FIRST PRINCIPLES INSIGHTS INTO OXYGEN TRANSPORT IN SOLID OXIDE FUEL CELL CATHODE MATERIALS BASED ON LANTHANUM STRONTIUM COBALT FERRITE

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Abstract
Lowering operating temperatures below 800 °C is critical for the viability of solid oxide fuel cell (SOFC) technology. Mixed ion-electron conducting (MIEC) cathodes increase the active region of the cathode by enabling bulk transport of oxygen ions. La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_3$ (LSCF) is the most common MIEC cathode; however, the properties of LSCF vary dramatically based on its elemental composition. Understanding the link between LSCF’s composition, electronic structure, and defect chemistry enables rational material design. This thesis applies density functional theory (DFT)-based methods to members of the LSCF family, linking oxygen ion transport to their electronic structure.

We show that creating oxygen vacancies in LaFeO$_3$ is more endothermic than in LaCoO$_3$ because Fe-O bonds are stronger than Co-O bonds and reducing Fe$^{3+}$ to Fe$^{2+}$ releases less energy than Co$^{3+}$ to Co$^{2+}$. Holes introduced by La vacancies in LaFeO$_3$ increase the oxygen vacancy concentration by several orders of magnitude. The low-spin state of Co$^{3+}$ in LaCoO$_3$ leads to the lowest oxygen vacancy formation energy among its near-degenerate magnetic configurations.

Holes arising from Sr substitutions in La$_{1-x}$Sr$_x$FeO$_3$ (LSF) and La$_{1-x}$Sr$_x$CoO$_3$ (LSC) partially delocalize over the Fe/Co and O sublattices. The extent to which the oxygen sublattice accepts the electrons left behind during oxygen vacancy formation is greater in LSF than LSC, leading to lower oxygen vacancy formation energies in LSF than in LSC.

Modeling LSCF yields the important insight that oxygen vacancies preferentially form between one Fe and one Co. The least favorable sites for oxygen vacancies are between two Co ions. Hence, too much Co in LSCF leads to too many unfavorable sites for oxygen vacancy formation and to lower ionic conductivity. Insufficient Co in LSCF
will yield a semiconducting electronic structure like LSF instead of the half-metallic behavior we predict for $y_{Co} = 0.25$. Fe-rich compositions should be preferred for LSCF and the commonly used $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ is close to the optimal composition.

This thesis establishes important guidelines for optimizing LSCF as a SOFC cathode. Choosing an Fe-rich composition of LSCF, employing A-site substoichiometry, and finding a way to encourage low-spin $Co^{3+}$ to form are critical directions enabling development of improved intermediate-temperature SOFC devices.
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“Praise be to the Father and to the Son and to the Holy Spirit:

as it was in the beginning, is now, and will be forever. Amen”*
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Chapter 1

Introduction

1.1 Motivation

The world faces an energy crisis. Developing and sustaining vibrant economies requires electrical power. Historically, this power has been supplied by burning fossil fuels (e.g., coal and oil). However, this course of action cannot be sustained due to the finite supply of fossil fuels. Burning fossil fuels has generated a significant increase in carbon dioxide (CO2) levels through the twentieth and into the twenty-first centuries. The resulting climate change looms as a significant threat to society moving forward.

Mitigating the effects of human-driven climate change requires alternative methods of producing electrical power. Specifically, a portfolio of efficient, clean, and economically viable technologies must be harnessed to replace existing power generation techniques. The chief sources of power will involve harnessing incoming solar energy, wind, and nuclear fusion. Although some of these technologies are emerging as the key players in a sustainable future, the need remains for technologies that can bridge this future and the current, combustion-based world. Solid oxide fuel cells (SOFCs) can serve this purpose because of their ability to handle common fuels (e.g., natural gas or syngas) in addition to hydrogen while offering superior efficiency to burning fuels in engines.
1.2 Solid Oxide Fuel Cells

1.2.1 Operating Principles

SOFCs are devices capable of generating electrical power by harnessing chemical energy in a variety of fuels.\textsuperscript{6-10} Four key processes happen in all fuel cells: (1) fuel is oxidized at the anode; (2) ions are transported through the electrolyte; (3) an oxidant is reduced at the cathode; and (4) electrons flow from the anode to the cathode through an external circuit, where it does useful work.\textsuperscript{6} Figure 1.1 illustrates the typical processes occurring in an SOFC.

![Figure 1.1. Schematic of an SOFC including the cell components, electrochemical reactions, and transport processes. The red arrows show heat transfer processes.](image)

The SOFC takes $O_2$ from the air and reduces it at the cathode. The $O^{2-}$ ions produced in this process diffuse through the solid electrolyte to the anode. These ions oxidize the fuel stream at the anode producing water vapor and releasing electrons into the anode. The voltage difference between the cathode and anode, resulting from the difference between the oxygen activities at the two electrodes, drives current through the external circuit (on
the right), accomplishing useful work. For simplicity, hydrogen is used as a fuel in this illustration, though other fuels may be used in SOFCs (vide infra).

Two key processes generate heat in an SOFC. Resistance to ionic transport through the electrolyte causes Ohmic heating. Excess heat released by the oxidation reaction causes additional heating. At steady-state, convective and radiative processes transfer heat to the product gases.\(^\text{11}\)

1.2.2 Benefits and Challenges

Harnessing a variety of fuels and employing relatively inexpensive materials are what make SOFCs attractive. The reductions of \(\text{CH}_4\) and \(\text{CO}\) become possible because of the temperature range in which SOFCs operate (500-1000 °C),\(^\text{7-10}\) eschewing the need of precious metal (i.e., platinum) electrodes required by low-temperature fuel cells (e.g., polymer exchange membrane fuel cells). Instead, ceramic materials with relatively inexpensive constituents are employed.\(^\text{12}\) Most existing SOFC technologies employ a yttria-stabilized zirconia (YSZ) electrolyte, Ni-YSZ cermet anode, and La\(_{1-x}\)Sr\(_x\)MnO\(_3\) (LSM) cathode.\(^\text{10}\) Stationary SOFC applications enable integration between the electrical power generated by the SOFC stack and the high quality heat available in the output streams due to the high operating temperatures.\(^\text{13}\) The net efficiency is the ratio of the DC power delivered by the fuel cell stack to the rate at which chemical energy enters the system. Powell et al. demonstrated a 1.7 kW system with a net efficiency of 57%.\(^\text{14}\) This system operated on methane with steam reforming to give syngas (\(\text{CO} + \text{H}_2\)). The net efficiency accounts for internal losses from the SOFC stack (Ohmic resistance and overpotentials), as well as losses accounting for the power used to operate the balance of
plant equipment (e.g., pumps and blowers). The system should retain its efficiency if power is increased by adding more cells within the stack.\textsuperscript{14}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image}
\caption{Illustration of the active region of the cathode with (a) a traditional La$_{1-x}$Sr$_x$MnO$_3$ cathode and (b) a mixed oxygen ion-electron conducting cathode (e.g., La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_3$). Red dots in part (a) indicate triple-phase boundaries. Red lines in part (b) show the active cathode surface.}
\end{figure}

While SOFCs derive benefits from their operating temperatures, use of the LSM cathode necessitates operating in the high-temperature regime ($T > 800$ °C). This places stringent chemical and thermal compatibility requirements on the materials that make up the cell. The coefficients of thermal expansion of all components must be closely matched to avoid buildup of thermal stress that can lead to cell failure.\textsuperscript{15} Similarly, the electrodes must not react with the electrolyte to form secondary phases (e.g., SrZrO$_3$ or La$_2$Zr$_2$O$_7$) that could hinder electrical or ionic conductivity. LSM meets these criteria and performs well as an electrocatalyst. At the same time, the high-temperature regime
necessitates the use of expensive La$_{1-x}$Sr$_x$CrO$_3$ interconnects. High temperatures are required because in LSM the oxygen reduction reaction (ORR) only occurs at the triple-phase boundary (TPB, see Figure 1.2a) where the cathode (LSM), electrolyte (YSZ), and gas phase meet. This limitation is imposed by the fact that LSM is a poor conductor of oxygen ions$^{16-19}$ leading to slow mass transport of oxygen ions to the cathode/electrolyte boundary. The limited reaction area causes sluggish ORR kinetics, leading to high cathode overpotentials. The cathode overpotential is then mitigated by employing a composite LSM/YSZ cathode and high operating temperature because kinetics improve with increased temperatures.$^{20}$ The restrictions imposed by the high-temperature regime limit the life-span of SOFC devices and hinder their commercialization.

Next-generation SOFCs will operate in the intermediate-temperature (IT) regime ($600-800$ °C) to enable use of less expensive interconnect materials and promote longer cell life.$^{21}$ Furthermore, lower operating temperatures should reduce the amount of heat lost in the product gas streams leading to more efficient SOFC devices. Developing IT-SOFCs requires finding cathode materials that exhibit lower cathode overpotential than the LSM-based cathodes currently in use.$^{22}$ Alternatively, mixed oxygen ion-electron conductors (MIECs) have the potential to significantly lower the cathode overpotential by increasing the cathode’s active region.$^{23}$ MIECs meet the requirement that the cathode be capable of conducting electrons (or holes). They also enable diffusion of oxygen ions through the bulk of the cathode, meaning that the ORR is no longer limited to the TPB (Figure 1.2b). Because the ORR rate is related to the availability of reaction sites, extending the active region of the cathode improves the kinetics and lowers the cathode overpotential at a given temperature. The key technological challenge for IT-SOFCs is
finding MIEC cathodes that demonstrate facile oxygen ion transport while still retaining sufficient electronic conductivity.\textsuperscript{18}

\subsection*{1.2.3 \textit{La}_{1-x}\textit{Sr}_x\textit{Co}_{1-y}\textit{Fe}_y\textit{O}_3 Cathodes}

The existing literature is full of studies reporting MIEC materials\textsuperscript{18,24–35} that perform better than the standard LSM cathodes. Of the materials, La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_3$ (LSCF) is the most studied and widely accepted MIEC cathode for IT-SOFCs.\textsuperscript{18,36,37} Making the most effective use of LSCF requires determining the ideal stoichiometries (x$_\text{Sr}$ and y$_\text{Fe}$) that maximize the ionic conductivity and electrocatalytic performance of LSCF.\textsuperscript{38,39} Macroscopic (\textit{e.g.}, synthesis method and sintering temperature), mesoscopic (\textit{e.g.}, porosity), and microscopic (\textit{e.g.}, composition) properties all play a significant role in determining the outcome of experimental investigations into SOFC cathode properties.\textsuperscript{40} This makes optimizing LSCF cathodes a multi-scale, multi-physics problem.\textsuperscript{41} However, rational design of LSCF cathodes must begin with atomic-scale insight allowing key properties of LSCF to be understood while controlling for the interference from effects associated with mesoscopic or macroscopic characteristics.

The first step is determining what insights can be gleaned from the atomic-scale to help scientists and engineers make rational choices when determining how to proceed with LSCF. The key properties of MIEC cathodes involve the transport of electronic carriers and oxygen ions. The former is governed by the electronic structure of the material. The latter involves understanding the defect chemistry and diffusion processes for oxygen ions in LSCF. While extensive measurements associated with these properties exist, the fundamental understanding to link these properties to atomic-scale properties remains elusive. Specifically, rational design of LSCF cathodes depends on an
understanding of how changing the material’s stoichiometry alters the material’s defect chemistry. Isolating effects associated with specific properties (e.g., the Sr$^{2+}$/La$^{3+}$ ratio) requires an understanding of the atomic-scale changes that the material undergoes in response to altering this property. Finally, the issue of the magnetic behavior of the Co$^{3+}$ ions in LSCF remains poorly addressed in the literature. LaCoO$_3$ is a specific composition of LSCF with a notoriously difficult magnetic structure. This arises from the fact that the Co$^{3+}$ ions have access to various magnetic states at temperatures far below those encountered in SOFCs. The role of magnetism in LSCF when Co$^{3+}$ ions are present must be understood, since this can play a significant role in the processes governing oxygen ion diffusion.

The issues presented above require a fundamental understanding at the atomic-scale of the processes that govern LSCF cathode performance (e.g., oxygen vacancy formation energies and activation energies for diffusion coefficients). Atomic-scale insights gained through first-principles calculations offer the chance to propose design principles for optimizing material compositions.$^{42,43}$ These calculations provide unbiased predictions of material properties, electronic structures, and defect formation energies. In fact, the only experimental input required is a general understanding of the crystal structure associated with these materials. The important LSCF compositions crystallize in a perovskite structure with possible rhombohedral, orthorhombic, tetragonal, or monoclinic distortions (vide infra). From these calculations it is possible to glean insights that enable a greater understanding of experimental data and provide guiding principles for designing improved MIEC cathode materials/compositions. This makes first-
principles studies of LSCF-related materials valuable for developing next-generation IT-SOFC cathodes.

1.3 Properties of La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_3$ Cathodes

1.3.1 Perovskite Crystal Structure

Most SOFC cathode materials crystallize in the perovskite (ABO$_3$) crystal structure. The ideal perovskite structure (Figure 1.3) has interpenetrating simple cubic lattices of rare earth/alkaline earth (A-site) and transition metal (B-site) cations. Oxygen ions occupy the face-centered sites of the A-site lattice. This leads to octahedral coordination of the B-site ion.

![Figure 1.3. Ideal cubic perovskite structure with A-site cations (green) at the corners of the cell, the B-site cation (brown) at the center of the cell, and the oxygen anions (red) occupying the face-centers.](image)

The $d$ manifold of the B-site cation is split according to crystal field theory into a set of threefold-degenerate $t_{2g}$ orbitals and a pair of degenerate $e_g$ orbitals (Figure 1.4). The splitting between the $t_{2g}$ and $e_g$ levels competes with exchange stabilization when determining the arrangement of the $d$ electrons. Furthermore, overlap between the $e_g$ orbitals of the TM $d$ manifold and the $p$ orbitals of the oxygen anions can lead to the formation of delocalized electronic states.
Figure 1.4. (Left) TM (blue sphere) ion octahedrally coordinated by oxygen atoms (red spheres). (Right) TM 3d manifold split into $t_{2g}$ ($3d_{xy}$, $3d_{xz}$, and $3d_{yz}$) and $e_g$ ($3d_{x^2}$ and $3d_{x^2-y^2}$) orbitals. The arrow labeled $\Delta_O$ indicates the octahedral splitting. Orbital isosurface colors: yellow (positive) and blue (negative).

The relative sizes of the ions occupying the A- and B-sites in the perovskite structure determine the stability of the structure’s cubic form. The Goldschmidt tolerance factor $t$ (Equation 1.1) employs the ionic radii ($r_A$, $r_B$, and $r_O$) to determine whether the structure will tend to distort from the standard cubic structure.\(^{48}\)

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$  \hspace{1cm} (1.1)

Perovskite materials retain the cubic form when $t$ is close to unity. However, most perovskite materials exhibit orthorhombic (e.g., LaFeO$_3$, chapter 3) or rhombohedral distortions (e.g., LaCoO$_3$, chapter 4).\(^{49}\) Ionic radii as reported by Shannon\(^{50}\) are usually
employed for the calculation of $t$. The perovskite structure in distorted form can remain stable for $0.75 < t \leq 1.0$.\textsuperscript{49} This stability makes the perovskite structure desirable because it can handle complex stoichiometries (e.g., LSCF), including A-site cation and oxygen anion nonstoichiometry (\textit{vide infra}).

Perovskite oxides with rare earth and alkaline earth ions on the A-site sublattice and TM ions on the B-site sublattice are ideal for MIEC applications because the chemical composition can be tuned to improve specific properties while the overall structure remains unchanged. The octahedral (or quasi-octahedral) coordination of the TM ions by $O^{2-}$ anions leads to materials with semiconducting properties (e.g., LaCoO$_3$ and LaFeO$_3$)\textsuperscript{51,52} or to materials with metallic properties (e.g., SrFeO$_3$).\textsuperscript{53} Furthermore, the perovskite structure is capable of accommodating the significant oxygen nonstoichiometries (e.g., ~3% oxygen vacancies in La$_{0.4}$Sr$_{0.6}$Co$_{0.2}$Fe$_{0.8}$O$_3$ at 700 °C and ambient pressure)\textsuperscript{54} required to facilitate oxygen ion conductivity for MIEC applications. A-site substoichiometry may exist as a result of intentionally synthesizing the material with less A-site cations than B-site cations\textsuperscript{55–57} or the fact that a precise 1:1 ratio of A-site to B-site cations is impossible to achieve. A-site vacancies occur more easily in perovskite structures than B-site vacancies\textsuperscript{58} because the B-site cations bond with the oxygen anions to form the backbone of the material.

1.3.2 Oxygen Diffusion Coefficients

The ionic conductivity of MIEC materials depends strongly on the diffusivity of the oxygen ions. Higher oxygen diffusion coefficients should lead to higher ionic conductivities. Three different oxygen diffusion coefficients are discussed in the literature. First, the self-diffusion coefficient ($D_0$) is the diffusion coefficient for oxygen
ions undergoing thermal motion. Second, the tracer-diffusion coefficient ($D_{o^*}$) measures
the rate at which $^{18}$O diffuses through the material. Finally, the chemical diffusion
coefficient ($D_{\text{chem}}$) arises from electrical conductivity relaxation experiments. While
values of the three diffusion coefficients will differ, trends should hold for all three
quantities. This is because $D_o = f D_{o^*}$ where $f$ is a constant usually taken as unity.$^{59}$
Likewise, $D_{\text{chem}} = \Gamma D_o$ where $\Gamma$ is the thermodynamic factor$^\dagger$ that depends on the defect
chemistry of the specific material being investigated. $\Gamma$ may cause $D_o$ and $D_{\text{chem}}$ to differ
significantly (e.g., two orders of magnitude).$^{60}$

For perovskite materials, oxygen diffusion occurs through a vacancy-mediated
mechanism. This leads to the oxygen diffusion coefficient being the product (Equation
1.2) of the oxygen vacancy concentration ($C_V$) and the vacancy diffusion coefficient ($D_v$).

$$D_o = C_v D_v$$

Two ways to increase $D_o$ exist: increase $C_V$ or increase $D_v$. Experimental evidence based
on single-crystal diffusion of oxygen through various materials related to LSCF indicates
that $D_v$ is relatively constant across materials.$^{61}$ However, $C_V$ can differ by orders of
magnitude depending on the defect chemistry of each material.$^{62-64}$ $C_V$ is usually
determined by thermogravimetry. Thermogravimetric data can be combined with defect
equilibrium models to predict thermodynamic quantities associated with the vacancy
formation process.

Measurements of the macroscopic quantities associated with oxygen ion transport
in perovskite materials can be accomplished reasonably well experimentally. However,
the precise results will depend on both the nature of the material as well as macroscopic

$^\dagger$ The expression for $\Gamma$ incorporates the temperature ($T$), the chemical potential of oxygen ($\mu_{O_2}$), and the
concentration of oxygen vacancies ($C_V$). The actual expression$^{18}$ is $\Gamma = \frac{1}{2RT} \frac{\partial \mu_{O_2}}{\partial C_V}$. 

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considerations, such as the synthesis method for creating the sample. These experiments only provide macroscopic observables, and they cannot probe the atomic-scale to understand the fundamental reasons why \( C_v \) depends strongly on the materials in question. We seek to supplement these experimental observations with fundamental insights into the defect chemistry of LSCF derived from first-principles calculations.

1.4 Thesis Outline

We provide atomic-scale insights into various materials of the LSCF family. We apply methods based on density functional theory (DFT) in order to properly account for the complex electronic structures encountered in these materials. These calculations enable us to investigate the electronic structure of the materials, including the complex magnetic behavior associated with Co\(^{3+}\) ions. In chapter 2, our methods are discussed in detail, with relevant computational details provided in each subsequent chapter.

The body of this thesis begins in chapter 3 with a detailed analysis of the electronic structure, defect chemistry, and oxygen transport mechanism of LaFeO\(_3\).\(^{65,66}\) We also present guidelines for increasing the oxygen vacancy concentration by linking trends in the vacancy formation energy in LaMO\(_3\) (M = Cr, Mn, Fe, Co) materials to basic chemical descriptors such as ionization potentials and TM-O bond dissociation energies.\(^{43}\) The final issue addressed in chapter 3 is that of A-site (La) substoichiometry. We show that small concentrations of La vacancies in LaFeO\(_3\) lead to charge compensation and an increase of several orders of magnitude in the oxygen vacancy concentration.

The magnetic nature of the first-row TM ions comes to the forefront when we investigate in chapter 4 the influence of the electron configuration of the Co\(^{3+}\) ions on the
electronic structure and defect chemistry of LaCoO$_3$. We analyze low spin (LS, $t_{2g}^6e_g^0$), intermediate spin (IS, $t_{2g}^5e_g^1$), high spin (HS, $t_{2g}^4e_g^2$), and a 1:1 mixture of HS:LS Co$^{3+}$ ions in LaCoO$_3$. We show that these configurations have similar energies, yet they significantly impact the oxygen vacancy formation energy.$^{67}$

In chapter 5, we study the effect of substituting Sr for La in the A-site sublattice to form La$_{1-x}$Sr$_x$FeO$_3$ (LSF)$^{65}$ and La$_{1-x}$Sr$_x$CoO$_3$ (LSC). We find that charge compensation between the holes introduced by Sr substitution and electrons left behind by oxygen vacancy formation makes LSF far more susceptible to forming oxygen vacancies than its parent material LaFeO$_3$. The same effect does not appear when we compare LSC to LaCoO$_3$. We analyze the extent to which the oxygen sublattice acts to accept excess electron density upon oxygen vacancy formation in each material, and we find that the oxygen sublattice in LSF plays a larger role than in LSC. This observation agrees with the relationship we had previously found for other materials (e.g., Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_{6-\delta}$ and La$_{1-x}$Sr$_x$MnO$_3$)$^{68}$

Our research efforts build toward being able to explain LSCF with all of its constituent members present. In chapter 6, we analyze the electronic structure and oxygen vacancy formation energy of LSCF using a quasirandom distribution of La/Sr and Co/Fe cations. Our efforts represent a step forward from previous DFT-based studies$^{69,70}$ of LSCF by presenting detailed calculations using traditional DFT and DFT+U methods. On the basis of chapter 4, we examine the various spin states of the Co$^{3+}$ ion in LSCF. We find that the DFT+U method provides an appropriate description of the electronic structure of LSCF ($x_{Sr}=0.50$, $y_{Co}=0.25$). We find that oxygen vacancies have a slight preference to form between one Co and one Fe ion. Forming an oxygen vacancy between
two Co ions requires more energy. Our analysis shows that a potential trade-off exists as the Fe:Co ratio is changed. Increasing $y_{\text{Co}}$ leads to improved electronic conductivity at lower concentrations; however, the effect becomes minimal as $y_{\text{Co}}$ changes from 0.25 to 0.50. At the same time, increased Co content means more oxygen sites coordinated by two Co ions. These are the sites least favorable for oxygen vacancy formation, so the oxygen vacancy concentration is expected to decrease with increasing $y_{\text{Co}}$. The optimal composition therefore features more Fe than Co, though it has sufficient Co to ensure that the electronic benefits of Co are fully present. These findings explain why $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ is the SOFC cathode composition encountered in most experimental studies.

Having provided detailed, atomic-scale insights into LSCF and some of its parent materials, we present a preliminary investigation of $\text{Sr}_{1-x}\text{K}_x\text{FeO}_3$ (SKFO) in chapter 7. We employed traditional DFT calculations because they provide reasonable agreement with known experimental behaviors of $\text{SrFeO}_3$. We find that the oxygen vacancy formation energy in $\text{SrFeO}_3$ becomes less endothermic as the oxygen vacancy concentration approaches zero. We attribute this finding to the fact that lower oxygen nonstoichiometry is correlated with a more ionic Fe sublattice, and that reducing the Fe sublattice in $\text{SrFeO}_3$ is generally favorable as it reduces the Fe ions toward their preferred $3^+$ oxidation state. The introduction of potassium substitutions in the creation of SKFO makes very little difference to the electronic structure. The holes introduced by potassium defects are delocalized over the Fe and O sublattices. We find that creating a potassium substitution is highly exothermic, indicating that SKFO remains stable when K substitutions are made. This result agrees with experimental observations of SKFO. We
also find that the holes introduced by potassium substitutions contribute to a slight lowering of the oxygen vacancy formation energy due to charge compensation effects. We find that SKFO shows some promise as a SOFC cathode material, although further investigations are required to assess its stability and to quantify the extent to which potassium substitutions make SKFO a better candidate material than SrFeO$_3$.

The remainder of this thesis includes chapter 8, which consists of conclusions summarizing our findings, and several appendices. Appendix A provides computational parameters and results of electronic structure analysis for reference materials discussed in the body of this thesis (e.g., the O$_2$ molecule, lanthanum metal, La$_2$O$_3$, strontium metal, SrO, potassium metal, and K$_2$O$_2$). Appendix B provides documentation for users of the Vienna Ab initio Simulation Package (VASP) based on the work presented in this thesis. Appendix C describes a small python program that was developed to calculate force constants and $\Gamma$-point phonon frequencies from the results of VASP calculations. The purpose is to allow the force constants to be derived from finite displacement calculations where the results are split across multiple VASP output files. Finally, Appendix D explains how to use the PHONOPY program in conjunction with VASP to compute phonon dispersion relationships, phonon densities of states, and phonon contributions to the energy, enthalpy, and free energy of a solid at finite (non-zero) temperatures.

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Chapter 2

Theoretical Background and Computational Methods‡

2.1 The Schrödinger Equation

Quantum mechanics provides the basic framework we use to understand how matter behaves. It provides a probabilistic description of how a system of low-mass particles is distributed in space and energy. The Schrödinger equation\(^1\) is the fundamental equation of quantum mechanics. Although the Schrödinger equation applies to both electronic and nuclear motion, the Born-Oppenheimer approximation\(^2\) separates and neglects any coupling between them. Thus, it is acceptable for the materials studied in this thesis to treat the nuclei as classical particles while still accounting for quantum mechanical effects through the motion of electrons.

Most properties of solid-state materials can be obtained by solving the time-independent Schrödinger equation (Equation 2.1).

\[
-\sum_{j=1}^{N} \frac{\hbar^2}{2m_e} \nabla_j^2 \Psi(\{x_j\}) + V(\{R_\alpha\}, \{x_j\})\Psi(\{x_j\}) = E\Psi(\{x_j\})
\]

2.1

In the preceding equation, \(\hbar\) is Planck’s constant divided by 2\(\pi\), \(j\) is an index running over all of the electrons, \(m_e\) is the electron mass, \(\Psi\) is the time-independent electronic wavefunction, \(V(\{R_\alpha\}; \{x_j\})\) is the potential energy including the nuclear-electron

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Reproduced in part with permission from Ritzmann, A. M., Muñoz-García, A. B., Pavone, M., Keith, J. A. & Carter, E. A. Ab Initio DFT+U Analysis of Oxygen Vacancy Formation and Migration in La\(_{1-x}\)Sr\(_x\)FeO\(_3\)-\(\delta\) (\(x = 0, 0.25, 0.50\)). *Chem. Mater.* 25, 3011-3019 (2013). Copyright 2013 American Chemical Society.
attraction and electron-electron repulsion, $E$ is the energy associated with $\Psi$, $\{\mathbf{R}_n\}$ is the set of nuclear positions, and $\{\mathbf{x}_j\}$ is the set of electronic coordinates (spatial and spin).

The time-independent Schrödinger equation is an eigenvalue problem. The eigenfunctions $\Psi_i(\{\mathbf{x}_j\})$ correspond to stationary states, $i$, where the material’s electron density does not change over time. Each eigenfunction, $\Psi_i(\{\mathbf{x}_j\})$, has a corresponding eigenvalue that is the electronic energy ($E_i$). The wavefunctions, $\Psi_i(\{\mathbf{x}_j\})$, depend on the spatial and spin coordinates of each electron. Furthermore, the Pauli exclusion principle requires that $\Psi_i(\{\mathbf{x}_j\})$ be antisymmetric with respect to exchanging the coordinates of any two electrons. This requirement has two practical consequences: 1) $\Psi_i(\{\mathbf{x}_j\})$ can naturally be written in terms of determinants of one-electron functions, and 2) the concept of exchange energy arises as a result of the permutational antisymmetry requirement. The exchange energy comes from terms that are similar to, but weaker than, the Coulombic interactions between electrons.

Solutions to the Schrödinger equation with one electron are known for various potentials (e.g., spherical potential). However, the problem becomes analytically intractable for systems containing multiple ($N$) electrons. Furthermore, the wavefunction depends on $3N$ degrees of freedom, and thus it quickly grows in complexity with the addition of each electron. This necessitates approximations to find viable solutions that reasonably describe the material of interest.

2.2 Density Functional Theory

Among the approximate quantum mechanical methods, density functional theory (DFT) has great power for finding the electronic ground state of a system. Hohenberg and Kohn proved that the ground-state electron density (a function of three spatial variables)
has a one-to-one mapping to the ground-state wavefunction and energy. They also proved that the variational principle holds for the electron density. The best approximation of the ground-state electron density is therefore obtained when the energy is minimized with respect to the electron density. The Hohenberg-Kohn (HK) theorems apply to systems with nondegenerate ground states. Expansion of the HK theorems to systems with degenerate ground states requires the constrained search formalisms proposed by Levy\textsuperscript{8–10} and Lieb\textsuperscript{11,12}.

2.2.1 Kohn-Sham Density Functional Theory

Although Hohenberg and Kohn proved the fundamental theorems underpinning DFT calculations,\textsuperscript{7} Kohn and Sham\textsuperscript{13} provided the basic formalism for using DFT. The electronic energy can be written as a functional of the electron density ($\rho$) according to Equation 2.2.

$$E[\rho] = T_S[\rho] + J[\rho] + E_{\text{ext}}[\rho] + E_{\text{XC}}[\rho]$$  \hspace{1cm} 2.2

This functional contains the kinetic energy $T_S[\rho]$, the Hartree (electron-electron repulsion) energy $J[\rho]$, the energy associated with the interaction of the electrons with the external potential (here, the nuclear-electron attraction) $E_{\text{ext}}[\rho]$, and the exchange-correlation (XC) energy $E_{\text{XC}}[\rho]$. The second and third terms, $J[\rho]$ and $E_{\text{ext}}[\rho]$, can be written exactly from classical electrostatic theory. Therefore, Equation 2.2 can be rewritten in the form of Equation 2.3.

$$E[\rho] = T_S[\rho] + \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{4\pi\varepsilon_0|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 d\mathbf{r}_2 + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} + E_{\text{XC}}[\rho]$$  \hspace{1cm} 2.3

Unfortunately, no universal forms are known for $T_S[\rho]$ and $E_{\text{XC}}[\rho]$. Kohn and Sham worked around the first of these issues by suggesting that the electron density be expanded in a single determinant ($\Psi$) of one-electron functions ($\phi_i$).
In Equation 2.4, \( \hat{A} \) is the antisymmetry operator. This allows the non-interacting kinetic energy to be calculated using the kinetic energy operator from quantum mechanics (Equation 2.5).

\[
T_S[\rho] = -\sum_{j=1}^{N} \frac{\hbar^2}{2m_e} \int \varphi^*(\mathbf{x}_j) \nabla^2 \varphi(\mathbf{x}_j) d\mathbf{x}_j
\]  

Equation 2.5

The electron density is related to the one-electron functions as specified in Equation 2.6.

\[
\rho = \sum_{j=1}^{N} \varphi_j^* \varphi_j
\]  

Equation 2.6

A careful distinction must be made at this time: the Kohn-Sham (KS) formalism solves for the ground-state energy and electron density of a system of interacting electrons; however, the kinetic energy is approximated as that of a non-interacting system with the same electron density as the interacting system. The part of the kinetic energy that arises from interactions between electrons is considered small and is theoretically combined into the XC functional. Within the KS formalism, the only unknown is the XC functional. Many approximations exist for the XC functional; these will be discussed in a subsequent section.

The KS Hamiltonian takes on a mean-field form that separates the N-electron problem into N, coupled one-electron equations (Equation 2.7).

\[
-\frac{\hbar^2}{2m_e} \nabla^2 \varphi_j(\mathbf{r}) + [V_{\text{ext}}(\mathbf{r}) + J(\rho(\mathbf{r})) + V_{\text{XC}}(\rho(\mathbf{r}))] \varphi_j(\mathbf{r}) = \epsilon_j \varphi_j(\mathbf{r})
\]  

Equation 2.7

Equation 2.7 is a mean-field Schrödinger-like equation where the potential is the sum of the external potential, the Hartree potential, and the XC potential. The last two terms
depend on the electron density, and therefore the equations must be solved self-consistently. Solutions to the KS Hamiltonian give one-electron orbitals ($\varphi_i$) that exist for the purpose of constructing the density. There is no physical meaning to these orbitals.

2.2.2 Periodic Boundary Conditions

Solid-state calculations employ periodic boundary conditions in order to satisfy the translational invariance found in the bulk of a crystal. A periodic potential causes the one-electron solutions to the Schrödinger equation take on the form of Bloch states (Equation 2.8).\(^{14,15}\)

$$\varphi_{jk}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \phi_{jk}(\mathbf{r}) \tag{2.8}$$

The one-electron states ($\varphi_{jk}$), called bands in the following discussion, have the form of a planewave $e^{i\mathbf{k} \cdot \mathbf{r}}$ multiplied by a function ($\phi_{jk}$) with the same periodicity as the potential. For a crystalline solid, the periodicity of the potential is defined by the lattice vectors of the unit cell or supercell employed in the calculations. The bands given by the Bloch theorem above have discrete energies at each $\mathbf{k}$ vector residing in the first Brillouin zone (BZ).\(^{15}\) The infinite crystal has a continuous spectrum of $\mathbf{k}$ vectors residing in the first BZ. Properties (e.g., the electron density) must be obtained by integrating over these $\mathbf{k}$ vectors.

In practice, integration is performed by sampling a finite set of $\mathbf{k}$ vectors (often called $\mathbf{k}$ points). In semiconductors, bands have occupation numbers of zero or one depending on whether they lie below the Fermi level (i.e., in the core and valence bands) or above the Fermi level (i.e., in the conduction band). Fractional occupations may occur in metals for bands that cross the Fermi level. Practical considerations demand\(^{16}\) that the
band occupancies be multiplied by a smearing function that smooths out the occupancies for bands lying near the Fermi level. This enables treating electrons at finite (non-zero) temperatures. Smearing functions may be written in a Gaussian form\textsuperscript{16} or using Methfessel and Paxton’s smearing functions of arbitrary order\textsuperscript{17} (usually the first-order expansion is used). Gaussian smearing is appropriate for insulators and semiconductors while Methfessel-Paxton smearing is appropriate for metals. Calculations at fixed geometries may employ the tetrahedron method with Blöchl corrections\textsuperscript{18} to perform the integration using a more accurate interpolation scheme instead of a smearing scheme. The tetrahedron method with Blöchl corrections\textsuperscript{18} is used to refine the total energy and obtain more accurate densities of states for the geometry obtained after optimization.

### 2.2.3 Exchange-Correlation Functionals

DFT calculations must rely on approximate XC functionals since the true XC functional remains unknown. From a conceptual standpoint, the easiest approximation for the XC functional is to assume that the XC energy density depends only on the electron density at each point in space. This is called the local density approximation (LDA).\textsuperscript{19} LDA functionals work best with metallic systems that have slowly varying electron densities. LDA calculations tend to overbind systems, leading to bond lengths and cell volumes smaller than those found experimentally.

The generalized gradient approximation (GGA) expresses the XC energy using the electron density and the gradient of the electron density.\textsuperscript{20,21} GGA functionals are often called semi-local because the gradient term introduces information about nearby variations in the density. GGA functionals generally offer better accuracy than LDA.
functionals; however, they tend to underbind crystals and usually give cell parameters larger than those found experimentally.\textsuperscript{22}

XC functionals that use the Laplacian of the density are called meta-GGA functionals; however, we restrict our analysis to the LDA and GGA functional forms. Specifically, the LDA functional of Perdew and Zunger,\textsuperscript{19} and the GGA functional of Perdew, Burke, and Ernzerhof\textsuperscript{21} are used in this work. LDA, GGA, and meta-GGA functionals are discussed extensively in an account by Zhao and Truhlar.\textsuperscript{23}

2.3 Self-Interaction Error and the DFT+$U$ Method

2.3.1 The Origin of Self-Interaction Error

DFT and Hartree-Fock (HF) calculations both make mean-field approximations by choosing a single Slater determinant to represent the many-electron wavefunction (or pseudo-wavefunction in DFT). HF theory contains exact exchange but fails to include electron correlation while DFT simulations approximate the XC energy using a functional of the density (\textit{vide supra}). Equation 2.3 contains the exact form of the Hartree energy, written in terms of the electron density. Consider a hypothetical DFT calculation on a one electron system. The electron density would describe the single electron, but the Hartree term would give a positive contribution to the energy. This repulsion is clearly spurious, and it should be cancelled by an exchange term of exactly the same magnitude. In HF theory, this exact exchange term is present, and the spurious self-interaction error (SIE) is avoided. However, approximate XC functionals give rise to inexact cancellation of this term allowing the single electron to interact with itself. This problem generalizes to systems with many electrons, and it is the cause of catastrophic failure in the electronic structure descriptions obtained by traditional DFT methods for certain classes of
materials (e.g., DFT-LDA calculations incorrectly predict metallic ground states for the semiconductors CoO and FeO).\textsuperscript{24} The SIE is largest when highly-localized \(d\) and \(f\) orbitals are partially occupied on atoms in the material. The preceding discussion suggests that looking at HF theory should offer plausible solutions to the SIE problem.

### 2.3.2 The DFT+U Method

The most common method used to correct for SIE in DFT calculations is the DFT+U method.\textsuperscript{25,26} This method adds a model HF potential to the Hamiltonian to account for intra-atomic Coulomb and exchange interactions. The correction is only applied to specified orbitals through on-site, angular-momentum-dependent density matrices. While multiple formulations of the DFT+U method exist, the work in this thesis uses the rotationally-invariant formalism proposed by Dudarev \textit{et al.}\textsuperscript{26} The DFT+U energy is formulated according to Equation 2.9.

\[
E_{\text{DFT+U}} = E_{\text{DFT}} + \sum_{I,\ell,m,\sigma} \frac{U_{I\ell} - J_{I\ell}}{2} (n_{I\ell m\sigma} - n_{I\ell m\sigma}^2)
\]  \textsuperscript{2.9}

The DFT+U energy is the DFT energy (within the LDA or GGA) plus a correction term summed over all of the sites (I), angular momentum (\(\ell\)), magnetic quantum number (m), and spin (\(\sigma\)). Only the difference between the average on-site Coulomb (\(U_{I\ell}\)) and average on-site exchange (\(J_{I\ell}\)) interactions between electrons residing in orbitals with common I, \(\ell\), and \(\sigma\) enters into the correction. This difference, denoted as \(U_{\text{eff}}\), is nonnegative since both \(U_{I\ell}\) and \(J_{I\ell}\) are nonnegative with the former being provably larger than or equal to the latter. This work applies \(U_{\text{eff}}\) to the \(d\) manifold of first-row transition metal ions, and all other \(U_{\text{eff}}\) terms are set to zero.
The results of a DFT+U calculation depend on the value of $U_{\text{eff}}$ employed. $U_{\text{eff}}$ values are often chosen to match experimental data. Predictions made on the basis of empirically derived $U_{\text{eff}}$ values are limited by the choice and quality of the experimental data used. Several years ago, a method for determining $U_{1\ell}$ and $J_{1\ell}$ from first-principles was developed in the Carter group.\textsuperscript{27,28} This method removes empiricism from the choice of $U_{\text{eff}}$. Unrestricted HF calculations on ionic clusters carved out of a bulk crystal and electrostatically embedded in a point charge array are used to calculate the $U_{1\ell}$ and $J_{1\ell}$ parameters. Capping effective core potentials are used in place of the nearest positive point charges to prevent electron density from spuriously spilling out into the point charge array. Progressively larger clusters are employed until the value of $U_{\text{eff}}$ converges. An application of this method to low-spin Co$^{3+}$ ions may be found in Chapter 4.

Alternative methods to computing $U_{\text{eff}}$ have been developed by applying linear response theory to DFT calculations.\textsuperscript{29–31} The Carter group’s more rigorous approach avoids the SIE-contaminated traditional DFT calculations when computing the $U_{\text{eff}}$ value as a correction for SIE, and were recently shown to be more robust than the linear response theory approach.\textsuperscript{32} DFT+U calculations require slightly more computational time than regular DFT calculations.

2.3.3 Hybrid DFT Methods

HF theory was the inspiration for the DFT+U method that approximately corrects for SIE. Sensibly, others have incorporated exact exchange through actual HF exchange terms.\textsuperscript{33–35} This gives rise to hybrid DFT where a portion of the exchange energy from the XC functional is replaced with a portion of the exact exchange computed from HF theory. Adamo and Barone suggest, on the basis of perturbation theory arguments, that
25% is the correct fraction of exchange energy to replace with exact exchange.\textsuperscript{33} The two hybrid functionals employed in this work are PBE0\textsuperscript{33} and HSE06.\textsuperscript{34,35} The HSE06 functional screens the exact exchange so that only short-range interactions are taken into account.

While hybrid DFT is expected to overcome failures due to SIE, the functionals have met with mixed success. The well-known divergence of HF theory for metallic systems is a major drawback to these methods.\textsuperscript{36} Introducing a fraction of exact exchange raises the predicted fundamental gap in many materials.\textsuperscript{37} This likely results from the fact that periodic HF usually predicts fundamental gaps in far excess of experimental values. The hybrid DFT functionals perform well when used to estimate lattice constants. However, the largest drawback to the use of hybrid DFT calculations is their cost. The hybrid DFT calculations reported in this thesis required approximately two orders of magnitude more computational time than the corresponding DFT or DFT+U calculations.

\textbf{2.4 Computational Details}

KS-DFT calculations were carried out using the Vienna Ab initio Simulation Package (VASP) version 5.2.2.\textsuperscript{38–40} Interactions between the nuclei and frozen-core electrons with the valence electrons were treated using the projector augmented-wave (PAW) method.\textsuperscript{41} The computational details are specified in each chapter for the specific materials investigated.

\textbf{2.5 Density of States and Density Difference Plots}

\textit{2.5.1 Density of States Plots}

Periodic DFT, DFT+U, and hybrid DFT calculations typically solve for the electronic structure of a crystal. The density of states (DOS) is the number of electronic
states per eV at a given energy. The site- and angular-momentum-projected DOS (PDOS) is typically used when interpreting the electronic structure. The PDOS shows the energies at which specific atomic states contribute. PDOS plots in this thesis are averaged over the sites containing the same element. For ferromagnetic materials, the PDOS is plotted such that positive values correspond to $\alpha$-spin states and negative values correspond to $\beta$-spin states. For antiferromagnetic materials, the majority spin states are plotted as positive values and minority spin states as negative values.

2.5.2 Density Difference Plots

The electron density ($\rho$) is also a result of a DFT, DFT+U, or hybrid DFT calculation. Changes in $\rho$ due to a chemical or physical process reveal, e.g., rearrangements in $d$ orbital occupations or oxidations/reductions. The density difference ($\Delta \rho$) for oxygen vacancy formation is defined by Equation 2.10.

$$\Delta \rho = \rho_{\text{defective}} + \rho_{O} - \rho_{\text{host}}$$  \hspace{1cm} 2.10

$\rho_{\text{defective}}$ is the electron density of the supercell with an oxygen vacancy, $\rho_{O}$ is the electron density of an isolated oxygen atom at the site from which it was removed, and $\rho_{\text{host}}$ is the electron density of the supercell without an oxygen vacancy. The $3P$ ground state of the O atom has one out of the three $p$ orbitals doubly occupied. Allowing this asymmetric occupation would bias $\rho_{O}$, so fractional occupation of all three $p$ orbitals is imposed to retain spherical symmetry even though this doesn’t correspond to the actual ground state of the oxygen atom. $\Delta \rho$ plots are isosurface or contour plots showing regions where electron density increased and regions where it decreased.
2.6 Oxygen Vacancy Formation Energies

The simplest approximation of the vacancy formation enthalpy ($\Delta H_{f,\text{vac}}$) uses only electronic energies and neglects thermal and vibrational effects:

$$\Delta E_{f,\text{vac}} = E_{\text{defective}} - E_{\text{perfect}} + \frac{1}{2} E_{O_2}$$ \hspace{1cm} (2.11)

Approximating $\Delta H_{f,\text{vac}}$ at absolute zero includes the zero point energy (ZPE) contributions

$$\Delta H_{f,\text{vac}}(0) = \Delta E_{f,\text{vac}} + \sum_{i=1}^{3(N-1)} \frac{1}{2} \hbar \nu_{i,\text{defective}} - \sum_{j=1}^{3N-3} \frac{1}{2} \hbar \nu_{j,\text{perfect}} + \frac{1}{2} \left( \frac{1}{2} \hbar \nu_{O_2} \right)$$ \hspace{1cm} (2.12)

where $\hbar$ is Planck’s constant and the $\nu$’s are vibrational frequencies calculated within the harmonic oscillator (H.O.) approximation and $N$ is the number of atoms in the perfect supercell. Approximating $\Delta H_{f,\text{vac}}$ at finite temperature involves integrating the heat capacities ($C_p$) from absolute zero to the temperature of interest. $C_p$ values for the solids (the sums in Equation 2.13) are calculated using the H.O. approximation for vibrational contributions while $C_p$ for $O_2$ also includes effects from the rigid-rotor (R.R.) and ideal gas (I.G.) approximations for rotational and translational contributions. Because the PV contributions to enthalpy for solids should be negligible, we assume that the internal energy of each solid is equivalent to its enthalpy, while the enthalpy of gas phase $O_2$ includes the PV term via its constant pressure heat capacity.

$$\Delta H_{f,\text{vac}}(T) = \Delta H_{f,\text{vac}}(0) + \sum_{i=1}^{3(N-1)} \frac{\hbar \nu_{i,\text{defective}}}{\nu_{i,\text{defective}} / k_B T - 1} - \sum_{j=1}^{3N-3} \frac{\hbar \nu_{j,\text{perfect}}}{\nu_{j,\text{perfect}} / k_B T - 1} + \frac{1}{2} \left( \int_0^T C_{P,O_2}(T')dT' \right)$$ \hspace{1cm} (2.13)

Calculating the free energy of oxygen vacancy formation ($\Delta G_{f,\text{vac}}$) requires the entropy of the solids and $O_2$ as a function of temperature.

$$\Delta G_{f,\text{vac}}(T) = \Delta H_{f,\text{vac}}(T) - T \Delta S_{f,\text{vac}}(T)$$ \hspace{1cm} (2.14)
\[
\Delta S_{\text{f,vac}}(T) = S_{\text{vib,defective}}(T) - S_{\text{vib,perfect}}(T) + \frac{1}{2} S_{O_2}(T) \quad (2.15)
\]

Computing entropies can be accomplished by applying the H.O. approximation to the \( \Gamma \)-point frequencies of the solids and the I.G., R.R., and H.O. approximations\(^6\) to the \( O_2 \) molecule. Further refinement of the entropies from the solids may be achieved by accounting for phonon dispersion using the PHONOPY software package.\(^{42,43}\)

### 2.7 Oxygen Diffusion Coefficients

The oxygen diffusion coefficient for a vacancy-mediated hopping mechanism is given by the product of the oxygen vacancy concentration \( (C_v) \) and the vacancy diffusion coefficient \( (D_v) \). \( C_v \) is determined from \( \Delta G_{f,vac} \) through equilibrium calculations.

Transition state theory is used to determine \( D_v \). The activation barrier \( (\Delta H_{\text{mig}}) \) is the difference between the energy of the transition state and the initial minimum energy state.

The migration pathway is obtained using the climbing image nudged elastic band (CINEB) method\(^{44-46}\) as implemented in the VASP transition state theory tools from the University of Texas.\(^{47}\)

Following previous work in our group,\(^{48-50}\) we use transition state theory to express \( D_v \) in terms of the activation barrier \( (\Delta H_{\text{mig}}) \), the jump length \( (a) \), the attempt frequency \( (\nu_0) \) and the entropy of activation \( (\Delta S^\ddagger) \) where \( k_B \) is Boltzmann’s constant (Equation 2.16).

\[
D_v = \frac{1}{6} \nu_0 a^2 e^{-\Delta S^\ddagger/k_B} e^{-\Delta H_{\text{mig}}/k_B T} \quad (2.16)
\]

The factor of one sixth arises from diffusion in three dimensions. The attempt frequency is the ratio of the product of the real \( \Gamma \)-point frequencies at the initial state to those at the transition state. Thermal expansion is accounted for by the \( e^{-\Delta S^\ddagger/k_B} \) term.\(^{48,49}\)
2.8 Vibrational Frequencies

Vibrational (phonon) frequencies are used to calculate thermal corrections and diffusion coefficients. Computing frequencies requires determining the Hessian matrix consisting of second derivatives of the total energy with respect to atomic displacements. For a crystalline material with \( N \) atoms, the Hessian is a \( 3N \times 3N \) matrix since each atom can be displaced in the x-, y-, and z-directions.

\[
H_{i\alpha,j\beta} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 E}{\partial x_{i\alpha} \partial x_{j\beta}} = -\frac{1}{\sqrt{m_i m_j}} \frac{\partial F_{i\alpha}}{\partial x_{j\beta}} \tag{2.17}
\]

In Equation 2.17, each element of the Hessian matrix involves the displacement of atom \( i \) in the direction \( \alpha \) and atom \( j \) in the direction \( \beta \). \( \alpha \) and \( \beta \) can be the x-, y-, or z-directions. The quantities \( m_i \) and \( m_j \) are the masses of atoms \( i \) and \( j \). The last part of Equation 2.17 exploits the relationship \( F_{i\alpha} = -\frac{\partial E}{\partial x_{i\alpha}} \). The eigenvalues of the Hessian matrix are the vibrational frequencies squared. Positive and negative eigenvalues therefore correspond to real and imaginary frequencies, respectively. The eigenvectors of the Hessian are the displacements associated with each frequency in mass-weighted coordinates. Small, finite displacements and finite differences of forces derived therefrom are employed to construct the Hessian matrix in this work.

2.9 Thermal Corrections for the \( O_2 \) Molecule

In our studies of oxygen vacancy formation, the departing oxygen atom is referenced to \( \frac{1}{2}O_2 \) (g). Although we employ vacancy formation energies (and enthalpies) for most of this thesis, the entropy change associated with liberating gas-phase molecules provides a strong driving force in favor of creating oxygen vacancies. Here we explain how the ideal gas, rigid-rotor, and harmonic oscillator approximations may be applied to
compute the thermal correction that accounts for the enthalpic and entropic contributions to the free energy of the O\textsubscript{2} molecule at non-zero temperature and pressure.

The chemical potential of oxygen ($\mu_O = \frac{1}{2} g_{O_2}$) is referenced to one-half of the partial molar Gibbs free energy of O\textsubscript{2} (g). Computing $g_{O_2}$ requires including thermal effects from molecular vibration, rotation and translation. We include these effects through the standard ideal gas, rigid rotor, and harmonic oscillator approximations.\textsuperscript{6} The analysis starts with considering the canonical partition function (Q) for an ensemble with constant temperature, volume, and number of molecules. The Helmholtz free energy of the system (A) is related to the partition function through Equation 2.18.

$$A = -k_B T \ln(Q)$$

(2.18)

The chemical potential is the Gibbs free energy (G) per molecule of O\textsubscript{2}. To calculate this quantity, we require expressions for the enthalpy (H) and the entropy (S) of the O\textsubscript{2} molecule as a function of temperature and pressure. At zero temperature, the enthalpy and internal energies are equivalent and expressed as the sum of the electronic energy and the zero point energy (ZPE).

$$H(0 \text{ K}) = U(0 \text{ K}) = E_{\text{electronic}} + \frac{1}{2} h \nu$$

(2.19)

In this expression, $E_{\text{electronic}}$ is the total energy from a DFT-based calculation, $h$ is Planck’s constant and $\nu$ is the vibrational frequency of the O\textsubscript{2} molecule. Integrating the constant pressure heat capacity ($C_p$) from absolute zero to the temperature of interest (e.g., 700\degree C) gives the thermal contribution to the enthalpy. Equation 2.20 expresses this contribution in terms of the partition function Q.\textsuperscript{51}

$$H(T) - H(0 \text{ K}) = k_B T^2 \frac{\partial \ln(Q)}{\partial T} + k_B T$$

(2.20)
Finally, the entropy is calculated according to Equation 2.21.

\[
S = -\left(\frac{\partial A}{\partial T}\right)_V = k_B \ln(Q) + k_B T \frac{\partial \ln Q}{\partial T}_V
\]  

(2.21)

At this point, all that remains is to express \( Q \) in terms of known quantities of the diatomic molecule. For an ensemble of \( N \) indistinguishable particles, the partition function takes the form

\[
Q = \frac{q^N}{N!}
\]  

(2.22)

where \( q \) is the molecular partition function. This smaller partition function can then be decomposed into electronic \( (q_e) \), rotational \( (q_r) \), translational \( (q_t) \) and vibrational \( (q_v) \) contributions.

\[
q = q_e q_r q_t q_v
\]  

(2.23)

For a diatomic molecule, the separate partition functions are given in Table 2.1.

**Table 2.1.** Individual contribution partition functions for a diatomic molecule.\(^6\)

<table>
<thead>
<tr>
<th>Contribution</th>
<th>Partition Function</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic</td>
<td>( q_e = g_e )</td>
<td>( g_e ) is the electronic degeneracy</td>
</tr>
<tr>
<td>Rotational</td>
<td>( q_r = \frac{\pi^2 m r_e^2 k_B T}{h^2} )</td>
<td>( r_e ) is the equilibrium bond length and ( m ) is molecule’s mass</td>
</tr>
<tr>
<td>Translational</td>
<td>( q_t = \left(\frac{2\pi k_B T m}{h^2}\right)^{3/2} V )</td>
<td>( m ) is the mass of the molecule and ( V = k_B T / P ) (ideal gas)</td>
</tr>
<tr>
<td>Vibrational</td>
<td>( q_v = \frac{1}{1 - e^{-h v / k_B T}} )</td>
<td>( v ) is the vibrational frequency of the diatomic molecule</td>
</tr>
</tbody>
</table>
Combining the individual partition functions with Equations 2.21, 2.22, and 2.23 gives an expression for the entropy of the diatomic molecule (Equation 2.24).\(^{51}\)

\[
S = k_B \left( \left[ \ln(g_e) \right] + \left[ \ln(q_l) + \frac{5}{2} \right] + \left[ \ln(q_r) + 1 \right] + \left[ \ln(q_v) + \frac{h\nu}{k_BT} \frac{1}{\left( \frac{h\nu}{e^{\frac{h\nu}{k_BT}} - 1} \right)} \right] \right)
\] (2.24)

Likewise, the thermal contribution to the enthalpy is given by combining Equations 2.20, 2.22 and 2.23 with the individual partition functions.\(^{6}\)

\[
H(T) - H(0 \text{ K}) = k_B T \left( \frac{7}{2} + \frac{h\nu}{k_BT} \frac{1}{\left( \frac{h\nu}{e^{\frac{h\nu}{k_BT}} - 1} \right)} \right)
\] (2.25)

Finally, the Gibbs free energy (G) may be calculated from the preceding expressions by combining the enthalpy with the entropy (both at the specified temperature). This results in Equation 2.26.

\[
G(T) = E_{\text{electronic}} + \frac{1}{2} h\nu + k_B T \left( \frac{7}{2} + \frac{h\nu}{k_BT} \frac{1}{\left( \frac{h\nu}{e^{\frac{h\nu}{k_BT}} - 1} \right)} \right) - TS(T)
\] (2.26)

Finally, the G(T) in Equation 2.26 is also the chemical potential of O\(_2\) because it is the free energy per molecule at the specified temperature and pressure.

Computed bond lengths and vibrational frequencies for the O\(_2\) molecule (Appendix A) were used to validate this model against thermodynamic data available in the NIST Webbook.\(^{52}\) Enthalpic contributions were within 1 kJ mol\(^{-1}\) and entropies...
within 1 J mol\(^{-1}\) K\(^{-1}\) for temperatures up to 1200 K. These errors are negligible compared to uncertainties inherent in DFT calculations.

References


Chapter 3.

Defect Chemistry and Oxygen Diffusion in LaFeO$_3$**

3.1 Introduction

Understanding the fundamental science governing oxygen transport in the target solid oxide fuel cell (SOFC) La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_3$ (LSCF) requires a valid, successful, and insightful model for the parent material LaFeO$_3$. This material removes the complexity of chemical substitutions found in LSCF (e.g., Sr for La, Co for Fe), and allows us to gain insight into how the defect chemistry and oxygen transport mechanisms work in Fe-rich materials resembling the common LSCF composition La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$. This chapter will therefore provide an initial validation of our DFT-based methods for describing oxygen transport in LSCF-related materials. We will build upon this study to address A-site (Sr for La) and B-site (Co for Fe) substitutions in later chapters.

Experimental investigations of conductivity, defect chemistry, and oxygen transport in LaFeO$_3$ provide the necessary information for validating our model of LaFeO$_3$. For consistency with the existing literature on defect chemistry in ionic solids, we use Kröger-Vink$^{1,2}$ notation to label each defect. LaFeO$_3$ crystallizes in the perovskite structure with an orthorhombic distortion.$^{3,4}$ This material is an insulator with low p-type

** Portions of this chapter were adapted from the following three papers with permission:
Reproduced with permission from Ritzmann, A. M., Muñoz-García, A. B., Pavone, M., Keith, J. A. & Carter, E. A. Ab Initio DFT+U Analysis of Oxygen Vacancy Formation and Migration in La$_{1-x}$Sr$_x$FeO$_{3-δ}$ (x = 0, 0.25, 0.50). Chem. Mater. 25, 3011-3019 (2013). Copyright 2013 American Chemical Society.
conductivity under ambient oxygen partial pressure (e.g., p-type for \( P_{O_2} > 10^{-5} \) Pa at 1000°C).\(^5,6\) The Fe ions have G-type antiferromagnetic order below the remarkably high Néel temperature (\( T_N = 750 \) K).\(^7\) For LaFeO\(_3\), the defect chemistry and the conductivity become intimately related because p-type conductivity implies the existence of holes, which can compensate electrons left behind when a neutral oxygen atom departs from the lattice. Under oxygen-poor conditions (e.g., \( P_{O_2} < 10^{-7} \) Pa at 1000°C), the material becomes slightly n-type as the oxygen vacancy (\( V_{O}^{\text{\textstruct{}}\text{\textstruct{}}} \)) concentration becomes sufficient to make electrons the majority carriers (instead of holes). With decreasing \( P_{O_2} \), the Seebeck coefficient goes from positive to negative, indicating that electrons (instead of holes) become the majority charge carriers (only at very low \( P_{O_2} \)).\(^5\) The material decomposes at extremely low oxygen partial pressures because of the accumulation of \( V_{O}^{\text{\textstruct{}}\text{\textstruct{}}} \). The generally low conductivity of LaFeO\(_3\) renders it unsuitable for practical use in SOFCs; the fundamental insights that we derive from this material inform our discussion of the defect chemistry and oxygen transport in other, more suitable cathode materials.

Experimental investigations of oxygen transport in LaFeO\(_3\) have shown that diffusion occurs via a vacancy-mediated hopping process.\(^8\) The large ionic radius of oxygen precludes the formation of interstitial defects. The resulting self-diffusion coefficient (\( D_0 \)) has the form:

\[
D_0 = C_v D_v
\]  

(3.1)

where \( C_v \) is the concentration of oxygen vacancies and \( D_v \) is the vacancy diffusion coefficient. \( D_v \) takes an Arrhenius form where the activation enthalpy (\( \Delta H_{\text{mig}} \)) is the energy barrier for an oxygen ion hopping into an unoccupied neighboring site. \( V_{O}^{\text{\textstruct{}}\text{\textstruct{}}} \), \( V_{La}/// \),
and holes (h') are the main point defects present in LaFeO₃ under ambient oxygen partial pressures.⁵ In LaFeO₃, the oxygen vacancies do not interact.⁹ The free energy of oxygen vacancy formation (∆Gᵥ,vac) governs the vacancy concentration. Therefore, the sum of ∆Hᵥ,vac and ∆Hᵥ,mig defines the apparent activation energy for the oxygen diffusion coefficient where A is the preexponential factor which contains the entropy of oxygen vacancy formation.

\[
D_0 = Ae^{-(\Delta H_{v,vac} + \Delta H_{v,mig})/k_BT}
\]  

(3.2)

Computational studies have already provided some microscopic insight into defect chemistry and ionic transport in LaFeO₃. Jones and Islam¹⁰ studied defect chemistry and ion migration in LaFeO₃ using classical potentials. However, conclusions drawn from simulations using classical, empirically-based potentials run the risk of depending strongly on the particular parameterization of the potentials rather than representing the true physics. By contrast, first-principles quantum mechanics calculations based on density functional theory (DFT) can offer unbiased insights by being free from system-dependent parameters. Indeed, several electronic structure descriptions of LaFeO₃ have been provided using DFT.¹¹–¹⁵ Unfortunately, these predictions may suffer from self-interaction errors that cause DFT to fail for strongly correlated materials (e.g., first row late transition metal oxides).¹⁶ To mitigate these errors, the DFT+U method¹⁷ has been applied to understanding the electronic structure¹⁸–²⁰ and defect chemistry¹⁴,¹⁵,²¹,²² of LaFeO₃.

Of specific note, the theoretical work by Mastrikov et al.¹⁵ provided the first DFT calculation of the migration barrier for LaFeO₃. However, their calculations used DFT
within the generalized gradient approximation (GGA) for which the self-interaction error may be significant. They also incorrectly employed a ferromagnetic model for the strongly antiferromagnetic \( \text{LaFeO}_3 \),\(^7\) as well as the ‘soft’ oxygen projector augmented-wave (PAW) potential from the VASP library;\(^{23,24}\) however, this ‘soft’ potential trades accuracy in certain properties for increased speed. The ‘soft’ PAW potential significantly overestimates the bond length of the \( \text{O}_2 \) molecule (1.30 Å calculated compared to 1.21 Å found experimentally), although the bond dissociation energy (BDE) shows better agreement with experiment than the value obtained using the ‘regular’ PAW potential. To obtain accurate results, we choose to use the ‘regular’ potential because it provides a better estimation of the \( \text{O}_2 \) bond length (1.23 Å). Likewise, the ‘regular’ PAW potential overestimates the BDE of \( \text{O}_2 \) by 0.84 eV (see Appendix A). This overestimation is somewhat smaller than the 1.11 eV overbinding obtained with the all-electron DFT-GGA using large Gaussian basis sets.\(^\ddagger\ddagger\) By correctly describing the antiferromagnetic state of \( \text{LaFeO}_3 \) and using the ‘regular’ oxygen PAW potential, we provide a more accurate description of the defect chemistry and oxygen migration in \( \text{LaFeO}_3 \). Furthermore, we provide the first DFT-based computation of the oxygen diffusion coefficient in \( \text{LaFeO}_3 \), leading to surprising insights.

This chapter is organized in the following manner: in section 3.2, we describe the computational details used for modeling \( \text{LaFeO}_3 \). In section 3.3, we then discuss the bulk properties and electronic structures of \( \text{LaFeO}_3 \) obtained with standard DFT, DFT+U, and

\(^{\ddagger\ddagger}\) All-electron DFT calculations with the GGA functional of Perdew, Burke, and Ernzerhof\(^{25}\) on \( \text{O}_2 \) overestimate the BDE by 1.11. This value is obtained by extrapolating energies obtained with the correlation-consistent basis sets (cc-pVTZ, cc-pVQZ, and cc-pV5Z)\(^{26}\) to the complete basis set limit according to the formula of Peterson and Dunning.\(^{27}\) These calculations were performed with MOLCAS.\(^{28}\) The BDE calculation used \( \text{O}_2 \) in its \( ^3\Sigma_g^- \) (\( ^1\text{B}_1 \) in \( \text{D}_{2h} \) symmetry) ground state and the \( \text{O} \) atom in its \( ^3\text{P} \) (\( ^3\text{B}_1 \) in \( \text{D}_{2h} \) symmetry) ground state. For more information, please see Appendix A.
hybrid DFT methods, establishing the validity of our model for LaFeO₃. In section 3.4, we discuss the oxygen defect chemistry of LaFeO₃. In section 3.5, we address oxygen migration in LaFeO₃ and calculate diffusion coefficients. Although we obtain reasonable results for some quantities in section 3.5, we find a significant deviation from experiment in our final Do calculation. Therefore, in section 3.6, we show how reevaluating the defect chemistry of LaFeO₃ explains the deviations found in section 3.5, leading to reasonable agreement between our calculated Do values and experiment. Finally, in section 3.7, we summarize our results and provide the key conclusions from the work in this chapter.

3.2 Computational Details for LaFeO₃

We employed three structural models to study LaFeO₃. First, an orthorhombic unit cell of LaFeO₃ (Figure 3.1a) corresponding to the experimental structure was used to validate the DFT+U model. Second, a pseudocubic 2 × 2 × 2 supercell of the simple perovskite unit cell containing 40 atoms (Figure 3.1b) was used to calculate the free energy of oxygen vacancy formation and the oxygen migration enthalpy. Previous studies have used the 40-atom cell to study oxygen vacancies in LaMO₃ (M=Cr,Mn,Fe,Co,Ni) perovskite materials.²¹,²² We constrained the lattice vectors of the second cell to remain cubic, but internal ionic relaxations were allowed. This model successfully captures the known cooperative tilting of the FeO₆ octahedra (Figure 3.1b). Finally, a 160-atom supercell (Figure 3.1c) was used to compute oxygen and lanthanum vacancy formation energies. These defect formation energies were converged to 0.03 eV when compared to a larger calculation containing 320 atoms. The vacancy-vacancy distances were ~7.9 Å in the 40-atom pseudocubic cell and ~11.25 Å in the 160-atom cell.
Figure 3.1 Structural models used for LaFeO₃: (a) orthorhombic unit cell, (b) pseudocubic cell, and (c) 160-atom supercell. Color designations: Sr (green), Fe (brown), O (red).

Our spin-polarized DFT calculations used both the local density approximation (LDA) and the GGA to describe electron exchange and correlation. To correct for self-interaction error, our DFT+U calculations employed $U_{\text{eff}}=4.3$ eV for Fe$^{3+}$ from Mosey et al.\textsuperscript{29} originally determined from first-principles for Fe$_2$O$_3$. We also tested the far more expensive Heyd, Scuseria, and Ernzerhof (HSE) hybrid functional, which explicitly includes exact exchange.\textsuperscript{30,31} Interactions of the nuclei and frozen core electrons with the valence electrons were modeled using the PAW method\textsuperscript{23} where the PAW potentials were taken from the VASP library\textsuperscript{24} for La ($5s^25p^66s^25d^1$ valence), Fe ($4s^23d^6$ valence) and ‘standard’ O ($2s^22p^4$ valence). We used $4 \times 4 \times 3$, $4 \times 4 \times 4$, and $2 \times 2 \times 2$ Monkhorst-Pack\textsuperscript{32} k-point meshes for the orthorhombic (20-atom), pseudocubic (40-atom), and 160-atom supercells, respectively. The denser k-point sampling used in the 40-atom supercell (compared to the orthorhombic unit cell) reflects the fact that there needed to be consistency in the k-point sampling for LaFeO₃ and La$_{1-x}$Sr$_x$FeO₃ ($x=0.25$ and 0.50). The
latter materials required denser k-point sampling in order to obtain proper electronic structures. The planewave basis was cut off at a kinetic energy of 750 eV. These parameters converge the total energies to within 5 meV/formula unit. Relaxations were performed with Gaussian smearing ($\sigma = 0.05$ eV), and we refined the final energies using the tetrahedron method with Blöchl corrections. The overall magnetism was fixed at 1 $\mu_B$ when $V_{La}$ is present and 0 $\mu_B$ without $V_{La}$. The migration pathway was obtained using the climbing image nudged elastic band (CINEB) method as implemented in the VASP transition state theory tools from the University of Texas. Vibrational frequencies were obtained by constructing the Hessian matrix from finite displacements (0.02 Å) of all atoms around the equilibrium oxygen vacancy geometry and the transition state geometry in the 40-atom supercell.

3.3 Bulk Properties and Electronic Structure of LaFeO$_3$

We first determine the most appropriate electronic structure method for treating LaFeO$_3$ using the orthorhombic unit cell (Figure 1a). Table 3.1 compares structural, electronic, and magnetic properties for antiferromagnetic LaFeO$_3$ calculated with various DFT, DFT+U, and hybrid DFT functionals. Notably, pure DFT-LDA incorrectly predicts a metallic structure for LaFeO$_3$ while pure DFT-GGA predicts a gap for LaFeO$_3$. However, pure DFT-GGA significantly underestimates the gap and Fe magnetic moments. These errors likely arise from electron self-interaction inherent in pure density functionals that can be ameliorated with DFT+U; indeed, LDA+U and GGA+U give more accurate gaps and magnetic moments. For completeness, we tested the more expensive HSE hybrid functional with a calculation at the GGA+U geometry. The magnetic moment from the HSE calculation agreed with the DFT+U calculation;
however, HSE gave an eigenvalue gap far in excess of the experimental optical gap.

From this, we conclude that DFT+U theory provides a sufficient description of LaFeO₃.

Table 3.1. Experimental and calculated\textsuperscript{a} lattice constants (a, b, c), axial and equatorial Fe-O bond lengths (r\textsubscript{z} and r\textsubscript{xy}, respectively), axial and equatorial O-Fe-O bond angles (\(\alpha\textsubscript{z}\) and \(\alpha\textsubscript{xy}\), respectively), bulk modulus (B\textsubscript{0}), eigenvalue gap (E\textsubscript{g}) and Fe magnetic moment (\(\mu\textsubscript{Fe}\)) for orthorhombic LaFeO₃.

<table>
<thead>
<tr>
<th>Property</th>
<th>Experiment</th>
<th>LDA</th>
<th>LDA+U</th>
<th>GGA</th>
<th>GGA+U</th>
<th>HSE\textsuperscript{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>a / Å</td>
<td>5.553\textsuperscript{b}</td>
<td>5.352</td>
<td>5.462</td>
<td>5.556</td>
<td>5.572</td>
<td>----</td>
</tr>
<tr>
<td>b / Å</td>
<td>5.563\textsuperscript{b}</td>
<td>5.273</td>
<td>5.472</td>
<td>5.653</td>
<td>5.627</td>
<td>----</td>
</tr>
<tr>
<td>c / Å</td>
<td>7.862\textsuperscript{b}</td>
<td>7.509</td>
<td>7.711</td>
<td>7.885</td>
<td>7.901</td>
<td>----</td>
</tr>
<tr>
<td>r\textsubscript{z} / Å</td>
<td>2.009\textsuperscript{b}</td>
<td>1.905</td>
<td>1.971</td>
<td>2.025</td>
<td>2.028</td>
<td>----</td>
</tr>
<tr>
<td>r\textsubscript{xy} / Å</td>
<td>2.007\textsuperscript{b}</td>
<td>1.903</td>
<td>1.976</td>
<td>2.046</td>
<td>2.035</td>
<td>----</td>
</tr>
<tr>
<td>(\alpha\textsubscript{z}) / °</td>
<td>156.32\textsuperscript{b}</td>
<td>160.21</td>
<td>155.99</td>
<td>153.54</td>
<td>153.80</td>
<td>----</td>
</tr>
<tr>
<td>(\alpha\textsubscript{xy}) / °</td>
<td>157.22\textsuperscript{b}</td>
<td>161.89</td>
<td>157.01</td>
<td>153.72</td>
<td>154.69</td>
<td>----</td>
</tr>
<tr>
<td>B\textsubscript{0} / GPa</td>
<td>----</td>
<td>206</td>
<td>188</td>
<td>155</td>
<td>157</td>
<td>----</td>
</tr>
<tr>
<td>E\textsubscript{g} / eV</td>
<td>2.1\textsuperscript{c}</td>
<td>Metal</td>
<td>2.31</td>
<td>0.75</td>
<td>2.53</td>
<td>3.63</td>
</tr>
<tr>
<td>(\mu\textsubscript{Fe}) / (\mu\textsubscript{B})</td>
<td>4.6 ± 0.2\textsuperscript{d}</td>
<td>0.78-0.89</td>
<td>4.1</td>
<td>3.7</td>
<td>4.2</td>
<td>4.1</td>
</tr>
</tbody>
</table>

[a] All DFT+U calculations were performed with an \textit{ab initio}-obtained U\textsubscript{eff} = 4.3 eV.
[b] Ref 4 (Room temperature).
[c] Ref 6 (Optical gap).
[d] Ref 7.
[e] DFT-HSE single point calculation performed at the GGA+U geometry.

Compared to LDA+U, GGA+U results give better lattice vectors and Fe-O bond lengths, all of which deviate from experiment by no more than 1.6%. Previously, Shein \textit{et al.}\textsuperscript{20} reported a bulk modulus of \(~198\) GPa for LaFeO₃ calculated with LDA+U with U\textsubscript{eff} = 5.4 eV chosen to reproduce the experimental band gap and magnetic moment in LaFeO₃.\textsuperscript{19}
Our LDA+U value of 188 GPa, calculated with the \textit{ab initio} $U_{\text{eff}} = 4.3$ eV agrees well with their calculations, while our GGA+U value was 157 GPa. We expect the actual bulk modulus lies between these values, but to the best of our knowledge, experimental measurements are not available to confirm this expectation.

For the different functionals/methods discussed above, the projected density of states (PDOS, Figure 3.2) for LaFeO$_3$ clearly illustrate why we must address self-interaction error. The DFT-LDA density of states is metallic (with states crossing the Fermi level), indicating that this functional fails catastrophically for LaFeO$_3$. The DFT-GGA performs better, giving a small-gap semiconductor. However, the LDA or GGA functionals alone are sufficient to describe LaFeO$_3$. When we correct for self-interaction error using DFT+U calculations, we obtain results which show better agreement with experiment (e.g., Fe magnetic moments) and that reflect our chemical intuition about the Fe$^{3+}$ ion. Specifically, the PDOS from the LDA+U and GGA+U calculations show that the Fe$^{3+}$ ion is high spin (essentially no Fe 3$d$ majority states above the Fermi level), although hybridization between O 2$p$ and Fe 3$d$ states leads to some occupied states with partial Fe 3$d$ character. This hybridization is characteristic of partially covalent bonding between the Fe and O ions, resulting in Fe magnetic moments lower than the full high spin Fe$^{3+}$ value of $\mu_{\text{Fe}} = 5.0$ $\mu_B$ (actual value $4.6 \pm 0.2$ $\mu_B$ from experiment$^7$). The partially covalent character of the Fe-O interactions arises due to the unoccupied minority spin $e_g$ states on the Fe ions overlapping with the occupied 2$p$ orbitals on the O ions. The Fe-O overlap leads to averaging of the Fe 3$d$ $e_g$ spins (therefore occupying both majority and minority spin channels), as expected in covalent bonds with singlet spin couplings.
Figure 3.2. Projected densities of states for stoichiometric LaFeO$_3$ using (top) LDA and GGA and (bottom) LDA+U and GGA+U. Positive PDOS gives the majority spin states, while negative PDOS gives the minority spin states. The dotted line indicates the Fermi level, below which the occupied and above which the states are unoccupied. Color designations: O 2$p$ states (red) and Fe 3$d$ states (black).

On the basis of the results presented, we will confine ourselves to the DFT+U method with the GGA functional for the remainder of our discussion on LaFeO$_3$. We justify this choice on the basis of the agreement between theory and experiment for GGA+U calculations for both structural and electronic properties.
3.4 Oxygen Vacancy Formation in LaFeO₃

The energy cost for oxygen vacancy formation determines the nonstoichiometry of LaFeO₃. We compute this energy by comparing the energy of the supercell with an oxygen vacancy (a neutral oxygen atom is removed) to the same cell without an oxygen vacancy (referenced to half the energy of a gas phase O₂ molecule in its triplet ground state). The vacancy concentrations are 1/24 (4.2%, δ=0.125) and 1/96 (1.0%, δ=0.03125) in the pseudocubic (40-atom) and sqs (160-atom) supercells, respectively. These vacancy concentrations exceed the experimental range for LaFeO₃ (0.008-0.01%, T=900-1200°C),³⁸ but reaching that tiny concentration is cost prohibitive. We examine the trend as cell size increases to see if we have reached the limit where the vacancies no longer interact as a means to model the limit of ultralow vacancy concentration; the values shown below are converged to within 0.03 eV, as mentioned earlier.

The simplest approximation of the vacancy formation enthalpy (∆H_f,vac) uses only electronic energies and neglects thermal and vibrational effects:

\[
\Delta E_{f,\text{vac}} = E_{\text{defective}} - E_{\text{perfect}} + \frac{1}{2}E_{O_2}
\]  

(3.3)

Approximating ∆H_f,vac at absolute zero includes the zero point energy (ZPE) contributions

\[
\Delta H_{f,\text{vac}}(0) = \Delta E_{f,\text{vac}} + \sum_{i=1}^{3(N-1)-3} \frac{1}{2}h\nu_i,\text{defective} - \sum_{j=1}^{3N-3} \frac{1}{2}h\nu_j,\text{perfect} + \frac{1}{2}\left(\frac{1}{2}h\nu_{O_2}\right)
\]

(3.4)

where h is Planck’s constant and the ν’s are vibrational frequencies calculated within the harmonic oscillator (H.O.) approximation and N is the number of atoms in the perfect supercell. Approximating ∆H_f,vac at finite temperature involves integrating the heat
capacities \( (C_p) \) from absolute zero to the temperature of interest. \( C_p \) values for the solids (the sums in Equation 5) are calculated using the H.O. approximation for vibrational contributions while \( C_p \) for \( O_2 \) also includes effects from the rigid-rotor and ideal gas approximations for vibrational, rotational, and translational contributions.\(^{39}\) Because the PV contributions to enthalpy for solids should be negligible, we assume that the internal energy of each solid is equivalent to its enthalpy, while the enthalpy of gas phase \( O_2 \) includes the PV term via its constant pressure heat capacity.

\[
\Delta H_{f,vac}(T) = \Delta H_{f,vac}(0) + \sum_{i=1}^{3(N-1)-3} \left( \frac{h \nu_{i,\text{defective}}}{k_B T} \right) - \sum_{j=1}^{3N-3} \left( \frac{h \nu_{j,\text{perfect}}}{k_B T} \right) + \frac{1}{2} \left( \int_0^T C_{p,O_2}(T') dT' \right) \tag{3.5}
\]

Calculating the free energy of oxygen vacancy formation \( (\Delta G_{f,vac}) \) requires the entropy of the solids and \( O_2 \) as a function of temperature.

\[
\Delta G_{f,vac}(T) = \Delta H_{f,vac}(T) - T \Delta S_{f,vac}(T) \tag{3.6}
\]

\[
\Delta S_{f,vac}(T) = S_{\text{vib,defective}}(T) - S_{\text{vib,perfect}}(T) + \frac{1}{2} S_{O_2}(T) \tag{3.7}
\]

Gryaznov et al. showed that including vibrational effects of the solids can significantly impact oxygen vacancy formation free energies in LSCF.\(^{40}\) We express the vibrational enthalpy and entropy as the sum of contributions from harmonic oscillators with the \( \Gamma \)-point phonon frequencies of the perfect and defective crystals.\(^{41}\) We computed the vibrational frequencies for the entire 40-atom supercell and found that all frequencies were real except for the three acoustic modes which were essentially zero. Sampling the Brillouin zone (BZ) beyond the \( \Gamma \)-point resulted in unphysical imaginary frequencies in some regions of the BZ. We attribute this issue to approximating the Hessian matrix using finite differences of forces and to the constraint that the lattice vectors remain cubic. To
avoid issues arising from these unphysical imaginary frequencies, we only use the Γ-point phonon frequencies in our LaFeO₃ calculations.

<table>
<thead>
<tr>
<th></th>
<th>Computed (this work)</th>
<th>Experimental (ref. 38)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE_{f,vac} / eV</td>
<td>4.06</td>
<td>5.1 ± 1.1[a]</td>
</tr>
<tr>
<td>ΔH_{f,vac}(T=0 K) / eV</td>
<td>4.02</td>
<td></td>
</tr>
<tr>
<td>ΔH_{f,vac}(T=600°C) / eV</td>
<td>3.93</td>
<td></td>
</tr>
<tr>
<td>ΔH_{f,vac}(T=700°C) / eV</td>
<td>3.92</td>
<td></td>
</tr>
<tr>
<td>ΔH_{f,vac}(T=800°C) / eV</td>
<td>3.91</td>
<td>5.1 ± 1.1[a]</td>
</tr>
<tr>
<td>ΔH_{f,vac}(T=900°C) / eV</td>
<td>3.90</td>
<td></td>
</tr>
<tr>
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<td>3.90</td>
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</tr>
<tr>
<td>ΔG_{f,vac}(T=600°C) / eV</td>
<td>3.07</td>
<td>3.9 ± 1.1</td>
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<td>ΔG_{f,vac}(T=700°C) / eV</td>
<td>2.97</td>
<td>3.8 ± 1.1</td>
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<tr>
<td>ΔG_{f,vac}(T=800°C) / eV</td>
<td>2.87</td>
<td>3.6 ± 1.1</td>
</tr>
<tr>
<td>ΔG_{f,vac}(T=900°C) / eV</td>
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<td>3.5 ± 1.1</td>
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<tr>
<td>ΔG_{f,vac}(T=1000°C) / eV</td>
<td>2.68</td>
<td>3.3 ± 1.1</td>
</tr>
</tbody>
</table>

[a] Experimental enthalpy determined from the van ’t Hoff equation over the temperature range 600-1200°C

We computed ΔH_{f,vac} and ΔG_{f,vac} for an oxygen vacancy in LaFeO₃ using the 40- and 160-atom supercells (figure 3.1 b and c, respectively). ΔE_{f,vac}, ΔH_{f,vac}(T=0 K), ΔH_{f,vac}(T), and ΔG_{f,vac}(T) at temperatures ranging from 600°C to 1000°C are given in Table 3.2. The experimental data are taken from reference 38 for the reaction given in Equation 3.8 (corresponding to the reduction of two Fe ions from Fe³⁺ to Fe²⁺).

$$2\text{Fe}^{3+} + \text{O}^{2-} \rightarrow 2\text{Fe}^{2+} + V^{\bullet\bullet} + \frac{1}{2}\text{O}_2(g) \quad (3.8)$$

Our calculations predict reaction energies (enthalpies and free energies) 0.6-1.2 eV below experiment. We predict vacancy formation energetics that lie below, or just inside, the
lower bound for the experimental values (taking into account the 2σ error bars given in reference 38). The difference between the computed and experimental reaction energies comes in part from the known overbinding of the O₂ molecule by DFT-GGA; this is the appropriate reference state for our GGA+U calculations because the U parameter is only applied to the Fe d electrons. Correcting for the DFT-GGA error in the O₂ bond energy raises our reaction energies by 0.42 eV (see Appendix A). This correction brings our results into better agreement with experiment; however, the difference between our calculated values and experiment remains large. Fortunately, we reproduce the experimental trend of increased temperature significantly reducing ∆G\textsubscript{f,vac}. Chemical intuition tells us that the entropic contribution to ∆G\textsubscript{f,vac} should be large because each mole of vacancies liberates 0.5 moles of O₂ vapor. Indeed, we find that the O₂ molecule is almost entirely responsible for the thermal variation in ∆G\textsubscript{f,vac} (the solid vibrations contribute a maximum of 0.1 eV to ∆G\textsubscript{f,vac} at 1000°C).

In LaFeO₃, creating an oxygen vacancy leads to reduced magnetic moments and Bader charges\textsuperscript{42} on the two Fe ions adjacent to the vacancy (Table 3.3). These results show that the two electrons from the oxygen vacancy reduce the adjacent Fe ions (from Fe\textsuperscript{3+} to Fe\textsuperscript{2+}) by localizing in their d manifold (Figure 3.3). Reducing high spin Fe\textsuperscript{3+} to Fe\textsuperscript{2+} requires that the added electron occupy a minority spin d orbital. As no other minority spin d electrons are present on the Fe ion, no gain in d-d exchange energy exists to offset the additional Coulomb repulsion associated with adding another electron to the d manifold, giving rise to the high vacancy formation energy\textsuperscript{22}. 

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Table 3.3. Magnetic moments ($\mu_B$) and Bader charges ($e$) for LaFeO$_3$ with and without an oxygen vacancy (VO$^{**}$) in the pseudocubic (40-atom) cell.$^{[a,b,c]}$

<table>
<thead>
<tr>
<th></th>
<th>without VO$^{**}$</th>
<th>with VO$^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{Fe}$</td>
<td>4.16</td>
<td>4.17 ± 0.01</td>
</tr>
<tr>
<td>$\mu_{Fe^*}$</td>
<td>----</td>
<td>3.59</td>
</tr>
<tr>
<td>$q_{Fe}$</td>
<td>1.70</td>
<td>1.69 ± 0.01</td>
</tr>
<tr>
<td>$q_{Fe^*}$</td>
<td>----</td>
<td>1.25</td>
</tr>
<tr>
<td>$q_{La}$</td>
<td>2.08</td>
<td>2.06 ± 0.02</td>
</tr>
<tr>
<td>$q_{Sr}$</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>$q_{O^-}$</td>
<td>-1.26</td>
<td>-1.27 ± 0.01</td>
</tr>
</tbody>
</table>

[a] Uncertainties give the range of calculated values (for different defect configurations) relative to the calculated mean.

[b] Fe* indicates the iron ions adjacent to the oxygen vacancy.

[c] VO$^{**}$ (in Kröger-Vink notation)$^1$ denotes an oxygen vacancy where a neutral oxygen atom has been removed.

Figure 3.3. (a) Electron density difference plot for oxygen vacancy formation in LaFeO$_3$. Isosurfaces at +0.075 (yellow) and -0.075 (blue) $e^{-} \text{Å}^{-3}$ (+/- 12.5% of the average charge density). Fe atoms lie in the center of the two yellow isosurfaces, while an O atom lies inside the blue isosurface. Color designations: Sr (green), Fe (brown), O (red).

(b) Schematic representation of the electronic rearrangement upon vacancy formation in LaFeO$_3$. 

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The preceding discussion regarding electron rearrangement upon Vo” formation relates to two fundamental concepts that enable us to understand trends in Vo” formation energies ($\Delta E_{f,vac}$) in LaMO$_3$ materials (where M is Cr, Mn, Fe, Co). This comparative study used the pseudocubic cell (Figure 3.1b) for all calculations. Our results reproduced a non-monotonic trend in $\Delta E_{f,vac}$ across the period (Figure 3.4). The behavior in each material was similar: forming Vo” caused the reduction of two neighboring transition metal ions. The observed trend can be explained in terms of two basic observables: the M$^{2+} \rightarrow$ M$^{3+}$ ionization energy and the M-O bond strength. The third ionization potential of the metal ion gives a qualitative measure of the expected energy gained by reducing the M$^{3+}$ ion to M$^{2+}$ (higher ionization potential corresponds to greater energy gain upon reduction). The M-O bond strength, e.g., taken from M-O and M$^+$-O molecules in the gas phase, gives a measure of how much energy will be required to break the M-O bonds when forming an oxygen vacancy.

Vo” formation involves breaking two M-O bonds and reducing two M$^{3+}$ ions to M$^{2+}$. These observables, though measured on bare ions or gas phase molecules, provide key descriptors for $\Delta E_{f,vac}$. Lower $\Delta E_{f,vac}$ correlates with higher M$^{2+} \rightarrow$ M$^{3+}$ ionization potential and weaker M-O bonds (figure 3.4). Mn and Co have the weakest M-O bond strengths and the highest ionization energies. Although LaMnO$_3$ and LaCoO$_3$ are expected to have similar $\Delta E_{f,vac}$ values, the magnetic flexibility of the Co$^{3+}$ ion gives LaCoO$_3$ its lower vacancy formation energy (see Chapter 4).
Figure 3.4. (top) Oxygen vacancy formation energies ($\Delta E_{f,vac}$) from GGA+U (blue line) and HSE (green line) calculations and experiment\textsuperscript{38,43,44} (gray line), (middle) M$^{2+}$$\rightarrow$M$^{3+}$ ionization potentials (IP)$^{45}$ (red line), and (bottom) M-O bond dissociation energies (BDEs)$^{46}$ (black line) for M=Cr, Mn, Fe, Co. $\Delta E_{f,vac}$ averaged over low spin and high spin states for Co. All values in eV.

Based on the M$^{2+}$$\rightarrow$M$^{3+}$ ionization energies, we would expect LaCrO$_3$ and LaFeO$_3$ to have the highest $\Delta E_{f,vac}$, and indeed that is true. However, LaCrO$_3$ has an even higher
$\Delta E_{f, \text{vac}}$ than LaFeO$_3$ primarily because Cr-O bonds are stronger than Mn-O, Fe-O, or Co-O bonds. This results from Cr$^{3+}$ having empty $e_g$ orbitals into which the O$^{2-}$ ions can donate electron density, forming donor-acceptor bonds. Fe$^{3+}$ has two electrons in the $e_g$ orbitals that interact repulsively with the O$^{2-}$ ions leading to lower Fe-O cohesion in the LaMO$_3$ crystal compared to Cr, but higher cohesion than Mn or Co. Therefore, the two observables we have discussed provide guidelines for rationally designing LaMO$_3$-based cathode materials. First, minimizing the strength of the M-O bonds will make VO$^{\bullet\bullet}$ formation less costly and will lead to higher VO$^{\bullet\bullet}$ concentrations. Second, maximizing the M$^{2+} \rightarrow$ M$^{3+}$ ionization potential ensures that the greatest energy gain from the localized reduction associated with VO$^{\bullet\bullet}$ formation. The latter point is associated with maximizing the increase in $d$-$d$ exchange interactions upon reduction. For LaFeO$_3$, no new exchange interactions are introduced upon reduction (Figure 3.3b), which explains the low Fe$^{2+} \rightarrow$ Fe$^{3+}$ ionization energy. Additionally, Fe-O bonds are stronger than Mn-O or Co-O bonds, which makes oxygen vacancy formation even more costly in LaFeO$_3$.

We compute $\Delta H_{f, \text{vac}}$ and $\Delta G_{f, \text{vac}}$ values with the hope of obtaining oxygen vacancy concentrations ($C_v$) in reasonable agreement with experiment. On the basis of our results, we expect to predict $C_v$ values in excess of experiment. Computing $C_v$ requires solving for the equilibrium governed by $\Delta G_{f, \text{vac}}$ (equation 3.9).

$$K_9 = e^{-\Delta G_{f, \text{vac}}^{0}/k_B T} = \frac{C_v P_{O_2}^{1/2}}{(1-C_v)(1-2C_v)} \approx C_v P_{O_2}^{1/2}$$  \hspace{1cm} (3.9)

The partial pressure of O$_2$ enters equation 3.9 in atmospheres (atm) because $\Delta G_{f, \text{vac}}^{0}$ is computed for 1 atm of O$_2$ (g). The approximation which allows us to obtain the final expression in equation 3.9 is valid only if the vacancy concentration is negligibly small.
When we compute $C_v$, we find that the approximation is justified (the computed $C_v$ remains below $1 \times 10^{-6}$), and we predict vacancy concentrations far lower than experiment. We will explain the origin of this discrepancy (section 3.6); however, we must first address oxygen migration in LaFeO$_3$.

**Figure 3.4.** Calculated and experimental$^8$ oxygen vacancy concentrations (mole fraction) over the range of experimental temperatures. Experiments in reference 8 were carried out between 600-1200°C, but experimental data was only tabulated between 900-1100°C. Computed values and experimental values at $P_{O_2} = 53$ torr. Experimental data (red circles) and computed data (blue line with triangles).
3.5 Oxygen Migration in LaFeO$_3$

Oxygen migration will lead to long-range diffusion once a significant concentration of oxygen vacancies exists in LaFeO$_3$. We obtained the minimum energy pathway for oxygen migration in LaFeO$_3$ using the CINEB method. We confirm the curved migration pathway (Figure 3.5a) previously predicted by Jones and Islam using classical potentials.$^{10}$ Our calculated oxygen migration barrier ($\Delta H_{\text{mig}}$ with $x_{\text{Sr}}=0$) is 0.79 eV (Figure 3.5b), agreeing nearly perfectly with the measured migration barrier of 0.77 eV obtained from oxygen tracer diffusion measurements$^{47}$ while falling below the value of 1.10 eV obtained from conductivity relaxation experiments.$^{48}$ Our study attempts to model the self-diffusion coefficient (D$_0$) for LaFeO$_3$ which most closely resembles the tracer diffusion coefficient (D$_0^*$) and is further from the chemical diffusion (D$_{\text{chem}}$) coefficient obtained from conductivity relaxation experiments. Therefore, our calculated migration barrier is in good agreement with experiment when compared against the experimental results of greatest similarity. Our results agree well with the Mastrikov et al.’s reported migration barrier of 0.75 eV;$^{15}$ however, their DFT-GGA analysis utilized ferromagnetic LaFeO$_3$ and the less-accurate ‘soft’ oxygen PAW potential available in VASP. The similarity in the computed barriers, in spite of several methodological differences indicates that steric/electrostatic effects play a dominant role in determining the migration barrier. While ref. 15 indicates negligible charge transfer from the migrating oxygen ion to the Fe ion at the center of the migration pathway, we find a different charge transfer accompanies oxygen diffusion in LaFeO$_3$. As mentioned earlier, oxygen migration involves hopping from an occupied site into an adjacent vacant site. These sites are each coordinated to two Fe ions, and one of these Fe ions is adjacent to
both the initial and final sites. The magnetic moment of the Fe ion proximal to the
migration (FeA, which is coordinated to the vacancy in both the initial and final states)
remains low (relative to the bulk $\mu_{Fe}$) throughout the migration process. The two other Fe
ions are coordinated to the vacant site in the initial state (FeB) or the final state (FeC).
Before migration, FeA and FeB have lower magnetic moments arising from the adjacent
oxygen vacancy while FeC shows a bulk-like magnetic moment. After migration, FeA and
FeC have lower magnetic moments while FeB now has a bulk-like magnetic moment.
During migration, there is an abrupt switch in the magnetic moments of FeB and FeC
corresponding to an electron transferring from FeB to FeC. An ionic picture explains the
origin of this electron transfer. The vacancy lies between FeA and FeB in the initial state
and FeA and FeC in the final state. In each state, the ions adjacent to the vacancy are in the
+2 oxidation state. Thus, FeA remains Fe$^{2+}$ throughout the migration process. FeB starts as
Fe$^{2+}$ and becomes Fe$^{3+}$ while FeC undergoes the reverse transformation. Since the total
number of electrons in the cell remains unchanged, an electron must transfer from FeB to
FeC during the migration process. The potential energy surface along the migration
pathway is slightly asymmetric because the electron transfer happens after the transition
state. This means that the transition state more closely resembles the $\xi=0.25$ image while
the $\xi=0.75$ image has a different magnetic structure. Since the $\xi=0.75$ image is linked to
the transition state by a spring, it is pulled to a higher energy on account of the abrupt
magnetic transition that occurs.
Following previous work in our group,\textsuperscript{49,50} we use transition state theory to express $D_v$ in terms of the activation barrier ($\Delta H_{\text{mig}}=0.79$ eV), the jump length ($a=2.96$ Å), the attempt frequency ($\nu_0=3.66\times10^{12}$ Hz) and the entropy of activation ($\Delta S^\ddagger=-2.71k_B$ at 700°C) where $k_B$ is Boltzmann’s constant (Equation 3.10).

\[
D_v = \frac{1}{6} \nu_0 a^2 e^{-\Delta S^\ddagger / k_B} e^{-\Delta H_{\text{mig}} / k_B T}
\]  

(3.10)

The factor of one sixth arises from diffusion in three dimensions. Our computed values of $D_v$ agree extremely well with experimental data (Figure 3.6) indicating that we have properly modeled the migration process. However, our computed oxygen diffusion coefficients will show significant deviation from experiment because we cannot (thus far) accurately predict the oxygen vacancy concentration. In the following sections, we will explain the origin of this discrepancy.
3.6 Lanthanum Vacancies in LaFeO$_3$

Despite quantitative agreement between experimental values and the computed reaction enthalpies and migration barriers, we found the predicted LaFeO$_3$ $V_0^{**}$ concentrations were orders of magnitude below the experimental values (vide supra). Therefore, some additional factor not yet considered is necessary to account for the experimentally observed $V_0^{**}$ concentrations. Vibrational and other thermal effects do not sufficiently explain the disagreement, as they were part of our initial calculations. Accounting for the known overbinding of the O$_2$ molecule by density functional theory (DFT) only increases the deviation from experiment. However, as mentioned above,
samples of LaFeO$_3$ tend to be slightly substoichiometric in La,$^{38}$ which had not been accounted for in previous modeling and could be responsible for the discrepancy.

\( \nabla_{\text{La}}^{++/} \) formation free energies (\( \Delta G_{f,\text{vac},\text{La}} \), Equation 3.11) involve the free energy difference between defective (\( G_{\text{defective}} \)) and perfect (\( G_{\text{perfect}} \)) crystals plus a lanthanum atom (referenced to the lanthanum chemical potential, \( \mu_{\text{La}} \), that depends on the external conditions).

\[
\Delta G_{f,\text{vac},\text{La}} = G_{\text{defective}} - G_{\text{perfect}} + \mu_{\text{La}} \tag{3.11}
\]

We propose two different limits for calculating \( \mu_{\text{La}} \). Under oxygen poor conditions (e.g., ultra-high vacuum experiments), La metal provides the reference for \( \mu_{\text{La}} \). Oxygen rich conditions require referencing \( \mu_{\text{La}} \) using La$_2$O$_3$ and the free energy per molecule of O$_2$. See Appendix A for reference DFT calculations of La metal and La$_2$O$_3$. These two limits, respectively, correspond to the defect formation reactions shown in Equations 3.12 and 3.13 in which \( \La^{x}_{\text{La}} \) represents a lanthanum ion in its normal, +3, oxidation state in the host material.

\[
\La^{x}_{\text{La}} \rightarrow \nabla_{\text{La}}^{++/} + 3h^* + \text{La (metal)} \quad \text{[oxygen poor]} \tag{3.12}
\]

\[
\La^{x}_{\text{La}} + \frac{3}{4}O_2(g) \rightarrow \nabla_{\text{La}}^{++/} + 3h^* + \frac{1}{2}\La_2O_3(s) \quad \text{[oxygen rich]} \tag{3.13}
\]

For the purpose of calculating \( \Delta G_{f,\text{vac},\text{La}} \), we neglect the vibrational contributions from solids. We previously showed that solid vibrations contribute negligibly to the oxygen vacancy formation free energy (\( \Delta G_{f,\text{vac},O} \)) in LaFeO$_3$ (\textit{vide supra}).$^{51}$ We account for vibrational, rotational, and translational contributions from the O$_2$ molecule through the harmonic oscillator, rigid-rotor, and ideal gas approximations (see Chapter 2). Further analysis of possible coupling between oxygen transport and low-energy, anharmonic
crystal modes (such as octahedral rotations) requires accurate, detailed dynamics simulations which are beyond the scope of this study. We believe that the results obtained through including the most relevant thermal contributions (specifically, the thermal variation of the chemical potential arising from the large entropy of a gas phase species) provide a sufficiently accurate description of the LaFeO$_3$ system. We find that, at 700°C, the free energies for reactions 3.12 and 3.13 are 11.4 eV and 4.33 eV, respectively. Since the SOFC cathode operates under oxygen rich conditions, we confine our analysis of $V_{\text{La}^{III}}$ formation to Equation 3.13 for the remainder of this discussion. $V_{\text{La}^{III}}$ formation is more endoergic than $V_{\text{O}^{II}}$ formation in stoichiometric LaFeO$_3$ (3.04 eV at 700°C).‡‡ While this seems to validate neglecting $V_{\text{La}^{III}}$, we will prove this assumption wrong for LaFeO$_3$.

We now consider the effect of $V_{\text{La}^{III}}$ on the electronic structure of LaFeO$_3$. One $V_{\text{La}^{III}}$ (per 32 formula units) introduces three hole states which extend just above the Fermi energy (Figure 3.7). The modeled concentration of $V_{\text{La}^{III}}$ (3.125%) exceeds the estimated experimental $V_{\text{La}^{III}}$ concentration (approximately 0.07%). However, this concentration yields $V_{\text{La}^{III}}$ formation energies within 0.03 eV of a larger calculation containing 320-atoms ($[V_{\text{La}^{III}}]=1.5625\%$). This indicates that our model is converged with respect to the limit of infinitely dilute $V_{\text{La}^{III}}$. Bader charge analysis indicates that the iron ions retain their charge ($q_{\text{Fe}}=1.70$ with and without $V_{\text{La}^{III}}$) while the oxygen sublattice loses charge ($q_{\text{O}}=-1.24$ with $V_{\text{La}^{III}}$ vs. $q_{\text{O}}=-1.26$ without $V_{\text{La}^{III}}$). While the Bader charges for oxygen seem similar, the small difference adds up to 1.76 electrons (over the entire

‡‡ Readers may note that this value (3.04 eV) differs from the value of 2.97 eV for $\Delta G_{f,vac}(T=700^\circ C)$ in table 3.2. The difference is that the value in table 3.2 includes contributions from solid vibrations, whereas this value only includes thermal effects from the O$_2$ molecule. The small difference between these numbers validates our decision to neglect solid vibrations for the remainder of this chapter.
160-atom supercell), accounting for the majority of the Bader charge of the La ion before the V_{La///} is created (q_{La}=2.08 before V_{La///}). Therefore, the holes delocalize over the oxygen sublattice.

Figure 3.7. Projected density of states (PDOS) for LaFeO$_3$ with a lanthanum vacancy (1/32 La sites vacant). The inset plot shows the region around the Fermi level showing the mixed Fe 3$d$ O 2$p$ nature of the hole states (the states to the right of the dashed line). Fe 3$d$ states in black and O 2$p$ states in red.

The presence of holes in the lattice dramatically changes the defect chemistry of LaFeO$_3$. Without V_{La///}, we found$^{22,51}$ that V$_{O^-}$ formation involves reducing the adjacent Fe ions (Equation 3.9). However, charge compensation (Equation 3.14) between the electrons from V$_{O^-}$ and the holes from V_{La///} should result in a decrease in $\Delta G_{f,vac,O}$. 

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We find a significant reduction in $\Delta G_{\text{f,vac,O}}$ in the presence of $V_{\text{La}^{III}}$ ($\Delta G_{14} = -0.34$ eV compared to $\Delta G_9 = 3.04$ eV at 700°C, where the subscripts refer to the numbered equations above without the chapter prefix). $V_{O}^{**}$ is slightly more stable adjacent to $V_{\text{La}^{III}}$ compared to far away from $V_{\text{La}^{III}}$ (only 0.06 eV different at 700°C). This small energy difference provides thermodynamic evidence that $V_{\text{La}^{III}}$ do not strongly trap $V_{O}^{**}$. Our results show how $V_{\text{La}^{III}}$ promote faster oxygen diffusion by making $V_{O}^{**}$ formation energetically favorable without trapping $V_{O}^{**}$.

A full analysis of the defect chemistry of LaFeO$_3$ requires considering the equilibrium between each of the defect formation reactions in Equations 3.9, 3.13, and 3.14. The equilibrium constants can easily be computed from the free energies ($\Delta G^0(T)$) for each of these reactions. We express these constants in terms of the extents of the three reactions ($\xi_9$, $\xi_{13}$, and $\xi_{14}$) which are related to the concentrations of the different defects as described by Equation 3.9 (vide supra) and Equations 3.15 and 3.16. In these equations, $k_B$ is Boltzmann’s constant and $T$ is the absolute temperature.

$$K_{13} = e^\frac{-\Delta G_{13}}{k_B T} = \frac{[V_{\text{La}^{III}} h^*]^3}{(1-V_{\text{La}^{III}}) P_{O_2}^{3/4}} = \frac{\xi_{13} (3\xi_{13} - 2\xi_{14})^3}{(1-\xi_{13}) P_{O_2}^{3/4}}$$

$$K_{14} = e^\frac{-\Delta G_{14}}{k_B T} = \frac{[V_{O}^{**} P_{O_2}^{1/2}]^2}{h^* P_{O_2}} = \frac{\xi_{14} P_{O_2}^{1/2}}{(3\xi_{13} - 2\xi_{14})^2}$$

In these expressions, the concentrations are expressed in terms of occupancies (mole fractions) and the extents of reaction correspond to the numbered equations above. We solve for the extents of reaction using Mathematica$^{52}$ and reject solutions which fail to
meet the criteria that $0 \leq \xi_i \leq 1$ (i=9, 13, 14) and $3\xi_{13} - 2\xi_{14} > 0$ (which ensures that the hole concentration is positive). All $\Delta G^0$ values are calculated with $P_{O_2} = 1$ atm meaning that the $P_{O_2}$ values entering the expressions above are expressed in atmospheres.

**Figure 3.8.** Calculated and experimental\textsuperscript{8} oxygen vacancy concentrations (mole fraction) over the range of experimental temperatures. Experiments in ref. 8 were carried out between 600-1200°C, but experimental data was only tabulated between 900-1100°C. Computed values and experimental values at $P_{O_2} = 53$ torr. Experimental data (red circles), computed data considering V\textsubscript{La}/// (black line with squares), computed data neglecting V\textsubscript{La}/// (dashed blue line with triangles).

Comparing two calculations side-by-side shows that V\textsubscript{La}/// play a significant role in promoting V\textsubscript{O}** in LaFeO\textsubscript{3} (Figure 3.8). As shown above (Figure 3.6), neglecting V\textsubscript{La}/// leads to $C_v$ values orders of magnitude below those obtained experimentally. When V\textsubscript{La}/// contribute to the defect chemistry, the calculation involves solving the coupled equations 3-14 and 3-15. This leads to calculated $C_v$ in far better agreement with experiment. Our calculated values (black line, Figure 3.8) lie approximately one order of magnitude below
the experimental values; however, this represents a very substantial improvement over the values computed neglecting the $\text{V}_{\text{La}^{III}}$ contribution.

Having established significantly better quantitative agreement with experimental $\text{V}_{\text{O}^{\text{IV}}}$ concentrations, we can calculate oxygen diffusion coefficients. Our computed values of $D_v$ agree extremely well with experimental data (Figure 3.6) indicating that we have properly modeled the migration process. Since $\text{V}_{\text{La}^{III}}$ in reality exist in extremely low concentrations (less than ppm), the migration calculation was performed in the absence of $\text{V}_{\text{La}^{III}}$ (vide supra).

![Figure 3.9](image.png)

**Figure 3.9.** Computed and experimental oxygen diffusion coefficients ($D_0$). Experimental data (triangles and black lines), computed $D_0$ considering $\text{V}_{\text{La}^{III}}$ (dashed blue line with squares), computed $D_0$ neglecting $\text{V}_{\text{La}^{III}}$ (green line with triangles).

When we combine the $C_v$ values from above with the $D_v$ values, we obtain results that clearly affirm our assertion that $\text{V}_{\text{La}^{III}}$ play an integral role in increasing the oxygen
diffusivity of LaFeO₃. The Do values calculated without considering Vₖₓₓ differ from experiment by orders of magnitude whereas our values including the effects of Vₖₓₓ show significantly better agreement with experiment (Figure 3.9). From this graph, we can see that the small concentration of Vₖₓₓ (approximately 6.6×10⁻⁷ at 700°C) raises the oxygen diffusion coefficient by six orders of magnitude. This finding demonstrates that A-site substoichiometry can be deliberately used as an alternative strategy to p-type substitutions (e.g., Sr substituting for La) for increasing oxygen diffusivity in SOFC cathodes.

3.7 Conclusions

We have presented a complete GGA+U analysis of oxygen transport in LaFeO₃. We showed that the GGA+U method offers the best agreement with experiment for structural parameters and Fe magnetic moments when compared to other DFT-based methods. We demonstrated that oxygen vacancy formation in perfectly stoichiometric (La/Fe=1) LaFeO₃ requires reducing the two Fe sites adjacent to the vacancy. This process has a high endoergicity primarily because of increased intra-atomic electron-electron repulsion and the absence of additional on-site exchange interactions for the reducing electron (it becomes the only minority spin Fe 3d electron). We computed the minimum energy pathway for oxygen migration in LaFeO₃ and showed that we accurately predicted the oxygen migration barrier and vacancy diffusion coefficient (Dᵥ) for this material. However, our computed oxygen vacancy concentrations disagreed with experiment by orders of magnitude. To explain this discrepancy, we explored the role of lanthanum vacancies in changing the defect chemistry of LaFeO₃. We found that the holes
introduced by a lanthanum vacancy delocalize over the oxygen sublattice. These holes provided favorable charge compensation for the electrons released upon oxygen vacancy formation. When we combined the lanthanum and oxygen defect chemistries, coupled through the charge compensation process, we were able to compute oxygen vacancy concentrations and oxygen diffusion coefficients in good agreement with experiment.

This work clearly demonstrates the enormous impact of La vacancies in raising the oxygen vacancy concentration in LaFeO$_3$. This effect, in turn, increases the observed oxygen diffusion coefficient. Specifically, the La vacancies introduce holes that compensate the electrons released when an oxygen vacancy forms. This results in favorable oxygen vacancy formation free energies leading to orders of magnitude higher oxygen vacancy concentrations than would be expected if La vacancies were not present. This also indicates a methodological point that La vacancies must be accounted for when computing oxygen vacancy formation energies in stoichiometric materials. In cases where Sr substitution dramatically lowers the oxygen vacancy formation energy, then La vacancies in the pure material (no Sr substitutions) are likely to play a large role in enhancing the oxygen diffusivity. Our results also indicate that A-site substoichiometry offers a powerful way to increase the oxygen diffusivity.
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Chapter 4

Defect Chemistry and Oxygen Diffusion in LaCoO₃§§

4.1 Introduction

The previous chapter provided the first step of our description of the complex solid oxide fuel cell (SOFC) cathode material, La₁₋ₓSrₓCo₁₋ₓFeₓO₃ (LSCF). The second parent material of LSCF with the LaMO₃ form is LaCoO₃. LaFeO₃ provides a simple platform for modeling, because the magnetic interactions between Fe ions are strongly antiferromagnetic. In contrast, the magnetic interactions between Co³⁺ ions in LaCoO₃ bring a new level of complexity into the electronic structure analysis. Specifically, the Co³⁺ ions in LaCoO₃ exist (and likely coexist) in various magnetic configurations (vide infra). Hitherto, an insufficient, atomic-level understanding of the physical and chemical properties of LaCoO₃ has inhibited the rational design of LaCoO₃-based SOFC cathode materials. More importantly, the relationship between magnetism and oxygen transport in LaCoO₃ has remained largely unexplored.

Co³⁺ ions introduce complex magnetic behavior in LaCoO₃ by occupying octahedral sites surrounded by oxygen ions (the slight rhombohedral distortion is customarily neglected).¹ This crystal field splits the d orbitals into a triply-degenerate set of t₂g orbitals below a doubly-degenerate set of e_g orbitals. Combining the crystal field

splitting with the $3d^6$ valence configuration leads to three local spin states for $\text{Co}^{3+}$: low spin ($\text{LS}, t_{2g}^6 e_{g}^0$), intermediate spin ($\text{IS}, t_{2g}^5 e_{g}^1$), and high spin ($\text{HS}, t_{2g}^4 e_{g}^2$). The IS state should display a strong Jahn-Teller (JT) distortion that breaks the degeneracy of the $e_g$ orbitals. $\text{LaCoO}_3$ exhibits nonmagnetic behavior at low temperatures, so the $\text{Co}^{3+}$ ions remain in the LS spin state below 90 K.\textsuperscript{2,3} The material undergoes a nonmagnetic-to-paramagnetic transition below 100 K\textsuperscript{4} and an insulator-to-metal transition around 500 K.\textsuperscript{5–8} Disagreement arises regarding the spin state of the $\text{Co}^{3+}$ ions above the onset of the first transition. Some X-ray diffraction experiments\textsuperscript{9} suggest the existence of IS $\text{Co}^{3+}$ ions while other soft X-ray absorption and circular dichroism experiments\textsuperscript{10} indicate that a mixture of HS and LS $\text{Co}^{3+}$ ions coexist. Another X-ray absorption study finds a continuous LS to IS transition around 90 K.\textsuperscript{11} All of these interpretations are consistent with the observed magnetic susceptibility of $\text{LaCoO}_3$. The second transition from insulator to metal has been interpreted as a transition from localized to delocalized $e_g$ bands.\textsuperscript{2} Neutron diffraction data show that $\text{LaCoO}_3$ undergoes anomalous thermal expansion resulting from the magnetic transitions.\textsuperscript{12} Consensus regarding the $\text{Co}^{3+}$ spin state in $\text{LaCoO}_3$ above 90 K remains elusive.

Numerous theoretical studies have attempted to solidify consensus regarding the relevant spin states of the $\text{Co}^{3+}$ ions. Unfortunately, Kohn-Sham density functional theory (KS-DFT), within either the local density approximation (LDA) or generalized-gradient approximation (GGA) treatment of electron exchange and correlation, generally fails to properly describe LS $\text{LaCoO}_3$ (predicting metallic instead of insulating behavior).\textsuperscript{13,14} Therefore, many studies have employed the DFT+U method to investigate the electronic and magnetic structure of $\text{LaCoO}_3$.\textsuperscript{15–21} The DFT+U method requires a
parameter $U_{\text{eff}}=U-J$ that represents the difference between the spherically averaged Coulomb ($U$) and exchange ($J$) interactions for electrons of a specified angular momentum ($d$ electrons in this case) on the same site (each Co ion in this case). Knížek and coworkers, using a $U_{\text{eff}} = 5.4$ eV, showed that the IS state becomes favored over the low spin state in LaCoO$_3$ as the lattice expands. The same authors later chose $U_{\text{eff}} = 2.7$ eV to show that a mixed HS/LS state was more stable than the IS state. These contradictory results demonstrate that different $U_{\text{eff}}$ parameters lead to different conclusions. A more desirable first-principles description of LaCoO$_3$ requires an unbiased choice of $U_{\text{eff}}$, such as a $U_{\text{eff}}$ determined from ab initio calculations that exactly account for the Coulomb and exchange interactions between $d$ electrons on a single Co$^{3+}$ site. Multiple studies have employed $U_{\text{eff}}$ values derived from the linear-response method to study multiple spin configurations of LaCoO$_3$. Laref et al. used this approach to determine that $U_{\text{eff}}$ depends on the Co$^{3+}$ spin state with the values of $U_{\text{eff,LS}}=7.22$ eV, $U_{\text{eff,IS}}=7.05$ eV, and $U_{\text{eff,HS}}=6.65$ eV. They conclude that the first magnetic transition involves populating the IS state within a matrix of LS Co$^{3+}$ ions. A theoretically predicted low energy LS-IS transition agrees with earlier studies using large $U_{\text{eff}}$ values ($U_{\text{eff}} > 5$ eV) but contradicts the results obtained with lower $U_{\text{eff}}$ values. Hybrid DFT calculations have been used to understand the electronic structure and oxygen vacancy formation energy in LaCoO$_3$. However, the computational expense of the hybrid functionals renders them unfeasible for modeling larger supercells required to study oxygen transport in LaCoO$_3$. Beyond DFT and DFT+U supercell model studies, Hozoi et al. used an embedded cluster model with multi-reference singles and doubles configuration interaction used to treat the cluster and an embedding potential derived.
from periodic Hartree-Fock calculations of LS LaCoO$_3$. This study investigated the spin states of Co in the cluster and found a spin-state ordering of LS $<$ HS $<$ IS. However, the small cluster size and the embedding potential imposed an artificial constraint whereby only local excitations to the IS and HS states within a LS background were modeled. In summary, standard DFT calculations fail catastrophically for LaCoO$_3$, DFT+$U$ calculations reach different conclusions depending on the $U_{\text{eff}}$ parameter chosen, and the embedded calculations fail to account for long-range distortions which may affect the relative stability of different spin states.

No consensus exists regarding the relevant spin states of Co$^{3+}$ above 90 K. Nonetheless, many experimental and theoretical investigations have addressed oxygen transport in LaCoO$_3$. Experiments show that LaCoO$_3$ has higher oxygen diffusivity than other common LaMO$_3$ perovskites (M=Mn,Fe). Oxygen diffusion in LaCoO$_3$ occurs via a vacancy-mediated hopping mechanism. This mechanism gives rise to a diffusion coefficient that is the product of two quantities: the vacancy concentration and the vacancy diffusion coefficient. The free energy of oxygen vacancy formation ($\Delta G_{f,\text{vac}}$) determines the oxygen vacancy concentration ($C_v$). The vacancy diffusion coefficient ($D_v$) takes an Arrhenius form with the activation energy determined from the enthalpic barrier ($\Delta H_{\text{mig}}$) to the hopping process. Therefore, the overall diffusion coefficient depends on the $\Delta G_{f,\text{vac}}$ and $\Delta H_{\text{mig}}$. Experimental data provide an overall description of oxygen diffusion in LaCoO$_3$; however, rational design of materials based on LaCoO$_3$ requires understanding the fundamental physics that govern the oxygen transport process. Theoretical studies (using DFT+$U$ calculations) have addressed oxygen vacancy formation in LaCoO$_3$. Recently, Mastrikov et al. computed the vacancy
formation enthalpy and migration enthalpy in IS LaCoO₃ using a 40-atom supercell model and found that their calculated barrier agreed well with the experimentally observed migration barrier.³⁵ On the other hand, their oxygen vacancy formation enthalpy (3.64 eV) is significantly higher than the experimental oxygen vacancy formation enthalpy (2.17 eV). These significant deviations from experiment mean that oxygen diffusion constants derived from these theoretical data will not be accurate. Hong, et al., addressed O₂ surface exchange kinetics on LaCoO₃ and used DFT+U and hybrid DFT calculations to investigate how the Co spin state affects the oxygen vacancy formation energy.²⁷ These authors find that larger Co³⁺ magnetic moments lead to lower oxygen vacancy formation energies, in contrast to what we find and argue for here (vide infra). They attribute the trends in the oxygen vacancy formation energies to changes in the O 2p band center, which they use as a descriptor of the Co-O bond strength. This finding, the first to address the impact of Co spin state on oxygen vacancy formation, underscores the need for more refined understanding of the oxygen defect chemistry in LaCoO₃, while the migration barrier should also be analyzed considering additional spin states of the Co³⁺ ion.

We have just explained the controversy regarding the spin state of Co³⁺ in LaCoO₃ and reviewed literature that provides some atomic-level insight into oxygen diffusion in LaCoO₃. Experiments and theory fail to conclusively find that one magnetic configuration of LaCoO₃ dominates above 90 K. In fact, experimentalists have found that invoking a mixture of LS, IS, and HS Co³⁺ ions is necessary to explain the anomalous thermal expansion seen in LaCoO₃.¹² Additionally, Raman spectroscopy²⁷ indicates that all three configurations coexist above 90 K. This insight proves that any
conclusive description of physical processes in LaCoO$_3$ must account for a variety of Co$^{3+}$ spin states.

We present an *ab initio* DFT+U study of oxygen transport in LaCoO$_3$ that focuses on the effects of different spin states of Co$^{3+}$. As explained below, we determine a unique and unbiased *ab initio* value of U$_{\text{eff}}$ for Co$^{3+}$ using the method of Mosey, Liao, and Carter.$^{37}$ We apply the DFT+U method to four magnetic configurations of LaCoO$_3$: LS, IS, HS, and a 1:1 mixture of HS and LS. We analyze the effects of different spin states on the crystal structure, electronic structure, oxygen vacancy formation, and oxygen migration in LaCoO$_3$. Our results show that the oxygen diffusion coefficient depends significantly on the magnetic configuration of LaCoO$_3$. From these results, we provide insights into how to rationally design materials based on LaCoO$_3$.

### 4.2 Methods and Computational Details

The *ab initio* value of U$_{\text{eff}}$ for Co$^{3+}$ was determined from unrestricted Hartree-Fock (UHF) calculations on clusters carved out of a Co$_3$O$_4$ crystal, embedded in a point charge array according to the method described in ref. $^{37}$ using the GAMESS software package.$^{38,39}$ This method involves first evaluating the Coulomb and exchange integrals between UHF molecular orbitals and then taking a weighted average of these integrals based on the extent to which $d$ orbitals on the central ion (here one of the octahedrally coordinated Co$^{3+}$ ions) contribute to the specific MOs. The weights were determined by Mulliken population analysis$^{40}$ as implemented in GAMESS. Therefore, this U$_{\text{eff}}$ value is determined without experimental input (apart from the experimental crystal structure used for the embedded cluster). The Stuttgart effective core potential$^{41}$ (ECP) for O and
the large-core Hay-Wadt ECP\textsuperscript{42} for Co (which subsume two and 18 core electrons, respectively) along with the corresponding double-zeta basis sets for the valence electrons were employed. UHF calculations were performed on cluster models (Figure 4.1) of Co\textsubscript{3}O\textsubscript{4} in its spinel structure,\textsuperscript{43} which were electrostatically embedded using a point charge array containing more than 6800 point charges. Formal charges were used to assign +2, +3, and –2 to the appropriate point charges while those on the boundary of the point charge array were reduced according to Evjen’s method.\textsuperscript{44} The clusters were capped with Al\textsuperscript{3+} and Mg\textsuperscript{2+} Hay-Wadt ECPs\textsuperscript{45} (where the Al\textsuperscript{3+} ECPs replace Co\textsuperscript{3+} ions and the Mg\textsuperscript{2+} ECPs replace Co\textsuperscript{2+} ions). Al\textsuperscript{3+} and Mg\textsuperscript{2+} were chosen to replace capping Co\textsuperscript{3+} and Co\textsuperscript{2+} ions, respectively, because the ionic radii of the corresponding species are nearly identical.\textsuperscript{46} No basis functions were centered on the capping ECPs so these ECPs only provide Pauli repulsion to prevent unphysical leaking of electron density into the point-charge array. UHF calculations were converged such that all clusters up to Co\textsubscript{13}O\textsubscript{38}\textsuperscript{43−} had an energy change less than 0.1 $\mu$Ha. We converged the two largest clusters to an energy change no larger than 22 $\mu$Ha. While these clusters are highly charged, all cluster calculations were performed on cationic clusters because of the capping ECPs. The central Co ion remains positively charged throughout the calculations, having a Mulliken charge of +1.35 in the CoO\textsubscript{6}\textsuperscript{9−} and +1.15 in the Co\textsubscript{26}O\textsubscript{68}\textsuperscript{68−} cluster.
Figure 4.1. Clusters of Co3O4 used in the calculation of U, J, and U-J. (a) Co3O4 F43m unit cell, (b) CoO69-, (c) Co2O1014-, (d) Co4O1620-, (e) Co7O2631-, (f) Co13O3843-, (g) Co25O6867-, (h) Co26O6868-, and (i) Co33O8687-. Color designations: Co (blue), O (red), Mg2+ capping ECP (pink), and Al3+ capping ECP (light blue).

Different structural models were needed to capture the different spin states and observables for LaCoO3. Two cells were employed to describe the bulk crystal and electronic structure of LaCoO3: the R3c unit cell (Figure 4.2a) for the LS state and the I2/a cell (Figure 4.2b) for the IS, HS, and LS/HS states. The LS state cannot undergo a JT distortion, so the standard R3c unit cell can be used. However, the IS, HS, and HS/LS states may demonstrate JT distortions, so the I2/a cell was chosen to accommodate this possibility. Calculating oxygen vacancy formation energies and oxygen migration pathways required larger cells, so the pseudocubic supercell (40 atoms, Figure 4.2c) and the 2×2×2 R3c supercell (80 atoms, Figure 4.2d) were employed. For the supercells, we
allowed the atomic coordinates to break symmetry allowing for some stabilization from JT distortions.

![Figure 4.2.](image)

Figure 4.2. (a) Rhombohedral and (b) monoclinic unit cells of LaCoO₃. (c) Pseudocubic and (d) 2×2×2 rhombohedral supercells used for oxygen vacancy calculations in LaCoO₃. Color designations: La (green), Co (blue), and O (red).

KS-DFT⁴⁷,⁴⁸ calculations with periodic boundary conditions were performed with the Vienna ab initio Simulation Package (VASP) version 5.2.2.⁴⁹⁻⁵¹ The nuclei and core electrons were represented within the projector-augmented wave (PAW) formalism.⁵² We used standard potentials from the VASP library⁵³ with the following valence configurations: La (5s²5p⁶6s²5d¹), Co (4s²3d⁷), and ‘regular’ O (2s²2p⁴). Integration over
the first Brillouin zone was performed with Gaussian smearing ($\sigma=0.05$ eV) on a $4\times4\times4$ Monkhorst-Pack\textsuperscript{54} $k$-point mesh for the 10-atom $R\bar{3}c$ unit cell of LaCoO$_3$. A $3\times3\times2$ $k$-point mesh was used for the 20-atom $I2/a$ unit cell, and a $2\times2\times2$ $k$-point mesh was used for the 40-atom pseudocubic cell and 80-atom rhombohedral supercell (a $2\times2\times2$ supercell of the $R\bar{3}c$ unit cell). The planewave basis set was truncated at 750 eV. Total energies were converged to within 1 meV/atom using these parameters. Electron exchange and correlation was treated with the local density approximation (LDA) and the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE).\textsuperscript{55} LDA+U and GGA+U calculations were performed using the rotationally invariant scheme of Dudarev, \textit{et al.}\textsuperscript{56} We compare the performance of LDA+U and GGA+U calculations, noting which predictions are most meaningful in light of their ability to reproduce known observables. Since the DFT+U approach can exhibit metastable states,\textsuperscript{57} we carefully examined the initial and final states of our calculations to ensure that comparisons between LDA+U and GGA+U were made between equivalent minima. Each magnetic state was constructed through varying the initial guess for the Co magnetic moments (LS=0, IS=±2, HS=±4, where this quantity is the difference between alpha and beta electrons on a given site). Oxygen migration pathways were determined using the climbing-image nudged elastic band (CINEB) method\textsuperscript{58–60} as implemented in the VASP transition state theory tools developed at the University of Texas (\texttt{http://theory.cm.utexas.edu/vtsttools/}). Structures and migration pathways were optimized until the force on each atom fell below 0.03 eV/Å. Vibrational frequencies were obtained by constructing the Hessian matrix (second derivatives of total energy with respect to ion positions) using finite displacements of atoms (0.02 Å displacements). For the larger supercells, we constructed
a subset of the Hessian consisting of groups of atoms surrounding the oxygen vacancy or migration pathway.  

We employed several tools for analyzing the electronic structure of LaCoO$_3$ in multiple spin states and the absence or presence of an oxygen vacancy. Atom- and angular-momentum-projected densities of states (PDOS) were obtained from single-point calculations using the tetrahedron method with Blöchl corrections. For convenience, PDOS plots show positive values for the majority spin states and negative values for the minority spin states. All PDOS plots were shifted such that the Fermi energy (the energy above which there are no occupied states) equals zero. We also used Bader’s atoms in molecules approach, as implemented by Professor Henkelman’s group at the University of Texas, to partition the electron density in our calculations. Density difference plots showing how electrons rearrange upon oxygen vacancy formation require a reference density for the oxygen atom. For this purpose, we computed the oxygen atom in a triplet state, but we allowed the minority electron to fractionally occupy the three p-orbitals to obtain a spherical charge density. This is required so that we do not bias our density difference plots through an arbitrary choice of $x$, $y$, or $z$ for the doubly occupied 2$p$ orbital. Finally, the magnetic moments we report were obtained by integrating the spin density within a sphere around each atom. The radii for the spheres were determined for each element by the PAW potentials we used (vide supra).

4.3 Determining $U_{\text{eff}}$ for Co$^{3+}$

Conclusions drawn from previous DFT+U studies of LaCoO$_3$ have depended strongly on the chosen value of the $U_{\text{eff}}$ parameter (vide supra). For less empirical predictions, we determine the $ab\ initio$ value of $U_{\text{eff}}$ for Co$^{3+}$ from UHF calculations on
embedded cluster models of Co₃O₄. We choose Co₃O₄ (spinel structure), the simplest cobalt oxide that contains Co³⁺ ions, to give us the most transferable U_{eff} value for Co³⁺ ions in an oxide material. While the U_{eff} value in principle depends on structure and magnetic state, we require a consistent U_{eff} value so that energy differences are valid (i.e., derived from the same Hamiltonian). The U_{eff} value for LS Co³⁺ is most appropriate since it represents the ground state of LaCoO₃ and Co₃O₄. Furthermore, at low temperature (T < 5 K), the Co³⁺-O²⁻ distances are 1.93 Å and 1.91 Å for LaCoO₃ and Co₃O₄, respectively. The spinel structure (Co₃O₄) also features tetrahedrally coordinated HS Co²⁺ ions. These Co²⁺ ions align antiferromagnetically with one another. The greatest discrepancies between Co₃O₄ and LaCoO₃ are the presence of Co²⁺ in Co₃O₄ and the different octahedral linkage in the spinel (edge shared) and perovskite (corner shared) structures. We calculate the values of U, J, and U_{eff}=U-J among the d electrons on the central Co³⁺ ion in the cluster. With expanding cluster size, the central Co ion should become increasingly bulk-like. We find (Figure 4.3) that U_{eff} converges to 4.0 eV in a cluster of Co₃₃O₈₆. Our result agrees reasonably well with the value U=5 eV obtained for LS Co³⁺ in LaCoO₃ by fitting X-ray photoemission data with a parameterized configuration interaction model for a CoO₆ cluster. Likewise, our U_{eff} value is reasonable when compared with the values for other 3+ transition metal ions: Cr³⁺ = 3.2 eV, Fe³⁺ = 4.3 eV. Our U_{eff} value for Co³⁺ disagrees significantly with the values obtained from linear-response theory which are 6.7 eV for LS Co³⁺ in Co₃O₄ and 7.22 eV for LS Co³⁺ in LaCoO₃. Another linear-response study obtains the U_{eff} value for LS Co³⁺ as a function of structure, giving rise to unreasonable values in excess of 8 eV. Based on this, it seems that linear-response theory can overestimate U_{eff}. This may arise
because the linear-response method of calculating U_{eff} derives the self-interaction error correction using a theory (DFT-LDA) which already contains self-interaction error. Thus results from those calculations should be interpreted with caution.

**Figure 4.3.** U (orange), J (blue), and U-J (black) for Co^{3+} ions in clusters obtained from Co_3O_4. The converged value of U-J is 4.0 eV. This value is converged to 0.3 eV (the difference between the Co_{26}O_{68}^{68-} and Co_{33}O_{86}^{87-} clusters).

### 4.4 Bulk Structural and Electronic Properties of LaCoO_3

To validate the transferability of our *ab initio* U_{eff} value for Co^{3+} from Co_3O_4 to LaCoO_3, we compare experimental observables to those from LDA+U and GGA+U calculations for different Co^{3+} spin configurations (Table 4.1). We find that the IS state only exists in a ferromagnetic (FM) configuration while the HS state only converges in the antiferromagnetic (AFM) configuration. This may explain why the IS state is routinely found when researchers perform FM DFT+U calculations on LaCoO_3.\textsuperscript{15,16} Although FM and AFM solutions exist for the HS/LS configuration of LaCoO_3, we use an AFM model for this state (in keeping with the paramagnetism of LaCoO_3 above 90 K). We require that LS Co^{3+} ions have HS Co^{3+} neighbors (and vice versa) with the HS Co^{3+}
aligned antiferromagnetically with one another. Periodic boundary conditions necessitate imposing such order to model a paramagnetic material. Experimental quantities obtained at low temperature ($T < 90$ K) should be compared to the LS state while observables obtained at room temperature (or higher) should be compared with the magnetic states. As expected, the LDA+U functional gives equilibrium volumes ($V_o$) smaller than the experimental volumes while the GGA+U functional gives volumes larger than experiment. The optimized lattice constants for both of these functionals follow the same trend as the equilibrium volume. The only exception is the LS case where both functionals underestimate the lattice constant. The GGA+U functional slightly overestimates the LS equilibrium volume because it overestimates the angle between the lattice vectors (61.3° compared to 61.0° from experiment) while the LDA+U angle (61.1°) is in better agreement with experiment. However, neither functional offers a significant advantage in terms of structural parameters. The GGA+U functional gives bulk moduli ($B_o$) in agreement with room temperature experiments (comparing IS, HS, and HS/LS with experiment) while the LDA+U values are much higher. Finally, the eigenvalue gap between the highest occupied band and the lowest unoccupied band ($E_g$), which provides a crude estimate of the band gap, is larger than the experimental gap (0.6 eV from optical spectroscopy and 0.9 eV from soft X-ray absorption spectroscopy); however, the eigenvalue gap is close enough that we can reasonably trust both our LDA+U and GGA+U calculations for LaCoO$_3$. Note that the IS state is predicted to be metallic, indicating that it does not play a significant role in the electronic structure of LaCoO$_3$ at temperatures below 500 K (below which LaCoO$_3$ is an insulator).
discussion of the spin state energetics is provided later (vide infra). These results suggest that our DFT+U calculations properly capture the physics of LaCoO$_3$.

**Table 4.1.** Equilibrium volumes per formula unit, f.u.($V_0$), lattice constants ($a$, $b$, $c$), bulk moduli ($B_0$), and eigenvalue gaps ($E_g$) of LaCoO$_3$ in different spin states calculated with LDA+U and GGA+U using the *ab initio* value $U_{\text{eff}}=4.0$ eV, as compared with experiment. $V_0$ and $a$ values for LS LaCoO$_3$ should be compared to the 5 K value while the IS, HS/LS, and HS states should be compared with the 295 K value. The LS (5 K) structure is rhombohedral and requires only one lattice constant ($a$). The IS, HS/LS, and HS states were analyzed in the monoclinic cell which has three separate lattice constants ($a$, $b$, and $c$). $B_0$ and $E_g$ measurements were conducted at room temperature; therefore these properties should be compared only to IS, HS/LS, and HS state predictions.

<table>
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<th>Property</th>
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<th>GGA+U</th>
</tr>
</thead>
<tbody>
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<td>$V_0$ (Å$^3$/f.u.)</td>
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<td>56.50</td>
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<td>53.96</td>
<td>53.82</td>
</tr>
<tr>
<td>$b$ / Å</td>
<td>5.426 (5 K)$^a$</td>
<td>5.246</td>
<td>5.375</td>
</tr>
<tr>
<td>$c$ / Å</td>
<td>5.370 (295 K)$^b$</td>
<td>5.312</td>
<td>5.350</td>
</tr>
<tr>
<td>$B_0$ (GPa)</td>
<td>7.640 (295 K)$^b$</td>
<td>7.605</td>
<td>7.466</td>
</tr>
<tr>
<td>$E_g$ (eV)</td>
<td>120$^c$, 150$^d$</td>
<td>222</td>
<td>203</td>
</tr>
<tr>
<td>$q_La$</td>
<td>0.6$^e$, 0.9$^f$</td>
<td>0.87</td>
<td>Metal</td>
</tr>
</tbody>
</table>

$^a$ Ref. 12
$^b$ Ref. 9
$^c$ Ref. 1
$^d$ Ref. 71 at room temperature
$^e$ Ref. 69: optical gap
$^f$ Ref. 70: gap from soft X-ray absorption at room temperature

Having validated our *ab initio* DFT+U method against measured bulk properties of LaCoO$_3$, we now consider how the spin state of Co affects the electronic structure of LaCoO$_3$ using Bader analysis$^{63-65}$ (Table 4.2) and PDOS (Figure 4.4). First, the Bader charge on La ($q_{\text{La}}$) shows negligible variation with the magnetic configuration, indicating that the significant interactions occur between the other atoms (Co and O). Bader analysis reveals that $q_{\text{Co}}$ becomes significantly more positive with increasing magnetic moment on the Co ion. Correspondingly, $q_{\text{O}}$ becomes more negative as $\mu_{\text{Co}}$ increases. These trends indicate that the system becomes increasingly ionic for higher $\mu_{\text{Co}}$. This is also consistent
with the fact that the HS state has the largest eigenvalue gap (Table 4.1), suggesting that it is the most ionic. Analyzing the PDOS reveals strong hybridization of Co $3d$ and O $2p$ states in all spin states, based on their overlapping energies. Consistent with a diamagnetic state, the LS PDOS is perfectly symmetrical with regard to majority and minority spin states, and the Co $3d$ states contribute to both the valence and conduction bands. This result agrees with the crystal field picture of LS LaCoO$_3$ in which Co$^{3+}$ has a $t_{2g}^6e_g^0$ electron configuration. The IS state is half-metallic with a wide Co $3d$ band crossing the Fermi level in the majority spin states. This delocalization is consistent with the $t_{2g}^5e_g^1$ electron configuration that has a half-filled $e_g$ band. The JT distortion is insufficient to limit the delocalization of the $e_g$ electrons resulting in the metallic state. The HS state of LaCoO$_3$ has all of the majority Co $3d$ states in the valence band (as expected for the $t_{2g}^4e_g^2$ configuration). The minority Co $3d$ states are very broad in the valence band (consistent with one of three $t_{2g}$ orbitals being occupied). The conduction band has no significant majority spin states and significant minority Co $3d$ peaks indicating that most of the minority Co $3d$ states are unoccupied. The HS/LS configuration shows a convolution of LS and HS states in LaCoO$_3$. Specifically, the large peak at low energy corresponds to the HS Co ions and the increased density of Co $3d$ states at the top of the valence band is consistent with the LS Co ions. Additionally, the conduction band has majority Co $3d$ states (consistent with LS Co ions) and the sharp peak in the minority channel (consistent with HS Co ions). Finally, we note that in all cases, the O $2p$ states fall almost entirely in the valence band, corresponding to their essentially closed-shell character.
Table 4.2. Magnetic moments ($\mu_{Co}$) and Bader charges ($q$) of LaCoO$_3$ in different spin states calculated with LDA+U and GGA+U with the \textit{ab initio} value $U_{\text{eff}}=4.0$ eV.

<table>
<thead>
<tr>
<th>Property</th>
<th>LDA+U</th>
<th>GGA+U</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LS (FM)</td>
<td>IS (FM)</td>
</tr>
<tr>
<td>$\mu_{Co}$ ($\mu_B$)</td>
<td>0.00</td>
<td>1.94</td>
</tr>
<tr>
<td>$q_{La}$ ($e$)</td>
<td>2.06</td>
<td>2.05</td>
</tr>
<tr>
<td>$q_{Co}$ ($e$)</td>
<td>1.25</td>
<td>1.31</td>
</tr>
<tr>
<td>$q_{O}$ ($e$)</td>
<td>-1.10</td>
<td>-1.12</td>
</tr>
</tbody>
</table>

The nature of the transition from nonmagnetic to paramagnetic behavior around 90 K remains controversial, and experiments suggest that a mixture of spin states is responsible for the paramagnetism.\textsuperscript{12} To investigate this issue, we computed the equation of state (energy vs. volume, Figure 4.5) for each spin state using LDA+U and GGA+U calculations. We found it sobering that the two sets of calculations give completely opposite qualitative trends. The low spin state (nonmagnetic) is the low temperature ground state and should have the lowest energy among the different spin configurations. LDA+U calculations properly predict this. However, the GGA+U calculations incorrectly predict that the LS state has the highest equilibrium energy. Finally, our hybrid DFT calculations using the HSE06\textsuperscript{72,73} functional indicate that, although this functional mostly uses GGA (PBE) exchange and correlation, the inclusion of short-range exact exchange gives a reasonable ordering of LS < HS. Others have shown that the B3LYP\textsuperscript{74} hybrid functional produces a reasonable spin state ordering for LaCoO$_3$.\textsuperscript{25} While hybrid functionals offer an alternative to LDA+U for analyzing the ordering of spin states, we believe that significant insight can be gleaned by examining the LDA+U energetics.
When considering which spin states occur above 90 K, we rely on the LDA+U results. We find that an equal mixture of HS and LS Co ions is slightly favored over the IS state. However, the HS/LS mixture and the IS state have similar energies, meaning that both states may contribute to the paramagnetism of LaCoO₃. Finally, the HS state lies more than 0.1 eV/f.u. above the mixed HS/LS state indicating that a purely HS state is less stable than a mixture of HS and LS Co³⁺ ions. Overall, LDA+U data, which we
believe are more meaningful in this situation, support the notion that the nonmagnetic-to-paramagnetic transition arises from Co$^{3+}$ ions being excited into the HS state within a background that is mostly LS in nature. Since our electronic structure calculations indicate that the IS state is metallic, this latter state most likely only exists above the insulator to metal transition (500 K). The IS and HS/LS spin states probably coexist at SOFC operating temperatures, proving that a thorough analysis of oxygen transport in LaCoO$_3$ must include Co spin state effects.

Figure 4.5. Energy vs. volume for LaCoO$_3$ with different spin states of Co. LDA+U gives (reasonable) LS < HS/LS < IS < HS ordering while GGA+U gives (unreasonable) HS < IS < HS/LS < LS ordering.
4.5 Oxygen Diffusion in LaCoO₃

Analyzing the effects of different Co spin states on oxygen transport requires understanding the oxygen diffusion mechanism. Experiments show that oxygen diffusion occurs via a vacancy-mediated hopping mechanism. Again, when diffusion occurs via this mechanism, two parameters control the oxygen diffusion coefficient (D₀): Cᵥ and Dᵥ (Equation 4.1).

\[
D₀ = \frac{Cᵥ}{C₀} Dᵥ = \frac{Cᵥ}{3 - Cᵥ} Dᵥ
\]  

(Cᵥ and C₀ are the oxygen vacancy and oxygen concentrations, respectively. We express these quantities in moles/mole LaCoO₃. This accounts for the factor of 3 in the denominator of Equation 4.1. ∆Gᵣ,vac governs Cᵥ (vide infra) while Dᵥ adopts an Arrhenius form (Equation 4.2).

\[
Dᵥ = A e^{-\Delta H_{mig}/k_BT} = \frac{1}{6} v₀ a^2 e^{-\Delta S^\parallel/k_B} e^{-\Delta H_{mig}/k_BT}
\]  

The righthand side of Equation 4.2 arises from transition state theory where v₀ is the attempt frequency, a is the jump length, ∆S^\parallel is the entropy difference between the initial and transition states, the factor of 1/6 arises from diffusion in three dimensions, and ∆Hₘᵢᵍ is the enthalpic barrier to migration. In light of the controversy over the different spin states in LaCoO₃ (vide supra), our analysis of oxygen transport will show how different Co spin states alter the oxygen vacancy formation process (e.g., ∆Gᵣ,vac) and the oxygen migration process (e.g., ∆Hₘᵢᵍ).

Oxygen vacancies play a fundamental role in the oxygen transport mechanism in LaCoO₃ (vide supra). We therefore analyze how the magnetic state of Co³⁺ changes the
fundamental physics of oxygen vacancy formation. Since experiments indicate that oxygen vacancies interact negligibly with one another in LaCoO₃, we require a model which reproduces the dilute limit of oxygen vacancies. We first computed $\Delta E_{f,\text{vac}}$ (Equation 4.3), which neglects thermal effects (vide infra), in the pseudocubic (40-atom) and $2\times2\times2$ rhombohedral (80-atom) supercells.

$$\Delta E_{f,\text{vac}} = E_{\text{defective}} - E_{\text{perfect}} + \frac{1}{2} E_{O_2}$$ (4.3)

We find that $\Delta E_{f,\text{vac}}$ decreases by as much as 0.48 eV when increasing the supercell size from pseudocubic to rhombohedral (Table 4.3). Thus, vacancy-vacancy interactions (arising from periodic boundary conditions) are significant in the pseudocubic cell. We further increased the rhombohedral supercell size from $2\times2\times2$ (80 atoms) to $3\times3\times3$ (270 atoms), and we found that the LDA+U LS oxygen vacancy formation energy decreases by only 0.12 eV. This difference is sufficiently small to show that the $2\times2\times2$ rhombohedral supercell reasonably represents the limit of dilute oxygen vacancies in LaCoO₃. The vacancy concentration in this cell is 2.1% ($\delta=0.0625$), which roughly corresponds with the vacancy concentrations determined from thermogravimetry (e.g., $\delta\approx0.01$ at 950°C and $P_{O_2}=0.01$ atm). Our larger supercell LDA+U and GGA+U calculations of the vacancy formation energy as a function of spin state (Table 4.3) show that the LS state is the best environment for oxygen vacancy formation. Note that the trends from the 80-atom supercell are reproduced in the pseudocubic 40-atom cell for GGA+U but not for the LDA+U calculations. From this point forward, we ignore the LDA+U oxygen vacancy formation energies because of the well-known overbinding of LDA compared to the GGA, leading to spuriously high vacancy formation energies.
within LDA+U. As a last point, we predict that the HS state has the highest oxygen vacancy formation energy, and the HS/LS state falls in between these two extremes. This indicates that changing the operating conditions (e.g., increasing the total pressure should stabilize the LS state, though the oxygen partial pressure should be kept constant to avoid lowering $C_v$) or making small modifications to the chemical composition that preserve more LS Co$^{3+}$ ions may offer a rational means of increasing the oxygen vacancy concentration (and thus the ionic conductivity) of LaCoO$_3$.

Table 4.3. Oxygen vacancy formation energy ($\Delta E_{f,\text{vac}}, \text{eV}$) in LaCoO$_3$ for different Co spin configurations in the pseudocubic and 2×2×2 rhombohedral supercells.

<table>
<thead>
<tr>
<th>Spin State</th>
<th>LDA+U</th>
<th>GGA+U</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pseudocubic</td>
<td>2×2×2 rhombohedral</td>
</tr>
<tr>
<td>LS</td>
<td>3.27</td>
<td>2.79</td>
</tr>
<tr>
<td>IS</td>
<td>2.85</td>
<td>----</td>
</tr>
<tr>
<td>HS</td>
<td>3.07</td>
<td>2.94</td>
</tr>
<tr>
<td>HS/LS</td>
<td>----</td>
<td>3.02</td>
</tr>
<tr>
<td>Experiment$^a$</td>
<td>2.2 eV</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Ref. 78  
$^b$ We could not obtain the IS state in the 2×2×2 rhombohedral supercell (*vide infra*)  
$^c$ The HS/LS state cannot be constructed with the proper antiferromagnetism in the pseudocubic cell.

Electronic structure analysis offers a way to explain why the oxygen vacancy formation energy changes with magnetic state. When we analyze the electronic structure of LS and HS LaCoO$_3$ in the presence and absence of an oxygen vacancy using the GGA+U results, we find that Co ions adjacent to the vacancy have magnetic moments around 2.5 $\mu_B$ (Table 4.4). Additionally, these ions have significantly reduced charges in the presence of an oxygen vacancy, indicating that they accept the electrons released when the vacancy forms. Since two Co ions were bound to the vacant oxygen site, each accepts one electron resulting in a localized reduction from Co$^{3+}$ to Co$^{2+}$ on these sites.
We find that, regardless of whether the oxygen vacancy is formed in HS or LS LaCoO$_3$, the final state of these ions is always high spin Co$^{2+}$. This occurs because the exchange stabilization of aligning the $d$ shell in Co$^{2+}$ is greater than the penalty introduced by the crystal field splitting. These effects are nearly balanced in Co$^{3+}$ (leading to the complex magnetic behavior of LaCoO$_3$); however, in Co$^{2+}$ the crystal field splitting is reduced compared to Co$^{3+}$, so the exchange stabilization effect dominates.

We can explicitly verify that the final state after oxygen vacancy formation is high spin Co$^{2+}$ by looking at an electron density difference plot that shows how the electrons rearrange upon vacancy formation in LS LaCoO$_3$ (Figure 4.6). Around the Co ions adjacent to the vacancy, we not only see an increase in electron density, we also see a region of decreased electron density. This demonstrates that a rearrangement occurs in the $d$ manifold of the Co ions, as required by the reduction of LS Co$^{3+}$ to HS Co$^{2+}$. This also explains why LS LaCoO$_3$ is more receptive to oxygen vacancies than HS LaCoO$_3$. The rearrangement in the $d$ manifold allows for additional exchange stabilization in LS LaCoO$_3$ that cannot be gained in HS LaCoO$_3$. HS/LS LaCoO$_3$ behaves slightly differently than its magnetically homogenous counterparts. In this state, the HS Co ion adjacent to the vacancy demonstrates the same reduced magnetic moment as occurs in the HS state. Similarly, the LS Co ion adjacent to the vacancy shows an increased magnetic moment of 1.9 $\mu_B$. 


**Table 4.4.** Magnetic moments ($\mu_{Co}$) and Bader charges ($q$) in the 2×2×2 rhombohedral supercell before and after the creation of an oxygen vacancy (V$_{O^{**}}$) determined using GGA+U calculations with $U_{eff}$ = 4.0 eV. Co* indicates a cobalt ion adjacent to the vacant oxygen site.

<table>
<thead>
<tr>
<th></th>
<th>LS Before V$_{O^{**}}$</th>
<th>After V$_{O^{**}}$</th>
<th>HS/LS Before V$_{O^{**}}$</th>
<th>After V$_{O^{**}}$</th>
<th>HS Before V$_{O^{**}}$</th>
<th>After V$_{O^{**}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{Co}$ ($\mu_B$)</td>
<td>0.0-0.1</td>
<td>0.0-0.1</td>
<td>3.0</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_{Co^*}$ ($\mu_B$)</td>
<td>+++</td>
<td>2.6</td>
<td>2.6$^a$</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_{La}$ ($e$)</td>
<td>2.09</td>
<td>2.08 ± .01</td>
<td>2.09</td>
<td>2.08</td>
<td>2.10</td>
<td>2.08 ± .01</td>
</tr>
<tr>
<td>$q_{Co}$ ($e$)</td>
<td>1.31</td>
<td>1.30</td>
<td>1.54</td>
<td>1.28</td>
<td>1.52</td>
<td>1.52</td>
</tr>
<tr>
<td>$q_{Co^*}$ ($e$)</td>
<td>+++</td>
<td>1.20</td>
<td>1.29$^a$</td>
<td>1.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_{O}$ ($e$)</td>
<td>-1.13</td>
<td>-1.15 ± .02</td>
<td>-1.17</td>
<td>-1.17 ± .01</td>
<td>-1.21</td>
<td>-1.21 ± .01</td>
</tr>
</tbody>
</table>

$^a$ One HS ion adjacent to the oxygen vacancy and another nearby HS ion show reduced magnetic moments and Bader charges.

To compensate for the fact that the LS Co increases its magnetic moment more than the HS Co reduces its magnetic moment, another HS Co (approximately the same distance from the LS Co ion as the first one) also reduces its magnetic moment. Bader analysis indicates that this second HS Co also undergoes reduction (q is significantly reduced from 1.53 to 1.29 $e$) while showing that the LS Co ion adjacent to the vacancy does not undergo a reduction (q insignificantly changes from 1.28 to 1.27). Taken together, the magnetic moments and Bader charges for HS/LS show that the oxygen vacancy reduces two HS Co$^{3+}$ sites to HS Co$^{2+}$ (only one of the two is adjacent to the oxygen vacancy) while causing a magnetic transition from LS Co$^{3+}$ to IS Co$^{3+}$ for the LS Co$^{3+}$ ion adjacent to the vacancy. This detailed analysis demonstrates that a single description of oxygen vacancy formation in LaCoO$_3$ will not account for significant changes in the oxygen vacancy formation process caused by different Co$^{3+}$ spin states.
Figure 4.6. Electron density difference for low spin LaCoO$_3$ ($\Delta \rho = \rho_{\text{defective}} + \rho_{O} - \rho_{\text{host}}$) calculated with the GGA+U functional. Volumetric plot (top) with isosurfaces at +0.03 $e/\AA^3$ (yellow) and -0.03 $e/\AA^3$ (blue). Ions (except those around the vacancy) are shown in reduced size for clarity. Color designations: cobalt (blue), lanthanum (green) and oxygen (red). Contour plot (bottom) on the (211) plane intersecting the oxygen vacancy site and its two nearest Co ions. Figure created with VESTA.\textsuperscript{79,80}

Our previous work on La$_{1-x}$Sr$_x$FeO$_3$ (LSF)\textsuperscript{81} demonstrated the relevance of taking into account thermal corrections to the oxygen vacancy formation energy. In agreement with Gryaznov, \textit{et al.},\textsuperscript{82} we found that the thermal contributions from the perfect and
defective LSF solids contributed significantly to $\Delta G_{f,\text{vac}}$. We expect that LaCoO$_3$ will show similar contributions from the solids, so we provide oxygen vacancy formation energies (Table 4.5) using different levels of approximation for the thermal corrections (see ref. 81 for equations). The approximations are as follows: $\Delta E_{f,\text{vac}}$ neglects all thermal corrections, $\Delta H_{f,\text{vac}}(0 \text{ K})$ includes zero-point energy (ZPE) corrections, $\Delta H_{f,\text{vac}}(700^\circ\text{C})$ includes ZPE corrections plus the heat capacity ($C_p$) integrated from absolute zero to 700$^\circ$C, and $\Delta G_{f,\text{vac}}(700^\circ\text{C})$ includes $\Delta H_{f,\text{vac}}(700^\circ\text{C})$ and entropic ($S$) terms. We determined $C_p$ and $S$ for the solid phases by using the harmonic oscillator approximation with the vibrational frequencies determined from a cluster of atoms within the supercell containing the departing oxygen ion and the two cobalt ions around the defect site. We provide an LDA+U and GGA+U analysis of phonon frequencies in LS LaCoO$_3$ in the supporting information. For the solid phases, we neglected PV terms in the enthalpy and assumed that the constant volume heat capacity equals $C_p$. We chose this cluster for the vibrational frequency calculations based on comparing clusters of increasing size (up to 16 atoms) and seeing that the thermal contributions to the vacancy formation enthalpies and free energies were converged to 0.02 eV for the small cluster. We used the standard ideal gas, rigid rotor, and harmonic oscillator approximations for homonuclear diatomic molecules to determine $C_p$ and $S$ for O$_2$(g). We account for the PV contribution to the enthalpy of O$_2$(g) by integrating $C_p$ instead of $C_v$. The large entropic contribution to $\Delta G_{f,\text{vac}}$ arises from the vacancy formation process releasing an oxygen atom from the lattice to form half of an O$_2$(g) molecule. For LaCoO$_3$, the thermal corrections only make a small impact on the enthalpies of vacancy formation. The significant entropic contribution from the gas-phase O$_2$ molecule gives rise to large thermal contributions in
ΔG_{f,vac}. A correction (ΔE = 0.42 eV) for the known overbinding of O₂ by DFT-GGA was derived by subtracting the experimental O₂ bond dissociation energy (BDE) from the computed O₂ BDE and dividing by 2 (since \( \frac{1}{2}O_2(g) \) is the product of oxygen vacancy formation). This correction shifts the vacancy formation energies upwards because it destabilizes the products (specifically the \( \frac{1}{2}O_2 \)).

Table 4.5. Oxygen vacancy formation energies (eV) in LaCoO₃ for different Co spin states with different approximations to the thermal contributions. Thermal corrections use P_{O₂} = 1 atm for the ideal gas approximation. Calculations performed at the GGA+U level in the 2×2×2 rhombohedral supercell. Values in parentheses reflect a correction for the known overbinding of O₂ by DFT-GGA.

<table>
<thead>
<tr>
<th>Spin State</th>
<th>ΔE_{f,vac}</th>
<th>ΔH_{f,vac}(0K)</th>
<th>ΔH_{f,vac}(700°C)</th>
<th>ΔG_{f,vac}(700°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS</td>
<td>0.90 (1.32)</td>
<td>0.85 (1.27)</td>
<td>0.84 (1.26)</td>
<td>-0.08 (0.34)</td>
</tr>
<tr>
<td>HS</td>
<td>1.89 (2.31)</td>
<td>1.86 (2.28)</td>
<td>1.83 (2.25)</td>
<td>0.99 (1.41)</td>
</tr>
<tr>
<td>HS/LS</td>
<td>1.45 (1.87)</td>
<td>1.44 (1.86)</td>
<td>1.40 (1.82)</td>
<td>0.62 (1.04)</td>
</tr>
</tbody>
</table>

Experiment

2.2

1.2

We do not present the vacancy formation process in IS LaCoO₃ because we were unable to stabilize that configuration within the 2×2×2 rhombohedral supercell. This lack of convergence is likely due to the supercell not accommodating the JT distortion required by the IS state. We did obtain the vacancy formation energy for the FM IS state in the pseudocubic supercell, and found it exceeds the LS state value by 0.28 eV (within GGA+U theory in the pseudocubic supercell). Others have also investigated oxygen vacancy formation in IS LaCoO₃ in the pseudocubic cell. Lee, et al. employed an optimized U_{eff} value of 3.3 eV for Co³⁺ obtained by fitting the reaction enthalpy for forming LaCoO₃ from CoO, La₂O₃, and O₂. Their oxygen vacancy formation energy in the FM IS state, including an empirical correction for the known DFT-GGA overbinding
of O$_2$, is between 2.5 and 3 eV, somewhat higher than experiment. Recently published work by Mastrikov, et al.$^{35,36}$ used DFT-GGA to calculate the oxygen vacancy formation energy for the IS FM configuration of LaCoO$_3$ in a rhombohedral variant of the 40-atom supercell. Their reported values of $\Delta E_{f,vac} = 3.42$ eV and 3.64 eV far exceed experiment, and the errors likely result from the well-known misrepresentation of the LaCoO$_3$ electronic structure by DFT-GGA (as opposed to GGA+U or hybrid DFT). Additionally, our results show that the 40-atom supercell they used probably produces a significant overestimation of $\Delta E_{f,vac}$, and larger supercells should be employed to determine whether their value is converged.

As mentioned earlier, Hong, et al. examined surface exchange kinetics of LaCoO$_3$ using both experimental methods and DFT-based calculations.$^{27}$ As in our present study, they investigated $\Delta E_{f,vac}$ for various Co magnetic moments. In contrast to our study here, they predicted that the LS state would have the highest $\Delta E_{f,vac}$ (~3.5 eV), for both GGA+U and hybrid functional calculations in the 40-atom supercell. Lower $\Delta E_{f,vac}$ values (derived from GGA+U) of ~2.7 eV and ~2.4 eV were reported for the ferromagnetic IS and HS states, respectively. These spin states experienced dramatic decreases in $\Delta E_{f,vac}$ to 1.3 eV and 1.4 eV, respectively, with hybrid functionals. Such large changes are not surprising given the significant differences between our calculations and those of Hong, et al. They utilized the 40-atom supercell that we showed to be insufficient for describing oxygen vacancy formation in LaCoO$_3$. Numerical differences between their work and ours include the $U_{eff}$ value (empirically fit value of 3.3 eV vs. $ab$ initio value of 4.0 eV), slightly different GGA functionals (PW-91 vs. PBE), and the use of a lower planewave kinetic energy cutoff (600 eV vs. 750 eV). In
order to obtain results for a specific spin state, Hong, et al. fixed the overall magnetization of the cell. In contrast, we allow free relaxation of the spin density, only constraining antiferromagnetic solutions to have equal numbers of alpha and beta electrons. Finally, they do not report the magnetization of the final states they obtained for any of the spin states they examined. These differences, especially the last one, may explain some of the differences in our values. Our argument for the reduced vacancy formation energy in the LS state comes from well-founded physical arguments: the extra intra-atomic exchange stabilization gained by the final state relaxing from LS Co$^{2+}$ to HS Co$^{2+}$ lowers the oxygen vacancy formation energy for the low spin state (*vide supra*).

Though Hong, et al. rely on the O 2$p$ band center as a measure of the Co-O bond strength, this metric depends on the methodology (*e.g.*, GGA functional, PAW potential) and does not account for final state relaxations which may lower the cost of breaking the bond. Additionally, the bands provided by DFT are of limited value because they have no physical meaning (in the KS formalism, orbitals or bands are used only as a convenience for evaluating the kinetic energy term and are not unique). Given our use of larger supercells, more accurate numerical parameters, and physical arguments based on $d$ orbital occupations and charge reorganization, we expect our predictions to be more reliable than those of Hong, et al.

Oxygen vacancy formation energies determine the oxygen vacancy concentration. However, theoretical oxygen vacancy concentrations are rarely reported for SOFC cathode materials. Commonly, a Boltzmann factor is used to compute the vacancy concentration (Equation 4.4).\(^{75,76}\)

$$\frac{C_v}{3 - C_v} = \exp\left(-\frac{\Delta H_{f,\text{vac}}}{k_B T}\right)$$

(4.4)
$C_v$ is the oxygen vacancy concentration (moles/mole LaCoO$_3$), $\Delta H_{f, vac}$ is the enthalpy of vacancy formation, $k_B$ is Boltzmann’s constant, and $T$ is the absolute temperature. When employing Equation 4.4 to compute $C_v$, we increase $\Delta H_{f, vac}$ by 0.42 eV to account for the known overbinding of O$_2$ by DFT-GGA (*vide supra*). This expression works well for dilute, non-interacting vacancies in situations where the departing atom is referenced to a solid (e.g., Ni vacancies in NiAl$^{75}$). In our case, forming the vacancy leads to a gaseous product and a large, positive entropy change (Equation 4.5). We employ Kroger-Vink notation$^{85}$ where Vo$^{**}$ represents an oxygen vacancy, Co$^x_{Co}$ and O$^x_{O}$ are Co$^{3+}$ and O$^{2-}$ in the crystal, and the grouping $\{Co^f_{Co} - V^{**}_{0} - Co^f_{Co}\}$ represents a vacancy cluster where two Co$^{3+}$ ions near the vacancy have been reduced to Co$^{2+}$.

$$2Co^x_{Co} + O^x_{O} \rightarrow \{Co^f_{Co} - V^{**}_{0} - Co^f_{Co}\} + \frac{1}{2}O_2(g) \quad (4.5)$$

The large entropic change arising from forming O$_2$(g) necessitates using equilibrium approaches to compute $C_v$ as illustrated in Equation 4.6.$^{86}$ Recall that we defined $C_v$ in terms of moles/mole LaCoO$_3$ (*vide supra*).

$$K = \exp\left(\frac{-\Delta G^0_{f, vac}}{k_B T}\right) = \frac{[\{Co^f_{Co} - V^{**}_{0} - Co^f_{Co}\}]^{1/2}P_{O_2}^{1/2}}{[Co^x_{Co}]^2[O^x_{O}]} = \frac{C_vP_{O_2}^{1/2}}{(1 - 2C_v)^2(3 - C_v)} \quad (4.6)$$

The computed vacancy concentrations using Equation 4.4 (traditional method) and Equation 4.6 (equilibrium method) are shown in Figure 4.7 where the partial pressure of O$_2$ is 49 torr, corresponding to the experimental conditions.$^{31}$ All equilibrium calculations were carried out with 0.42 eV added to $\Delta G_{f, vac}$ to compensate for the known overbinding of the O$_2$ molecule by DFT-GGA (*vide supra*). These results confirm our previous
assertion that different spin states in LaCoO$_3$ lead to large changes (2-3 orders of magnitude) in oxygen vacancy concentrations. We also observe that the LS spin state gives the highest oxygen vacancy concentration, in agreement with our reported $\Delta H_{f,vac}$ and $\Delta G_{f,vac}$ values. The traditional method always gives far lower oxygen vacancy concentrations than the equilibrium method because it neglects the positive entropy contribution from the O$_2$ molecule. The slopes of the LS and HS/LS curves are less negative than the experimental value because the slope is controlled by the enthalpy of vacancy formation (which we underestimate with respect to experiment). The HS curve has a similar slope to the experimental concentration because its adjusted $\Delta H_{f,vac}$ agrees well with experiment. As expected, the HS/LS and LS results predict $C_v$ values greater than experiment. The HS/LS and HS $C_v$ curves bracket the experimental curve in agreement with their adjusted $\Delta G_{f,vac}$ values lying below and above, respectively, the experimental value. Physically, a mixture of Co$^{3+}$ spin states contribute to LaCoO$_3$, so a proper comparison between our results and the experimental $C_v$ data is not possible. For example, if the material had more HS than LS Co$^{3+}$ ions, then we would expect the $C_v$ curve to shift downward with respect to the HS/LS curve (toward the experimental values) because the trend is toward lower $C_v$ with increasing HS Co$^{3+}$. The curves in Figure 4.7 become steeper for larger $\mu_{Co}$, mirroring the trend we found for $\Delta H_{f,vac}$ (the slope is, approximately, -$\Delta H_{f,vac}/k_B$). A valid comparison with experimental $C_v$ data requires larger length/time (e.g., Monte Carlo) simulations that account for thermal population of different Co$^{3+}$ spin states and the effect of magnetic heterogeneity on the oxygen vacancy formation energies. Such simulations are beyond the scope of this work. The trends we find provide sufficient atomic-level insight into how various Co$^{3+}$ spin
states affect oxygen transport in LaCoO$_3$. Our results demonstrate that engineering LaCoO$_3$-based cathode materials to have higher LS Co$^{3+}$ concentrations should improve the oxygen diffusivity of these materials. This effect will be largest for pure LaCoO$_3$.

**Figure 4.7.** Oxygen vacancy concentrations ($C_v$, moles per mole LaCoO$_3$) as a function of temperature computed for the LS (red), HS/LS (blue), and HS (green) spin states of LaCoO$_3$. Solid lines use the equilibrium method while dashed lines employ the traditional method as discussed in the text. Experimental data (gray area) from Ishigaki *et al.*$^{31}$ where $C_v$ was estimated as the ratio of the vacancy diffusion coefficient ($D_v$) to the oxygen tracer diffusion coefficient ($D_{O^*}$) multiplied by a constant factor of 1.0 or 0.69.$^{31,32}$ Tabulated experimental data points (black circles) from ref. 31.

Our discussion of oxygen vacancy formation in LaCoO$_3$ shows that the Co$^{3+}$ spin state significantly affects the concentration of oxygen vacancies by altering $\Delta G_{f,\text{vac}}$. Completely understanding oxygen ion transport in LaCoO$_3$ requires considering how the migration process couples to the magnetic configuration of Co$^{3+}$. For this purpose, we identified the minimum energy pathways for oxygen migration in the LS and HS/LS states using GGA+U calculations (Figure 4.8). We did not investigate oxygen migration in the HS state because it probably does not occur independently (*vide supra*). Migration
in the IS state was previously studied by Mastrikov, et al.\textsuperscript{35,36} The pathways (parts a and d) show slightly curved behavior consistent with the prediction made by Islam and Jones for LaFeO\textsubscript{3}.\textsuperscript{87} The predicted migration barriers (parts b and e) are 0.69 eV and 0.49 eV for LS and HS/LS LaCoO\textsubscript{3}, respectively, while the experimental migration barrier from tracer diffusion experiments is $0.78 \pm 0.22$ eV obtained for $700^\circ C < T < 1000^\circ C$.\textsuperscript{31} Tsvetkov et al.\textsuperscript{77} obtained $1.08 \pm 0.10$ eV for the migration barrier using polarization experiments. Tracer diffusion experiments provide a better comparison for our computed barriers because they do not involve an electric potential gradient (present in the polarization experiments). Our calculated barrier for LS LaCoO\textsubscript{3} is comparable to the value of 0.71 eV obtained by Mastrikov et al.;\textsuperscript{35} however, a fair comparison between these theoretical barriers is not possible — their result is for the IS state and our result is for the LS state. Mastrikov et al. proposed that higher charge transfer from the migrating O ion to the central B ion at the transition state in (A,A')(B,B')O\textsubscript{3} materials correlates with a lower migration barrier.\textsuperscript{35} In agreement with Mastrikov et al.’s finding for IS LaCoO\textsubscript{3}, we find almost no change in the charge of the migrating oxygen ($\Delta q \leq 0.02$ e) at the transition state (compared to its charge at the initial state) for both LS and HS/LS LaCoO\textsubscript{3}. Therefore, although the data presented by Mastrikov, et al. show this correlation for Ba\textsubscript{1-x}Sr\textsubscript{x}Co\textsubscript{1-y}Fe\textsubscript{y}O\textsubscript{3} (BSCF) and LSCF, this does not explain the difference in the computed barrier heights for LS and HS/LS LaCoO\textsubscript{3}. In the experimental temperature range, the correct comparison should be between our HS/LS value and the experiment, where we see our value falls just slightly below the lower end of experimental range. Below we offer insight into this discrepancy.
In addition to obtaining different barriers for LS and HS/LS LaCoO$_3$, we find that the magnetic configuration produces different electronic behavior during oxygen migration. In particular, we see that the magnetic moments of the Co ions surrounding the migration pathway evolve differently in LS than in HS/LS LaCoO$_3$. In LS LaCoO$_3$, oxygen migration involves a magnetic moment crossover between two of the Co ions surrounding the migration pathway (Figure 4.8c). We explain this in terms of an ionic picture. Initially, the vacancy resides between Co$_A$ and Co$_B$ (see Figure 4.8a). This means that Co$_A$ and Co$_B$ exist in a reduced state (HS Co$^{2+}$) while Co$_C$ remains in the LS Co$^{3+}$ configuration. In the final state, the vacancy resides between Co$_A$ and Co$_C$, which
now exhibit the HS Co$^{2+}$ state while Co$_B$ becomes LS Co$^{3+}$. Therefore, Co$_B$ is oxidized (Co$^{2+} \rightarrow$ Co$^{3+}$) while Co$_C$ is reduced (Co$^{3+} \rightarrow$ Co$^{2+}$) during the oxygen migration process. This indicates that the migration process couples to an electron transfer from Co$_B$ to Co$_C$, which is opposite to the motion of the oxygen ion. We previously demonstrated this same behavior in LaFeO$_3$. HS/LS LaCoO$_3$ does not exhibit this coupling between oxygen ion migration and electron transfer because of the structure of the defect. Our earlier analysis of oxygen vacancy formation in HS/LS LaCoO$_3$ demonstrated that two HS Co$^{3+}$ ions undergo reduction while the LS Co$^{3+}$ ion adjacent to the vacancy becomes IS Co$^{3+}$. The two HS Co$^{3+}$ (Co$_B$ and Co$_C$ in Figure 4.8d) ions that undergo reduction bracket the diffusion pathway, and their magnetic moments remain essentially constant throughout the migration process. The IS Co$^{3+}$ ion (Co$_A$ in Figure 4.8d) shows a small variation in its magnetic moment along the diffusion pathway, reaching a minimum at the transition state. Because Co$_A$, Co$_B$, and Co$_C$ bracket the diffusion pathway and their charge/magnetism remains constant throughout the migration (see Figure 4.8(d,f)), no electron transfer couples to the oxygen ion migration in HS/LS LaCoO$_3$. However, in order for long range transport to occur, an electron transfer is required such that two Co$^{2+}$ ions bracket the migration pathway for the next jump. While modeling such an electron transfer is beyond the scope of this thesis, we expect that accounting for this electron transfer will increase the observed barrier for oxygen migration leading to better agreement with the experimental measurements.

The difference in oxygen migration between HS/LS and LS LaCoO$_3$ is not just an electronic and magnetic issue. The barrier in HS/LS LaCoO$_3$ is significantly lower than in LS LaCoO$_3$ (Table 4.6). To fully analyze the differences between LS and HS/LS
LaCoO$_3$, we calculate their oxygen diffusion coefficients using transition state theory. As seen earlier, the calculated barrier for LS LaCoO$_3$ is in reasonable agreement with the experimental data$^{31}$ while the calculated barrier for HS/LS LaCoO$_3$ falls below the measured value. Our underestimation of the observed barrier for HS/LS LaCoO$_3$ may result from the inability of our model to include the electron transfer step required to set up the next migration step leading to long range transport as noted above. $D_v$ for LS and HS/LS LaCoO$_3$ are in fair agreement with experiment at 700°C. Since diffusion measurements occur at high temperature, it is of course surprising that the LS state (only stable up to 90 K) shows such good agreement with experiment. We compute the oxygen diffusion coefficient assuming our value of $C_v$ (using Equation 4.6) and using the experimental $C_v$ value at 700°C in order to see how these differences affect $D_0$. The result is a large discrepancy between experiment and theory for the LS state while the agreement is better – though still off - for the HS/LS state. Using the $C_v$ value from experiment, we are nearly within one order of magnitude of experiment. Clearly, the oxygen diffusion coefficient depends strongly on the spin state of the Co$^{3+}$ ions, though primarily through $C_v$.

<table>
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<tr>
<th>Parameter</th>
<th>LS LaCoO$_3$ Calculated</th>
<th>HS/LS LaCoO$_3$ Calculated</th>
<th>LaCoO$_3$ Experimental$^{31}$</th>
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<tr>
<td>a (Å)</td>
<td>2.82</td>
<td>2.61</td>
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</tr>
<tr>
<td>$\nu_0$ (THz)</td>
<td>8.53</td>
<td>6.31</td>
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<td>$\Delta S^\ddagger /k_B$ [700°C]</td>
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<td>-2.16</td>
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<td>$\Delta H_{\text{mig}}$ (eV)</td>
<td>0.69</td>
<td>0.47</td>
<td>0.78 ± 0.22</td>
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<td>ZPE(TS)–ZPE(Min) (eV)</td>
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<td>-0.01</td>
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<tr>
<td>$A$ (cm$^2$/s) [700°C]</td>
<td>$7.3 \times 10^{-3}$</td>
<td>$6.2 \times 10^{-3}$</td>
<td>$1.59 \times 10^{-2}$</td>
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<tr>
<td>$D_v$ (cm$^2$/s) [700°C]</td>
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<td>$2.58 \times 10^{-5}$</td>
<td>$1.43 \times 10^{-6}$</td>
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<tr>
<td>$D_0$ (cm$^2$/s) [700°C] (C, from eq. 6)</td>
<td>$3.17 \times 10^{-7}$</td>
<td>$7.64 \times 10^{-10}$</td>
<td>$9.20 \times 10^{-13}$</td>
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<tr>
<td>$D_0$ (cm$^2$/s) [700°C] (C, from expt.)</td>
<td>$1.34 \times 10^{-12}$</td>
<td>$1.58 \times 10^{-11}$</td>
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</table>
4.6 Conclusions

We have presented an analysis of the effect of Co spin state on oxygen transport in LaCoO$_3$ using detailed first-principles quantum mechanics calculations. Our results provide new understanding regarding the intricacy of LaCoO$_3$, specifically the interrelation of spin state with oxygen ion diffusivity. First, we calculated a new ab initio value of $U_{\text{eff}} = 4.0$ eV for LS Co$^{3+}$ ions using the method of Mosey, Liao, and Carter.$^{37}$ We showed how LDA+U and GGA+U calculations lead to different spin state orderings with only LDA+U being reasonable. We then demonstrated that the presence of LS Co$^{3+}$ ions leads to lower oxygen vacancy formation energies. We also showed that the spin state alters the vacancy migration process and thus the vacancy diffusion coefficient. On the whole, these results confirm that the spin state of the Co$^{3+}$ ions critically influences oxygen transport in LaCoO$_3$.

The results of our study indicate that modifying the operating conditions (e.g., operating pressure) or the material composition (e.g., doping) to increase the number of LS Co$^{3+}$ ions at higher temperatures may offer a route toward improving the ionic conductivity of LaCoO$_3$. The results we provided also form the initial basis for a library of diffusion coefficients, derived from first principles, which can be used for longer time and length scale simulations (e.g., kinetic Monte Carlo). Such an analysis including transitions between spin states, oxygen vacancy formation, and oxygen migration would provide a more complete description of oxygen ion conductivity in LaCoO$_3$. 

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4.7 Supporting Information: Vibrational Frequency Analysis of Low Spin LaCoO$_3$

The ability of different DFT-based methods to describe the vibrational spectrum of LaCoO$_3$ has garnered significant interest in recent years.$^{21,24,25}$ These studies have employed LDA+U, PBE0, and B3LYP calculations to compute the gamma point frequencies for LaCoO$_3$ and to compare them with experiment. To augment the existing literature, we report frequencies for low spin LaCoO$_3$ computed with LDA+U and GGA+U (Table 4.7).

Before we discuss our results, one computational note is required. While VASP can compute and report gamma point frequencies, it does not assign the symmetries to each frequency. Instead, we used Phonopy$^{88}$ (version 1.8.3.2) to diagonalize the Hessian matrix at the gamma point of the Brillouin zone. Using Phonopy allowed us to assign symmetries to the obtained frequencies for comparison with the existing literature. The Phonopy frequencies agreed with those reported by VASP.
Table 4.7. Gamma point phonon frequencies (in cm\(^{-1}\)) for low spin LaCoO\(_3\) obtained with LDA+U and GGA+U calculations. For comparison, experimental\(^8,89\) and theoretical frequencies\(^21,24,25\) from the literature are also reported. All calculations were performed with planewave basis sets unless otherwise noted with the LCAO (linear combination of atomic orbitals) designation. The values in parentheses are the percentage errors with respect to the experimental frequencies.\(^e,f\)

<table>
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<tr>
<th>Mode</th>
<th>Experiment</th>
<th>LDA+U(^a)</th>
<th>GGA+U(^a)</th>
<th>PBE0(^b)</th>
<th>PBE0 – LCAO(^b)</th>
<th>B3LYP – LCAO(^c)</th>
<th>LDA+U(^d)</th>
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<td>Raman Active</td>
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<tr>
<td>(e_g)</td>
<td>86(^e)</td>
<td>93 (+8)</td>
<td>80 (-8)</td>
<td>57 (-34)</td>
<td>104 (-21)</td>
<td>106 (-23)</td>
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<td>176 (+2)</td>
<td>173 (+1)</td>
<td>178 (+3)</td>
<td>178 (+3)</td>
<td>188 (+9)</td>
<td>174 (+1)</td>
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<td>(a_{1g})</td>
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<td>280 (+7)</td>
<td>298 (+14)</td>
<td>280 (+7)</td>
<td>257 (-1)</td>
<td>343 (+31)</td>
<td>253 (-3)</td>
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<td>438 (+1)</td>
<td>448 (+3)</td>
<td>480 (+11)</td>
<td>409 (-5)</td>
</tr>
<tr>
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<td>613 (+5)</td>
<td>631 (+8)</td>
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<td>448 (-23)</td>
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<tr>
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<td>177(^f), 174(^f)</td>
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<td>0.2i</td>
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<td>654</td>
<td>----</td>
<td>----</td>
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\(^a\) This Work  
\(^b\) Ref. 24  
\(^c\) Ref. 25  
\(^d\) Ref. 21  
\(^e\) Ref. 89 at 5 K  
\(^f\) Ref. 8 temperature not specified  
\(^g\) Ref. 90 at 9 K
For the Raman modes, both LDA+U and GGA+U show respectable agreement with experiment. The LDA+U values differ from experiment by at most 8%, while the GGA+U frequencies deviate from experiment by a maximum of 14%. Generally, the LDA+U frequencies exceed experiment, while the GGA+U values fall below experiment. This trend agrees with the fact that LDA+U overbinds the crystal, while GGA+U slightly underbinds the crystal (vide supra, Table 4.1). The respective results obtained with LDA+U and GGA+U agree with experiment, as well as the values obtained with the hybrid PBE0 functional in a planewave basis set. Using a Gaussian basis set appears to have little effect on the accuracy of the frequencies obtained with the PBE0 functional. However, using the B3LYP hybrid functional to predict the Raman frequencies of LaCoO$_3$ is an exercise in futility, as three of the five frequencies have greater than 10% deviation from experiment. The B3LYP functional was not designed for solid state systems containing transition metals, so it is unsurprising to see it struggle with a system such as LaCoO$_3$. Finally, comparing our LDA+U results to the literature values for LDA+U, computed with a different $U_{eff}$ value (7.8 eV) and different pseudopotentials, yielded frequencies which have nearly the same accuracy as our results. Our LDA+U frequencies exceed the experimental frequencies (as expected due to overbinding), whereas ref. 21 reports frequencies below experiment, which is not expected from an LDA-derived theory. This becomes especially noticeable for the highest frequency Raman mode, where ref. 21 deviates from experiment by 23%. Taken together, these results provide evidence that our ab initio $U_{eff}$ value is superior to the higher value used in ref. 21.
The assignment of the symmetries to the infrared frequencies reported by experiment is a difficult task. Indeed, neither ref. 8 or ref. 90 explicitly combines the symmetries with the reported frequencies. Instead, ref. 8 discusses five peaks in the infrared reflection spectrum in terms of $3(A_2u+Eu) + 2Eu$ modes. The three $(A_2u+Eu)$ modes are assigned to the external ($177 \text{ cm}^{-1}$), bending ($315 \text{ cm}^{-1}$), and stretching ($540 \text{ cm}^{-1}$) modes arising from the cubic perovskite lattice. Based on our reading of ref. 8, the $a_{2u}$ and $e_u$ components of these modes should be lumped together because they are not reported separately. The additional modes arise from zone folding due to the rhombohedral unit cell containing two formula units (compared to the one formula unit in the cubic perovskite cell); therefore, these are two independent $e_u$ modes at $242 \text{ cm}^{-1}$ and $411 \text{ cm}^{-1}$, respectively. We next analyze the six infrared modes reported in ref. 90 and attempt to assign their symmetries. While eight phonon modes should be visible in rhombohedral LaCoO$_3$, ref. 90 only observes six frequencies. These are described as belonging to three bands of phonon frequencies in the range of $180 \text{ cm}^{-1}$, $330 \text{ cm}^{-1}$, and $600 \text{ cm}^{-1}$. Since these three bands are assigned to the external, bending, and stretching modes of the cubic perovskite cell, we take the frequencies closest to these ranges and assign them to the $3(a_{2u} + e_u)$ combinations, like we did when analyzing the frequencies from ref. 8. In this case, the external mode is assigned to the peak at $174 \text{ cm}^{-1}$, the bending mode to the peak at $328 \text{ cm}^{-1}$, and the stretching mode to the peaks at $550 \text{ cm}^{-1}$ and $582 \text{ cm}^{-1}$. This leaves the $240 \text{ cm}^{-1}$ and $411 \text{ cm}^{-1}$ modes as zone folding modes, in good agreement with ref. 8. Note that our assignments differ from those in ref. 24.

We see that these assignments have merit when compared with our LDA+U and GGA+U results, though some problems remain. Specifically, the lowest $a_{2u}$ and $e_u$ modes
(corresponding to the external mode) are split by \(\sim 33 \text{ cm}^{-1}\). This is by no means a large splitting, but it does cast doubt on the validity of assigning the same frequency to the \(a_{2u}\) and \(e_u\) components of the external mode. For the external mode, our LDA+U results agree well with experiment, while our GGA+U results are slightly below the experiments. For the bending mode, we again see significant splitting between our \(a_{2u}\) and \(e_u\) modes (71 cm\(^{-1}\) and 53 cm\(^{-1}\) for LDA+U and GGA+U, respectively). The \(e_u\) mode agrees well with experiment in both cases; however, we predict that the \(a_{2u}\) mode should lie significantly lower than the assigned experimental frequencies. The stretching mode has the highest frequencies and, again, the LDA+U results seem to agree pretty well with experiment, while the GGA+U results remain below the experimental frequencies. For the zone folding modes, both the LDA+U and GGA+U results show reasonable agreement with experiment. Given the uncertainty in assigning the experimental infrared frequencies, our LDA+U and GGA+U frequencies both indicate respectable agreement with experiment.

Compared to other functionals, our LDA+U results have approximately the same accuracy as hybrid DFT for the infrared active modes. Our GGA+U results are slightly worse than the hybrid DFT results. Both the B3LYP and PBE0 functionals give approximately the same accuracy for the infrared frequencies. The previously reported LDA+U infrared frequencies are vastly different from experiment. The errors most likely arise from numerical issues with the pseudopotentials used, the high \(U_{\text{eff}}\), or failure to converge the energies to a sufficiently tight threshold (e.g., \(10^{-7} \text{ eV}\)) when computing the forces. For our results and the reported hybrid DFT results, the maximum deviation is between 12-21\%. The GGA+U has the largest deviations of this data set (excluding the
LDA+U results from ref. 21. However, these deviations are not so different from the hybrid DFT deviations to necessitate using the far more expensive hybrid functionals, which require approximately 100 times the computational time as a GGA+U calculation.

In conclusion, comparing our LDA+U and GGA+U gamma point phonon frequencies with experimental values demonstrates that the DFT+U method does indeed provide reasonable predictions of vibrational frequencies. The obtained Raman modes had a maximum deviation of 14% from experiment, which is far lower than the maximum deviation for any hybrid functional reported in the literature. Our LDA+U frequencies show better agreement with the experimental infrared frequencies; however, the GGA+U results seem equally reasonable, as well. The hybrid functionals perform slightly better on the infrared modes, although the gain in accuracy is not worth the increased computational cost. Finally, the LDA+U results from ref. 21 fail to accurately predict the infrared frequencies of LaCoO₃, likely due to some numerical problem or choice of parameters. This analysis establishes that the DFT+U method provides reasonably accurate frequencies for LaCoO₃.

References


Chapter 5

Electronic Structure and Oxygen Vacancies in La$_{1-x}$Sr$_x$FeO$_3$ and La$_{1-x}$Sr$_x$CoO$_3$***

5.1 Introduction

The preceding chapters provided thorough analyses of LaFeO$_3$ (Chapter 3) and LaCoO$_3$ (Chapter 4) as oxygen ion conductors. The next step towards understanding La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_3$ (LSCF) is establishing the role of substituting Sr$^{2+}$ for La$^{3+}$. Using first-principles calculations enables us to isolate this effect independent of other changes (e.g., increased oxygen nonstoichiometry or crystal quality). In this chapter, we will explain how the presence of Sr$^{2+}$ affects La$_{1-x}$Sr$_x$FeO$_3$ (LSF, $x_{Sr}=0.25$, and 0.50) and La$_{1-x}$Sr$_x$CoO$_3$ (LSC, $x_{Sr}=0.25$, 0.50). We will first discuss LSF, followed by LSC.

5.2 La$_{1-x}$Sr$_x$FeO$_3$ Introduction

In LSF, oxygen diffusion occurs via a vacancy-mediated hopping mechanism.$^{1,2}$ The resulting self-diffusion coefficient ($D_o$) has the form:

$$D_o = C_V D_V$$

(5.1)

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Reproduced with permission from Ritzmann, A. M., Muñoz-Garcia, A. B., Pavone, M., Keith, J. A. & Carter, E. A. Ab Initio DFT+U Analysis of Oxygen Vacancy Formation and Migration in La$_{1-x}$Sr$_x$FeO$_3$-$\delta$ ($x = 0, 0.25, 0.50$). Chem. Mater. 25, 3011-3019 (2013). Copyright 2013 American Chemical Society.
Portions of this chapter were reproduced, with permission, from the supporting information from Ritzmann, A. M., Dieterich, J. M. & Carter. E. A. Density Functional Theory +U Analysis of the Electronic Structure and Defect Chemistry of LSCF (La$_{0.5}$Sr$_{0.5}$Co$_{0.25}$Fe$_{0.75}$O$_{3-\delta}$), Phys. Chem. Chem. Phys. 18, 12260-12269 (2016) – Reproduced by permission of the Royal Society of Chemistry.
where $C_v$ is the concentration of oxygen vacancies and $D_v$ is the vacancy diffusion coefficient. $D_v$ takes an Arrhenius form where the activation enthalpy ($\Delta H_{\text{mig}}$) is the energy barrier for an oxygen ion hopping into an unoccupied neighboring site. In LSF, the oxygen vacancies do not interact.\(^3\) The free energy of oxygen vacancy formation ($\Delta G_{\text{f,vac}}$) governs the vacancy concentration. Therefore, the sum of $\Delta H_{\text{f,vac}}$ and $\Delta H_{\text{mig}}$ defines the apparent activation energy for the oxygen diffusion coefficient where $A$ is the preexponential factor which contains the entropy of oxygen vacancy formation.

\[
D_0 = Ae^{-(\Delta H_{\text{f,vac}} + \Delta H_{\text{mig}})/k_BT}
\]

(5.2)

Oxygen diffusion measurements on LSF (for $x_{\text{Sr}}=0$, 0.1 and 0.25) indicate that $x_{\text{Sr}}$ does not significantly affect $\Delta H_{\text{mig}}$.\(^2\) However, thermogravimetric analysis shows that increasing $x_{\text{Sr}}$ significantly raises the oxygen vacancy concentration.\(^4\)

Adding Sr clearly improves oxygen transport in LSF, but a conclusive explanation of the fundamental physics driving this improvement remains absent. In addition to vacancy mediated oxygen transport, the defect chemistry and electrical conductivity of LSF are intimately related. The host material, LaFeO$_3$, is a G-type antiferromagnetic insulator,\(^5\) although lanthanum vacancies ($V_{\text{La}}^{///}$ in Kröger-Vink notation\(^6\)) lead to low p-type conductivity at ambient oxygen partial pressure.\(^7\) Furthermore, while similar ABO$_3$ materials La$_{1-x}$Sr$_x$MnO$_3$ and La$_{1-x}$Sr$_x$CoO$_3$ become metallic when $x > 0.2$, LSF remains an antiferromagnetic semiconductor for $x < 0.9$.\(^8,9\) Substitutional defects ($\text{Sr}_{\text{La}}$), lanthanum vacancies ($V_{\text{La}}^{///}$) oxygen vacancies ($V_O^-$), and electrons/holes play important roles in the defect chemistry of LSF.\(^3\) Large ionic radii suppress interstitial defects within the perovskite structure.
Computational studies have already provided some microscopic insight into defect chemistry and ionic transport in LSF. Jones and Islam\textsuperscript{10} studied defect chemistry and ion migration in LSF using classical potentials. However, conclusions drawn from simulations using classical, empirically-based potentials run the risk of depending strongly on the particular parameterization of the potentials rather than representing the true physics. By contrast, first-principles quantum mechanics calculations based on density functional theory (DFT) can offer unbiased insights by being free from system-dependent parameters. Indeed, several electronic structure descriptions of LaFeO$_3$ have been provided using DFT.\textsuperscript{11–15} Unfortunately, these predictions may suffer from self-interaction errors that cause DFT to fail for strongly correlated materials (\textit{e.g.}, first row late transition metal oxides).\textsuperscript{16} To mitigate these errors, the DFT+U method\textsuperscript{17} has been applied to understanding the electronic structure\textsuperscript{18–20} and defect chemistry\textsuperscript{14,15,21,22} of LaFeO$_3$. However, these previous studies did not consider either the Sr substitution or oxygen migration in LaFeO$_3$. While the perspective of Kuklja \textit{et al.} discounts the DFT+U method for complex oxide materials (\textit{e.g.}, LSCF),\textsuperscript{14} its validity for LSF remains an open question.

Here we present an \textit{ab initio} DFT+U\textsuperscript{23} analysis of the electronic structure and oxygen vacancy formation process in LSF ($x_{\text{Sr}}$=0, 0.25 and 0.50) and oxygen migration in LaFeO$_3$. We clearly show how electron-deficient A-site substitutions enhance oxygen migration in LSF. This insight is highly relevant to rationally designing iron-based SOFC cathode materials. Our study considers all possible arrangements of La/Sr for a given composition within a 40-atom supercell and considers larger cells (160-atom) cells designed to reproduce the random distribution of La/Sr in LSF. We show that DFT+U
successfully models these materials and that Sr substitution has a large effect on the oxygen vacancy formation enthalpy, which in turn has a dramatic effect on ion conductivity.

5.3 Computational Methods for \( \text{La}_{1-x}\text{Sr}_x\text{FeO}_3 \)

We employed two structural models to study LSF. A pseudocubic \( 2 \times 2 \times 2 \) supercell of the simple perovskite unit cell containing 40 atoms was used to calculate the free energy of oxygen vacancy formation and the oxygen migration enthalpy. Previous studies have used the 40-atom cell to study oxygen vacancies in \( \text{LaMO}_3 \) (\( M=\text{Cr,Mn,Fe,Co,Ni} \)) perovskite materials.\(^{21,22} \) We constrained the lattice vectors of the second cell to remain cubic, but internal ionic relaxations were allowed. This model successfully captures the known cooperative tilting of the FeO\(_6\) octahedra (Figure 5.2a). To address the role of Sr substitution, we considered all unique arrangements of La and Sr within the La sublattice (Figure 5.2b). We study the G-type antiferromagnetic state of LSF which is consistent with neutron diffraction experiments.\(^{24} \) For validation, we used a 160 atom supercell of LSF to consider the effects of lower oxygen vacancy concentrations on our predictions. We generated the 160-atom supercell using the special quasirandom structures method (sqs) to determine the La/Sr arrangement which best resembles the random alloy.\(^{25} \) The cell was generated using the mcsqs code in version 3.0 of the Alloy Theoretic Automatic Toolkit (ATAT)\(^{26-28} \) by first enumerating all possible supercells of the \( \text{LaFeO}_3 \) orthorhombic unit cell (ensuring G-type antiferromagnetism in the resulting cells) for a specified number of atoms. To minimize vacancy-vacancy
interactions, we screened for supercells which maximized the distance from an oxygen atom to its periodic image.

Figure 5.1 a) Pseudocubic cell used for modeling LSF, b) all unique La/Sr arrangements for $x=0$, 0.25 and 0.50, and c) 160-atom supercells for $x=0$, $x=0.25$ and $x=0.50$. Structures visualized with VESTA. Color designations: Fe (brown), O (red), La (green), Sr (pink). For clarity, we omit the Fe and O atoms when presenting the La/Sr arrangements in parts b and c.
Finally, for the best candidate cells, we used the mcsqs code to find the La/Sr arrangement which best reproduced random mixing on the A-site sublattice for $x_{Sr}=0.25$ and $x_{Sr}=0.50$. Both compositions yielded supercells (Figure 5.1c) with the same shape and matched the random alloy pair-correlation functions to a cutoff of 8.8 Å. The vacancy-vacancy distances were ~7.9 Å in the 40-atom pseudocubic cell and ~11.25 Å in the SQS cells. Calculations for other $x_{Sr}$ values (e.g., $x_{Sr}=0.125$) would require significantly larger supercells and were not undertaken in this study.

The energy cost for oxygen vacancy formation determines the nonstoichiometry of LSF. We compute this energy by comparing the energy of the supercell with an oxygen vacancy (a neutral oxygen atom is removed) to the same cell without an oxygen vacancy (referenced to half the energy of a gas phase O$_2$ molecule in its triplet ground state). The vacancy concentrations are $1/24$ (4.2%, $\delta=0.125$) and $1/96$ (1.0%, $\delta=0.03125$) in the pseudocubic (40-atom) and sqs (160-atom) supercells, respectively. These vacancy concentrations are reasonable for $x=0.25$ and $x=0.50$ (1% and 4% respectively). The simplest approximation of the vacancy formation enthalpy uses only electronic energies and neglects thermal and vibrational effects:

$$
\Delta E_{f,\text{vac}} = E_{\text{defective}} - E_{\text{perfect}} + \frac{1}{2} E_{O_2}
$$

Approximating $\Delta H_{f,\text{vac}}$ at absolute zero includes the zero point energy (ZPE) contributions

$$
\Delta H_{f,\text{vac}}(0) = \Delta E_{f,\text{vac}} + \sum_{i=1}^{3(N-1)-3} \frac{1}{2} h \nu_{i,\text{defective}} - \sum_{j=1}^{3N-3} \frac{1}{2} h \nu_{j,\text{perfect}} + \frac{1}{2} \left( \frac{1}{2} h \nu_{O_2} \right)
$$

where $h$ is Planck’s constant and the $\nu$’s are vibrational frequencies calculated within the harmonic oscillator (H.O.) approximation and $N$ is the number of atoms in the perfect
supercell. Approximating $\Delta H_{f,\text{vac}}$ at finite temperature involves integrating the heat capacities ($C_p$) from absolute zero to the temperature of interest. $C_p$ values for the solids (the sums in Equation 5.5) are calculated using the H.O. approximation for vibrational contributions while $C_p$ for O$_2$ also includes effects from the rigid-rotor and ideal gas approximations for vibrational, rotational, and translational contributions.$^{30}$ Because the PV contributions to enthalpy for solids should be negligible, we assume that the internal energy of each solid is equivalent to its enthalpy, while the enthalpy of gas phase O$_2$ includes the PV term via its constant pressure heat capacity.

$$\Delta H_{f,\text{vac}}(T) = \Delta H_{f,\text{vac}}(0) + \sum_{i=1}^{3(N-1)-3} \frac{h v_{i,\text{defective}}}{k_B T_i} - \sum_{j=1}^{3N-3} \frac{h v_{j,\text{perfect}}}{k_B T_j} + \frac{1}{2} \left( \int_0^T C_p,O_2(T')dT' \right)$$

Calculating the free energy of oxygen vacancy formation ($\Delta G_{f,\text{vac}}$) requires the entropy of the solids and O$_2$ as a function of temperature.

$$\Delta G_{f,\text{vac}}(T) = \Delta H_{f,\text{vac}}(T) - T \Delta S_{f,\text{vac}}(T)$$

$$\Delta S_{f,\text{vac}}(T) = S_{\text{vib,defective}}(T) - S_{\text{vib,perfect}}(T) + \frac{1}{2} S_{O_2}(T)$$

Gryaznov et al. showed that including vibrational effects of the solids can significantly impact oxygen vacancy formation free energies in LSCF.$^{31,32}$ We express the vibrational enthalpy and entropy as the sum of contributions from harmonic oscillators with the $\Gamma$-point phonon frequencies of the perfect and defective crystals.$^{33}$ We computed the vibrational frequencies for the entire 40-atom supercell and found that all frequencies were real except for the three acoustic modes which were essentially zero. Sampling the Brillouin zone (BZ) beyond the $\Gamma$-point resulted in unphysical imaginary frequencies in some regions of the BZ. We attribute this issue to approximating the Hessian matrix using
finite differences of forces and to the constraint that the lattice vectors remain cubic. To
avoid issues arising from these unphysical imaginary frequencies, we only use the Γ-
point phonon frequencies in our calculations. For each composition, we compute the
vibrational effects using frequencies calculated in the pseudocubic cell with the isotropic
La/Sr arrangements only (rightmost distributions of Sr shown in Figure 5.1c).

Electronic energies were obtained from spin-polarized Kohn-Sham DFT\textsuperscript{34,35} and
DFT + U\textsuperscript{17} calculations with periodic boundary conditions using the Vienna Ab Initio
Simulation Package (VASP)\textsuperscript{36–38} version 5.2.2. The nuclei and core electrons were
represented within the frozen-core projector-augmented wave\textsuperscript{39} approach using standard
potentials for Fe (4s\textsuperscript{2} 3d\textsuperscript{6}), La (5s\textsuperscript{2} 5p\textsuperscript{6}s\textsuperscript{2} 5d\textsuperscript{1}), Sr (4s\textsuperscript{2} 4p\textsuperscript{6}s\textsuperscript{2}) and ‘regular’ O (2s\textsuperscript{2} 2p\textsuperscript{4}) from
the VASP library, where the outer core/valence electrons shown in parentheses are self-
consistently optimized.\textsuperscript{40} Electron exchange and correlation was evaluated within the
generalized gradient approximation (GGA) using the functional of Perdew, Burke, and
Ernzerhof (PBE),\textsuperscript{41} although we also performed validation calculations (\textit{vide infra}) with
the local density approximation (LDA) and the more expensive hybrid functional of
Heyd, Scuseria, and Ernzerhof (HSE).\textsuperscript{42} The pseudocubic and SQS LSF calculations
required 4 × 4 × 4 and 3 × 3 × 3 Monkhorst-Pack \textit{k}-point meshes, respectively. The
planewave basis set was converged at a kinetic energy cutoff of 750 eV. Integration over
the first BZ used Gaussian smearing (σ=0.05 eV) during structural relaxations. The
tetrahedron method with Blöchl corrections\textsuperscript{43} for BZ integration was used after geometry
optimization to obtain projected density of states (PDOS), refined energies, and the final
charge density for Bader analysis.\textsuperscript{44,45} Total energies were converged to within 5
meV/formula unit with these numerical settings. The $\text{U}_{\text{eff}}$ parameter for Fe\textsuperscript{3+} (4.3 eV) in
the DFT+U calculations was derived from unrestricted Hartree-Fock calculations on electrostatically embedded Fe₂O₃ clusters in earlier work. The transferability of this Ueff value was recently validated by applying it in the study of the double-perovskite MIEC material Sr₂FeMoO₆. The energies of defective cells were calculated at the lattice constants of the perfect cell. We used the lattice vectors obtained at absolute zero because thermal expansion results in only minor changes in the lattice vectors (~1%) from low temperature to SOFC temperatures.

5.4 Results and Discussion for La₁₋ₓSrₓFeO₃

5.4.1 Bulk Properties of La₁₋ₓSrₓFeO₃

The structural behavior of LSF under increased Sr content may appear counterintuitive. Sr²⁺ has a larger ionic radius (1.44 Å) than La³⁺ (1.36Å), but when Sr²⁺ substitutes for La³⁺, the unit cell volume actually decreases (Figure 5.2a). Shorter Fe-O bonds accompany this decrease (Figure 2b), while Fe-O-Fe bond angles increase toward 180° (Figure 2c). This trend reproduces the experimental trends found in LSF, but the underlying cause only becomes clear upon examination of the electronic structure discussed next.
As alluded to earlier, Sr substitution introduces holes into the lattice of LSF to maintain charge neutrality in the crystal. We determine the nature of the hole states that form upon Sr-substitution in LSF by analyzing its electronic structure, as represented by its PDOS (Figure 5.3). In LaFeO$_3$, a clear gap is visible above the Fermi level (Figure 5.3a). For $x_{Sr}=0.25$ (Figure 5.3b) and $x_{Sr}=0.50$ (Figure 5.3c), the hole states introduced by Sr substitution appear just above the Fermi level. While the valence band now crosses the
Fermi level, the gap remains clear. Thus, the GGA+U method correctly predicts p-type semiconductivity for these compositions. Furthermore, the PDOS indicate the hole states have mixed Fe $3d$ and O $2p$ character and hence are at least somewhat delocalized (\textit{vide infra}), in contrast to the assumption of hopping type, localized carriers that was employed in analyzing the conductivity and Seebeck coefficients of LSF.$^3$

\textbf{Figure 5.3.} GGA+U PDOS for Fe $3d$ (black) and O $2p$ (red) states in LSF. a) $x=0$, b) $x=0.25$ and c) $x=0.50$ in the pseudocubic (40-atom) cell. Positive values represent majority spin states while negative values represent minority spin states.
Besides affecting the DOS, Sr substitution also affects the magnetic moment and charge on each atom (Table 5.1). Increasing Sr-content decreases magnetic moments of a corresponding number of Fe ions; holes therefore appear to affect the Fe sublattice. However, with increasing Sr content, the Fe and La Bader charges remain essentially unchanged. The Bader charge on O becomes less negative by only 0.04 electrons per O atom for each 0.25 increase in Sr mole fraction. Surprisingly, this small difference, when distributed over the entire oxygen sublattice, accounts for nearly all of the electrons lost due to holes arising from Sr substitution, indicating hole delocalization on the oxygen sublattice. Moreover, the fact that the charge on Fe does not change but the Fe magnetic moments are reduced indicates increased Fe-O bond covalency upon Sr substitution rather than hole localization on Fe as had been suggested previously. Our results agree with Patrakeev et al.’s 2005 study which found no activation energy for carrier mobility in LSF (x ≤ 0.5) indicating band-like semiconducting behavior.
Table 5.1. Magnetic moments (μB) and Bader charges (e) for LSF with x=0, x=0.25 and x=0.50 with and without an oxygen vacancy (Vo**) in the pseudocubic (40-atom) cell.[a,b,c]

<table>
<thead>
<tr>
<th></th>
<th>x = 0</th>
<th>x = 0.25[c]</th>
<th>x = 0.50[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no V₀</td>
<td>with V₀</td>
<td>no V₀</td>
</tr>
<tr>
<td>μFe</td>
<td>4.16</td>
<td>4.17 ± 0.01</td>
<td>4.07 ± 0.12</td>
</tr>
<tr>
<td>μFe*</td>
<td>----</td>
<td>3.59</td>
<td>----</td>
</tr>
<tr>
<td>qFe</td>
<td>1.70</td>
<td>1.69 ± 0.01</td>
<td>1.70</td>
</tr>
<tr>
<td>qFe*</td>
<td>----</td>
<td>1.25</td>
<td>----</td>
</tr>
<tr>
<td>qLa</td>
<td>2.08</td>
<td>2.06 ± 0.02</td>
<td>2.09</td>
</tr>
<tr>
<td>qSr</td>
<td>----</td>
<td>----</td>
<td>1.59</td>
</tr>
<tr>
<td>qO</td>
<td>-1.26</td>
<td>-1.27 ± 0.01</td>
<td>-1.22 ± 0.01</td>
</tr>
</tbody>
</table>

[a] Uncertainties give the range of calculated values (for different defect configurations) relative to the calculated mean.

[b] Fe* indicates the iron ions adjacent to the oxygen vacancy.

[c] Vo** (in Kröger-Vink notation) denotes an oxygen vacancy where a neutral oxygen atom has been removed.

[d] Values are reported for the isotropic La/Sr distributions when xSr=0.25 and xSr=0.50 (rightmost distributions in Figure 5.1c).

[e] ‘×4’ indicates four Fe ions (out of eight) within the supercell have this magnetic moment.

5.4.2 Oxygen Vacancy Formation in La1-xSrxFeO3

Now we describe fundamental characteristics of oxygen vacancy formation in LSF. Each La/Sr arrangement shown in Figure 5.1b has several potential oxygen vacancy sites. Two Fe ions and four La/Sr ions coordinate each oxygen atom in LSF. We calculated vacancy formation energies for removing an oxygen ion in each La/Sr environment present for each unit cell shown Figure 5.1b, leading to one, seven and fifteen unique oxygen vacancy calculations for xSr=0, xSr=0.25, and xSr=0.50, respectively. Vacancy formation energies (Table 5.2) are calculated using Equations 5.3-
5.7. The vibrational effects significantly impact the free energy of oxygen vacancy formation, but they do not alter the general trends. Therefore, we use the oxygen vacancy formation enthalpy at 700°C (Equation 4) for qualitative analysis and direct comparison to the experimentally-derived enthalpy. From $x_{Sr}=0$ to $x_{Sr} = 0.25$, our results show a steep decline in oxygen vacancy formation energy, which agrees with experimental measurements ($T=600-1200^\circ C$) in this range (Figure 5.4).\textsuperscript{4} Since our GGA+U results slightly overestimate the equilibrium lattice constants (compared to experiment), our calculation already accounts for the small (~1\%) elongation of the lattice vectors due to thermal expansion.\textsuperscript{49} From $x_{Sr} = 0.25$ to $x_{Sr} = 0.5$, the oxygen vacancy formation enthalpy decreases in the pseudocubic cell while the remaining sqs cells and experiment show relatively constant values in this range. Below, we discuss why the pseudocubic and sqs models differ.

\textbf{Table 5.2.} Average GGA+U oxygen vacancy formation energies (in eV) for LSF with $x_{Sr}=0$, 0.25 and 0.50 in the pseudocubic (40-atom) and sqs (160-atom) supercells.\textsuperscript{[a]}

\begin{center}
\begin{tabular}{cccccc}
\hline
$x_{Sr}$ & $\Delta E_{f,vac}$ & $\Delta H_{f,vac}(0)$ & $\Delta H_{f,vac}(700^\circ C)$ & $\Delta G_{f,vac}(700^\circ C)$ \\
\hline
\textbf{Pseudocubic Cell (40 atoms)}\textsuperscript{[a]}
0 & 4.05 & 4.01 & 3.99 & 3.04 \\
0.25 & 0.71 ± 0.17 & 0.82 ± 0.17 & 0.69 ± 0.17 & 0.14 ± 0.17 \\
0.50 & 0.02 ± 0.28 & 0.09 ± 0.28 & -0.01 ± 0.28 & -0.67 ± 0.28 \\
\hline
\textbf{Sqs Cell (160 atoms)}\textsuperscript{[b]}
0.0 & 4.06 & 4.02 & 4.00 & 3.06 \\
0.25 & 0.14 & 0.25 & 0.12 & -0.44 \\
0.50 & 0.31 & 0.38 & 0.28 & -0.39 \\
\hline
\end{tabular}
\end{center}

\textsuperscript{[a]} Uncertainties give the range of calculated values (for different defect configurations) relative to the calculated mean.

\textsuperscript{[b]} Vibrational contributions are assumed to be the same as those found in the pseudocubic cell.
Figure 5.4. GGA+U vacancy formation enthalpy at 700°C in LSF as a function of Sr content. Experimental results from ref. 4, DFT-GGA results from ref. 15, average 40-atom results (gray line), all 40-atom results (gray circles), and 160-atom results (red line and squares). Even better agreement between our computed oxygen vacancy formation enthalpies and experimental values would be obtained with a correction for the known overbinding of the O₂ molecule by DFT-GGA (vide infra). The small scatter in our 40-atom results indicates that the local chemical environment has a minimal effect on the oxygen vacancy formation enthalpy. [a]Experimental results from ref 4 are the reported reaction enthalpies determined over the range of 600°C-1200°C for 2Fe³⁺ + O²⁻ → 2Fe²⁺ + V₀ + ½O₂ (x=0) and 2Fe⁴⁺ + O²⁻ → 2Fe³⁺ + V₀ + ½O₂ (x=0.25, 0.50) in LSF. Because they are determined from a fit using the van’t Hoff equation, the experimental values are temperature-independent. Experimental uncertainties represent 2σ. [b]DFT-GGA results from Mastrikov et al. (ref. 15) obtained using the 40-atom pseudocubic supercell with ferromagnetic ordering.

Adding Sr initially causes a large drop in ΔHᵢ, vac leading to improved bulk oxygen transport. Bader charges and magnetic moments in LSF with and without an oxygen vacancy (Table 5.1) help explain this decrease. As previously discussed in Chapter 3, a lack of exchange stabilization for the reduced Fe ions adjacent to an oxygen vacancy in LaFeO₃ leads to a relatively large ΔHᵢ, vac (computed 4.0 eV, experimental 5.1 eV). The presence of Sr significantly alters oxygen vacancy formation. Little electron density localizes on the Fe sites adjacent to the vacancy in xₛᵣ=0.25; instead, the average charge
on the oxygen ions becomes more negative, indicating that creating the vacancy provides electrons which disperse across the oxygen sublattice. As discussed earlier, the holes introduced by Sr substitution withdraw charge from the oxygen sublattice. Creating a vacancy generates electrons, and these electrons compensate the holes arising from Sr substitution. The Fe ion remains in the favorable $+3$ oxidation state that has a half-filled $d$-shell, thereby maximizing the $d$-$d$ exchange stabilization with no additional Coulomb repulsion as suffered in LaFeO$_3$ vacancy formation. The electronegative oxygen ions regain the charge they lost when Sr substituted for La. Similar to the $x_{Sr}=0.25$ LSF, the oxygen vacancies in $x_{Sr}=0.50$ LSF provide electrons which compensate some of the holes residing on the oxygen sublattice. The process of creating an oxygen vacancy is essentially the same in $x_{Sr}=0.25$ and $x_{Sr}=0.50$, involving favorable charge compensation and no added Coulomb repulsion on Fe ions, which leads to very low oxygen vacancy formation energies. Our results for La$_{0.5}$Sr$_{0.5}$FeO$_3$ differ significantly from the DFT-GGA results of Mastrikov et al.$^{15}$ who found that vacancy formation leads to charge localization on the Fe ions adjacent to the vacancy (as we found for LaFeO$_3$). This difference leads to a large disagreement between the computed oxygen vacancy formation enthalpies (0.28 eV in this work vs. 3.39-3.60 eV from ref. 15). Our results show far greater agreement with experiment than the DFT-GGA results. Our improved agreement with experiment likely arises from using computational methods that more accurately represent the La$_{1-x}$Sr$_x$FeO$_3$ family of materials (specifically, using GGA+U method, treating the antiferromagnetic order appropriately, and using the ‘normal’ instead of ‘soft’ PAW potential for oxygen).
Recall that our pseudocubic model predicts a decrease in $\Delta H_{f,vac}$ from $x_{Sr}=0.25$ to $x_{Sr}=0.50$ (Figure 5.4) which differs from experiment. In the previous paragraph, we showed that charge compensation occurs in both cases and facilitates oxygen vacancy formation. However, the ratio of vacancies to holes ($V_O/Sr_{La}^{\prime}$) differs in each case. Specifically, $x=0.25$, $V_O/Sr_{La}^{\prime}=0.5$ in the pseudocubic model, which is the limit for charge compensation (two holes compensating one vacancy). When $x_{Sr}=0.50$, additional uncompensated holes are present in the pseudocubic supercell so $V_O/Sr_{La}^{\prime}$ is less than 0.5.

Increasing the size of our supercell model lowers the oxygen vacancy formation energy for $x_{Sr}=0.25$ while leaving $x_{Sr}=0.0$ and $x_{Sr}=0.50$ basically untouched because the $x_{Sr}=0.25$ calculation no longer occurs at the charge compensation limit. Thus, the $\Delta H_{f,vac}$ values for $x_{Sr}=0.25$ and $x_{Sr}=0.50$ are similar. The narrow scatter in our 40-atom oxygen vacancy formation enthalpies (obtained for various local environments and for different La/Sr arrangements) indicates that the multiple minimum problem sometimes encountered for DFT+U is not a likely source of error in our calculations. This does not explain why our $\Delta H_{f,vac}$ values at 700°C in the 160-atom sqs cell are 1.1, 0.88 and 0.72 eV below the experimental values, for $x=0.00$, $x=0.25$ and $x=0.50$, respectively. We attribute this difference primarily to the known overbinding of $O_2$ by DFT-GGA, which would shift our values upward by at least 0.42 eV (half of the difference between the bond dissociation energy, $D_0$, calculated with DFT-GGA and determined experimentally), in better agreement with experiment.

Using the relationships described above as well as the thermal corrections for $O_2$ (see Chapter 2), we calculate the oxygen vacancy formation free energy ($\Delta G_{f,vac}$) as a function of temperature over the range 500-1000°C (Figure 5.5). For the purpose of
comparison, we also plot the $\Delta G_{f,\text{vac}}$ using $\Delta H_{0,\text{vac}}^0$ and $\Delta S_{0,\text{vac}}^0$ determined from the experiments of Mizusaki et al.$^4$

![Figure 5.5](image-url)  

**Figure 5.5.** Free energies of oxygen vacancy formation for LaFeO$_3$ (green, $x=0$), La$_{0.75}$Sr$_{0.25}$FeO$_3$ (orange, $x=0.25$), and La$_{0.50}$Sr$_{0.50}$FeO$_3$ (black, $x=0.50$). The dashed lines provide the experimental data from reference 4 (assuming that $\Delta G_{f,\text{vac}} = \Delta H_{0,\text{vac}}^0 - T\Delta S_{0,\text{vac}}^0$ and the standard enthalpies and entropies are independent of temperature).

We note that the computed values fall significantly below the experimental values, but this observation is consistent with our earlier discussion. Applying a correction for the overbinding of O$_2$ would shift the calculated lines upward by approximately 0.42 eV and yield significantly better agreement with experiment. The fact that the slopes of the calculated and experimental data are similar indicates that the entropy of vacancy formation does not have a strong temperature dependence. Finally, the ordering of
$x_{Sr}=0.25$ and $x_{Sr}=0.50$ vacancy formation free energies is reversed in the calculated data compared with experiment; however, the difference between these two lines is very small, such that the two are essentially equal in both the experimental results and the computed results.

**5.5 $La_{1-x}Sr_xCoO_3$ Background**

LSC-based SOFC cathodes demonstrate significantly higher electronic conductivities than LSF-based cathodes.\(^7\)\(^{,56}\) Unfortunately, thermal incompatibility with YSZ has limited the usefulness of LSC cathodes.\(^57\) Recent experimental work has renewed interest in this material in conjunction with other La-Sr-Co-O phases (e.g., $La_{2-x}Sr_xCoO_4$). Experiments by Sase *et al.* have shown that the heterointerface of LSC with $La_{2-x}Sr_xCoO_4$ displays orders of magnitude increases in the oxygen surface exchange coefficient ($k$).\(^58\) As previously discussed in Chapter 1, $k$ is a measure of the ease with which reduction and incorporation occur on the surface of a material. The high-correlation between $k$ and $D_O$\(^59\) suggests that this heterointerface will also improve oxygen diffusivity. Furthermore, applying tensile strain to LSC increases $k$ and $D_O$.\(^60\) As our aforementioned studies of $LaCoO_3$ (Chapter 4) showed that the magnetic configuration of the $Co^{3+}$ ion significantly impacted the oxide ion diffusivity, we believe that the relationship between oxygen nonstoichiometry and the magnetic behavior of LSC may also provide insights into how the presence of Co affects ion conduction in LSCF. However, the effect of nonstoichiometry on the magnetic properties of LSC has received very little attention.\(^61\) Therefore, we present an *ab initio* analysis LSC to elucidate the
atomic-level effects of Sr substitutions and oxygen vacancies on LSC’s electronic
structure.

LSC behaves differently than LSF with respect to the addition of Sr$^{2+}$. Whereas
LSF remains a semiconductor when $x_{Sr} < 0.90$, LSC becomes metallic when $x_{Sr} \geq 0.25$. Electron delocalization leads to the intermediate spin state of Co$^{3+}$ becoming the
dominant magnetic configuration. While the general behavior of LSC is well-known
with respect to Sr substitution, important electronic structure features such as the role of
the oxygen sublattice remain unclear.

5.6 Computational Details for La$_{1-x}$Sr$_x$CoO$_3$

The computational details for LSC are very similar to those for LSF (vide supra). We perform both DFT-GGA and GGA+U calculations to see whether the GGA+U
method can handle metallic LSC. We employ the 40-atom pseudocubic supercell (Figure
5.6a and 5.6b) in the same way we did for LSF, and we use an 80-atom SQS cell (Figure
5.6c) to examine the effects of using larger supercells. The 80-atom SQS cell exactly
matches the first- and second-nearest-neighbor pair-correlation functions of a perfectly
random alloy. For the structures in Figure 5.6b and 5.6c, the minimum distances between
an atom and its periodic image are 7.7 Å and 9.4 Å, respectively. The SQS cells can be
constructed from the ideal cubic perovskite cell (lattice vectors $\mathbf{a}_c$, $\mathbf{b}_c$, and $\mathbf{c}_c$) as a
supercell with lattice vectors $\mathbf{a}_{sqs} = 2\mathbf{a}_c + \mathbf{b}_c + \mathbf{c}_c$, $\mathbf{b}_{sqs} = 2\mathbf{a}_c - \mathbf{b}_c - \mathbf{c}_c$, and $\mathbf{c}_{sqs} = -\mathbf{a}_c + 2\mathbf{b}_c$ 

For both the 40-atom and 80-atom supercells, we used a $4 \times 4 \times 4$ Monkhorst-
Pack k-point mesh. First-order Methfessel-Paxton smearing ($\sigma = 0.10$ eV) was used to
model the metallic LSC. This smearing width ensures that the electronic entropy remained below 5 meV/f.u. The planewave basis set was truncated at a kinetic energy of 750 eV.

Figure 5.6. Structures used for modeling LSC. a) The pseudocubic (40-atom) cell, b) the unique La/Sr arrangements for $x_{\text{Sr}}=0.25$ and $x_{\text{Sr}}=0.50$ in the pseudocubic cell, and c) the 80-atom SQS cell matching the pair correlation functions of a random alloy for first- and second-nearest-neighbor arrangements. Color designations: Co (blue), O (red), La (green), and Sr (pink). For clarity, we omit the Co and O atoms when presenting the La/Sr arrangements in parts b and c.
5.7 Results and Discussion for La$_{1-x}$Sr$_x$CoO$_3$

We begin by analyzing DFT-GGA and GGA+U calculations for LSC ($x_{Sr}=0.25$ and 0.50). The reason we re-check the methodology for LSC is that as noted above, unlike LSF, the specified compositions have metallic character.\textsuperscript{56} We employ the 40-atom pseudocubic supercell (Figure 5.6a) with isotropic La/Sr distributions for this purpose (furthest right in Figure 5.6b). Table 5.3 and Figure 5.7 give the results of these calculations.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>DFT-GGA</th>
<th>GGA+U</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_0$</td>
<td>54.61\textsuperscript{a,63} &lt;sup&gt;54.64\textsuperscript{63}&lt;sup&gt;</td>
<td>54.64\textsuperscript{63}&lt;sup&gt;</td>
</tr>
<tr>
<td>$a_{pc}$</td>
<td>7.59\textsuperscript{b} &lt;sup&gt;7.59\textsuperscript{b}</td>
<td>7.70 &lt;sup&gt;7.68 &lt;sup&gt;</td>
</tr>
<tr>
<td>$q_{La}$</td>
<td>---- &lt;sup&gt;7.59\textsuperscript{b} &lt;sup&gt;7.59\textsuperscript{b}</td>
<td>2.09 &lt;sup&gt;2.10 &lt;sup&gt;</td>
</tr>
<tr>
<td>$q_{Sr}$</td>
<td>---- &lt;sup&gt;7.59\textsuperscript{b} &lt;sup&gt;7.59\textsuperscript{b}</td>
<td>1.59 &lt;sup&gt;1.59 &lt;sup&gt;</td>
</tr>
<tr>
<td>$q_{Co}$</td>
<td>---- &lt;sup&gt;7.59\textsuperscript{b} &lt;sup&gt;7.59\textsuperscript{b}</td>
<td>1.36 &lt;sup&gt;1.39 &lt;sup&gt;</td>
</tr>
<tr>
<td>$q_{O}$</td>
<td>---- &lt;sup&gt;7.59\textsuperscript{b} &lt;sup&gt;7.59\textsuperscript{b}</td>
<td>-1.11 &lt;sup&gt;-1.08 &lt;sup&gt;</td>
</tr>
<tr>
<td>$\mu_{Co}$</td>
<td>1.5 \textsuperscript{62} &lt;sup&gt;1.8 \textsuperscript{61}</td>
<td>1.44-1.54 &lt;sup&gt;1.62-1.64 &lt;sup&gt;</td>
</tr>
</tbody>
</table>

\textsuperscript{a}For $x_{Sr} = 0.25$, the values of the equilibrium volume from ref. 63 for $x_{Sr} = 0.2$ and $x_{Sr} = 0.3$ were averaged.

\textsuperscript{b}The pseudocubic lattice constants were derived by double the cube-root of the equilibrium volume (per formula unit). This gives a lattice constant that can properly be compared to our data.

We find that both computational methods properly predict metallic behavior for LSC; however, the GGA+U method gives disparate Co magnetic moments. The PDOS
from the GGA+U calculations is half-metallic with a gap in the $\beta$-spin channel. These features result from the GGA+U method attempting to force integer occupations in the Co $3d$ manifold. Our data thus show that the +U correction leads to unphysical electron localization in LSC. On the other hand, the DFT-GGA calculations perform very well for LSC. The Co magnetic moments remain essentially homogeneous, and the PDOS shows that a fully metallic system has developed. DFT-GGA values are consistent with experimental measurements of $\mu_{\text{Co}}$ in La$_{0.50}$Sr$_{0.50}$CoO$_3$, which found values of 1.5 $\mu_B$ and 1.8 $\mu_B$. A large peak in the $\beta$-spin PDOS at the Fermi level agrees with previous DFT-GGA calculations on LSC. Based on these results, we will use DFT-GGA exclusively in the following discussion of LSC.
Figure 5.7. DFT-GGA (top) and GGA+U (bottom) PDOS for LSC \( x_{Sr} = 0.25 \) (left) and \( x_{Sr} = 0.50 \) (right) in the pseudocubic cell with isotropic La/Sr arrangements (furthest right in Figure 5.6b).

The Bader charges indicate that a significant portion of the hole density is delocalized on the oxygen sublattice. The following analysis uses the DFT-GGA results for the transition from \( x_{Sr} = 0.25 \) to \( x_{Sr} = 0.50 \). As with LSF, the Bader charges of the oxygen ions show a small increase from \( x_{Sr} = 0.25 \) to \( x_{Sr} = 0.50 \) (\(+0.03 \text{ e per ion}\)). However, this small difference becomes significant when summed over the twenty-four oxygen ions in the cell. Replacing two La\(^{3+}\) ions with Sr\(^{2+}\) ions removes 2 e from the cell, but the difference in Bader charges between these two ions indicates that 1.0 e are withdrawn from the Co and O sublattices. The remaining 1.0 e reflects the 0.5 e per site difference in the Bader charges of La and Sr. Our Bader analysis therefore shows that 0.72 e comes
from the O sublattice, while 0.24 $e$ comes from the Co sublattice. The remaining 0.04 $e$ is accounted for by the slight increase in the Bader charge of the La ions.

Analyzing various La/Sr distributions (Figure 5.6b) enables us to understand how Sr substitution affects the properties of LSC. The total energies for pseudocubic cells with different La/Sr arrangements and $x_{Sr}=0.25$ differ by a maximum of 9 meV f.u.$^{-1}$. The most stable La/Sr arrangement for $x_{Sr}=0.25$ has the two Sr ions adjacent to one another. However, these small energy differences compete with configurational entropy (approximately 10 meV f.u.$^{-1}$ at 700°C) that tries to drive the system toward randomness. Meanwhile, the story changes for $x_{Sr}=0.50$. The maximum energy difference in this case is 65 meV f.u.$^{-1}$, while the configurational entropy is approximately the same as with the $x_{Sr}=0.25$ case. The most stable configuration for $x_{Sr}=0.50$ alternates between SrO and LaO planes, sandwiching CoO$_3$ planes in the (001) direction (leftmost arrangement in Figure 5.6b). The isotropic La/Sr distribution (rightmost arrangement in Figure 5.6b) is 35 meV f.u.$^{-1}$ less stable than any other arrangement. The results for $x_{Sr}=0.50$ indicate that a driving force for Sr segregation may exist. This agrees with the experimental work of Señaris-Rodriguez and Goodenough who found that La$_{1-x}$Sr$_x$CoO$_3$ contains Sr-rich regions with ferromagnetic order embedded in Sr-poor regions resembling LaCoO$_3$.$^{64}$ Although we do not observe a large driving force for segregation at lower Sr content ($x_{Sr}=0.25$), our pseudocubic cell contains insufficient Sr ions to draw a firm conclusion about the driving force for Sr segregation at that composition.

$^{***}$ Configurational entropy is calculated as $S = -k_B \sum_{n=1}^{N} P_n \ln(P_n)$ for $N$ configurations. The Boltzmann weights for each configuration of 8 f.u. (Figure 5.6b) were used to compute the configurational entropy for the pseudocubic cell. The entropic contribution at 700°C was then estimated by multiplying the absolute temperature (973 K) by the configurational entropy that we obtained and dividing by eight (the number of f.u. in the cell).
Table 5.4. Bader charges \( (q_{\text{La}}, q_{\text{Sr}}, q_{\text{Co}}, \text{and} q_{\text{O}} \text{ in } e) \) and \( \text{Co and total magnetic moments} \ (\mu_{\text{Co}} \text{ and } \mu_{\text{Tot}} \text{ in } \mu_{\text{B}}) \) for \( \text{LSC} \ (x_{\text{Sr}}=0.25 \text{ and } 0.50) \) in the SQS cell. The range from the minimum to maximum value of each quantity is given.

<table>
<thead>
<tr>
<th></th>
<th>( x_{\text{Sr}}=0.25 )</th>
<th>( x_{\text{Sr}}=0.50 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_{\text{La}} )</td>
<td>2.07 – 2.09</td>
<td>2.07 – 2.10</td>
</tr>
<tr>
<td>( q_{\text{Sr}} )</td>
<td>1.59 – 1.60</td>
<td>1.60</td>
</tr>
<tr>
<td>( q_{\text{Co}} )</td>
<td>1.36 – 1.39</td>
<td>1.39 – 1.42</td>
</tr>
<tr>
<td>( q_{\text{O}} )</td>
<td>-1.12 – -1.10</td>
<td>-1.10 – -1.06</td>
</tr>
<tr>
<td>( \mu_{\text{Co}} )</td>
<td>1.50 – 1.73</td>
<td>1.48 – 1.92</td>
</tr>
<tr>
<td>( \mu_{\text{Tot}} )</td>
<td>29.86</td>
<td>33.81</td>
</tr>
</tbody>
</table>

The magnetic moments and Bader charges (Table 5.4) in the SQS cell show greater fluctuations than what we have found for the isotropic \( \text{La/Sr} \) arrangement in the pseudocubic cell (e.g., \( \mu_{\text{Co}} = 1.44-1.54 \mu_{\text{B}} \) in the pseudocubic cell and \( \mu_{\text{Co}} = 1.50-1.73 \mu_{\text{B}} \) in the SQS cell for \( x_{\text{Sr}} = 0.25 \)). This difference arises from the fact that each Co ion has the same surrounding La/Sr environment in the isotropic pseudocubic cell, while the Co ions in the SQS cell have different local La/Sr environments. The magnetic moments are dispersed throughout the given range, indicating that Co ions in certain local environments are more receptive to receiving electrons.

5.8 \textit{Oxygen Vacancy Formation in La}_{1-x}\textit{Sr}_x\textit{CoO}_3

To compare the behaviors of LSC and LSF, we want to first understand how Sr substitution affects the defect chemistry of LSC. We have previously shown that adding Sr to LSF allows a charge compensation mechanism that greatly reduces \( \Delta H_{\text{f,vac}} \) (and \( \Delta G_{\text{f,vac}} \)). Fe ions strongly prefer the +3 oxidation state, and the holes introduced by Sr substitution agitate both the Fe ions and O sublattice. To make our comparison between
LSC and LSF, we start by analyzing the energetics and electronic structure changes associated with $V_0^+$ formation in LSC.

We employ the same approach with the 40-atom supercell for LSC as we used for LSF (*vide supra*). For each cell in Figure 5.6b, we remove a neutral oxygen atom from every unique La/Sr environment, which is defined by the four A-site ions surrounding the oxygen vacancy site. The data obtained from this procedure are presented in Figure 5.8. Changing the composition from $x_{Sr}=0.25$ to $x_{Sr}=0.50$ decreases $\Delta H_{f,vac}$ by an average of 0.6 eV. The data in Figure 5.8 indicates that $V_0^+$ shows a slight preference toward sites surrounded by La ions. This trend seems opposed to the fact that increasing $x_{Sr}$ from 0.25 to 0.50 decreases $\Delta H_{f,vac}$; therefore, an explanation is necessary. Although increasing the overall Sr composition leads to an increase in hole concentration and lowers $\Delta H_{f,vac}$, the La ions provide a more flexible local environment to accommodate the electronic rearrangement induced by a nearby $V_0^+$. The higher polarizability of La ($31.1 \text{ Å}^3$) compared to Sr ($27.6 \text{ Å}^3$ and $23.5 \text{ Å}^3$) provides evidence that the La ions will undergo rearrangement easier than the Sr ions. Since the polarizabilities for the ionic species are not readily available, the atomic polarizabilities were used for this argument. Since La$^{3+}$ has the same electron configuration as Xe and Sr$^{2+}$ the same electron configuration as Kr, the polarizabilities of these noble gases offer information about how the ionic species will behave. Once again, the data support our assertion as Xe ($4.044 \text{ Å}^3$) has a larger polarizability than Kr ($2.4844 \text{ Å}^3$). This trend can be rationalized on the basis that La$^{3+}$ has 18 electrons more than Sr$^{2+}$ and more electrons lead to increased polarizability.
Figure 5.8. \( V_0 \) formation energies (\( \Delta E_{f,vac} \), eV) as a function Sr content (mole fraction). The data at \( x_{Sr}=0.25 \) and \( x_{Sr}=0.50 \) are derived from PBE calculations whereas the data at \( x_{Sr}=0 \) are derived from PBE+U calculations. In all cases, \( \Delta E_{f,vac} \) is derived from a consistent Hamiltonian (all terms in the expression are calculated at the same level of theory), but we choose the best level of theory for \( x_{Sr}=0 \), \( x_{Sr}=0.25 \), and \( x_{Sr}=0.50 \). The data are colored according to the local La/Sr environment (see color legend).

Analyzing how \( \Delta H_{f,vac} \) changes across the spectrum of \( x_{Sr}=0 \) to \( x_{Sr}=0.50 \) leads to a methodological issue. We find that the DFT+U method is absolutely essential for describing \( \text{LaCoO}_3 \); however, the same method performs poorly for \( \text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3 \) and \( \text{La}_{0.50}\text{Sr}_{0.50}\text{CoO}_3 \). For analysis (Figure 5.8), we have used the \( \Delta H_{f,vac} \) values obtained with the best level of theory for each composition. This qualitative comparison proves insightful in spite of the fact that the energy difference obtained with two different methods should not be compared. We find that adding Sr initially has only a small effect on \( \Delta H_{f,vac} \). The energetics for \( \text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3 \) line up well with the values obtained for
high spin and high spin/low spin LaCoO$_3$ (see Chapter 4 for more details). Comparison to
experiment sheds light on whether this is a methodological effect or a physical effect.
Analysis of thermogravimetry data shows that adding Sr has a small effect initially (up to
$x_{Sr}=0.1$), but, thereafter, $\Delta H_{f,vac}$ continues to decrease as $x_{Sr}$ increases.$^{66}$ The $\Delta H_{f,vac}$
values obtained from the DFT-GGA calculations are significantly higher than the
experimental values ($\Delta H_{f,vac} = 1.3$ eV and $0.7$ eV for stoichiometric LSC when $x_{Sr}=0.25$
and $0.50$, respectively).$^{66}$ The too-high $\Delta H_{f,vac}$ values indicate that the supercell may be
too small, leading to significant vacancy-vacancy repulsive interactions. However,
consistent with LSF (vide supra), we see a decrease in the value of $\Delta H_{f,vac}$ from $x_{Sr}=0.25$
to $x_{Sr}=0.50$ (~0.6 eV) in our calculations. Computing vacancy formation energies using
the larger SQS cells discussed above can help quantify any errors associated with
vacancy-vacancy interactions that may arise from periodic boundary conditions.
Preliminary results indicate that the SQS cell gives $\Delta E_{f,vac}$ values around 1.0 eV for $x_{Sr} = 0.25$.
The SQS cell produces $\Delta E_{f,vac}$ values below experiment, consistent with the DFT-
GGA overbinding of the O$_2$ molecule. In fact, correcting for the overbinding of O$_2$ (vide
supra) by adding 0.42 eV to $\Delta E_{f,vac}$ brings our results into good agreement with
experiment.

We use Bader analysis to understand the reason why $\Delta E_{f,vac}$ decreases with
increasing $x_{Sr}$. The data in Table 5.5 indicate that La and Sr ions undergo little-to-no
change when an oxygen vacancy forms. The Co sublattice undergoes a reduction, with
the most significant reductions on the sites adjacent to the vacancy (Co* in Table 5.5).
For $x_{Sr} = 0.25$, the Co sublattice gains 0.61 e when an oxygen vacancy forms while the
oxygen sublattice, excluding the vacant site, gains 0.46 e.
Table 5.5. Bader charges ($q_{La}$, $q_{Sr}$, $q_{Co}$, and $q_o$ in $e$) for stoichiometric and nonstoichiometric LSC obtained from DFT-GGA calculations in the pseudocubic cell with isotropic La/Sr arrangements (furthest right in Figure 5.6b). Co* refers to a Co site adjacent to an oxygen vacancy.

<table>
<thead>
<tr>
<th></th>
<th>$x_{Sr}=0.25$</th>
<th></th>
<th>$x_{Sr}=0.50$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without $V_0^-$</td>
<td>With $V_0^-$</td>
<td>Without $V_0^-$</td>
</tr>
<tr>
<td>$q_{La}$</td>
<td>2.09</td>
<td>2.07</td>
<td>2.10</td>
</tr>
<tr>
<td>$q_{Sr}$</td>
<td>1.59</td>
<td>1.58, 1.59</td>
<td>1.59</td>
</tr>
<tr>
<td>$q_{Co}$</td>
<td>1.36</td>
<td>1.32</td>
<td>1.39</td>
</tr>
<tr>
<td>$q_{Co^*}$</td>
<td>----</td>
<td>1.17, 1.18</td>
<td>----</td>
</tr>
<tr>
<td>$q_o$</td>
<td>-1.11</td>
<td>-1.13 ± 0.02</td>
<td>-1.08</td>
</tr>
</tbody>
</table>

The preceding analysis accounts for 1.07 $e$ of the 1.11 $e^-$ left behind when the vacancy forms, and the small remainder is distributed in the La/Sr sublattice. Therefore, forming the oxygen vacancy leaves behind electrons that localize significantly on the Co sublattice.

Preliminary results indicate that the localization effect is even more pronounced for LSC in the larger SQS cells. The difference between the pseudocubic and SQS results arises because the repulsion between the vacancy and its periodic images in the pseudocubic cell drives greater charge delocalization.

5.9 Comparison Between $La_{1-x}Sr_xFeO_3$ and $La_{1-x}Sr_xCoO_3$

As previously discussed, the physical and chemical properties of LSF differ significantly from those of LSC. Specifically, LSF is an antiferromagnetic semiconductor, whereas LSC becomes a ferromagnetic metal. We have already explained why LaFeO$_3$ has a lower oxygen vacancy concentration than LaCoO$_3$; however, the question now becomes why the opposite is true after Sr is added. We can analyze this by looking at the extent to which the electrons from the oxygen vacancy delocalize over the...
O sublattice. The extent of this delocalization (\(\lambda\)) can be expressed according to Equation 5.8, where \(q\) indicates the charge obtained from Bader analysis and \(N\) is the number of oxygen ions in the stoichiometric cell.

\[
\lambda = \frac{(N - 1)((q_{O,nonstoichiometric}) - (q_{O,stoichiometric}))}{(q_{O,stoichiometric})} \tag{5.8}
\]

We find that increasing \(\lambda\) leads to lower \(\Delta E_{\text{f,vac}}\) for a variety of materials. The trend for LSC and LSF is presented in Figure 5.9.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.9.png}
\caption{Oxygen vacancy formation energy (\(\Delta E_{\text{f,vac}}\) in eV) as a function of the delocalization degree \(\lambda\) (dimensionless). As defined in Equation 5.8, \(\lambda\) gives the extent to which the electrons released upon \(V_0\) creation delocalize over the oxygen sublattice.}
\end{figure}

The same trend holds for \(\text{La}_{1-x}\text{Sr}_x\text{MnO}_3\) (\(x_{\text{Sr}}=0.0, 0.25,\) and 0.50). Since the oxygen sublattice in LSF is more active in accepting electrons upon oxygen vacancy formation than the oxygen sublattice in LSC, the oxygen vacancy formation energies are lower in LSF than in LSC. The activity of the oxygen sublattice is directly related to the relative

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\textsuperscript{67} Credit for this idea belongs to my coworkers Ana B. Muñoz-García and Michele Pavone. We discussed it in an account of our research published in 2014.\textsuperscript{67}
ease of reducing the B-site cation. In this case, Fe$^{3+}$ is much harder to reduce than Co$^{3+}$, so the oxygen sublattice in LSF will play a larger role than in LSC. To conclude, the stronger effect of Sr substitution on LSF (compared to LSC) indicates that LSCF-based cathodes should contain more Fe than Co to promote higher oxygen vacancy concentrations; however, the presence of Co helps improve the electronic conductivity of LSCF.  

5.10 Conclusions

We have presented a detailed first-principles quantum mechanics analysis showing how Sr substitution influences oxygen transport in LSF that provides a deeper understanding of oxygen transport in LSF cathodes. Specifically, we clarify the fundamental role of A-site dopants in promoting oxygen vacancy formation and therefore oxide ion transport in IT-SOFCs with MIEC cathodes. After showing the DFT+U method’s capability of successfully modeling LSF, we demonstrated that the holes introduced by Sr substitution have mainly O 2$p$ character. In LaFeO$_3$, the reduction of Fe$^{3+}$ ions to Fe$^{2+}$ is unfavorable and leads to a large $\Delta H_{f,vac}$ value (see Chapter 3). With Sr present, the electrons left behind when a vacancy forms compensate for the holes introduced by Sr. The resulting $\Delta H_{f,vac}$ is significantly lower than that in LaFeO$_3$, resulting in more oxygen vacancies and easier oxygen transport. GGA+U calculations indicate significant increases oxygen diffusivity will occur with increasing Sr concentration because of the corresponding increase in oxygen vacancies.

This refined illustration provided by the DFT+U method shows how the interplay between electron-deficient substitutions, iron ions, and the oxygen sublattice can improve
oxygen transport in LSF. As found in Sr$_2$FeMoO$_6^{46-48}$ based materials, the electrons from an oxygen vacancy in LSF (x > 0) distribute over the oxygen sublattice which produces very favorable oxygen vacancy formation enthalpies. This insight has wide potential application to iron-based SOFC cathode materials, but this should still be con-firmed by experiment. Further theoretical studies will address how substitutions in the transition metal site (B-site doping) can further improve oxygen transport in LSF-based SOFC cathodes.

We have also presented a detailed DFT-GGA analysis of the electronic structure and defect formation processes in LSC. We find that the metallic nature of LSC renders the GGA+U method inaccurate for this material. This work shows that Sr substitution in LSC has significantly less impact on $\Delta H_{f,vac}$ compared with LSF. Further, $\Delta H_{f,vac}$ is larger in LSC than LSF. This result lies in stark contrast to the significantly lower $\Delta H_{f,vac}$ in LaCoO$_3$ compared with LaFeO$_3$. This result arises from the fact that the oxygen sublattice participates to a much larger degree in the oxygen vacancy formation process in LSF compared to LSC.

References


Chapter 6

Electronic Structure and Oxygen Vacancy Formation in LSCF (La\textsubscript{1-x}Sr\textsubscript{x}Co\textsubscript{1-y}Fe\textsubscript{y}O\textsubscript{3-δ})

6.1 Introduction

Solid oxide fuel cells (SOFCs)\textsuperscript{1,2} are a clean and efficient technology for generating electrical power from a variety of fuels.\textsuperscript{3-5} Making SOFCs technologically and economically viable depends on lowering their operating temperature from the high (800-1000 °C) to the intermediate temperature (IT, 600-800 °C) regime.\textsuperscript{6,7} The key issue necessitating high temperature operation is the cathode overpotential\textsuperscript{8} arising from slow oxygen reduction reaction (ORR) rates on the traditional, La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3}-based (LSM) cathodes. Specifically, the LSM cathodes are poor oxygen ion conductors.\textsuperscript{9,10} Consequently, the ORR only occurs at the three-phase boundary (TPB) where the cathode, electrolyte, and oxidizing gas come into contact. One method for increasing the rate of oxygen reduction is to employ a mixed ion-electron conducting (MIEC) material.\textsuperscript{2,11} Because bulk oxygen ion transport occurs in MIEC materials, oxygen ions may react on surface sites where the cathode and gas phases come into contact instead of only at the TPB.\textsuperscript{11,12} The cathode then transports the oxygen ions to the electrolyte. Ideally, this leads to increased active areas, higher ORR rates, and lower cathode overpotentials.

\textsuperscript{§§§} This chapter is adapted, with permission, from Ritzmann, A. M., Dieterich, J. M. & Carter, E. A. Density Functional Theory +U Analysis of the Electronic Structure and Defect Chemistry of LSCF (La\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{0.25}Fe\textsubscript{0.75}O\textsubscript{3-δ}). Phys. Chem. Chem. Phys. 18, 12260-12269 (2016) – Reproduced by permission of the Royal Society of Chemistry.
Among candidate MIECs, the La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_3$ (LSCF) family of materials has demonstrated significant potential.\textsuperscript{13–17} Macroscopic observations have revealed that LSCF demonstrates sufficiently high electronic and ionic conductivities for use in IT-SOFC applications.\textsuperscript{13} Furthermore, SOFCs employing LSCF generally exhibit lower polarization losses than equivalently constructed LSM-based SOFCs.\textsuperscript{12} Systematic improvements of these MIECs are hampered because the diversity of synthesis methods, morphologies, and cell architectures (anode-supported vs. cathode-supported) make comparing research findings difficult.\textsuperscript{18,19} Theoretical work can be used to test design strategies. Although rational design of SOFC cathodes requires the consideration of multiple length and time scales;\textsuperscript{20} the most important decision is choosing the optimal elemental composition.\textsuperscript{21} This process ideally will start with detailed, first-principles quantum mechanics studies of the electronic structure and defect chemistry of LSCF. Armed with the insights from these studies, researchers should be able to subsequently make reasonable choices regarding the cathode microstructure, the method of synthesis, and even fuel cell construction.

A paucity of first-principles quantum mechanics studies on LSCF makes rational design quite difficult. Previous investigations by various groups have used first-principles methods based on density functional theory (DFT) to investigate the electronic structure and defect chemistry of materials related to LSCF.\textsuperscript{22–31} These investigations demonstrated that Sr substitutions (Sr$_{La}^{+/}$ in Kröger-Vink notation)\textsuperscript{32} play a crucial role in lowering the oxygen vacancy formation energy ($\Delta G_{f,vac}$).\textsuperscript{27} Sr$_{La}^{+/}$ defects produce holes that are partially
delocalized across the oxygen sublattice, causing the oxygen sublattice to become susceptible to formation of oxygen vacancies ($V_O$).\textsuperscript{31} To date, three key studies exist that address LSCF in its full chemical makeup. These investigations may use different DFT-based methodologies (DFT-GGA\textsuperscript{25,29} and GGA+U\textsuperscript{24}), but they all arrive at a common conclusion.\textsuperscript{24,25,29} Specifically, they each find that $V_O$ defects preferentially occur in oxygen sites between Co ions. While this insight is critical in understanding the ionic conductivity of LSCF, the authors do not provide the electronic structure analysis necessary to truly understand MIEC materials. Furthermore, all three studies employ a 40-atom pseudocubic structure to obtain their results. This structure severely limits the possible La/Sr and Co/Fe arrangements that can be considered. The size of this cell may also be the reason for Gryaznov et al.’s conclusion that the local Co/Fe arrangement significantly impacts the phonon contribution to $\Delta G_{\text{f,vac}}$.\textsuperscript{29}

The preceding discussion prompts two major questions, which lie at the heart of rationally optimizing the chemical composition of LSCF. First, how does the electronic structure of LSCF differ from its parent materials, La$_{1-x}$Sr$_x$CoO$_3$ and La$_{1-x}$Sr$_x$FeO$_3$? Second, how does the mixture of Co and Fe ions impact the defect chemistry and ionic conductivity of LSCF?

To answer these questions, we present a DFT-based investigation of LSCF. Employing a cell that attempts to mimic the random distribution of La/Sr and Co/Fe ions in LSCF enables us to more accurately model the material as it exists in reality. To ensure that a proper methodology is used for studying the defect chemistry in LSCF, the electronic structures of LSCF are computed with DFT-GGA and GGA+U. We use these electronic structure results to interpret the electronic behavior of LSCF. Moreover, the
pseudorandom model employed enables us to take into account the effect on $\Delta G_{f,\text{vac}}$ of the local ionic environment surrounding the $V_0^-$ site. This analysis then yields insights regarding a fundamental trade-off that arises when optimizing the chemical composition of LSCF.

6.2 Computational Methods

We modeled the distribution of La/Sr ions and Co/Fe ions in LSCF using the special quasirandom structures (SQS) method. We used the Monte Carlo SQS code (mcsqs) from the Alloy Theoretical Automated Toolkit (ATAT) developed by Professor Axel van de Walle and collaborators. SQS cells are relatively small unit cells that approximate the disorder in a random alloy. SQS cells are usually chosen to match the pair correlation functions of the random alloy out to the largest possible distance. In this work, we employ an SQS cell containing 80 atoms (16 formula units) with the composition La$_{0.5}$Sr$_{0.5}$Co$_{0.25}$Fe$_{0.75}$O$_3$ (vide infra). This reasonably approximates the commonly used experimental composition, La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$.

We performed spin-polarized Kohn-Sham DFT calculations using the Vienna Ab Initio Simulation Package (VASP), version 5.2.2. We employed the generalized gradient approximation (GGA) exchange-correlation (XC) functional of Perdew, Burke, and Ernzerhof (PBE). Additionally, we performed GGA+$U^{50-52}$ calculations using the PBE functional and the rotationally invariant formulation of Dudarev et al. In this formulation, only the difference between the average on-site Coulomb ($U$) and exchange ($J$) interactions enters into the calculation. We applied the on-site correction to the 3$d$ manifolds of Fe$^{3+}$ and Co$^{3+}$. To avoid biasing the calculations, we employed a value of $U_{\text{eff}} = U-J = 4.0$ eV for both ions. This value was determined from first-principles for
Co\textsuperscript{3+} \textsuperscript{30} using the method of Mosey, Liao, and Carter.\textsuperscript{53} The value of 4.3 eV derived\textsuperscript{53} for Fe\textsuperscript{3+} is close enough to 4.0 eV that using the latter for both transition metals (TMs) will have negligible effect on the results.

We found that truncating the planewave basis set at a 750 eV kinetic energy cutoff and a 4 × 4 × 4 Γ-centered k-point mesh yielded total energies converged to 5 meV/f.u. The projector augmented-wave (PAW) method\textsuperscript{54,55} was used to represent the interaction between the valence electrons and nuclei plus frozen core electrons. We employed the PAW potentials labeled La (6s\textsuperscript{2}5d\textsuperscript{1}), Sr\textsubscript{sv} (semi-core electrons treated as valence electrons, 4s\textsuperscript{2}4p\textsuperscript{6}5s\textsuperscript{2}), Fe (4s\textsuperscript{2}3d\textsuperscript{6}), Co (4s\textsuperscript{2}3d\textsuperscript{7}), and ‘regular’ O (2s\textsuperscript{2}2p\textsuperscript{4}) from the library supplied by the VASP developers.\textsuperscript{55} Integration over the first Brillouin zone was performed using first-order Methfessel-Paxton\textsuperscript{56} smearing (σ = 0.1 eV) during geometry optimizations. This smearing width ensures that the electronic entropy is no greater than 5 meV per formula unit (1 meV/atom). Single-point energies and densities of states (DOS) were obtained for the optimized geometries using the tetrahedron method with Blöchl corrections.\textsuperscript{57} In one case, the stoichiometric cell with low-spin Co\textsuperscript{3+} ions (\emph{vide infra}) computed with the GGA+U method, instabilities with the tetrahedron method calculation necessitated obtaining the single-point energy and DOS using Gaussian smearing with a reduced width (σ = 0.05 eV).

Electron density differences (Δρ) were computed according to Equation 6.1 where ρ\textsubscript{defective} is the electron density of the supercell with an oxygen vacancy, ρ\textsubscript{host} is the electron density of the supercell without any vacancies, and ρ\textsubscript{O} is the electron density of an isolated oxygen atom placed at the vacant site. Each electron density was computed with the ions fixed in the positions of the host supercell.
\[ \Delta \rho = \rho_{\text{defective}} + \rho_O - \rho_{\text{host}} \] (6.1)

\( \rho_O \) was determined for the oxygen atom in its triplet state. Gaussian smearing (\( \sigma = 0.05 \) eV) was employed to avoid biasing our calculations through the double occupation of single \( p \) orbital. Instead, each \( O_p \) orbital had an average occupation of \( 4/3 \) e.

6.3 Results and Discussion

6.3.1 Structural Model for LSCF

We employed the SQS method in order to develop a reasonable model for LSCF. Finding a reasonable SQS cell required two constraints. First, we treated the La/Sr sublattice separate from the Co/Fe sublattice; we consider this constraint to be reasonable given the usual locations of A vs. B site ions in the perovskite ABO\(_3\) structure. The final cell contains randomized La/Sr positions and randomized Co/Fe positions. Second, we looked for cells that gave the largest possible minimum image distance between oxygen vacancies. With these constraints, we can confidently sample a (locally) random configuration of cations with minimal vacancy-vacancy interactions. The cell in Figure 6.1 has a minimum image distance of 9.46 Å between oxygen vacancies and matches pair correlation functions of a random alloy for all nearest-neighbors on the La/Sr sublattice (up to 4.03 Å) and all nearest-neighbors on the Co/Fe sublattice (up to 3.96 Å). This model corresponds to a realistic\(^{58}\) oxygen nonstoichiometry (\( \delta \)) of 0.0625 when one oxygen atom is removed from the lattice.
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Figure 6.1: The 80-atom unit cell with quasirandom distributions of La/Sr and Fe/Co. The composition is 1:1 La:Sr and 3:1 Fe:Co. Atomic colors: La (green), Sr (pink), Co (blue), Fe (brown), O (red). The minimum image distance between oxygen vacancies is 9.46 Å for this cell. This figure was created using VESTA.59

6.3.2 Electronic Structure Analysis of LSCF

Using the structural model shown in Figure 6.1, we aim to understand the electronic structure of LSCF. We previously showed that changing the spin state of Co$^{3+}$ could significantly alter the oxygen vacancy formation energy in LaCoO$_3$.30 The possible spin states of Co$^{3+}$ are low-spin (LS, $t_{2g}^6e_g^0$), intermediate-spin (IS, $t_{2g}^5e_g^1$), and high-spin (HS, $t_{2g}^4e_g^2$), where the $t_{2g}$ and $e_g$ orbitals result from the $d$ manifold splitting in the presence of an octahedral crystal field. Furthermore, our work on La$_{1-x}$Sr$_x$FeO$_3$ and La$_{1-x}$Sr$_x$CoO$_3$ (LSF and LSC, respectively) showed that GGA+U calculations were best for LSF$^{27}$ and DFT-GGA calculations were best for LSC (Chapter 5), indicating that we must test both methodologies for LSCF. We restrict our calculations to ferromagnetic (FM) ordering of the TM cations based-on experimental evidence of low temperature FM behavior in LSCF.$^{60}$ Six possible combinations of calculation-type and initial Co$^{3+}$ spin state are enumerated in Table 6.1, along with whether or not the calculation resulted in a unique electronic structure (instead of leading to a result also obtained with a different set
of parameters and/or theory). The total energies after geometry optimization are reported so that comparisons may be made between tests of the same calculation type (DFT-GGA or GGA+U).

**Table 6.1**: Ferromagnetic test calculations performed on La$_{0.5}$Sr$_{0.5}$Co$_{0.25}$Fe$_{0.75}$O$_3$ to analyze the calculation type (DFT-GGA or GGA+U) and initial guess for the Co$^{3+}$ magnetic state (LS, IS, HS). The unique result column indicates whether the combination of calculation type and initial Co$^{3+}$ spin state gave a magnetic configuration and total energy that differed from other calculations. When two calculations collapsed to the same result, the unique result designation was awarded to the initial condition that had the closer match to the final result.

<table>
<thead>
<tr>
<th>Test</th>
<th>Calculation Type</th>
<th>Co$^{3+}$ Spin State</th>
<th>Unique Result?</th>
<th>Relative Energy (eV)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DFT-GGA</td>
<td>LS</td>
<td>No</td>
<td>----</td>
</tr>
<tr>
<td>2</td>
<td>DFT-GGA</td>
<td>IS</td>
<td>Yes</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>DFT-GGA</td>
<td>HS</td>
<td>No</td>
<td>----</td>
</tr>
<tr>
<td>4</td>
<td>GGA+U</td>
<td>LS</td>
<td>Yes</td>
<td>1.39</td>
</tr>
<tr>
<td>5</td>
<td>GGA+U</td>
<td>IS</td>
<td>No</td>
<td>----</td>
</tr>
<tr>
<td>6</td>
<td>GGA+U</td>
<td>HS</td>
<td>Yes</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*Relative energy compared to the lowest energy state obtained with the same calculation type. DFT-GGA and GGA+U total energies cannot be directly compared.

The data above show the difference between DFT-GGA and GGA+U calculations. The DFT-GGA results favor the IS state for Co$^{3+}$. The GGA+U calculations, however, stabilize both the HS and LS states for Co$^{3+}$ in LSCF, with HS being the ground state. The reason for this difference is that the GGA+U method penalizes fractional occupations in the $d$ manifold, while no such penalty exists in DFT-GGA calculations. Thus, the relative positions of the oxygen 2$p$, cobalt 3$d$, and iron 3$d$ states become relevant for determining which model, if either, offers an appropriate physical description of LSCF.

We therefore plot (Figure 6.2) the projected density of states (PDOS) for each of the unique results listed in Table 6.1. We also present magnetic moments and Bader charges$^{61–63}$ (Table 6.2) for each set of results.
Figure 6.2: PDOS for each of the unique results identified in Table 6.1. Plots are presented in the following order: GGA/IS (top), GGA+U/HS (middle), and GGA+U/LS (bottom). Majority (alpha-spin) states have positive PDOS values, while minority (beta-spin) states have negative PDOS values. Color guide: Fe 3d states (black), Co 3d states (blue), and O 2p states (red).
The PDOS in Figure 6.2 demonstrate that the DFT-GGA and GGA+U descriptions differ significantly for LSCF. Specifically, the DFT-GGA calculation yields a completely metallic state with significant peaks in the minority TM 3d orbitals at the Fermi energy. Conversely, the GGA+U description opens a gap in the minority spin channel. In both descriptions, the majority spin channel contains a flat region of majority spin states spanning the Fermi energy. These states are hybrid TM 3d and O 2p states.

The GGA+U/LS PDOS is smoother than the other PDOS plots because it was computed with small-width (0.01 eV) Gaussian smearing instead of the tetrahedron method with Blöchl corrections, which avoids the numerical instabilities that arose when using the latter method on that system.

Table 6.2: Bader charges (q\text{Co}, q\text{Fe}, q\text{La}, q\text{Sr}, and q\text{O} in e), magnetic moments (\mu\text{Co} and \mu\text{Fe} in \mu_B), and equilibrium volumes (V_0 in Å³/f.u.) for the unique results identified in Table 6.1. Column headers indicate the calculation type and initial Co³⁺ spin state.

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>GGA/IS</th>
<th>GGA+U/HS</th>
<th>GGA+U/LS</th>
</tr>
</thead>
<tbody>
<tr>
<td>q\text{Co}</td>
<td>----</td>
<td>1.34</td>
<td>2 \times 1.55, 2 \times 1.40</td>
<td>1.30</td>
</tr>
<tr>
<td>q\text{Fe}</td>
<td>----</td>
<td>1.58 ± 0.01</td>
<td>1.73</td>
<td>1.72</td>
</tr>
<tr>
<td>q\text{La}</td>
<td>----</td>
<td>2.09</td>
<td>2.09</td>
<td>2.09 ± 0.01</td>
</tr>
<tr>
<td>q\text{Sr}</td>
<td>----</td>
<td>1.60</td>
<td>1.60</td>
<td>1.59</td>
</tr>
<tr>
<td>q\text{O}</td>
<td>----</td>
<td>-1.12 ± 0.01</td>
<td>-1.17 ± 0.02</td>
<td>-1.15 ± 0.01</td>
</tr>
<tr>
<td>\mu\text{Co}</td>
<td>----</td>
<td>1.47 ± 0.08</td>
<td>2.0, 2.1, 2.9, 3.0</td>
<td>0.28 – 0.39</td>
</tr>
<tr>
<td>\mu\text{Fe}</td>
<td>----</td>
<td>2.92 ± 0.04</td>
<td>3.98 ± 0.07</td>
<td>3.84–3.96</td>
</tr>
<tr>
<td>V_0</td>
<td>60.9⁺</td>
<td>57.6</td>
<td>59.9</td>
<td>58.9</td>
</tr>
</tbody>
</table>

⁺ Calculated from reported density for La\text{0.6Sr0.4Co0.2Fe0.8O3} (6.08 g/cm³)\text{₃³⁹}

Further quantifying the electronic structure results using Bader charge analysis (Table 6.2) shows that adding the +U correction significantly alters the nature of the TM and O sites. The GGA+U results paint a more ionic picture of LSCF than do the DFT-GGA results. This finding is expected given the physics introduced by the GGA+U method; however, certain salient points arise. First, the magnetic moments of the Fe ions
increase by approximately 1 $\mu_B$ from the DFT-GGA to the GGA+U results. If the Fe ions are in the 3+ oxidation state, as is apparent from XANES and EXAFS experiments,\textsuperscript{64,65} we expect a magnetic moment closer to 5 $\mu_B$ for HS Fe$^{3+}$. In this regard, the GGA+U results agree with experiment far better than the DFT-GGA results. Second, the electrical conductivity of LSCF ($x_{Sr} = 0.4$, $y_{Fe} = 0.8$) increases with temperature, up to temperatures of 500 °C.\textsuperscript{58} This indicates that LSCF is a semiconductor in this temperature range, although the increase is less than one order of magnitude over the range of 100-500 °C, hinting that the band gap is very small. Therefore, the DFT-GGA calculation fails on a qualitative level by predicting a strongly metallic system. The GGA+U calculations, on the other hand, predict a half-metallic system, which agrees better with experiment.

Analyzing the GGA+U results for the HS Co$^{3+}$ ground state illustrates how the insights we gleaned from the parent materials of LSCF remain relevant for the compound itself. The GGA+U values for $\mu_{Fe}$ (3.98 ± 0.07 $\mu_B$) and $q_{Fe}$ (1.73 $e$) agree with the values we reported in our analysis of La$_{0.5}$Sr$_{0.5}$FeO$_3$ ($\mu_{Fe} = 3.73$ and 4.11 $\mu_B$ and $q_{Fe} = 1.70$ $e$).\textsuperscript{27} Likewise, the range of GGA+U values for $q_{Co}$ (1.40 and 1.55 $\mu_B$) agrees with the value we reported for HS Co$^{3+}$ in LaCoO$_3$ ($q_{Co} = 1.52$ $e$).\textsuperscript{30} The values of $\mu_{Co}$ indicate that Co remains flexible in its magnetic configuration. Given the quasirandom arrangement of atoms in our model, the Co ions do not all experience the same local environment, causing their Bader charges and magnetic moments to vary depending on position. Finally, we also note that the Bader charge for oxygen in the GGA+U calculation agrees with that reported for La$_{0.5}$Sr$_{0.5}$FeO$_3$ in our previous work ($q_{O} = -1.18$ ± 0.03 $e$).\textsuperscript{27} Thus, the descriptions provided by our earlier models offer significant insight into the behavior
of LSCF. The following section therefore refers to the GGA+U analysis of LSCF with HS Co$^{3+}$.

![Figure 6.3. PDOS plots for La$_{0.50}$Sr$_{0.50}$FeO$_3$, La$_{0.50}$Sr$_{0.50}$Co$_{0.25}$Fe$_{0.75}$O$_3$, and La$_{0.50}$Sr$_{0.50}$Co$_{0.50}$Fe$_{0.50}$O$_3$ computed using the DFT+U method. The Co ions are in the HS state for all of these calculations. La$_{0.50}$Sr$_{0.50}$FeO$_3$ results are the same as those presented in our previous work. Positive values denote majority spin ($\alpha$ for FM ordering) DOS while negative values denote minority spin ($\beta$ for FM ordering) DOS. Color designations: O 2$p$ states (red), Fe 3$d$ states (black), and Co 3$d$ states (blue).]
6.3.3 Electronic Structure of $\text{La}_{0.50}\text{Sr}_{0.50}\text{Co}_{y}\text{Fe}_{1-y}\text{O}_3$ with $y = 0.0$, $0.25$, and $0.50$

Mixing Co and Fe on the B-site sublattice may help improve the electronic conductivity of LSCF, when compared with the Co-free material LSF. To investigate the atomic-level changes associated with increasing Co content, we modeled $\text{La}_{0.50}\text{Sr}_{0.50}\text{Co}_{0.50}\text{Fe}_{0.50}\text{O}_3$ in addition to the $\text{La}_{0.50}\text{Sr}_{0.50}\text{Co}_{0.25}\text{Fe}_{0.75}\text{O}_3$ results reported above and the previously reported $\text{La}_{0.50}\text{Sr}_{0.50}\text{FeO}_3$ results. The PDOS for each of these compositions (Figure 6.3) reveals that adding Co significantly changes the electronic structure of the material. The DFT+U calculations predict semi-metallic behavior for the compounds containing Co compared with the p-type semiconducting behavior demonstrated by $\text{La}_{0.50}\text{Sr}_{0.50}\text{FeO}_3$. Surprisingly, changing the Co content from $y_{\text{Co}} = 0.25$ to $y_{\text{Co}} = 0.50$ has little impact on the electronic structure. Combining these observations leads to the conclusion that the electronic structure of LSCF is not terribly sensitive to the mole fraction of cobalt. Therefore, Tai et al.’s observation that the electronic conductivity increases with increasing cobalt content requires an investigation of how Co influences the $V^\cdot_0$ formation process. If Co ions significantly impact $\Delta G_{f,\text{vac}}$, then the increase in conductivity may be a result of an increase in ionic conductivity. This increase, in turn, requires a higher oxygen diffusion coefficient.

6.3.4 Oxygen Vacancy Formation in LSCF

Oxygen vacancy formation plays a considerable role in determining the oxygen diffusion coefficient. The key descriptor is $\Delta G_{f,\text{vac}}$, but we can also use the energy change for $V^\cdot_0$ formation ($\Delta E_{f,\text{vac}}$) to analyze trends (Equations 6.2-6.3). This analysis depends on the assumption that thermal contributions from the solids are equal in each of the cases we analyze. The key thermal contribution arises from the O$_2$ molecule; however, this is a
constant difference between \( \Delta G_{f,vac} \) and \( \Delta E_{f,vac} \) and so does not affect trends. Our assumption that the thermal contributions from the host and defective solids cancel is reasonable since they only differ by one atom out of 80, although further investigation would be required to fully ensure its validity. In the following equations, the subscripts refer to the host (stoichiometric cell) and defective cell containing one oxygen vacancy. The subscript \( O_2 \) refers to the gas-phase molecule.

\[
\Delta E_{f,vac} = E_{\text{defective}} + \frac{1}{2} E_{O_2} - E_{\text{host}} \tag{6.2}
\]

\[
\Delta G_{f,vac} = G_{\text{defective}} + \frac{1}{2} G_{O_2} - G_{\text{host}} \tag{6.3}
\]

Moreover, three possible oxygen vacancy formation reactions may occur. These processes differ in the TM centers that are reduced by the electrons left behind when an oxygen vacancy forms. In Kröger-Vink notation, these processes are shown in Equations 6.4–6.6 as:

\[
O_\text{O}^x + 2\text{Fe}^x_{\text{Fe}} \rightarrow V_\text{O}^- + 2\text{Fe}^{'/}_{\text{Fe}} + \frac{1}{2} O_2(g) \tag{6.4}
\]

\[
O_\text{O}^x + 2\text{Co}^x_{\text{Co}} \rightarrow V_\text{O}^- + 2\text{Co}^{'/}_{\text{Co}} + \frac{1}{2} O_2(g) \tag{6.5}
\]

\[
O_\text{O}^x + \text{Fe}^x_{\text{Fe}} + \text{Co}^x_{\text{Co}} \rightarrow V_\text{O}^- + \text{Co}^{'/}_{\text{Co}} + \text{Fe}^{'/}_{\text{Fe}} + \frac{1}{2} O_2(g) \tag{6.6}
\]

The three possible processes exist because each oxygen ion sits adjacent to two TM ions. Thus, it is possible that zero, one, or two of these TM ions is a Co ion and vice-versa for an Fe ion. While we employ the notation above to discuss the process of oxygen vacancy formation, our previous results indicate that the oxygen sublattice receives most of the electron density left behind when the oxygen vacancy forms. Even so, previous studies
of LSCF have localized the electrons on the TM centers adjacent to the vacancy.\textsuperscript{25,26} One of the benefits of our structural model is the quasirandom distribution of La/Sr and Fe/Co. Therefore, we can analyze oxygen vacancy formation energies in LSCF ($x_{\text{Sr}}=0.5$, $y_{\text{Fe}}=0.75$) to determine whether changing the local TM metal environment or the surrounding La/Sr environment significantly impacts the oxygen vacancy formation energy. The local environment is defined in terms of the two TM neighbors and four La/Sr ions surrounding the vacant site.

Our analysis of the local environment effects using GGA+U calculations is presented in Figure 6.4. We have previously shown that the magnetic state of the Co$^{3+}$ ion is important in LaCoO$_3$.\textsuperscript{30} Some calculations of LSCF containing V$_0$ resulted in the formation of LS Co$^{3+}$ ions. These calculations are designated with the symbol “X” in Figure 6.4. These results should be questioned because the transition from HS or IS Co$^{3+}$ to LS Co$^{3+}$ should be unfavorable while the lattice is undergoing a reduction (\textit{i.e.}, during V$_0$ formation).\textsuperscript{30} Therefore, we omit these results from the following analysis.
In Figure 6.4, we see that the local La/Sr environment plays only a minor role in determining the oxygen vacancy formation energy. Variations in the oxygen vacancy formation energy exist between different La/Sr environments, but difference between the four La and four Sr environments is less than 0.1 eV indicating that there is no single preferred La/Sr environment. However, we do observe a slight (~0.3 eV) preference for oxygen vacancies to occupy sites between Fe and Co ions (one Co-O bond broken). Itoh and Nakayama used in-situ XANES and EXAFS analysis of the Fe and Co K-edges in
LSCF to show that $V_0^-$ form near Co ions.\textsuperscript{65} Since this attraction between oxygen vacancies and Co ions is rather slight, the trapping effect is minimal at SOFC operating temperatures. Likewise, an oxygen ion residing between two Co ions is trapped by $\sim 0.1$ eV compared to residing between two Fe ions and by $\sim 0.4$ eV compared to residing between one Fe and one Co ion. Our finding that the $V_0^-$ prefers to form between one Fe$^{3+}$ and one Co$^{3+}$ ion qualitatively disagrees with previous theoretical studies that predicted $V_0^-$ would preferentially form in sites between Co$^{3+}$ ions.\textsuperscript{24–26} The qualitative difference between our results and previous theoretical studies arises from our use of the more accurate ‘regular’ instead of ‘soft’ PAW potential for oxygen and our choice to employ a larger supercell with quasirandomly distributed cations. Of these two differences, the use of a larger supercell with a realistic distribution of cations gives us reason to believe that our results more accurately represent the material as synthesized experimentally. The reported defect formation energies (0.89-1.69 eV) should be corrected for the overbinding of O$_2$ by DFT-GGA. Adding 0.84 eV to the energy of the O$_2$ molecule brings the bond energy into agreement with experiment.\textsuperscript{28} Thus, the correction for the defect formation energies is 0.42 eV, bringing our corrected results (1.31-2.11 eV) into much better agreement with the experimentally derived defect formation energy ($\sim 1.8$ eV) at the oxygen nonstoichiometry ($\delta = 0.0625$) used in our defect calculations.\textsuperscript{58}

We find some interesting behavior in the analysis of how the electron density rearranges after an oxygen vacancy is formed (Table 6.3, Figure 6.5). From the magnetic moments and Bader charges, we can see that the Fe ions undergo only minor changes in response to the oxygen vacancy, even when the Fe ions are adjacent to the vacant site.
Table 6.3: Fe and Co magnetic moments (µ in µB) and Bader charges (q in e) for La0.5Sr0.5Co0.25Fe0.75O3-δ for an oxygen vacancy located between two Fe ions and one each of Co and Fe ions.

<table>
<thead>
<tr>
<th></th>
<th>Fe-VO' -Fe</th>
<th>Fe- VO' -Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>µFe</td>
<td>4.03 ± 0.06</td>
<td>4.04 ± 0.04</td>
</tr>
<tr>
<td>µFe*</td>
<td>3.81, 3.84</td>
<td>3.94</td>
</tr>
<tr>
<td>µCo</td>
<td>2.85, 2.27, 2.32, 2.39</td>
<td>2.95, 2.13, 2.49</td>
</tr>
<tr>
<td>µCo*</td>
<td>----</td>
<td>2.91</td>
</tr>
<tr>
<td>qFe</td>
<td>1.72 ± 0.03</td>
<td>1.73</td>
</tr>
<tr>
<td>qFe*</td>
<td>1.62</td>
<td>1.63</td>
</tr>
<tr>
<td>qCo</td>
<td>1.54, 1.37, 1.36, 1.37</td>
<td>1.55, 1.39, 1.36</td>
</tr>
<tr>
<td>qCo*</td>
<td>----</td>
<td>1.45</td>
</tr>
<tr>
<td>qLa</td>
<td>2.09 ± 0.01</td>
<td>2.09 ± 0.01</td>
</tr>
<tr>
<td>qSr</td>
<td>1.59</td>
<td>1.59 ± 0.01</td>
</tr>
<tr>
<td>qO</td>
<td>-1.18 ± 0.02</td>
<td>-1.19 ± 0.02</td>
</tr>
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</table>

VO' represents an oxygen vacancy in Kröger-Vink notation. Fe* and Co* denote sites adjacent to the vacancy location. Uncertainties are plus/minus one standard deviation.

Since Fe* ions are adjacent to oxygen vacancies, their Bader volumes are greater than usual leading to small reductions (from $1.73 \text{ e}$ to $1.62/1.63 \text{ e}$) like those reported in Table 6.3. The Co ions undergo only a slightly larger reduction (from $1.40 \text{ e}/1.55 \text{ e}$ to $1.36-1.55 \text{ e}$), and Figure 6.5 indicates that some of the Co ions undergo rearrangements in their $d$ manifold.

The major redistribution of electron density occurs at the oxygen vacancy site itself (yellow spheroids in Figure 6.5) and around the Co$^{3+}$ ions. Specifically, the Co$^{3+}$ ions undergo changes to their magnetic state as illustrated by the redistribution of the electrons in the $d$ manifold around some of the Co sites. Interestingly, at least one of the Co ions remains inert during the vacancy formation process. We attribute this observation to differences in the local environment for each Co ion arising from our use of a quasirandom model.
Figure 6.5: Electron density differences after the formation of oxygen vacancies in local environments corresponding to (a) Fe-Vo°⁻Fe and (b) Fe-Vo°⁻Co. Isosurfaces show increased/decreased (yellow/blue) electron density (0.02 e⁻ bohr⁻¹). For clarity, only the Co ions and TM ions adjacent to the oxygen vacancy are shown. In each image, the round yellow region corresponds to an increase in electron density at the vacant site. In all cases, the vacancy is surrounded by 2 La and 2 Sr ions. Color designations: Fe (brown), Co (blue), and O (red). This figure was created using VESTA.59

The preference for vacancies to form near Co ions is because Co-O bonds are weaker than Fe-O bonds, and also because more energy is gained by reducing Co³⁺→Co²⁺ than Fe³⁺→Fe²⁺.23

In addition, we see that the oxygen sublattice plays a small role in accommodating the changes in electron density. On average, each oxygen ion receives 0.01-0.02 e upon vacancy formation. This accounts for approximately half of the electron density that must be redistributed when the vacancy forms. The remainder of the electron density is split between the TM ions adjacent to the vacancy and Co ions in the cell. For the purpose of comparison, we employ the degree of delocalization (λ) introduced in Chapter 5 (and ref. 31).

\[
\lambda = \frac{(N - 1)(\langle q_{O,\text{nonstoichiometric}} \rangle - \langle q_{O,\text{stoichiometric}} \rangle)}{\langle q_{O,\text{stoichiometric}} \rangle} \quad (6.7)
\]
In Equation 6.7, N is the number of oxygen ions in the perfect cell, $<q_{O,\text{nonstoichiometric}}>$ is the average Bader charge on the oxygen sublattice in the defective cell, and $<q_{O,\text{stoichiometric}}>$ is the average Bader charge on the oxygen ions in the perfect cell. The numerator of Equation 6.7 gives the number of extra electrons on the oxygen sublattice after VO$^{\cdot\cdot}$ formation. When we normalize by the Bader charge of an oxygen ion in a perfect sublattice (i.e., the number of electrons released into the lattice upon VO$^{\cdot\cdot}$ formation), we obtain a quantity that represents the extent to which the oxygen sublattice absorbs the excess charge.

Figure 6.6: (a) The variation of $\Delta E_{\text{f,vac}}$ (in eV) with $\lambda$ (dimensionless) for La$_{0.5}$Sr$_{0.5}$CoO$_3$ (green triangle), La$_{0.5}$Sr$_{0.5}$Co$_{0.25}$Fe$_{0.75}$O$_3$ (red squares), and La$_{0.5}$Sr$_{0.5}$FeO$_3$ (blue circle). (b) The variation of $\lambda$ with the number of Co-O bonds broken during VO$^{\cdot\cdot}$ formation for La$_{0.5}$Sr$_{0.5}$Co$_{0.25}$Fe$_{0.75}$O$_3$.

Comparing the role of the oxygen sublattice in LSCF to that in LSC and LSF (Figure 6.6) demonstrates that the extent to which the reduction delocalizes over the oxygen sublattice generally goes as $\lambda_{\text{LSC}} < \lambda_{\text{LSCF}} < \lambda_{\text{LSF}}$, although exceptions exist in our data. Different local Fe/Co environments for LSCF lead to changes in $\lambda$, and these
variations subsequently cause significant changes in $\Delta E_{f,vac}$. The similarity between the variation of $\Delta E_{f,vac}$ and $\lambda$ with the number of Co-O bonds broken (Figures 6.4 and 6.6, respectively) gives a counterintuitive result. Previously, we have seen that increasing $\lambda$ lowers $\Delta E_{f,vac}$, however, the lowest $\Delta E_{f,vac}$ values for LSCF appear on the lower end of the spectrum of $\lambda$ values (see Figure 6.6(a)). This implies that adding Co initially leads to greater localization of electrons from an oxygen vacancy on the nearby TM sites. The fact that this leads to a decrease in $\Delta E_{f,vac}$ can be explained by the ability of the Co$^{3+}$ ions to change their magnetic states to accommodate the additional electron density. It may also be explained, in part, by the fact that hybrid TM 3$d$ and O 2$p$ states occupy the energies close to the Fermi level (Figure 6.3b) in La$_{0.50}$Sr$_{0.50}$Co$_{0.25}$Fe$_{0.75}$O$_{3-\delta}$. Therefore, delocalizing the electron charge onto the oxygen sublattice will also cause electron density to appear on the TM sublattice. Increasing the number of Co ions adjacent to the vacant site from one to two leads to greater delocalization (Figure 6.6b) but relatively higher $\Delta E_{f,vac}$ (Figure 6.4b). $\lambda$ is largest when the vacancy resides between two Co$^{3+}$ ions because these cases lead to the largest increase in $\mu_{Co}$ upon oxygen vacancy formation. This drives electron density into the $e_g$ orbitals pushing more electron density onto the O sublattice. We hypothesize that the reason this leads to higher $\Delta E_{f,vac}$ values is that the oxygen sublattice is forced to accept more electron density than it would under ideal circumstances (e.g., when the vacancy forms between one Fe and one Co ion).

Taken together all of these results indicate that oxygen vacancy formation between Fe and Co sites is more favorable than the oxygen vacancy formation between only Fe sites or only Co sites. This observation potentially has a twofold impact on the performance of LSCF as a cathode material. First, having Co-V$_O^{-}$-Fe sites leads to lower
defect formation energies and, thus, higher oxygen vacancy concentrations. Second, Co-
$\text{VO}^-\text{-Fe}$ sites might act as traps that limit the number of vacancies actually able to
participate in oxygen transport. The second point is mitigated by the small ~0.3 eV
difference in $\Delta E_{v,\text{vac}}$ between Co-$\text{VO}^-\text{-Fe}$ and Fe-$\text{VO}^-\text{-Fe}$ configurations. Even so, the
percolation paths that avoid Co-$\text{VO}^-\text{-Fe}$ configurations become the important pathways
for oxygen ion migration. The fact that Co-$\text{VO}^-\text{-Co}$ configurations are rare in
La$_{0.50}$Sr$_{0.50}$Co$_{0.25}$Fe$_{0.75}$O$_{3-\delta}$ makes them of minor importance to our discussion. Since Co-
$\text{VO}^-\text{-Co}$ configurations do not trap like Co-$\text{VO}^-\text{-Fe}$ configurations, increasing the Co
content will have the mixed effect of increasing the number of trapping (Co-$\text{VO}^-\text{-Fe}$)
configurations as well as the number of non-trapping (Co-$\text{VO}^-\text{-Co}$) sites.

Based on the preceding analysis, it appears that increasing the Co content has a
mixed impact on oxygen transport. Higher Co concentrations increase the oxygen
vacancy formation energy causing a reduction in the oxygen vacancy concentration. At
the same time, higher Co concentration ought to reduce the number of trapping sites
leading to more free oxygen vacancies. However, it is known that the presence of Co
increases the conductivity of LSCF when compared with LSF.$^{58}$ Thus, the reduction in
oxygen ion mobility is balanced by the increase in electronic conductivity for LSCF. Our
formation energy predictions (Figure 6.4b) indicate that high Co concentrations might be
counterproductive for $\text{VO}^-$ formation, so this tradeoff appears to be maximized with
higher Fe concentrations. The preceding discussion explains why the standard LSCF
cathode composition (La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$) works well under experimental conditions.
6.4 Conclusions

In summation, we analyzed DFT-based models for LSCF, finding that the GGA+U method gave a far better description of the electronic structure of LSCF than did traditional DFT-GGA. Furthermore, we carefully accounted for the possible magnetic states of the Co$^{3+}$ ion in deciding how to model LSCF. Our results showed that previous studies on the parent materials of LSCF (e.g., LaCoO$_3$, LaFeO$_3$, and La$_{1-x}$Sr$_x$FeO$_3$) provided insights that remain relevant for the target material. We employed a quasirandom model to simulate oxygen vacancy formation in LSCF and found that the oxygen vacancies had a slight preference to form between Fe and Co ions. This correlates with the Co ions rearranging their $d$ electrons in response to a nearby oxygen vacancy. Finally, we showed that the GGA+U results gave rise to oxygen vacancy formation energies consistent with experiment when a correction was made for the overbinding of the O$_2$ molecule by DFT-GGA.

Our results showed that the presence of Co in LSCF serves to improve the electronic conductivity by making it a semi-metal with a smaller minority spin gap than that found in La$_{0.50}$Sr$_{0.50}$FeO$_3$; however, too high Co content will reduce the oxygen vacancy concentration because Co-VO··-Co configurations have higher VO·· formation energies. Oxygen sites between Fe and Co ions may wind up trapping vacancies; however, the trapping effect is small (~0.3 eV). Fundamentally, a tradeoff must occur between the increased electronic conductivity and decreased ionic mobility resulting from adding Co to LSCF. We find that increasing the Co content from $y_{Co} = 0.25$ to $y_{Co} = 0.50$ has minimal effect on the electronic structure. This finding indicates that increasing $y_{Co}$ above 0.25 will negligibly impact the electrical conductivity. Therefore, Fe-rich
compositions should be preferred to Co-rich compositions, because higher Co concentrations do not improve the electronic conductivity and may reduce the ionic conductivity by introducing more Co-Vo⁻-Co sites that exhibit higher oxygen vacancy formation energies. This trade-off explains why the standard LSCF composition (La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3}) is close to optimal for the SOFC cathode.

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Chapter 7

Electronic Structure and Defect Chemistry of SrFeO_{3-\delta} and Sr_{1-x}K_xFeO_{3-\delta}

7.1 Introduction

In the previous chapters, we have explained the electronic structure and defect chemistry of La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta} (LSCF) and provided insights for optimizing LSCF to use as a solid oxide fuel cell cathode (SOFC) material. Our description began with the parent materials, LaFeO_3 and LaCoO_3, before progressing into the more respectively complex compositions La_{1-x}Sr_xFeO_3 and La_{1-x}Sr_xCoO_3, and finally analyzing the behavior of LSCF with all elements present in the lattice. In this chapter, we will focus on one more parent material SrFeO_{3-\delta} and its transformation into an alternative SOFC cathode material in the form of Sr_{1-x}K_xFeO_{3-\delta} (SKFO).

While La_{1-x}Sr_xCo_{1-y}Fe_yO_3 remains the reference mixed ion-electron conducting (MIEC) cathode,^{2-5} many other cathode materials show promising electrochemical behavior. These include Ba_{1-x}Sr_xCo_{1-y}Fe_yO_3 (BSCF), Sr_2Fe_{2-x}Mo_xO_6 (SFMO), and Sr_{1-x}K_xFeO_3 (SKFO).^{1,6,7} Many experimental studies have illuminated the structural properties, oxygen transport mechanisms, and electrochemical performance of LSCF, BSCF, and SFMO.^{7-13} Far less is known about SFKO. Hou, et al. showed that cathodes of Sr_{0.9}K_{0.1}FeO_3 (with a La_{1-x}Sr_xGa_{1-y}Mg_yO_3, or LSGM, electrolyte and Sr_2MgMoO_6 anode) produced a satisfactory maximum current density of 680 mW cm^{-2} at 800°C.^{1} They observed no loss in the observed power density over the course of 50 cycles from open circuit voltage (OCV) to 0.4 V and back to OCV.^{1} The obtained power density
competes with LSCF-based cells. Even better, the SFKO cathodes contain no Co, which improves their cost-effectiveness.

In light of the promising experimental results presented above, we seek to understand the role K plays in making SKFO a viable cathode. Understanding the role of K in SKFO first requires analyzing the electronic structure and oxide ion diffusivity in the parent material SrFeO$_{3-\delta}$ (SFO). In oxygen-rich conditions, SFO adopts a cubic perovskite structure with disordered vacancies. This phase displays metallic conductivity (desirable for a MIEC cathode), although a helical antiferromagnetic arrangement complicates the magnetic properties of SFO.$^{14-16}$ However, the Néel temperature for SFO in the perovskite phase is only 134 K,$^{14}$ meaning that the material behaves paramagnetically at SOFC operating temperatures. Formally, SFO contains Fe$^{4+}$ ($3d^4$) ions that can easily reduce to Fe$^{3+}$ ($3d^5$) due to the stability of the half-filled $d$-shell in Fe$^{3+}$. This makes SFO susceptible to large nonstoichiometries (e.g., $\delta=0.20$ at 800°C).$^1$

Several structures of SrFeO$_3$ featuring vacancy ordering have been reported. This presents an issue for SOFC performance because ordered structures effectively reduce the number of oxygen vacancies free to participate in ionic transport. Experimental investigations have found phases with ordered oxygen vacancies for $\delta=0.125$, 0.25, and 0.50.$^{17}$ However, the order-disorder transitions for $\delta=0.125$ and $\delta=0.25$ occur at 250°C and 320°C, respectively. The only vacancy-ordered phase relevant at SOFC operating temperatures therefore is the Brownmillerite phase (SrFeO$_{2.5}$), with an order-disorder transition at 830°C. The ordering of oxygen vacancies in SrFeO$_{2.5}$ leads to low electrical conductivity.$^{18}$ This means that care must be taken to avoid the transition from SrFeO$_{3-\delta}$ to SrFeO$_{2.5}$. Hou et al. found a tetragonally distorted perovskite structure for SKFO.
(xK=0.10) with K substituents distributed randomly over the Sr sublattice. Two questions arise from this discussion: First, do K substitutions beneficially alter the electronic structure of the material? Second, do the holes introduced by K substitutions lower the oxygen vacancy formation energy leading to improved ionic conductivity?

Theoretical analysis using density functional theory (DFT)-based methods can provide the fundamental understanding necessary to answer the first of the preceding questions. DFT and DFT+U studies have examined the band structure and bulk energetics of SrFeO$_3$ (or Sr$_8$Fe$_8$O$_{23}$)$_{\text{16,19–24}}$. Matar$^{25}$ (using DFT-LDA) and Shein et al.$^{21}$ (using LDA+U) concluded that the ferromagnetic (FM) state had the lowest energy among the collinear magnetic configurations. This result was contradicted by Hamdad et al., whose LAPW+lo calculations with the GGA+U method (U = 0.49 eV) determined that the ground state of SFO was G-type antiferromagnetic (AFM)$^{24}$. The fact that different theoretical methods predict different magnetic ground states makes checking the lowest energy collinear arrangement a necessary part of any DFT-based analysis. The actual spin-spiral ground state of SrFeO$_3$ was investigated by Li et al.$^{16}$, but they found that the stabilization of the spin-spiral (relative to the FM state) using LDA+U calculations is only 3 meV/f.u. The uncertainty associated with the approximate exchange-correlation (XC) functional used in Kohn-Sham (KS) DFT calculations makes this stabilization insignificant. Furthermore, the spin-spiral and FM states have (essentially) equal energies, indicating that FM descriptions of SrFeO$_3$ likely capture the essential physics. Few studies have attempted to address both the oxygen vacancy formation energy$^{26,27}$ and oxygen migration energy barrier using DFT$^{26–28}$. 
We present a detailed DFT-based analysis of the electronic structure, phase stability, and defect chemistry of SrFeO$_3$. We analyze how the defect chemistry affects the electronic structure of these materials, providing insight necessary to optimize the operating conditions for SOFCs using this material. Subsequently, we introduce K ions into SrFeO$_3$ in order to examine whether K substitutions improve the electronic and/or ionic conductivity of SFO.

![SrFeO$_3$ periodic cells](image)

**Figure 7.1.** SrFeO$_3$ periodic cells: (a) cubic unit cell, (b) $2\times2\times2$ supercell, (c) 80-atom (rhombohedral) supercell, and (d) $3\times3\times3$ supercell. Color designations: Sr (green), Fe (brown), and O (red). Structural images were produced using VESTA.$^{29,30}$

7.2 Computational Details

We employed four structures to model SrFeO$_3$. Figure 7.1 shows the structures used to analyze the electronic structure and defect formation energies in perovskite SFO. The basic electronic structure of SrFeO$_3$ was computed for the cubic (primitive)
perovskite unit cell (space group 221, Pm\(\bar{3}\)m, Figure 7.1a). Although SrFeO\(_{3-\delta}\) can undergo orthorhombic and tetragonal distortions, we restrict our analysis of SrFeO\(_3\) to the cubic perovskite structure, because the other perovskite phases convert back to the cubic phase at SOFC operating temperatures.\(^{31}\) Defect chemistry analysis requires supercells large enough to minimize interactions between defects and their own periodic images. For this purpose, we used the supercells of the primitive cell enumerated in Table 7.1 to model the specified defects. Possible defects include oxygen (Vo\(^−\)) and strontium (Vs\(r//\)) vacancies, as well as K substitutions (Ks\(r/)\). To see how these defects (Vs\(r//\) or Ks\(r/)\) influenced Vo\(^−\) formation, we tested whether proximity of Vo\(^−\) to Vs\(r//\) or Ks\(r/)\) significantly altered the Vo\(^−\) formation energies. We employed a FM configuration for the Fe ions because we find that it is the lowest energy collinear magnetic alignment (\textit{vide infra}). Studying defect chemistry requires using supercell models for which non-collinear models become prohibitively complex and expensive.

<table>
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<th>Lattice Vectors</th>
<th>Defects Studied</th>
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<td>None</td>
</tr>
<tr>
<td>b</td>
<td>40</td>
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</tr>
<tr>
<td>c</td>
<td>80</td>
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<td>Vo(^−), Vs(r//), Ks(r/))</td>
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<tr>
<td>d</td>
<td>135</td>
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<td>Vo(^−), Vs(r//)</td>
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</table>

We performed spin-polarized KS-DFT\(^{32,33}\) calculations using the Vienna Ab initio Simulation Package (VASP) version 5.2.2.\(^{34-36}\) Electron XC was treated within the local density approximation (LDA)\(^{37,38}\) and the generalized gradient approximation (GGA) of
Perdew, Burke, and Ernzerhof. The projector augmented-wave (PAW) method was used to describe the interaction of nuclei plus frozen core electrons with the valence electrons. The PAW potentials taken from the VASP library were labeled Sr\_sv (4s\(^2\)4p\(^6\)5s\(^2\)), K\_sv (3s\(^2\)3p\(^6\)4s\(^1\)), Fe (4s\(^2\)3d\(^6\)), and ‘regular’ O (2s\(^2\)2p\(^4\)). The “\_sv” appended to the Sr and K PAW potentials indicates that the s and p semi-core states were treated explicitly as self-consistently optimized valence states in our calculations. Self-interaction errors produced by pure DFT functionals are often significant for first row transition metal cations. To assess the role of self-interaction error in our DFT calculations, we also used the rotationally invariant DFT+U method with \( U_{\text{eff}} = U - J = 4.3 \) eV. This \( U_{\text{eff}} \) value was derived for Fe\(^{3+}\) from first-principles calculations. A small increase in \( U_{\text{eff}} \) would be appropriate for Fe\(^{4+}\) because \( U_{\text{eff}} \) increases by 0.6 eV from Fe\(^{2+}\) to Fe\(^{3+}\). However, we expect that \( U_{\text{eff}} = 4.3 \) eV will give qualitatively accurate results suitable for answering the questions posed in this chapter. We used a 8 × 8 × 8 Monkhorst-Pack k-point mesh for the cubic unit cell. Correspondingly, we used 4 × 4 × 4 and 3 × 3 × 3 Monkhorst-Pack k-point meshes for the 40- and 135-atom supercells, respectively. A 6 × 6 × 6 Γ-point-centered k-point mesh was used for the 80-atom supercell. During relaxations, first-order Methfessel-Paxton smearing (\( \sigma = 0.1 \) eV) was used for integrating over the first Brillouin zone. A 750 eV kinetic energy cutoff was used to truncate the planewave basis. These numerical parameters converged the total energies to 5 meV/f.u. and kept the electronic entropy below 5 meV/f.u. during the relaxations. Energies and densities of states (DOS) were refined at the relaxed geometries using the tetrahedron method with Blöchl corrections. We disabled the use of symmetry
in our calculations to ensure a consistent description of the host and defective crystal lattices.

7.3 Electronic Structure Analysis of Stoichiometric SrFeO$_3$

To ensure that we obtain an appropriate model for SrFeO$_3$, we compare the performance of traditional DFT-LDA and DFT-GGA methods with the LDA+U and GGA+U methods for computing the electronic structure of FM SrFeO$_3$ in its primitive cubic cell (Table 7.2 and Figure 7.2). Γ-point vibrational analysis properly yields twelve real optical phonon modes and three acoustic phonon modes for FM structures obtained with each method in the primitive unit cell containing five atoms. These results confirm that we have obtained valid minimum energy structures. Our DFT-GGA results confirm that the FM configuration is indeed the lowest energy collinear state for SrFeO$_3$ (by 66 meV f.u.$^{-1}$). The spin vectors on neighboring Fe sites are nearly aligned because the spin-spiral in SrFeO$_3$ propagates slowly.$^{16}$ The spin-spiral thus resembles the FM configuration more closely than any collinear AFM configuration.$^{25}$ Our results (Table 7.2) show that the DFT-GGA gives the best agreement with experiment for the lattice constant and Fe magnetic moment. To our knowledge, no experimental value for the bulk modulus of SrFeO$_3$ exists; however, our LDA+U bulk modulus (164 GPa, $U_{\text{eff}}=4.3$ eV) shows reasonably good agreement with the LDA+U bulk modulus reported by Shein et al.$^{21}$ (171 GPa, $U_{\text{eff}}=5.4$ eV). We expect that the actual value of the bulk modulus lies within the range of our computed values (131-188 GPa), with our DFT-GGA value (141 GPa) providing the best estimate of this property.
Table 7.2. Lattice constant (a in Å), Fe magnetic moment (μFe in μB), bulk modulus (B₀ in GPa), and Bader charges (qSr, qFe, and qO in e) of ferromagnetic SrFeO₃ cubic perovskite structure computed with various DFT-based methods and XC functionals. Data are reported for the ideal cubic perovskite unit cell (5 atoms, Figure 7.1a). The lattice constant and μFe are compared with experiment. DFT+U results used the ab initio value U_{eff,Fe}=4.3 eV. Uncertainties in the bulk modulus values give the 95% confidence range from our curve fit and do not account for errors arising from the approximate methods and XC functionals.

<table>
<thead>
<tr>
<th>Property</th>
<th>Experiment</th>
<th>DFT-LDA</th>
<th>DFT-GGA</th>
<th>LDA+U</th>
<th>GGA+U</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3.850⁹</td>
<td>3.746</td>
<td>3.858</td>
<td>3.784</td>
<td>3.904</td>
</tr>
<tr>
<td>μFe</td>
<td>2.7 ± 0.4⁹</td>
<td>2.50</td>
<td>2.88</td>
<td>3.61</td>
<td>3.84</td>
</tr>
<tr>
<td>B₀</td>
<td>----</td>
<td>188 ± 1</td>
<td>141 ± 1</td>
<td>164 ± 2</td>
<td>131 ± 3</td>
</tr>
<tr>
<td>qSr</td>
<td>----</td>
<td>1.54</td>
<td>1.58</td>
<td>1.53</td>
<td>1.59</td>
</tr>
<tr>
<td>qFe</td>
<td>----</td>
<td>1.47</td>
<td>1.66</td>
<td>1.61</td>
<td>1.68</td>
</tr>
<tr>
<td>qO</td>
<td>----</td>
<td>-1.00</td>
<td>-1.08</td>
<td>-1.05</td>
<td>-1.09</td>
</tr>
</tbody>
</table>

⁹ Reference 14

Understanding how DFT and DFT+U methods with LDA and GGA functionals affect the electronic structure of SrFeO₃ clarifies which combination of theory and functional provides the best description of SrFeO₃. We therefore plot the atom-projected DOS (PDOS, Figure 7.2) for FM, cubic SrFeO₃. The DFT-LDA and DFT-GGA electronic structures both show the metallic nature of SrFeO₃ with a β-spin peak just above the Fermi energy for the Fe 3d states. This behavior is consistent with high-spin (HS) Fe^{4+} ions (3d⁴ electron configuration). A purely HS 3d⁴ configuration would have no Fe 3d minority-spin contribution to the valence band. However, hybridization between the O 2p states and Fe 3d states explains the existence of small, minority-spin Fe 3d contributions in the valence band. Similarly, hybridization of the Fe 3d and O 2p states leads to contributions from the O 2p states in the conduction band. The hybridization between the α-spin Fe 3d and O 2p states agrees with the analysis of X-ray photoemission spectra performed by Bocquet et al.⁴⁸,⁴⁹ Their parameter-based configuration interaction model showed that the ground state of SrFeO₃ involves significant charge-transfer from
the oxygen 2p orbitals into the Fe 3d levels, leading to a combination of high-spin 3d⁴ and 3d⁵\(^L\) (\(L\) indicates a hole in an O 2p orbital) for the ground state of SrFeO₃.\(^{48}\) The DFT+U results resemble the regular DFT results, although a gap now exists in the minority-spin channel. This reduces the metallic character of the SrFeO₃ ground state and leads to excessively large values for the Fe magnetic moment (Table 7.1). Furthermore, the hybridization between Fe 3d and O 2p states is significantly lower with the DFT+U description, as illustrated by the decreased presence of O 2p states above the Fermi energy and lower overlap between the Fe 3d and O 2p peaks across the spectrum of energies displayed.

**Figure 7.2.** PDOS for SrFeO₃ computed with DFT (LDA and GGA) and DFT+U (LDA and GGA) methods. Positive PDOS values correspond to \(\alpha\) (up) spin states while negative PDOS corresponds to \(\beta\) (down) spin states. Color designations: Fe 3d states (blue) and O 2p states (red).
Our results contradict the assertion by Hamdad et al. that the +U correction is required to describe SrFeO$_3$.\textsuperscript{24} Although the DFT-LDA calculations give a similar electronic structure to the DFT-GGA calculations for SrFeO$_3$, DFT-LDA is far worse at describing oxygen defects in perovskite materials.\textsuperscript{50} Since the DFT-GGA results agree best with experimental lattice constants and electronic structure observations, we will use DFT-GGA exclusively for the remainder of our SrFeO$_3$ calculations.

7.4 Defect Chemistry of SrFeO$_3$

7.4.1 Oxygen Vacancy Formation in SrFeO$_3$

Creating a complete defect chemistry model for SrFeO$_{3-\delta}$ requires analyzing several possible defects. For clarity, we use the Kröger-Vink\textsuperscript{51} notation when discussing various defects in SrFeO$_3$. We assume that the Fe (B-site) sublattice is fully stoichiometric.\textsuperscript{52} Large concentrations of oxygen vacancies (V$_{O^{2-}}$) exist in SrFeO$_{3-\delta}$.\textsuperscript{15} Based on our previous work with LaFeO$_3$ (Chapter 3),\textsuperscript{53} we expect that strontium vacancies (V$_{Sr^{\oplus}}$) may exist in SrFeO$_3$. Coexistence of V$_{O^{2-}}$ and V$_{Sr^{\oplus}}$ SrFeO$_{3-\delta}$ should result in charge compensation, and the proximity of the defects may significantly impact their formation energies. Considering the distance between coupled defects thus adds another dimension to the defect model. We reference all of our defect calculations to O$_2$ (g) and SrO (s), as SOFC cathodes operate at intermediate-to-high temperatures (T > 500 °C) in an oxidizing atmosphere.

We begin by analyzing V$_{O^{2-}}$ formation in the cubic (perovskite) phase of SrFeO$_{3-\delta}$ without V$_{Sr^{\oplus}}$ present. As indicated in Table 7.1, we study V$_{O^{2-}}$ formation in the 40-, 80-, and 135-atom supercells (Figure 7.1b-d). We model a single V$_{O^{2-}}$ defect in each cell
yielding $\delta=0.125$, $\delta=0.0625$, and $\delta=0.037$, respectively. The \( \text{Vo}^{\text{+}} \) formation energy $\Delta E_{f,\text{vac}}$ is calculated according to Equation 7.1 and plotted as a function of $\delta$ in Figure 7.3.

$$
\Delta E_{f,\text{vac}} = E_{\text{V}_O^{\text{+}}\text{present}} - E_{\text{host}} + \frac{1}{2}E_{\text{O}_2}
$$

(7.1)

Here, $E_{\text{V}_O^{\text{+}}\text{present}}$ is the total energy of the cell with an oxygen vacancy, $E_{\text{host}}$ is the total energy of the stoichiometric supercell, and $E_{\text{O}_2}$ is the energy of the O$_2$ molecule in a large box. Increasing the supercell size does not yield convergence to a limit of dilute vacancies. Instead, $\Delta E_{f,\text{vac}}$ decreases faster with decreasing $\delta$. This trend resembles what was previously found for Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_{6.5}$.\textsuperscript{54} The similarity in the trends exhibited by these materials indicates that this behavior likely holds for perovskite materials with Sr for the A-site ion and an Fe-rich B-site sublattice.

**Figure 7.3.** Oxygen vacancy formation energy ($\Delta E_{f,\text{vac}}$) as a function of the oxygen nonstoichiometry ($\delta$).
As discussed in previous chapters, an upward shift of 0.42 eV should be made to the $\Delta E_{\text{f,vac}}$ values presented in Figure 7.3. The values with and without the correction are reported in Table 7.3, along with the Fe magnetic moments and the Bader charges for each of the perfect and defective cells. We find that the charge distributions differ significantly between the 40- and 135-atom supercells. Specifically, the 135-atom supercell is more ionic than the 40-atom cell. This difference is most pronounced when the VO$^{\cdots}$ is not present. Furthermore, the response of the Fe$^*$ ions (those adjacent to the VO$^{\cdots}$) differs between the cells. The 40-atom supercell has Fe$^*$ ions with magnetic moments that decrease upon VO$^{\cdots}$ formation (2.88 $\mu_B$ to 2.70 $\mu_B$). The opposite holds true for the 80-atom supercell (2.87 $\mu_B$ to 2.98 $\mu_B$). Finally, the 135-atom supercell exhibits a negligible difference between the magnetic moments of the Fe$^*$ ions and the remaining Fe ions (2.88 $\mu_B$ vs. 2.87 $\mu_B$). The Bader charges reveal that the oxygen sublattice plays a large role in accommodating the electron density left behind after VO$^{\cdots}$ formation in the 40-atom supercell (-1.04 e to -1.08 e). This effect becomes smaller in the 80-atom supercell (-1.05 e to -1.08 e) and disappears in the 135-atom supercell (-1.08 e to -1.08 e). In all three supercells, the Bader charges on the oxygen ions with the VO$^{\cdots}$ present are -1.08 e, indicating that there is an ionic limit to the O sublattice. The Fe sublattice in the 135-atom supercell is reduced upon VO$^{\cdots}$ formation (1.67 e to 1.61 e). This result is expected because the electronic states at the Fermi level of SrFeO$_3$ are mainly $\beta$-spin Fe $d$ states. The metallic nature of the $\beta$-spin Fe $d$ bands in SrFeO$_3$ explains why the reduction is seen across the entire sublattice, and the additional reduction observed on the Fe$^*$ ions (adjacent to the VO$^{\cdots}$) can be explained by the fact that the Bader volumes of these two
ions are enlarged to include the volume originally occupied by the now-departed oxygen ion.

Table 7.3. Oxygen vacancy formation energies (ΔE_{f,vac} in eV), magnetic moments (μ_{Fe} and μ_{Fe*} in μB), and Bader charges (q_{Fe}, q_{Fe*}, q_{Sr}, and q_{O} in e). Fe* indicates an Fe ion adjacent to an oxygen vacancy (Vo**). ΔE_{f,vac} values in parentheses contain a +0.42 eV correction for the overbinding of the O₂ molecule by DFT-GGA.

<table>
<thead>
<tr>
<th></th>
<th>40-atom (δ = 0.125)</th>
<th>80-atom (δ = 0.0625)</th>
<th>135-atom (δ = 0.037)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No Vo**</td>
<td>With Vo**</td>
<td>No Vo**</td>
</tr>
<tr>
<td>ΔE_{f,vac}</td>
<td>1.66 (2.08)</td>
<td>1.27 (1.69)</td>
<td>0.95 (1.37)</td>
</tr>
<tr>
<td>μ_{Fe}</td>
<td>2.88</td>
<td>2.95 ± 0.01</td>
<td>2.87</td>
</tr>
<tr>
<td>μ_{Fe*}</td>
<td>----</td>
<td>2.70</td>
<td>----</td>
</tr>
<tr>
<td>q_{Fe}</td>
<td>1.54</td>
<td>1.53</td>
<td>1.55</td>
</tr>
<tr>
<td>q_{Fe*}</td>
<td>----</td>
<td>1.48</td>
<td>----</td>
</tr>
<tr>
<td>q_{Sr}</td>
<td>1.58</td>
<td>1.59</td>
<td>1.60</td>
</tr>
<tr>
<td>q_{O}</td>
<td>-1.04</td>
<td>-1.08 ± e</td>
<td>-1.05</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The exact reason that the Bader charge analysis differs between these structural models is likely due to the way in which each supercell constrains the movement of the FeO₆ octahedra. Ironically, the larger 135-atom supercell constrains the octahedral rotations more than the 40-atom supercell because it contains an odd number (three) of octahedra spanning the width of the cell. This leads the 135-atom supercell to structurally and electronically resemble the ideal cubic unit cell. Since stoichiometric SrFeO₃ is known to exhibit the basic cubic perovskite structure, this means that the 135-atom supercell provides the most realistic electronic structure description out of the three supercell models presented. The overall trend of ΔE_{f,vac} decreasing with supercell size depends most strongly on two factors: 1) the reduction of interactions between oxygen vacancies and their periodic images; and 2) the larger supercells formally containing more Fe⁴⁺ ions to be reduced to Fe³⁺. The driving force for Vo** formation therefore is
strongest when the oxygen nonstoichiometry is smallest. At higher oxygen
nonstoichiometries, the partial reduction of the Fe sublattice decreases the driving for
oxygen vacancy formation because the Fe sublattice begins closer to its ideal +3
oxidation state. In fact, the oxygen nonstoichiometries measured by thermogravimetric
experiments\textsuperscript{15} are in excess of $\delta = 0.15$ for $P_{O_2} = 1$ atm and $T > 500$ °C, meaning that the
material naturally has oxygen nonstoichiometries in excess of any modeled here.

7.4.2 Strontium Vacancy Formation in SrFeO$_3$

In addition to VO$^{\bullet\bullet}$ defects, we must consider the possibility and role of VSr$^{\parallel}$
defects in SrFeO$_3$. Our previous work on LaFeO$_3$ showed that lanthanum vacancies
(VLa$^{\parallel}$) caused the VO$^{\bullet\bullet}$ concentration to increase by several orders of magnitude due to
favorable charge compensation. We first address the viability of VSr$^{\parallel}$ formation in SrFeO$_3$
by calculating the strontium vacancy formation energy ($\Delta E_{f,vac,Sr}$). In oxygen-rich (\textit{i.e.},
high $P_{O_2}$) conditions applicable to SOFC operation, VSr$^{\parallel}$ formation is referenced to SrO in
the B1 phase (NaCl structure). Equations 7.2 and 7.3 describe this process, where one Sr
ion is removed from the SrFeO$_3$ lattice.

$$\text{SrFeO}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{Sr}_{1-x}\text{FeO}_3 + \text{SrO (s)} \quad (7.2)$$

$$\Delta E_{f,vac,Sr} = E_{V_{Sr}^{\parallel} \text{present}} + E_{\text{SrO}} - E_{\text{host}} - \frac{1}{2} E_{\text{O}_2} \quad (7.3)$$

In Equation 7.3, $E_{V_{Sr}^{\parallel} \text{present}}$ is the total energy of the supercell with a VSr$^{\parallel}$ defect present,
$E_{\text{SrO}}$ is the total energy \textit{per formula unit} of the B1 phase of SrO, $E_{\text{host}}$ is the total energy
of the stoichiometric supercell, and $E_{\text{O}_2}$ is the energy of the O$_2$ molecule in a large box.

See Appendix A for details and validation of our SrO calculations.
We employ the 80- and 135-atom supercells (Figure 7.1c-d) to analyze \( \text{VSr}^{\|/} \). The \( \Delta E_{\text{f,vac,Sr}} \) values and relevant electronic structure parameters (magnetic moments and Bader charges) are reported in Table 7.4.

**Table 7.4.** Strontium vacancy formation energies (\( \Delta E_{\text{f,vac,Sr}} \) in eV), magnetic moments (\( \mu_{\text{Fe}} \) in \( \mu_B \)), and Bader charges (\( q_{\text{Fe}}, q_{\text{Sr}}, \) and \( q_{\text{O}} \) in e). \( \Delta E_{\text{f,vac,Sr}}^c \) contains a -0.42 eV correction for the overbinding of the \( \text{O}_2 \) molecule by DFT-GGA. Uncertainties are plus/minus one standard deviation. \( \Delta E_{\text{f,vac,Sr}}^c \) values corrected for the overbinding of the \( \text{O}_2 \) molecule are reported in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>80-atom (x =0.0625)</th>
<th>135-atom (x = 0.037)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E_{\text{f,vac,Sr}} )</td>
<td>2.14 (1.72)</td>
<td>2.00 (1.58)</td>
</tr>
<tr>
<td>( \mu_{\text{Fe}} )</td>
<td>2.87</td>
<td>2.90 (2.87-2.93)</td>
</tr>
<tr>
<td>( q_{\text{Fe}} )</td>
<td>1.55 ±0.03</td>
<td>1.67 ±0.02</td>
</tr>
<tr>
<td>( q_{\text{Sr}} )</td>
<td>1.60</td>
<td>1.58 ±0.01</td>
</tr>
<tr>
<td>( q_{\text{O}} )</td>
<td>-1.05 ±0.02</td>
<td>-1.08 ±0.03</td>
</tr>
</tbody>
</table>

The supercell size plays a minimal role in the value of \( \Delta E_{\text{f,vac,Sr}} \), with the larger supercell reducing the cost to form \( \text{VSr}^{\|/} \) defects by only 0.14 eV. This indicates that the interactions between the vacancy and its periodic images are minimal. Once again, the supercells differ in the way that charge redistributes upon vacancy formation. In the 80-atom supercell, the Fe sublattice is oxidized by 0.05 e per site, while the O sublattice is oxidized by 0.02 e per site, accommodating the holes formed by the departure of the Sr ion. The holes are therefore split among the Fe (0.8 e) and O (0.96 e) sublattices. The 135-atom supercell yields counterintuitive behavior. Forming a \( \text{VSr}^{\|/} \) causes a small reduction of 0.03 e per site on the Fe sublattice, while the oxygen sublattice is oxidized by 0.03 e per site. Although these changes are of the same magnitude, it is important to remember that there are three times as many O sites as Fe sites, meaning the O sublattice donates triple the amount of electron density accepted by the Fe sublattice. This distinction is important because the O sublattice must provide the electrons required to
reduce $\frac{1}{2}O_2$ to $O^2_-$ in the SrO product, as well as the electrons that reduce the Fe sublattice upon Sr vacancy formation.

The main result from Table 7.4 is that the $\Delta E_{f,vac,Sr}^c$ values are similar to the $\Delta E_{f,vac}^c$ values reported for the $Vo^{\cdot\cdot}$ formation in Table 7.3. This would initially lead us to expect similar concentrations of $Vo^{\cdot\cdot}$ and $Vs_{Sr//}$ defects. However, these concentrations are governed by the free energy of vacancy formation ($\Delta G_{f,vac}$ for $Vo^{\cdot\cdot}$ and $\Delta G_{f,vac,Sr}$ for $Vs_{Sr//}$).

The critical difference between $\Delta E$ and $\Delta G$ is that the free energy accounts for entropic contributions, which arises mainly from the gas-phase $O_2$ molecule. $Vo^{\cdot\cdot}$ formation releases $O_2$ molecules, leading to an entropic driving force for this process. Conversely, $Vs_{Sr//}$ formation binds oxygen from the gas phase into solid SrO, leading to an entropic penalty. Our calculations of the free energy of the $O_2$ molecule using the ideal gas, rigid-rotro, and harmonic oscillator approximations (Chapter 2) show that the difference between the defect formation energies and the defect formation free energies is approximately 1.0 eV at 700 °C. We thus conclude that $Vo^{\cdot\cdot}$ formation occurs far more easily than $Vs_{Sr//}$ formation.

7.4.3 Simultaneous Formation of Oxygen and Strontium Vacancies in SrFeO$_3$

The preceding section established that $Vs_{Sr//}$ may exist under SOFC operating conditions. This leads to the question of whether or not charge compensation from the holes introduced by $Vs_{Sr//}$ and the electrons introduced by $Vo^{\cdot\cdot}$ will lead to lower formation energies and increased defect concentrations. Such an effect could enhance the oxygen diffusion coefficient in SrFeO$_3$, leading to improved ionic transport through the cathode bulk. The chemical process is changed (Equation 7.4) when considering coupled
defects capable of undergoing charge compensation, where one Sr ion and one O ion are removed from the lattice and a formula unit of SrO is produced. 

\[
\text{SrFeO}_3 \rightarrow \text{Sr}_{1-x}\text{FeO}_3 - \delta + \text{SrO} \text{ (s)}
\]  

(7.4)

Here, the species written as \(\text{Sr}_{1-x}\text{FeO}_3 - \delta\) contains one \(V_{\text{Sr}}/\) and one \(V_O^\circ\). No \(O_2\) molecule appears in Equation 7.4, so it becomes apparent that the entropic driving forces previously discussed are balanced for creating the defect pair. The energy cost \((\Delta E_{V_{\text{Sr}}/ + V_O^\circ}, \text{Equation 7.5})\) for this process is one descriptor that helps us understand the extent to which defect pairs may arise.

\[
\Delta E_{V_{\text{Sr}}/ + V_O^\circ} = E_{V_{\text{Sr}}/ + V_O^\circ \text{ present}} + E_{\text{SrO}} - E_{\text{host}}
\]  

(7.5)

Here, \(E_{V_{\text{Sr}}/ + V_O^\circ \text{ present}}\) is the total energy of the supercell containing one defect pair.

Another descriptor of interest is the additional energy cost of forming the oxygen vacancy once the Sr vacancy is already present. This tells us if charge compensation significantly reduces \(\Delta E_{f, \text{vac}}\) and promotes higher \(V_O^\circ\) concentrations. This second descriptor is calculated using Equation 7.1 with the \(E_{\text{host}}\) term replaced by the total energy of the supercell and with one \(V_{\text{Sr}}/\) already present \((E_{V_{\text{Sr}}/ \text{ present}})\). The value of \(\Delta E_{V_{\text{Sr}}/ + V_O^\circ}\) and the value of derived value of \(\Delta E_{f, \text{vac}}\) with one \(V_{\text{Sr}}/\) present are presented in Table 7.5.

In this case, both the 80- and 135-atom supercells were employed. We tested whether proximity between the defects made a significant different by placing the \(V_O^\circ\) adjacent to the \(V_{\text{Sr}}/\) and by placing the \(V_O^\circ\) as far from the \(V_{\text{Sr}}/\) as could be achieved within our supercell model.
Table 7.5. Defect pair formation energies ($\Delta E_{V_{Sr}^//+V_O^-}$ in eV) and the uncorrected formation energy ($\Delta E_{f,vac}$ in eV) for $V_O^{\text{**}}$ with a $V_{Sr}^//$ already present. Adjacent indicates that the two defects are on neighboring sites, while distant indicates that the defects were separated by the maximum distance possible within the given supercell. Corrected $\Delta E_{f,vac}$ values are reported in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>80-atom (x, $\delta =0.0625$)</th>
<th>135-atom (x, $\delta =0.037$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adjacent</td>
<td>Distant</td>
</tr>
<tr>
<td>$\Delta E_{V_{Sr}^//+V_O^-}$</td>
<td>2.97</td>
<td>3.07</td>
</tr>
<tr>
<td>$\Delta E_{f,vac}$</td>
<td>0.83 (1.25)</td>
<td>0.93 (1.35)</td>
</tr>
</tbody>
</table>

Analyzing the data presented in Table 7.5 reveals only a 0.1 eV preference for defects to form on adjacent sites instead of distant sites. This difference is almost identical for both supercell models used, indicating that any attraction between the defects is short-ranged. The charge compensation effect between $V_O^{\text{**}}$ and $V_{Sr}^//$ is relatively small in SrFeO$_3$. Comparing the $\Delta E_{f,vac}$ values from the second row of Table 7.5 to the $\Delta E_{f,vac}$ values in Table 7.3 reveals that a significant (~0.4 eV) reduction occurs in the 80-atom supercell, but that this reduction essentially disappears for the 135-atom supercell. This means that $V_{Sr}^//$ may enable additional $V_O^{\text{**}}$ to form when $\delta = 0.0625$; however, the introduction of holes does not impact $V_O^{\text{**}}$ formation energies when $\delta = 0.037$. The main reason for this result may be found by examining the Bader charges in Table 7.4. $V_{Sr}^//$ formed in the 80-atom supercell caused an oxidation of both the Fe and O sublattices. The Fe ions thus were pushed toward higher oxidation states, and subsequent $V_O^{\text{**}}$ formation provided electrons to bring the Fe ions back into a more reasonable state. In the 135-atom supercell, the O sublattice donated the electrons to reduce the Fe sublattice and $\frac{1}{2}$O$_2^-$ to O$_2^-$ in the SrO product. This effect, in turn, means that there is no significant driving force from the Fe sublattice to obtain electrons and return to a better
oxidation state. The presence of \( \text{V}_{\text{Sr}^{2+}} \) fails to significantly reduce the cost to form \( \text{V}_{\text{O}^{2-}} \) at small \( \delta \) for this reason.

The small, sometimes negligible charge compensation effect found in \( \text{SrFeO}_3 \) should be compared to our findings for \( \text{LaFeO}_3 \). In \( \text{LaFeO}_3 \), the free energy of \( \text{V}_{\text{O}^{2-}} \) decreased by more than 3 eV in the presence of \( \text{V}_{\text{La}^{2+}} \). This meant that charge compensation played a significant role in coupling the \( \text{V}_{\text{La}^{2+}} \) and \( \text{V}_{\text{O}^{2-}} \) concentrations. The difference in the charge compensation effect between these two materials is striking, and can be explained through two arguments: First, the Fe sublattice is formally in the +3 oxidation state for \( \text{LaFeO}_3 \) and the +4 oxidation state in \( \text{SrFeO}_3 \). This causes \( \Delta E_{\text{f,vac}} \) to be large (4.06 eV)*** in \( \text{LaFeO}_3 \), because the Fe\(^{3+}\) ions have a stable, HS 3\(d^5\) electron configuration. The Fe\(^{4+}\) ions in \( \text{SrFeO}_3 \) prefer to be reduced to Fe\(^{3+}\), providing a driving force for \( \text{V}_{\text{O}^{2-}} \) formation. Second, the band gap of \( \text{LaFeO}_3 \) causes electrons and holes introduced by vacancies to be localized on the Fe ions. The metallic nature of \( \text{SrFeO}_3 \) leads to situations where the holes and electrons are mostly delocalized. This distributes any discomfort the \( \text{SrFeO}_3 \) lattice experiences as a result of defect formation. The driving force to compensate holes introduced by a cation vacancy through forming \( \text{V}_{\text{O}^{2-}} \) is therefore ameliorated.

### 7.5 Electronic Structure of \( \text{Sr}_{1-x}\text{K}_x\text{FeO}_3 \)

Our interest in \( \text{SrFeO}_3 \) stems from the discovery of Hou, et al. that \( \text{Sr}_{0.9}\text{K}_{0.1}\text{FeO}_3 \) is a plausible SOFC cathode material for intermediate temperature applications.\(^1\) We begin by considering the effect of K substitutions (\( \text{K}_{\text{Sr}^{2+}} \)) on the electronic structure of

*** This value was obtained in a 160-atom supercell as described in Chapter 3.
SrFeO₃. The following preliminary results rely on analyzing the effects in the 40- and 80-atom supercells described earlier (Figure 7.1b-c).

We place a single K atom in the 40-atom pseudocubic cell (Sr₀.₈₇₅K₀.₁₂₅FeO₃) in an attempt to stay close to the composition reported in ref. 1. We investigate substituting both one K atom and two K atoms in the 80-atom supercell, resulting in compositions of Sr₀.₉₃₇₅K₀.₀₆₂₅FeO₃ and Sr₀.₈₇₅K₀.₁₂₅FeO₃, respectively. With two K atoms present, we analyze the scenario where they are nearest-neighbors on the A-site sublattice. In Figure 7.4, we present the PDOS for Sr₁₋ₓKₓFeO₃. Although K is present in these cells, the 4s and 3p states from the K atoms do not have a significant presence near the Fermi level. We therefore focus on the Fe 3d and O 2p states as previously done for SrFeO₃.
Figure 7.4. Projected densities of states (PDOS) for SrFeO$_3$ (top), Sr$_{0.9375}$K$_{0.0625}$FeO$_3$ (middle), and Sr$_{0.875}$K$_{0.125}$FeO$_3$ (bottom) in the 40-atom (left) and 80-atom (right) supercells. Sr$_{0.9375}$K$_{0.0625}$FeO$_3$ cannot be modeled in the 40-atom supercell. Color designations: Fe 3$d$ states (blue) and O 2$p$ states (red).
Whether K is present or absent, the PDOS contain the same features. All compositions exhibit a pair of broad peaks in the $\alpha$-spin channel for the Fe 3$d$ states and a strong Fe 3$d$ peak in the $\beta$-spin channel beginning just below the Fermi level. This peak in the $\beta$-spin Fe 3$d$ states is the primary cause of the metallic conductivity in Sr$_{1-x}$K$_x$FeO$_3$. We also observe that the significant hybridization between the Fe 3$d$ and O2$p$ states remains when K is present. We therefore can see that the electronic structure of SrFeO$_3$ is essentially preserved up to 12.5% K$_{Sr}$/ on the A-site sublattice. The PDOS (Figure 7.4) for Sr$_{1-x}$K$_x$FeO$_3$ confirms the metallic conductivity observed experimentally for SKFO above 350 °C. We cannot evaluate the experimentalists’ assertion that a polaronic mechanism governs electronic transport below this temperature.

We augment our analysis of the PDOS shown in Figure 7.4 by presenting the Fe magnetic moments and Bader charges for all species (Table 7.6) in the same cells and compositions. This process establishes how the SrFeO$_3$ lattice responds to K$_{Sr}$/ introduction. We find that both the Fe and O sublattices are oxidized in the presence of K$_{Sr}$/.

Specifically, we observe an increase in the Fe Bader charge of 0.02-0.03 e per site for each K atom added (moving right by one column in Table 7.6). Likewise, we observe an increase in the O Bader charge of 0.01-0.02 e per site. The lattice must find a way to accommodate each K$_{Sr}$/ leading to 0.78 e ($q_{Sr} – q_K$ in the second, fourth, and fifth columns of data in Table 7.6) no longer being available to the lattice. The extent of each hole is obtained as the difference between the Sr and K Bader charges, which is consistent across both cells. In the 40-atom supercell, the Fe sublattice is oxidized by 0.22 e, while the O sublattice is oxidized by 0.53 e when one K atom is introduced. The Sr sublattice is oxidized by a negligible 0.03 e. In the 80-atom supercell, the first K$_{Sr}$/ oxidizes the Fe
sublattice by 0.30 e and the O sublattice by 0.43 e. The second KSr/ oxidizes the Fe sublattice by 0.40 e and the O sublattice by 0.37 e. The small remainders of 0.05 and 0.01 e required to make the total oxidation 0.78 e (vide supra) for the formation of the first and second KSr/, respectively, are taken from the Sr sublattice and produce a negligible effect on the average Sr Bader charge.

Table 7.6. Fe magnetic moments ($\mu_{Fe}$ in $\mu_B$) and Bader charges ($q_{Fe}$, $q_{Sr}$, $q_K$, and $q_O$ in e) for Sr$_{1-x}$K$_x$FeO$_3$ with $x_K = 0$, 0.0625, and 0.125. $x_K = 0.0625$ cannot be modeled in the 40-atom supercell.

<table>
<thead>
<tr>
<th></th>
<th>40-atom Supercell</th>
<th>80-atom Supercell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_K = 0$</td>
<td>$x_K = 0.125$</td>
</tr>
<tr>
<td>$\mu_{Fe}$</td>
<td>2.88</td>
<td>2.84</td>
</tr>
<tr>
<td>$q_{Fe}$</td>
<td>1.54</td>
<td>1.56</td>
</tr>
<tr>
<td>$q_{Sr}$</td>
<td>1.58</td>
<td>1.58</td>
</tr>
<tr>
<td>$q_K$</td>
<td>----</td>
<td>0.80</td>
</tr>
<tr>
<td>$q_O$</td>
<td>-1.04</td>
<td>-1.02</td>
</tr>
</tbody>
</table>

From the preceding analysis, we conclude that the holes introduced by KSr/ substitutional defects are delocalized across both Fe and O sublattices. This conclusion is consistent with the presented PDOS (Figure 7.4), which show significant hybridization between the O 2$p$ and Fe 3$d$ states.

7.6 Defect Chemistry of Sr$_{1-x}$K$_x$FeO$_3$

7.6.1 Potassium substitutions in Sr$_{1-x}$K$_x$FeO$_3$

We begin our analysis of the defect chemistry of SKFO by analyzing the energy change associated with creating KSr/ substitutions. We perform this analysis in the 80-atom supercell (Figure 7.1c). Equation 7.6 presents the chemical process associated with the K substitution, transforming SrFeO$_3$ into Sr$_{1-x}$K$_x$FeO$_3$. Equation 7.7 is used to calculate the energy change associated with forming n KSr/ substitutions ($\Delta E_{f,K_{Sr/}}$).
\[
\text{SrFeO}_3 + n\text{KO}_2(s) \rightarrow \text{Sr}_{1-x}\text{K}_x\text{FeO}_3 + n\text{SrO} (s) + \frac{n}{2}\text{O}_2(g)
\] (7.6)

\[
\Delta E_{fK_{Sr}} = \frac{1}{n} \left( E_{K\text{present}} + nE_{\text{SrO}} + \frac{n}{2}E_{\text{O}_2} - E_{\text{host}} - \frac{n}{2}E_{\text{KO}_2} \right)
\] (7.7)

In Equation 7.7, \(n\) is the number of substitutional defects formed to create the appropriate composition \(\text{Sr}_{1-x}\text{K}_x\text{FeO}_3\) in the 80-atom supercell. We consider the \(n = 1\) case (\(x_K = 0.0625\)) and the \(n = 2\) case (\(x_K = 0.125\)). \(\text{SrO}\) and \(\text{KO}_2\) are the most stable oxides for each of these cations (Appendix A), so these serve as the reference materials in Equation 7.6. Equation 7.7 allows us to calculate the cost per \(K_{Sr}/\) formed. In this case, \(E_{K\text{present}}\) is the total energy of the 80-atom cell with one or two \(K_{Sr}/\) defects present, \(E_{\text{host}}\) is the total energy of \(\text{SrFeO}_3\) in the 80-atom cell, \(E_{\text{SrO}}\) is the total energy per formula unit of \(\text{SrO}\) in its B1 (NaCl) structure, and \(E_{\text{KO}_2}\) is the total energy per formula unit of \(\text{KO}_2\).

**Table 7.7.** Formation energies (\(\Delta E_{f,K_{Sr}}\) in eV) for \(K_{Sr}/\) substitutional defects at various concentrations (\(x_K\)). Results are reported in the 80-atom supercell for one \(K_{Sr}/\) (\(x_K = 0.0625\)) and two \(K_{Sr}/\) (\(x_K = 0.125\)) defects present in the cell. The distance between the two K ions (\(d_{K-K}\) in Å) is presented so that any tendency for \(K_{Sr}/\) defects to cluster can be evaluated. \(\Delta E_{f,K_{Sr}}\) values in parentheses include the +0.42 eV correction for the overbinding of the \(\text{O}_2\) molecule.

<table>
<thead>
<tr>
<th>(x_K)</th>
<th>(d_{K-K})</th>
<th>(\Delta E_{f,K_{Sr}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0625</td>
<td>----</td>
<td>-5.64 (-5.22)</td>
</tr>
<tr>
<td>0.125</td>
<td>3.85</td>
<td>-5.62 (-5.20)</td>
</tr>
<tr>
<td>0.125</td>
<td>5.44</td>
<td>-5.61 (-5.19)</td>
</tr>
<tr>
<td>0.125</td>
<td>6.67</td>
<td>-5.62 (-5.20)</td>
</tr>
<tr>
<td>0.125</td>
<td>7.70</td>
<td>-5.62 (-5.20)</td>
</tr>
</tbody>
</table>

The formation energies for \(K_{Sr}/\) are reported in Table 7.7. Two key observations arise from the data presented in this table: First, forming \(K_{Sr}/\) defects is highly exothermic. Second, the formation energy per \(K_{Sr}/\) does not change for higher \(x_K\) or increased \(K_{Sr}/-K_{Sr}/\) separation. The exothermicity of forming \(K_{Sr}/\) defects indicates that
the material should remain stable up to and beyond \( x_k = 0.125 \) as experimentally observed.\(^1\) The second observation indicates that there is no strong driving force to prevent \( \text{K}_{\text{Sr}^/} \) defects from residing close to one another. This result is consistent with the hole introduced by \( \text{K}_{\text{Sr}^/} \) being highly delocalized (\textit{vide supra}). We therefore expect that the true crystal will not show any ordering of K and Sr ions on the A-site sublattice.

7.6.2 Oxygen Vacancy Formation in \( \text{Sr}_{1-x}\text{K}_x\text{FeO}_3 \)

The motivation for choosing SKFO over \( \text{SrFeO}_3 \) is that the introduction of holes should lower the \( \text{Vo}^{\prime\prime} \) formation energy, leading to higher \( \text{Vo}^{\prime\prime} \) concentrations and improved oxide ion diffusivity. However, we must determine whether or not this hypothesis holds. If it does hold, to what extent do the holes from \( \text{K}_{\text{Sr}^/} \) reduce the \( \text{Vo}^{\prime\prime} \) formation energy? We address these questions by computing the \( \text{Vo}^{\prime\prime} \) formation energy in the 80-atom supercell (Figure 7.1c) with one \( \text{K}_{\text{Sr}^/} \) present. Whenever two defects are present, the proximity of these defects may impact the formation energies. However, our previous discussion of \( \text{K}_{\text{Sr}^/} \) defects (\textit{vide supra}) leads us to believe that proximity between defects makes very little difference in the energetics.

<table>
<thead>
<tr>
<th>( \text{d}<em>{\text{K}</em>{\text{Sr}^/}-\text{V}_0} ) (Å)</th>
<th>( \Delta E_{\text{f,vac}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.77</td>
<td>1.10 (1.52)</td>
</tr>
<tr>
<td>4.71</td>
<td>1.09 (1.51)</td>
</tr>
<tr>
<td>6.08</td>
<td>1.15 (1.57)</td>
</tr>
</tbody>
</table>

The \( \text{Vo}^{\prime\prime} \) formation energies for various \( \text{K}_{\text{Sr}^/} - \text{V}_0^{\prime\prime} \) distances are presented in Table 7.8. The data confirm our expectation that there is no significant effect from the proximity of the two defects. This result is consistent with the metallic nature of SKFO.
The VO\textsuperscript{″} formation energies are computed using the optimized geometries containing both the Ks/ and VO\textsuperscript{″} defects; however, they have not been refined using the tetrahedron method with Blöchl corrections.\textsuperscript{47} Instead, they are computed using the smearing method employed during relaxations (first-order Methfessel-Paxton smearing\textsuperscript{46} with $\sigma = 0.1$ eV).

This difference should not impact the overall trend, as the total energies obtained with these two methods differ by less than 10 meV per 80-atom supercell for the supercells without VO\textsuperscript{″}.

The $\Delta E_{f,\text{vac}}$ values in Table 7.8 (1.09-1.15 eV) must then be compared to the $\Delta E_{f,\text{vac}}$ value (1.27 eV) obtained in the same supercell in the absence of Ks/ (Table 7.3). This minor difference in $\Delta E_{f,\text{vac}}$ indicates that the VO\textsuperscript{″} formation is easier because of a small charge compensation effect. The limitation of our preliminary study is that we have only investigated the scenario where $x_K$ and $\delta$ are equal to one another. The material, as synthesized by Hou et al., has $\delta = 0.06$ at room temperature.\textsuperscript{1} It therefore would be beneficial to consider the case where $x_K > \delta$ (e.g., two Ks/ in our 80-atom supercell).

Exploring different ratios of Ks/ to VO\textsuperscript{″} is beyond the scope of this work; however, such an investigation should yield insight into the VO\textsuperscript{″} formation process when more holes are present in the supercell.

7.7 Conclusions

We presented a detailed DFT-GGA study of SrFeO\textsubscript{3}. The oxygen vacancy formation energy was found to decrease sharply with increasing supercell size. This result mirrors the trend found in Sr\textsubscript{2}Fe\textsubscript{1.5}Mo\textsubscript{0.5}O\textsubscript{6} by Muñoz-García et al.\textsuperscript{54} Bader charge analysis indicated that the larger supercells allowed the Fe sublattice to be reduced to a larger extent upon oxygen vacancy formation. This reduction is favorable since it takes
Fe from a +4 towards a +3 oxidation state. We found that strontium vacancies are likely to exist in SrFeO₃, though they will exist in much smaller concentrations than oxygen vacancies. Strontium vacancies made minimal difference in the oxygen vacancy formation energy when the two defects were combined. We attribute this finding to the metallic nature of SrFeO₃, leading to the delocalization of holes and electrons introduced by the defects.

Substituting potassium for strontium to form Sr₁₋ₓKₓFeO₃ had minimal effect on the electronic structure, meaning we found metallic behavior for Sr₁₋ₓKₓFeO₃ consistent with experimental observations above 350 °C.¹ We cannot evaluate the experimental assertion that polaronic conductivity occurs below this temperature. We found that potassium substitutions have a large and exothermic formation energy. This finding indicates that the material will remain stable for potassium concentrations of up to xₖ = 0.125, possibly greater. The holes introduced by potassium substitution slightly lowered the oxygen vacancy formation energy. The small reduction in the oxygen vacancy formation energy indicates that further investigation is needed to understand the relationship between the potassium concentration and the oxygen vacancy formation energy.

The preceding paragraphs raised the question of potassium-to-oxygen-vacancy ratio for future investigation. One additional issue that needs to be investigated using first-principles calculations is the phase equilibrium between the disordered SrFeO₃ (metallic) and ordered SrFeO₂.₅ (insulating) phases. One key, unanswered question is whether or not adding potassium to these phases changes the equilibrium in favor of the
metallic, disordered SrFeO$_3$ phase. Addressing these issues will significantly clarify the utility of Sr$_{1-x}$K$_x$FeO$_3$ as an SOFC cathode.

References

9. Endler-Schuck, C., Joos, J., Niedrig, C., Weber, A. & Ivers-Tiffée, E. The chemical oxygen surface exchange and bulk diffusion coefficient determined by impedance spectroscopy of porous La$_{0.58}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$–$\delta$ (LSCF) cathodes. *Solid State Ion.* **269**, 67–79 (2015).


Chapter 8

Conclusions

This work aimed to provide fundamental insights regarding how members of the La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_3$ (LSCF) family of compounds behave as solid oxide fuel cell (SOFC) cathodes. We set out to glean atomic-scale insights that lead to design principles for rationally optimizing the elemental composition of LSCF for use as a SOFC cathode. Specifically, our objective was to isolate differences in electronic structure and oxygen diffusivity associated with specific changes to the material. What are the characteristic features of these materials that make LSCF a good mixed oxygen ion-electron conductor (MIEC)? What principles can we extract from these insights that will help engineers rationally design improved MIEC cathodes? Our work started with investigating how the electronic structure, defect chemistry, and oxygen diffusivity of the parent materials LaFeO$_3$ (Chapter 3) and LaCoO$_3$ (Chapter 4) differ. We then isolated effects associated with substituting Sr$^{2+}$ for La$^{3+}$ to form La$_{1-x}$Sr$_x$FeO$_3$ (LSF) and La$_{1-x}$Sr$_x$CoO$_3$.

Portions of this chapter were adapted from the following publications with permission:


Ritzmann, A. M., Muñoz-García, A. B., Pavone, M., Keith, J. A. & Carter, E. A. Ab Initio DFT+U Analysis of Oxygen Vacancy Formation and Migration in La$_{1-x}$Sr$_x$FeO$_{3-δ}$ (x = 0, 0.25, 0.50). *Chem. Mater.* 25, 3011-3019 (2013). Copyright 2013 American Chemical Society.


This work was presented in Chapter 5. We then looked at the behavior of LSCF with mixing on both the La/Sr and Co/Fe sublattices (Chapter 6). Finally, we presented a preliminary investigation of potassium substitution in the compound Sr$_{1-x}$K$_x$FeO$_3$ (Chapter 7). The following pages furnish a cumulative view of the insights offered in this thesis.

Chapter 3 presented a complete GGA+U analysis of oxygen transport in LaFeO$_3$. We showed that the GGA+U method offers the best agreement with experiment for structural parameters and Fe magnetic moments when compared to other DFT-based methods. We determined that oxygen vacancy (V$_{O^-}$) formation in perfectly stoichiometric (La/Fe=1) LaFeO$_3$ requires reducing the two Fe sites adjacent to the vacancy. This process has a high endoergicity primarily because of increased intra-atomic electron-electron repulsion and the absence of additional on-site exchange interactions for the reducing electron (it becomes the only minority spin Fe 3$d$ electron). We computed the minimum energy pathway for oxygen migration in LaFeO$_3$ and accurately predicted the oxygen migration barrier and vacancy diffusion coefficient ($D_v$) for this material. However, our computed V$_{O^-}$ concentrations disagreed with experiment by orders of magnitude. To more deeply investigate this discrepancy, we explored the role of lanthanum vacancies in changing the defect chemistry of LaFeO$_3$. We found that the holes introduced by a lanthanum vacancy delocalize over the oxygen sublattice. These holes provided favorable charge compensation for the electrons released upon V$_{O^-}$ formation. When we combined the lanthanum and oxygen defect chemistries, coupled through the charge compensation process, predicted V$_{O^-}$ concentrations and oxygen diffusion coefficients were brought into good agreement with experiment.
This work clearly demonstrates the enormous impact of La vacancies in raising the Vo\textsuperscript{−} concentration in LaFeO\textsubscript{3}. This effect, in turn, increases the observed oxygen diffusion coefficient. Specifically, the La vacancies introduce holes that compensate the electrons released when an Vo\textsuperscript{−} forms. This results in favorable Vo\textsuperscript{−} formation free energies leading to orders of magnitude higher Vo\textsuperscript{−} concentrations than would be expected if La vacancies were not present. This also indicates a methodological point that La vacancies must be accounted for when computing Vo\textsuperscript{−} formation energies in stoichiometric materials. In cases where Sr substitution dramatically lowers the Vo\textsuperscript{−} formation energy, then La vacancies in the pure material (no Sr substitutions) are likely to play a large role in enhancing the oxygen diffusivity. Our results also indicate that A-site substoichiometry offers a powerful way to increase the oxygen diffusivity.

Chapter 4 presented an analysis of the effect of Co spin state on oxygen transport in LaCoO\textsubscript{3} using detailed first-principles quantum mechanics calculations. Our results provide new understanding regarding the intricacy of LaCoO\textsubscript{3}, specifically the interrelation of spin state with oxygen ion diffusivity. First, we calculated a new \textit{ab initio} value of U\textsubscript{eff} = 4.0 eV for low-spin (LS) Co\textsuperscript{3+} ions using the method of Mosey, Liao, and Carter.\textsuperscript{6} We showed how LDA+U and GGA+U calculations lead to different spin state orderings with only LDA+U being reasonable. We then determined that the presence of LS Co\textsuperscript{3+} ions leads to lower Vo\textsuperscript{−} formation energies. We also found that the spin state alters the vacancy migration process and thus the vacancy diffusion coefficient. On the whole, these results confirm that the spin state of the Co\textsuperscript{3+} ions critically influences oxygen transport in LaCoO\textsubscript{3}. 
The results of our study indicate that modifying the operating conditions (e.g., operating pressure) or the material composition (e.g., doping) to increase the number of LS Co\(^{3+}\) ions at higher temperatures may offer a route toward improving the ionic conductivity of LaCoO\(_3\). The results we provided also form the initial basis for a library of diffusion coefficients, derived from first principles, which can be used for longer time and length scale simulations (e.g., kinetic Monte Carlo). Such an analysis including transitions between spin states, V\(_{O}^{-}\) formation, and oxygen migration would provide a more complete description of oxygen ion conductivity in LaCoO\(_3\).

Chapter 5 presented a detailed first-principles quantum mechanics analysis showing how Sr substitution influences oxygen transport in LSF, which provides a deeper understanding of oxygen transport in LSF cathodes. Specifically, we clarify the fundamental role of A-site dopants in promoting V\(_{O}^{-}\) formation and therefore oxide ion transport in intermediate temperature (IT)-SOFCs with MIEC cathodes. After showing the DFT+U method’s capability of successfully modeling LSF, we investigated the nature of the holes introduced by Sr substitution, determining them to have mainly O 2p character. In LaFeO\(_3\), the reduction of Fe\(^{3+}\) ions to Fe\(^{2+}\) is unfavorable and leads to a large \(\Delta H_{f,\text{vac}}\) value (see Chapter 3). With Sr present, the electrons left behind when a vacancy forms compensate for the holes introduced by Sr. The resulting \(\Delta H_{f,\text{vac}}\) is significantly lower than that in LaFeO\(_3\), resulting in more oxygen vacancies and easier oxygen transport. GGA+U calculations indicate significant increases in oxygen diffusivity will occur with increasing Sr concentration because of the corresponding increase in oxygen vacancies.
This refined illustration provided by the DFT+U method shows how the interplay between electron-deficient substitutions, iron ions, and the oxygen sublattice can improve oxygen transport in LSF. As found in Sr$_2$FeMoO$_6$\textsuperscript{7-9} based materials, the electrons from an V$_{O}^{−}$ in La$_{1-x}$Sr$_x$FeO$_3$ ($x > 0$) distribute over the oxygen sublattice which produces very favorable V$_{O}^{−}$ formation enthalpies.\textsuperscript{10} This insight has wide potential application to iron-based SOFC cathode materials, but this should still be confirmed by experiment.

Chapter 5 also presented a detailed DFT-GGA analysis of the electronic structure and defect formation processes in LSC. We find that the metallic nature of LSC renders the GGA+U method inaccurate for this material. This work shows that Sr substitution in LSC has significantly less impact on $\Delta H_{f,vac}$ compared with LSF. Further, $\Delta H_{f,vac}$ is larger in LSC than LSF. This result lies in stark contrast to the significantly lower $\Delta H_{f,vac}$ in LaCoO$_3$ compared with LaFeO$_3$. This outcome arises from the fact that the oxygen sublattice participates to a much larger degree in the V$_{O}^{−}$ formation process in LSF compared to LSC.\textsuperscript{10}

Chapter 6 analyzed DFT-based models for LSCF, finding that the GGA+U method gave a far better description of the electronic structure of LSCF than did traditional DFT-GGA. Furthermore, we carefully accounted for the possible magnetic states of the Co$^{3+}$ ion in deciding how to model LSCF. Our results showed that previous studies on the parent materials of LSCF (\textit{e.g.}, LaCoO$_3$, LaFeO$_3$, and La$_{1-x}$Sr$_x$FeO$_3$) provided insights that remain relevant for the target material. We employed a quasirandom structure model to simulate V$_{O}^{−}$ formation in LSCF and found that the oxygen vacancies had a slight preference to form between Fe and Co ions. This correlates with the Co ions rearranging their $d$ electrons in response to a nearby V$_{O}^{−}$. Finally, we
showed that the GGA+U results gave rise to $V_{O^-}$ formation energies consistent with experiment when a correction was made for the overbinding of the $O_2$ molecule by DFT-GGA.

Our results suggested that the presence of Co in LSCF serves to improve the electronic conductivity by making it a semi-metal with a smaller minority spin gap than that found in $La_{0.50}Sr_{0.50}FeO_3$; however, too high Co content will reduce the $V_{O^-}$ concentration because Co-$V_{O^-}$-Co configurations have higher $V_{O^-}$-formation energies. Oxygen sites between Fe and Co ions may wind up trapping vacancies; however, the trapping effect is small (~0.2 eV). Fundamentally, a tradeoff must occur between the increased electronic conductivity and decreased ionic mobility resulting from adding Co to LSCF. We find that increasing the Co content from $y_{Co} = 0.25$ to $y_{Co} = 0.50$ has minimal effect on the electronic structure. This finding indicates that increasing $y_{Co}$ above 0.25 will negligibly impact the electrical conductivity. Therefore, Fe-rich compositions should be preferred to Co-rich compositions, because higher Co concentrations do not improve the electronic conductivity and may reduce the ionic conductivity by introducing more Co-$V_{O^-}$-Co sites that exhibit higher $V_{O^-}$ formation energies. This trade-off explains why the standard LSCF composition ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$) is close to optimal for the SOFC cathode.

Chapter 7 presented a detailed DFT-GGA study of $SrFeO_3$. The $V_{O^-}$ formation energy was found to decrease sharply with increasing supercell size. This result mirrors the trend found in $Sr_2Fe_{1.5}Mo_{0.5}O_6$ by Muñoz-García et al. Bader charge analysis indicated that the larger supercells allowed the Fe sublattice to be reduced to a larger extent upon $V_{O^-}$ formation. This reduction is favorable since it takes Fe from a +4
towards a +3 oxidation state. We found that strontium vacancies are likely to exist in SrFeO$_3$, though they will exist in much smaller concentrations than oxygen vacancies. Strontium vacancies made minimal difference in the VO$^{--}$ formation energy when the two defects were combined. We attribute this finding to the metallic nature of SrFeO$_3$, leading to the delocalization of holes and electrons introduced by the defects.

Substituting potassium for strontium to form Sr$_{1-x}$K$_x$FeO$_3$ had minimal effect on the electronic structure, meaning we found metallic behavior for Sr$_{1-x}$K$_x$FeO$_3$ consistent with experimental observations above 350 °C. We cannot evaluate the experimental assertion that polaronic conductivity occurs below this temperature. We found that potassium substitutions have a large and exothermic formation energy. This finding indicates that the material will remain stable for potassium concentrations of up to $x_K = 0.125$, possibly greater. The holes introduced by potassium substitution slightly lowered the VO$^{--}$ formation energy. The small reduction in the VO$^{--}$ formation energy indicates that further investigation is needed to understand the relationship between the potassium concentration and the VO$^{--}$ formation energy.

The preceding paragraphs raised the question of potassium-to-oxygen-vacancy ratio for future investigation. One additional issue that needs to be investigated using first-principles calculations is the phase equilibrium between the disordered SrFeO$_3$ (metallic) and ordered SrFeO$_{2.5}$ (insulating) phases. One key, unanswered question is whether or not adding potassium to these phases changes the equilibrium in favor of the metallic, disordered SrFeO$_3$ phase. Addressing these issues will significantly clarify the utility of Sr$_{1-x}$K$_x$FeO$_3$ as an SOFC cathode.
This thesis has demonstrated the power of DFT-based methods for understanding defect chemistry in materials related to LSCF. Specifically, we have shown how \( V_{O^-} \) formation energies are influenced by the electronic structure of the perovskite. The complexity of this system makes rational optimization of LSCF’s composition difficult; however, we have identified characteristic features that lead to higher \( V_{O^-} \) concentrations and, thus, to better ionic conductivity. The electronic structure of LSCF is enhanced by mixing Co and Fe on the B-site sublattice. Furthermore, we have shown that adding Sr is generally favorable for increasing \( V_{O^-} \) concentrations because the holes introduced by Sr substitution compensate for the electrons left behind when an \( V_{O^-} \) forms. In general, the benefit gained from Sr substitution is stronger in Fe-rich compositions because the holes partially oxidize the Fe sublattice, moving it away from its preferred 3+ oxidation state. Initially mixing some Co into \( \text{La}_{1-x}\text{Sr}_x\text{FeO}_3 \) to give LSCF enhances the electrical conductivity of LSCF; however, too much Co increases the concentration of unfavorable sites (between two Co ions) for \( V_{O^-} \) formation. The ideal Co concentration in LSCF balances these considerations. Two additional insights from this thesis may prove powerful in optimizing the composition of LSCF: employing A-site substoichiometry and making Co\(^{3+} \) ions low-spin offer exciting avenues that could further enhance the ionic conductivity of LSCF.

The insights presented in this thesis offer important suggestions for rationally improving the MIEC performance of LSCF and related materials. This work prepares the way for improved SOFC devices operating in the intermediate-temperature regime.
References


5. Ritzmann, A. M., Dieterich, J. M. & Carter, E. A. Density Functional Theory +U Analysis of the Electronic Structure and Defect Chemistry of LSCF (La$_{0.5}$Sr$_{0.5}$Co$_{0.25}$Fe$_{0.75}$O$_{3-\delta}$). *Phys. Chem. Chem. Phys.* **18**, 12260-12269 (2016).


Appendix A

Reference State Calculations

A.1 Electronic Structure of O₂

The energy of the O₂ molecule in the gas phase has entered into equations for oxygen vacancy formation and A-site vacancy formation energies. The discussion will start with qualitative models for bonding in O₂. Using these simple models as reference, comparisons will be made between computed quantities and experiment, as well as between different levels of theory. This analysis shows the extent to which Kohn-Sham density functional theory (DFT)¹,² with certain exchange-correlation (XC) functionals predicts exceedingly high bond strengths for O₂. This leads to a simple correction for the DFT overbinding of O₂ referenced in the preceding work.

A.1.1 Qualitative Descriptions of Bonding in O₂

Explaining the bonding in O₂ at its equilibrium geometry requires the use of molecular orbital (MO) theory.³ MO theory provides a qualitative description of a molecule’s electronic structure by assuming that linear combinations of atomic orbitals (LCAO) can accurately represent the molecule’s orbitals. Within MO theory, the strongest mixing occurs between atomic orbitals of the same symmetry with similar energy and the highest overlap.

*Figure A.1. Lewis dot structure for the O₂ molecule.*
Various qualitative descriptions of $O_2$ offer simple ways to understand its electronic structure. The Lewis dot structure for $O_2$ (Figure A.1) describes $O_2$ with a double bond, though it does not indicate the triplet ground state of $O_2$. On the other hand, the MO diagram for $O_2$ (Figure A.2) shows that the bonding in $O_2$ consists of three bonds (from the $3\sigma$ and $1\pi$ orbitals) offset by two electrons in the degenerate $1\pi^*$ pair of antibonding orbitals. Formally, this leads to a bond order\(^n\) of two in agreement with the Lewis dot structure. However, Hund’s rules require that the two $1\pi^*$ electrons be coupled in a triplet state, leading to the observed ground state of $O_2$ ($^3\Sigma_g^-$).

\[ n \text{bonding} - n \text{antibonding} = \frac{1}{2} \]

where $n_{\text{bonding}}$ and $n_{\text{antibonding}}$ are the number of electrons in bonding and antibonding orbitals, respectively. (Ref. 4, Pg. 341)

**Figure A.2.** Molecular orbital diagram for $O_2$ in its equilibrium geometry.

\(^n\) In MO theory, the bond order is expressed as $\frac{1}{2} (n_{\text{bonding}} - n_{\text{antibonding}})$, where $n_{\text{bonding}}$ and $n_{\text{antibonding}}$ are the number of electrons in bonding and antibonding orbitals, respectively. (Ref. 4, Pg. 341)
A.1.2 Overbinding of \( \text{O}_2 \) in Traditional DFT

Understanding the overbinding of the \( \text{O}_2 \) molecule by traditional DFT calculations requires comparison between bond dissociation energies (BDEs) computed with DFT-LDA, DFT-GGA,\(^5\) and hybrid DFT (HSE06 functional).\(^6,7\) Computational details for these calculations may be found following the discussion of the results. The computed and experimental BDE values including zero-point energy (ZPE) corrections are presented in Table A.1. The BDE is called \( D_0 \) when ZPE corrections are included, and it is calculated according to Equation A.1.

\[
D_0 = E_{\text{O}_2} + \frac{1}{2} h \nu_{\text{O}_2} - 2E_{\text{O}} \tag{A.1}
\]

Here, \( E_{\text{O}_2} \) is the total energy (electronic + nuclear-nuclear repulsion) of the \( \text{O}_2 \) molecule at its equilibrium bond length, \( E_{\text{O}} \) is the total energy of the O atom, \( h \) is Planck’s constant, and \( \nu_{\text{O}_2} \) is the vibrational frequency of the \( \text{O}_2 \) molecule. Both the \( \text{O}_2 \) molecule and O atom are treated in their triplet ground states (\( ^3\Sigma_g^- \) and \( ^3\text{P} \), respectively).

### Table A.1

Computed BDE (\( D_0 \) in eV), vibrational frequency (\( \nu_{\text{O}_2} \) in cm\(^{-1}\)) and equilibrium bond length (\( r_e \) in Å) values for \( \text{O}_2 \) computed with various DFT-based methods compared to experiment.

<table>
<thead>
<tr>
<th>Method</th>
<th>( D_0 )</th>
<th>( \nu_{\text{O}_2} )</th>
<th>( r_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT-LDA</td>
<td>7.40</td>
<td>1632</td>
<td>1.220</td>
</tr>
<tr>
<td>DFT-GGA</td>
<td>5.96</td>
<td>1571</td>
<td>1.232</td>
</tr>
<tr>
<td>Hybrid DFT (HSE06)</td>
<td>5.08</td>
<td>1730</td>
<td>1.210</td>
</tr>
<tr>
<td>Experiment</td>
<td>5.12(^8)</td>
<td>1580.19(^9)</td>
<td>1.20752(^9)</td>
</tr>
</tbody>
</table>

The data in Table A.1 reveal that all of the methods obtain a reasonable equilibrium bond length, with the largest deviation being the DFT-GGA overestimating the bond length by 2.0%. The vibrational frequency values are in reasonably good agreement with experiment, although the hybrid DFT method overestimates this quantity by 9.4%. The \( D_0 \) values differ significantly from experiment. Specifically, DFT-LDA overbinds the \( \text{O}_2 \) molecule by 2.287 eV, while the DFT-GGA overbinds the \( \text{O}_2 \) molecule by 0.84 eV. These are non-trivial differences that require special attention. The oxygen vacancy formation energy is written (e.g., Equation 3.3 in the
thesis) in terms of energies of the supercell with an oxygen vacancy (defective crystal), half of the O₂ molecule, and the supercell without a defect (host crystal). We shift the energy of the O₂ molecule upward by 0.84 eV to account for this systematic flaw in the DFT-GGA methodology.

The DFT and hybrid DFT calculations were carried out using VASP version 5.2.2¹⁰⁻¹² with the O₂ molecule in a large (30 Å × 9.1 Å × 9.2 Å) box. Interactions between the valence electrons and the nuclei plus core electrons were represented using the projector augmented-wave (PAW) method.¹³ We employed the ‘regular’ PAW potential for oxygen (2s²2p⁴) from the VASP library.¹⁴ The planewave kinetic energy cutoff was set to 900 eV, and k-point sampling was limited to the Γ-point. The electronic structure calculation was considered converged when the total energy changed by less than 1 × 10⁻⁶ eV. Gaussian smearing with a narrow width (σ = 0.0001 eV) was employed to ensure integer occupation of the orbitals. The overall magnetism of the molecule/atom was fixed to ensure a triplet state was obtained. The screening parameter was set to the recommended value of ω = 0.2 Å⁻¹ for the hybrid DFT calculations using the HSE06 functional.⁶,⁷

A.2 Lanthanum Metal

Under oxygen-poor conditions, the reference state for La is its pure metallic state. La undergoes two phase changes prior to melting (T_{\text{mel}}=918°C).¹⁵ In this case, we report calculations for the dhcp (α), fcc (β), and bcc (γ) phases and compare the computed structural parameters to experimental values (Table A.2). We obtain the correct phase ordering for La, with $E_\alpha < E_\beta$ (α→β transition occurs at 310°C) and $E_\beta < E_\gamma$ (β→γ transition occurs at 865°C). We obtain lattice constants within 0.8% of experiment, and our bulk modulus value is close to experiment.¹⁵ Note that the energy difference between α and β is 8 meV/atom, indicating that choosing either phase as a reference for La is reasonable. Since solid oxide fuel cells operate above 310°C, we choose the β phase as a reference for reaction 3.12 in Chapter 3.
Table A.2. Calculated quantities for La in different phases obtained with DFT-GGA calculations. Experimental data from ref. 15 in parentheses (when available).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Energy (eV/atom)</th>
<th>Lattice Constants (Å)</th>
<th>Bulk Modulus, B0 (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α (dhcp)</td>
<td>-4.929</td>
<td>a: 3.765 (3.774)</td>
<td>c: 12.079 (12.171)</td>
</tr>
<tr>
<td>β (fcc)</td>
<td>-4.921</td>
<td>a: 5.285 (5.303)</td>
<td></td>
</tr>
<tr>
<td>γ (bcc)</td>
<td>-4.806</td>
<td>a: 4.226 (4.26)</td>
<td></td>
</tr>
</tbody>
</table>

These calculations were performed with VASP using the PAW potential for La described earlier. We used a planewave basis set truncated at 750 eV and 9 × 9 × 3 (Γ-point-centered), 7 × 7 × 7 (Monkhorst-Pack16), and 9 × 9 × 9 (Monkhorst-Pack16) k-point meshes for α-, β-, and γ-La, respectively. We used the 4-atom cubic fcc cell for β-La and the two-atom cubic bcc cell for γ-La. These parameters converged the total energies to 1 meV/atom. Relaxations were performed using first-order Methfessel-Paxton smearing17 (σ = 0.20 eV), which ensured that the electronic entropy remained below 1 meV/atom. Final energies were refined with the tetrahedron method with Blöchl corrections.

A.3 Lanthanum Oxide

Under oxygen-rich conditions, the formation of a lanthanum vacancy in LaFeO3 involves oxidizing the material and forming La2O3 as a product (reaction 3.13 in Chapter 3). We modeled the hexagonal phase of La2O3, which exists above 600°C.18 As with pure La, we compare our results to experiment (Table A.3) and find very good agreement for the structural parameters. La2O3 is a large-gap (6.4 eV)19 insulator, and we find that DFT-GGA significantly underestimates the band gap of this material. However, our results are consistent with previously reported DFT-GGA eigenvalue gaps,20 which are too low due to the lack of derivative discontinuity in the XC potential and other known errors in pure DFT. However, the gap is large enough to ensure a proper electronic structure of an insulator, which is all that matters in this application. These results confirm the appropriateness of our model for La2O3.
Table A.3. Physical quantities for hexagonal La$_2$O$_3$ obtained with DFT-GGA calculations compared with experimental values.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Calculated (DFT-GGA)</th>
<th>Experimental Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a: 3.94 Å</td>
<td>a: 3.94 Å$^a$</td>
<td></td>
</tr>
<tr>
<td>c: 6.18 Å</td>
<td>c: 6.13 Å$^a$</td>
<td></td>
</tr>
<tr>
<td>Oxygen position parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>u*: 0.247</td>
<td>u*: 0.245$^a$</td>
<td></td>
</tr>
<tr>
<td>v*: 0.355</td>
<td>v*: 0.355$^a$</td>
<td></td>
</tr>
<tr>
<td>Bulk modulus, $B_0$</td>
<td>119 GPa</td>
<td>113 GPa$^b$</td>
</tr>
<tr>
<td>Band gap, $E_g$</td>
<td>3.8 eV</td>
<td>6.4 eV$^c$</td>
</tr>
<tr>
<td>Energy</td>
<td>-41.920 eV/f.u.</td>
<td>----</td>
</tr>
</tbody>
</table>

---

a. Ref. 21
b. Ref. 22
c. Ref. 19

The resulting density of states (DOS) shows that La$_2$O$_3$ is a ligand-to-metal charge transfer conductor (Fig. A.3). The valence band maximum consists of O 2$p$ states, while the conduction band minimum consists of La 4$f$ states. Both nonmagnetic and ferromagnetic (FM) initial conditions converged to a nonmagnetic ground state. This result is consistent with the experimental observation of diamagnetism in La$_{1.9}$Co$_{0.1}$O$_3$ and the absence of ferromagnetism in La$_2$O$_3$.$^{23}$

Figure A.3. Projected DOS (PDOS) for La$_2$O$_3$. The minority- and majority-spin channels are symmetric because the solution is nonmagnetic. This material is a ligand-to-metal charge transfer insulator because the valence band maximum contains O 2$p$ states, while the conduction band minimum consists of La 4$f$ states.
We performed spin-polarized DFT calculations of hexagonal La$_2$O$_3$ using VASP version 5.2.2. The planewave basis set was truncated at 750 eV, and we employed a $12 \times 12 \times 8$ Monkhorst-Pack k-point mesh. Relaxations were performed with Gaussian smearing ($\sigma = 0.05$ eV) until the atomic forces were all below 0.01 eV/Å, and we refined the final energies with the tetrahedron method with Blöchl corrections. These numerical parameters converge the total energy to 5 meV/formula unit. We tried both nonmagnetic and ferromagnetic initial guesses to see if a magnetic state would be obtained, but all initial conditions converged to the same nonmagnetic ground state.

A.4 Strontium Oxide

The energy of SrO arises in the equations for calculating the strontium vacancy formation energy and the potassium substitution energy in SrFeO$_3$. SrO exists in two phases, the B1 phase (NaCl structure) and B2 phase (CsCl structure) as shown in Figure A.4. The B1 phase is the stable phase at room temperature, while the B2 phase exists under high pressure ($P > 35$ GPa). The important quantity therefore is the energy of B1-SrO obtained using DFT-GGA calculations. To validate our approach, we present results for both phases and show that the B1 phase is more stable than the B2 phase.
First, we computed the equations of state for B1- and B2-SrO and fit them with the Murnagahan equation of state (Figure A.5).\(^{28}\) The results show that the B1 phase is 0.83 eV/f.u. more stable than the B2 phase.
The equilibrium volume for the B2 phase is lower than the B1 phase, consistent with the B2 phase being favored at high pressures. Our model shows good agreement with experiment for the lattice constants (within 1.5%) and bulk modulus (within 8%) of B1-SrO (Table A.4). We also present the data for the B2 phase for completeness. Our bulk modulus ($B_0 = 84$ GPa) and lattice constant ($a = 5.208$ Å) for B1-SrO agree reasonably well with previous DFT-GGA results ($B_0 = 86$ GPa, $a=5.197$ Å),\cite{29} with the small discrepancies arising from differences in the basis set and core electron representation. As commonly occurs with DFT-GGA calculations,\cite{30,31} the computed band gap ($E_{\text{gap}}$) is severely underestimated compared to experimental values.

**Table A.4.** DFT-GGA lattice constant ($a$), bulk modulus ($B_0$), bulk modulus pressure derivative ($B_0'$), band gap ($E_{\text{gap}}$), and equilibrium total energy, as compared to available experimental data.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>B1-SrO (this work)</th>
<th>B1-SrO (experiment)</th>
<th>B2-SrO (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ / Å</td>
<td>5.208</td>
<td>5.1326$^{22}$</td>
<td>3.143</td>
</tr>
<tr>
<td>$B_0$ / GPa</td>
<td>84</td>
<td>88 ± 7$^{33}$</td>
<td>90</td>
</tr>
<tr>
<td>$B_0'$</td>
<td>4.3</td>
<td>6.0 ± 0.7$^{33}$</td>
<td>8.36</td>
</tr>
<tr>
<td>$E_{\text{gap}}$ / eV</td>
<td>3.28</td>
<td>5.7 eV$^{34}$</td>
<td>2.79</td>
</tr>
<tr>
<td>Energy / eV f.u.$^{-1}$</td>
<td>-12.109</td>
<td>----</td>
<td>-11.279</td>
</tr>
</tbody>
</table>

We performed spin-polarized DFT calculations of B1-SrO and B2-SrO with VASP version 5.2.2. The planewave basis set was truncated at 750 eV, and we employed an $8 \times 8 \times 8$ Monkhorst-Pack\cite{16} k-point mesh for B1-SrO and B2-SrO. Calculations were performed with Gaussian smearing ($\sigma = 0.05$ eV). The lattice constant was computed from the equilibrium volume obtained by fitting the Murnaghan equation\cite{28} to the energy vs. volume data. We refined the final energies at the equilibrium structure using the tetrahedron method with Blöchl corrections.\cite{24} These numerical parameters converge the total energy to 2 meV/formula unit.
A.5 Potassium Superoxide

When we investigated potassium substitution in SrFeO$_3$, we needed to reference potassium to the most stable compound containing potassium and oxygen. Basic chemistry would lead us to believe that potassium oxide (K$_2$O) should be most stable; however, reviewing the literature tells us that potassium superoxide (KO$_2$) is the major product formed in the combustion of potassium.$^3$

![Figure A.6. Tetragonal crystal structure of KO$_2$. Color designations: K (purple) and O (red). Figure created with VESTA.$^{27}$](image)

KO$_2$ crystallizes in a tetragonal lattice (Figure A.6).$^{36}$ Formally, the structure contains superoxide O$_2^-$ ions and K$^+$ ions. It exhibits antiferromagnetic behavior at temperatures below 7.1 ± 0.5 K.$^{37}$ The results of our calculation are summarized in Table A.5. Our structural results are within 4% of the experimental values. We observe magnetic ordering consistent with the one described in the literature.$^{37}$ Sheets of ferromagnetically aligned O$_2^-$ ions lie parallel to the (00l) planes and are aligned antiferromagnetically with one another.
Table A.5. DFT-GGA and experimental lattice constants (a and c in Å), O-O bond length in the O$_2^-$ ion (d$_{O-O}$ in Å), and magnetic moment of the O$_2^-$ ion ($\mu_{O_2^-}$ in µB) for KO$_2$.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Calculated (This Work)</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5.58</td>
<td>5.704 ± 0.005\textsuperscript{38}</td>
</tr>
<tr>
<td>c</td>
<td>6.94</td>
<td>6.699 ± 0.005\textsuperscript{38}</td>
</tr>
<tr>
<td>d$_{O-O}$</td>
<td>1.36</td>
<td>1.28 ± 0.02,\textsuperscript{38} 1.32-1.35\textsuperscript{39}</td>
</tr>
<tr>
<td>$\mu_{O_2^-}$</td>
<td>0.77</td>
<td>----</td>
</tr>
</tbody>
</table>

Consistent with previous DFT\textsuperscript{40} and DFT+U\textsuperscript{41} calculations, we found metallic behavior for KO$_2$ (Figure A.7). The PDOS show that the Fermi level lies in the middle of a band consisting of minority O 2$p$ states.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{PDOS.png}
\caption{PDOS for KO$_2$. Positive PDOS corresponds to majority-spin states, while negative PDOS corresponds to minority-spin states. Color designations: O 2$p$ (red) and K 3$p$ (black).}
\end{figure}

This is not surprising, as the O$_2^-$ ion has three electrons in the degenerate $\pi^*$ states.\textsuperscript{42} This assertion assumes that the MO structure for O$_2$ (Figure A.2) is not disrupted significantly by the crystal field arising from the surrounding cations. Both of the DFT-based studies cited\textsuperscript{40,41} employ spin-orbit coupling to describe KO$_2$. We do not employ spin-orbit coupling for our description of KO$_2$ in order to keep a consistent Hamiltonian for the calculations that determine the energies used to calculate the K substitution formation energy (Equation 7.7 in the thesis).
We performed spin-polarized DFT calculations of KO$_2$ with VASP version 5.2.2. The planewave basis set was truncated at 750 eV, and we employed a $9 \times 9 \times 6$ Monkhorst-Pack$^{16}$ k-point mesh. Calculations were performed with Gaussian smearing ($\sigma = 0.05$ eV). The structure was optimized until the external pressure was below 0.15 kBar and the forces were below 0.01 eV/Å. We refined the final energies at the equilibrium structure using the tetrahedron method with Blöchl corrections.$^{24}$ These numerical parameters converge the total energy to 3 meV/formula unit.

References


22. McClure, J. P. High pressure phase transitions in the lanthanide sesquioxides. (University of Nevada, Las Vegas, 2009).


Appendix B

Using VASP Effectively

B.1 Introduction

This thesis relies upon results obtained with VASP (version 5.2.2). This Appendix discusses how to use VASP effectively. The emphasis is on documenting the most important settings for Kohn-Sham density functional theory (KS-DFT), DFT+U, and hybrid DFT calculations. While VASP mainly performs DFT-based calculations, it is also capable of performing other ab initio calculations (e.g., G₀W₀, self-consistent GW, and 2nd order Möller-Plesset perturbation theory).¹⁵

VASP allows the user to perform many different quantum mechanical calculations depending on the parameters specified in the input files. In this appendix, we will review the structure of each input file (as of VASP 5.2.2) and clarify the key parameters that govern the accuracy and convergence behavior of the calculation.

B.2 VASP Background

VASP is a highly efficient code for performing KS-DFT calculations on a variety of systems. VASP works with ultrasoft pseudopotentials and projector augmented-wave (PAW) potentials, though ultrasoft pseudopotentials are no longer

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¹⁵ The GW family of calculations take a DFT, DFT+U, or hybrid DFT wavefunction and refine it to solve for quasiparticle energies using a self-energy operator. GW is not an acronym; the term GW comes from the fact that the self-energy operator is expanded using a Green’s function approach. For greater detail, please consult the dissertation, “First Principles Evaluation of the Photocatalytic Properties of Cuprous Oxide,” by Leah Isseroff Bendavid (Princeton University, 2013).
maintained by the VASP developers. Local density approximation (LDA) and
generalized gradient approximation (GGA) exchange-correlation (XC) functionals are
available. The LDA functional in VASP uses the Perdew-Zunger parameterization\textsuperscript{15} of
the Ceperley-Alder quantum Monte Carlo results.\textsuperscript{16} VASP provides two sets of potentials
for GGA calculations: one for the functional of Perdew and Wang (PW91),\textsuperscript{17,18} and one
for the functional of Perdew, Burke, and Ernzerhof (PBE).\textsuperscript{19} Recently released PAW
potentials no longer directly support the PW91 functional. The DFT+U method is
available for use with PAW potentials for either the LDA or PBE XC functional. VASP
versions starting with 5.2.11 allow users to apply van der Waals corrections through the
DFT+D\textsuperscript{20} method with the choice of D2, D3, Becke-Jonson damped D3,\textsuperscript{23} and
Tkatchenko-Scheffler\textsuperscript{24,25} parameterizations now available. Hybrid density functionals,
which replace a portion of the approximate exchange with exact exchange (e.g., PBE0,\textsuperscript{9}
HSE,\textsuperscript{10,11} and B3LYP\textsuperscript{26}), are also available, though these calculations should use a PBE
PAW potential (POTCAR file). Finally, VASP contains modules for performing higher
accuracy calculations based on the GW quasi-particle approximation\textsuperscript{27–32} and 2\textsuperscript{nd} order
Møller-Plesset perturbation theory (MP2).\textsuperscript{33,34}

VASP also evaluates forces from the DFT-based energies. This enables molecular
dynamics within the microcanonical (NVE), canonical (NVT), and isothermal-isobaric

\textsuperscript{xvi} "The use of ultrasoft pseudopotentials is at your own risk and the potentials are no longer maintained or
updated."\textsuperscript{14} In 1999, G. Kresse and D. Joubert published a paper entitled, "From ultrasoft pseudopotentials
to the project augmented-wave method."\textsuperscript{9} In this work, the authors established that PAW potentials
outperformed ultrasoft pseudopotentials for all the systems they tested. The ultrasoft potentials had good
accuracy for nonmagnetic systems (on par with the PAW potentials) but lost accuracy when dealing with
magnetic systems (e.g., bcc iron).

\textsuperscript{xvii} Since MP2 perturbation theory requires the orbital (band) energies, the entire virtual spectrum must be
calculated to use this module. This means calculating as many bands as there are planewaves in the
calculation. Since calculations can frequently have $10^3$-$10^4$ planewaves, this results in a very large virtual
space as well as difficult calculations.
(NPT) ensembles. Structural optimizations, including independent or simultaneous optimization of ion positions and lattice parameters, are easy to perform with VASP. Dynamical matrix calculations in VASP use either a finite displacement or DFT perturbation algorithms to determine the gamma-point phonon modes and frequencies. VASP is capable of recognizing and utilizing the symmetry of the crystal, and it will lower the symmetry in cases where the magnetic configuration supplied (as an initial guess) lowers the overall symmetry (e.g., antiferromagnetic systems have lower magnetic symmetry than one would infer from the nuclear positions and lattice vectors).

In the following, we will discuss the basics of executing VASP (section B.3), the POSCAR file (section B.4), the POTCAR file (section B.5), the KPOINT file (section B.6), and, most importantly, the INCAR file (section B.7). We will provide example files illustrating the structure of each file.

**B.3 Running VASP Calculations**

VASP must be executed from the directory containing the INCAR, POTCAR, and KPOINT files (as well as the POSCAR file, so long as a nudged elastic band (NEB) calculation is not being performed). The best solution around this issue is to have a submit script in the working directory (i.e., the directory containing INCAR) which executes only a handful of commands. The submit script should prepare the environment by loading or unloading modules as needed. The script should change the working directory (i.e., cd) to the directory from which the script was submitted (e.g., $PBS_O_WORKDIR under the pbs scheduler\textsuperscript{34,35} or $SLURM_SUBMIT_DIR under the slurm scheduler\textsuperscript{36}).
B.4 The POSCAR File

VASP obtains the geometry (cell parameters, ion positions) from the POSCAR file. VASP must run in the directory containing this file except in NEB calculations (*vide infra*). The POSCAR file has a fairly simple format, yet the format can handle many different methods of inputting the geometry information. In the following paragraph, we will outline the POSCAR format for a standard calculation.

LaCoO₃ R-3c at 5 K from Radaelli and Cheong, 2002

1.000000000000
5.3447942734 0.0000000000 0.0000000000
2.5903153255 4.6751569320 0.0000000000
2.5903153255 1.5261453543 4.4190465823
Co La O
2 2 6
Direct
0.000000000 0.0000000000 0.0000000000
0.5000000000 0.5000000000 0.5000000000
0.2500000000 0.2500000000 0.2500000000
0.7500000000 0.7500000000 0.7500000000
0.8026580210 0.6973419790 0.2500000000
0.1973419790 0.3026580210 0.7500000000
0.2500000000 0.8026580210 0.6973419790
0.7500000000 0.1973419790 0.3026580210
0.6973419790 0.2500000000 0.8026580210
0.3026580210 0.7500000000 0.1973419790

**Figure B.1**: A sample POSCAR file containing the geometry for LaCoO₃ in the unit cell. Lattice parameters and nuclear positions were obtained at 5 K by Radaelli and Cheong, Phys. Rev. B, 2002.³⁷

Figure B.1 provides a basic example of a POSCAR file for a system discussed in this thesis (chapter 4). Figure B.2 is a visual representation of the cell defined by the POSCAR file in Figure B.1. We will now explain the structure of the POSCAR file. The first line contains a title for the system, while the second line contains a scaling factor for the lattice constants. This factor is usually set to one; however, it may be used to quickly scan a range of lattice constants. The third, fourth, and fifth lines give the lattice vectors in x, y, and z components. The vectors specified in lines three, four, and five are scaled
by the factor on line two. The sixth line contains the atomic symbols for each ion type in
the cell and serves as a convenience for software that reads the POSCAR file. The
seventh line contains the number of atoms for each ion type corresponding to those found
on the previous line. Note that the numbers on the seventh line correspond to the number
of ions for each type in the order they are encountered in the POTCAR file. The eighth
line contains one of two options: either direct or Cartesian. VASP only reads the first
letter of this line and, if it finds a “d” or “D,” then it will read the coordinates on the
following lines as fractional coordinates. However, if it finds any of the letters “c,” “C,”
“k,” or “K,” then it will read the following lines as Cartesian coordinates. After the line
indicating direct or Cartesian, the position of each ion is specified in the given coordinate
system. There should be one line per ion. After specifying the positions of each ion, it is
then possible to set the velocity of each ion, as in the case of a molecular dynamics
simulation.

**Figure B.2:** The unit cell for LaCoO$_3$ at 5 K.$^{26}$ Atoms are Co (blue), La (green), and O
(red). Note that the Co atoms at the boundary are replicated; there are only two unique Co
atoms in the cell.
VASP provides a method for constraining the motion of the ions. This constraint is determined by inserting a line that reads selective dynamics on the line before direct or Cartesian. Selective dynamics allows the user to specify which atoms are allowed to move and in which directions. In addition to specifying selective dynamics, the user must provide an additional three entries on each line corresponding to the ion positions. These three additional entries are of the form T or F, and each entry indicates whether or not that specific ion is allowed to move in the x, y, or z directions. Selective dynamics is most useful for calculating dynamical matrices where computing every displacement in one calculation is not feasible (Appendix C). This flag is also useful for slab calculations, where the middle layer or bottom layer is fixed in the bulk positions. Consult the VASP manual for more information regarding the POSCAR file (found online at http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html).8

B.5 The POTCAR File

The POTCAR file contains the pseudopotential or PAW potential definitions required for VASP. The potentials used by VASP are provided by the VASP developers. These files can be found in compressed form on the Tiger cluster in the directory /home/EAC/VASP/potentials. In this directory, there are two sets of potentials: the first is from 2003, while in the second is from 2012. While little or no change occurred for most potentials from 2003 to 2012, the latter set includes potentials specifically designed for GW calculations. This thesis uses the potentials from the first set (2003); however, new users should test both sets of potentials and, if possible, use the newer set (2012). Creating a POTCAR file for a system containing multiple elements requires
concatenating the POTCAR files for each individual element in the appropriate order. This is usually done by executing zcat, followed by each of the compressed POTCAR files from the potentials directory in their appropriate order. The output of this command should be redirected (using the > operator) to a file named POTCAR in the appropriate directory. Once a suitable POTCAR has been created, it may be copied and reused as needed. As the POTCAR format is lengthy and not well documented, we will refrain from providing an example of this file here.

Two additional details require discussion. First, the XC functional specified in the POTCAR file dictates the XC functional used in the calculation. However, this can be overridden by using the GGA tag in the INCAR file, though use of this tag is not recommended and should be used with extreme caution. Note that it is essential to use PAW potentials that all use the same XC functional. Second, some elements have a selection of PAW potentials available, which usually have the designations _h (hard) or _s (soft). Hard potentials have larger fluctuations in the core region and therefore require a higher planewave kinetic energy cutoff. Soft potentials are smoother and require a lower kinetic energy cutoff; however, these potentials are sometimes less accurate than regular or hard potentials. If no _h or _s designation appears, then the potential is neither particularly hard nor soft and is called regular in our terminology. For metallic elements, designations of _pv indicate that semi-core p orbitals (e.g., the 3p orbitals of chromium) are treated explicitly. Likewise, a designation of _sv indicates that semi-core s orbitals (e.g., the 3s orbitals on chromium) are treated explicitly. Usually, _sv implies _pv, as well, i.e., the s and p semi-core orbitals are both treated explicitly.
The simplest way to mess up a VASP calculation is to have the order of elements used in the POTCAR file differ from the order used in the POSCAR file (*vide supra*). We recommend choosing a set order for the elements in a set of calculations and then using the same POTCAR file for all of the calculations. This type of consistency ensures that the right potential is assigned to each atom.

### B.6 The KPOINTS File

Periodic calculations require sampling sufficient k-points to obtain reasonable integrated values where the integration is over the first Brillouin zone. VASP uses the parameters found in the KPOINTS file to determine how to construct this mesh. The file is relatively simple: it is usually five-lines long. Figure B.3 shows a sample KPOINTS file.

```
LaCoO3 R-3c at 5 K from Radaelli and Cheong, 2002
0            ! Automatic Mesh Generation
Monkhorst-Pack
 4 4 4          ! Mesh dimensions
0.0 0.0 0.0      ! Mesh shift
```

**Figure B.3:** A sample KPOINTS file for a $4 \times 4 \times 4$ Monkhorst-Pack k-point mesh.

The first line of the KPOINTS file is a description of the system (much like the first line of the POSCAR file). This is one of three redundant places to specify the name of the system. This line has no effect on numerics, but it is a way to keep track of different k-point meshes being utilized. The second line gives the number of k-points to be specified. A value of 0 (zero) on the second line activates automatic k-point generation, which is recommended. The third line specifies the grid type (Monkhorst-Pack or Gamma-point-centered) when automatic generation is used. The fourth line specifies the number of k-points along each of the reciprocal lattice vectors. The fifth line specifies the shift for the
mesh. We recommend leaving the fifth line as “0.0 0.0 0.0.” Monkhorst-Pack k-point meshes are typically used for most calculation; however, hexagonal cells require Γ-point-centered k-point meshes.

When automatic k-point generation is not used, the k-point mesh is specified with different entries starting on the third line. The third line can read as either Cartesian or reciprocal - only the first letter of the line matters. Starting on the fourth line, the k-points are listed in the appropriate coordinate system. For each k-point, a weight is given based on symmetry, i.e., how many k-points are degenerate with the k-point listed. The weights for the k-points do not have to sum to one; VASP will renormalize before starting the calculation, although the same is not done for the weights of the tetrahedra specified later. After listing the k-points, the connectivity for tetrahedra must be specified only if the user is asking for the tetrahedron method for integration. This is done by placing “tetrahedra” on the line after the last k-point. The following line gives the number of tetrahedra and the volume weight of a single tetrahedron (note that all tetrahedra must have the same volume, and the weight is simply the volume of the tetrahedron over the volume of the Brillouin zone). Then, the file ends with a series of lines containing four integers that are the vertices of the tetrahedra. The tetrahedron method (with Blöchl corrections) is not appropriate for computing forces during relaxation. Therefore, the tetrahedron method should be used to obtain final energies and electronic densities of states with a single-point calculation at the converged geometry.

It is generally unwise to enter k-points and tetrahedra by hand unless there is a compelling reason to do so. However, k-points may require manual entry when
calculating band structures (band energy plots). In this case, it is important to first converge the electron density with a regular k-point mesh using a self-consistent field (SCF) calculation and then run the band structure calculation with the charge density frozen. Alternatively, one could generate the standard k-mesh for a system (found in IBZKPT after the calculation starts) and then add the desired k-points to the file (having copied IBZKPT to KPOINTS), giving all of the added k-points zero weight. The latter is probably the safest way to ensure that the band structure is obtained for a converged electron density.

Overall, letting VASP generate the k-point mesh for the system is the safest and most reliable way to ensure accurate sampling of the Brillouin zone. To obtain accurate results, the k-point density should be converged by increasing the k-point sampling along each reciprocal vector in a proportionate manner. This means that longer lattice vectors in real space require less k-points in reciprocal space, and vice versa. The k-point density (mesh size) should be increased until the total energy changes by less than 1 meV/atom. Generally, the converged meshes will be fairly dense for metallic systems and sparse for semiconductors/insulators. This type of study is illustrated in table B.1.

Table B.1: A k-point convergence study for low-spin LaCoO$_3$ in the rhombohedral unit cell (10 atoms). The first column shows the k-point mesh used, the second column shows the total energy (eV) for the given k-point mesh, and the third column shows the energy (eV) relative to an $8 \times 8 \times 8$ k-point mesh. Monkhorst-Pack k-point meshes are used here. Convergence (to 0.001 eV/atom) is reached with the $4 \times 4 \times 4$ k-point mesh.

<table>
<thead>
<tr>
<th>k-point Mesh</th>
<th>Total Energy</th>
<th>Relative Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \times 2 \times 2$</td>
<td>-75.763</td>
<td>0.132</td>
</tr>
<tr>
<td>$4 \times 4 \times 4$</td>
<td>-75.895</td>
<td>-0.003</td>
</tr>
<tr>
<td>$8 \times 8 \times 8$</td>
<td>-75.892</td>
<td>0</td>
</tr>
</tbody>
</table>
B.7 The INCAR File

The INCAR file governs how a VASP calculation proceeds. It defines the parameters for the calculation, and, sometimes, it determines the type of calculation performed. In the following pages, we will provide a detailed description of key flags for VASP and how they operate. A good portion of this section is redundant to the information found in the VASP guide; however, we hope that this section helps clarify the most important parameters that enter into VASP calculations. This section is not exhaustive, as there are additional parameters that we do not discuss. The flags discussed here are valid for VASP 5.2.2, unless we indicate that a newer version of VASP is required to take advantage of a given parameter or feature.

B.7.1 Initialization

The first set of flags discussed in this appendix tells VASP how to initialize itself. The initialization process is complicated, but we offer the following explanation. VASP looks at the tag ISTART (*vide infra*) to see if the calculation is a new job or the continuation of a previous job. If the calculation is a new job, then the INIWAV flag tells VASP how to initialize the wavefunction. If the calculation is a continuation, then VASP looks at the ICHARG tag to determine how to initialize the charge density. If no CHGCAR and WAVECAR files are present in the directory, then VASP internally resets and treats the calculation as if it were a new job.

**KEYWORD:** ISTART

**VALUE:** An integer specifying whether or not to use existing information to initialize the calculation.

**DISCUSSION:** ISTART can have a value of 0, 1, or 2.
ISTART=0 indicates that VASP should treat the calculation as a new job. Therefore, VASP will initialize the orbitals according to the INIWAV value (vide infra) and will ignore any WAVECAR file that is present in the directory.

ISTART=1 instructs VASP to use the WAVECAR file in the current directory to initialize the orbitals. This value is the default if WAVECAR is present in the directory, and its use is highly recommended. If WAVECAR is not present or is incompatible with the current calculation (i.e., incorrect number of bands or k-points), then ISTART is reset to zero.

ISTART=2 instructs VASP to read the WAVECAR file and keep the same set of planewaves even if the cell shape and/or ENCUT have changed. According to the VASP GUIDE, “always restart with ISTART=1 except if you really know what you are looking for.” The essence of this flag is that it allows continuation of a calculation using a constant basis set even when the cell shape/volume changes. Since mismatches between the planewave basis set and the cell shape lead to Pulay stresses, ISTART=1 is a better way to restart a calculation because it constructs the appropriate planewaves for the cell shape defined by POSCAR.

**KEYWORD:** ICHARG

**VALUE:** An integer specifying how VASP should initialize the charge density.

**DISCUSSION:** ICHARG can take various values.

ICHARG=0 computes the charge density from the initial orbitals (e.g., when WAVECAR is provided). This is the best restart option because VASP begins right where it ended the previous calculation.
ICHARG=1 reads the charge density from CHGCAR and extrapolates from the old geometry to the new geometry. This option should be used when continuing calculations where the user has chosen not to write the wavefunction (planewave coefficients) to a file. This usually occurs when the wavefunction file will exceed the capacity of the disk to which it is written (or the user’s quota on the given filesystem).

ICHARG=2 creates an initial guess that is the superposition of atomic densities. This becomes the default if ISTART=0. This option is appropriate when no electron density is available from a previous calculation.

NOTE: Adding 10 to any of these options allows for a non-self-consistent calculation, where the charge density is frozen while the planewave coefficients are updated. Freezing the charge density is appropriate when performing a single-point calculation with a different smearing method (e.g., tetrahedron method with Blöchl corrections instead of Methfessel-Paxton smearing) on an already converged electron density. In this type of calculation, VASP optimizes the planewave coefficients to minimize the electronic energy subject to the constraint that they reproduce the frozen electron density. Users should be careful about freezing the electron density unless the nuclei remain fixed in the same positions as the previous calculation.

**KEYWORD:** INIWAV

**VALUE:** An integer specifying how to initialize the planewave coefficients.

**DISCUSSION:** This parameter should always be set to 1 (the default).
INIWAV=1 initializes the wavefunction with random numbers. INIWAV=0 constructs orbitals from the planewaves with the lowest kinetic energies. NOTE: INIWAV has no meaning if ISTART≠0.

**B.7.2 Keywords Governing the Electronic Structure Calculation**

**KEYWORD**: ENCU

**VALUE**: A positive real number. The default value is the largest ENCU read from POTCAR.

**DISCUSSION**: ENCU determines the size of the planewave basis set. A planewave with reciprocal vector $\mathbf{G}$ has the kinetic energy

$$T = \frac{\hbar^2}{2m_e} \nabla^2 e^{\mathbf{G} \cdot \mathbf{x}} = \frac{\hbar^2 | \mathbf{G} |^2}{2m_e}$$

The kinetic energy of a planewave must satisfy the relationship

$$\frac{\hbar^2 | \mathbf{G} + \mathbf{k} |^2}{2m_e} < \text{ENCUT}$$

for inclusion in the basis set. Note that this formulation leads to a different number of planewaves at each k-point. This parameter must be increased until the total energy converges to 1 meV/atom (using a converged k-point mesh). Generally, metals require lower ENCU values, while transition metal oxides tend to require the high ENCU values. Converged ENCU depends primarily on
the PAW potential used, and it must be converged again if the PAW potential is changed.

**KEYWORD:** ALGO

**VALUE:** A string or character indicating the algorithm that should be used for optimizing the electronic structure.

**DISCUSSION:** This flag chooses among the most commonly used algorithms for the SCF calculation. An alternative flag, IALGO, takes an integer that specifies the algorithm more precisely. ALGO is a shortcut to setting IALGO to the right value for the type of algorithm desired. The options for this flag are:

- **Fast** – Perform a few iterations using Davidson’s method before switching to the RMM-DIIS algorithm. The flag NELMDL controls the number of iterations before the algorithm switch.

- **Normal** – Use Davidson’s method for solving the electronic structure problem.

- **All** – Use the all-bands simultaneous conjugate-gradient method. This is one of the most stable algorithms available. However, this algorithm is slow to converge. The user must set the TIME flag (*vide infra*) to a reasonable value (generally 0.1 – 0.4).

- **VeryFast** – Use only RMM-DIIS for the electronic structure calculation. We advise against this setting because the ALGO=Fast setting should be nearly as fast, and the initial Davidson iterations can improve the stability of the optimization.
**Trick**: In some very difficult cases, the standard algorithms (Fast and Normal) lead to spurious electronic structures. This occurs frequently when dealing with near degenerate magnetic states (*e.g.*, the spin state of Co$^{3+}$ in LaCoO$_3$). In VASP 5.3.2 and later, the combination ALGO=ALL, TIME=0.15, LSUBROT=.FALSE., is quite powerful for finding the appropriate minimum.\textsuperscript{xviii} This method takes many iterations to converge, though it does work quite well. Fortunately, only one electronic structure calculation is required with these settings; the resulting WAVECAR will contain a wavefunction that is already converged. Future ionic iterations can go back to the ALGO=Normal setting and should avoid spurious electronic structures. The trick of avoiding subspace rotation (LSUBROT=.FALSE.) is recognized in VASP 5.3.2 and newer.

**KEYWORD**: NELM

**VALUE**: An integer specifying the maximum number of iterations for an ionic iteration.

**DISCUSSION**: Optimizing the electronic structure of a material at a given geometry requires performing a SCF calculation. After the maximum number of iterations, VASP computes the forces and proceeds to the next ionic step as long as geometry optimization or molecular dynamics have been selected. Note that while VASP will issue a warning if the electronic structure does not converge, it will not stop at this point. Generally, this flag should be set very high to ensure that the calculation reaches convergence. A reasonable value for NELM is 300. If the SCF calculation takes this many iterations, then the geometry or initial guess

\textsuperscript{xviii} This insight came from Dr. Florian Libisch, a former postdoc in the Carter group.
is very poor. A careful analysis of the interatomic distances and the initial magnetic moments chosen is the best way to address a system that refuses to converge. If there is no issue with the geometry or initial magnetic moments, then consider changing ALGO to NORMAL or ALL (vide supra).

**KEYWORD:** NELMIN

**VALUE:** An integer specifying the minimum number of iterations for the SCF calculation at each ionic iteration.

**DISCUSSION:** Ensuring that VASP performs a minimum number of SCF iterations at each ionic step is a way to improve accuracy without changing the convergence criterion EDIFF (vide infra). When using a loose threshold for the SCF iterations, progressively better electron densities can be obtained by setting this value to a manageable number of iterations. Generally, we recommend a NELMIN value below 10. Only in the case of a loose convergence criterion would raising NELMIN to 15-20 iterations have any benefit.

**KEYWORD:** NELMDL

**VALUE:** An integer specifying the mixing delay for the SCF calculation. A positive integer applies the delay at every ionic step, and a negative integer applies the delay to just the first ionic iteration.

**DISCUSSION:** VASP uses a mixing algorithm, which combines the Fock matrices from the previous and current iterations and can help improve convergence. However, when using an initial electron density that is a
superposition of atomic densities, one should set NELMDL to a value below 10 iterations (4 is a reasonable value). During the mixing delay, the electron density is fixed and the planewave coefficients are optimized to reproduce that same density. Since the default behavior is to initialize the planewave coefficients randomly, it makes sense to set this keyword, unless a WAVECAR file is supplied for the initial guess.

**KEYWORD:** TIME

**VALUE:** A floating point number indicating the step size for ALGO=ALL.

**DISCUSSION:** This parameter controls how aggressively VASP will operate when using the all-bands conjugate gradient method. The default value is 0.4, which seems to work well. In sensitive cases, lowering this value to 0.1 or 0.15 is recommended. TIME is irrelevant if ALGO=Fast.

**KEYWORD:** LSUBROT (VASP 5.3 or later)

**VALUE:** A Boolean (.TRUE. or .FALSE.) value indicating whether or not to perform subspace rotation during the all-bands conjugate gradient optimization.

**DISCUSSION:** In versions of VASP before 5.3, ALGO=ALL included a step at each SCF iteration, in which the subspace was rotated to find the best subspace possible. In sensitive cases, this can be turned off (for VASP 5.3 only) to force the optimizer to use greater caution during the SCF calculation. This flag should be used as a last resort and accompanied by a small value for the TIME parameter. Lastly, when using this parameter, NELM should be sufficiently large enough to
allow for a long SCF calculation (usually more than 100 iterations are needed when starting from a superposition of atomic densities). Use this flag for a single point calculation to obtain an optimized wavefunction. Then proceed with ALGO=NORMAL using the WAVECAR obtained from the first calculation.

**KEYWORD:** LREAL

**VALUE:** .TRUE., .FALSE., or Auto (default).

**DISCUSSION:** LREAL determines whether or not the PAW\(^7,9\) projection operators should be evaluated in real-space (fast but not as accurate) or reciprocal space (slow but more accurate). Generally, VASP recommends using LREAL=.TRUE. for “large” supercells. When relaxing structures, we recommend using LREAL=.TRUE. in conjunction with a lower energy convergence criterion (EDIFF) and (possibly) a lower planewave cutoff (ENMAX). Once the structure nears a minimum, ENMAX must be increased back to the converged value, EDIFF should be returned to \(1 \times 10^{-5}\) eV, and LREAL must be set to .FALSE. in order to ensure accurate forces near the minimum, and, thus, an accurate structure. Making this transition when the maximum force goes below 0.1 eV Å\(^{-1}\) is a reasonable approach. For all density of states (DOS) calculations, LREAL=.FALSE. is a necessity.

**KEYWORD:** NUPDOWN

**VALUE:** The net magnetization for the entire cell (difference in total \(\alpha\) and \(\beta\) \(e^-\)).
DISCUSSION: NUPDOWN is used to control the net magnetization for the entire cell. There are at least two instances where this becomes important: (1) when computing an isolated atom or molecule with a known ground state (e.g., \text{NUPDOWN}=2 for $^3\text{P}$ O – the oxygen atom in its ground state), and (2) when simulating an antiferromagnetic state where the net magnetization is zero. In the latter instance, NUPDOWN ensures that the system does not drift away from the open-shell singlet state during the unrestricted calculation. This flag should not be used to isolate a specific magnetic state of a transition metal ion in a crystal (e.g., Co$^{3+}$ in LaCoO$_3$). In that case, the magnetism should be allowed to fluctuate so that the computed value can be compared with experiment.

KEYWORD: ISPIN

VALUE: An integer indicating whether or not to perform a spin-polarized (ISPIN=2) or non-spin-polarized (ISPIN=1) calculation. The default value is ISPIN=1.

DISCUSSION: ISPIN takes one of the two values given above. In the language of quantum chemistry, ISPIN=1 corresponds to a restricted calculation, while ISPIN=2 corresponds to an unrestricted calculation. The former calculation involves assuming that the $\alpha$ and $\beta$ Kohn-Sham orbitals are identical. Thus, only one set of orbitals is optimized. The spin-polarized calculation optimizes each $\alpha$ and $\beta$ orbital independently. Magnetic systems require spin-polarized calculations and ISPIN=2 should be chosen in most cases. If a system is nonmagnetic, the
spin-polarized calculation should collapse to a state where the $\alpha$ and $\beta$ Kohn-Sham orbitals are symmetrical. If this happens, it may indicate that future calculations can be performed without spin-polarization. Spin-polarized calculations require twice the memory compared to non-spin-polarized calculations; however, the computational cost is worthwhile to ensure that no artifacts arise from the lack of accounting for spin-polarization.

**KEYWORD:** EDIFF

**VALUE:** A floating point value (in eV) specifying the energy convergence criterion for the SCF calculations that VASP performs. The default value is $1 \times 10^{-4}$.

**DISCUSSION:** EDIFF is one of the most important parameters in a VASP calculation. It specifies the largest energy difference between two SCF iterations at convergence. A large value of EDIFF (e.g., EDIFF = 0.01) produces a quick calculation susceptible to inaccuracies. Smaller values of EDIFF (e.g., $1 \times 10^{-5}$) give well-converged charge densities and geometries. Greater accuracy (EDIFF = $1 \times 10^{-7}$) is required when small differences in the forces become important (e.g., during frequency calculations). Decreasing EDIFF imposes better optimization of the planewave coefficients, which leads to more accurate properties. This accuracy is achieved at the cost of increasing the number of SCF iterations required for convergence.
**KEYWORD:** MAGMOM  

**VALUE:** A list of numbers that give the initial magnetic moments on each atom. One entry per atom is required.

**DISCUSSION:** MAGMOM provides one of the most powerful tools in VASP for changing the initial guess for the charge density (i.e., when a CHGCAR file is not provided). MAGMOM specifies for each site the quantity $n_\alpha - n_\beta$. Values may be positive or negative. Using this flag, antiferromagnetic states can be sought and specific magnetic states (e.g., intermediate spin for the Co$^{3+}$ ion) can be targeted. VASP recognizes when the MAGMOM input lowers the symmetry of the system, and it responds by using the lower symmetry (as of VASP 4.4.4).^{14}

**KEYWORD:** NBANDS  

**VALUE:** The number of bands that VASP should compute.

**DISCUSSION:** NBANDS tells VASP how many bands (occupied and virtual) to compute for each spin channel. The recommended value is $n_{\text{electrons}}/2 + n_{\text{ions}}/2$, which obviously would need to be adjusted for, e.g., ferromagnetic materials. However, certain cases necessitate more bands in the calculation. Small unit cells may require more bands because the $n_{\text{ions}}/2$ term may only provide one or two excess bands. Metallic systems containing many partially filled bands may require more virtual orbitals than those given by the suggested value. Ferromagnetic systems may require more bands because the number of occupied $\alpha$-spin bands is greater than the default value. Finally, some algorithms converge better with extra unoccupied bands (specifically, ALGO=FAST). Choosing this value carefully
plays a role in efficiently using computational resources. If the value of NBANDS is excessively large, then the calculation takes longer than necessary because VASP must compute additional virtual bands that do not contribute to the ground state electron density. However, if the value of NBANDS is too small, then the calculation may converge poorly. Generally, the recommended value works well. If convergence issues or runtime errors occur during a calculation, then the user should consider increasing NBANDS.

**NOTE:** NBANDS is automatically changed by VASP to be a multiple of NPAR (VASP 5.2.2). This is to say that the most efficient use of resources has NBANDS as an integer multiple of the number of cores used in the calculation.

**KEYWORD:** NPAR

**VALUE:** An integer specifying how VASP distributes work in parallel jobs.

**DISCUSSION:** NPAR tells VASP how many bands to work on at a given time. In general, setting NPAR to the number of cores per node seems to be a reasonable value. The keyword NCORE is only available in VASP 5.3 and later. NCORE tells VASP how many cores should work on a single band at one time. Setting NCORE to the number of cores per node is highly effective. Further parallelization can be achieved using the keywords NSIM and LPLANE. For more information, consult the VASP GUIDE (ref. 14).

*B.7.3 Keywords Governing DOS and Brillouin Zone Integration*

**KEYWORD:** ISMEAR

**VALUE:** An integer specifying the type of smearing to be used in the calculation.
DISCUSSION: Choosing the correct smearing method is one of the critical decisions that a VASP user must make. Below, three common and useful choices are discussed.

ISMEAR=1 tells VASP to use Methfessel-Paxton smearing\textsuperscript{38} (1\textsuperscript{st} order). Integer values greater than zero specify the order of Methfessel-Paxton smearing to be employed (generally 1\textsuperscript{st} or 2\textsuperscript{nd} order). Methfessel-Paxton smearing is appropriate for metallic systems, and applying it to the wrong material can lead to spurious occupation numbers (e.g., less than zero).

ISMEAR=0 tells VASP to use Gaussian smearing. This method is appropriate for insulators and semiconductors. Gaussian smearing tends to force occupation numbers to zero or two (or one, for spin-polarized calculations).

ISMEAR=-5 tells VASP to use the tetrahedron method with Blöchl corrections.\textsuperscript{39} This smearing method should be avoided for ion relaxation and frequency calculations because it can lead to errors of up to 10\% in the forces for metallic systems.\textsuperscript{14} However, it should be used to obtain the final energy and DOS for a system. Gamma-point-centered k-point meshes should be used for ISMEAR=-5.

**KEYWORD:** SIGMA

**VALUE:** The smearing width in eV.

**DISCUSSION:** SIGMA specifies the width of the smearing function used to integrate over the first Brillouin zone. The value of SIGMA should be decreased
until the entropic contribution to the electronic energy is less than 1 meV/atom. The default value of 0.2 eV may work; however, semiconductors often require values as low as 0.05 eV. SIGMA is irrelevant if ISMEAR=-5.

**KEYWORD:** PREC  
**VALUE:** Tells VASP how precise to be with the fast Fourier Transform (FFT) grids and other numerical parameters.  
**DISCUSSION:** The PREC tag tells VASP how much the user is willing to trade accuracy for computational speed. Possible values are: “Low,” “Medium,” “High,” “Normal,” “Accurate,” and “Single.” These tags have the effect of determining the size of the FFT and fine FFT grids used by VASP. Use of PREC=Accurate is recommended to avoid wrap-around errors in the FFT calculations. The default value is Normal for VASP 5.x (and Medium for VASP 4.x). This flag also controls the number of grid points for evaluating the PAW projection operators in real space.

**KEYWORD:** LORBIT  
**VALUE:** An integer indicating how VASP should write the DOSCAR and PROCAR output files.  
**DISCUSSION:** LORBIT is used to tell VASP how much information the user desires regarding the DOS. LORBIT = 11 is recommended so that VASP writes DOSCAR with the total DOS and the projected DOS. The size of the PROCAR and DOSCAR files may be reduced by specifying LORBIT = 10 only if the
projected DOS is not required. The options LORBIT = 0, 1, or 2 are not recommended because they require the specification of a Wigner-Seitz radius (RWIGS tag) in the INCAR file. Since PAW potentials are now standard for VASP calculations, the radius of the PAW sphere is used (LORBIT = 10 or 11) and RWIGS is ignored. Choosing LORBIT = 11 also results in an extended PROCAR file.

**KEYWORD:** NEDOS

**VALUE:** An integer specifying the number of points at which to sample the DOS.

**DISCUSSION:** NEDOS tells VASP how many points (energies) to print out in the DOSCAR file. VASP evenly samples the energy range from minimum (EMIN) to maximum (EMAX) energies. EMIN and EMAX may be specified in the INCAR file, but VASP can determine their values on its own. A high value of NEDOS is recommended for accurate DOS figures; however, excessively high values lead to rough, jagged plots. As such, a value between 1000-3000 is appropriate for NEDOS. A value ending in 1 is important if the user specifies EMIN and EMAX with the objective of obtaining easy-to-read energy values in the DOSCAR file. When NEDOS ends with a 1, then the number of intervals for which the DOS is calculated becomes a multiple of 10.

**KEYWORD:** GGA

**VALUE:** A string specifying an alternative GGA XC functional to be used.
**DISCUSSION:** This keyword originally was intended to allow users to run GGA calculations with PAW potentials built for LDA calculations. With the advent of the PBE PAW potentials, this keyword became far less important. It is now used to specify alternative GGA functionals to be used in calculations where the supplied PAW potential is either a LDA- or PBE-based potential. Users must ensure that they understand the implications of using this keyword before including it in their input. The following options are listed in the VASP documentation.

- **GGA=PE** specifies that VASP should use the PBE functional.\(^{19}\)
- **GGA=91** tells VASP to use the Perdew-Wang 91 GGA functional.\(^{17,18}\)
- **GGA=RP** asks for a revised PBE calculation according to the RPBE functional of Hammer, Hansen and Nørskov.\(^{40}\)
- **GGA=AM05** selects the AM05 GGA functional proposed by Armiento and Mattsson.\(^{41–43}\)
- **GGA=PS** requests the PBEsol functional of Perdew *et al.* This functional is a revised form of the PBE functional designed to improve predictions for solids and surfaces.\(^{44}\)
- **GGA=B3** is required to run B3LYP\(^{26}\) calculations in VASP. Additionally, the following parameters must be specified: LHFCALC=.TRUE., AEXX=0.2, AGGAX = 0.72, AGGAC = 0.81, and ALDAC=0.19. These keywords are discussed further in section B.7.5.\(^{45}\)
B.7.4 Keywords Governing Ionic Motion

VASP has the capability of optimizing ionic (nuclear) coordinates and cell parameters using the electronic structure calculations as described above. The following section elucidates the keywords that govern the geometry optimization portion of the calculation. Although VASP can perform molecular dynamics in the microcanonical (NVE), canonical (NVT), and isothermal-isobaric (NPT) ensembles, this section does not cover such simulations.

**KEYWORD:** NSW

**VALUE:** The maximum number of ionic iterations in the calculation.

**DISCUSSION:** At each geometry, VASP performs an electronic structure calculation that determines the electronic energy, electron density, and Hellmann-Feynman forces on the nuclei. These forces are then used to update the positions of the nuclei according to the algorithm specified by IBRION.

**KEYWORD:** IBRION

**VALUE:** An integer specifying the algorithm for nuclear geometry optimization.

**DISCUSSION:** VASP offers several methods for optimizing the geometry. This optimization involves minimizing the total energy (i.e., electronic energy plus nuclear-nuclear repulsion) in terms of the nuclear coordinates.

**IBRION=1:** VASP uses a quasi-Newton method to update the nuclear positions. Specifically, the RMM-DIIS algorithm is used. IBRION=1 performs best when the initial geometry is close to the optimal geometry.
**IBRION=2**: VASP uses a conjugate gradient algorithm to update the ionic positions. This method is slower to converge than IBRION=1; however, it performs better when the geometry is far from convergence.

**IBRION=3**: VASP uses a damped molecular dynamics algorithm to move the nuclei. The forces are scaled by the factor POTIM. Additionally, this algorithm looks at the direction of the instantaneous force and velocity for each nucleus. Whenever $\mathbf{F} \cdot \mathbf{v}$ is negative, the velocity is set to zero and the simulation continues. $\mathbf{F} \cdot \mathbf{v} < 0$ indicates that the nucleus has overshot its ideal position. By resetting the nuclear velocity to zero, VASP avoids the situation in which the nucleus vibrates back and forth around its ideal position. In general, IBRION=3 is a good fallback when the quasi-Newton and conjugate gradient methods act too aggressively and update the geometry to a place where the electronic structure changes. Also, IBRION=3 performs well in NEB calculations, where the forces on the nuclei depend on both a spring force and the Hellmann-Feynman forces (see below for more information on NEB calculations). IBRION =3 combines well with POTIM = 0.15 to give a robust, albeit slow, method for finding minima when the initial structure is a poor representation of the equilibrium structure.

**IBRION=5 and 6**: VASP uses a finite displacement algorithm to perform a vibrational analysis (Γ point phonon frequencies). Frequencies are determined by diagonalizing the Hessian matrix that consists of second derivatives of the total energy with respect to the nuclear Cartesian
displacements. The first derivative of the total energy with respect to the
displacement of one nucleus in one of the Cartesian coordinates is the
negative of the corresponding force component on that nucleus. Therefore,
the Hessian is written as

\[
H_{i\alpha,j\beta} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 E}{\partial \mathbf{r}_{i\alpha} \partial \mathbf{r}_{j\beta}} = -\frac{1}{\sqrt{m_i m_j}} \frac{\partial F_{i\alpha}}{\partial \mathbf{r}_{j\beta}}
\]

In the preceding equation, the index \(i\alpha\) specifies the nucleus \(i\) in the
Cartesian direction \(\alpha\) (\(\alpha = x, y,\) or \(z\)). The index \(j\beta\) is decomposed in the
same way. Thus, each entry in the Hessian matrix is the derivative of the
force on nucleus \(i\) in the direction \(\alpha\) when nucleus \(j\) is displaced in the
direction \(\beta\). The partial derivative is approximated using finite differences
when IBRION=5 or 6, and NFREE determines the order of the finite
difference approximation. However, VASP defaults to NFREE=2, which
uses central finite differences with one point on either side of equilibrium.
NFREE=1 uses a one-sided approximation and is “strongly
discouraged.”\(^{14}\) IBRION=5 ignores symmetry and performs each ionic
displacement. Since numerical approximations can lead to a small
asymmetry in the Hessian matrix with IBRION=5, VASP symmetrizes the
matrix by averaging it with its transpose (symmetry here refers to matrix
symmetry and not the symmetry of the nuclear system). IBRION=6 uses
symmetry to identify the unique nuclear displacements and gives an
appropriately symmetrized Hessian. To calculate elastic constants, use
IBRION=6 and ISIF=3.
**IBRION=7 and 8:** VASP uses density functional perturbation theory to perform a vibrational analysis.\textsuperscript{31–33} See the preceding discussion for the theory behind the vibrational analysis. As with above, IBRION=7 ignores nuclear symmetry, while IBRION=8 uses the system’s symmetry to reduce the workload. The VASP guide notes that “Born effective charges and piezoelectric constants can be calculated by specifying LEPSILON=.TRUE.”\textsuperscript{14}

**KEYWORD:** ISIF  
**VALUE:** An integer specifying how the forces and stress tensor are calculated and constraints on the geometry optimization.  
**DISCUSSION:** ISIF gives the user the control over whether or not to calculate the stress tensor. If the stress tensor is fully calculated, then ISIF also determines which components of the structure are relaxed. Calculating the stress tensor is computationally demanding and can also add significant cost per ionic iteration (the stress tensor, like atomic forces, is calculated after the electronic structure has been converged at the current geometry). The following describes the relevant values of ISIF.  

**ISIF=0:** VASP calculates the forces but not the stress tensor. If NSW is greater than 1, then the nuclei are relaxed. This is the recommended setting for single-point calculations and for ionic relaxations in a fixed cell.
ISIF=1: VASP calculates the forces and the trace of the stress tensor. This gives an accurate total pressure, but it does not give accurate components of the stress tensor. If NSW is greater than 1, then the nuclei are relaxed but the cell shape/size remains constant. When performing ionic relaxations, this tag allows the user to monitor the pressure and determine whether or not the cell shape/size is reasonable. At equilibrium, the external pressure should be 0 kBar; however, absolute values less than 0.5 kBar indicate well-converged cell parameters. Larger values indicate that the cell shape or size should be optimized.

ISIF=2: VASP computes the forces and complete stress tensor. If NSW is greater than 1, then the nuclear positions are allowed to relax while the cell shape/size remains fixed.

ISIF=3: VASP computes the forces and complete stress tensor. If NSW is greater than 1, then the nuclear positions and the cell shape/size are optimized. Calculations that use ISIF=3 should reach the optimal geometry; however, the size of the planewave basis set is not adjusted to reflect the new cell shape. This leads to the possible exclusion of some planewaves that fall below the threshold specified by ENCUT. Therefore, calculations using ISIF=3 must be restarted after initial convergence is reached to see if the Pulay stress requires further optimization. The process should be repeated until the geometry is converged on the first ionic iteration (indicating that the basis set at the first iteration still gives a converged geometry).
**ISIF=4**: VASP computes the forces and complete stress tensor. If NSW is greater than 1, then the nuclear positions and cell shape are optimized subject to the constraint of keeping the cell volume constant. The same warnings arise for ISIF=4 as they do for ISIF=3.

**ISIF=5**: VASP computes the forces and complete stress tensor. If NSW is greater than 1, then the cell shape is optimized with fixed nuclear fractional coordinates and constant cell volume. The same warnings for ISIF=3 apply to calculations with ISIF=5.

**ISIF=6**: VASP computes the forces and complete stress tensor. If NSW is greater than 1, then the cell shape and volume are optimized subject to fixed nuclear fractional coordinates. See ISIF=3 for a discussion of the issues with optimizations that involve changing the cell shape/size.

**ISIF=7**: VASP computes the forces and complete stress tensor. If NSW is greater than 1, then the cell volume is optimized while the nuclear positions and cell shape remain constant. See the warnings for ISIF=3, as they apply to this situation as well.

**NOTE**: In order to converge geometries with a specific shape (*i.e.*, a cubic cell) but without internal symmetry, it is possible to alternate calculations with both ISIF=0 and ISIF=7 until the geometry converges on the first iteration for these settings. This situation arose for perovskites that have a pseudocubic structure, yet the TM-O₆ octahedra needed to rotate freely inside the cell. ISIF=7 allowed the cell to remain cubic while volume was optimized, and then ISIF=0 allowed the ionic positions to be optimized.
**KEYWORD:** POTIM

**VALUE:** The scaling factor for forces in geometry optimization, the displacement (in Å) for vibrational calculations, or the time step for molecular dynamics.

**DISCUSSION:** The meaning of POTIM depends on the value of IBRION. If IBRION=1, 2, or 3, then POTIM gives the scaling factor for the forces. The default is POTIM=0.5, and this value works well for the conjugate gradient and quasi-Newton methods. For the damped molecular dynamics method, a smaller value is needed. For vibrational calculations (IBRION=5-8), POTIM specifies the size of the atomic displacements in Å. If IBRION=0, then POTIM specifies the time step for the molecular dynamics simulation.

**KEYWORD:** EDIFFG

**VALUE:** The force cutoff for geometry optimization (specified in eV/Å).

**DISCUSSION:** EDIFFG determines the maximum allowable force on a single nucleus for a converged geometry. If the maximum atomic force is greater than EDIFFG, then VASP will update the nuclear positions and perform another ionic iteration (i.e., if NSW iterations have not already been performed).

---

*B.7.5 Keywords Governing DFT+U and Hybrid DFT Calculations*

VASP supports both DFT+U\(^{6-8}\) and hybrid DFT\(^{9-11}\) methods for correcting the self-interaction error inherent in any approximate XC functional. The following
parameters instruct VASP to run LDA+U or GGA+U calculations, the choice of which depends on the XC functional specified in the POTCAR file.

**PARAMETER:** LDAU

**VALUE:** .TRUE. for DFT+U calculations or .FALSE. for regular DFT calculations.

**DISCUSSION:** When set to .TRUE., LDAU tells VASP to use the DFT+U method.

**KEYWORD:** LDAUTYPE

**VALUE:** 2 for the rotationally invariant form of Dudarev *et al.*\(^8\) or 1 for the original LDA+U method of Liechtenstein *et al.*\(^7\)

**DISCUSSION:** The default value (2) is recommended as it is the rotationally invariant form proposed by Dudarev *et al.*\(^8\) This formalism depends only on the difference between U and J, where U is the average on-site Coulomb interaction for the specific orbitals being corrected while J is the average on-site exchange interaction for these specific orbitals. Thus, it is possible to enter the value of \(U = U-J = U_{\text{eff}}\) and \(J = 0\) using the appropriate keywords.

**KEYWORD:** LDAUL

**VALUE:** An integer array specifying the angular momentum of the orbitals to be treated with DFT+U for each atom type (use -1 to avoid applying DFT+U to orbitals on a specific element).
DISCUSSION: The LDAUL keyword requires one entry per atom type listed in the POSCAR file (and found in the POTCAR file). The order corresponds to the order in which the elements are found in the POTCAR file. Generally, transition metals require DFT+U applied to the \(d\) manifold (angular momentum = 2). Lanthanides and actinides may require DFT+U to be applied to the \(f\) manifold (angular momentum = 3). An example for LaCoO\(_3\), where the elements are specified in the order Co – La – O in the POTCAR file, is LDAUL = 2 -1 -1.

NOTE: VASP issues a warning (to the standard output) and continues to perform a standard DFT calculation when failing to have one entry per element in the POTCAR file.

KEYWORD: LDAUU

VALUE: An array of values specifying the \(U\) value for each element.

DISCUSSION: As with LDAUL (see above), this keyword is a list that contains one entry for each atom type found in the POTCAR file. LDAUU is used to specify the \(U\) value for the orbitals specified by LDAUL. Entries must be provided even for elements that are not receiving the DFT+U treatment (set these entries to zero). As with LDAUL, failing to have sufficient entries will cause VASP to default back to standard DFT calculations.

KEYWORD: LDAUJ

VALUE: A list of \(J\) values for the orbitals of each element specified via LDAUL and POTCAR.
DISCUSSION: If using LDAUTYPE=2, then the input is entered where LDAUU contains the U_{eff} values and LDAUJ is a list of zeros (one for each element found in the POTCAR file). As with LDAUL and LDAUU, failing to enter a value for each element in the POTCAR file will result in VASP performing a standard DFT calculation.

KEYWORD: LDAUPRINT

VALUE: An integer specifying the verbosity of the DFT+U output from VASP.

DISCUSSION: The default value of 0 (zero) gives silent behavior. Although this significantly reduces the output from VASP, it does make differentiating DFT+U calculations DFT calculations difficult. A better option is LDAUPRINT=1, which causes the on-site density matrix to be printed at each iteration. The extra output helps the user to recognize whether or not the DFT+U calculation was actually performed.

KEYWORD: LHFCALC

VALUE: .TRUE. to include exact (Hartree-Fock) exchange or .FALSE. to avoid calculating exact exchange.

DISCUSSION: Use this keyword to perform hybrid DFT calculations (PBE0\(^{15}\), HSE06\(^{16,17}\) or B3LYP\(^{18}\)). When performing hybrid DFT calculations, the ALGO keyword should be set to Damped, All, or Normal (though use Normal with caution). The VASP Guide\(^{14}\) recommends ALGO=Damped and TIME=0.4 when LHFCALC=.TRUE.

KEYWORD: AEXX
VALUE: The contribution (in decimal form) of exact exchange to include in place of the approximate exchange from the standard XC functionals.

DISCUSSION: This keyword is used to control how much exact exchange is included in the calculation. For PBE0 and HSE06 calculations, this should be set to 0.25. By default, VASP subtracts this quantity from 1 for scaling the GGA contribution to the exchange energy.

KEYWORD: ENCUTFOCK

VALUE: The kinetic energy cutoff for the exact exchange FFT grid.

DISCUSSION: This keyword is not supported starting in VASP 5.2.4; however, it is important in VASP 5.2.2. Omitting ENCUTFOCK leads to a slower but more accurate calculation. The other option is ENCUTFOCK=0, in which VASP uses the smallest FFT grid that encompasses the planewave energy cutoff. Setting ENCUTFOCK=0 leads to a 2-3x increase in speed, but it has the effect of introducing small energy differences and noises in the forces. However, given the computational expense of hybrid DFT calculations, using ENCUTFOCK=0 makes sense for finding the ground-state geometry. The electronic structure can then be refined by omitting ENCUTFOCK. In later versions of VASP, this has been superseded by the PRECFOCK keyword.

KEYWORD: HFSCREEN

VALUE: The screening parameter for HSE$^{10,11}$ calculations in Å$^{-1}$.

DISCUSSION: For HSE06 calculations, this parameter should be set to 0.2. Other values should be used with discretion. This parameter controls how the exact exchange is screened (applied at close range and phased out at long range).
**KEYWORD:** NKREDX, NKREDY, NKREDZ

**VALUE:** The factor by which the k-point mesh should be down-sampled when evaluating exact exchange. NKREDX applies to the reciprocal lattice vector, NKREDY to the second reciprocal lattice vector, and NKREDZ to the third reciprocal lattice vector.

**DISCUSSION:** VASP supports using reduced k-point meshes to save time and memory when evaluating exact exchange. The k-points along the first reciprocal lattice vector are the number of k-points along this vector specified in the KPOINTS file divided by NKREDX. Reducing the k-point mesh can affect the accuracy of the calculations; however, the savings in computational time and resources may necessitate using these parameters.

**B.7.6 Keywords Governing NEB Calculations**

VASP has the ability to find transition states using two methods: the dimer method\(^47,48\) and the NEB method.\(^49\)–\(^51\) A transition state is characterized by a single imaginary vibrational frequency. This corresponds to the maximum potential energy along one normal mode and the minimum potential energy along all of the other normal modes. The NEB method is a well-tested technique for finding minimum energy pathways and transition states given that the starting and ending geometries are known. In the case of diffusion via a vacancy hopping mechanism, the two geometries have a vacancy (e.g., an oxygen vacancy) in appropriate, adjacent locations.

When running NEB calculations, VASP requires a very strict directory structure. The NEB calculation consists of a number of images (geometries) interpolated between the starting and ending geometries. VASP takes the INCAR, POTCAR, and KPOINTS
files from the execution directory. This directory should then have subdirectories numbered 00, 01, 02, … N\text{images}+1, where N\text{images} is the number of images allowed to move and the endpoints remain fixed. OUTCAR files for the respective geometries should be copied into the 00 and N\text{images}+1 subdirectories. This allows the energy to be detected for the endpoints. In each subdirectory, a POSCAR file is required. This is the geometry from which the calculation will start. The calculation continues until the NEB force on each image is zero. The NEB method adds a spring force to connect adjacent images together.

The following section documents the relevant tags that must be added for NEB calculations. These are the tags that should be used with the VASP transition state theory code by Professor Henkelman’s group at the University of Texas.\textsuperscript{52} This code must be compiled into VASP in order for these tags to fully work.

**KEYWORD:** ICHAIN

**VALUE:** Set to 0 (zero) to run NEB calculations.

**DISCUSSION:** Values other than zero are not well-documented, so this parameter should be set to 0 (zero) for NEB calculations and otherwise omitted.

**KEYWORD:** IMAGES

**VALUE:** The number of moving images (geometries) in the NEB calculation.

**DISCUSSION:** Geometries for the start and end of the band reside in subdirectories 00 and the value of IMAGES+1. The directories 01, 02, …, IMAGES contain POSCAR files defining geometries that will be optimized
subject to the NEB spring force. Simple pathways can be isolated with 3 or 5 images, while complex pathways may require significantly more images (20-30).

**KEYWORD:** SPRING

**VALUE:** The spring constant (in eV/Å²) preceded by a negative sign.

**DISCUSSION:** A negative value of SPRING is used to specify the spring constant in the NEB calculation. A spring force replaces the force tangent to the elastic band, and the spring helps to ensure that the images remain evenly spaced (approximately). The default value seems to work well in most situations.

**KEYWORD:**  LCLIMB

**VALUE:** .TRUE. for climbing image NEB calculations or .FALSE. for standard NEB calculations.

**DISCUSSION:** The climbing image NEB method applies the standard NEB method to all of the images except for the one with the greatest energy. This image is driven to the transition state by moving it along the tangent in the direction that increases energy. At the end, the forces on all of the atoms in the highest energy image should be zero because it will have arrived at a transition state. This method is used to identify the transition state geometry. In general, this flag should be turned on once there is a reasonable approximation to the minimum energy pathway. If the pathway is likely to be symmetrical (e.g., oxygen diffusion in LaCoO₃), then this flag works well as long as an odd number of images are chosen. In that case, the central image should be driven to the transition state.
B.7.7 Keywords Governing Output

VASP allows the user to control whether or not it writes certain files. Specifically, the CHGCAR and WAVECAR files may be written or suppressed. The all-electron charge density from a PAW-DFT computation can be written, as well.

**KEYWORD:** LCHARG

**VALUE:** .TRUE. to write the CHGCAR file at the end of the calculation.

**DISCUSSION:** CHGCAR is a file containing the valence charge density and, as an ASCII text file, can become very large. However, this file is used to initialize continuation calculations. Unless the charge density is not required for further work, this should be set to .TRUE.

**KEYWORD:** LWAVE

**VALUE:** .TRUE. to write the WAVECAR file.

**DISCUSSION:** If the resulting geometry and charge density of the calculation will be used for further calculations, the best way to restart a calculation is to use a WAVECAR file. However, this file contains all of the planewave coefficients for the Kohn-Sham orbitals at each k-point. Although this is a binary file, it can be quite large (especially for large systems). Sometimes, the file size necessitates setting LWAVE=.FALSE.

**KEYWORD:** LAECHG

**VALUE:** .TRUE. to write the all-electron charge density.

**DISCUSSION:** When set to .TRUE., LAECHG causes VASP to write three files. The first, AECCAR0, contains the frozen core electron density associated with the PAW potentials. The second, AECCAR1, contains the initial valence charge density.
density. The third, AECCAR2, contains the final valence charge density. The all-electron charge density is obtained when the charge densities from AECCAR0 and AECCAR2 are summed.xix

B.7.8 Example INCAR File

```plaintext
SYSTEM = LaCoO3 from Spectroscopic Data
ISTART = 1
ICHARG = 1
INIWAV = 1

NELM = 300
NELMIN = 8
ALGO = FAST
TIME = 0.4
LREAL = .FALSE.
ISPIN = 2
EDIFF = 1E-5
MAGMOM = 0 0 0 0 0 0 0 0 0 0
ENCUT = 750
NBANDS = 80

ISMEAR = 0
SIGMA = 0.05
PREC = accurate
LORBIT = 11
NEDOS = 1200

LDAU = .TRUE.
LDAUTYPE = 2
LDAUL = 2 -1 -1
LDAUU = 4.0 0.0 0.0
LDAUJ = 0.0 0.0 0.0
LDAUPRINT = 2

EDIFFG = -.01
NSW = 30
IBRION = 2
ISIF = 3
POTIM = 0.5

LWAVE = .TRUE.
LCHARG = .TRUE.
```

Figure B.4: Example INCAR file for LaCoO₃ using the DFT+U method. U_{eff} = 4.0 eV for the Co^{3+} d manifold. The calculation involves ionic relaxation, including cell optimization.

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xix Adding two charge density files from VASP is easily accomplished using the sumchg.pl script from the VASP TST scripts collection as provided by Prof. Henkelman’s group at the University of Texas.⁴²
References


Appendix C

Obtaining Vibrational Frequencies Using Multiple VASP Calculations

C.1 Motivation

As discussed in Chapter 2 of this thesis, vibrational contributions from solid phases should be included when calculating the free energies of vacancy formation. These contributions depend on the vibrational frequencies of the system. The vibrational frequencies are obtained by diagonalizing the Hessian matrix formed from the second derivatives of the total energy with respect to atomic displacements.

\[
H_{i\alpha,j\beta} = \frac{1}{\sqrt{m_im_j}} \frac{\partial E}{\partial x_{i\alpha}\partial x_{j\beta}} = -\frac{1}{\sqrt{m_im_j}} \frac{\partial F_{i\alpha}}{\partial x_{j\beta}}
\]

These entries can be rewritten in terms of the derivative of a force component (\(\alpha\)) on one nucleus (\(i\)) with respect to the displacement of a second nucleus (\(j\)) along one of the Cartesian unit vectors (\(\beta\)). This is a matrix of size \(3N \times 3N\), where \(N\) is the number of atoms in the system. VASP does not provide an analytical expression for obtaining the entries in the Hessian matrix; instead, it can approximate the Hessian by either finite differences\(^1\) or density functional perturbation theory.\(^2-4\) The work in this thesis uses the former method for obtaining the Hessian matrix. The vibrational frequencies are the square roots of the eigenvalues of the Hessian matrix.

The selective dynamics tag in VASP enables the user to specify a set of displacements to be calculated. The combination of an atom and a direction is called a degree of freedom (DOF), and VASP will then diagonalize the subset of the Hessian corresponding to the motion for the DOFs selected. This functionality provides a means
for approximating the vibrational contributions to defect formation by looking at the vibrations of atoms near the defect. To ensure that this procedure is reasonable, the user must keep adding shells of atoms around the defect until the vibrational contribution to the free energy is converged. Convergence applies to the energy difference between the defective and host cells. Unfortunately, VASP will only provide the frequencies for the DOFs involved in one calculation. This requires the user to recompute the forces for DOFs associated with inner shells when adding an additional shell of atoms. This is both a waste of resources and a time-sink, since the most time consuming part of the vibrational calculation is optimizing the electronic structure for each atomic displacement.

To address the situation above, Prof. Henkelman’s group from the University of Texas has provided code that will compute frequencies for a Hessian compiled from multiple VASP calculations. However, this code uses one-sided finite differences to approximate the derivatives, and the VASP guide strongly recommends against using one-sided finite differences for frequency calculations. Therefore, a new solution is necessary for using the forces obtained during multiple VASP calculations to form the complete or partial Hessian matrix. This appendix illuminates the work we did to solve this problem by developing our own python program.

C.2 Program Description

Our python program takes an arbitrary number of OUTCAR files and determines the DOFs analyzed in the complete set of calculations. Using the forces obtained for each displacement, the program constructs central finite differences to estimate the derivatives
needed for the Hessian matrix. If no displacements occur, or if only one displacement occurs, for a DOF, the program ignores that DOF when constructing the Hessian matrix.

The python program reads through the OUTCAR files, and it creates an object for each displacement that holds the positions and forces. These objects are defined by the class PositionsAndForces. The first OUTCAR file read is used to determine the masses of each ion. Once all of the OUTCAR files have been parsed, the collection of PositionAndForces objects are inspected and paired to determine which DOFs have been analyzed in the complete set of calculations. The result of this process is a collection of DegreeOfFreedom objects that hold information about which atom was displaced, the direction and size of the displacement, and the forces on all of the atoms for the positive and negative displacements. Finally, the DegreeOfFreedom objects are used to form the Hessian matrix, which is diagonalized using the Numpy package.xx

In order to provide integration with the PHONOPY program7 (appendix D), our program has a flag, “--fc” that forces it to write a file named MYFC. This file is in the same format as the FORCE_CONSTANTS file created and used by PHONOPY. This allows our program to provide the input needed for investigating phonon dispersion with PHONOPY.

C.3 Program Validation

Validating our program means ensuring that it can accurately reproduce the frequencies obtained from VASP calculations. This is done in two stages: (1) we use the program to analyze a single OUTCAR file and ensure that the frequencies match those reported by VASP; and (2) we take the single OUTCAR file, break the ionic steps into multiple files, and ensure that our program can piece together the Hessian matrix from

multiple files while still reporting accurate vibrational frequencies. The results of these two tests are shown in table C.1.

**Table C.1**: Vibrational frequencies (in cm$^{-1}$) for SrO (B1 structure) obtained using three methods for the same system. The first results are those reported by VASP. The second results are those reported by our program when applied to the same OUTCAR file. The third results are those reported by our program after the OUTCAR file was broken into multiple files. $i$ is used to indicate imaginary frequencies.

<table>
<thead>
<tr>
<th>VASP Frequencies</th>
<th>Single OUTCAR Test</th>
<th>Multiple OUTCAR Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>306.8</td>
<td>306.8</td>
<td>306.8</td>
</tr>
<tr>
<td>306.7</td>
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<td>306.7</td>
</tr>
<tr>
<td>306.6</td>
<td>306.6</td>
<td>306.6</td>
</tr>
<tr>
<td>225.4</td>
<td>225.4</td>
<td>225.4</td>
</tr>
<tr>
<td>224.7</td>
<td>224.7</td>
<td>224.7</td>
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<tr>
<td>224.6</td>
<td>224.6</td>
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<tr>
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<tr>
<td>191.9</td>
<td>191.9</td>
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<td>122.5</td>
<td>122.5</td>
<td>122.5</td>
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<tr>
<td>122.3</td>
<td>122.3</td>
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<td>122.3</td>
<td>122.3</td>
<td>122.3</td>
</tr>
<tr>
<td>122.2</td>
<td>122.2</td>
<td>122.2</td>
</tr>
<tr>
<td>0.3$i$</td>
<td>0.2$i$</td>
<td>0.2$i$</td>
</tr>
<tr>
<td>0.4$i$</td>
<td>0.4$i$</td>
<td>0.4$i$</td>
</tr>
<tr>
<td>0.4$i$</td>
<td>0.4$i$</td>
<td>0.4$i$</td>
</tr>
</tbody>
</table>

Our program successfully reproduces the frequencies from VASP with a maximum error of 0.1 cm$^{-1}$. The discrepancies arise from the fact that our program reads the forces from the OUTCAR file (6 decimal places), while VASP has access to the full floating point
value it calculated. This makes a difference for the smallest imaginary frequency. The three imaginary frequencies are translational modes for the atoms with the cell. They should be zero; however, the approximate derivatives used to build the Hessian lead to a small quantity of noise in the actual results. From table C.1, our program is validated and ready for use on other systems.

C.4 User’s Manual

Our program is entitled vasp_frequencies.py and can be located on the Tiger cluster in the directory /home/EAC/VASP/scripts. It has been tested with Python version 2.6.6. It has not been tested with any version of Python 3 because the two versions of Python are incompatible with one another.

C.4.1 Input

The program is called with a very simple syntax:

```
vasp_frequencies.py [--fc] <OUTCAR_FILES>
```

From the arguments passed to the program, two things are determined. First, the program looks to see if the --fc flag was provided and responds appropriately. Second, the program interprets the remaining arguments, <OUTCAR_FILES> above, as a list of OUTCAR files to be read and analyzed. There is no internal limit to the number of OUTCAR files specified in this manner. The user should be aware that files can be specified by relative or absolute paths. In either case, if the path or file name contains a space, the argument must be placed in quotation marks or it will be interpreted as two separate values and the program will stop when it does not find a file corresponding to part of the path.
C.4.2 Output

The program will provide simple output. First, the program writes out the files that it is processing. Next, the DOFs with complete finite differences are written in a zero-based indexing scheme. For this part of the output, the first atom in the geometry is atom 0 and the directions are given as x=0, y=1, and z=2. Finally, the program prints all of the frequencies from its calculation and indicates whether they are real or imaginary. Frequencies are reported in terahertz (THz, $10^{12}$ s$^{-1}$) and wavenumbers (cm$^{-1}$). For any imaginary frequencies, the mass-weighted displacements corresponding to the eigenvector along that mode are printed. Dividing each atom’s displacement by its mass transforms the printed eigenvector from mass-weighted to Cartesian coordinates.

C.4.2 Limitations

Our program only works with VASP OUTCAR files. It assumes that ISIF=5 was used for the calculations (see Appendix B). If symmetry was used (ISIF=6) or density functional perturbation theory (ISIF=7 or 8), then the program is not applicable. Finally, the program checks to make sure that each calculation has the same geometry for the first iteration. This results from the fact that VASP always performs the first iteration at the given geometry before displacing any atoms. Thus, the program will inform the user if they are attempting to use OUTCAR files for two different initial geometries. In that case, a warning is issued and the program terminates.

References


Appendix D

Using PHONOPY for Phonon Dispersion Calculations

D.1 Motivation

Recent work by Gryaznov et al.\textsuperscript{1} demonstrated that phonon dispersion may contribute up to 0.5 eV when calculating the oxygen vacancy formation free energies in La\textsubscript{1-x}Sr\textsubscript{x}Co\textsubscript{1-y}Fe\textsubscript{y}O\textsubscript{3-δ}. These results forced us to consider the effects of phonon dispersion in our own calculations. We found problems with the phonon spectrum in the pseudocubic cell (chapter 2) that Gryaznov et al. had also used. However, the PHONOPY package\textsuperscript{2,3} was integral to our ability to compute phonon densities of states (DOS) and dispersion curves using the data we obtained with VASP. In this appendix, we document how to use PHONOPY.

D.2 Background

PHONOPY is a package of programs, written in Python, for analyzing vibrational effects in solids. We discuss using PHONOPY for calculations relevant to this thesis and ignore its other capabilities. PHONOPY calculates phonon frequencies at various points in reciprocal space. These are given by diagonalizing the dynamical matrix

\[ D_{\alpha i, \beta j} = \frac{1}{\sqrt{m_i m_j}} \Phi_{\alpha i, \beta j} \exp(i \mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)) \]

where \( m_i \) and \( m_j \) are the masses of atoms \( i \) and \( j \), \( \mathbf{r}_i \) and \( \mathbf{r}_j \) are the positions of atoms \( i \) and \( j \), \( \mathbf{q} \) is a reciprocal wave vector, and \( \Phi_{\alpha i, \beta j} \) is the second derivative of the energy with respect to displacing atom \( i \) in the direction \( \alpha \) and displacing atom \( j \) in the direction \( \beta \). The values for \( \mathbf{q} \) run over the first Brillouin zone (chapter 2). The dynamical matrix is diagonalized for each wave vector \( \mathbf{q} \), and the corresponding eigenvalues are the
vibrational frequencies squared. Thus, negative eigenvalues produce imaginary frequencies, while positive eigenvalues produce real frequencies. Formulas for the constant volume heat capacity, Helmholtz free energy, and entropy may be found on the PHONOPY website: http://phonopy.sourceforge.net/theory.html.

D.3 Running PHONOPY

PHONOPY is run by loading the appropriate module on the Tiger cluster. Once the module is loaded, the user must execute PHONOPY once to post-process the data from a VASP calculation, generating the FORCE_CONSTANTS file that PHONOPY uses as input. A second calculation generates the desired output.

D.3.1 Post-Processing VASP Results for Use with PHONOPY

PHONOPY has its own format for storing the force constants, \( \Phi_{\alpha\beta,ij} \), in a file called FORCE_CONSTANTS. To generate the FORCE_CONSTANTS file, PHONOPY must be instructed to read the information from a vasprun.xml file. This is accomplished by executing the following command:

```
phonopy --fc vasprun.xml
```

The preceding syntax assumes that PHONOPY is executed in the directory containing vasprun.xml. This works in the case where the VASP calculation involved displaces every atom in the cell in each Cartesian direction. If the complete displacements are separated into multiple OUTCAR files, the python program vasp_frequencies.py (appendix C) can also produce a file that works with PHONOPY. In this case, the resulting file is named MYFC to avoid overwriting any FORCE_CONSTANTS file already existing in the current directory. To use the file produced by vasp_frequencies.py, rename MYFC to FORCE_CONSTANTS.
D.3.2 Computing a Phonon DOS

Once a FORCE_CONSTANTS file has been generated, the next step is to use PHONOPY to calculate the desired output. A basic example of this is computing the phonon DOS. The resulting plot provides information about the spectrum of frequencies in the cell. Figure D.1 is a sample input file for PHONOPY that generates a phonon DOS.

```
ATOM_NAME=Co La O
DIM=1 1 1
FORCE_CONSTANTS=READ
MP=4 4 4
```

**Figure D.1:** A sample input file for PHONOPY to produce a phonon DOS for LaCoO₃. The DOS is produced using a 4 × 4 × 4 Monkhorst-Pack mesh.

We assume that the input from figure D.1 is saved in a file named band.conf. PHONOPY is then executed in one of two manners. The first option generates a file named band.yaml and works with or without an X server running locally.

```
phonopy band.conf
```

The second option requires the user to have a local X server running, but it produces the plot for immediate inspection. The ATOM_NAME keyword specifies the elements in the cell. The DIM keyword tells PHONOPY to create a supercell from the input unit cell by multiplying each integer by its corresponding lattice vector. DIM=1 1 1 tells PHONOPY to construct the dynamical matrix for the input cell. FORCE_CONSTANTS=READ informs PHONOPY that the FORCE_CONSTANTS file in the current directory contains the correct data to construct the dynamical matrix. The MP keyword specifies the dimensions of the k-point mesh to be used for dispersion calculations.
Figure D.2: A sample plot of the phonon DOS (arbitrary units) vs. frequency (THz) for LaCoO$_3$ in the low-spin state and the $R\bar{3}c$ unit cell. The frequencies are based on GGA+U electronic structure calculations$^{5-7}$ with the PBE functional$^8$ and U-J = 4.0 eV.

D.3.3 Computing Phonon Band Structures with PHONOPY

PHONOPY also calculates phonon band structures based on paths through the Brillouin zone specified in the input file. Phonon band structures show the variation of phonon frequencies and allow the user to identify acoustic and optical modes. For instance, the input in figure D.3 will generate a phonon band structure for LaCoO$_3$. 

---

296
ATOM_NAME = Co La O
DIM = 1 1 1
PRIMITIVE_AXIS = 1 0 0 0 1 0 0 0 1
FORCE_CONSTANTS = READ
BAND=0 0 0 0 0 -0.5 0.5 0.255 -0.255, 0.745 0.5 0.255 0.5
0.5 0.5 0 0 0 0.3775 0 -0.3775, 0.6225 0.3775 0 0.5 0.5 0
0.6225 0.6225 0.255 0.5 0.5 0.5, 0 0 -0.5 0.755 0.3775 0.3775
BAND_POINTS=101
BAND_LABELS=\Gamma L B1| B Z \Gamma X| Q F P1 Z| L P

**Figure D.3:** Input to generate the phonon band structure of LaCoO₃.

Running PHONOPY with the –p flag produces the plot on the local screen. Thus, the user must have a local X server running. The BAND tag specifies the coordinates, in reciprocal space, of the endpoints for each segment of the plot. The points are labeled using the BAND_LABELS tag. PHONOPY reads the input for BAND in sets of three numbers, and paths go from the first to the second point, from the second to the third point, etc. If PHONOPY encounters a comma after a point, the next path begins with the subsequent point and ends with the point thereafter. Figure D.3 illustrates input where the paths are constructed from $\Gamma \rightarrow L \rightarrow B1$, then from $B \rightarrow Z \rightarrow \Gamma \rightarrow X$, then from $Q \rightarrow F \rightarrow P1 \rightarrow Z$, and finally from $L \rightarrow P$. The input from figure D.3 and the FORCE_CONSTANTS file derived from GGA+U calculations with the PBE functional and U-J = 4.0 eV both yield the phonon band structure in figure D.4.
Figure D.4: Phonon frequencies (in THz) along paths between high symmetry points in the Brillouin zone. Labels for the high-symmetry points in reciprocal space from Setyawan and Curtarolo.⁹

D.3.4 Computing Thermal Corrections Using PHONOPY

PHONOPY enables users to compute thermal corrections due to phonons, including the effects of dispersion. Thermal corrections account for finite temperature effects in the solid. PHONOPY assumes that the cell volume remains constant. In this way, it provides estimates of the phonon contribution to the internal energy, heat capacity, Helmholtz free energy, and entropy. Because solids usually have low coefficients of thermal expansion, the Helmholtz free energy is a good approximation to
the Gibbs free energy for solid phases. Computing the thermal contributions to the energy of a system using PHONOPY is accomplished using an input file similar to the one shown in figure D.5.

```
ATOM_NAME=Co La 0
DIM=1 1 1
FORCE_CONSTANTS = READ
   MP=4 4 4
   TPROP=.TRUE.
   TMIN=873.15
   TMAX=1273.15
   TSTEP=100
```

**Figure D.5**: Example input file for calculating thermal contributions using PHONOPY.

The input shown in figure D.5 tells PHONOPY to calculate the thermal corrections for LaCoO₃ over the range 873.15-1273.15 K (600-1000°C). Table D.1 shows the results. TSTEP determines step-size between consecutive temperatures. The values reported in Table D.1 are the vibrational contributions to the internal energy (E) and Helmholtz free energy (F) at each of the specified temperatures. When these values are added to the total (electronic and ionic) energies from the electronic structure calculation, the result gives the E or F (depending on the correction used) of the cell at each temperature. The corrections for E in Table D.1 are positive because higher temperature increases the phonon population leading to higher internal energy. On the other hand, F is negative in Table D.1 because raising the temperature creates additional vibrational entropy and the net quantity $F = E - TS$ (where $T$ is the temperature) becomes negative.
Table D.1: Thermal corrections due to phonons in LaCoO₃. The columns give the temperature (T in K), Helmholtz free energy (F in kJ/mol), entropy (S, in J/mol.K), heat capacity (Cᵥ in J/mol.K), and internal energy (E in kJ/mol), respectively.

<table>
<thead>
<tr>
<th>T</th>
<th>F</th>
<th>S</th>
<th>Cᵥ</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>873.15</td>
<td>-178.2</td>
<td>460.1</td>
<td>243.0</td>
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</tr>
<tr>
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<td>247.9</td>
</tr>
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<td>245.1</td>
<td>272.4</td>
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<td>-327.6</td>
<td>532.3</td>
<td>245.8</td>
<td>296.9</td>
</tr>
<tr>
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<td>-381.8</td>
<td>552.4</td>
<td>246.4</td>
<td>321.5</td>
</tr>
</tbody>
</table>

References