Simulation Studies of Extended Defects in the Model System of the Functional Oxide Strontium Titanate

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vorgelegt von

M. Sc.
Amr Hazem Helmy Ramadan
aus Giza, Ägypten

Berichter: Priv.-Doz. Dr. Roger A. De Souza
Univ.-Prof. Dr. rer. nat. Arne Lüchow

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Previously Published Work

Part of the work reported in this thesis was previously published or prepared for publication


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1 Introduction

Electronic devices have shown great progress over the last few decades, with exponential growth in both power and efficiency as well as an exponential decrease in size. For conventional silicon-based technology this advancement was achieved through the pursuit of perfection on the atomic scale.\cite{1} So much so, that the limiting factor for further progress is not necessarily a lack of understanding of but rather the physical limitations of conventional silicon-based materials.\cite{2-4} This terminal point, prophesised again and again in the past $\sim 50$ years, has fuelled a search for novel materials that would allow further technological advancement. Thus functional oxides emerged as one of the future prospects of electronic materials. This new class of materials brought with it a shift in paradigm, from the strive for perfection to the utilisation of designed imperfection.\cite{5,6}

Oxide materials typically refer to ionic inorganic compounds comprised of oxygen anions—as the term suggests—and metal cations. Such compounds have been found to exhibit a plethora of different properties, such as varying forms of magnetism, of electrical conductivity, and of chemical activity.\cite{7-9} The wide variety of properties found in oxide materials are not necessarily native to the perfect structure but may also stem from the systems’ imperfections, their various defects. It has been found that, depending on the type and number density of defects within a system, an oxide material will show considerable differences in behaviour. As a result thereof, varying the type and amount of imperfections has become the method with which the desired properties of oxide materials can be finely tuned.\cite{5}

The advantage of using defects to manipulate a system’s properties is based, among other things, on the length scale of defects, which is in the sub-nanometre regime and thus already beyond the physical limitations of silicon-based technology. In light of this, an understanding of how the presence of various defects influences the properties of an oxide system is of fundamental importance such that the devices of the future can be tailored to their respective applications.

This thesis focuses on the perovskite-oxide class of materials, specifically the model system strontium titanate (ST). SrTiO$_3$ is an ideal system for fundamental research due to the good understanding of its bulk properties combined with the great versatility exhibited in its properties and its high-symmetry structure.\cite{10-17} The goal
of this work is to expand our knowledge by investigating the effects of extended defects on the microscopic and macroscopic properties of SrTiO$_3$. To this end, a brief introduction to the various types of defects (see Section 1.1) and an overview of the basic properties of the bulk strontium titanate system (see Section 1.2) will be presented.

1.1 Defects

Generally speaking, defects are deviations from a perfect crystal lattice. They can be categorised according to their dimensionality, ranging from zero-dimensional up to three-dimensional. Extended defects, a main aspect of the presented studies, are all defects which extend in at least one dimension, i.e. one- to three-dimensional defects. In the following, the various types of defects will be introduced according to their dimensionality.

1.1.1 Point Defects

Point defects or zero-dimensional (0D) defects, are imperfections in the lattice which—as the term suggests—do not extend in any spatial directions. There are various types of point defects, e.g. vacancies, with the regular lattice site being vacant [see Fig. 1.1(a)], interstitials with species being located at the normally vacant interstitial sites in the lattice [see Fig. 1.1(b)] and foreign defects where extrinsic atoms/ions (commonly referred to as dopants or impurities) reside in the host lattice at either an interstitial site or by replacing a native atom/ion of the lattice [see Fig. 1.1(c)].

![Figure 1.1: (a) Schematic of a vacancy (white square) in a two dimensional lattice. (b) Schematic of an interstitial species. (c) Schematic of a substituted lattice position (small black spot).](image)

The equilibrium concentration of point defects in a given system is determined by the equilibrium constant of the respective equilibrium reactions, such as the
intrinsic Schottky, Frenkel, Anti-Frenkel and band-excitation equilibria, and by extrinsic factors in the form of dopants/impurities and surrounding atmosphere. Furthermore, the electroneutrality condition must be fulfilled as the system (including the various point defects) must overall remain charge neutral. Knowledge of the various equilibrium point-defect concentrations is of significant importance as various properties, such as diffusivity, conductivity and optical characteristics, are governed by them.\textsuperscript{[13–15,18]}

Kröger–Vink Notation

For the sake of clarity, point defects will be referred to using the Kröger–Vink notation\textsuperscript{[19]}, as shown in Figure 1.2.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{kröger-vink_notation.png}
\caption{Schematic description of the conventional Kröger–Vink notation, with species $S$ on sublattice site $G$ with excess charge $\varepsilon$ relative to the ideal host lattice.}
\end{figure}

The notation consists of three parts: the species of interest ($S$); the sublattice site ($G$) at which the species is located; and the excess charge with respect to the ideal lattice ($\varepsilon$).

The species and sublattice sites are referred to by their respective chemical symbols, with the exception of vacancy species and interstitial sites which are referred to by $V$ and $i$, respectively. A negative excess charge is referred to by $'$, a positive charge by $\cdot$ and a neutral one by $\times$. In SrTiO$_3$, for example, a strontium vacancy (V$_{Sr}^\varepsilon$) has a twofold negative excess charge relative to the strontium ion on its regular site (Sr$_{Sr}^\varepsilon$).

1.1.2 Line Defects

Line defects or one-dimensional (1D) defects are also known as dislocations. There are two extreme types of dislocations: edge and screw dislocations. In this study edge dislocations are investigated, which—simply speaking—can be described by the insertion of an excess lattice plane or lattice planes which do not pass through
the entire lattice [cf. Figs. 1.3(a) and (b)]. This results in lattice distortions near the termination of the excess half-plane. The defining characteristic of an edge dislocation is its Burgers’ vector \( \mathbf{b} \). It describes the excess distance required to complete a path around the edge dislocation relative to the perfect lattice. The direction of the Burgers’ vector is perpendicular to the direction of the edge dislocation [see Fig. 1.3(b)]. A main difference between a screw dislocation and an edge dislocation is that the Burgers’ vector of a screw dislocation is parallel to the direction of dislocation. As mentioned, edge and screw dislocations are the two extreme types of dislocations; most dislocations are of a mixed edge/screw nature.

A common occurrence at dislocations is their dissociation into partial dislocations accompanied by the formation of an antiphase domain boundary [see Figure 1.3(c)]. Dislocations dissociate when the excess energy of the partial dislocations and the accompanying antiphase domain boundary is lower than the excess energy of the undisassociated dislocation.\(^{20–22}\)

The presence of line defects may locally alter the equilibrium distribution of point defects if dislocations are electrostatically charged (see Chapters 2 and 5). Such effects result in locally altered macroscopic properties (e.g. diffusivity and conductivity) as will be detailed throughout this work. Similar effects are also observed for screw dislocations; however as they are beyond the scope of the investigations presented here, the interested reader is referred to Refs. [20–22] for more details.

![Figure 1.3](image.png)

**Figure 1.3:** (a) Schematic perfect lattice without dislocations. (b) Schematic of an inserted half-plane, resulting in an edge dislocation with surrounding distortion of the lattice. The difference between the blue paths in the undisturbed lattice (top right) and around the dislocation (centre) results in the Burgers’ vector, as indicated by the red arrow. (c) A schematic of a dissociated dislocation with an anti-phase domain boundary.
1.1.3 Planar Defects

Two-dimensional (2D) defects are frequently referred to as interfaces. Two important types of interfaces are solid-gas interfaces or solid-solid interfaces. Irrespective of the type of interface, the defining characteristic of a planar defect is that the atomic planes forming the interface have a different surrounding environment (e.g. different coordination geometries) compared to the bulk of the compound. The altered environment at the interface may have considerable effects on the system’s properties. Such effects include, but are not limited to, changes in the point-defect distribution in the vicinity of the interface, similar to the interactions of 1D defects with point defects (see Chapters 2, 3 and 5). Thus the presence of an interface can alter or even dominate the material properties in their proximity.\(^{[18]}\) This work is focussed on solid-solid interfaces of which several heterogeneous, \textit{i.e.} interfaces composed of different compounds (see Chapters 3 and 4), and homogeneous systems, \textit{i.e.} interfaces composed of a single compound (see Chapter 5) have been investigated.

Grain Boundaries

Grain boundaries, homogeneous planar defects, are the boundaries that form between two grains of identical material which are misoriented with respect to one another. Depending on the misorientation of the grains, one may differentiate between two extreme cases: twist and tilt boundaries. Similar to the case of 1D defects (dislocations), most grain boundaries are a result of a combination of the two misorientation types and are referred to as mixed boundaries.

Each grain boundary is uniquely defined by five independent macroscopic degrees of freedom (DOF) which can be used to rotate one grain into perfect coincidence with the second grain: the misorientation angle (1 DOF), the rotation axis (2 DOFs), and the grain-boundary plane normal (2 DOFs). These degrees of freedom are commonly represented as \( \theta \ [h_\theta \ k_\theta \ l_\theta] \ (h_{GB} \ k_{GB} \ l_{GB}).^{[23]} \) Beyond the five macroscopic degrees of freedom, three microscopic degrees of freedom exist. The microscopic DOFs are in the form of a translation vector, that characterises the parallel and perpendicular rigid body translation of two grains with respect to one another. These three translational degrees of freedom are independent of the five macroscopic degrees of freedom and are determined through the minimum energy configuration of the grain boundary and thus cannot be chosen arbitrarily.\(^{[23]}\)

Other than the type of misorientation, grain-boundaries can also be differentiated by the degree of misorientation, the misorientation angle (\( \theta \)). Low-angle boundaries are generally accommodated by an arrangement of one-dimensional defects:
Twist boundaries are accommodated by a network of screw dislocations, and tilt boundaries are accommodated by an array of edge dislocations. With increasing misorientation angle, the separation of the 1D defects decreases. The angle at which the accommodating line defects can no longer be discerned as individual dislocations is the transition point to high-angle boundaries.[24]

![Diagram of grain boundary](image)

**Figure 1.4:** Schematic depiction of a symmetric tilt grain boundary. $d_{\text{Frank}}$ represents the distance between dislocations and $\theta$ the tilt angle. $|\mathbf{b}|$ is the Burgers’ vector, indicated by the blue arrow. (Schematic based on Ref. [18])

Low-angle tilt grain boundaries for which the grain-boundary planes of both grains are crystallographically equivalent are symmetric-tilt boundaries. The five DOFs of symmetric tilt boundaries are then reduced to $\theta \mid \{h_G k_G l_G\} \mid \{h_{GB} k_{GB} l_{GB}\}$, where the curly brackets denote the family of equivalent grain-boundary plane normals with the Miller indices $h_{GB}$, $k_{GB}$ and $l_{GB}$. The lattice discontinuity at such low-angle tilt boundaries is accommodated by an array of edge dislocations with a specific separation between them,

$$d_{\text{Frank}} = \frac{|\mathbf{b}|}{2 \sin (\theta/2)}$$  \hspace{1cm} (1.1)

for a given tilt angle ($\theta$) and Burgers’ vector ($|\mathbf{b}|$).[21] Equation (1.1) is also known as Frank’s formula. A schematic representation of such a boundary is shown in Figure 1.4.

The edge dislocations result in two regimes of strain: a compressive strain regime due to the excess lattice plane, and a tensile strain regime at the termination of the excess lattice plane (see Figure 1.4). Investigating dislocations by means
of low-angle symmetric tilt grain boundaries has several advantages for both experimental and theoretical investigations. Namely, the boundaries consist of a well-defined array of pure edge dislocations that are stable against annihilation at high temperatures.

### 1.1.4 Volume Defects

For the sake of thoroughness, volume defects or three-dimensional (3D) defects are mentioned only briefly. They refer to macroscopic defects (e.g. inclusions and pores). However, as they extend beyond the length scales of interest to this study, the reader is referred to Refs. [18, 25] for more information.

### 1.2 Strontium Titanate

Strontium titanate (SrTiO$_3$), the model material for the family of perovskite oxides (ABO$_3$) for reasons of its high symmetry structure and its chemical and physical stability over a wide range of temperatures$^{[16,26,27]}$, is the system of interest for the studies presented in this thesis.

While the cubic phase of SrTiO$_3$ is stable up to its melting point ($\approx$ 2350 K), other non-cubic phases exist at low temperatures. The oxide structure transitions from cubic to tetragonal at $T = 110$ K, and at $T = 65$ K a further transition from tetragonal to orthorhombic symmetry takes place.$^{[28]}$

Beyond the structural stability, the system also exhibits good chemical stability, as it is capable of accommodating small deviations from the nominal cation stoichiometry of 1:1, remaining single phase for ratios $0.995 \leq \text{SrO}/\text{TiO}_2 \leq 1.002$. $^{[29]}$ Excess TiO$_2$ beyond the stability limit results in the exsolution of TiO$_2$ as a second phase, while in the case of excess SrO, a new phase is formed in order to accommodate the non-stoichiometry, the Ruddlesden–Popper phases of general composition Sr$_{n+1}$Ti$_n$O$_{3n+1}$. $^{[30–32]}$

With regards to point defects in bulk SrTiO$_3$, their behaviour has been elucidated to a degree unrivalled by any other complex oxide$^{[13–16,33–35]}$, which allows for the quantitative examination of the interactions of extended defects (e.g. dislocations and interfaces) with point defects$^{[36–38]}$.

This study, specifically, focuses on the investigation of the effects of extended defects on the surrounding structure and point-defect distribution in SrTiO$_3$. To this end, a general introduction regarding strontium titanate’s bulk structure and point-defect properties is presented prior to the investigation of the system’s interactions with extended defects.
1.2.1 Cubic Perovskite Structure

Figure 1.5: (a) Crystallographic unit cell of SrTiO$_3$ with Sr at the origin and Ti at the centre; (b) alternative representation of the crystallographic unit cell with Ti at the origin and Sr at the centre; (c) view along the $\langle 100 \rangle$ direction indicating the alternating planes of SrO and TiO$_2$ within the structure. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii).

SrTiO$_3$ crystallises in the high-symmetry cubic space group $Pm\bar{3}m$ (No. 221) at room temperature. The crystallographic unit cell is depicted in Figure 1.5. The unit cell can be generated with either Sr or Ti positioned at the origin, as they occupy the Wyckoff positions 1a and 1b with the same site symmetry ($m\bar{3}m$), yielding two equivalent representations of the same structure [see Figures 1.5(a) and 1.5(b)]. The experimental lattice constant at room temperature is $a = 3.905\ \text{Å}$ \cite{39}.

Figure 1.6: (a) Cuboctahedral (12-fold) coordination of Sr by O; (b) octahedral (6-fold) coordination of Ti by O; and octahedral (6-fold) coordination of O by four Sr and two Ti. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii).

For the atomistic investigations of grain boundaries presented in this study (see Chapter 5) it is often useful to view the perovskite structure in terms of alternating SrO and TiO$_2$ planes along the $\langle 100 \rangle$ direction, forming units of SrTiO$_3$ [see Figure
1.5(c).
Figure 1.6 shows the coordination polyhedra of the different sites. Sr occupies the A-site in the $\text{ABO}_3$ perovskite structure and is cuboctahedrally (12-fold) coordinated by oxygen [see Figure 1.6(a)]; the B-site is occupied by 6-fold (octahedrally) coordinated Ti with oxygen being the coordinating species [see Figure 1.6(b)]; and the O-sites are also octahedrally coordinated, by four Sr and two Ti ions, respectively [see Figure 1.6(c)].

1.2.2 Bulk Defect Chemistry of Strontium Titanate

The equilibrium defect chemistry of a system is determined by the relevant equilibrium reactions and their corresponding equilibrium constants. In the case of the nominally undoped $\text{SrTiO}_3$ under dry conditions (such that water incorporation can be ignored\cite{40}), the point-defect chemistry is defined by three equilibrium reactions\cite{10–17}:

(I) The electronic equilibrium

\[
\text{nil} \rightleftharpoons e^+ + h^+ \tag{1.2}
\]

\[
K_{\text{eh}}(T) = c_{e^+} c_{h^+} = K_{\text{eh}}^0 \exp \left( -\frac{\Delta H_{\text{gap}}}{k_B T} \right) \tag{1.3}
\]

(II) The oxide reduction equilibrium

\[
\text{O}_2^\ast \rightleftharpoons V_{\text{O}}^\ast + 2e^+ + \frac{1}{2}\text{O}_2(g) \tag{1.4}
\]

\[
K_{\text{red}}(T) = c_{V_{\text{O}}^\ast}^2 c_{e^+}^2 a_{\text{O}_2}^{0.5} = K_{\text{red}}^0 \exp \left( -\frac{\Delta H_{\text{red}}}{k_B T} \right) \tag{1.5}
\]

(III) The partial Schottky equilibrium

\[
\text{Sr}_{\text{Sr}}^\ast + \text{O}_2^\ast \rightleftharpoons V_{\text{Sr}}^\ast + V_{\text{O}}^\ast + \text{SrO(g)} \tag{1.6}
\]

\[
K_{\text{Sch}}(T) = c_{\text{Sr}_{\text{Sr}}^\ast} c_{\text{V}_{\text{O}}^\ast} a_{\text{SrO}} = K_{\text{Sch}}^0 \exp \left( -\frac{\Delta H_{\text{Sch}}}{k_B T} \right) \tag{1.7}
\]

$c_{\text{def}}$ refers to the concentration of the respective defect species and $K(T)$ to the equilibrium constant of the corresponding defect equilibrium. $\Delta H_{\text{gap}}$, $\Delta H_{\text{red}}$ and $\Delta H_{\text{Sch}}$ are enthalpies of band-gap excitation, reduction and partial Schottky disorder, respectively. $a_{\text{O}_2}$ and $a_{\text{SrO}}$ are the activities of oxygen and strontium oxide and are approximately equal to the numerical value of the respective partial pressure in bar.
For the relevant electroneutrality condition one must consider that nominally un-
doped strontium titanate is actually weakly doped with acceptor impurities (e.g. 
$Al^{13+}$), resulting in a fixed acceptor concentration ($c_{Acc}'$). Furthermore, the 
temperatures of interest in this study ($\leq 1000$ K) are much lower than the tem-
peratures at which cation diffusion in SrTiO$_3$ becomes relevant$^{[42,43]}$. Thus the 
concentration of cation vacancies ($V_{Sr}'$) can be considered frozen in from higher 
temperatures and consequently is regarded as an additional fixed acceptor con-
centration independent of the SrO activity resulting in a fixed effective acceptor 
concentration

$$c_{Acc}' = c_{Acc}' + 2c_{V_{Sr}}'.$$  \hspace{1cm} (1.8)

With the considerations described, the electroneutrality condition can be formulated as

$$c_{Acc}' + c_{e'} = 2c_{V_{O}}'' + c_{h'}.$$  \hspace{1cm} (1.9)

The resulting set of three equations [Eqns. (1.3), (1.5) and (1.9)] with three un-
knowns ($c_{V_{O}}''$, $c_{e'}$ and $c_{h'}$) can then be solved consistently for a fixed acceptor 
concentration (of the order of $10^{18}$ cm$^{-3}$) for given $T$ and $a$O$_2$ (independent of 
c$_{V_{Sr}}''$ and $a$SrO), with the relevant equilibrium constants ($K_{eh}$ and $K_{red}$) taken from 
literature$^{[14,15,44]}$ (see summarised values in Table 1.1).

**Figure 1.7:** Kröger–Vink diagram for point defects ($c_{V_{O}}''$, $c_{e'}$ and $c_{h'}$) in weakly acceptor-
doped SrTiO$_3$ with $T = 973$ K and $c_{Acc}' = 7 \cdot 10^{17}$ cm$^{-3}$ at various $p$O$_2$. 

10
The determined equilibrium defect concentrations for bulk SrTiO$_3$ for $T = 973$ K and $c_{Acc} = 7 \cdot 10^{17}$ cm$^{-3}$ as a function of $p_{O_2}$ are shown in Figure 1.7. From this Kröger–Vink diagram it becomes apparent that for $-20 \leq \log_{10} (p_{O_2}/\text{bar}) \leq 0$, the point defect chemistry in bulk strontium titanate is dominated by the acceptor dopants and the compensating oxygen vacancies.

Table 1.1: Energies and pre-exponential factors required for the determination of the equilibrium concentration of point defects in SrTiO$_3$ (see text).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{Acc}'$</td>
<td>$0.7 \cdot 10^{18}$ cm$^{-3}$</td>
<td>[33]</td>
</tr>
<tr>
<td>$K_{eh}^0$</td>
<td>$7.5 \cdot 10^{45}$ cm$^{-6}$</td>
<td>[44]</td>
</tr>
<tr>
<td>$K_{red}^0$</td>
<td>$6.6 \cdot 10^{68}$ cm$^{-9}$</td>
<td>[44]</td>
</tr>
<tr>
<td>$\Delta H_{\text{gap}}$</td>
<td>3.46 eV</td>
<td>[44]</td>
</tr>
<tr>
<td>$\Delta H_{\text{red}}$</td>
<td>5.58 eV</td>
<td>[44]</td>
</tr>
</tbody>
</table>

1.3 Outline

Having presented the basic structural and defect-chemical properties of SrTiO$_3$, the various computational methods used in this study will be explained in Chapter 2. Three interface systems comprising ST are investigated in this thesis. The first is the SrTiO$_3$ | Y:ZrO$_2$ | SrTiO$_3$ heterostructure and will be discussed in Chapter 3 with a focus on the origin of the highly unusual conductivity of the system. Possible effects of an equilibrium redistribution of point-defects across the interfaces on the conductance and oxygen diffusion will be investigated within a well-established thermodynamic framework (see Section 2.2).

The second system, the SrTiO$_3$ | SrO heterostructure, will be investigated with regards to the interface structure as well as the possible influence it may have on the memristive properties of ST (see Chapter 4). Conclusions will be drawn through the combination of both the computational results and the experimental findings obtained through the collaborative nature of the investigations.

The third and final topic of this thesis deals with homogeneous interfaces comprised of SrTiO$_3$, specifically low-angle symmetric tilt grain boundaries (see Chapter 5). Detailed investigations of the interface structure and the corresponding defect properties will be discussed and compared with various findings in literature.
Computational Methods

The investigation of extended defects across various length scales requires the utilisation of multiple methods in order to properly capture the properties of interest. Specifically two approaches are employed in the studies presented, atomistic simulations and a continuum approach with finite-element calculations. Atomistic simulations are typically used to investigate atomic length scales (Å up to a few hundred nm) and the continuum approach is used for the investigation of macroscopic length scales (0.1 µm – 1000 µm). The two methods and their application within the presented studies are introduced below.

2.1 Atomistic Simulations

The focus of atomistic simulation methods is typically at the Å scale up to the nm scale, where atoms/ions are treated explicitly with respect to their short- and long-range interactions between one another. In this way system-specific properties can be determined which are not directly attainable through experimental procedures, such as defect energies or migration paths and barriers.

The atomic-scale interactions within a system can be described using several methods, among them the quantum mechanical approach employing density functional theory and classical methods employing empirical pair potentials. Each method has its advantages and its drawbacks. The quantum mechanical approach generally yields results with good accuracy but is computationally very expensive and is currently limited to small systems, typically comprising a few hundred atoms. Even with these limitations, the use of density functional theory does not guarantee a good description of point-defect properties within a system (e.g. the migration barrier of oxygen ions in SrTiO$_3$ is regularly underestimated$^{[45]}$). Simulations using empirical pair potentials have the advantage of being considerably simpler and computationally less taxing, allowing for simulations with up to several million species$^{[46]}$. This often comes at the cost of simulation accuracy, for which reason empirical pair potential simulations are more frequently used for the investigation of trends and relative quantities rather than absolute quantities.
As the systems of interest in this work are of considerable size (treatment of interfaces requires large systems with more than $10^3$ ions), with resource limitations prohibiting extensive density functional theory simulations, classical methods employing empirical pair potentials will be used.

### 2.1.1 General Utility Lattice Program

The General Utility Lattice Program (GULP) is a stand-alone program developed by Julian Gale\(^{[47]}\) for atomistic simulations focused on the application of static lattice dynamics.\(^a\) The GULP code is employed for all the atomistic simulations presented here. All tools required for the investigations conducted are implemented within its code.\(^b\)

### 2.1.2 Empirical Pair Potentials

An empirical pair potential (EPP) is typically comprised of two parts \([\text{see Eq. (2.1)}]\), one of which accounts for the Coulomb interactions (long-range interactions), while the other is used to describe the van-der-Waals and Pauli interactions (short-range interactions). The long-range interactions are described with a Coulomb term sufficiently well, which is used in virtually all EPP simulations of ionic systems, although the ionic charges may be the nominal valences or some fraction thereof. For the short-range interactions, by contrast, a broad spectrum of functions is available \((\text{e.g. Buckingham, Morse and Lennard-Jones potentials})\). Each function describes certain properties of a system well, while other properties are less adequately described. The choice of potential type depends on the characteristics to be investigated.

Preferably, the selected pair potential will be transferable between systems \((\text{for the same pair of interacting species})\), stable with regards to the desired simulations, and describe the structure as well as the physical and defect-chemical properties well. This is a tall order, and it is unlikely any one potential will achieve all these goals. Therefore, a compromise, depending on the intended study and the properties of interest, must be made. Due to this difficulty of finding the perfect potential for SrTiO\(_3\), a large number of potentials have been derived in literature\(^{[48–56]}\).

The atomistic simulations in this study were performed with a rigid ion model employing partial ionic charges. As usual, long-range interactions are described with a Coulomb term, but the short-range interactions are modelled with a Morse-

\(^a\)http://nanochemistry.curtin.edu.au/gulp/

\(^b\)Example input files for the employed methods can be found in the Appendix.
potential with an additional repulsive term [see Eq. (2.1)].

\[ V_{EPP}^{ii}(r) = \frac{z_iz_je^{2}}{4\pi\varepsilon_0r} + D_{ij}\left\{\left[1 - e^{-a_{ij}(r-r_{eq})}\right]^{2} - 1\right\} + \frac{C_{ij}}{r^{12}} \]  

(2.1)

The empirical parameters, in this case, are the ionic charges \((z_i \text{ and } z_j)\), the energy-well depth \((D_{ij})\), the energy-well width \((a_{ij})\), the equilibrium distance \((r_{eq})\) and the parameter \(C_{ij}\). The third term \((C_{ij}/r^{12})\) is an additional repulsive term, which gains in importance when performing molecular dynamics simulations, as it prevents inter-ion distances from becoming unphysically small.

The form of the potential as well as the values for the empirical parameters are those determined by Pedone et al.[54] (see Table 2.1). They reproduce both experimental bulk and defective lattice properties of SrTiO\(_3\) very well (see Tables 2.2 and 2.3 below)[57,58] and thus have proven to be transferable to perovskites as they were initially developed for various binary oxides and glasses[54].

<table>
<thead>
<tr>
<th>Table 2.1: Parameters of the empirical pair potentials as derived by Pedone et al.[54]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_{ij} / \text{eV})</td>
</tr>
<tr>
<td>Sr(^{1.2+}) ... O(^{1.2-})</td>
</tr>
<tr>
<td>Ti(^{2.4+}) ... O(^{1.2-})</td>
</tr>
<tr>
<td>O(^{1.2-}) ... O(^{1.2-})</td>
</tr>
</tbody>
</table>

### 2.1.3 Bulk Simulations

Due to the difficulties in finding a suitable set of EPPs, it is necessary to perform basic simulations to determine whether certain properties are comparable to experimental values prior to performing extensive and more complex simulations which may push the limits of the simple EPPs. The most commonly checked perfect lattice properties are the lattice parameters as well as the bulk modulus. In order to determine these quantities, a simulation of the perfect lattice is performed.

A good initial configuration of the simulation cell is obtained from the experimentally determined structure (see Section 1.2). All degrees of freedom are optimised freely until a minimum energy configuration is obtained. As evidenced by the summary in Table 2.2, various experimental and computational investigations of perfect lattice properties are adequately reproduced by the EPPs. This indicates that the selected potentials are transferable from SrO and TiO\(_2\) to SrTiO\(_3\) as it captures both the bulk physical properties as well as the system’s structure well.[57–59]
Table 2.2: Comparison of computational and experimental properties of the perfect lattice: lattice parameter $a$, bulk modulus $B$, $G/(1 - \nu)$ with shear modulus $G$ and Poisson’s ratio $\nu$. Adapted from Ref. [57] with permission from The Royal Society of Chemistry.

<table>
<thead>
<tr>
<th></th>
<th>$a$ / Å</th>
<th>$B$ / GPa</th>
<th>$G/(1 - \nu)$ / GPa</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPP calculations</td>
<td>3.919</td>
<td>169</td>
<td>143</td>
<td>This study</td>
</tr>
<tr>
<td>DFT calculations</td>
<td>3.898 – 3.969</td>
<td>173</td>
<td>146</td>
<td>[45]</td>
</tr>
<tr>
<td>Experiment</td>
<td>3.92</td>
<td>183</td>
<td>149</td>
<td>[61]</td>
</tr>
<tr>
<td>Experiment</td>
<td>3.905</td>
<td>179</td>
<td>150</td>
<td>[63]</td>
</tr>
</tbody>
</table>

2.1.4 Defect Simulations

If perfect lattice properties can be reproduced, the simulation of point-defect process can be performed. There are two general approaches for the simulation of point-defect processes, namely the Mott–Littleton approach\textsuperscript{[64]} and the supercell approach.

Mott–Littleton Approach

![Figure 2.1: Scheme of the Mott–Littleton approach indicating the defect centre and regions I, IIa and IIb. Region IIb extends to infinity.](image)

The Mott–Littleton approach is an approximation and is valid for the investigation
of infinitely dilute point-defect processes. Within this approximation, two spherical regions (region I and region II) are defined around a defect centre in the perfect lattice (see Figure 2.1). The point defect(s) of interest (e.g. an interstitial, vacancy, impurity or a combination thereof) is placed at or around the defect centre. Then all ion positions within region I are optimised explicitly to a minimum energy configuration. Region II is subdivided into regions IIa and IIb (see Figure 2.1), wherein the ionic configurations in region IIa are minimised in an approximating fashion as the effects of the defect(s) of interest (at the defect centre) are much weaker compared to their interactions with region I. Region IIb is a dielectric and elastic continuum which constitutes the perfect lattice. Herein the ionic positions are optimised such that the ions at the edge of region IIa transition (preferably without discontinuity in the energy landscape) into the perfect lattice structure.

**Supercell Approach**

A supercell is the definition of a new translational unit cell which is comprised of multiples of the original unit cell. Figure 2.2 shows an example $3 \times 3 \times 3$ supercell of SrTiO$_3$, where the unit cell with five ions (left) is multiplied by three in all directions, resulting in the supercell containing 135 ions (right).

![Figure 2.2: On the left is the crystallographic unit cell of SrTiO$_3$ and on the right is a $3 \times 3 \times 3$ supercell of SrTiO$_3$. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii).](image)

The supercell approach distinguishes itself from the Mott–Littleton approach through its ease of application as it maintains three-dimensional translational symmetry. This method is mostly limited by computational costs, as the simulation of an infinitely dilute defect would require a supercell with an infinite number of ions. Thus the supercell method is mainly used in cases where the Mott–Littleton approach is not a viable option (e.g. non-dilute defects). The supercell size is
typically chosen in a way to obtain a defect concentration of the order of 1%. This approach becomes ideal when investigating the properties of concentrated defects, since these can be simulated with a smaller cell. However, within this approach the defect ordering is not random. Due to the use of translational symmetry in the simulations, the defect(s) will always be located at the same position within the repeat units of the supercell and may result in undesired interactions of with their translational images (often referred to as image interactions).

**Point-Defect Processes**

Irrespective of the method employed to investigate point-defect processes, Mott–Littleton or supercell approach, the activation energy of point-defect processes (e.g. vacancy formation, ion migration and defect reactions) can be determined by comparing various defect states. In the following, the approach to determining the migration path and barrier of an ion will be illustrated with the example of oxygen-ion motion in SrTiO₃.

![Diagram of SrTiO₃ unit cell and defect energy](image)

**Figure 2.3:** (a) Unit cell of SrTiO₃ indicating the (100) and (110) migration paths. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii). (b) Relative defect energy of an oxygen ion for the two migration paths; the activation energy is indicated by the grey arrows. Adapted from Ref. [57] with permission from The Royal Society of Chemistry.

The migration of oxygen in SrTiO₃ occurs by a vacancy mechanism along the octahedral edges of the TiO₆ octahedra [see Figures 1.6(b) and 2.3(a)]. In order to determine the migration path and the position of the saddle point, the energy hyper-surface between the initial and the final position of the migrating species is systematically scanned. This is achieved through multiple defect simulations where the migrating oxygen ion is fixed at various positions on the plane of migration between the initial and final state of the migration process (see Figure 2.3). The
scan of the energy hyper-surface along the migration direction reveals a maximum, indicative of proximity to the saddle-point configuration. In order to confirm that a saddle-point configuration has been found, further systematic scans of the energy hyper-surface in the directions perpendicular to the migration direction are necessary. In these linearly independent directions, it is expected to find energy minima at the position of the energy maximum along the migration direction (not shown). A saddle-point configuration (also referred to as a transition state) has been found once these conditions have been fulfilled.

For oxygen-migration along the \( \langle 110 \rangle \) direction in \( \text{SrTiO}_3 \) one finds a curved migration path as schematically depicted in Figure 2.3(a). For \( \langle 100 \rangle \) migration a linear migration path is found.

**Table 2.3:** Comparison of computational and experimental activation enthalpies for oxygen-vacancy migration \( \Delta H_{\text{mig,V}_0} \) and strontium vacancy migration \( \Delta H_{\text{mig,V}_{\text{Sr}}} \).

Adapted from Ref. [57] with permission from The Royal Society of Chemistry.

<table>
<thead>
<tr>
<th>Method</th>
<th>( \Delta H_{\text{mig,V}_0} )/eV</th>
<th>( \Delta H_{\text{mig,V}_{\text{Sr}}} )/eV</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPP calculations</td>
<td>0.63</td>
<td>4.01</td>
<td>This study</td>
</tr>
<tr>
<td>DFT calculations</td>
<td>0.27(-)0.49</td>
<td>3.68</td>
<td>[45]</td>
</tr>
<tr>
<td>DFT calculations</td>
<td>0.53</td>
<td>3.96</td>
<td>[65]</td>
</tr>
<tr>
<td>DFT calculations</td>
<td>0.51</td>
<td>3.96</td>
<td>[66]</td>
</tr>
<tr>
<td>DFT calculations</td>
<td>0.58</td>
<td>3.96</td>
<td>[67]</td>
</tr>
<tr>
<td>Nuclear spin relaxation</td>
<td>0.62</td>
<td>3.96</td>
<td>[68]</td>
</tr>
<tr>
<td>Anelastic relaxation</td>
<td>0.60(+)0.007</td>
<td>3.96</td>
<td>[69]</td>
</tr>
<tr>
<td>Chemical diffusion</td>
<td>0.65(+)0.06</td>
<td>3.96</td>
<td>[70]</td>
</tr>
<tr>
<td>Isotope diffusion</td>
<td>0.62(+)0.08</td>
<td>4.0(+)0.3</td>
<td>[33]</td>
</tr>
<tr>
<td>Isotope diffusion</td>
<td></td>
<td>3.54(+)0.14</td>
<td>[43]</td>
</tr>
<tr>
<td>Isotope diffusion</td>
<td></td>
<td></td>
<td>[71]</td>
</tr>
</tbody>
</table>

Figure 2.3(b) shows the defect energy plotted against the projected distance along the migration path. In the case of cubic bulk \( \text{SrTiO}_3 \) one finds that the energy profile is symmetric about its centre, due to the high-symmetry structure of the system and the initial and final positions being symmetry equivalent. This is not always the case for structures with a lower symmetry (e.g. at dislocations or in triclinic systems).

The migration barrier is determined as the difference between the transition-state energy and the energy of the initial state [indicated by the arrows in Figure 2.3(b)],

\[
\Delta E_{\text{mig}} = E_{\text{trans}} - E_{\text{initial}}.
\]  

(2.2)
If the initial and final states are inequivalent, the migration barrier for forward and reverse jumps will be different. Thus the difficulty in determining the migration energy lies in finding the correct transition state. The migration enthalpies for oxygen-vacancy and strontium-vacancy migration in SrTiO$_3$ were determined with the Mott–Littleton method with the scanning procedure described above and compared to computational and experimental values found in literature. Table 2.3 shows that beyond the perfect lattice properties, the defective lattice properties can also be modelled successfully with the EPPs developed by Pedone et al.$^{[54]}$ It is worth noting again that the employed empirical pair potentials reproduce $\Delta H_{\text{mig,V}}$ better than various density functional theory studies which to date underestimate the experimental result of approximately 0.62 eV.$^{[45,68-70]}$

### 2.2 Thermodynamic Treatment of Extended Defects

When looking at length-scales greater than a few hundred nm, it is generally ill-advised to investigate such systems with atomistic simulation techniques due to the excessive computational costs. Thus the investigation of effects that occur on length-scales ranging from tenths of microns up to several microns, such as the effects of extended defects on the surrounding point-defect distribution, is performed using a continuum approach, namely with finite-element calculations. Figure 2.4 shows different constructs that can be used to model extended defects.

![Figure 2.4: Schematics of various geometric constructs for the investigation of extended defects using finite-element simulation techniques (not to scale). (a) Schematic of the geometry of a surface–bulk finite-element model; (b) Schematic of the geometry of a grain-boundary finite-element model; (c) Schematic of the geometry for a solid-solid heterogeneous interface finite-element model.](image)

The altered structure of an extended defect (e.g. dislocations, surfaces, heterogeneous interfaces and grain boundaries) leads to changes in the local defect
formation energies compared to those in the unperturbed bulk lattice. The resulting difference in formation energies (the altered thermodynamic driving energies) determine the electric potential, which, in turn, determines the point-defect distributions. This series of relationships can be represented in a simple diagram\cite{38}:

\[
\begin{align*}
\text{altered structure} & \quad \downarrow \\
\text{thermodynamic driving energy} & \quad \downarrow \\
\text{electric potential} & \quad \downarrow \\
\text{point-defect distributions}
\end{align*}
\]

Specifically, the presence of an electric potential leads to a redistribution of the point defects (electrons, electron holes and ionic defects) in the vicinity of the interface. The corresponding equilibrium distribution results in zones (near the extended defect) where an electro-neutrality condition is no longer applicable, the so-called space-charge zones or layers. Their general thermodynamic treatment and a description of the driving forces has previously been reported in literature\cite{38,44,57,72} and will be presented in the following.

### 2.2.1 Electrochemical Potential

The derivative of the Gibbs free energy with respect to the number of particles in a system is the electrochemical potential \([\partial G_i / \partial N_i = \tilde{\mu}_i(x)]\). Contrary to the chemical potential, the electrochemical potential also accounts for electrostatic contributions and for dilute, non-interacting defects it has the form\cite{73}

\[
\tilde{\mu}_i^I(x) = \mu_i^{\ast, I} + k_B T \ln \left( \frac{c_i^I(x)}{N_i^I - c_i^I(x)} \right) + z_i e \phi(x). \tag{2.3}
\]

\(\mu_i^{\ast, I}\) is the standard chemical potential, \(c_i(x)\) is the concentration of species \(i\), and \(\phi(x)\) is the electric potential. \(N_i\) refers to the number of sites per unit volume for species \(i\) and the superscripted Roman numeral indicates the phase described by the quantity (cf. Figure 2.4).

The interest here is in the equilibrium defect distribution in the vicinity of extended defects, so the equilibrium condition,

\[
\tilde{\mu}_i^I(x) = \tilde{\mu}_i^{II}(\infty) = 0, \tag{2.4}
\]
is applicable to the mobile defects. ∞ refers to a position far away from the extended defect, in the electroneutral bulk. Combining Equations (2.3) and (2.4), an expression for the spatial dependence of the mobile defect concentrations (perpendicular to the extended defect) can be determined:

\[
c_i^I(x) = \frac{N_i^I c_i^{II}(\infty) \exp \left\{ -\frac{ze_i[\phi(x) - \phi(\infty)] + \Delta\mu_i^\circ}{k_B T} \right\}}{N_i^{II} c_i^{II}(\infty) + c_i^I(\infty) \exp \left\{ -\frac{ze_i[\phi(x) - \phi(\infty)] + \Delta\mu_i^\circ}{k_B T} \right\}}.
\] (2.5)

\[
\Delta\mu_i^\circ = \mu_i^{\circ, I} - \mu_i^{\circ, II}
\]
is the difference in standard chemical potential relative to the reference state at \(x = \infty\) and is equivalent to the conduction band offset (CBO) and the valence band offset (VBO) for electrons (\(e^\prime\)) and holes (\(h^\prime\)), respectively. For ionic defects \(\Delta\mu_V^\circ\) is the difference in the vacancy formation energies. Note that if \(c_i^I(x)\) refers to the same phase as the reference state (at \(x = \infty\)), then \(\Delta\mu_i^\circ = 0\). Defects which cannot react (within a reasonable time frame) to the electrochemical potential are considered to be immobile. Thus, they are not expected to follow the same behaviour given by Eq. (2.5) and have a fixed concentration profile independent of \(\phi(x)\).

Bulk SrTiO\(_3\) defect concentrations \([c_i^{II}(\infty)]\) for various \(T\) and \(pO_2\) are obtained by utilising the extensive knowledge of the defect chemistry of SrTiO\(_3\) in conjunction with defect chemical calculations (see Section 1.2).\[14,15,44\]

\(\Delta\mu_i^\circ\) is the driving energy for the point-defect redistribution in the vicinity of extended defects, resulting in the formation of space-charge layers. The number of sites per unit volume (\(N_i^I\) and \(N_i^{II}\)) account for changes in site density between e.g. Phase I and Phase II, which may result in considerable concentration gradients across the interface.

Once the driving forces are known, the space-charge potential \([\phi(x)]\) can be calculated in order to determine the equilibrium point-defect distribution in the vicinity of extended defects. In the case of \(\Delta\mu_i^\circ\), the value can be obtained directly from atomistic simulations. The electric-potential profile \([\phi(x)]\) can be determined with the help of Poisson’s equation.

### 2.2.2 Poisson’s Equation

In electrostatics, Poisson’s equation links the 2\(^{nd}\) derivative of the electric potential \(\phi\) with the space-charge density \(\rho(x)\),

\[
-\varepsilon_r\varepsilon_0 \frac{d^2\phi}{dx^2} = \rho(x) = \sum_i e z_i c_i(x),
\] (2.6)
where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ the relative permittivity, $e$ the elementary charge and $z_i$ the charge number of defect species $i$.

Combining the expression for the spatial dependence of the defect concentrations [Equation (2.5)] with Poisson’s equation, one obtains a partial differential equation (PDE). In the following example, a system comprised of bulk SrTiO$_3$ and a thin surface region (1 nm) corresponding to the geometry of Figure 2.4(a) is used to present the procedure. Only immobile acceptor species ($\text{Acc}'$) and mobile oxygen vacancies ($\text{V}_\text{O}$) are considered within the example. The relevant PDEs are as follows for the surface region [with the second term being $c_{\text{V}_\text{O}^\text{surface}}(x)$],

$$-\varepsilon\varepsilon_0 \frac{d^2 \phi}{dx^2} = e z_{\text{Acc}'} c_{\text{Acc}'}$$

$$+ \frac{e z_{\text{V}_\text{O}'} N_{\text{V}_\text{O}}^\text{surface} c_{\text{V}_\text{O}}^\text{bulk}(\infty)}{N_{\text{V}_\text{O}}^\text{bulk} - c_{\text{V}_\text{O}}^\text{bulk}(\infty) + c_{\text{V}_\text{O}}^\text{bulk}(\infty)} \exp \left\{ - \frac{e z_{\text{V}_\text{O}'} [\phi(x) - \phi(\infty)] + \Delta \mu_{\text{V}_\text{O}}^{\text{surface}}}{k_B T} \right\},$$

and for the bulk region [with the second term being $c_{\text{V}_\text{O}}^\text{bulk}(x)$],

$$-\varepsilon\varepsilon_0 \frac{d^2 \phi}{dx^2} = e z_{\text{Acc}'} c_{\text{Acc}'}$$

$$+ \frac{e z_{\text{V}_\text{O}'} N_{\text{V}_\text{O}}^\text{bulk} c_{\text{V}_\text{O}}^\text{bulk}(\infty)}{N_{\text{V}_\text{O}}^\text{bulk} - c_{\text{V}_\text{O}}^\text{bulk}(\infty) + c_{\text{V}_\text{O}}^\text{bulk}(\infty)} \exp \left\{ - \frac{e z_{\text{V}_\text{O}'} [\phi(x) - \phi(\infty)]}{k_B T} \right\}.\tag{2.7}$$

Note as $c_{\text{V}_\text{O}}^\text{bulk}(x)$ refers to the same phase as the reference state at $x = \infty$, then $\Delta \mu_{\text{V}_\text{O}}^{\text{bulk}} = 0$ [see Eq. (2.8)]. Furthermore, $N_{\text{V}_\text{O}}$ is assumed to be equal in both surface and bulk region ($N_{\text{V}_\text{O}}^\text{surface} = N_{\text{V}_\text{O}}^\text{bulk}$) and the immobile acceptor concentration ($c_{\text{Acc}'}$) is taken to be the expected bulk concentration, constant throughout the entire system. The Neumann boundary conditions are used to solve the PDEs, with

$$\frac{d\phi(0)}{dx} = \frac{d\phi(\infty)}{dx} = 0 \text{ V m}^{-1} \tag{2.9}$$

for the boundaries at $x = 0$ and $x = \infty$ (located in electroneutral bulk region) of the system. The solution of the differential equation yields the electric potential profile and thus the sought-after equilibrium distribution of mobile defects.

Figure 2.5 shows the resulting equilibrium defect distributions from the simulations of the example system described. In the case of no driving force, $\Delta \mu_{\text{V}_\text{O}}^{\text{surface}} = 0$ eV, there is no defect redistribution (as long as $N_{\text{V}_\text{O}}^\text{surface} = N_{\text{V}_\text{O}}^\text{bulk}$), the resulting electric potential is 0 V and the concentration of the mobile oxygen vacancies is constant.
throughout the simulation volume [see Figure 2.5(b)].

![Diagram showing equilibrium defect distribution for immobile acceptor dopants and mobile oxygen vacancies and corresponding electric potential \(\phi(x)\) for a 1 nm surface layer at \(T = 973\,\text{K}, p\text{O}_2 = 0.1\,\text{bar}\) and \(c_{\text{Acc}} = 7 \cdot 10^{23}\,\text{m}^{-3}\) for (a) \(\Delta \mu_{\text{Vo}}^{\phi} = -1\,\text{eV}\), (b) 0 eV, and (c) 1 eV.]

**Figure 2.5:** Equilibrium defect distribution for immobile acceptor dopants and mobile oxygen vacancies and corresponding electric potential \(\phi(x)\) for a 1 nm surface layer at \(T = 973\,\text{K}, p\text{O}_2 = 0.1\,\text{bar}\) and \(c_{\text{Acc}} = 7 \cdot 10^{23}\,\text{m}^{-3}\) for (a) \(\Delta \mu_{\text{Vo}}^{\phi} = -1\,\text{eV}\), (b) 0 eV, and (c) 1 eV.

For \(\Delta \mu_{\text{Vo}}^{\phi} = -1\,\text{eV}\), which is equivalent to a favourable formation of oxygen vacancies in the surface layer, the determined electric potential profile combined with Equation (2.5) yields the redistribution of oxygen vacancies from the bulk phase into the surface layer which results in a depletion space-charge zone near the surface. The vacancy concentration is reduced by approximately three orders of magnitude and increases to the bulk value over ca. 100 nm [see Figure 2.5(a)]. The resulting space charge potential in this case is positive.

In the third case, \(\Delta \mu_{\text{Vo}}^{\phi} = 1\,\text{eV}\), oxygen vacancies redistribute from the surface layer into the bulk phase. In this case the effect of the redistribution appears minute relative to \(\Delta \mu_{\text{Vo}}^{\phi} = -1\,\text{eV}\), as the amount of redistributed vacancies that can be removed from the surface region is considerably smaller than the amount of vacancies in the bulk phase. Nonetheless, there is a slight increase in the oxygen vacancy concentration near the surface layer and a corresponding negative electric potential [see Figure 2.5(c)].

Once the equilibrium distribution of mobile defects is known, the spatial dependence of several related properties, e.g. diffusivity and conductivity\(^{[74]}\) can be
determined. The contribution of the mobile species to the conductivity ($\sigma_i$) of a system, for example, is given by

$$\sigma_i(x) = z_i e u_i c_i(x),$$

(2.10)

and can be determined with the knowledge of the species’ mobilities ($u_i$) in addition to their equilibrium distribution.

### 2.2.3 Space-Charge Effects on Oxygen Diffusion

As the diffusion coefficient of oxygen depends on the oxygen vacancy concentration\(^{[33]}\) ($c_{V_O}$) according to Equation (2.11),

$$D^*_O(x) = f^* D_{V_O} \frac{c_{V_O}(x)}{N_V - c_{V_O}(x)},$$

(2.11)

it stands to reason that oxygen diffusion (perpendicular to the extended defect) will be affected by the presence of a space-charge zone. $f^*$ is the tracer-correlation factor which, for perovskite-type oxides with a dilute concentration of oxygen vacancies, is equal to 0.69.\(^{[75]}\) $D_{V_O}$ and $D^*_O(x)$ are the oxygen-vacancy diffusivity and the spatially dependent oxygen-diffusion coefficient, respectively.

With the solution of Poisson’s equation yielding the spatial dependence of the oxygen-vacancy concentration in the presence of extended defects (see previous section) the spatial behaviour of the oxygen diffusivity is accessible and can be used to numerically solve Fick’s second law,

$$\frac{\partial n^*}{\partial t} = \frac{\partial}{\partial x} \left[ D^*_O(x) \frac{\partial n^*}{\partial x} \right],$$

(2.12)

in order to obtain, for example, a simulated isotope penetration profile which traverses a space-charge zone (perpendicular to the extended defect). $n^*$ is the isotope fraction.

Based on the example discussed above for the electrostatics model, Figure 2.6 shows simulated diffusion profiles as well as the corresponding oxygen diffusivity for three different values of $\Delta \mu_{V_O}^c$.

For $\Delta \mu_{V_O}^c = 0$ eV, corresponding to no defect redistribution, the diffusion coefficient of oxygen is spatially independent and results in a penetration profile [see\(^c\)

\(^c\)Values for the vacancy diffusivity and the surface exchange coefficient for SrTiO$_3$ were taken from literature\(^{[33]}\).
Figure 2.6: Simulated oxygen-penetration profiles and corresponding oxygen diffusivity for $T = 973 \text{ K}$, $p_{O_2} = 0.1 \text{ bar}$, $\epsilon_{Aco} = 7 \cdot 10^{23} \text{ m}^{-3}$, and $t_{ex} = 30 \text{ min}$ through a 1 nm surface layer into a bulk phase. Bulk values for $D_{O}^{v,v}$ and $k_s^*$ were taken from literature.\textsuperscript{[33]} (a) $\Delta \mu_{O}^{v,v} = -1 \text{ eV}$, with (b) showing the first 300 nm of the profile; (c) $\Delta \mu_{O}^{v,v} = 0 \text{ eV}$, with (d) showing the first 300 nm of the profile; (e) $\Delta \mu_{O}^{v,v} = 1 \text{ eV}$, with (f) showing the first 300 nm of the profile.

Figures 2.6(c) and 2.6(d)] exactly equivalent to that of the analytical solution of Eq. (2.12),

$$
\frac{n^* - n_{bg}}{n_{gas} - n_{bg}} = \text{erfc} \left( \frac{x}{2\sqrt{D_{O}^* t_{ex}}} \right) - \exp \left[ \frac{k_s^*}{D_{O}^*} x + \left( \frac{k_s^*}{D_{O}^*} \right)^2 D_{O}^* t_{ex} \right] \text{erfc} \left( \frac{x}{2\sqrt{D_{O}^* t_{ex}}} + \frac{k_s^*}{D_{O}^*} \sqrt{D_{O}^* t_{ex}} \right),
$$

(2.13)
for a semi-infinite medium with surface exchange and spatially constant oxygen diffusivity\textsuperscript{[76].} Here $n_{\text{bg}}$ and $n_{\text{gas}}$ are the background-isotope concentration and the isotope enrichment in the gas phase, respectively. $k_s^*$ is the surface exchange coefficient and $t_{ex}$ is the diffusion time.

In the case of vacancy redistribution to the surface layer ($\Delta \mu_{\text{V}O}^\circ = -1 \text{ eV}$), $D_O^*$ has a sharp drop of roughly three orders of magnitude from the bulk value towards the surface, which results in a diffusion profile consisting of two features [cf. Figures 2.6(a) and 2.6(b)]. The first feature (ca. $0 - 50 \text{ nm}$) is the result of the depletion space-charge zone, while the second feature corresponds to the bulk diffusion in SrTiO\textsubscript{3}.

In the last example ($\Delta \mu_{\text{V}O}^\circ = 1 \text{ eV}$) [Figures 2.6(e) and 2.6(f)], the oxygen diffusivity in bulk strontium titanate is negligibly affected by the oxygen-vacancy redistribution from the surface layer into the bulk layer. The corresponding penetration profile is, therefore, very similar to the case with no vacancy redistribution, with the exception of the initial isotope fraction being slightly lower due to the strong depletion of oxygen vacancies in the surface layer.

### 2.2.4 Experimental Approach

Typically an experiment yields an isotope-penetration profile, consequently rather than predicting a diffusion profile, the requirement is to describe a diffusion profile. In this case, equilibrium experiments are used as a method to probe the presence of a space-charge layer, and determine both the electric potential and $\Delta \mu_{\text{V}O}^\circ$\textsuperscript{[33]}. $D_O^*(x)$ can be expressed as a function of the electric potential and the difference in standard electrochemical potential by combining Equations (2.5) and (2.11), assuming the dilute limit:

\[
D_O^*(x) = D_O^*(\infty) \exp \left\{ - \frac{z_{\text{V}O}^* e [\phi(x) - \phi(\infty)] + \Delta \mu_{\text{V}O}^\circ}{k_B T} \right\} \tag{2.14}
\]

Equation (2.14) is then fit to describe a measured isotope penetration profile in order to obtain $\phi(x)$ and subsequently determine the thermodynamic driving energy ($\Delta \mu_{\text{V}O}^\circ$). With a successful fit, the determined values can be used to determine the equilibrium defect distribution—without solving Poisson’s equation—with the help of Equation (2.5).

In an ideal scenario, both approaches—solving Poisson’s equation and probing the electric potential using an isotope exchange experiment—will lead to the same results. This can serve as a self-consistency check.
2.2.5 COMSOL Multiphysics

For the studies presented here, the numerical solution of Poisson’s equation and the simulation of isotope penetration profiles were performed with the commercial finite-element code COMSOL Multiphysics (COMSOL AB, Stockholm, Sweden).
3 Ionic Conduction in the SrTiO$_3$ and Y:ZrO$_2$ Heterostructure

Parts of this chapter were previously published by De Souza and Ramadan, Phys. Chem. Chem. Phys. (2013) [77].

3.1 Introduction

There is much debate surrounding the emergence of colossal ionic conductivity in highly strained films of yttria-stabilised zirconia (YSZ). In their seminal study

![Graph showing ionic conductivity of ST|YSZ|ST trilayers for YSZ layer thickness ranging from 1 – 62 nm. Also included are the data of a single crystal (sc) of YSZ and a thin film (tf) 700 nm thick taken from Ref. [78] with the same nominal composition. The grey arrow indicates the reported increase in conductivity of 8 orders of magnitude. From Ref. [79]. Adapted with permission from AAAS.](image)

**Figure 3.1:** Ionic conductivity of the ST|YSZ|ST trilayers for YSZ layer thickness ranging from 1 – 62 nm. Also included are the data of a single crystal (sc) of YSZ and a thin film (tf) 700 nm thick taken from Ref. [78] with the same nominal composition. The grey arrow indicates the reported increase in conductivity of 8 orders of magnitude. From Ref. [79]. Adapted with permission from AAAS.
García-Barriocanal et al. reported an enhancement in the ionic conductivity of YSZ by a factor of $10^8$ at $T = 500 \text{ K}$ for a thin (1 nm), epitaxial layer of YSZ sandwiched between thicker layers (10 nm) of SrTiO$_3$ (ST) on a SrTiO$_3$ substrate (see Fig. 3.1). Such an enormous increase, it was said, resulted from the tensile strain of 7% within the YSZ film and disorder of oxygen ions at the interface.$^{[79]}$

There are two strands to the intense debate that surrounds this report. One strand is concerned with the physical limits to the enhancement of the ionic conductivity in a fluorite-structured electrolyte through strain.$^{[80–85]}$ To date no theoretical study has come close to the $10^8$ enhancement reported from experiment, although enhancements of $\sigma^e / \sigma^{e=0} \approx 10^4$ at $T = 500 \text{ K}$ for strains of $\epsilon = 4\%$ have been predicted.$^{[81,83,85]}$ This is nevertheless a considerable enhancement, in contrast to enhancements by factors of 2–5 typical of composition optimisation, and suggests a promising path towards superior electrolyte performance in micro-solid oxide fuel cell (micro-SOFC) applications.

**Figure 3.2:** Temperature dependence of the conductivities of ST substrate and ST|YSZ|ST heterostructure as determined by García-Barriocanal et al.$^{[79]}$. The arrow indicates the resulting conductivity of the heterostructure with the correction for the ST substrate thickness according to Guo$^{[86]}$. From Ref. [86]. Adapted with permission from AAAS.

The second strand of the debate is focussed on the nature (ionic or electronic) of the conductivity of the ST|YSZ|ST heterostructure.$^{[86–89]}$ It is this strand that is
the subject of this investigation. Guo, in a comment\cite{86} on the original report\cite{79}, showed that the conductance $Y$ of a 1 mm thick ST substrate is not negligible, and that—taking this non-negligible conductance into account—the conductivity enhancement $\sigma_{\text{het}}/\sigma_{\text{ST}}$ is only ca. $10^3$, with ST providing the main contribution (see Fig. 3.2). In view of $V_O^-$ and $h^+$ being the majority charge carriers in ST under oxidising conditions (see Section 1.2),\cite{114–16,90} Guo concluded that the measured conductivity of the heterostructure is due to electron holes in SrTiO$_3$ and not oxygen vacancies in YSZ.

![Figure 3.3: Temperature dependence of the conductance of 10 nm ST film (black triangles), 10 nm YSZ film (black squares), ST|YSZ 1 nm|ST as determined by Cavallaro et al.\cite{89} (blue circles) and conductance ST|YSZ 1 nm|ST according to García-Barriocanal et al.\cite{79} (red circles). From Ref. [89]. Adapted with permission from Elsevier.](image)

In response to Guo’s comment, García-Barriocanal et al.\cite{88} maintained their initial assertion of enhanced conductivity of the ST|YSZ|ST heterostructure. They considered their d.c. and a.c. values for the heterostructure’s conductance, and found that the former did indeed agree with Guo’s data for single crystal ST $[Y_{\text{dc,het}} = Y_{\text{dc,ST}}]$, but the latter were ca. 3 orders of magnitude higher $[Y_{\text{ac,het}} \gg Y_{\text{ac,ST}}]$ (see Fig. 1 of Ref. [88]). And it was $Y_{\text{ac,het}}$ they argued, that corresponded to ionic transport in YSZ, with $Y_{\text{dc,het}}$ corresponding to electronic transport in ST. Cavallaro et al.\cite{89} grew ST|YSZ|ST heterostructures themselves and found that,
although their YSZ layer was non-continuous (i.e. it consisted of isolated YSZ islands), the conductance of the heterostructure was significantly higher than the conductance of single crystal ST (see Fig. 3.3). In addition, the conductance of the heterostructure was observed to decrease with decreasing oxygen partial pressure—a finding consistent with p-type electronic conduction in ST but not with ionic conduction in YSZ. Thus, according to Guo\textsuperscript{[86]} and Cavallaro \textit{et al.}\textsuperscript{[89]} the conductivity of ST|YSZ|ST arises from electron holes in ST. The reason for the enhanced conductivity of the heterostructure, as measured by García-Barriocanal \textit{et al.}\textsuperscript{[79]} and Cavallaro \textit{et al.},\textsuperscript{[89]} is unclear, however.

### 3.2 Results

In the following a careful reexamination of the data available from previous reports (Figures 3.1, 3.2 and 3.3) will be undertaken in order to unambiguously determine the defect species responsible for the conductance in the low temperature regime ($330 \leq T/K \leq 550$). Consequently, the possibility of defect redistribution across the interface with respect to its effects on both the conductance and the diffusion behaviour will be discussed.

#### 3.2.1 Factors Contributing to the Conductivity

Fig 3.4 shows selected data taken from three studies\textsuperscript{[79,86,89]} First, an examination of the measured conductivity of ST: the agreement between the data acquired by Guo\textsuperscript{[86]} and by Cavallaro \textit{et al.}\textsuperscript{[89]} is reasonable, given that the (acceptor) impurity concentration may vary between samples. Also plotted in Fig. 3.4 is the ionic conductivity calculated for single-crystal substrate ST with the Nernst-Einstein equation

$$\sigma_{Vo} = \frac{4e^2D_{Vo}c_{Vo}}{k_B T}.$$  \hspace{1cm} (3.1)

$c_{Vo}$ is the concentration of oxygen vacancies, assumed here to be determined by fixed-valence acceptor-like impurities at a level typical of nominally undoped ST substrates: $c_{A\text{ac}} = 2c_{Vo} = 10^{18} \text{ cm}^{-3}$. $D_{Vo}$ is the diffusivity of oxygen vacancies in SrTiO\textsubscript{3} and extrapolated from a global expression derived by De Souza \textit{et al.}\textsuperscript{[33]} $D_{Vo}/\text{cm}^2\text{s}^{-1} = 7 \times 10^{-3} \exp (-0.67 \text{eV}/k_B T)$; this expression for $D_{Vo}$ was used because it describes data obtained for ST from three different experimental studies (tracer diffusion\textsuperscript{[33]} chemical diffusion\textsuperscript{[91]} and electrocoloration\textsuperscript{[92]} that are consistent with each other over a wide range of temperatures. The excellent
Figure 3.4: Conductivity $\sigma$ of SrTiO$_3$|YSZ|SrTiO$_3$ heterostructures and of SrTiO$_3$ single crystal substrates. A - ST|YSZ|ST, measured by García-Barriocanal et al.,$^{[79]}$ and corrected for the thickness of the substrate according to Guo;$^{[86]}$ B - ST|YSZ|ST, converted from conductance values measured by Cavallaro et al.$^{[89]}$ assuming a square substrate of thickness $d = 1$ mm; C - ST, converted from conductance values measured by Cavallaro et al.$^{[89]}$ assuming a square substrate thickness of $d = 1$ mm; D - ST, measured by Guo;$^{[86]}$ E - ST, ionic conductivity calculated from vacancy diffusivity. The grey lines have the same slope as the black line and thus act as guides to the eye for the purpose of indicating, with black arrows, deviations from the grey lines (see text). Adapted from Ref. [77] with permission from the PCCP Owner Societies.

agreement in Fig. 3.4 between the predicted and experimental values of $\sigma_{\text{ST}}$, both in terms of absolute magnitude and activation enthalpy, strongly suggests that the measured conductivity of SrTiO$_3$—in the temperature range $300 < T/\text{K} < 550$—is overwhelmingly ionic.

The $p$-type electronic conductivity of ST is insignificant at these low temperatures because the rate of oxygen surface exchange goes to zero,$^{[93]}$ and as a consequence, the sample is not in equilibrium with the surrounding oxygen atmosphere. The internal electronic equilibria are still active, however, and they serve to lower drastically the concentration of electron holes, and thus the electron-hole conductivity.$^{[13,14]}$ In contrast, the concentration of oxygen vacancies is fixed, frozen-in at the temperature at which the surface “shuts off”; and since the vacancies are
mobile (a mobility that is of course unaffected by the inactive equilibrium), a significant and predominant ionic conductivity results. Defect chemical calculations\cite{94} predict a theoretical equilibrium hole conductivity in ST at $T = 500\,\text{K}$ of $\sigma_{h,\text{eq}} = 5 \times 10^{-4}\,\text{S}\,\text{cm}^{-1}$ (difficult to attain in practice due to extremely long equilibration times—see below) and a hole conductivity of ST quenched from e.g. $T_{\text{qch}} = 700\,\text{K}$ to $T = 500\,\text{K}$ of $\sigma_{h,\text{qch}} = 5 \times 10^{-10}\,\text{S}\,\text{cm}^{-1}$, which is much lower than the ionic conductivity at this temperature.

At what temperature does the exchange of oxygen with the surroundings start to become active? Since an active exchange equilibrium

$$\frac{1}{2}\text{O}_2 + V^\circ_O \rightleftharpoons \text{O}_O^\infty + 2h^\dagger,$$  

(3.2)
generates electron holes and thus results in predominant $p$-type conduction under oxidising conditions, the critical temperature $T_{\text{crit}}$ is the temperature at which the experimentally measured conductivity deviates significantly from the calculated ionic conductivity. In Fig. 3.4, such a deviation is apparent in the data of Cavallaro et al.\cite{89} for single crystal ST from $T_{\text{crit}} = 550\,\text{K}$ upwards; similar deviations can be identified for ST|YSZ|ST at the highest temperature ($T_{\text{crit}} = 530\,\text{K}$) examined by García-Barriocanal et al.\cite{79} and from $T_{\text{crit}} = 550\,\text{K}$ upwards for ST|YSZ|ST measured by Cavallaro et al.\cite{89} (all three points are marked with arrows in Fig. 3.4). The fact that these three temperatures are close provides additional confirmation (in addition, that is, to the similar activation enthalpies determined for ST|YSZ|ST\cite{79} and ST,\cite{86} and to the enhanced conductivity being observed for a non-continuous YSZ layer\cite{89}) that the conductivity of the heterostructure stems from ST. Furthermore, the critical temperature of $T_{\text{crit}} = 540\,\text{K}$ is consistent with the conductance of the heterostructure depending on oxygen partial pressure at $T = 723\,\text{K}$ (Ref. [89]), but being independent of oxygen partial pressure at $T < 500\,\text{K}$ (Ref. [79]), because ST cannot react—within a reasonable timescale—to changes in the surrounding atmosphere at temperatures below $T_{\text{crit}}$.

It is worth noting, although the surface “opens” the sample to the surrounding atmosphere at $T_{\text{crit}} \approx 540\,\text{K}$, equilibrium is not established immediately because the equilibration kinetics are exceedingly sluggish. Extrapolating data for the chemical surface incorporation coefficient $k^\delta$ for an ST surface covered with Ag (Ref. [33]) to the temperatures of interest, one obtains equilibration times of $\tau_{\text{eq}} > 6\,\text{years}$ at $T = 550\,\text{K}$, falling to $\tau_{\text{eq}} < 11\,\text{hours}$ at $T = 800\,\text{K}$. Thus the conductance data for ST and for ST|YSZ|ST acquired by Cavallaro et al.\cite{89} refer, in all probability, to equilibrium only at the highest temperatures examined. At temperatures below $T_{\text{crit}}$, all experimental data in Fig. 3.4 refer to the quenched state. Returning to
Fig. 3.4, one is still confronted with the discrepancy of ca. 3 orders of magnitude between $\sigma_{ST}$ and $\sigma_{het}$. Therefore, the statement of García-Barriocanal et al.\cite{79,88} regarding the d.c. conductance of ST\|YSZ\|ST, is considered anew. They disregarded $Y_{het}^{dc}$ because they claimed that it represented the electronic contribution (from ST), whereas $Y_{het}^{ac}$ referred to the ionic contribution (from YSZ). In the light of Fig. 3.4, this argument is clearly invalid: the d.c. conductance at $550 > T / K > 300$ can be unambiguously assigned to an ionic transport process in ST, namely the migration of oxygen vacancies. It is unclear to what charge transport process in ST the a.c. conductance reported by García-Barriocanal et al.\cite{79,88} refers.

### 3.2.2 Space-Charge Effects on the Conductance

Despite the measured d.c. conductance being an ionic transport process, one glaring inconsistency remains. The conductance of the ST\|YSZ\|ST heterostructure reported by Cavallaro et al.\cite{89} is larger than the conductance of ST, as shown in Fig. 3.4, even though they determined $Y_{het}^{dc}$. Thus based on the data of Cavallaro et al.\cite{89} there is a conductivity enhancement, whereas based on the argument above regarding the data of García-Barriocanal et al.\cite{79,88} there is none. Although this outstanding issue remains unresolved, one major possibility can be discounted at this juncture.

One possibility for enhanced conductivity in heterostructures is the redistribution of mobile charge-carriers resulting in the formation of space-charge layers.\cite{38,95,96} The redistribution of oxygen vacancies between YSZ and ST in a ST\|YSZ\|ST heterostructure has, therefore, been examined.\cite{3} Defect re-distribution in this case is driven not only by vacancy concentrations being different but also by the standard chemical potentials of oxygen vacancies $\mu_{\text{V}_O}^\circ$ being different in YSZ and in ST;\cite{38,83} and this redistribution takes place until, in equilibrium, the electrochemical potential of oxygen vacancies is constant across the heterostructure (see Section 2.2). In the (one-dimensional, continuum-based) calculations, the electrochemical potential of oxygen vacancies is assumed to take the form of Equation (2.3). The only quantity required for these calculations that is not known [see Eq. (2.3)] is the standard chemical potential of oxygen vacancies, or to be specific, the difference, $\Delta \mu_{\text{V}_O}^\circ$, defined here as $\Delta \mu_{\text{V}_O}^\circ = \mu_{\text{V}_O}^\circ,\text{YSZ} - \mu_{\text{V}_O}^\circ,\text{ST}$. Therefore, $\Delta \mu_{\text{V}_O}^\circ$ is used as a parameter.

Equilibrium charge-carrier concentration profiles for vacancy redistribution from ST to YSZ at $T = 500 \text{ K}$ are shown in Fig. 3.5(a). One perceives large changes in $c_{\text{V}_O}^{\text{ST}}$, but hardly any change in $c_{\text{V}_O}^{\text{YSZ}}$. This is because the number of vacancies

---

\*Dopant cations in YSZ and ST were assumed to be immobile.
Figure 3.5: (a) Equilibrium charge-carrier concentration profiles in an ST\YSZ\ST heterostructure at $T = 500$ K, resulting from redistribution of oxygen vacancies from ST to YSZ, $\Delta \mu_{V^*O} = -0.5$ eV. The arrow indicates the position of the YSZ layer. (b) The excess conductance in YSZ arising from vacancy redistribution from ST to YSZ, $\Delta Y_{YSZ}$, compared as a function of temperature $T$ with the conductance of 1 nm of ST ($Y_{ST}$) and of 1 nm of YSZ ($Y_{YSZ}$). Adapted from Ref. [77] with permission from the PCCP Owner Societies.

transferred per unit area is large compared with the number of vacancies per unit area in the bulk ST phase, but small compared with the number of vacancies per unit area present in the bulk YSZ phase. Integrating the conductivity profile over the thickness of the YSZ layer,

$$Y_{YSZ}^{layer} = \int_{YSZ} \sigma_{V^*O}(x) \, dx = \left[ \frac{4e^2D_{V^*O}}{k_B T} \right] \int_{YSZ} c_{V^*O}(x) \, dx,$$

and subtracting the bulk contribution of

$$Y_{YSZ}^{bulk} = \int_{YSZ} \sigma_{V^*O}(\infty) \, dx = \left[ \frac{4e^2D_{V^*O}}{k_B T} \right] c_{V^*O}(\infty) \int_{YSZ} \, dx$$

yields the excess conductance $\Delta Y_{YSZ} = Y_{YSZ}^{layer} - Y_{YSZ}^{bulk}$ due to defect redistribution. To obtain the data plotted in Fig. 3.5(b), the calculations shown in Fig. 3.5(a) were repeated at other temperatures. The excess conductance $\Delta Y_{YSZ}$ is seen to be negligible in comparison with the conductance $Y$ of the ST substrate (and also in comparison with the native conductance of 1 nm of YSZ). Making $\Delta \mu_{V^*O}$ more negative will increase $\Delta Y_{YSZ}$ but the increase will only be small (less than an order of magnitude) because the vacancy site fraction in YSZ is already appreciable.[83] It is therefore evident that the accumulation of oxygen vacancies in the YSZ layer can play no major role in contributing to the measured conductance of the heterostructure.
Figure 3.6: (a) Equilibrium charge-carrier concentration profiles in an ST\YSZ\ST heterostructure at $T = 500$ K, resulting from redistribution of oxygen vacancies from YSZ to ST, $\Delta \mu_{V^0} = +0.5$ eV. The arrow indicates the position of the YSZ layer. (b) The excess conductance in ST arising from vacancy redistribution from YSZ to ST, $\Delta Y_{ST}$, compared as a function of temperature $T$ with the conductance of 1 mm of ST ($Y_{ST}$) and of 1 nm of YSZ ($Y_{YSZ}$). Adapted from Ref. [77] with permission from the PCCP Owner Societies.

In Fig. 3.6(a) the alternative case is considered: the transfer of vacancies from YSZ to ST. In this instance, one can remove a large number of vacancies from YSZ and add them to an initially small number in ST, and thus the changes in vacancy concentration in both YSZ and ST are evident. The excess conductance from the space-charge layers in ST, $\Delta Y_{ST}$, calculated as a function of temperature is shown in Fig. 3.6(b). $\Delta Y_{ST}$ is over two orders of magnitude lower than $Y_{ST}$, and this difference cannot be lessened considerably by increasing $\Delta \mu_{V^0}$, because most of the vacancies have already been transferred from the 1 nm YSZ layer. Thus in this case, too, space-charge effects do not contribute significantly to the measured conductance. This leads to the conclusion that a re-distribution of mobile charge carriers cannot account for the enhanced conductance observed experimentally (irrespective of the direction of redistribution).

3.2.3 Space-Charge Effects on the Diffusivity

Although space-charge effects do not account for the experimentally observed enhanced conductance (see above), strong depletion of oxygen vacancies may account for an unusual feature in an $^{18}$O penetration profile perpendicular to a multilayer ST\YSZ\ST structure observed by Cavallaro et al.[89]. The isotope profile displayed an abrupt drop before the YSZ layer was reached (see Fig. 8 of Ref. [89]). The observed fall in the isotope fraction can be reproduced qualitatively by decreasing the tracer diffusion coefficient $D_0(x)$ in the vicinity of the interface.
Specifically, the isotope profile was calculated according to procedures detailed in Section 2.2,[33,72] for transport through a homogeneous bulk phase and then into a space-charge layer depleted of oxygen vacancies. Exemplary results for the predicted variation in $D_{\text{O}}^{*}(x)$ and the resultant $^{18}\text{O}$ penetration profile are shown in Fig. 3.7.

![Graph showing calculated $^{18}\text{O}$ penetration profile for isotope diffusion through 145 nm ST$|1$ nm YSZ$|10$ nm ST, with redistribution of vacancies from ST to YSZ. The dashed vertical line indicates the position of the YSZ layer. Adapted from Ref. [77] with permission from the PCCP Owner Societies.]

Although the abrupt drop in the $^{18}\text{O}$ fraction is reproduced qualitatively, it is only possible by increasing the acceptor concentration and by decreasing the vacancy diffusivity from the values for single crystal ST. With $\Delta \mu_{\text{V}_\text{O}}^{\text{c}} = -1.0 \text{ eV}$, for example, the dopant concentration in the top ST layer had to be increased by an order of magnitude while $D_{\text{V}_\text{O}}^{\text{c}}$ had to be decreased by three and a half orders of magnitude; other combinations of $\Delta \mu_{\text{V}_\text{O}}^{\text{c}}$, $c_{\text{V}_\text{O}}^{\text{ST}}$, and $D_{\text{V}_\text{O}}^{\text{ST}}$ (not shown) also yield this unusual profile shape. The large alterations of $c_{\text{V}_\text{O}}^{\text{ST}}$ and $D_{\text{V}_\text{O}}^{\text{ST}}$ from the values for single crystal ST should not be counted as evidence against the space-charge model, since ST thin films are known to possess substantially different defect concentrations from those of single crystal substrates.[97–99] Nevertheless, the abrupt drop in the measured $^{18}\text{O}$ profile only indicates a local decrease in tracer diffusion coefficient $D_{\text{O}}^{*}(x)$.
before the interface. It does not indicate why such a decrease occurs. Although
the formation of a space-charge layer is one possible explanation, it is not the only
possibility: cation interdiffusion between YSZ and ST during film growth\textsuperscript{[89]}, for
example, may also produce such an effect.
The outstanding issue of the enhanced conductance, however, remains unsolved.
The measurement geometry is, therefore, tentatively suggested as another possible
contributing factor. In the study of Cavallaro \textit{et al.}\textsuperscript{[89]} the electrodes for the conduc-
tance measurements were placed on top of the ST|YSZ|ST heterostructure, which
means that the various layers (ST, YSZ, ST and the ST substrate) are not simply
connected in parallel. The simulation of impedance spectra for such a measurement
geometry is left for future study.
In summary, the detailed analysis of published conductivity data for single crystal
ST substrates and ST|YSZ|ST heterostructures leads one to cast doubts on the
reported conductivity enhancement of ST|YSZ|ST heterostructures.

3.3 Conclusion

From the investigations performed, it is unambiguously clear that the migration
of oxygen vacancies in the temperature range of 300 \(\leq T \:/K \leq 550\) is the main
contribution to the conductivity of SrTiO\textsubscript{3}. It is this process that is observed in the
ST|YSZ|ST heterostructures, as the activation energy at temperatures below \(T_{\text{crit}}\)
is the same for the different measurements. Beyond \(T_{\text{crit}}\) electronic processes start
to contribute significantly to the system’s conductivity as the surface exchange
becomes active. This interpretation is supported by the observation of the same
traits in the various experimental measurements found in literature.\textsuperscript{[79,89]} The fact
that the measured conductance is ionic in nature does not provide an explanation
for the enhanced conductivity of the heterostructure. However, the possibility of
space-charge layers playing a role can be discounted as the excess conductance due
to vacancy redistribution is found to be negligible compared to the conductance
of the ST substrate. Although the vacancy redistribution may not play a role in
the enhanced conductivity of the system, it can, nevertheless, be used to explain
the unusual isotope profile shape found in literature\textsuperscript{[89]}, as the diffusion through a
depletion space-charge zone in SrTiO\textsubscript{3} near the interface can reproduce the abrupt
drop observed experimentally. Thus, the formation of equilibrium space-charge
layers is a phenomenon that should always be included in the consideration of
properties at extended defects.
4 Oxygen Migration across a SrTiO$_3$|SrO Interface

 Parts of this chapter were previously published by Bäumer, Schmitz, Ramadan, Du, Skaja, Feyer, Müller, Arndt, Jia, Mayer, De Souza, Schneider, Waser and Dittmann, Nat. Commun. (2015$^{[100]}$).

4.1 Introduction

Among the many applications of SrTiO$_3$ is its potential use as a resistive switch: the application of an electrical bias switches the resistivity of the material from a high resistive state (HRS) to a low resistive state (LRS)$^{[101–105]}$. This characteristic is also known as memristive behaviour. Due to the physical limitations of silicon based technology, memristive devices have received much attention for their potential applications in data storage. The widely accepted mechanism for the resistive switching process in transition metal oxides is the valence-change mechanism and describes the switching process in terms of a nanoscale redox reaction.$^{[106–111]}$

Generally, the switching process is performed by applying a set voltage to switch the system from the HRS to the LRS, thus reducing the system locally and forming a switching filament. Preferably the device remains in the LRS without decay until a reset operation is performed, with a bias opposite to the one applied in the set process, to return the device to the original oxidised HRS. The term retention failure describes the case where the switched device decays (without the application of a reset operation) back to the high resistive state over a short period of time.

The desired properties for the large-scale application of memristive devices are not only high uniformity, high endurance (high cyclability of the switching process) and scalability down to the nanometre regime, but also ultra-nonlinear switching kinetics, combining extremely fast switching times (tens of nanoseconds) and retention times exceeding a decade with no more than an order of magnitude separating the read and write voltages of the device.$^{[112,113]}$ This is commonly referred to as the voltage–time dilemma.

The memristive properties of strontium titanate are known to vary depending
on its morphology, where single-crystalline samples are known to exhibit retention failure after short time spans\textsuperscript{[102,104,105]} and (poly- or single-crystalline) thin films—with considerable amounts of extended defects—have enhanced retention behaviour\textsuperscript{[101,105]}.

Here a comprehensive collaborative study of the memristive properties of SrTiO\textsubscript{3}, where both experimental and simulation techniques were employed, is presented. Before discussing the performed simulations, a brief overview of the experimental findings within the collaboration is given.

**Overview of the Experimental Results**

Within the collaborative investigation of the retention behaviour of SrTiO\textsubscript{3}, C. Bäumer, C. Schmitz, H. Du, K. Skaja, V. Feyer, P. Müller and B. Arndt performed an extensive set of experiments on a variety of switching devices\textsuperscript{[100]} The investigated samples were prepared by means of pulsed laser deposition (PLD): 2 nm SrTiO\textsubscript{3} (the switching film) was deposited on a Nb-doped strontium titanate (Nb: SrTiO\textsubscript{3}) substrate which served as the bottom electrode for the electrical measurements. For the top electrode 30 nm of gold were sputter-deposited on the switching device and structured by optical lithography and reactive ion-beam etching into 10 \( \mu \)m \( \times \) 10 \( \mu \)m electrode pads. The device geometry is shown in Fig. 4.1(a).

![Schematic of SrTiO\textsubscript{3} switching device geometries](image)

**Figure 4.1:** Schematic of SrTiO\textsubscript{3} switching device geometries. (a) Geometry without retention stabilisation layer; (b) Geometry with retention stabilisation layer.

Only \( \sim \) 20% of the devices with the described geometry exhibited stable retention, i.e. retention failure occurred in most of the devices. Careful spectromicroscopic analyses, employing X-ray photoemission electron microscopy (XPEEM), of the
switched devices (after delamination of the top electrode) revealed a reduced and locally confined switching filament containing Ti$^{3+}$. Devices which were switched back showed no Ti$^{3+}$ spectral contributions, thus indicating local redox reactions to be the fundamental mechanism for resistive switching in SrTiO$_3$. Upon closer examination of the devices exhibiting stable retention characteristics it was found that SrO segregation occurred in the vicinity of the switching filament. No evidence of such a phase separation was found in the devices with retention failure, leading to the conclusion that SrO may play an important role in the stabilisation of the retention behaviour.

In order to investigate the effects of the phase separation, devices with an alternative geometry [see Fig. 4.1(b)], which included an intentional additional 1 nm stabilisation layer (deposited by PLD), were prepared and subsequently examined with regards to their retention behaviour. The inclusion of SrO as an artificial layer led to enhanced device uniformity and retention properties compared to the counter parts without the intentional stabilisation layer.

The question at hand is how the retention-stabilisation layers contribute to the enhanced retention of the system. To this end, two further oxides, other than SrO, were deposited as stabilisation layers in order to gain insight into the mechanisms at play in the enhancement of the retention properties, specifically YSZ and Al$_2$O$_3$. The oxides used as stabilisation layers are wide band-gap insulators, but differ in their mass-transport properties. YSZ is a prototypical representative of a fast oxygen-ion conductor due to its high concentration of oxygen vacancies\cite{114–121} whereas Al$_2$O$_3$ is known for exceedingly sluggish oxygen transport and very low oxygen-vacancy concentrations\cite{121–129}. The devices with YSZ stabilisation layers showed frequent retention failure, while those with Al$_2$O$_3$ layers showed improved retention behaviour similar to that observed with the SrO layers.

Combining the experimental results of Bäumer et al.\cite{100} with the atomistic simulations of the switching interface structure SrTiO$_3$ | SrO presented here should therefore shed light on the processes relevant in preventing retention failure.\textsuperscript{a}

\section*{4.2 Results}

Prior to the discussion of the results concerning the interface structure, brief preliminary investigations of the SrO system with respect to bulk and defect properties will be presented. Furthermore, the compatibility of the rock-salt structure with the perovskite structure will be assessed with regards to the interface

\textsuperscript{a}The computational details are described in Section 2.1.
structure.

4.2.1 Strontium Oxide

As the current interest lies in the behaviour of oxygen ions within the interface system, it is pertinent to know the behaviour of oxygen ions in bulk SrO as well as in bulk SrTiO$_3$ using the same set of potentials. Since the empirical pair potentials of Pedone et al.\cite{54} were developed for SrO among other binary oxides, they are the ideal set to use for the investigation of both SrO and the SrTiO$_3$|SrO heterostructure as they have proven to be capable of describing both systems (see Section 2.1). The oxygen-transport properties of bulk SrTiO$_3$ have been previously discussed (see Section 2.1), while the properties of bulk SrO will be briefly investigated at this point. Specifically, a closer look at the oxygen migration process in SrO will be taken.

![Crystallographic unit cell of strontium oxide. Sr in large blue and O in small red spheres (no relationship to real ionic radii).](image)

**Figure 4.2:** Crystallographic unit cell of strontium oxide. Sr in large blue and O in small red spheres (no relationship to real ionic radii).

SrO crystallises in the cubic rock-salt structure with the space group $Fm\bar{3}m$ (No. 225) and a lattice constant of $a = 5.16$ Å\cite{130,131} (see Figure 4.2). From Table 4.1 it is clear that the empirical pair potentials of Pedone et al.\cite{54}, as expected, describe the bulk properties of SrO fairly well.

As both oxygen and strontium are octahedrally coordinated by their respective counter-ions, the assumption is made that the oxygen migration will occur along the octahedral edges (the $\langle 110 \rangle$ direction). Whether the ion migration within the rock-salt structure follows a curved or a linear path in the lattice is currently unclear. Investigations in the literature indicate that the exact migration path may depend on the difference of electronegativity ($\Delta$EN) of the constituent ions; large $\Delta$EN lead to linear paths and small differences lead to curved paths.\cite{133,134} In the case of SrO, $\Delta$EN $\approx$ 2.5 (which is appreciable) and indicates a linear path.
Table 4.1: Comparison of computational and experimental properties of the perfect SrO lattice: lattice parameter $a$ and bulk modulus $B$.

<table>
<thead>
<tr>
<th></th>
<th>$a$ /Å</th>
<th>$B$ /GPa</th>
<th>Ref.</th>
</tr>
</thead>
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<td>76</td>
<td>This study</td>
</tr>
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<td>5.15</td>
<td>76</td>
<td>[54]</td>
</tr>
<tr>
<td>Experiment</td>
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<td>88</td>
<td>[130]</td>
</tr>
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<td>Experiment</td>
<td>5.16</td>
<td></td>
<td>[131]</td>
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<tr>
<td>Ab-initio calculations</td>
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<td>106</td>
<td>[132]</td>
</tr>
</tbody>
</table>

to be probable. However, in order to confirm the actual migration path and determine the migration barrier, the energy hyper-surface (between the initial and final position of the migrating oxygen ion) is systematically scanned for the saddle-point configuration (as described in Section 2.1).

![Schematic representation of oxygen migration](image)

**Figure 4.3:** Schematic representation of the oxygen migration along an octahedral edge (left) and the hyper-surface energies of the migrating ion along the straight path indicated in the schematic (right). Sr in large blue and O in small red spheres (no relationship to real ionic radii).

Figure 4.3 shows the energies of the migrating ion (right) scanned along the linear path indicated in the schematic (left). Scanning in the directions perpendicular to the migration direction at the maximum energy (not shown) revealed that the oxygen migration takes place along a linear path, as the scans showed energy minima at the position of the maximum found along the migration direction. This is confirmed through the use of various other sets of empirical pair potentials (not shown)$^{51,52}$, leading to the conclusion that O migration in SrO occurs along a linear path with an activation energy of $\approx 1.4$ eV.
4.2.2 Interface Structure between SrTiO$_3$ and SrO

In order to perform simulations on an epitaxial SrTiO$_3$|SrO interface, it is necessary to understand how the two bulk compounds fit together at the interface, i.e. which lattice planes form the interface. SrTiO$_3$ is known to form Ruddlesden–Popper phases in the presence of excess SrO$^{[30,31]}$ and the Ruddlesden–Popper structures can be grown through epitaxial deposition of SrO on SrTiO$_3$.$^{[135]}$ Therefore, the interface structure for the investigation of oxygen migration is assumed to be equivalent to the Ruddlesden–Popper phase interface between rock-salt and perovskite structured oxides.

![Diagram of SrTiO$_3$ and SrO interface]

Figure 4.4: The optimised simulation cell of the SrTiO$_3$|SrO interface structure projected on the ac-face. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii).

The crystallographic lattice planes that form the interface are, therefore, the (001) plane in SrTiO$_3$ and the (011) plane in SrO. The corresponding lattice constant in SrO, $a^{[011]}$(SrO) = $a$(SrO)/$\sqrt{2}$ = 3.642 Å, is smaller than the lattice constant of SrTiO$_3$ [$a$(SrTiO$_3$) = 3.923 Å], resulting in a lattice mismatch of 7%. The heterostructure will therefore consist of SrTiO$_3$ under compressive strain and SrO under tensile strain.

In order to mimic the experimental investigations performed on the heterostructure$^{[100]}$, the simulation cell was constructed with similar dimensions for the SrTiO$_3$ and the SrO layer, consisting of $\approx$ 2.2 nm of SrTiO$_3$ and $\approx$ 1.2 nm SrO [see Fig. 4.1(b)]. It was subsequently optimised by minimising all degrees of freedom at constant pressure (see Figure 4.4). Due to the lattice mismatch, SrTiO$_3$ shows compressive strain of the order of ca. 1% parallel to the interface (in-plane), while
SrO exhibits tensile strain of the order *ca.* 6% in-plane. It is expected that SrO accommodates most of the lattice mismatch as SrTiO$_3$ constitutes most of the simulation cell.

### 4.2.3 Oxygen Migration in SrTiO$_3$|SrO Heterostructures

As discussed above, a retention failure is believed to be caused by the reoxidation of the switching filament. For the SrTiO$_3$|SrO heterostructure, three different scenarios could be employed to prevent this reoxidation:

(I) *Oxygen storage capability.* Similar to the oxygen exchange between different oxide layers in oxide dual-layer memory elements under applied electric fields\textsuperscript{[136]}, oxygen from SrTiO$_3$ could be incorporated into SrO (as interstitials or into existing vacancies) during the *set* operation. The SrO layer can be regarded as an oxygen reservoir. This may lead to a new (meta-)stable oxygen distribution between the two adjacent oxides, eliminating the driving force for reoxidation of the SrTiO$_3$ without applied electric fields and therefore leading to improved retention times.

(II) *Surface reaction rate of oxygen incorporation.* If the storage of additional oxygen in the retention-stabilisation layer is impeded due to a lack of available lattice sites (no vacancies available and unfavourable energy of formation for oxygen interstitials), oxygen must be excorporated from the retention-stabilisation layer during the *set* operation in order to form the switching filament. In this case, reoxidation of the SrTiO$_3$ during *reset* or retention failure inevitably requires the incorporation and diffusion of additional oxygen into the heterostructure from the surroundings. Since conduction band electrons contribute to the rate determining step in the incorporation of oxygen into the oxide lattice\textsuperscript{[137,138]}, this step might be impeded in SrO due to the comparably large band-gap (between 5 and 6.5 eV). The inhibited oxygen incorporation may therefore be responsible for the enhanced retention times of the heterostructures.

(III) *Diffusion rate.* At the same time, the oxygen needs to migrate from the top surface into the conductive filament within the SrTiO$_3$ after the incorporation into the retention-stabilisation layer. Given the fast diffusion rates in SrTiO$_3$\textsuperscript{[33,34]} the improved retention of the heterostructures may be caused by slower ambipolar diffusion rates within the SrO. If the incorporation rate of the retention-stabilisation layer was as fast as in SrTiO$_3$, slow diffusion
through the retention-stabilisation layer may become the rate-determining step and thus retard the reoxidation of the switching filament.

![Diagram](image)

**Figure 4.5**: Top: Illustration of the simulation cell of the heterostructure, with the simulated migration path indicated schematically by black arrows. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii). Bottom: Energies of the sites and saddle points corresponding to an oxygen vacancy migrating through the heterostructure. The x axis is scaled to the fractional coordinates of the c axis of the simulation cell. All plotted energies are referenced to the average vacancy formation in the SrTiO$_3$ regime of the simulation cell. The dotted line serves as a guide to the eye for the change in energy during the migration process and the vertical dashed line indicates the position of the interface between SrTiO$_3$ and SrO. Adapted from Ref. [100] with permission under the CC-BY 4.0 license.

To clarify which of the effects (I–III) are responsible for the improved retention times, the oxygen migration in the heterostructure is first described through static
lattice simulations. The formation process of the SrO layer (through phase separation during electrical treatments or intentional deposition by pulsed laser deposition as previously described) is known to result in considerable amounts of point defects such as anion and cation vacancies. Therefore, the migration of oxygen by a vacancy mechanism within the SrTiO$_3$|SrO heterostructure is analysed.

In Fig. 4.5, the site and saddle-point energies corresponding to the migration of an oxygen vacancy through the heterostructure are shown. One notices a considerable difference in the migration barriers in the two materials, with the barriers in SrO (ca. 1.2 eV) being twice as high as those in SrTiO$_3$ (ca. 0.6 eV). This suggests that, once oxygen ions are incorporated into SrO under an electric field (which lowers the barrier for migration$^{[139-141]}$), their return is hindered. There are also small differences in the site energies within SrTiO$_3$ (this is due to the biaxial strain arising from lattice mismatch) and between SrTiO$_3$ and SrO (suggesting a small amount of vacancy redistribution from SrO to SrTiO$_3$$^{[138]}$, see also preceding chapter). The migration barriers in the heterostructure do not differ significantly from the barriers in the bulk compounds, indicating that the effects of the lattice mismatch play a minor role.

On the basis of these calculations, it is possible to conclude that impeded oxygen transport within the SrTiO$_3$|SrO heterostructure (mechanism III) could in fact lead to improved retention times. At the same time, one cannot exclude that mechanisms I and II play a similar role in SrO, as oxygen incorporation reactions and the defect structure in SrO are not well understood. However, the combination of the experimental findings (where YSZ stabilisation layers lead to frequent retention failure of the switching device$^{[100]}$) and the simulation results suggest the exclusion of mechanism I (oxygen storage capability) as a stabilisation factor.

The improved retention behaviour observed for both SrO (which the simulations reveal to have larger activation enthalpies for oxygen migration) and Al$_2$O$_3$ stabilisation layers indicates that mechanisms II and III play a greater role than mechanism I in the switching process. As both oxides are wide band-gap insulators, it is not possible to isolate one of the two effects (surface reaction rate and diffusion rate for oxygen) as the main cause for the improved retention behaviour. Nonetheless, since YSZ is also a wide band-gap insulator (and does not enhance the retention properties) one may tentatively posit that mechanism III has a larger influence on the retention behaviour than mechanism II.
4.3 Conclusion

Simulations supporting the experimental investigations within the collaboration were performed to determine the mechanisms at play in improving the retention behaviour of SrTiO$_3$. While the computational results on their own are inconclusive, one finds—when taking the experimental evidence into account—that both surface-reaction and diffusion rate in the stabilisation layer may be rate-determining for the retention behaviour of switching devices. The oxygen-storage capability of the stabilisation layer (on its own) is found to be neither mandatory nor sufficient to obtain enhanced retention properties. Although the results may suggest mechanism III to be the most effective stabilisation factor, a better separation of the effects of mechanisms II and III may be achieved through further experimental investigations wherein the surface-reaction rate is varied; for example by switching in various atmospheres, or by varying the rate of oxygen diffusion through altering the defect chemistry of the stabilisation layers. Future investigations may also entail the investigation of point-defect redistribution across an interface driven by a difference in the standard chemical potential of the defect species.
5 Low-Angle Grain Boundaries in SrTiO₃

Parts of this chapter were previously published by Metlenko, Ramadan, Gunkel, Du, Schraknepper, Hoffmann–Eifert, Dittmann, Waser and De Souza, Nanoscale (2014) 571 and by Ramadan and De Souza, Acta Materialia (2016) 142.

5.1 Introduction

The perovskite oxide strontium titanate (SrTiO₃) has long been considered a model material for studying experimentally the structures of grain boundaries in the huge family of perovskite-type oxides. This is because it combines high mechanical and chemical stability with a simple, high-symmetry cubic structure [16,26,27] (see Section 1.2). In addition, SrTiO₃ provides an ideal oxide material in which the interactions of grain boundaries with point defects may be examined quantitatively [36–38] due to the extensive knowledge of the point-defect chemistry in bulk SrTiO₃ [13–15] (see Section 1.2). This knowledge allows strong conclusions to be drawn for interfacial behaviour.

Low-angle grain boundaries in SrTiO₃, in particular, have received much attention because—consisting of a periodic array of dislocations—they allow for structure-property relationships to be elucidated [38,143–147] and for the properties of dislocations to be studied. Thus, not only the atomistic structures of selected [100] low-angle boundaries have been investigated [148–154], but also the boundaries’ resistance to charge transport [57,143–147], their interactions with oxygen vacancies [38,57], and their influence on oxygen diffusion [57]. It has furthermore been suggested [155] that dislocations constitute the active filaments in resistive switching devices of SrTiO₃, but recent evidence militates against this view [57,141,156].

Despite the concerted effort, there is much debate, still, regarding the structure of low-angle [100] tilt grain boundaries in SrTiO₃. These interfaces are reported variously to consist of one type [153], two types [148,151,154], or even three types [152] of dislocation cores. The dislocations, furthermore, may be aligned [148,152,153], or non-aligned in a zigzag pattern [151,154]. In addition there are reports of considerable
cation disorder at the dislocation cores\textsuperscript{[152,153]}, and also reports in which no such disorder was observed\textsuperscript{[148,151,154]}. All studies do agree, though, that dislocations are oxygen-deficient and dissociated; and that the average dislocation separation at a given [100] tilt boundary is given by Frank’s Formula\textsuperscript{[21]} [see Equation (1.1)].\textsuperscript{a}

The general aims of this study are to investigate the effects of the tilt angle ($\theta$) on the dislocation structure, the grain-boundary structure, the excess energy and the excess volume for both stoichiometric and oxygen-deficient dislocation cores. To this end, well-established static atomistic simulation techniques\textsuperscript{[157–159]} with high-quality empirical pair potentials\textsuperscript{[54]} (see Section 2.1) are employed. The grain-boundary simulation cells were prepared according to the procedure detailed below, in accordance with general grain-boundary theory (see Section 1.1).

Based on the results, several apparent discrepancies in the literature regarding the atomistic structure of low-angle grain boundaries can be resolved. Specifically, one finds that various dislocation configurations are possible at [100] (0 1 1) symmetric tilt boundaries in SrTiO$_3$: the dislocations may be equally spaced or not; they may display one or two types of dislocation cores; and they may be aligned or not. Furthermore, it will be demonstrated that it is possible to predict the specific dislocation configuration (spacing, type and alignment) based solely on knowledge of the grain-boundary plane. With the data obtained from the atomistic simulations, the effect of symmetric tilt boundaries on the behaviour of point-defects is predicted within a well-established thermodynamic framework\textsuperscript{[38,44,83]} (as described in Section 2.2).

### 5.2 Simulation of Symmetric-Tilt Grain Boundaries

In order to investigate symmetric-tilt grain boundaries employing atomistic simulation techniques, a periodic simulation cell with such grain boundaries is required. The tilt-boundary angle ($\theta$) is given by the angle between the planes of the two grains forming the boundary, which for cubic systems is determined by

$$
\cos \theta = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \sqrt{h_2^2 + k_2^2 + l_2^2}},
$$

where $h_i$, $k_i$ and $l_i$ are the Miller indices of the planes. For all SrTiO$_3$ interfaces simulated in this study the rotation axis is parallel to the [100] direction and the grain-boundary normal prior to the rotation is the [001] direction. Thus, for all\textsuperscript{a} for these tilt boundaries the Burgers’ vector, $|\mathbf{b}| = a$(SrTiO$_3$), where $a$ is the lattice constant of SrTiO$_3$.\textsuperscript{[143,144,148,152,153]}

\textsuperscript{a}For these tilt boundaries the Burgers’ vector, $|\mathbf{b}| = a$(SrTiO$_3$), where $a$ is the lattice constant of SrTiO$_3$.\textsuperscript{[143,144,148,152,153]}
investigated boundaries, \( h_1 = h_2 = 0 \). Furthermore, \( k_1 = k_2 = 1 \), so that the only remaining variable is \( l \). As only symmetrical tilt boundaries are investigated, \( |l_1| = |l_2| \) in all cases. These conditions lead to discrete tilt angles, which can be determined using Eq. (5.1). The individual parameters concerning the investigated tilt angles are given in Table 5.1.

**Table 5.1:** Summary of the simulation cell parameters for the various tilt-angles \( \theta \) as well as the corresponding grain-boundary planes. \( d_{\text{Frank}} \) is the distance between dislocations as determined by Frank’s formula and corresponds to the determined average dislocation separation for all investigated grain boundaries. From Ref. [142].

<table>
<thead>
<tr>
<th>( \theta /^\circ )</th>
<th>( h )</th>
<th>( k )</th>
<th>( l )</th>
<th>( a / \text{Å} )</th>
<th>( b / \text{Å} )</th>
<th>( c / \text{Å} )</th>
<th>( d_{\text{Frank}} / \text{nm} )</th>
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</table>

The initial geometric configurations of the tilt boundaries in this study were constructed with the GBStudio package\[160\]. The implemented procedure will be described using the 6.0° tilt angle [corresponding to the boundary plane (0119)] as an example.

The first step is to merge two tilted grains into a periodic structure (as illustrated in Figure 5.1 on page 54). The resulting configuration contains two (anti-parallel) boundaries (indicated by the green arrows), one at the centre and the other at the edge of the simulation cell. The angle between the two grains is 6.0°. The boundaries are separated by a large bulk-structured regime, 20 unit cells in width (ca. 75 Å), in order to prevent interactions of the two boundaries with each other. This initial structure—in its current form—cannot be used to perform atomistic simulations due to overlapping ions and large voids present at the boundaries,
In intermediate gray and red spheres (no relationship to real time radii),
indicate the periodic unit (unit cell) of the structure and the green arrows mark the position of the two boundaries. The black rectangle indicates the periodic simulation cell of the symmetric unit. The black rectangle indicates the periodic simulation cell of the symmetric unit.

Figure S1: 2D projection of the initial periodic simulation cell of the symmetric unit.
Figure 5.2: 2D projection of the modified periodic simulation cell of the symmetric 6.0° [100] (0119) tilt boundary. The black rectangle indicates the periodic unit (unit cell) of the structure and the green arrows mark the position of the two boundaries. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii).
Figure 5.3: 2D projection of the optimized periodic simulation cell of the symmetric 60° [0110] (0 1 1 9) Pt boundary containing two complementarily grain boundaries. The black rectangle indicates the periodic unit (unit cell) of the structure and the green arrow marks the position of the two boundaries. Si in large blue, Ti in intermediate grey and O in small red spheres (no relabelling to real ionic radii).
wherein the overlapping ions are more detrimental than the voids. Therefore, the initial structure is modified to reduce the degree of overlap and the magnitude of the voids, while maintaining the stoichiometry of SrTiO$_3$. Such modifications correspond to either removing or shifting entire SrTiO$_3$ units within the structure, wherein equivalent boundaries are treated in an identical manner.

Figure 5.2 (see page 55) shows the simulation cell after the necessary modifications, prior to the optimisation. This modified structure containing 3750 ions (750 formula units of SrTiO$_3$) is then used as the input structure for atomistic simulations; the optimised tilt-boundary structure (see Figure 5.3 on page 56) is obtained through minimising all degrees of freedom at constant pressure. The result is the point-defect free stoichiometric 6.0° [1 0 0] (0 1 19) grain-boundary simulation cell. On the basis of the defect-free grain-boundary cell the defect calculations are performed at constant volume with the techniques described in Chapter 2.

This procedure is repeated for various grain boundary planes to obtain the different tilt boundary angles investigated here. Creating tilt boundary simulation cells in this manner has several advantages, one of which is the formation of two anti-parallel grain boundaries, resulting in macroscopically unstrained systems. Another is the maintained comparability of the tilt-boundary cells which are all created in an analogous manner with the same approximate separation between the boundaries.

Thirteen symmetric tilt boundaries with misorientation angles varying between $\theta = 3.0^\circ$ and $\theta = 22.6^\circ$ (see Table 5.1) were prepared and studied in both stoichiometric and oxygen-deficient forms.

5.3 Results

In the following, the properties of symmetric tilt boundaries will be presented with respect to the structural motifs of the dislocations and those of the grain boundaries, the boundaries’ excess thermodynamic quantities, and their influence on point defects. Finally a discussion of the data available in literature in comparison to the results obtained from the atomistic simulations will be presented.

5.3.1 Grain-Boundary Structure

Initial examination of the thirteen (energy-minimised) stoichiometric boundaries shown in Figure 5.4 (on page 58) reveals several common characteristics. First, all boundaries consist of an array of edge dislocations. Second, the average separation of dislocations is consistent with the theoretical values calculated with Frank’s
Figure 5.4: Full repeat units of the optimised thirteen stoichiometric symmetrical $\theta$ [100] (0 1 1) tilt boundaries simulated in this study. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii). From Ref. [142]. Reproduced with permission from Elsevier.
Figure 5.5: Full repeat units of the optimised thirteen oxygen deficient symmetrical $\theta [100] (01\bar{1})$ tilt boundaries simulated in this study. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii). From Ref. [142]. Reproduced with permission from Elsevier.
formula (see Table 5.1). Third, all simulated interfaces consist of non-dissociated dislocations. The thirteen corresponding fully oxygen-deficient boundaries are shown in Figure 5.5 (on page 59). (As a supercell approach employing a simulation cell with a thickness of two-unit-cells was used, the removal of one oxygen ion corresponds to the removal of every other oxygen ion from a column; and the removal of two oxygen ions corresponds to the removal of an entire column.) Here, the interfaces consist of dissociated dislocation cores, but otherwise these oxygen-deficient boundaries maintain the same common traits as those observed for the stoichiometric boundaries.

5.3.1.1 Dislocation Types

![Dislocation core structures at a 6.0°[1 0 0] (0 1 1 9) tilt boundary for the stoichiometric cases, and after the removal of half and an entire column of oxygen ions from the structure. (a) Stoichiometric TiO₂-type core, (b) TiO₂-type core with half an oxygen column removed, (c) fully oxygen-deficient TiO₂-type core, (d) stoichiometric SrO-type core, (e) SrO-type core with half an oxygen column removed, (f) fully oxygen-deficient SrO-type core. The column, from which oxygen ions were removed, is circled in black. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii). Adapted from Ref. [57] with permission from The Royal Society of Chemistry.](image)

All relaxed structures of the stoichiometric low-angle tilt grain boundaries, shown in Figure 5.4, have two types of dislocation cores: one is terminated with tita-
nium and oxygen columns (TiO$_2$-type core); the other, with strontium and oxygen columns (SrO-type core). These core structures are shown in detail in Figures 5.6(a) and 5.6(d) for the 6.0° [1 0 0] (0 1 19) boundary. They were first suggested by Zhang et al.$^{[16]}$ and were subsequently predicted by Ferré et al.$^{[60]}$ by means of a Peierls–Nabarro approach.

There is experimental evidence directly from electron energy loss spectroscopy (EELS)$^{[16,162]}$ and indirectly from electrical measurements$^{[143-145]}$ that edge dislocation cores in ST are oxygen deficient. Therefore, the effect of removing oxygen ions from the simulation cell was examined. The ion columns at the dislocations cores, from which oxygen ions were removed, are indicated in Fig. 5.6(a) and 5.6(d).

![Dislocation core structures](image)

**Figure 5.7:** Dislocation core structures at a 22.6° [1 0 0] (0 1 5) tilt boundary for the stoichiometric cases, and after the removal of half and an entire column of oxygen ions from the structure. (a) Stoichiometric TiO$_2$-type core, (b) TiO$_2$-type core with half an oxygen column removed, (c) fully oxygen-deficient TiO$_2$-type core, (d) stoichiometric SrO-type core, (e) SrO-type core with half an oxygen column removed, (f) fully oxygen-deficient SrO-type core. The column, from which oxygen ions were removed, is circled in black. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii).

The removal of an entire oxygen-ion column from a dislocation core results in substantial structural relaxation, as shown in Fig. 5.6(c) and 5.6(f). In both cases, the TiO$_2$-type and the SrO-type core, there is now a plane of ions running through
the centre of a dislocation (from the top to the bottom of each image), and the structure is essentially symmetrical. Such non-stoichiometric core structures were proposed by Zhang et al.\textsuperscript{[161]} from an analysis of high-resolution transmission electron microscopy (HR-TEM) images obtained for a 5.4° low-angle tilt grain boundary in ST [see Fig. 6(B and C) of Zhang et al.\textsuperscript{[161]}]; essentially, the dislocation cores are dissociated with a unit cell of antiphase domain boundary. The removal of every other oxygen ion from a column at the dislocation core did not produce the same degree of structural changes: the core structures remained close to the stoichiometric cases [see Figures 5.6(b) and 5.6(e)] and thus indicate that a high degree of oxygen deficiency is required at the specified column for the dislocations to dissociate as observed experimentally.

The structural changes accompanying the removal of an oxygen column are not limited only to the 6.0° boundary, but are observed for all studied tilt angles, even the extreme case of the 22.6° tilt angle (see Figures 5.5 and 5.7). The respective segregation energies for the various tilt angles are discussed in Section 5.3.2.2.

5.3.1.2 Dislocation Arrangement

![Diagram](image)

**Figure 5.8:** Representation of all $2^3$ descriptor combinations for the $\theta$ [1 0 0] (0 1 1) symmetric tilt grain-boundaries in SrTiO$_3$ with even and uneven values of $l$. E/NE refer to equidistant/non-equidistant dislocations, A/NA refer to aligned/non-aligned dislocations and AL/ST refer to alternating/single type dislocation cores. Options that are crossed out are forbidden by the crystal chemistry of SrTiO$_3$; bracketed, grey options are possible but have been found to be energetically unfavourable; blue options are energetically favoured and are therefore the most likely descriptor combinations. From Ref. [142]. Reproduced with permission from Elsevier.
Close inspection of Figs. 5.4 and 5.5 reveals two important differences between the various boundaries. Although all boundaries have the same basic structural units (dislocations), the distortion of these structural units increases with increasing tilt angle, an effect that is clearly visible when comparing the extreme cases (3.0° and 22.6° boundaries). In addition, some boundaries consist of equidistant dislocations, while others (θ = 3.0°, 7.2° and 8.2°) consist of non-equidistant dislocations (see Fig. 5.4 or 5.5). Those boundaries that consist of equidistant dislocations display an average separation of $d_{\text{Frank}} = (n + 0.5) \cdot a$ and have boundary planes with uneven values of Miller index $l$. The boundaries with non-equidistant dislocations display an average separation of $d_{\text{Frank}} = n \cdot a$ and have even values of $l$.

In the following, the structural properties of stoichiometric and oxygen-deficient symmetric tilt boundaries are considered according to their nominal dislocation separation. The three descriptors that characterise the dislocation arrangement are found to be equidistant/non-equidistant, aligned/non-aligned and alternating/single type. That is, in total there are $2^3$ combinations. Based on crystal chemistry—and as described in detail in the following sections—one finds that not all of these eight combinations are possible (see Figure 5.8).

**Boundaries with** $d_{\text{Frank}} = (n + 0.5) \cdot a$

In this study, most of the investigated boundaries fall into the category of $d_{\text{Frank}} = (n + 0.5) \cdot a$. All these boundaries (see Figs. 5.4 and 5.5) are characterised by dislocations that are equidistant, alternating between TiO$_2$-type and SrO-type and aligned exactly along the interface.

Based on crystal chemical arguments (see below), it is apparent that the descriptors are not independent of one another and therefore not all combinations are possible (see Figure 5.8). If, for example, the dislocation configuration is changed from alternating to single type (by making the dislocations at one interface in the cell only TiO$_2$-type, which automatically makes the other boundary in the cell have SrO type dislocations to maintain global SrTiO$_3$ stoichiometry, see Figure 5.9), and then the ions are allowed to relax to a minimum energy configuration, one finds that both interfaces display non-equidistant, non-aligned and single type dislocation cores [see Figure 5.10(b)].

Specifically, this alternative configuration exhibits individual dislocation separations that switch between $n \cdot a$ and $(n + 1) \cdot a$, thus maintaining the average spacing of $(n + 0.5) \cdot a$. The single type dislocations at each boundary are a result of the dislocation spacings being a full multiple of the SrTiO$_3$ lattice constant. With the boundary consisting of single type dislocations, the dislocations can no longer
be aligned (due to the crystal structure), and are *non-aligned* in a zigzag pattern. Figure 5.10 compares the discussed traits for the oxygen deficient 5.5° [100] (0 1 21) boundary with dissociated dislocation cores.

![Diagram](image)

**Figure 5.9:** Complementary grain boundaries in an optimised 5.5° [1 0 0] (0 1 21) system with non-equidistant, non-aligned and same type dislocations at the boundary. The grain boundary on the upper side comprises of only TiO₂-type dislocation cores, the boundary on the lower side comprises solely of SrO-type cores. The individual space between two dislocations is indicated by the arrows and given in units of \( a(\text{ST}) \). Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii). From Ref. [142]. Adapted with permission from Elsevier.

In the *equidistant, aligned* and *alternating* boundary configuration, the dislocations alternate in type (between SrO- and TiO₂-type cores) due to the distance between the cores being a multiple of the perovskite-oxide lattice constant plus an extra half unit. As the cores alternate in type the perovskite structure allows for the cores to be aligned. Although a non-aligned configuration of equidistant alternating dislocations is possible (see Fig. 5.8), preliminary calculations reveal the aligned
configuration to be energetically more favourable, in agreement with general grain-boundary theory\textsuperscript{[22]}.

![Diagram](image)

**Figure 5.10:** Oxygen-deficient 5.5° [1 0 0] (0 1 2 1) tilt boundaries with dissociated dislocations. (a) Boundary with equidistant, alternating and aligned dislocations. (b) Two boundaries with non-equidistant, single type and non-aligned dislocations; one with only TiO\textsubscript{2} cores (left) and the other with only SrO cores (right). Dislocations are arranged in a “zigzag” pattern. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii). From Ref. [142]. Adapted with permission from Elsevier.

Thus, knowledge of the nominal average dislocation separation at a boundary [as given by Equation (1.1)] in combination with an understanding of the arrangement of ions in the perovskite structure allows for a prediction of expected boundary configurations. If one considers the excess grain-boundary energy (see Section 5.3.2) for the two different dislocation arrangements, one finds that they differ by ca. 0.1%. This energy difference is of the same order of magnitude as the accuracy of the simulations; one can, therefore, regard the different boundary configurations to be
energetically degenerate. In light of this degeneracy, the dislocation configuration that actually forms may be governed by the chemical composition [specifically by the activity of SrO (TiO$_2$) as a chemical component]. For example, if two SrO-excess (single-phase) crystals of SrTiO$_3$ are bonded to create the tilt boundary, the resulting interface will tend to consist of single type (SrO-type) dislocations.

Changing the individual dislocation spacing from that of Frank’s formula beyond half a lattice spacing, for example from $(n + 0.5) \cdot a$ to $(n - 0.5) \cdot a$ and $(n + 1.5) \cdot a$, though possible, is found to be energetically unfavourable relative to the equidistant case [$d = (n + 0.5) \cdot a$]. Increasing the difference between the individual spacing further is increasingly unfavourable. Incidentally, the limiting case here corresponds to the faceted boundary with individual spacings of $0.5a$ and $(2n + 0.5) \cdot a$.

**Boundaries with $d_{\text{Frank}} = n \cdot a$**

Three of the investigated boundaries fulfil the criterion of $d_{\text{Frank}} = n \cdot a$, specifically the boundaries having boundary planes (0138), (0116) and (0114) with corresponding angles of 3.0°, 7.2° and 8.2°. Similar to the boundaries discussed in the previous section, these interfaces also have two possible dislocation configurations [and these are different to $d_{\text{Frank}} = (n + 0.5) \cdot a$]. Either the boundaries consist of non-equidistant, aligned, and alternating dislocation cores (see Figures 5.4 and 5.5) or the dislocations are equidistant, non-aligned, and single type [as shown in Fig. 5.11 for the 7.2° [100] (0116) boundary]. Other possibilities (see Figure 5.8) can be disregarded as they are energetically unfavourable, as discussed in the preceding section.

Again, the two possible configurations can be understood in terms of the nominal average dislocation separation combined with the consideration of the perovskite structure. As the average separation is a full multiple of the SrTiO$_3$ lattice constant, equidistant dislocations can only be of single type (SrO or TiO$_2$) and are therefore non-aligned [see Figure 5.11(b)]. In order to obtain alternating dislocation cores at the boundary, the individual dislocation separations will alternate between $(n - 0.5) \cdot a$ and $(n + 0.5) \cdot a$ while maintaining the average separation of $d_{\text{Frank}} = n \cdot a$.

In this case, too, the energy difference between the two dislocation configurations at the grain boundary is very small (of the order of 0.1%), hence indicating that (within the accuracy of the simulation approach) there is no preferential configuration.

From the rules described above, it is concluded that only two types of edge dislocations (SrO-type and TiO$_2$-type dislocations) are found to form [100] symmetric tilt boundaries in SrTiO$_3$. Furthermore, there are four distinct energetically favourable
dislocation arrangements for $\theta$ [100] (01l) symmetric tilt boundaries in SrTiO$_3$. For even $l$, the resulting dislocation separation according to Frank’s formula will be $d_{\text{Frank}} = n \cdot a$, which leaves two possible dislocation configurations; either 1) non-equidistant, aligned, and alternating or 2) equidistant, non-aligned, and single type. For uneven values of $l$, the resulting dislocation separation will be $d_{\text{Frank}} = (n + 0.5) \cdot a$ and the boundaries also have two possible dislocation configurations; either 1) equidistant, aligned, and alternating or 2) non-equidistant, non-aligned, and single type. The other possible descriptor combinations listed in Figure 5.8 are not considered because preliminary calculations reveal them to be unfavourable or because they can be excluded due to the crystal chemistry of SrTiO$_3$.

![Dislocation Diagram](image)

Figure 5.11: Oxygen-deficient 7.2° [1 0 0] (01 16) tilt boundaries with dissociated dislocations. (a) Boundary with non-equidistant, alternating and aligned dislocations. (b) Two boundaries with equidistant, single type and non-aligned dislocations; one with only TiO$_2$ cores (left) and the other with only SrO cores (right). Dislocations are arranged in a “zigzag” pattern. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii). From Ref. [142]. Adapted with permission from Elsevier.

It is emphasised that the possible tilt angles for symmetric-tilt grain boundaries are not limited to the specific angles presented in this study: they can vary freely. In or-
order to obtain, for instance, a tilt-angle somewhere between 8.2° and 8.8°, angles that correspond to the grain-boundary planes (0 1 13) and (0 1 14), the grain-boundary plane of (0 2 27) would be a possibility, as according to Equation (5.1) the resulting tilt angle is 8.5°. With regards to the arrangement of the dislocations at such a tilt boundary, a combination of the possible arrangements for the [100] (0 1 14) and [100] (0 1 13) boundaries is to be expected, in accordance with conventional grain-boundary theory[21]. Atomistic simulations (not shown) confirm that for the 8.5° [100] (0 2 27) interface the resulting dislocation arrangement is indeed a combination of the arrangement at the [100] (0 1 14) and [100] (0 1 13) boundaries.

5.3.2 Grain-Boundary Properties

Having elucidated the structural motifs of low-angle symmetric-tilt grain boundaries in SrTiO₃ according to simple rules based on the crystal chemistry of the cubic perovskite structure, the focus is now shifted to the investigation of the boundaries’ properties, such as excess grain-boundary quantities and vacancy segregation energies.

5.3.2.1 Excess Grain-Boundary Quantities

The excess thermodynamic quantities of a grain boundary are defined as the difference between the value of that property for a system containing the boundary and its value in a system without the boundary, normalised to the area of the boundary. The excess energy of a stoichiometric grain boundary is therefore given by

$$\Delta_f E_{GB} = \frac{E_{cell} - n E_{Bulk}}{2A_{GB}}, \quad (5.2)$$

where $E_{cell}$ is the internal energy of the simulation cell, $E_{Bulk}^{SrTiO_3}$ is the internal energy of a single unit cell of SrTiO₃, and $A_{GB}$ is the cross-sectional area of the grain boundary simulation cell (with the factor of two arising from the cell containing two grain boundaries). $n$ is the number of SrTiO₃ units in the grain-boundary simulation cell. It is emphasised that the two most stable arrangements of dislocations at a boundary for a given angle are not relevant to the energy as they are energetically degenerate (as discussed in Section 5.3.1).

The excess grain-boundary volume is obtained in an analogous way and is given by

$$\Delta_f V_{GB} = \frac{V_{cell} - n V_{Bulk}^{SrTiO_3}}{2A_{GB}}, \quad (5.3)$$
where $V_{\text{cell}}$ is the volume of the simulation cell and $V_{\text{Bulk}}^{\text{SrTiO}_3}$ the volume of a single unit cell of SrTiO$_3$.

**Figure 5.12:** (a) Determined excess grain-boundary energies of stoichiometric SrTiO$_3$ tilt boundaries for different tilt-angles $\theta$ and corresponding fit of the Read–Shockley equation. (b) Determined excess grain-boundary volume for different tilt-angles $\theta$. From Ref. [142]. Adapted with permission from Elsevier.

The excess grain-boundary quantities determined from the simulations are consistent with the order of magnitude determined for different tilt boundaries, with the excess energy ranging up to $1.5 \text{J m}^{-2}$ and the values of the excess volume up to $0.8 \text{Å}^3 \text{Å}^{-2}$ for the investigated $\theta$-range (see Figure 5.12).$^{[163–166]}$ The excess grain-boundary quantities are—by definition—zero at $0^\circ$.

With increasing angle, a monotonous increase in the excess energy of the stoichiometric boundaries is seen. Investigations of metal systems$^{[24,167,168]}$ indicate that the grain-boundary energy varies smoothly with the misorientation angle for [100] symmetric tilt boundaries, though not, e.g., for [110] boundaries. A similar behaviour is observed here for [100] symmetric tilt boundaries in SrTiO$_3$. The excess grain-boundary volume shows a similar increase with tilt-angle.

Analytically, the excess energy of a low-angle tilt grain boundary can be described with two energy terms ($E_{\text{core}} + E_{\text{elastic}}$) that account for the strain energy of dislocations. The core energy ($E_{\text{core}}$) is commonly assumed to be negligible compared with the elastic energy outside the core region ($E_{\text{elastic}}$) and is therefore generally ignored. For the elastic term Read & Shockley$^{[20,169]}$ derived a simple expression, based on Hookean elasticity theory, to describe the excess energy of a low-angle grain boundary, namely

$$\Delta fE_{\text{GB}} = E_{\text{elastic}} = E_0\theta \left[ \ln \left( \frac{b}{2\pi r_0} \right) + 1 - \ln \theta \right],$$  \hspace{1cm} (5.4)$$

where $E_0$ is a constant which depends only on the elastic properties of the material and is equal to $Gb / [4\pi (1 - \nu)]$. $G$ and $\nu$ are the shear modulus and the
Poisson ratio, respectively. The only unknown parameter is \( r_0 \), the dislocation core radius. Equation (5.4) is only valid for grain boundaries with sufficiently large dislocation separations; a detailed derivation of the above expression can be found elsewhere\(^{[20,22,169]}\).

With \( G \) and \( \nu \) being determined directly from the simulation (see Table 2.2 in Section 2.1), Equation (5.4) can be fitted to the data shown in Figure 5.12(a) to determine a value for \( r_0 \). When fitting these data, however, it quickly becomes apparent that it is not possible to fit the entire range of angles from \( 3^\circ \) up to \( 23^\circ \). A good fit was found when limiting the range of angles to \( 0 \leq \theta \leq 9^\circ \) [see Figure 5.12(a)]. This gives a dislocation core radius of \( 2.54 \) Å, which—though small—appears to be reasonable as it is in the same order of magnitude as the Burgers’ vector\(^{[22]}\). Note: \( E_{\text{core}} \) is evidently negligible for this range of angles, as the excess energies determined from the simulations include both energy contributions \( (E_{\text{core}} + E_{\text{elastic}}) \). Similar limitations of the analytical expression have been reported in literature for metal systems\(^{[168]}\).

### 5.3.2.2 Vacancy Segregation Energies

There are various possibilities to examine the energetics of oxygen-deficient grain boundaries. One option is to compare the energy of the fully oxygen-deficient structures (four dislocation cores, each missing a column of ions) with the energy to remove a column of ions from the bulk region. An alternative is to compare the formation energy of an isolated vacancy at the different core types with the formation energy of an isolated vacancy in the bulk (point defects at infinite dilution). This segregation energy (which may be concentration dependent) is the quantity that is required for the thermodynamic treatment of point-defect redistribution at extended defects\(^{[36,38]}\). Here, in order to be able to predict space-charge potentials (see below), the segregation of isolated vacancies is investigated.

Figure 5.13 shows the vacancy segregation energies at the two types of dislocation cores as a function of tilt angle. The segregation energies were determined according to

\[
\Delta_t E_{\text{seg}}^{\text{VO}} = \Delta_t E_{\text{VO}}^\text{GB} - \Delta_t E_{\text{VO}}^\text{Bulk},
\]

with the oxygen-vacancy formation energy in the bulk, \( \Delta_t E_{\text{VO}}^\text{Bulk} \), being determined separately for each tilt angle.

Some slight scatter in \( \Delta_t E_{\text{seg}}^{\text{VO}} \) is apparent in Fig. 5.13. The scatter, though small, was also observed in the reference bulk values, possibly indicating that the size of the simulation cells may be insufficient to converge the bulk values. Larger simulation cells, however, cannot be simulated with the GULP code on a reasonable timescale.
Nevertheless one sees that the segregation energies are negative for all investigated angles, indicating that oxygen vacancies form preferentially at the dislocation cores. Furthermore, the energies indicate that the oxygen deficiency is favoured at the SrO-type dislocation cores relative to the TiO$_2$-type cores. In particular, one perceives that in both cases the segregation energy is approximately constant for angles up to approximately $9^\circ$ and thereafter begins to decrease in absolute magnitude with increasing angle.

With the segregation energies of Fig. 5.13 (assuming they are independent of the vacancy concentration), and the number of preferential sites for vacancies within a dislocation core given by $N_{\text{core}}^{V_O} = (2r_0a_{\text{Frank}})^{-1}$, it is now possible to predict the space-charge potential and the degree of oxygen deficiency for all the low-angle tilt grain boundaries. These calculations are based on the thermodynamic treatment of space-charge formation detailed in Ref. [38] (see Section 2.2), and employ for simplicity a one-dimensional, continuum approach. This one-dimensional treatment is sufficient as long as the extent of the space-charge zone (here $ca. 150$ nm) is much greater than the dislocation separation (here, the largest value is $\approx 7.5$ nm).
Figure 5.14: (a) Calculated vacancy redistribution profile across a 4.2°[100](0127) symmetric tilt-boundary comprised of equidistant, aligned, and alternating dislocation cores. (b) Space-charge potential $\Phi_0$ in dependence of tilt-angle for various grain-boundary configurations. The data was determined for a temperature of $T = 973$ K, an oxygen activity of $aO_2 = 0.1$ and an acceptor-impurity concentration of $c_{\text{dop}}^{\text{bulk}} = 7 \cdot 10^{17}$ cm$^{-3}$. The bulk electron ($c_e^{\text{bulk}}$), electron hole ($c_h^{\text{bulk}}$) and oxygen-vacancy ($c_{\text{O}}^{\text{vac}}$) concentrations were obtained according to the procedure detailed elsewhere\cite{43,83} (see Section 1.2). From Ref. \cite{142}. Adapted with permission from Elsevier.

In Figure 5.14(a), the equilibrium concentrations of the mobile defects across a 4.2°[100](0127) symmetric tilt-boundary are shown; of particular importance is the substantial accumulation of oxygen vacancies within the grain-boundary core and their strong depletion in the adjacent bulk phase. Electrons and holes follow the electric potential profile set up by the re-distribution of oxygen vacancies. Fig. 5.14(b) shows that the space-charge potential, $\Phi_0$, is highest for the alternating and SrO-type boundaries, while the TiO$_2$-type boundaries (with the smaller absolute segregation energies) tend to exhibit much lower space-charge potentials and thus much weaker point-defect redistribution. In general for all three types of boundary, $\Phi_0$ increases with increasing $\theta$ up to 9°, after which it decreases. This behaviour can be understood by considering $N_{\text{core}}^{\text{V}_\text{O}}$, which continuously increases with tilt-angle, and $\Delta_{\text{V}_\text{O}}E_{\text{V}_\text{O}}^{\text{seg}}$, which is constant up to $\theta = 9^\circ$ and then decreases in magnitude. Thus, the initial, small increase in $\Phi_0$ is due to the fact that $N_{\text{core}}^{\text{V}_\text{O}}$ increases with $\theta$ at constant $\Delta_{\text{V}_\text{O}}E_{\text{V}_\text{O}}^{\text{seg}}$, whereas the subsequent decrease in $\Phi_0$ results from the decrease in the magnitude of $\Delta_{\text{V}_\text{O}}E_{\text{V}_\text{O}}^{\text{seg}}$ being more important than the further increase in $N_{\text{core}}^{\text{V}_\text{O}}$. As previously inferred for metal systems\cite{24,170}, the presence of a transition between very low-angle and low-angle boundaries is suggested. It is not a transition between low-angle and high-angle boundaries because each of the investigated boundaries fulfils the criterion of a low-angle grain boundary\cite{24}: each interface consists of an array of discrete and clearly discernible dislocations. The transition between
very low-angle and low-angle boundaries is suggested to occur at $\theta = 9^\circ$ for three reasons. First, close visual inspection of the dislocation cores suggest a subtle change in their structure in the range of $8^\circ - 10^\circ$. Second, the analytical expression of Read and Shockley describes the excess grain-boundary energy up to $\theta = 9^\circ$. And third, the vacancy segregation energies are constant up to this value.

### 5.3.2.3 Oxygen Migration at Dislocations

From investigations of metals\textsuperscript{[171,172]} and semiconductors\textsuperscript{[173]} it is generally asserted that one-dimensional defects (e.g. dislocations) provide fast pathways within which mass transport occurs more rapidly than in the regular crystal. The common argument is that the atomic arrangements within dislocation cores are generally more open than in the regular crystal, suggesting less energetic hindrance (\textit{i.e.} lower activation enthalpies of migration) for the diffusing species and thus accelerated rates of mass transport. Whether this model holds true for all classes of crystalline materials, is unclear. Specifically, ionic oxides are more complex than other crystalline systems ultimately due to the crystal being composed of ions. In this case, a more open atomic arrangement within a dislocation core may not necessarily guarantee a lower activation enthalpy of migration. The migration jump of an ion along a dislocation core may involve the diffusing ion passing past ions of the same polarity—a process that is generally avoided in the bulk lattice in order to minimise Coulomb repulsion.

In the following, the oxygen deficient 6.0$^\circ$ [1 0 0] (0 1 19) grain boundary will be used as a model system to investigate the oxygen migration at dislocations. The migration process is investigated using the Mott–Littleton approach\textsuperscript{[64]} (see Section 2.1). For the determination of the migration energies, confirmation that a saddle-point configuration had been identified was obtained by systematically scanning the energy surface between the initial and final state.

In the $ABO_3$ perovskite structure, oxygen ions migrate by jumping along the $\langle 1 1 0 \rangle$ edges of the $BO_6$ octahedra into adjacent vacant sites.\textsuperscript{[174–179]} An alternative path—and one that might be relevant in the case of this grain boundary—is the $\langle 1 0 0 \rangle$ directions (see Section 2.1.4). Calculations of the activation energies for these two paths in the undisturbed bulk lattice of the simulation cell yield, as shown in Table 5.2, 0.63 eV and \textit{ca.} 4 eV, respectively.\textsuperscript{b} The huge difference in activation energies can be explained in terms of the respective saddle-point configurations: Migration along the $\langle 1 1 0 \rangle$ directions involves the large oxygen ion pushing through the small

\textsuperscript{b}They are thus in excellent agreement with values of $\Delta E_{\text{mig,V}}$ obtained for the analogous calculations performed on the cubic bulk ST cell as shown in Table 2.3 in Section 2.1.
aperture formed by two Sr ions and a Ti ion, and thus it is mainly steric hindrance that determines the migration barrier.\textsuperscript{174-179} Migration along the $\langle 100 \rangle$ directions involves the oxygen ion pushing past two oxygen ions and two strontium ions in the saddle-point configuration. Additional calculations (not shown) indicate that the Coulomb repulsion between the migrating oxygen ion and the two lattice oxygen ions provides the predominant contribution to the much higher activation energy.

![Image of TiO$_2$ and SrO cores](image)

**Figure 5.15:** Oxygen deficient dislocation cores of the 6.0° [1 0 0] (0 1 19) symmetric tilt grain boundary (top). The black circle indicates the face of the schematic cylindrical tube (bottom). The straight red arrows indicate the linear $\langle 100 \rangle$ migration path, the curved red arrows indicate the curved $\langle 110 \rangle$ migration path through the dislocation core. Sr in large blue, Ti in intermediate grey and O in small red spheres (no relationship to real ionic radii).

Having examined migration in the bulk, oxygen-ion migration along the fully oxygen-deficient [1 0 0] dislocation cores is now considered. The focus on these cores is due to their structures corresponding closely to the structures observed experimentally. As the cores are oxygen-deficient (i.e. no oxygen ions are present), oxygen ions first have to be introduced into the core. It is considered that introduction occurs by an oxygen ion executing a $[1 \bar{1} 0]$ jump into the empty space of the core, leaving a vacancy behind. Sitting now in the core, the ion either may jump back to its original site, executing a $[\bar{1} \bar{1} 0]$ jump; or it may jump out, executing a $[1 \bar{1} 0]$ jump, although this requires a second vacant site directly adjacent to the first site; or it may migrate directly along the $[1 0 0]$ direction for some time before executing a $[1 \bar{1} 0]$ out of the core. Each of these migration jumps were examined
individually at infinite dilution in Mott–Littleton calculations (the two jumps out of the core being equivalent); the results are summarised in Table 5.2. It is stressed that these two migration processes remove the problems associated with a truly one-dimensional migration path: If there were, for whatever reason, blockages or breaks in the path, no long-range migration would be possible. Figure 5.15 shows a schematic of the migration paths along a dislocation (in this case represented by a cylindrical tube).

Different activation energies are obtained for the $[110]$ and $[1\overline{1}0]$ jumps at the TiO$_2$ core because the initial and final sites for these jumps are not energetically equivalent: the oxygen ion (oxygen vacancy) prefers to reside outside (within) the dislocation core, and hence jumps into the core have a higher barrier than jumps out. The small difference in energies suggests significant disorder of oxygen ions over the two sites, in and outside of the core; this energy difference is probably underestimated as the calculations refer to a single oxygen ion in an otherwise empty core. For the SrO core, the energies are not activation energies as no barriers were found. The energies given are the differences in site energies between the initial and final positions, and they indicate a strong preference for the oxygen ion remaining outside the core. Overall, for this long-range migration process—the oxygen ion only jumping in a zigzag fashion along the $\langle 110 \rangle$ directions—the rate-limiting step will be either the jump into the core, and for both dislocation cores, the activation energy is higher than the corresponding value in bulk STO, or the availability of vacancies around the core, since the most likely jump of an ion, once in the core, is back to its original site.

Table 5.2: Activation energy for oxygen-ion migration in the bulk phase or along oxygen-deficient dislocation cores. The jumps in $[100]$, $[110]$ and $[1\overline{1}0]$ directions correspond to jumps along, into, and out of the dislocation core, respectively. Values for the SrO core are not migration energies (see text). Reproduced from Ref. [57] with permission from The Royal Society of Chemistry.

<table>
<thead>
<tr>
<th>Region</th>
<th>$\Delta E_{\text{mig, V}}^{[100]}$ / eV</th>
<th>$\Delta E_{\text{mig, V}}^{[110]}$ / eV</th>
<th>$\Delta E_{\text{mig, V}}^{[1\overline{1}0]}$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>3.98</td>
<td>0.63</td>
<td>0.63</td>
</tr>
<tr>
<td>TiO$_2$ core</td>
<td>3.43</td>
<td>0.75</td>
<td>0.49</td>
</tr>
<tr>
<td>SrO core</td>
<td>–</td>
<td>(1.38)</td>
<td>(-1.38)</td>
</tr>
</tbody>
</table>

For the $[100]$ path, it was only possible to determine an activation barrier for migration along the TiO$_2$ core: this is lower than the value in the bulk, possibly because the oxygen-ions in the saddle-point configuration are further apart and one of the nearest neighbours (a Sr ion) is missing in the saddle-point configuration.
(because of the dislocation core’s structure). Although no value was obtained for the [100] migration along the SrO core, a further lowering of the activation energy may be expected, as in this case, an oxygen ion is missing from the saddle-point configuration. Overall, for this long-range migration process—a combination of (110) and [100] jumps—the rate-limiting step will be the jump along the core (or possibly for the SrO core, the jump into the core), and here too, the activation energies are higher than the bulk value.

From these results two conclusions are drawn, one specific and one more general. First, bearing in mind that the energy hypersurface was only probed manually in static calculations (rather than performing molecular dynamic simulations), a tentative conclusion from the results of Table 5.2 is that there is no enhanced oxygen-ion migration along [100] dislocations in ST, contrary to the model assumed for metal and semiconductor systems. This conclusion is further supported by the lack of evidence for fast diffusion in experimental investigations of the diffusion along a grain boundary\textsuperscript{[57]}. Second, and more generally, one may tentatively conclude that, if the activation energy of ion migration is low such that migration in the regular lattice is facile, as oxygen-ion migration is in the perovskite-structured SrTiO\textsubscript{3} (and also in fluorite-structured YSZ\textsuperscript{[119,180,181]}), strong perturbation of the lattice, as at a dislocation core or a grain boundary, will increase the activation energy of migration. In contrast, if the activation energy of migration is high to begin with, the more open structure of a dislocation core can result in a decrease in the activation energy (cf. Al\textsubscript{2}O\textsubscript{3}, Ref. [128]).

5.3.3 Other Cubic $\text{A}^{II}\text{B}^{IV}\text{O}_3$ Perovskite Oxides

Within the same study of Pedone et al.\textsuperscript{[54]}, the authors developed further sets of empirical pair potentials (other than those of SrTiO\textsubscript{3}). The sets of potentials are of the same form as Eq. (2.1) (see Section 2.1) and can be applied to various $\text{ABO}_3$ perovskite oxides, specifically for $A = \text{Ca, Sr, Ba}$ and $B = \text{Ti, Zr, Sn}$. Broglia et al.\textsuperscript{[182]} developed an empirical pair potential for the Hf-O interactions independently, but according to the same form employed by Pedone et al., thus allowing for the investigation of $\text{AHiO}_3$ perovskites as well. Of the possible $A$- and $B$-site combinations, only a small subset exhibit the same cubic symmetry as SrTiO\textsubscript{3}, specifically BaZrO\textsubscript{3}, BaSnO\textsubscript{3} and BaHfO\textsubscript{3}. All remaining combinations have orthorhombic crystal symmetry (CaBO\textsubscript{3} and SrBO\textsubscript{3}) or tetragonal crystal symmetry (BaTiO\textsubscript{3}) at room temperature.\textsuperscript{[183–188]}

It is reasonable to assume that the simple rules derived to predict the type, arrangement and alignment of the dislocations at a given SrTiO\textsubscript{3} symmetric tilt boundary
(see Section 5.3.1) should be applicable to analogous perovskite structures. The simplest case for the application of these rules would be other cubic $\text{A}^{II}\text{B}^{IV}\text{O}_3$ phases of e.g. $\text{BaZrO}_3$, $\text{BaSnO}_3$ and $\text{BaHfO}_3$. That is, the same dislocation core structures and the same four possibilities for dislocation configurations at [1 0 0] low-angle tilt grain boundaries of cubic perovskite phases are expected. For the non-cubic phases ($\text{CaBO}_3$, $\text{SrBO}_3$ and $\text{BaTiO}_3$) the same general structural scheme should be valid. It may not, however, be directly apparent due to the distortion and tilting of the $\text{BO}_6$-octahedra common to the non-cubic perovskite phases.

![Figure 5.16: Stoichiometric dislocation core structures of 6.0°[1 0 0] (01 19) ABO$_3$ tilt boundaries. Top: BO$_2$-type cores. Bottom: AO-type cores. (a) and (b) BaZrO$_3$; (c) and (d) BaSnO$_3$; (e) and (f) BaHfO$_3$. Ba in large, B-site cations in intermediate and O in small spheres (no relationship to real ionic radii).](image)

In order to test the validity of the derived predictive rules, other 6.0° [1 0 0] (01 19) symmetric tilt-boundaries of cubic perovskite oxides were investigated with regards to dislocation core structure, excess grain-boundary energy and vacancy segregation energy.

The simulations of ABO$_3$ perovskite oxides were performed by Jana Parras within the framework of a student research project and the results thereof will be presented here. Figures 5.16 and 5.17 show the optimised dislocation core structures of the cubic perovskite systems BaZrO$_3$, BaSnO$_3$ and BaHfO$_3$ in both their stoichiometric and oxygen-deficient forms, respectively. Examination of the dislocation cores
indeed reveals analogous dislocation structures to those of SrTiO$_3$ (cf. Figure 5.6).

![Diagram of dislocation core structures](image)

**Figure 5.17**: Oxygen-deficient dislocation core structures of 6.0°[100](0119) $A$BO$_3$ tilt boundaries. Top: BO$_2$-type cores. Bottom: AO-type cores. (a) and (b) BaZrO$_3$; (c) and (d) BaSnO$_3$; (e) and (f) BaHfO$_3$. Ba in large, $B$-site cations in intermediate and O in small spheres (no relationship to real ionic radii).

As was the case for SrTiO$_3$, the stoichiometric dislocation cores appear to be undissociated (see Figure 5.16) and the fully oxygen-deficient cores (i.e. cores from which an entire oxygen column was removed) appear to be dissociated (see Figure 5.17). This behaviour indicates that a high degree of oxygen deficiency is necessary for the dissociation of the dislocation cores (as was observed for SrTiO$_3$). The structural relaxation of both the dissociated AO- and BO$_2$-type cores leads to the formation of an antiphase domain boundary with a plane of ions passing through the centre of the dislocation [from top to bottom in Figures 5.17(a)–(f)], thus making the core structure essentially symmetrical. Only the oxygen-deficient HfO$_2$-type core of BaHfO$_3$ does not reach the same degree of symmetry, the reason for the distortion of the core structure [see Figure 5.17(e)] being unclear at this point. As the Hf-O potential was developed separately by Broglia et al.$^{182}$, the discrepancy may be a result of a lower quality potential set compared to those initially derived by Pedone et al.$^{54}$ or it may be an effect specific to BaHfO$_3$. Investigations of bulk BaHfO$_3$ and its corresponding defect properties and defect interactions as well as experimental studies are necessary in order to gain insight in the mentioned observations at the grain boundary; such investigations are, however, beyond the
scope of the current studies. When examining the dislocation arrangement at the boundaries one finds the dislocations to be equidistant, aligned and alternating; a configuration which is applicable to a 6.0° [100] (0119) with an average dislocation separation of $d_{\text{Frank}} = 9.5 a(ABO_3)$ (see Table 5.1). Therefore, one may tentatively conclude that the simple rules derived for SrTiO$_3$ are also applicable to analogous cubic $A^{\text{II}}B^{\text{IV}}O_3$ perovskites.

![Diagram](image)

**Figure 5.18:** (a) Excess grain-boundary energies for 6.0° tilt-boundaries of cubic $ABO_3$ perovskite oxides. (b) Vacancy segregation energies of the AO- and BO$_2$-type cores. The data is plotted against the Goldschmidt tolerance factor.

When looking for trends across various $ABO_3$ perovskites the Goldschmidt tolerance factor ($t$) comes to mind$^{[190]}$, which is given by

$$t = \frac{r_A + r_O}{\sqrt{2} (r_B + r_O)}.$$  \hspace{2cm} (5.6)

$r_{A,B,O}$ denotes the ionic radius of species $A$, $B$ and $O$, respectively. The radii employed in this study are the ionic radii according to Shannon$^{[191]}$ for 12-fold coordinated doubly charged $A$-site cations, 6-fold coordinated $B$-site cations with an ionic charge of +4 and 6-fold coordinated $O$ with a negative ionic charge of −2. Essentially the value of the tolerance factor is an indicator of the system’s structure. For $t = 0.8 - 1.0$ the perovskite structure is expected; for values below 0.8 the perovskite structure is no longer stable and corundum- and ilmenite-type structures are prevalent; and for values greater than 1.0 additional structures, such as the calcite structure, are to be expected.$^{[190]}$ For perovskites, a tolerance factor of 1.0 corresponds to the ideal cubic structure, and the greater the deviation from 1.0 the less favourable the cubic structure is expected to be.

Figure 5.18 shows both the excess grain-boundary energies and the vacancy segre-

---

$^c$The alternative dislocation configuration was not investigated here.
gation energies of the investigated cubic perovskite oxides plotted against \((1 - t)\). The excess grain-boundary energies vary between 0.85 and 1.25 J m\(^{-2}\). Within this limited set of data, there does not appear to be a direct correlation to the tolerance factor. The same can also be said for the vacancy segregation energies, thus implying that the properties of grain-boundaries are not directly dependent on the Goldschmidt tolerance factor.

Figure 5.19: Dependence of the vacancy segregation energies of the \(AO\) and \(BO_2\)-type dislocation cores on the corresponding excess grain-boundary energies of the cubic \(ABO_3\) perovskite oxides. The solid lines serve to indicate an emerging trend.

Figure 5.19 shows the dependence of the vacancy segregation energies of the cubic \(ABO_3\) perovskite oxides on the corresponding excess grain-boundary energies. One observes a linear trend; the segregation energy decreases with increasing excess grain-boundary energy (for both \(AO\)- and \(BO_2\)-type dislocation cores). This behaviour indicates that the higher \(\Delta_f E_{GB}\) the easier it is for oxygen vacancies to be formed at the dislocation cores. This trend, however, must be considered with caution, as the data set consists of only four points and due to the doubts regarding the quality of the EPP for BaHfO\(_3\) (see above). Future investigations could include additional \(ABO_3\) perovskite oxides (not limited to the cubic phases) in order to determine whether the emerging trend is not a result of the limited data set.

Still, it is worth noting that the vacancy segregation energies are all negative, with the segregation to \(AO\)-type dislocation cores being favoured over the segregation
to $BO_2$-type cores (as was also observed for SrTiO$_3$). The fact that the vacancy segregation energies are negative may be indicative that grain-boundaries in $A^{II}B^{IV}O_3$ generally lead to the formation of depletion space-charge zones in their vicinity (see previous section).

5.4 Discussion

In the following, the apparent discrepancies in the literature regarding the atomistic structure of low-angle grain boundaries$^{[57,148,149,151–154]}$ are discussed based on the present simulation results. The focus is on three key aspects: dislocation types, oxygen stoichiometry and dislocation arrangement. Since cation non-stoichiometry is not always observed experimentally$^{[148,151,154]}$ and its extent may depend on several factors (including tilt angle), this complex aspect of symmetrical low-angle tilt grain boundaries in SrTiO$_3$ is left for future investigation.

5.4.1 Dislocation Types

Reports in literature agree on the fact that $[100]$ low-angle symmetrical tilt boundaries consist of an array of edge dislocations. The discrepancies arise when discussing the structure and type of the dislocations. According to the structure of SrTiO$_3$ there are—generally speaking—two basic types of $[100]$ edge dislocations, either the TiO$_2$- or SrO-type, and there have been several reports, both experimental and theoretical, confirming the two types$^{[57,148,151,154]}$.

Buban et al.$^{[152]}$, however, in their high-resolution transmission electron microscopy (HR-TEM) study reported three types of dislocation cores, which they termed elongated, composite and transformed cores. These core structures were determined by averaging over a multitude of separate HR-TEM images. One of the three types (the elongated core) corresponds closely to the two initially determined structures of Zhang et al.$^{[148]}$, while the other two types (the composite and transformed cores) appear to be strongly disordered variants of the two initial configurations. The most frequently observed case of Buban et al., is one with a large excess and a large deficiency of Ti and Sr, respectively, which led to the definition of the transformed core$^{[152]}$. The averaging technique employed by Buban et al.$^{[152]}$ to obtain their dislocation structures may, however, give misleading results. Namely, the multiple images that are averaged together could consist variously of TiO$_2$-type and SrO-type dislocations, of identical dislocations whose images are shifted with respect to one another, and of dislocations of similar (but not identical) disordered structures. In other words, one may question whether there are three very different
dislocation core structures.

What is not questioned is the observation of Buban et al.\textsuperscript{[152]} that there is considerable disorder in the tensile strain regime of some dislocation cores. This finding was recently confirmed in a HR-TEM study by Du et al.\textsuperscript{[153]}, who observed additional intensities in the tensile strain regime of the dislocations in a $6^\circ$ SrTiO$_3$ bicrystal, which were assigned to columns of titanium ions. With regards to the core structure, Du et al. only report a single dislocation core type\textsuperscript{[153]}, which corresponds to one of the two types predicted by Zhang et al. in 2002\textsuperscript{[148]}; the authors do not comment on the possibility of a second dislocation core type. It is concluded, therefore, that there are two basic types of dislocation core structure (SrO- and TiO$_2$-type) and disordered variants thereof.

5.4.2 Oxygen Stoichiometry

Previous investigations indicated\textsuperscript{[38,143–148,161]} that the formation of oxygen vacancies at the dislocation core is favoured relative to the bulk phase. Furthermore, as proposed by Zhang et al.\textsuperscript{[148]}, the experimentally observed oxygen deficiency can be explained by the removal of an entire oxygen column at the dislocation cores. The oxygen-deficient TiO$_2$- and SrO-type dislocation structures (see Section 5.3.1.1), also show a higher degree of symmetry and have a single plane of ions passing through the centre of the dislocation forming an anti-phase boundary, \textit{i.e.} the oxygen-deficient dislocation cores are dissociated in agreement with the experimental observations found in literature. The presented simulations confirm that the dissociation of the dislocation is a result of the oxygen deficiency and not the other way around, as initially argued\textsuperscript{[145,148]}. This dissociation behaviour is observed for all simulated tilt angles $3.0^\circ \leq \theta \leq 22.6^\circ$ (see Figure 5.5).

Although the removal of an entire oxygen column may seem unfeasible, the simulations show that a high degree of oxygen deficiency is required to obtain the dissociated core. The actual extent of the oxygen deficiency, however, is governed by thermodynamics and is thus dependent on thermodynamic parameters such as temperature, oxygen activity and dopant concentration, in addition to the vacancy formation energy at a dislocation relative to that in the bulk phase and the number of preferential sites for vacancies\textsuperscript{[38]}. Consequently, the extent of oxygen deficiency will also depend on the tilt angle, and also on the dislocation arrangement (alternating, single type SrO, single type TiO$_2$), as indicated by the vacancy segregation energies (see Figs. 5.13 and 5.14).
5.4.3 Dislocation Arrangement at Grain Boundaries

It has been postulated that a non-aligned 'zigzag' arrangement is more likely to occur at higher angles\textsuperscript{[151]}. The presented simulations reveal both aligned and non-aligned boundaries to be energetically degenerate (within the accuracy of the simulation methodology) for all angles, indicating that it is unlikely to be an effect that is induced by the tilt angle. Nonetheless, the tilt angle, in the form of the specific dislocation separation, does have an effect on the dislocation arrangement at the boundary. In the case of $d_{\text{Frank}} = n \cdot a$, the dislocations are arranged in a non-aligned (zigzag) pattern if they are single type and equidistant; and aligned and alternating if they are non-equidistant. In the alternate case, $d_{\text{Frank}} = (n + 0.5) \cdot a$, the opposite is valid, equidistant dislocations are aligned and alternating; and non-equidistant dislocations are of a single type and non-aligned. This differentiation is also consistent with the experimental results of Choi \textit{et al.}\textsuperscript{[151,154]}.

It remains unclear which type of boundary (aligned or non-aligned) will form preferentially. This uncertainty is further supported by the experimental observation of both aligned and non-aligned configurations for both 6° and 8° tilt boundaries\textsuperscript{[151]}. Choi \textit{et al.}\textsuperscript{[154]} recently determined the strain distribution along an aligned 6° and a non-aligned 10° grain boundary and found that for the case where the dislocations are aligned, the residual strain is mostly diluted between the dislocations, whereas for the grain boundary with the zigzag (non-aligned) pattern the strains between the dislocation cores remain to a greater extent\textsuperscript{[154]}. The strain analysis could be a possible indication that the aligned dislocations are favoured over those arranged in a zigzag pattern. Such an interpretation is, however, not unambiguous as the strain distribution was determined for two different tilt-angles. More accurate simulation approaches should be employed in the future to investigate the small energy difference between the two types of dislocation arrangement.

5.5 Conclusion

A systematic and detailed computational investigation of symmetrical low-angle $\theta[100]$ (0 1 l) tilt-boundaries in SrTiO$_3$ has been performed. The study reveals two basic types of boundaries, identified by their nominal dislocation separation with respect to the lattice constant of SrTiO$_3$. If $d_{\text{Frank}} = n \cdot a$, the excess energies indicate two specific dislocation arrangements to be the most stable:

1. Non-equidistant, aligned, alternating dislocation cores
2. *Equidistant, non-aligned, single type* dislocation cores

The second type occurs for \( d_{\text{Frank}} = (n + 0.5) \cdot a \) and leads to the following stable dislocation arrangements:

1. *Equidistant, aligned, alternating* dislocation cores

2. *Non-equidistant, non-aligned, single type* dislocation cores

Irrespective of the nominal dislocation separation, it was found that all boundaries can be formed with only two types of dislocation cores, the TiO\(_2\)- and the SrO-type cores. Symmetrical \([100]\) tilt boundaries with a boundary plane of \((0kl)\) with \(k \neq 1\) can be formed with a combination of the different dislocation separations of the \((01l)\) boundaries.

The investigation of other cubic \(A^{II}B^{IV}O_3\) perovskite phases (BaZrO\(_3\), BaSnO\(_3\) and BaHfO\(_3\)) revealed that they display the same behaviour according to the rules derived from the examination of SrTiO\(_3\). Specifically the same traits, that is, the same dislocation core structures and the same four possibilities for dislocation configurations at \([100]\) low-angle tilt grain boundaries were observed. For non-cubic phases (e.g. CaTiO\(_3\), BaTiO\(_3\) or MgSiO\(_3\)), the general structural scheme is expected to be valid but additional complexities cannot be excluded due to the distortion and tilting of the \(BO_6\)-octahedra.

Beyond the structural investigation of various symmetric SrTiO\(_3\) tilt boundaries, the excess grain-boundary quantities and vacancy segregation energies with respect to tilt angle were determined. The properties indicate dislocations to favour oxygen deficiency and are thus dissociated. Oxygen-ion migration along the dislocation cores is found to be hindered relative to the bulk lattice, contrary to the generally assumed model for non-ionic systems.

Finally, the investigation of the redistribution of mobile point defects reveals that the interaction of point defects with extended defects is not only governed by the structural motifs of grain boundaries, but also by the specific tilt angle, and by the dislocation arrangement, which in turn determine the effective segregation energies of said point defects.
6 Concluding Remarks

The objective of the presented thesis was to investigate various interfaces of the model perovskite-oxide strontium titanate. To this end three interface systems were studied employing a variety of computational techniques across different length-scales. The first system is the ST|YSZ|ST heterostructure, which was reported to exhibit extremely enhanced conductivity. The origins of the reported conductivity, however, were unclear and widely debated in the scientific community. The thorough re-examination of the literature data presented here led to the conclusion that the observed conductivity originates mainly from the ionic conductivity in ST. The cause of the conductivity enhancement relative to the conductivity of the constituent oxides (ST and YSZ), however, remains unclear. Finite-element modelling of the heterostructure within a well-established thermodynamic framework ruled out space-charge effects as an explanation for the increased conductivity of the system. The effects of depletion space-charge zones on the diffusivity of the heterostructure could, however, be identified as a potential explanation for the unusual $^{18}$O diffusion profile reported in literature.

The ST|SrO heterostructure, the second system of interest in this thesis, was investigated within a collaborative research project with regards to the effects of the interface on the memristive properties of SrTiO$_3$. Combining the experimental results obtained from the collaboration with complementing atomistic simulations, it was possible to determine the key factors in the design of redox-based memristive devices with enhanced retention properties. The investigations revealed that it is favourable to employ thin films of oxides with low rates of oxygen-diffusion (and slow surface-reaction rates) in order to obtain memristive SrTiO$_3$ devices with enhanced retention properties.

The third system of interest, symmetric-tilt grain boundaries in SrTiO$_3$, is investigated with respect to its structural and electrical properties. A wide range of low-angle tilt-boundary simulation cells were constructed according to conventional grain-boundary theory and optimised using atomistic simulation techniques. The resulting structures were carefully analysed with respect to the dislocation structures and arrangements at the grain boundary, such that a predictive model was derived to determine the arrangement of dislocations at a grain-boundary.
based on the knowledge of the grain-boundary plane. The general rules derived are expected to apply to all analogous perovskite oxide systems, especially the cubic $A^{II}B^{IV}O_3$ systems (for which it was shown in the preceding chapter). The excess thermodynamic quantities as well as the oxygen vacancy segregation energy to boundaries were determined and subsequently used as the required input for the thermodynamic treatment of the interactions of point-defects with extended defects. The thermodynamic model revealed that the electrical properties of the low-angle grain boundaries vary in a non-trivial manner with misorientation angle. The investigation of the symmetric tilt boundaries in ST was concluded with a discussion of the discrepancies in literature and how these can be resolved.

In summary, the findings show the necessity for combining the various aspects of structure, chemistry and physics in order to understand the thermodynamics of extended defects in complex functional oxide systems. Future work could employ dynamic investigation methods (e.g. Molecular Dynamics, Kinetic Monte Carlo) to investigate the influence of extended defects on the kinetic properties of the systems.
Bibliography


Appendix

A GULP Input Examples

In the following a few example input files for different GULP simulations will be presented in the form of minimal working examples (MWE). First the input code is shown and subsequently briefly explained.

A.1 Bulk Structure Optimisation

```plaintext
OPTI CONP COMP PROP NOSYM FULL
CELL
3.905 3.905 3.905 90.0 90.0 90.0
FRACTIONAL
Sr core 0.50 0.50 0.50
Ti core 0.00 0.00 0.00
O core 0.50 0.00 0.00

SPACE
221

SPECIES
Sr core 1.2
Ti core 2.4
O core -1.2

#SUPERCELL 3 3 3

MORSE
0 core Sr core 0.019623 1.886000 3.328330 0.0 0.0 20.0
0 core Ti core 0.024235 2.254703 2.708943 0.0 0.0 20.0
0 core O core 0.042395 1.379316 3.618701 0.0 0.0 20.0

LENNARD 12 6
0 core Sr core 3.0 0.0 0.0 20.0
0 core Ti core 1.0 0.0 0.0 20.0
```

*Detailed explanations for each of the commands can be found in the online guide to commands: [https://nanochemistry.curtin.edu.au/gulp/help/manuals.cfm](https://nanochemistry.curtin.edu.au/gulp/help/manuals.cfm)*
The first line of the input code contains the keywords, i.e. the procedures to be performed in the simulation. OPTI is the keyword that initiates the optimisation of the structure. CONP introduces the constant pressure constraint to the optimisation, similarly CONV constrains the simulation to constant volume. The keywords COMP and PROP invoke a comparison of the initially input structure with the optimised structure and a calculation of the properties of the optimised structure, respectively. NOSYM runs the optimisation in P1 symmetry after generating the unit cell using symmetry. FULL forces the NOSYM command to output the full, instead of the primitive, unit cell.

Lines 2 and 3 input the unit cell parameters $a$, $b$, $c$, $\alpha$, $\beta$ and $\gamma$. Lines 4 – 7 are the fractional coordinates of the ions within the structure and are followed by the symmetry of the structure given as the space group number (see lines 9 and 10). Lines 12 – 15 declare the ionic species and their charge according to the empirical pair potentials used. The SUPERCELL option on line 17 is used for the generation of a $3 \times 3 \times 3$ supercell of the initial input structure and is commented out by the # symbol. Lines 19 – 27 input the empirical pair parameters of the short range interactions according to the potential discussed in Section 2.1. Lines 29 – 31 specify additional outputs to the output of the optimisation. The DUMP option generates a new input file with the optimised structure after each optimisation iteration. The OUTPUT option is used to create structure files, in this case a crystallographic information file (cif) and an xyz-file of the optimised structure is created upon completion of the simulation.

### A.2 Defect Calculation

```
0 core 0 core 22.0 0.0 0.0 20.0
DUMP every 1 optimised_input.in
OUTPUT cif optimised_st.cif
OUTPUT xyz optimised_st.xyz
```

```100
```

```
OPTI CONP COMP PROP NOSYM FULL DEFE REGI
CELL
3.905 3.905 3.905 90.0 90.0 90.0
FRACTIONAL
Sr core 0.50 0.50 0.50
Ti core 0.00 0.00 0.00
O core 0.50 0.00 0.00

SPACE
221
```
When performing a defect simulation employing the Mott–Littleton method, two additional *keywords* are specified in line 1: `DEFE` and `REGI`. `DEFE` initialises a defect calculation after the bulk calculation and `REGI` outputs the ionic coordinates in region I (see Section 2.1) prior to optimisation.

Additional parameter specifications are required for the Mott–Littleton simulation (see lines 17 – 19). The `SIZE` option specifies the radii of regions I and IIa for the Mott–Littleton spheres. The `CENTRE` option specifies the centre of regions I and II in fractional coordinates relative to the initial input structure. The third option that needs to be specified is the type of defect, in this example a vacancy calculation is implemented by the option `VACANCY` followed by the fractional coordinates of the vacancy position. Defect options, such as, `INTERSTITIAL` and `IMPURITY` are also implemented within the GULP code.

In the case of Mott–Littleton simulations, only the `OUTPUT` command outputs the optimised structure of region I. The cif-file which is output during a defect calculation corresponds to the optimised bulk unit cell.

For defect calculations within the supercell approach it is sufficient to edit the fractional coordinates of the structure in an input file containing the entire supercell. The keywords `DEFE`, `REGI` and the options described above are not required. In order...
to accommodate supercells which are charged due to the defect(s) the keyword \texttt{Q0K} is required.

\subsection{Defect Migration}

```
OPTI CONP CONP PROP NOSYM FULL DEFE REGI
CELL
3.905 3.905 3.905 90.0 90.0 90.0
FRACTIONAL
Sr core 0.50 0.50 0.50
Ti core 0.00 0.00 0.00
O core 0.50 0.00 0.00
SPACE
221
SPECIES
Sr core 1.2
Ti core 2.4
O core -1.2
SIZE 20 35
CENTRE 0.25 0.25 0.00
VACANCY 0.50 0.00 0.00
VACANCY 0.00 0.50 0.00
INTERSTITIAL 01 0.25 0.25 0.00 fix
#SUPERCELL 3 3 3
MORSE
O core Sr core 0.019623 1.886000 3.328330 0.0 0.0 20.0
O core Ti core 0.024235 2.254703 2.708943 0.0 0.0 20.0
O core O core 0.042395 1.379316 3.618701 0.0 0.0 20.0
LENNARD 12 6
O core Sr core 3.0 0.0 0.0 20.0
O core Ti core 1.0 0.0 0.0 20.0
O core O core 22.0 0.0 0.0 20.0
DUMP every 1 optimised_input.in
OUTPUT cif optimised_st.cif
OUTPUT xyz region1_st.xyz
```

When examining ion migration, the Mott–Littleton approach can also be used. The difference compared to the simulation of an isolated defect is the inclusion of multiple defects in the same simulation (cf. lines 17 – 21). The present example is
for the investigation of oxygen migration in SrTiO$_3$. The two vacancies are included at the start and end position of the migration process. The interstitial oxygen ion is placed exactly between the two vacancies and fixed at that position using the $\text{fix}$ setting at the end of the $\text{INTERSTITIAL}$ option. Within the defect optimisation all ion positions surrounding the fixed interstitial are optimised to a minimum energy configuration. Finding the transition state (as discussed in Section 2.1) involves scanning the energy hyper-surface through multiple defect calculations wherein the interstitial position is varied.

The GULP code offers a few possibilities for automatically searching for the transition state, e.g. by not fixing the interstitial ion or using the $\text{TRANSITION\_STATE}$ keyword. However, these methods have been found to be unreliable as they require the interstitial to be placed at a position close to the transition state, information that is not always readily available.
# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0D</td>
<td>Zero-dimensional</td>
</tr>
<tr>
<td>1D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>A</td>
<td>Aligned</td>
</tr>
<tr>
<td>a.c.</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AL</td>
<td>Alternating</td>
</tr>
<tr>
<td>CBO</td>
<td>Conduction band offset</td>
</tr>
<tr>
<td>d.c.</td>
<td>Direct current</td>
</tr>
<tr>
<td>DOF</td>
<td>Degree of Freedom</td>
</tr>
<tr>
<td>E</td>
<td>Equidistant</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>EPP</td>
<td>Empirical pair potential</td>
</tr>
<tr>
<td>eq</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>GB</td>
<td>Grain boundary</td>
</tr>
<tr>
<td>GULP</td>
<td>General utility lattice program</td>
</tr>
<tr>
<td>HRS</td>
<td>High resistive state</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>LRS</td>
<td>Low resistive state</td>
</tr>
<tr>
<td>ML</td>
<td>Mott–Littleton</td>
</tr>
<tr>
<td>MWE</td>
<td>Minimal working example</td>
</tr>
<tr>
<td>Nb:SrTiO$_3$</td>
<td>Niobium doped strontium titanate</td>
</tr>
<tr>
<td>NA</td>
<td>Non-aligned</td>
</tr>
<tr>
<td>NE</td>
<td>Non-equidistant</td>
</tr>
<tr>
<td>PDE</td>
<td>Partial differential equation</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>sc</td>
<td>Single crystal</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cell</td>
</tr>
<tr>
<td>ST</td>
<td>Strontium titanate (SrTiO$_3$) and Single Type (see context)</td>
</tr>
<tr>
<td>tf</td>
<td>Thin-film</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>VBO</td>
<td>Valence band offset</td>
</tr>
<tr>
<td>XPEEM</td>
<td>X-ray photoemission electron microscopy</td>
</tr>
<tr>
<td>YSZ</td>
<td>Yttria-stabilised Zirconia (Y:ZrO$_2$)</td>
</tr>
</tbody>
</table>
C List of Symbols

\( \mathbf{a} \) Lattice constant
\( a_{\text{O}_2} \) Activity of oxygen
\( a_{\text{SrO}} \) Activity of strontium oxide
\( a_{ij} \) Morse energy potential well width
\( A_{\text{GB}} \) Cross-sectional area of a grain boundary
\( \mathbf{b} \) Burger’s vector
\( B \) Bulk modulus
\( C_{ij} \) Repulsive parameter in empirical pair potential
\( c_i \) Concentration of species \( i \)
\( d \) Substrate thickness
\( d_{\text{Frank}} \) Dislocation separation (according to Frank’s formula)
\( D_{ij} \) Morse energy potential well depth
\( D'_{\text{O}(x)} \) Oxygen diffusivity in dependence of \( x \)
\( D_{\text{VO}} \) Oxygen vacancy diffusivity
\( \Delta H_{\text{gap}} \) Band gap
\( E_{\text{initial}} \) Energy of the initial configuration
\( e' \) Electron
\( \Delta \text{EN} \) Difference in electronegativity
\( e \) Elementary charge
\( \Delta E_{\text{mig}} \) Migration barrier
\( \epsilon \) Strain
\( \epsilon_0 \) Vacuum permittivity
\( \epsilon_r \) Relative permittivity
\( E_{\text{core}} \) Elastic energy of a dislocation core
\( E_{\text{elastic}} \) Elastic energy
\( \Delta H_{\text{Sch}} \) Partial Schottky energy
\( E_{\text{trans}} \) Energy of the transition state
\( \Delta_l E_{\text{GB}} \) Excess grain-boundary energy
\( \Delta_l E_{\text{VO}}^{\text{seg}} \) Oxygen vacancy segregation energy
\( \Delta_f E_{\text{GB}} \) Oxygen vacancy formation energy at the grain boundary
\( \Delta_f E_{\text{VO}} \) Oxygen vacancy formation energy in the bulk region
\( \Delta E_{\text{mig},V_O} \) Migration energy of oxygen vacancies
\( E_{\text{cell}} \) Lattice energy of the simulation cell
\( E_{\text{Bulk}} \) Lattice energy of bulk SrTiO\(_3\)
\( f^* \) Tracer correlation factor
\( G \) Shear modulus
\( h, k, l \) Miller indices
\( \Delta H_{\text{mig},V_O} \) Migration enthalpy of oxygen vacancies
\( \Delta H_{\text{mig},V_{\text{Sr}}} \) Migration enthalpy of strontium vacancies
\( h^* \) Electron hole
\( \Delta H_{\text{red}} \) Enthalpy of reduction
\( \infty \) Refers to a spatial coordinate in a region far away from extended defects
\( k_B \) Boltzmann constant
\( k^\delta \) Chemical surface incorporation coefficient
\( K_{\text{eh}} \) Electronic equilibrium constant
\( K_{\text{eh}}^0 \) Pre-exponential factor of the electronic equilibrium
\( K_{\text{red}} \) Oxide reduction equilibrium constant
\( K_{\text{red}}^0 \) Pre-exponential factor of the oxide reduction equilibrium
\( k_s^* \) Surface exchange coefficient
\( K_{\text{Sch}} \) Partial Schottky equilibrium constant
\( K_{\text{Sch}}^0 \) Pre-exponential factor of the partial Schottky equilibrium
\( \mu_i^\circ \) Standard chemical potential of species \( i \)
\( \tilde{\mu}_i(x) \) Electrochemical potential of species \( i \) in dependence of \( x \)
\( n^* \) Isotope fraction
\( n_{\text{bg}} \) Background isotope fraction prior to the diffusion experiment
\( n_{\text{gas}} \) Isotope fraction of the enriched gas phase
\( N_i \) Number of sites for species \( i \) per unit volume
\( \nu \) Poisson ratio
\( \phi(x) \) Electric potential in dependence of \( x \)

\( \Phi_0 = \phi(0) \) Refers to the electric potential at the extended defect

\( pO_2 \) Partial pressure of oxygen

\( r \) Distance between ion pairs for Morse potential

\( r_0 \) Dislocation radius

\( r_{eq} \) Equilibrium distance for Morse potential

\( \rho(x) \) Space charge density in dependence of \( x \)

\( \sigma_i \) Conductivity of species \( i \)

\( \tau_{eq} \) Equilibration time

\( T \) Absolute temperature

\( t \) Goldschmidt tolerance factor

\( t_{ex} \) Isotope exchange time

\( \theta \) Tilt angle

\( u_i \) Mobility of species \( i \)

\( V \) Vacancy

\( V_{cell} \) Volume of the simulation cell

\( V_{Bulk}^{SrTiO_3} \) Volume of the bulk unit cell of \( SrTiO_3 \)

\( \Delta fV_{GB} \) Excess grain-boundary volume

\( x \) Spatial coordinate

\( Y \) Conductance

\( z_i \) Valence of species \( i \)
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Curriculum Vitae

Personal Data
Name: Amr Hazem Helmy Ramadan
E-Mail: amr.ramadan@rwth-aachen.de
Born: 1st October 1988
in Giza, Egypt

University Education and Research
10/2012–08/2016  Dissertation under supervision of Priv.-Doz. Dr. Roger A. De Souza at the Institute of Physical Chemistry, RWTH Aachen University: "Simulation Studies of Extended Defects in the Model System of the Functional Oxide Strontium Titanate"
Day of oral examination: 15.08.2016

10/2010–10/2012  Graduate Studies: Master of Science in Chemistry, RWTH Aachen University. Special fields:
a) Catalysis
b) Computational chemistry and spectroscopy
Master examination: 17.08.2012 M.Sc.RWTH

01/2012 – Master thesis under supervision of Priv.-Doz. Dr. Roger A. De Souza at the Institute of Physical Chemistry, RWTH Aachen University: "Defect distributions at interfaces between ABO₃ perovskite-type oxides"

09/2011 – Research project under supervision of Prof. Neil A. Allan and Priv.-Doz. Dr. Roger A. De Souza at the School of Chemistry, University of Bristol: "A study of the phase stability of Ruddlesden–Popper phases of SrTiO₃ and its defect energies"

02/2011 – Research project under supervision of Prof. Ulli Englert at the Institute of Inorganic Chemistry, RWTH Aachen University: “Tunable Crystal-to-Crystal Phase Transition in a Cadmium Chain Polymer”

Bachelor examination: 26.07.2010 B.Sc. RWTH

04/2010 – Bachelor thesis under supervision of Prof. Markus Albrecht at the Institute of Organic Chemistry, RWTH Aachen University: "Quinoline-8-ol derivatives for dinuclear triplestranded lanthanide(III) helicates"

School Education

16th May 2007 High School Diploma

06/2004–06/2007 Deutsche Evangelische Oberschule, Cairo, Egypt

06/2000–06/2004 Deutsche Schule Seoul, Seoul, South Korea

12/1998–06/2000 Deutsche Evangelische Oberschule, Cairo, Egypt


Personal Achievements

06/2013 Springorium commemorative coin award

10/2007–10/2012 German Academic Exchange Service — Full scholarship within the program "Deutsche Auslandsschulen"

10/2009–10/2012 Student advisor within the Mosaica program "Deutsche Auslandsschulen — Girls and boys go science..."

05/2011–08/2011 Student representative to the appointments committee for the Institute of Energy and Climate Research – Fundamental Electrochemistry (IEK-9)

10/2010–08/2011 Treasurer of the student association of chemists at the RWTH Aachen University

Aachen, August 29, 2016