$ ions. $Y^{3+}$ ions are found to segregate to the surface layer of $Zr^{4+}$ ions. The result that short-range NN type defects are favorable at the surface contradicts the behavior of the $Y^{3+}$ species in the bulk crystal, where long-range NNN type defects are energetically favorable. To test this result, we model the lowest energy short-range NN type structure found in the previous chapter, on the (111) surface.

The lowest energy short-range NN type defect cluster found in the bulk crystal is pictured in Figure 4.20. This defect cluster was found to have a very small energy barrier to $V_o^-$ reconstruction, with the $V_o^-$ able to migrate and form a more stable NNN type defect cluster. We consider this defect cluster on the YSZ (111) surface, and consider the NNN type defect that would exist if the $V_o^-$ were to migrate.

The $V_o^-$ was placed in the first sub-surface layer of $O^{2-}$ ions and in the first O-coordination sphere of both $Y^{3+}$ ions. One $Y^{3+}$ ion was placed in the surface layer of $Zr^{4+}$ ions, while the second was placed in the first sub-surface layer of $Zr^{4+}$ ions. The $V_o^-$ was then moved between the first and second O-coordination spheres of the dopant $Y^{3+}$ ions but remains in the sub-surface layer of $O^{2-}$ ions. This creates the NN and NNN type defect structures. Both NN and NNN defects have an equilateral triangle geometry of the $Y^{3+}$ - $V_o^-$ - $Y^{3+}$ cluster, which was found to be energetically favorable in the bulk material. The unrelaxed
geometries of the structures are pictured in Figure 5.10, while the formation energy of the defect clusters are compared in Table 5.1.

![Unrelaxed NN Surface Defect](image1)

![Unrelaxed NNN Surface Defect](image2)

**Figure 5.10:** Left: unrelaxed geometry of the lowest energy NN defect cluster identified in bulk 3.2m% YSZ, modeled on the (111) surface of 3.2 mol% YSZ. Right: unrelaxed geometry of the equivalent NNN defect cluster modeled on the (111) surface of 3.2 mol% YSZ.

<table>
<thead>
<tr>
<th>NN structure</th>
<th>NNN structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defect Formation Energy / eV</td>
<td>-1.7</td>
</tr>
</tbody>
</table>

**Table 5.1:** Formation energy per defect of an NN defect on the YSZ surface vs the formation energy of the equivalent NNN type defect structure.

It is clear from the energetics recorded in Table 5.1 that the NN type defect structure is energetically unfavorable compared to the NNN type defect. The NN type defect cluster is found to be 1.7 eV less stable than the NNN type defect cluster following a relaxation
of the atomic positions. The findings presented in this section match our results for the
bulk crystal, where we showed that short-range NN type structures are energetically un-
favorable.

5.5 Generating 3.2 mol% YSZ Surface Structures

Thus far we have outlined the convergence requirements of a YSZ surface model, deter-
mined the energetic preference for yttrium segregation, and established the instability
of NN type defect structures on the (111) surface. We now generate a set of symmetry
inequivalent NNN surface defect structures, using the method previously developed in the
chapter Chemical Descriptors of Yttria Stabilised Zirconia at Low Defect Concentration.

In addition to using a potential model to pre-screen structures, we add a geometric consid-
eration to our defect structure search. Having shown that short-range defect structures
with NN geometries are unfavorable compared to long-range NNN type structures, we
only consider NNN type structures in our structure search. The procedure to generate all
the possible NNN defect structures in the slab model, and compute their energies with
the point charge model implemented in GULP is outlined below. The process was fully
automated using the python programming language:

1. Label the atomic position of the first O\(^{2-}\) ion in the GULP cell file as O\(_0\). This
   introduces the location of the first V\(_{\bar{O}}\).

2. Determine the distance between the V\(_{\bar{O}}\) and each Zr\(^{4+}\) site. Reject Zr\(^{4+}\) atomic sites
   that are NN, NNNN or greater from the V\(_{\bar{O}}\). This only leaves NNN sites.

3. Iterate over the NNN Zr\(^{4+}\) sites changing any two Zr\(^{4+}\) ions into Y\(^{3+}\) ions.

4. Delete the O\(^{2-}\) ion to introduce the vacancy.

5. Start a list of structure number vs total energy.
6. Iterate over every possible structure and calculate the total energy using the point charge model, introduced in the chapter Parent Materials and Computational Details.

7. Sort the list of structure number vs total energies numerically.

8. Remove symmetry equivalents based on identical total energies.

9. Return a list of unique structure numbers and total energies.

45 symmetry inequivalent structures were discovered. As the simple point charge model of unrelaxed geometries does not provide reliable total or relative energies for the defects, the internal coordinates of the 45 structures were fully relaxed using the BMH potential. The internal coordinates of the unrelaxed 20 lowest energy structures predicted by the BMH potential, were then fully relaxed using PBE-DFT. Of the 20 structures, only 16 were successfully geometry optimized. Previously it was found that the BMH energetics of relaxed structures weakly correlated to the final relaxed DFT energies, hence we expect to capture the low energy structures as well as some high energy structures. The total BMH and DFT energies are plotted against each-other in Figure 5.11. The BMH energetics correlate weakly to the final DFT energies, however the correlation would be stronger if not for a cluster of four low energy structures predicted by DFT.

5.6 YSZ Surface Sites

The unrelaxed geometries of the four low energy structures predicted by DFT are pictured in Figure 5.12. Structure 1 is the lowest energy DFT structure after full relaxation of the atomic positions, while Structure 4 is the least energetically favorable of these four low energy DFT structures. The formation energy of the fully relaxed defect structures are recorded in Table 5.2.
The defect clusters have similar geometric characteristics. Each defect has one Y\(^{3+}\) ion in the surface layer of Zr\(^{4+}\) ions, while the second Y\(^{3+}\) ion remains in the bulk. In addition, the local geometries of the surface defect structures correspond to the three lowest energy defect clusters characterised in the bulk material, however the energetic ordering of the defect clusters changes in the slab model. In the bulk, the defect with the Y\(^{3+}\) - Y\(^{3+}\) ions lying on the metal sub-lattice along the line \(\langle 2 2 0 \rangle\) and separated by 7.2 Å was the lowest in energy. This is the least energetically favorable of the low energy defect structures in the YSZ slab model. The defect cluster with the Y\(^{3+}\) - Y\(^{3+}\) ions lying on the metal sub-lattice along the line \(\langle 1 1 0 \rangle\) and separated by 3.6 Å is the most energetically favorable in the slab, with the defect cluster with the Y\(^{3+}\) - Y\(^{3+}\) ions lying on the metal sub-lattice along the line \(\langle 2 1 0 \rangle\) being the second most favorable.

The unrelaxed geometries of Structures 1 and 2 are similar with the exception that the \(V_o^\cdot\) lies in a different sub-surface layer of O\(^{2-}\) anions. In Structure 1, the \(V_o^\cdot\) occupies the sub-surface layer of O\(^{2-}\) ions, while in Structure 2, the \(V_o^\cdot\) occupies the second sub-
Figure 5.12: The four low energy 3.2 mol% YSZ (111) surface structures calculated with DFT.
surface layer. Upon relaxation of the atomic positions in DFT, Structure 2 undergoes a reconstruction of the V\textsubscript{o}, and relaxes to a geometry that can be mapped back onto the unrelaxed geometry of Structure 1. The reconstruction of the V\textsubscript{o} is pictured in Figure 5.12. The reconstruction accounts for the identical formation energies of these defect clusters. This result suggests that there is an energetic preference for the V\textsubscript{o} to occupy the sub-surface layer of O\textsuperscript{2−} ions, a result that matches Reaxff modeling. In the case of Structures 3 and 4, the V\textsubscript{o} occupies the sub-sub-surface layer of O\textsuperscript{2−} ions and a reconstruction of the vacancy into the sub-surface layer does not appear to be possible as it would break the preferential equilateral triangle geometry of the Y\textsuperscript{3+} - V\textsubscript{o} - Y\textsuperscript{3+} cluster.

In addition, we observe that O\textsuperscript{2−} ions continue to relax along the imaginary X-point phonon modes of c-ZrO\textsubscript{2} in the YSZ slab model. This is pictured in the bottom centre panel of Figure 5.13.

Table 5.2: Formation energy per defect of the four low energy DFT YSZ surface structures

<table>
<thead>
<tr>
<th></th>
<th>Structure 1</th>
<th>Structure 2</th>
<th>Structure 3</th>
<th>Structure 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation Energy per Defect / eV</td>
<td>-3.5</td>
<td>-3.5</td>
<td>-3.3</td>
<td>-3.1</td>
</tr>
</tbody>
</table>

5.7 YSZ Water Chemistry

One reaction pathway proposed for hydrogen oxidation at the anode TPB in an SOFC is the spillover of H from nickel onto the YSZ surface. The H atoms then combine with O\textsuperscript{2−} ions to form −OH ions, which combine with an additional H atom to form water. Water then dissociates from the YSZ surface, and electrons are conducted through nickel to complete the oxidation of hydrogen. In addition, it has been shown that the polarisation resistance to hydrogen oxidation is reduced at high water partial pressures [38]. This has been attributed to an increase in the effective TPB due to hydroxylation of the YSZ surface [39] which allows hydrogen oxidation to occur away from the TPB, via the migration of −OH ions through a pseudo-Grotthus mechanism [29][58].
Figure 5.13: Top Left: unrelaxed Structure 2. Top Right: relaxed Structure 2 with $V_o$ reconstruction. Bottom Middle: relaxation along the bulk imaginary X-point phonon modes of $c$-ZrO$_2$ observed in the 3.2 mol% YSZ slab model.

To investigate the interaction between water and hydroxyl ions and the YSZ surface, we
consider the dissociation of a water molecule onto the low energy defect structure of YSZ, Structure 1 in Figure 5.12. This allows us to investigate the preferable chemical sites for water formation, the interaction between the surface sites and $\cdot OH$ and $H^+$ ions, and the energy barriers to water dissociation.

Water dissociation was investigating by modeling one $\cdot OH$ ion coordinated to one of the surface metal ions, and a $H^+$ ion coordinated to one of the surface $O^{2-}$ ions. There are 16 possible ways a water molecule can dissociate onto the low energy defect structure we have identified. We relax the geometries of all 16 structures using DFT. The surface sites are labeled in Figure 5.14, while the binding energies for the 16 water dissociations are recorded in Table 5.3.

Figure 5.14: A section of the lowest energy (111) YSZ surface defect structure, with labelled surface chemistry sites.

The results of Table 5.3 show that it is energetically favorable for the $\cdot OH$ ion to coordinate to the surface $Y^{3+}$ site. With the exception to the $Y_1 O_2$ combination, all geometries
Table 5.3: Binding energies of water on the YSZ (111) surface. $^\cdot$OH ions are coordinated to surface metal ions while H$^+$ ions are coordinated to surface O$^{2-}$ ions.

<table>
<thead>
<tr>
<th>Surface Locations of $^\cdot$OH and H$^+$ Species</th>
<th>Binding Energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr$_1$ O$_1$</td>
<td>-0.43</td>
</tr>
<tr>
<td>Zr$_1$ O$_2$</td>
<td>-0.25</td>
</tr>
<tr>
<td>Zr$_1$ O$_3$</td>
<td><strong>0.10</strong></td>
</tr>
<tr>
<td>Zr$_1$ O$_4$</td>
<td>-0.43</td>
</tr>
<tr>
<td>Zr$_2$ O$_1$</td>
<td><strong>-0.43</strong></td>
</tr>
<tr>
<td>Zr$_2$ O$_2$</td>
<td>-0.61</td>
</tr>
<tr>
<td>Zr$_2$ O$_3$</td>
<td>-0.56</td>
</tr>
<tr>
<td>Zr$_2$ O$_4$</td>
<td>-0.69</td>
</tr>
<tr>
<td>Zr$_3$ O$_1$</td>
<td>-0.69</td>
</tr>
<tr>
<td>Zr$_3$ O$_2$</td>
<td>-0.63</td>
</tr>
<tr>
<td>Zr$_3$ O$_3$</td>
<td>-0.56</td>
</tr>
<tr>
<td>Zr$_3$ O$_4$</td>
<td><strong>-0.44</strong></td>
</tr>
<tr>
<td>Y$_1$ O$_1$</td>
<td>-0.85</td>
</tr>
<tr>
<td>Y$_1$ O$_2$</td>
<td><strong>-0.03</strong></td>
</tr>
<tr>
<td>Y$_1$ O$_3$</td>
<td>-0.84</td>
</tr>
<tr>
<td>Y$_1$ O$_4$</td>
<td>-0.82</td>
</tr>
</tbody>
</table>

where the $^\cdot$OH ion is coordinated to the Y$^{3+}$ ion are energetically favorable compared to the geometries where the $^\cdot$OH is coordinated to the Zr$^{4+}$ ions. The energetic preference for $^\cdot$OH coordination to the surface Y$^{3+}$ ion can be rationalised through evaluating the relaxed geometries of the $^\cdot$OH and H$^+$ species.

When the $^\cdot$OH ion is coordinated to the Y$^{3+}$ ion, a reconstruction of the dissociated species occurs and the $^\cdot$OH and H$^+$ ions recombine to form a water molecule associatively adsorbed to the Y$^{3+}$ ion. The exception to this is the Y$_1$ O$_2$ combination, where the local geometry does not permit the $^\cdot$OH and H$^+$ ions to recombine and form water, nor can they form a hydrogen-bond. In this structure, the bridging O$^{2-}$ ion, which has the H$^+$ coordinated to it, does not neighbour the surface Y$^{3+}$ ion. A reconstruction is not possible in this structure leading to an energetically unfavorable geometry (highlighted in **bold** in Table 5.3).
The water molecule coordinated to the Y$^{3+}$ ion has one hydrogen hydrogen-bonded to a bridging surface O$^{2-}$ ion. The average Y$^{3+}$ - H$_2$O intermolecular separation is 2.42 Å, while the water molecule is distorted with bond lengths of 0.97 Å and 1.02 Å, and a bond angle of 112.4°. The average hydrogen-bond length between the surface and water molecule is 1.65 Å. The relaxed geometry of the lowest energy water adsorption (Y$_1$ O$_1$ combination) is pictured in Figure 5.15.

![Figure 5.15: A section of the lowest energy (111) YSZ surface defect structure, with water associatively adsorbed to the surface Y$^{3+}$ ion.](image)

For structures where the −OH ion is coordinated to a Zr$^{4+}$ ion, the water molecule remains dissociatively adsorbed to the surface. The average Zr$^{4+}$ - −OH bond length is 2.06 Å, while the average −OH bond length is 0.97 Å. The average bridging O$^{2-}$ - H$^+$ bond length is 1.0 Å. The energetics presented in Table 5.3 show that there are a number of unfavorable dissociations. These are highlighted in **bold**. These include: Zr$_1$ O$_3$, Zr$_2$ O$_1$, and Zr$_3$ O$_4$. These structures have unfavorable geometries, as the −OH and H$^+$ species do not neighbour each other and cannot form an additional hydrogen-bond. All other structures gain additional stability through a hydrogen-bond formed between the surface
−OH and the H⁺ species. The average −OH - H⁺ hydrogen bond length is 1.67 Å . The lowest energy dissociative adsorption is pictured in Figure 5.16.

Figure 5.16: A section of the lowest energy (111) YSZ surface defect structure, with water dissociatively adsorbed to a Zr⁴⁺ ion and surface O²⁻.

Finally the interaction between a water molecule and the YSZ surface was investigated. A water molecule was placed in the vacuum space above each surface metal ion site. The water and the slab were separated by 3.4 Å and the atomic positions allowed to relax. There appears to be an attraction between the water molecules and the YSZ surface. The water molecule relaxes towards the Zr⁴⁺ and Y³⁺ surface sites and the intermolecular distance between the surface metal ions and the water molecule decreases by 1.0 Å , to approximately 2.4 Å . An example is pictured in Figure 5.17. When the water molecule relaxes over the Y³⁺ site, the geometry pictured in Figure 5.15 is formed. Associative adsorption over the Y³⁺ site is 0.18 eV more favorable than associatively adsorption over the Zr⁴⁺ sites. Dissociative adsorption does not appear to be possible at the Y³⁺ site due
to the spontaneous reconstruction of the dissociated species.

Figure 5.17: A section of the lowest energy (111) YSZ surface defect structure, with water associatively adsorbed to a Zr$^{4+}$ ion.

The associative adsorption of water over the four different the Zr$^{4+}$ surface sites is recorded in the second column of Table 5.4. In addition, the fourth column of Table 5.4 records the change in adsorption energy between each associative adsorption, against the equivalent dissociative adsorption. Dissociative adsorption over Zr$^{4+}$ is generally endothermic with only three exothermic paths existing.

We approximate the energy barrier to the exothermic dissociation of water on the YSZ surface using a LST/QST search. In addition, we investigate the energy barrier associated with the migration of an $\cdot$OH ion, on the YSZ surface. Specifically we investigate the transition from a water molecule associatively adsorbed to a Zr$4+$ site, to the water molecule associatively adsorbed to the Y$^{3+}$ site. The reaction path is listed below:

1. H$_2$O associatively adsorbed to the Zr$_2$ site $\rightarrow$ H$_2$O dissociatively adsorbed to the Zr$_2$ and O$_4$ sites.

2. H$_2$O dissociatively adsorbed on the Zr$_2$ and O$_4$ sites $\rightarrow$ H$_2$O associatively adsorbed
The energetics of the two reaction paths are recorded in Figure 5.18. Energies are normalised to the energy of the water molecule associatively adsorbed to the Zr$^{4+}$ site. The geometries of the adsorbed species, and their transitions states are pictured in Figure 5.19.

There is a large energy barrier, approximately 0.5 eV, to water dissociation onto the YSZ surface. In addition, the results show that $-\text{OH}$ migration occurs via the dissociation of a water molecule from the surface, which proceeds to strongly bind to the Y$^{3+}$ site.

### 5.8 Chapter Conclusions

We have investigated the local defect structure and surface chemistry of the (111) YSZ surface at 3.2 mol%, using large scale \textit{ab initio} calculations. We have converged an accurate YSZ slab model using the dipole correction method to PBE-DFT, our slab model reproduces accurately the bulk energies of the Y$_2$O$_3$ defect clusters, when the defect clusters are modeled in the centre of the slab. This has has enabled us to investigate yttrium segregation to the (111) surface of YSZ, where we have shown a very large energetic pref-
Figure 5.18: Normalised energetics of water associatively or dissociatively adsorbed to varying YSZ surface sites, and the transition states between them. AA = Associative Adsorption, DA = Dissociative Adsorption.

Figure 5.19: Surface structures of water associatively or dissociatively adsorbed to varying YSZ surface sites, and the transition states between them.
We have gone on to identify the low energy Y$_2$O$_3$ defect clusters on the (111) YSZ surface at 3.2 mol%, using a joint Born-Mayer-Huggins empirical atomistic potential and PBE-DFT approach. Our results show that there is an energetic preference for the V$_{\gamma}$ to occupy the sub-surface layer of O$^{2-}$ ions, a result supported by ReaxFF atomistic potential modeling. In contrast to ReaxFF modeling, we do not find a low energy structure that has a nearest neighbour (NN) defect structure. The most probable explanation for this is the inadequacies in the energy expression provided by the force field. This supports our findings from previous bulk crystal work, and highlights the need for large scale DFT calculations when considering the surfaces of YSZ.

Four low energy surface defect clusters have been identified. The local geometries of these structures can be mapped back onto the local geometries of the low energy defect clusters identified in the bulk crystal. By considering water dissociation on our lowest energy surface defect structure, we have shown that it is preferable for water to associatively adsorb to the YSZ surface, and that this is optimal at the yttrium site. Dissociative adsorption of water is only possible over zirconium sites with the process generally being endothermic. Some exothermic paths for dissociative water adsorption exist, however there are large energy barriers to the process, as determined through LST/QST searches. Associative adsorption to the surface yttrium site is the global minimum of the system, and yttrium sites appear to act as a trap for water molecules.
In the chapter titled *Chemical Descriptors of Yttria Stabilised Zirconia at Low Defect Concentration* we outlined the relative importance of electrostatics and harmonic relaxation energies in predicting the likely low energy defect structures of 3.2 mol% YSZ, computed by DFT. Through this, we found that the total electrostatic energy of a point charge model, calculated at the unrelaxed geometries of the defects, correlated strongly to the energies of the final relaxed DFT structures of long-range structures, where the $V_\text{o}^-$ resides in the second or greater O-coordination sphere of $Y^{3+}$ ions. In contrast, it was found that the best available empirical atomistic potential only recreated a general trend of increasing DFT energies across the series of relaxed structures. In this chapter, the methodology is applied to investigate the 6.7 mol% YSZ system. 6.7 mol% is closer to the $Y_2O_3$ dopant concentration used in most commercial SOFCs (8 - 10 mol%).

Doubling the dopant concentration introduces a second $Y_2O_3$ defect cluster into the 2x2x2 supercell, and introduces an additional level of complexity. While at 3.2 mol% there were only 496 structures to consider after simple numerics were taken into account, at 6.7 mol% there are 4,530,960 possible structures to consider.

Introducing a second $Y_2O_3$ also introduces a second $V_\text{o}^-$ into the structure. As $V_\text{o}^-$ have effective charges of +2 relative to the lattice ions, it is expected that they repel one-another
and seek to maximise the distance between each other. However, based on diffuse neutron scattering results, it has been reported that $V_o$ preferentially associate in pairs along (1 1 1) directions at dopant concentrations between 10 and 24 mol%, without forming a phase with long range order [20][78][142]. Theoretical support for the short range ordering of vacancies in (1 1 1) directions has also been provided by DFT calculations at 17 mol%, and for the ordered compound $\text{Zr}_3\text{Y}_4\text{O}_{12}$ (40 mol%) [143][144], where the enumeration of all possible defect configurations through lattice algebra techniques clearly showed preference for this type of defect aggregation. Calculations at 6.7 and 10.4 mol% have also suggested that vacancies preferentially associate in (1 1 1) [12][151][180][181].

Ostanin et al. [12] studied several representative structures of YSZ 6.7 mol%, 10.4 mol% and 14.3 mol% where the $V_o$ were located in the second O-coordination sphere of yttrium ions (NNN type structures), however the relative positions of the $\text{Y}^{3+}$ ions and the exact defect topologies studied are unclear. The alignment of vacancy pairs in the (1 0 0), (1 1 0), (1 1 1) and (2 1 1) directions were considered. A key figure from their results is plotted in Figure 6.1, which shows how the energetics of the selected 6.7 mol% YSZ defect structures changes with respect to the orientation of the $V_o$ pair. The top panel shows that the (1 1 1) orientation of the vacancy pair is most favorable, while (1 0 0) is the least favorable. The second panel shows a cartoon of how the vacancy pair can align in (1 1 1) directions. There are three different orientations. The first, is one in which both vacancies neighbour a $\text{Zr}^{4+}$ ion, giving a six fold O-coordinated $\text{Zr}^{4+}$ ion. In this configuration the vacancy pair is separated by 4.43 Å ([111]-I). The second and third are variations whereby the vacancies neighbour one $\text{Zr}^{4+}$ ion respectively. The inter-atomic separation of these combinations are 8.86 Å ([111]-II) and 4.43 Å ([111]-III) respectively.

In addition, the electron paramagnetic resonance (EPR) spectrum of YSZ below 12 mol% contains a prominent trigonal (T centre) peak in samples that have been chemically reduced or exposed to ionizing radiation [145][146][147][148]. This peak has been
Figure 6.1: Ostanin et al.[12] results for $V_o - V_o$ alignment in YSZ, the top panel shows the energy of a 6.7mol% YSZ structure with the vacancy pair orientated in $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ and $\langle 211 \rangle$ orientations, the second panel shows a cartoon of the three different ways vacancies can align in $\langle 111 \rangle$ directions, and the third shows the relative energetics of each.

- Figure 6.1 -

assigned to a vacancy-vacancy pair lying in a $\langle 1 1 1 \rangle$ direction neighbouring a Ti$^{3+}$ impurity[149][150][151].

While there is evidence that vacancy pairs align in $\langle 1 1 1 \rangle$ directions, the lack of a well defined experimentally observed crystal structure, and the combinatorial complexity of the 6.7mol% system makes it difficult to know whether the low energy defect structures have actually been identified and studied. Through previous computational studies, only a handful of structures picked through experimental observations (such as the $V_o$ being NNN to a $Y^{3+}$ ion), have been considered. This makes it impossible to know if the low energy configuration of vacancy pair has been discovered.
6.1 Defect-Defect Interactions

Initially the interaction between isolated defects, relaxed in supercells of different volume and shape were investigated. We have already identified the lowest energy defect structure in a 2x2x2 supercell at 3.2 mol% (Figure 4.11). By modeling the same Y$'_Zr$ - V$_o$ - Y$'_Zr$ defect cluster in different supercells, the formation energy of the defect cluster at different dopant concentrations can be calculated. This gives an insight into the defect - defect interactions. In addition, the dependency of the formation energy on the spacial orientation of the defect can be established through modeling the defect in different shaped supercells at the same dopant concentration.

The isolated defect was relaxed using the DFT energy expression in six different supercells of the conventional c-ZrO$_2$ cell. Defect formation energies were calculated relative to the c-ZrO$_2$ and bixbyite Y$_2$O$_3$. The supercells studied included: 2x1x1 (YSZ 10.4 mol%), 2x2x1 (YSZ 6.7 mol%), 2x2x2 (YSZ 3.2 mol%), 4x2x1 (YSZ 3.2 mol%) and 4x2x2 (YSZ 1.6 mol%). The supercells and defect orientations are pictured in Figure 6.2.

By comparing the energetics of the isolated defect in the 4x2x1, 2x2x2 supercells, and the 4x2x2 supercells, the energy dependency on the spacial orientation of the defect was investigated. The 4x2x1 and 2x2x2 supercells have the same dopant concentration, but the periodicity of the defect changes between the two. The periodicity of the defect in the 2x2x2 supercell is 10.22 Å in x, y and z, while in the 4x2x1 supercell, it is 20.44 Å 10.22Å and 5.11Å in x, y and z respectively. This means the distance between defects is halved in the z direction. Studying the defect in the 4x2x2 cell allows the defect to be rotated giving two non-identical configurations. Defect formation energies of the unrelaxed structures are recorded in Table 6.1.

The results of Table 6.1 show that defects repel each other as the dopant concentration
Figure 6.2: 2x1x1, 2x2x1, 2x2x2, 4x2x1, 4x2x2 supercells of the lowest energy isolated defect structure discovered in chapter *Chemical Descriptors of Yttria Stabilised Zirconia at Low Defect Concentration*.

Table 6.1: Defect formation energies relative to c-ZrO$_2$ and bixbyite Y$_2$O$_3$, of an isolated defect with varying periodicity and dopant concentration. Energies given to 2 s.f.

<table>
<thead>
<tr>
<th>Defect Structure</th>
<th>2x1x1</th>
<th>2x2x1</th>
<th>4x2x1</th>
<th>2x2x2</th>
<th>4x2x2 1</th>
<th>4x2x2 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defect Formation Energy / eV</td>
<td>4.77</td>
<td>5.57</td>
<td>4.95</td>
<td>5.42</td>
<td>5.47</td>
<td>5.44</td>
</tr>
</tbody>
</table>
increases from 3.2 mol% to 6.7 mol%, with the formation energy increasing by approximately 0.15 meV. At 14.3 mol%, defects appear to attract each other with the formation energy decreasing by 0.2 eV between 6.7 and 14.3 mol%. In addition, there is an energy dependence on the orientation of the defect. The energy change is 0.47 eV between the 2x2x2 and 4x2x1 supercells, while it is 0.02 eV between the defect configurations in the 4x2x2 supercell. The results also show that 3.2 mol% YSZ modeled in a 2x2x2 supercell is a good approximation to the dilute limit, converging the defect formation energy to approximately 0.02 eV.

6.2 Generating 6.7 mol% YSZ Defect Structures

6.7 mol% YSZ was modeled by introducing two \( \text{Y}_2\text{O}_3 \) formula units into a 96 atom 2x2x2 supercell of the conventional c-ZrO2 cell. From the results of chapter *Chemical Descriptors of Yttria Stabilised Zirconia at Low Defect Concentration* and previous literature, it is known that defects with short-range interactions, where the V\(_{o}\) resides in the first O-coordination sphere of a Y\(^{3+}\) ion, are high in energy and unfavorable. We hence ignore all short-range structures and only consider long-range structures.

The procedure to generate all the possible defect structures with the geometric parameters outlined above, and compute their energies with the point charge model is outlined below. The process was fully automated using the python programming language:

1. Label the atomic position of the first O\(^{2-}\) ion in the GULP cell file as O\(_{0}\). This introduces the location of the first V\(_{o}\).

2. Iterate over all remaining O\(^{2-}\) ions to identify their locations. Label each new location O\(_{1}\), O\(_{2}\), O\(_{3}\),... O\(_{63}\). This determines the location of potential vacancy-vacancy pairs.

3. Loop over all possible vacancy-vacancy pairs.
4. Determine the distance between each vacancy-vacancy pair and each Zr\(^{4+}\) site. If the location of the potential V\(_o\) resides in the first coordination sphere of a Zr\(^{4+}\) ion (2.21 Å), reject that Zr\(^{4+}\) atomic site.

5. Iterate over every remaining Zr\(^{4+}\) site changing any four Zr\(^{4+}\) into Y\(^{3+}\) ions.

6. Delete the O\(^{2-}\) ions to introduce the two vacancies.

7. Start a list of structure number vs total energy.

8. Iterate over every possible structure and calculate the total energy using the point charge model.

9. Sort the list of structure number vs total energies numerically.

10. Remove symmetry equivalents based on identical total energies.

11. Return a list of unique structure numbers and total energies.

2857 symmetry inequivalent structures were discovered. The total electrostatic energy of the structures is plotted against structure number in Figure 6.1. This shows a near continuum in the energies vs structure number.

As the simple point charge model of unrelaxed geometries does not provide reliable total or relative energies for the defects, the internal coordinates of the 2857 were fully relaxed using the BMH potential. Previously it was found that the BMH energetics of relaxed structures weakly correlated to the final relaxed DFT energies. From this, an energy cut-off criteria (plotted in Figure 6.4) was used to reduce the number of structures to consider with DFT. As the BMH potential has been shown to predict many structures to be significantly higher or lower in energy than their DFT equivalents, it is expected that all the low energy defect structures will be captured, along with some structures that are high in energy. Structures up to an energy cut-off 0.35 eV were considered leaving 33
Figure 6.3: Electrostatic formation energies of 2857 6.4 mol% defect structures on the ideal lattice sites of c-ZrO$_2$.

structures to study with DFT. The structures are pictured in Figures 6.5, 6.6, 6.7 6.8, 6.9, and 6.10 where they are ordered with respect to increasing DFT energy i.e. structure 1 is the lowest energy structure when the structures are relaxed using the DFT energy expression.

Figure 6.4: Energy cut-off criteria determined from the results of the chapter Chemical Descriptors of Yttria Stabilised Zirconia at Low Defect Concentration.
Figure 6.5: Unrelaxed 6.7 mol% YSZ structures 1 - 6
Figure 6.6: Unrelaxed 6.7 mol% YSZ structures 7 - 12
Figure 6.7: Unrelaxed 6.7 mol% YSZ structures 13 - 18
Figure 6.8: Unrelaxed 6.7 mol% YSZ structures 19 - 24
Figure 6.9: Unrelaxed 6.7 mol% YSZ structures 25 - 30
Figure 6.10: Unrelaxed 6.7 mol% YSZ structures 31 - 33
6.3 6.7mol% YSZ Preliminary DFT Results

Initially we consider the formation energies of the 33 unrelaxed defect structures calculated using DFT and the simple point charge model. Figure 6.11 shows that the DFT formation energies correlate remarkably well to the total electrostatic formation energies computed from the point charge model, with an $R^2$ of 0.82.

Figure 6.11: Scatter graph showing the formation energy per defect at 6.7 mol%, calculated using DFT and point charge model at the unrelaxed geometries of the defects. The correlation between the two sets is very strong ($R^2$ of 0.82).

The internal coordinates of the 33 6.7mol% defect structures were then fully relaxed using the DFT and BMH energy expression. In Figure 6.12 the relative DFT defect formation energies of relaxed structures are plotted against the relative BMH formation energies. The results show that the BMH model energies do not correlate with the DFT energies, yielding an $R^2$ of 0. In Figure 6.13 the relative DFT defect formation energies are plotted against the relative electrostatic formation energies calculated at the unrelaxed geometries. The correlation between the two data sets is poor, with an $R^2$ of 0.2.
Figure 6.12: Scatter graph showing the formation energy per defect of relaxed structures calculated with the DFT and BMH energy expressions. The correlation between the two sets is zero, indicating that the empirical potential completely fails to reproduce the DFT energy differences.

Figure 6.13: Electrostatic formation energies of unrelaxed structures plotted against DFT formation energies of relaxed structures.

The lack of correlation between the BMH model energies and the DFT energies means that it is not possible to know whether the lowest energy structure we have computed with DFT is the minimum energy 6.7 mol% defect structure. Furthermore, the correlation between the electrostatic formation energies of the unrelaxed structures and the DFT
formation energies of relaxed structures has decreased from an $R^2$ of 0.75 in the 3.2 mol% system, to an $R^2$ of 0.2 at 6.7mol%. This indicates that the total electrostatic energy of the unrelaxed structures is a poor descriptor of the DFT energies at 6.7mol%. Figure 6.14 plots the relaxed BMH energetics against electrostatic energies of the structures, and the energy cut-off criteria applied. There is a weak correlation between the two ($R^2 = 0.31$), it can be concluded that the lowest energy structure predicted by the electrostatics was studied within the subset of 33 structures.

![Figure 6.14: Electrostatic energies of unrelaxed structures plotted against BMH energies of relaxed structures.](image)

It is apparent that the methodology used to pick 6.7 mol% structures to study with DFT is insufficient. We conclude that the database of DFT structures is currently too small to produce statistically meaningful results on the distribution of $V_{\text{O}}$ and $Y^{3+}$.

### 6.4 DFT Relaxation Energies

The relationship between the total DFT relaxation energies and the defect formation energies of the relaxed structures was assessed. Relaxation energies ($E_{\text{relaxation}}$) were computed using equation 6.1, where $E_{\text{unrelaxed}}$ is the total DFT energy of the unrelaxed
structure and $E_{\text{relaxed}}$ is the total DFT energy of the relaxed structure.

$$E_{\text{relaxation}} = E_{\text{relaxed}} - E_{\text{unrelaxed}}$$

(6.1)

Figure 6.15 plots the total relaxation energies of the structures vs their equivalent defect formation energies. There is a strong correlation between the two with an $R^2$ of 0.62. In the 3.2 mol% it was found that the total relaxation energy was not significant in determining the energetic ordering of the relaxed defect structures. Adding a second defect to the system changes this, with the ability of the ions to minimise the forces acting on them becoming significantly important.

Figure 6.15: total relaxation energies of the structures vs their equivalent defect formation energies.

Table 6.2 records the formation energy per defect of; the 6.7 mol% system modeled in the 2x2x1 supercell, and the 6.7 mol% system modeled in the 2x2x2 supercell. It is clear that the formation energy per defect is significantly lower in the 2x2x2 supercell (-0.67 eV). In this supercell, defects can cluster and pack. While the results of section titled *Isolated Defect-Defect Interactions* show that defects start to repel each other as the dopant...
concentration increases from 3.2 to 6.7mo%. The results of Table 6.2 hence suggest that clustering and packing allows defects to reduce their formation energy.

<table>
<thead>
<tr>
<th>Defect Structure</th>
<th>6.7mol% 2x2x1 supercell</th>
<th>6.7mol% 2x2x2 supercell</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_f$ per defect / eV</td>
<td>-0.16</td>
<td>-0.83</td>
</tr>
</tbody>
</table>

### 6.5 Geometric Descriptors of 6.7 mol% Defect Structures

From the preliminary DFT results it is clear that the DFT data set is currently too small to assess the major physical interactions at 6.7mol%. In addition, it is also not possible to assess the preferential orientations of the vacancy-vacancy pair or conclusively state that the minimum energy 6.7mol% defect structure has been identified. In the absence of a methodology that can be used to identify the lowest energy structure without computing the DFT energies of all 2857 symmetry inequivalent structures, we attempt to extend the methodology developed in the previous chapter, by developing an intuitive geometric understanding of the defect structures. Through a geometric understanding of the structures we hope to identify the criteria that defines whether a structure will be high in energy or low in energy.

#### 6.5.1 Energy Dependency on $V_\circ^-$ - $V_\circ^-$ Interatomic Distance and Crystallographic Orientation

We first investigate how the formation energy of the defects changes with the crystallographic orientation of the vacancy-vacancy pair. The electrostatic and BMH formation energies of the 2857 symmetry inequivalent structures were split into categories based on the orientation of the vacancy-vacancy pair. The vacancy-vacancy pair orientation has
an equivalent interatomic distance, this is listed in Table 6.3 along with the number of structures in each category. The vacancy-vacancy pair orientation with the highest symmetry has the fewest number of defect structures.

Table 6.3: Crystallographic orientations and interatomic distances of V\textsubscript{o} - V\textsubscript{o} pairs in YSZ

<table>
<thead>
<tr>
<th>Crystallographic Orientation</th>
<th>V\textsubscript{o} - V\textsubscript{o} Inter-atomic Distance / Å</th>
<th>Number of Structures in Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>⟨1 0 0⟩</td>
<td>2.55</td>
<td>511</td>
</tr>
<tr>
<td>⟨1 1 0⟩</td>
<td>3.61</td>
<td>807</td>
</tr>
<tr>
<td>⟨1 1 1⟩</td>
<td>4.43</td>
<td>42</td>
</tr>
<tr>
<td>⟨2 0 0⟩</td>
<td>5.11</td>
<td>128</td>
</tr>
<tr>
<td>⟨2 1 0⟩</td>
<td>5.71</td>
<td>431</td>
</tr>
<tr>
<td>⟨2 1 1⟩</td>
<td>6.26</td>
<td>394</td>
</tr>
<tr>
<td>⟨2 2 0⟩</td>
<td>7.23</td>
<td>239</td>
</tr>
<tr>
<td>⟨2 2 1⟩</td>
<td>7.67</td>
<td>269</td>
</tr>
<tr>
<td>⟨2 2 2⟩</td>
<td>8.86</td>
<td>35</td>
</tr>
</tbody>
</table>

Figure 6.16 shows the electrostatic formation energy per defect plotted against the reciprocal vacancy - vacancy interatomic separation. As V\textsubscript{o} have effective charges of +2 relative to the lattice ions, it is expected that they repel one-another and seek to maximise the distance between each other. Indeed, the results show that vacancy pairs repel each other with the average formation energy per vacancy pair category decreasing with decreasing reciprocal distance (R\textsuperscript{2} of 0.57). The exception to this seems to be the categories where the vacancy pair lies in a ⟨1 1 1⟩ type directions.

Figure 6.16 also shows that there is a large distribution in the energies per vacancy pair category, which is determined by the local distribution of Y\textsuperscript{3+} ions. While there is a good correlation between the average formation energy per vacancy pair category and decreasing reciprocal distance, the standard deviation away from the average formation energy within each category (approximately ± 2 - 3 eV), meaning that the interatomic separation of vacancy pairs is not a good descriptor of defect structure formation energies.
Figure 6.16: Electrostatic formation energy per defect plotted against the reciprocal vacancy - vacancy interatomic separation in reciprocal nanometers.

Figure 6.17 shows the formation energies of the relaxed BMH structures plotted against their reciprocal vacancy - vacancy interatomic separation. As was the case with the total electrostatic energy of the defects, the BMH model shows categories of structures with wide distributions of formation energies determined by the distribution of Y$^{3+}$ ions. Unlike the results for the electrostatic energies, the BMH model does not distinguish between vacancy - vacancy orientations and does not suggest that there is any repulsion between vacancy pairs.

To some extent the results presented above support the findings of previous experimental and DFT results[78][12]. The energetic ordering of the $\langle 1\ 0\ 0 \rangle$, $\langle 1\ 1\ 0 \rangle$, $\langle 1\ 1\ 1 \rangle$ and $\langle 2\ 1\ 1 \rangle$ correspond to previous DFT findings[12], with the set of structures within the $\langle 1\ 1\ 1 \rangle$ category appearing to be more favorable than the $\langle 1\ 0\ 0 \rangle$, $\langle 1\ 1\ 0 \rangle$, and $\langle 2\ 1\ 1 \rangle$ categories respectively. However, previous theoretical studies have only considered a few select structures. As the description of defect geometries provided in the literature is often incomplete, it is not possible to identify which structures within each sub-category
Figure 6.17: Born-Mayer-Huggins formation energy per defect plotted against the reciprocal vacancy-vacancy interatomic separation in nanometers.

were studied, or to know how accurate the reported relative energetics are. In addition, only vacancy pairs up to an interatomic separation of 6.26 Å have previously been considered. We have performed an exhaustive search, considering all structures up to an $V_o - V_o$ separation of 8.86 Å. The results of the exhaustive search suggest that there are many structures within the $\langle 2 1 0 \rangle$, $\langle 2 1 1 \rangle$, $\langle 2 2 0 \rangle$, and $\langle 2 2 1 \rangle$ categories that are lower in energy than the structures in the $\langle 1 1 1 \rangle$ category.

We have also made a distinction between a the vacancy-vacancy pair laying in a $\langle 1 1 1 \rangle$ direction, separated by 4.43 Å, and a vacancy-vacancy pair laying in a $\langle 1 1 1 \rangle$ direction, separated by 8.86 Å ($\langle 2 2 2 \rangle$). The category where the vacancy - vacancy pair lies in a $\langle 1 1 1 \rangle$ direction and separated by 4.43 Å is unusually low in energy given the interatomic separation of the vacancy pair. These structures are labelled [111]-I and [111]-II in Figure 6.1. In comparison, the category where the vacancy - vacancy pair lies in a $\langle 1 1 1 \rangle$ direction separated by 8.86 Å is unusually high in energy given its interatomic separation.
of the vacancy pair. These structures are labelled [111]-III in Figure 6.1.

Figure 6.18: Relaxed DFT formation energy per defect plotted against the reciprocal vacancy - vacancy interatomic separation in nanometers.

Figure 6.18 shows the formation energies of the relaxed DFT structures plotted against their reciprocal vacancy - vacancy interatomic separation. The data set is incomplete, as many vacancy pair categories are missing, and the number of structures within each category is too small to draw definitive conclusions on whether the highest or lowest energy structure within each category has been captured. Certainly, the preliminary DFT results do not support the findings of previous literature, with the ⟨1 1 1⟩ category, and V₀ inter-atomic separation of 4.43 Å, being energetically unfavorable. To reach a reliable conclusion on the DFT energies of 6.7 mol% structures, one must either compute the energy of every structure, or determine how the distribution of yttrium ions affects the total energy of the structures within each vacancy pair category. Through understanding the geometric distribution of yttrium ions, descriptors of how the defects pack and the likely low and high energy structures may be developed. This may enable the highest and lowest energy structures within each vacancy pair category to be identified. In contrast, computing the energies of all 2857 structures is estimated to take 10,000 kAU’s of the UK
national super computer, ARCHER.

6.5.2 Energy Dependency on Y\textsuperscript{3+} Ion Distribution

Doping at 6.7 mol\% introduces two V\textsubscript{o} and four Y\textsuperscript{3+} onto the crystal lattice of c-ZrO\textsubscript{2}. The defect cluster can hence be defined as a shape, where the vertices are the 3D coordinates of the dopant species. Possible shapes include; octahedra and planar sheets. To analyse the distribution of Y\textsuperscript{3+} ions within each structure, and indeed within each vacancy pair category, we consider a number of geometric descriptors including: the surface area, the volume, the volume to surface area ratio, the average Y\textsuperscript{3+} - V\textsubscript{o} interatomic distance, and the average Y\textsuperscript{3+} - Y\textsuperscript{3+} interatomic distance within each defect shape. Initially we consider the volume and surface area of the defect cluster.

Due the 3D nature of the defect cluster, it follows that there are multiple shapes that can be defined by six dopant species. We only consider the shape that occupies the smallest volume, this in turn gives an insight into the defect cluster packing. Initially the V\textsubscript{o} interatomic distance was calculated for each structure and the defect centered around the vacancy pair. Periodic images were then taken into account and the minimum distance between the center of the vacancy pair and each Y\textsuperscript{3+} ion calculated. This defines the positions of the six dopant species and the defect cluster. The volumes and surface areas of the defect clusters were calculated using a convex hull algorithm.

In mathematics, the convex hull of a set of \( n \) points, in an Euclidean plane or space, defined as the smallest convex set that contains all \( n \) points. For instance, when \( n \) is a bound subset of a plane, the convex hull may be visualised as the shape formed by a rubber band stretched around \( n \). This is pictured in Figure 6.19, where \( n \) is a set of sheep and the convex hull is the dashed line that contains all the sheep. For 3D shapes, and the 6.7 mol\% defect structures, the convex hull may look more like the 3D hull pictured in Figure 6.20. It follows that the surface area of a 3D convex hull is the sum of the triangles that map
its surface, while the volume is the sum of the tetrahedra formed by the barycentre of the set and the vertices of the convex hull. If the shape is a 2D sheet, the shape has no volume.

Figure 6.19: Example of a convex hull, $n$ corresponds to a set of sheep, the dashed line is the convex hull that contains all of the sheep, and the yellow sheep represent the vertices of the convex hull [13].

Figure 6.20: Example of a 3D convex hull, $n$ is a set of green vertices, the convex hull is made of a set of triangles (facets) that link all of the vertices [14].

Figure 6.21 plots the defect cluster volumes against their electrostatic formation energies. There is no correlation between the two. Figure 6.22 plots the average volume of the defect clusters within each $V_o$ category against the reciprocal interatomic separation of the $V_o$. 

170
Figure 6.21: Defect cluster volumes plotted against their electrostatic formation energies.

Figure 6.22: Average volume of the defect clusters within each $V_0$ category plotted against the reciprocal interatomic separation of the $V_0$.

Figure 6.22 shows that the average volume of the defect clusters increases with increasing $V_0$ interatomic separation until the $\langle 1 \ 1 \ 1 \rangle$ orientation is reached. After this there is a decrease in the average volumes of the defect clusters. The average volume of the defect clusters then steadily increases to the $\langle 2 \ 2 \ 0 \rangle$ category, before sharply rising in the case of the $\langle 2 \ 2 \ 0 \rangle$ and $\langle 2 \ 2 \ 2 \rangle$ categories. This observed trend closely resembles the trend in
DFT energies plotted in Figure 6.18, however the trend between defect cluster volumes and their final relaxed DFT energetics is poor, with an $R^2$ of 0.12, as plotted in Figure 6.23.

![Figure 6.23: Defect cluster volumes plotted against their relaxed DFT formation energies.](image)

Next the surface area of the defect clusters, and the volume to surface area ratio were considered. There is no trend between the surface area of the defect clusters and their electrostatic energies. There is also no trend between the electrostatic or DFT energies and the volume to surface area ratio. There is a trend in the surface area vs final relaxed DFT energies, with an $R^2$ of 0.42. This is plotted in Figure 6.24. It appears that defects that have smaller surface areas have a lower defect formation energy. The result may also suggest that a geometric descriptor of the defect structure energies, may have lower dimensionality than the volume ($\text{Å}^3$) or surface area ($\text{Å}^2$) i.e. the average interatomic distance between the $V_o$ and the $Y^{3+}$ ions (Å).

Finally we consider the average interatomic separation of the $V_o$ and the $Y^{3+}$ ions, as well as the average interatomic distance between the $Y^{3+}$ ions. The interatomic separation of the $V_o$ and the $Y^{3+}$ ions is defined as the average of eight values given in the matrix below, where $V_{oi}$ denotes the first oxygen vacancy etc. and $Y_1$ represents the first yttrium
Figure 6.24: Defect cluster surface plotted against their relaxed DFT formation energies.

\[
\begin{pmatrix}
Y_1 - V_{o1} & Y_1 - V_{o2} \\
Y_2 - V_{o1} & Y_2 - V_{o2} \\
Y_3 - V_{o1} & Y_3 - V_{o2} \\
Y_4 - V_{o1} & Y_4 - V_{o2}
\end{pmatrix}
\]

Through symmetry, the average \( Y^{3+} - Y^{3+} \) distance is the average of six values given in the 4 x 4 matrix below, \( Y_1 - Y_2 \), \( Y_1 - Y_3 \), \( Y_1 - Y_4 \), \( Y_2 - Y_3 \), \( Y_2 - Y_4 \), and \( Y_3 - Y_4 \).

\[
\begin{pmatrix}
Y_1 - Y_1 & Y_1 - Y_2 & Y_1 - Y_3 & Y_1 - Y_4 \\
Y_2 - Y_1 & Y_2 - Y_2 & Y_2 - Y_3 & Y_2 - Y_4 \\
Y_3 - Y_1 & Y_3 - Y_2 & Y_3 - Y_3 & Y_3 - Y_4 \\
Y_4 - Y_1 & Y_4 - Y_2 & Y_4 - Y_3 & Y_4 - Y_4
\end{pmatrix}
\]

For the complete set of 2857 structures, there is no trend between the average \( V_o - Y^{3+} \) interatomic separation and the total coulomb energy of the structures. However, within each \( V_o - V_o \) sub-set (excluding \( \langle 1 1 1 \rangle \)) there exist correlations between the two. Table 6.4 records the regression coefficients \((R^2)\) between the average \( V_o - Y^{3+} \) distance and the
total electrostatic energy of defect structures within each sub-set.

Table 6.4: Crystallographic orientations and regression coefficients ($R^2$) between the average $V_{o} - Y^{3+}$ distance and the total electrostatic energy of defect structures.

<table>
<thead>
<tr>
<th>$V_{o} - V_{o}$ Crystallographic Orientation</th>
<th>Regression Coefficient ($R^2$) of Average $Y - V_{o}$ Interatomic Distance Vs Total Electrostatic Energy of Defects</th>
</tr>
</thead>
<tbody>
<tr>
<td>⟨1 0 0⟩</td>
<td>0.56</td>
</tr>
<tr>
<td>⟨1 1 0⟩</td>
<td>0.47</td>
</tr>
<tr>
<td>⟨1 1 1⟩</td>
<td>0.00</td>
</tr>
<tr>
<td>⟨2 0 0⟩</td>
<td>0.57</td>
</tr>
<tr>
<td>⟨2 1 0⟩</td>
<td>0.65</td>
</tr>
<tr>
<td>⟨2 1 1⟩</td>
<td>0.70</td>
</tr>
<tr>
<td>⟨2 2 0⟩</td>
<td>0.32</td>
</tr>
<tr>
<td>⟨2 2 1⟩</td>
<td>0.56</td>
</tr>
<tr>
<td>⟨2 2 2⟩</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Figure 6.25 shows that the average $V_{o} - Y^{3+}$ distance of the defect clusters plotted against their relaxed DFT formation energies. As was the case with the surface area of the defect clusters, there is a weak trend between the average $V_{o} - Y^{3+}$ distance and the relaxed DFT energies, with an $R^2$ of 0.39. It appears that defects that have a smaller average $V_{o} - Y^{3+}$ distance have a lower defect formation energy.

Finally the correlation between the average $Y^{3+} - Y^{3+}$ interatomic separation and the total Coulomb and DFT energies was analysed. For the complete set of 2857 structures, there is no trend between the average $Y^{3+} - Y^{3+}$ interatomic separation and the total coulomb energy of the structures. There is also no correlation within each $V_{o} - V_{o}$ sub-set, with the exception of the ⟨1 1 1⟩ category. There is a reasonable negative correlation ($R^2$ of 0.5) within this category, suggesting that $Y^{3+}$ ions seek to become as far apart from each other as possible. This result is interesting given the geometric information previously collected.

We have shown that the structures within the ⟨1 1 1⟩ $V_{o} - V_{o}$ sub-set have uncharacteristically low total electrostatic energies when compared to defect structures within the
Figure 6.25: Average $V_o^-$ - $Y^{3+}$ distance of the defect clusters plotted against their relaxed DFT formation energies.

(1 1 0) and (2 0 0) sub-sets. The geometric data reveals that defect clusters with (1 1 0) $V_o^-$ pair orientations occupy unusually large volumes, and their electrostatic formation energies are not dependent on the attractive interaction between $Y^{3+}$ and $V_o^-$. Instead, their electrostatic formation energies are dependent on the electrostatic repulsion between $Y^{3+}$ - $Y^{3+}$ ions.

Figure 6.26 shows that the average $Y^{3+}$ - $Y^{3+}$ distance of the defect clusters plotted against their relaxed DFT formation energies. There is a very weak positive trend between the two, with an $R^2$ of 0.27. This result suggests that the smaller average $Y^{3+}$ - $Y^{3+}$ distance, the lower the defect formation energies, implying that the trend is weakly correlated to the attraction between $Y^{3+}$ - $Y^{3+}$ ions. This is contradictory to the electrostatic results.

### 6.6 Chapter Conclusions

We have applied the results of previous chapters to develop a methodology for selecting sensible 6.7mol% defect structures to study with DFT. Through reviewing the relative ac-
accuracy and importance of empirical potentials, electrostatics, and strain relaxation effects in predicting the DFT formation energies of thirty three 6.7 mol% YSZ structures, we find that, whereas the electrostatic energy of the unrelaxed structures calculated using a point charge model was a good predictor of the likely low energy 3.2 mol% defect structures, it is a poor predictor of the likely low energy 6.7 mol% defect structures. In addition, while it was found that the best available Born-Mayer-Huggins potential model recreated general trends in DFT energies at 3.2 mol%, it completely fails to reproduce DFT energy differences at 6.7 mol%.

In the absence of an easy to calculate, reliable predictor of the likely low energy DFT defect structures, we have attempted to correlate the formation energies of the structures to simple geometric descriptors. We have performed an exhaustive search on 2857 symmetry inequivalent structures, characterising every structure in terms of intuitive quantities, such as: $V_o^- - V_o^+$ separation, the average $V_o^- - Y^{3+}$ interatomic separation, the average $Y^{3+} - Y^{3+}$ interatomic separation, the surface area occupied by the defect cluster, and the volume of the defect cluster.
We can now explain the electrostatic formation energies of the defects in terms of intuitive attractive and repulsive interactions. The electrostatic formation energies of the defects decreases with increasing $V_0^- - V_0^-$ separation, due to the electrostatic repulsion between $V_0^-$. This allows us to split the structures into categories based on $V_0^- - V_0^-$ separation. Within each $V_0^- - V_0^-$ category, the formation energies of the defects strongly correlate to the distribution of the $Y^{3+}$ ions. With the exception of the $\langle 1\ 1\ 1 \rangle V_0^- - V_0^-$ category, the formation energy of the defects decreases with decreasing average $V_0^- - Y^{3+}$ distance, due to the electrostatic attraction between the two dopant species. The exception to this is the $\langle 1\ 1\ 1 \rangle$ category, where there is no correlation between the two. Instead the trend in electrostatic formation energies of these defects is correlated to the repulsion between $Y^{3+}$ ions.

Literature suggest that there is a preference for $V_0^-$ to align in $\langle 1\ 1\ 1 \rangle$ directions. While we have found no electrostatic or DFT energetic data to confirm this result, there is indeed something unique about this category of defect structures. The electrostatic formation energy of the structures where $V_0^-$ pair is aligned along the line $\langle 1\ 1\ 1 \rangle$, is unusually low in energy given their relative interatomic separation of the $V_0^-$. These defect clusters also occupy unusually large volumes, and they are the only structures to have a energy dependence on the repulsion between $Y^{3+}$ ions.

We have found weak trends between; the average $V_0^- - Y^{3+}$ interatomic separation, average $Y^{3+} - Y^{3+}$ interatomic separation, and the surface area occupied by the defect clusters, and the final relaxed DFT energies. Without a larger database of fully relaxed DFT energies, it is hard to determine if the results are statistically meaningful. This result highlights the combinatorial complexity of the 6.7mol% system, and establishes the need for further large scale DFT calculations, to produce an even larger database of 6.7 mol% defect structures.
Conclusions and Suggestions for Future Work

This thesis has established the relative accuracy and importance of empirical potentials, electrostatics and strain relaxation effects in predicting the DFT formation energetics of 3.2mol% YSZ structures. In turn, the chemical descriptors that can identify likely low energy defect structures of YSZ have been determined. It was found that the best available empirical potential poorly recreates the general trend of increasing DFT formation energies across a series of 28 symmetry inequivalent structures. The unreliability of the empirical potential can be analysed in terms of geometric considerations and the energy barriers associated with V_{o} reconstruction. The energy barriers predicted by DFT are not faithfully reproduced by the potential model and in addition, the connectivity between defect structures topologies on the potential energy surface is poorly described.

Low energy defect structures have NNN type geometries where the V_{o} resides in the second coordination sphere of a Y^{3+} ion and the first coordination sphere of a Zr^{4+} ion. This is optimal when the Y^{3+} - V_{o} - Y^{3+} defect cluster has equilateral triangle geometry. A very good predictor of the likely low energy NNN structures and indeed of all long-range NNNN and NNNNN type structures is the total electrostatic energy of a simple point charge model calculated at the unrelaxed geometries of the structures. In comparison, the total electrostatic potential calculated at the unrelaxed geometries is a poor descriptor of short-range NN structures, where the V_{o} resides in the first coordination shell of a Y^{3+} ion.
Strain effects are important and can be mapped in terms of relaxation along the imaginary X-point phonons of c-ZrO$_2$. Strain is only significant in determining the energetic ordering of high energy structures with short-range interactions. All long-range structures exploit relaxation along imaginary phonon modes to a similar extent. The results suggest that defects can be characterised by two regimes: long-range structures, whose relative energetics correlate to, or can be predicted by point charge electrostatics; and short-range structures, whose relative energetics correlate to, or can be predicted by a model containing point charge electrostatics plus a harmonic relaxation energy along the imaginary X-point phonon modes of c-ZrO$_2$. Establishing an analytical description of a destabilising force at short-range will allow both regimes to be incorporated into a single model.

Work presented in this thesis has also investigated the local defect structure and surface chemistry of the (111) YSZ surface at 3.2 mol%, using large scale \textit{ab initio} calculations. An accurate YSZ slab model was developed using the dipole correction method to PBE-DFT. The slab model presented within, reproduces accurately the bulk energies of the Y$_2$O$_3$ defect clusters, when the defect clusters are modeled at the centre of the slab. This has enabled analysis of yttrium segregation to the (111) surface of YSZ, where it was shown that there is a very large energetic preference for yttrium to segregate of approximately -2.05 eV.

Building on the results of previous sections, this thesis has identified the low energy Y$_2$O$_3$ defect clusters on the (111) YSZ surface at 3.2 mol%, using a joint Born-Mayer-Huggins empirical atomistic potential and PBE-DFT approach. The results show that there is an energetic preference for the $V_o$ to occupy the sub-surface layer of O$^{2-}$ ions, a result supported by ReaxFF empirical atomistic potential modeling. In contrast to ReaxFF modeling, there does not exist a low energy structure that has a nearest neighbour (NN) defect structure. A result that supports our studies of the bulk crystal.
Four low energy surface defect clusters were identified. The local geometries of these structures can be mapped back onto the local geometries of the low energy defect clusters identified in the bulk crystal. By considering water dissociation onto the lowest energy surface structure, results presented in this thesis show that water associatively adsorbs to the YSZ surface, and this is optimal when water adsorbs to the yttrium site. Dissociative adsorption of water is only possible over zirconium sites, with the process generally being endothermic. Some exothermic paths for dissociative water adsorption exist, however as determined through LST/QST searches, there are large energy barriers to this process. Associative adsorption to the surface yttrium site is the global minimum of the system, and yttrium sites appear to act as a trap for water molecules.

From studying 3.2 mol% YSZ, this thesis developed a methodology for selecting sensible 6.7mol% defect structures to study with DFT. Through reviewing the relative accuracy and importance of empirical potentials, electrostatics and strain relaxation effects in predicting the DFT the formation energetics of thirty three 6.7mol% YSZ structures, results presented in this thesis showed that, whereas the electrostatic energy of the unrelaxed structures calculated using a point charge model was a good predictor of the likely low energy 3.2 mol% defect structures, it is a poor predictor of the likely low energy 6.7 mol% defect structures. In addition, while it was found that the best available Born-Mayer-Huggins potential model recreated general trends in DFT energies at 3.2 mol%, it completely fails to reproduce DFT energy differences at 6.7 mol%.

In the absence of an easy to calculate, reliable predictor, of the likely low energy DFT 6.7mol% defect structures, work presented within has attempted to correlate the formation energies of the structures to simple geometric descriptors including: $V_{o} - V_{o}$ separation, the average $V_{o} - Y^{3+}$ interatomic separation, the average $Y^{3+} - Y^{3+}$ interatomic speration, the surface area occupied by the defect cluster, and the volume occupied by the defect
cluster. Through performing an exhaustive search on 2857 symmetry inequivalent structures, work presented within is able explain the electrostatic formation energies of the defects in terms of intuitive attractive and repulsive forces. The electrostatic formation energies of the defects decreases with increasing $V_\circ\cdot V_\circ$ separation, due to the electrostatic repulsion between the $V_\circ$. This allows the structures to be split into categories based on $V_\circ\cdot V_\circ$ separation. Within each $V_\circ\cdot V_\circ$ category, the formation energies of the defects correlate to the distribution of the $Y^{3+}$ ions.

With the exception of the $\langle 1\ 1\ 1 \rangle\ V_\circ\cdot V_\circ$ category, the formation energy of the defects decreases with decreasing average $V_\circ\cdot V_\circ$ - $Y^{3+}$ distance, due to the attraction between the two dopant species. The exception to this is the $\langle 1\ 1\ 1 \rangle$ category, where there is no correlation between the two. Instead, the trend in electrostatic formation energies is correlated to the repulsion between $Y^{3+}$ ions.

Literature suggests that there is a preference for $V_\circ$ to align in $\langle 1\ 1\ 1 \rangle$ directions. Work in this thesis has not produced any electrostatic or DFT energetic data to confirm this result, however there is indeed something unique about this sub-category of defect structures. The electrostatic energy of these structures is unusually low for the interatomic separation of the $V_\circ$. These defect clusters also occupy unusually large volumes, and are the only structures to have a strong energy dependence on the repulsion between $Y^{3+}$ ions.

There exist trends between; the average $V_\circ\cdot Y^{3+}$ interatomic separation, average $Y^{3+}\cdot Y^{3+}$ interatomic separation, and the surface area occupied by the defect clusters and the final relaxed DFT energies. Without a larger database of fully relaxed DFT energies, it is hard to determine if the results are statistically meaningful. This result highlights the combinatorial complexity of the 6.7mol% system, and establishes the need for further large scale DFT calculations on an even more 6.7 mol% defect structures.
The work presented in this thesis outlines the need for further research in three main areas, outlined below:

- Testing and Developing Improved Empirical Atomistic Potential Models for SOFC Anode TPB Models - Atomistic potential models will enable very fast simulations of the anode TPB and allow atomistic modeling to bridge length scales. In addition, a good potential model will enable modelers to consider the vast number of possible defect structures that are possible within YSZ, as well as consider the various interfaces and structures formed between YSZ and catalytic metal. The main aim would be to develop a empirical potential that can reproduce accurately the DFT energetics of 6.7 mol% and 10.4 mol% YSZ structures, something the best available Born-Mayer-Huggins (BMH) potential fails to do. The project would initially involve testing a recently published YSZ Reactive Force Field (ReaxFF) potential developed by A. van Duin and co-workers [71]. The project would involve comparing the ReaxFF energies of the bulk and surface YSZ defect structures studied within this thesis to determine if the potential recreates the DFT energy differences. If the potential works, the project would move to tackling more complicated challenges such as surfaces and interfaces, if not, the project would focus on refitting the existing BMH and developing a new potential. In conjunction with this, it would be interesting to investigate the destabilising interaction between $Y^{3+}$ ions and $V_o$ at short range, which leads to energetically unfavourable NN type defect structures. There is also scope to test a new dipole interatomic potential, to be published in 2015 [182].

- Modelling YSZ Surface Chemistry and Transition State Spectroscopic Signals - There is a large debate in the atomistic modeling community on the surface chemistry of YSZ and the electrochemistry occurring at the anode TPB in an SOFC. Early models developed by Shiskin and Ziegler [5] have been heavily criticised by Parinello and co-workers [29], and the mechanism for hydrogen oxidation at the TPB is still
debated. There exists a need to develop improved surface models of YSZ so that the chemistry at the TPB can be explored. As highlighted in a review this year [49] “The models in the published works to date are constructed without any attempts of validation of their atomic structure by experimental measurements. Indeed the pathway of fuel oxidation would in principle depend on such structural properties as dopant concentration on the YSZ surface, bond topology at the Ni/YSZ interface, etc.” We have developed an accurate surface model of the (111) surface of 3.2 mol% YSZ, and started investigating its surface chemistry. However, the combinatorial complexity of the defect structures created by doping YSZ to 6.7 and 9.3 mol% Y$_2$O$_3$ challenges the evaluation of the surface structures at higher dopant concentration. To proceed, we propose to calculate the spectroscopic signals, IR & Raman bond shifts, NMR signals etc. of chemical species adsorbed/absorbed onto the YSZ surface. This will enable us to propose a set of experiments that could be performed to validate the atomic structure of the YSZ surface.

- Calculating the Free Energy of YSZ Defect Structures - The work in this thesis has involved a large number of phonon calculations. From the phonon calculations it is possible to calculate the vibrational entropy of the structures and their total free energy. This in turn allows the stability of the defect structures to be investigated at high temperatures, extending the work presented from 0K to actual SOFC operating temperatures. Presented below are some preliminary results for the vibrational entropy of the structures calculated over the temperature range of 1000 - 1300K, as well as the phonon DOS of the minimum energy 3.2 mol% defect structure and the structure stabilised through relaxation of the oxygen anions along the imaginary X-point phonon mode of c-ZrO$_2$. It is apparent that the imaginary phonon modes of c-ZrO$_2$ have been stabilised in 3.2 mol% YSZ. The similarity between the DOS and the defect structures pictured in Figure 7.1 strongly suggests that atomic displacement along this phonon eigenvector is responsible for relaxing the local strain induced
by the dopant and vacancy. It would be interesting to investigate the vibrational properties of YSZ further.

Figure 7.1: Phonon DOS of c-ZrO₂ compared to the phonon DOS of the minimum energy structure relaxed along the imaginary X-point phonon eigen vector, and the minimum energy YSZ defect structure.

Figure 7.2: Vibrational entropy of seven 3.2 mol% YSZ defect structures across the temperature of operation of an SOFC (1000 - 1300K).
Bibliography


[20] Stefan T. Norberg, Stephen Hull, Istaq Ahmed, Sten G. Eriksson, Dario Marrocchelli, Paul A. Madden, Peng Li, and John T. S. Irvine. Structural Disorder in Doped Zirconias, Part I: The Zr$_{0.8}$Sc$_{0.2}$Y$_x$O$_{1.9}$ (0.0 ≤ x ≤ 0.2) System. *Chemistry of Materials*, 23:1356–1364, February 2011.


[65] Yanxing Zhang, Zhaoming Fu, Mingyang Wang, and Zongxian Yang. Oxygen vacancy induced carbon deposition at the triple phase boundary of the nickel/yttrium-


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8.1 Permissions

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Figure 1.6
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**Figure 1.7**

Title: Combined DFT and Microkinetic Modeling Study of Hydrogen Oxidation at the Ni/YSZ Anode of Solid Oxide Fuel Cells
Author: Salai Cheettu Ammal, Andreas Heyden
Publication: Journal of Physical Chemistry Letters
Publisher: American Chemical Society
Date: Oct 1, 2012
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Figure 1.8
Title: Oxidation of H\textsubscript{2}, CH\textsubscript{4}, and CO Molecules at the Interface between Nickel and Yttria-Stabilized Zirconia: A Theoretical Study Based on DFT
Author: M. Shishkin, T. Ziegler
Publication: The Journal of Physical Chemistry C
Publisher: American Chemical Society
Date: Dec 1, 2009
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**Figure 1.9**

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Figure 3.1
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Publication: Physical Review Letters
Title: First-Principles Determination of the Soft Mode in Cubic ZrO$_2$
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Figure 6.1

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8.2 Pseudopotentials

Below are the CASTEP input strings for the USP and NCP pseudopotentials used in this thesis. For more information, readers are directed to the CASTEP and Opium websites [183] [126].

8.2.1 USPs

Oxygen: 2|1.5|12.86|16.537|18.375|20UU:21UU(qc=6.25)|2p4.75
Zirconium: 3|2.1|2.1|1.05|8.5|10|11.4|40U=-2.005:50U=-0.17:41U=-1.195U=+0.1:42U=+0.25
Yttrium: 3|2|2|8.5|10|11.1|40U:50U:41UU:42UU
Hydrogen: 1|0.8|3.675|7.35|11.025|10UU(qc=6.4)

8.2.2 NCPs

Oxygen: o-optgga1.recpot
Zirconium: zr-optgga1.recpot
Yttrium: y-optgga1.recpot
8.3 CASTEP Cell Files

Below are the CASTEP cell files for the materials studied in this thesis. For more information on the cell file format, readers are directed to the CASTEP website [183].

8.3.1 c-ZrO₂ Primitive Cell

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0.00000 2.55500 2.55500
2.55500 0.00000 2.55500
2.55500 2.55500 0.00000
%ENDBLOCK LATTICE_CART

%BLOCK POSITIONS_FRAC
Zr 0.00 0.00 0.00
O 0.25 0.25 0.25
O -0.25 -0.25 -0.25
%ENDBLOCK POSITIONS_FRAC
```

8.3.2 c-ZrO₂ Supercell

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%BLOCK LATTICE_CART
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0.0000000000000 10.2200000000000 0.00000000000000
0.00000000000000 0.00000000000000 10.2200000000000
%ENDBLOCK LATTICE_CART

%BLOCK POSITIONS_FRAC
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Zr 0.000000000000000 0.250000000000000 0.750000000000000
Zr 0.250000000000000 0.000000000000000 0.750000000000000
Zr 0.500000000000000 0.500000000000000 0.000000000000000
Zr 0.500000000000000 0.750000000000000 0.250000000000000
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Zr 0.750000000000000 0.250000000000000 0.000000000000000
Zr 0.250000000000000 0.750000000000000 0.000000000000000
Zr 0.750000000000000 0.750000000000000 0.000000000000000

%ENDBLOCK POSITIONS_FRAC

8.3.3  t-ZrO$_2$ Primitive Cell

%BLOCK LATTICE_CART
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0.0000 3.5742 0.0000
0.0000 0.0000 5.1540
%ENDBLOCK LATTICE_CART

%BLOCK POSITIONS_FRAC
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O 0.5000000000000000 1.0000000000000002 0.7786552039643919
O 0.0000000000000000 0.5000000000000000 0.2213447960356081
O 0.0000000000000000 0.5000000000000000 -0.2786552039643919
Zr 0.5000000000000000 0.5000000000000000 0.5000000000000000

219
8.3.4 m-ZrO$_2$ Primitive Cell

%BLOCK LATTICE_CART
5.15000000000000 0.00000000000000 0.00000000000000
0.00000000000000 5.21200000000000 0.00000000000000
-0.852836320681048 0.00000000000000 5.24815769676629
%ENDBLOCK LATTICE_CART

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O 0.929988186572328 0.831734458940905 0.155292589721946
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O 0.070011813427670 0.168265541059095 -0.155292589721946
O 0.449570345218326 0.743092862624712 -0.020769192981217
O 0.070011927489004 0.331734458940906 0.344707304244240
O 0.929988072510994 0.668265541059094 0.655292695755760
O 0.449667432596967 0.756907137375288 0.479230807018783
O 0.550332567403032 0.243092862624712 0.520769192981217
Zr 0.724619537853955 0.539524174980813 0.291721417011410
Zr 0.275380462146043 0.460475825019187 -0.291721417011410
Zr 0.275459170363050 0.039524174980813 0.208263558976794
Zr 0.724540829636948 0.960475825019187 -0.208263558976794
%ENDBLOCK POSITIONS_FRAC
8.3.5  c-ZrO$_2$ 24 Layer (111) Slab

%BLOCK LATTICE_CART
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%ENDBLOCK LATTICE_CART

%BLOCK POSITIONS_FRAC
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O 0.500000004271115 0.000000008542229 -0.000378503863863
O 0.33333334076747 0.16666667038373 0.091041964090106
O 0.666666666666666 0.333333333333333 0.047171182480883
O 0.000000000000000 -0.000000000000001 0.137148828085599
O 0.333333333333333 0.666666666666666 0.091041968064114
O 0.166666677752688 0.833333322247311 0.047171183079962
O 0.66666644494624 0.833333322247311 0.047171183079962
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O 0.666666666666666 0.33333333333333 0.183514948736889
O 0.33333334157756 0.16666667078877 0.229300250020008

221
Zr 0.499999999569572 -0.000000000860855 0.206347731647303
Zr 0.333333333253739 0.16666666626869 0.297973852497984
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Zr 0.333333333333333 0.666666666666666 0.573346847970007
Zr 0.83333329386082 0.66666658772163 0.573346849896647
Zr 0.83333329386082 0.16666670613918 0.573346849896647
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Zr 0.666666666666666 0.333333333333333 0.663365191872722
Zr 0.16666672569138 0.83333327430861 0.663365189673497
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8.3.6  \( Y_2O_3 \) Primitive Cell

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224
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225
8.4 GULP Cell Files

Below are the GULP cell files for the materials studied in this thesis. For more information on the cell file format, readers are directed to the GULP website........

8.4.1 c-ZrO$_2$ Supercell

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fractional  
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229
|         | O shel 0.8750000000000000 0.8750000000000000 0.6250000000000000 | O core 0.6250000000000000 0.6250000000000000 0.3750000000000000 | O shel 0.6250000000000000 0.6250000000000000 0.3750000000000000 | O core 0.8750000000000000 0.3750000000000000 0.1250000000000000 | O shel 0.8750000000000000 0.3750000000000000 0.1250000000000000 | O core 0.6250000000000000 0.1250000000000000 0.8750000000000000 | O shel 0.6250000000000000 0.1250000000000000 0.8750000000000000 | O core 0.3750000000000000 0.8750000000000000 0.1250000000000000 | O shel 0.3750000000000000 0.8750000000000000 0.1250000000000000 | O core 0.1250000000000000 0.6250000000000000 0.8750000000000000 | O shel 0.1250000000000000 0.6250000000000000 0.8750000000000000 |
|---------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| Zr core | 0.0000000000000000 0.0000000000000000 0.0000000000000000 | 0.0000000000000000 0.0000000000000000 0.0000000000000000 | 0.0000000000000000 0.0000000000000000 0.0000000000000000 | 0.0000000000000000 0.5000000000000000 0.5000000000000000 | 0.0000000000000000 0.5000000000000000 0.5000000000000000 | 0.0000000000000000 0.7500000000000000 0.7500000000000000 | 0.0000000000000000 0.7500000000000000 0.7500000000000000 | 0.2500000000000000 0.0000000000000000 0.2500000000000000 | 0.2500000000000000 0.0000000000000000 0.2500000000000000 | 0.2500000000000000 0.0000000000000000 0.2500000000000000 | 0.2500000000000000 0.0000000000000000 0.2500000000000000 |
| Zr shel | 0.250000000000000 | 0.500000000000000 | 0.750000000000000 |
| Zr core | 0.500000000000000 | 0.000000000000000 | 0.500000000000000 |
| Zr shel | 0.500000000000000 | 0.000000000000000 | 0.500000000000000 |
| Zr core | 0.500000000000000 | 0.250000000000000 | 0.750000000000000 |
| Zr shel | 0.500000000000000 | 0.250000000000000 | 0.750000000000000 |
| Zr core | 0.750000000000000 | 0.000000000000000 | 0.750000000000000 |
| Zr shel | 0.750000000000000 | 0.000000000000000 | 0.750000000000000 |
| Zr core | 0.250000000000000 | 0.250000000000000 | 0.750000000000000 |
| Zr shel | 0.250000000000000 | 0.250000000000000 | 0.750000000000000 |
| Zr core | 0.250000000000000 | 0.500000000000000 | 0.250000000000000 |
| Zr shel | 0.250000000000000 | 0.500000000000000 | 0.250000000000000 |
| Zr core | 0.500000000000000 | 0.250000000000000 | 0.250000000000000 |
| Zr shel | 0.500000000000000 | 0.250000000000000 | 0.250000000000000 |
| Zr core | 0.250000000000000 | 0.500000000000000 | 0.500000000000000 |
| Zr shel | 0.250000000000000 | 0.500000000000000 | 0.500000000000000 |
| Zr core | 0.500000000000000 | 0.750000000000000 | 0.750000000000000 |
| Zr shel | 0.500000000000000 | 0.750000000000000 | 0.750000000000000 |
| Zr core | 0.000000000000000 | 0.500000000000000 | 0.000000000000000 |
| Zr shel | 0.000000000000000 | 0.500000000000000 | 0.000000000000000 |
| Zr core | 0.000000000000000 | 0.750000000000000 | 0.250000000000000 |
| Zr shel | 0.000000000000000 | 0.750000000000000 | 0.250000000000000 |
| Zr core | 0.750000000000000 | 0.250000000000000 | 0.500000000000000 |
| Zr shel | 0.750000000000000 | 0.250000000000000 | 0.500000000000000 |
| Zr core | 0.750000000000000 | 0.500000000000000 | 0.750000000000000 |
8.5 YSZ Defect Structures

This section specifies the YSZ defect structures using a numbering system. Numbers correspond to the lines in the “BLOCK POSITIONS_FRAC” of the CASTEP files that
need to be manipulated to recreate the YSZ defect structures pictured in Figures 4.2, 4.3, 4.4 4.5, 5.12, 6.5, 6.6, 6.7 6.8, 6.9, and 6.10. The number that proceeds the “O” in the YSZ structure name specifies the line in the “BLOCK POSITIONS_FRAC” that needs to be deleted to created the $V_\text{O}^\text{o}$, while the numbers that proceed the “Y” specify the lines that need to be turned into yttrium ions. The raw CASTEP DFT energy of the relaxed structure is also provided next to the structure number.

### 8.5.1 3.2 mol% YSZ

All structures are generated in the c-ZrO$_2$ supercell.

<table>
<thead>
<tr>
<th>YSZ Combination</th>
<th>YSZ Combination</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ 1</td>
<td>YSZ_combination_O_1_Zr_70_94</td>
<td>-74179.03593783</td>
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<tr>
<td>YSZ 2</td>
<td>YSZ_combination_O_1_Zr_65_66</td>
<td>-74178.95811312</td>
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<tr>
<td>YSZ 3</td>
<td>YSZ_combination_O_1_Zr_70_80</td>
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<td>YSZ 4</td>
<td>YSZ_combination_O_1_Zr_65_83</td>
<td>-74178.90511000</td>
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<td>YSZ 5</td>
<td>YSZ_combination_O_1_Zr_70_93</td>
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<td>YSZ 6</td>
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<td>YSZ 7</td>
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<td>YSZ 8</td>
<td>YSZ_combination_O_1_Zr_67_78</td>
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<td>YSZ 11</td>
<td>YSZ_combination_O_1_Zr_70_81</td>
<td>-74178.64164710</td>
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<td>YSZ 12</td>
<td>YSZ_combination_O_1_Zr_65_67</td>
<td>-74178.57802320</td>
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<td>YSZ 13</td>
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<td>YSZ 14</td>
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<td>YSZ 15</td>
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<td>YSZ 16</td>
<td>YSZ_combination_O_1_Zr_67_72</td>
<td>-74178.52825909</td>
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<td>YSZ 17</td>
<td>YSZ_combination_O_1_Zr_70_79</td>
<td>-74178.48842840</td>
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</table>
YSZ 18 YSZ\_combination\_O\_1\_Zr\_67.79 -74178.4754567 eV
YSZ 19 YSZ\_combination\_O\_1\_Zr\_67.73 -74178.45775959 eV
YSZ 20 YSZ\_combination\_O\_1\_Zr\_67.81 -74178.4186077 eV
YSZ 21 YSZ\_combination\_O\_1\_Zr\_65.71 -74178.3815967 eV
YSZ 22 YSZ\_combination\_O\_3\_Zr\_67.73 -74178.38093854 eV
YSZ 23 YSZ\_combination\_O\_1\_Zr\_65.71 -74178.37751189 eV
YSZ 24 YSZ\_combination\_O\_1\_Zr\_65.68 -74178.34635576 eV
YSZ 25 YSZ\_combination\_O\_1\_Zr\_65.70 -74178.29519261 eV
YSZ 26 YSZ\_combination\_O\_1\_Zr\_65.80 -74178.2338281 eV
YSZ 27 YSZ\_combination\_O\_1\_Zr\_67.68 -74178.1934258 eV
YSZ 28 YSZ\_combination\_O\_1\_Zr\_79.71 -74178.13987745 eV

8.5.2 3.2 mol% YSZ Slab

All structures are generated in the c-ZrO$_2$ 24 Layer (111) Slab.

YSZ 1 YSZ\_combination\_O\_5\_Zr\_67.71 -74176.20779564 eV
YSZ 2 YSZ\_combination\_O\_11\_Zr\_65.71 -74176.19845872 eV
YSZ 3 YSZ\_combination\_O\_11\_Zr\_65.74 -74176.01509050 eV
YSZ 4 YSZ\_combination\_O\_11\_Zr\_65.72 -74175.78573686 eV

8.5.3 6.7 mol% YSZ

All structures are generated in the c-ZrO$_2$ supercell.

YSZ 1 YSZ\_combination\_O\_14\_1\_Zr\_76.80_82_87 -72902.78513288 eV
YSZ 2 YSZ\_combination\_O\_14\_1\_Zr\_76.82_87_89 -72902.70596460 eV
YSZ 3 YSZ\_combination\_O\_11\_1\_Zr\_76.78_81_88 -72902.68301470 eV
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<th>Chemical Elements</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ 4</td>
<td>O:11, Zr:76,78,83,88</td>
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<tr>
<td>YSZ 5</td>
<td>O:14, Zr:73,76,82,87</td>
<td>-72902.65622433 eV</td>
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<td>YSZ 6</td>
<td>O:11, Zr:76,78,88,89</td>
<td>-72902.40732120 eV</td>
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<tr>
<td>YSZ 7</td>
<td>O:5, Zr:70,82,87,95</td>
<td>-72902.38530642 eV</td>
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<td>YSZ 8</td>
<td>O:3, Zr:78,82,83,87</td>
<td>-72902.37997093 eV</td>
</tr>
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<td>YSZ 9</td>
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<td>-72902.32575511 eV</td>
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<td>YSZ 11</td>
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<td>YSZ 14</td>
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<td>YSZ 15</td>
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<td>YSZ 16</td>
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<td>YSZ 17</td>
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<td>YSZ 18</td>
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<td>-72901.9927189 eV</td>
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<td>YSZ 19</td>
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<td>-72901.89746161 eV</td>
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<td>-72901.45822737 eV</td>
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</table>
YSZ 32 YSZ combination O_{11.1} Zr_{67.72} -72900.92727886 eV

YSZ 33 YSZ combination O_{8.1} Zr_{70.71} -72900.84964102 eV