# OPTOELECTRONIC PROPERTIES AND ENERGETICS OF DEFECTS AND IMPURITIES IN NIO STUDIED USING AB INITIO CALCULATIONS

by

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## DEDICATION

For my father.

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#### ABSTRACT

Nickel oxide (NiO) is a transparent conducting oxide (TCO) which has shown potential for applications in the next generation of memristors for non-volatile resistive RAM (RRAM), solar cells, spintronics, and other devices. Thus it is of interest to study the intrinsic defects responsible for this resistive switching mechanism as well as other impurities in order to improve desired characteristics. Density Functional Theory (DFT) based ab initio calculations are used to study the electronic and optical properties as well as the energetics and stability of defects and impurities when introduced into rock-salt NiO. Exchange-correlation effects were included in the calculations within the generalized gradient approximation where to better describe the d-orbitals of Ni and transition metal (TM) dopants a Hubbard potential U contribution was added (GGA+U). Results also considering a hybrid functional (HSE06) to treat the exchange correlation are shown for both the pristine and altered systems. NiO systems containing defects and impurities were studied using supercell grown along the [111] direction of 32 atoms to simulate the anti-ferromagnetic (AFM) configurations. Stability was investigated through the calculation of formation energies of these systems in order to discern what is most energetically favorable.

#### **1. INTRODUCTION AND MOTIVATION**

Nickel oxide (NiO) is a p-type transparent conducting oxide (TCO) which has shown potential for a wide array of different applications in the next generation of memristors for non-volatile resistive RAM (RRAM),<sup>1–3</sup> hole transport and extraction layers for organic LEDs and solar cells,<sup>4–7</sup>, pseudocapacitor electrodes in electrochemical supercapacitors,<sup>8,9</sup> and spintronic devices.<sup>10</sup> Thus it is of interest to study the intrinsic defects responsible for this resistive switching mechanism as well as various dopants in order to improve the desired material characteristics.

TCOs are, as the name implies, a classification of materials composed of O bound to some sort of cation. These types of materials are used anywhere from catalytic components to paint to semiconductors and may be generally divided into two types, n-type and p-type. n-type materials have conduction and electronic properties attributed to negative charge carriers, or electrons, while p-type materials attribute these to positive charge carriers, or holes. For most device applications one needs both n- and p-type materials, but a majority of TCOs fall within the n-type classification. Thus there is a desire in the field to find and explore possible applications of p-type TCO's, with pristine NiO being studied extensively over the past couple decades for this purpose.<sup>11–14</sup> However, there still remains more to be done in the form of understanding how the intrinsic defects contribute to the character of the material as well as exploring the introduction of various impurities and dopants.

The primary motivation for use of NiO in RRAM devices stems from a mechanism called resistive switching.<sup>15,16</sup> With the application of an electric field along with thermal effects, NiO may be placed in a low or high resistive state on demand that are then registered as a '0' or '1' to act as a bit, similar to how low and high voltage states are used in current memory devices. The driving force for this resistive switching is the formation of filaments in the material when this electric field is applied, which are the result of the migration of intrinsic defects when this field is applied. While there is some disagreement

in the literature as to which defect is more relevant for this mechanism, the majority of studies seem to suggest O vacancies as the primary driver of resistive switching in NiO and attributing the p-type character of the film to Ni vacancies.<sup>2,3,15,16</sup> There is place then for further and more accurate study of these systems and their energetics to help reinforce one conclusion or another and help improve the description of this important feature.

In order to improve device behavior, doping NiO with various elements and growing films in various device stacks has been investigated both experimentally and theoretically.<sup>1,8,15,17</sup> The selection of which elements to study was done by finding areas in the literature where there seemed some experimental interest, but the theoretical description could be improved or different options explored in order to help guide future experiment. To that end, the elements selected for this work were Cu, Ag, Fe, and C.

The electronic and optical character of Cu-doped NiO has been the subject of interest for the better part of a decade, with contributions from experimental and theoretical work.<sup>5,6,18,19</sup> Doping Ni<sub>1-x</sub>O with Cu<sub>x</sub> has been experimentally shown to improve transparency and conductivity, with optical band gap decreasing with increasing Cu concentration from 3.2 eV to 2.96 eV for x = 0% - 10%.<sup>18–20</sup> Other experiments have shown potential uses as a hole transport layer in scalable organic and inorganic cell fabrication.<sup>5,6,21,22</sup>

Moving down a row in the periodic table, Ag doping in NiO has also been investigated. With similar motivation and concentrations studied as Cu doping,<sup>23</sup> Ag doping offers another option to improve performance in both organic and inorganic perovskite solar cells by acting as a charge transport layer and improving the power conversion efficiency in these devices.<sup>7</sup> Although from the literature it appears less work has been done with Ag doping as opposed to Cu doping, Ag-doped NiO is a promising candidate for these devices and may offer improvement over the more studied Cu-doped material. Thus additional work is needed in order to determine the potential of Ag doping in NiO.

Although some work has been done with Fe-doped NiO, most studies have focused on its application for spintronic devices and are generally fabricated within O-Rich conditions<sup>24–26</sup> with more recent work placing Fe-doped NiO as a strong candidate for improving the well-known resistive switching behavior found in pristine NiO.<sup>2,15,27</sup> Experimentally studied in concentrations up to 20%,<sup>28</sup> the electronic and optical properties of Fe-doped NiO are of interest for potential use in improving NiO-based RRAM devices.

In recent work several papers have been published exploring the potential of growing NiO in contact with graphene films in order to create new devices for these same applications.<sup>29–33</sup> These heterostructures have been reported to yield improved electrochemical properties and observed 'synergistic effects'<sup>30</sup> and some work has been done exploring the effect the introduction C may have on NiO as well as Ni doping on graphene.<sup>31–33</sup> C is also reported to be commonly seen in fabricated films as an unintentional dopant.<sup>34</sup> However, current literature does not explore the energetics of C replacing Ni vs. C replacing O, nor does it completely describe the effect either case may have on the character and optical properties of the material.

For these reasons the defects and impurities selected here were investigated. In Chapter 2 the theoretical background of the primary tool used in this work, density functional theory (DFT), is reviewed along with the approximations used and its implementation within the computational code used to perform the calculations, the Vienna Ab initio Simulation Package (VASP). The method for calculating optical properties from the real and imaginary parts of the dielectric function and formation energies is described here as well. Following this, Chapter 3 presents results for the systems studied describing the electronic and optical characteristics for each defect or impurity investigated. Chapter 4 explores trends in the stability and energetics of NiO as a function of defect and doping concentration via formation energy calculations. Chapter 5 gives conclusions and suggestions for future work.

#### 2. THEORY AND METHODOLOGY

The basis of density functional theory (DFT) is rooted in what are known as the Hartree-Fock (HF) equations, the explicit solution of the Hamiltonian for an electron in a system of interacting nuclei and electrons incorporating the Pauli Exclusion principle. However, when one goes to actually evaluate these expressions for a non-trivial system they encounter an exponential growth in the resources necessary to evaluate it due to the the exchange-correlation component of the electron-electron interaction term, making the exact solution for most systems too computationally expensive to reasonably evaluate. Since computational time is finite, several approximations are made in order to come to a usable solution while trying to maintain as much accuracy as possible. While unavoidable with current technology, it is important to understand what these approximations are, how they are implemented within the tools used, and how they may affect and impose limitations on the results.

#### 2.1 Hartree-Fock Equations

Starting from the one-particle Schrödinger equation:

$$\hat{\mathbf{H}}\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = \epsilon\psi(\mathbf{r})$$
(1)

Where  $\hat{\mathbf{H}}$  is the Hamiltonian operator,  $\psi(\mathbf{r})$  is the wavefunction of a single particle, m is the mass of that particle,  $\hbar$  is the reduced Planck constant,  $\nabla$  is the standard vector differential operator such that  $\nabla^2$  is the Laplacian,  $V(\mathbf{r})$  is a potential term we will expand later,  $\epsilon$  is the energy eigenvalue, and where the first term of the Hamiltonian gives the kinetic contribution and the second the potential contribution.

If we improve our description and no longer consider a single isolated particle, but instead a system of N interacting particles we go from the single-electron wavefunction  $\psi_i(\mathbf{r})$  to the many-body wavefunction:

$$\Psi(\mathbf{r_1},...\mathbf{r_N}) = \prod_{i=1}^N \psi_i(\mathbf{r})$$
(2)

Using this in our previous expression, one obtains the many-body Schrödinger equation:

$$\hat{\mathbf{H}}\Psi(\mathbf{r}_{1},...\mathbf{r}_{N}) = \sum_{i=1}^{N} \left(-\frac{\hbar^{2}}{2m}\nabla_{i}^{2} + V(\mathbf{r}_{i})\right)\Psi(\mathbf{r}_{1},...\mathbf{r}_{N}) = E_{tot}\Psi(\mathbf{r}_{1},...\mathbf{r}_{N})$$
(3)

Where  $E_{tot}$  is the total energy of the many-body system. Expanding this for a system of electrons and nuclei we would expect find in a crystal lattice, we can break this apart into 5 terms for our Hamiltonian:

$$\hat{\mathbf{H}}\Psi = (T_n + T_e + U_{nn} + U_{en} + U_{ee})\Psi = E_{tot}\Psi$$
(4)

Where  $T_n$  is the kinetic contribution from the nuclei,  $T_{el}$  is the kinetic contribution from the electrons,  $U_{nn}$  is the potential contribution from the coulombic interaction between nuclei,  $U_{en}$  is the potential contribution from the coulombic interaction between nuclei and electrons, and  $U_{ee}$  is the potential contribution from the coulombic interaction between electrons. Evaluating each remaining term for a system of N electrons with summation indices i, j, and M nuclei with summation indices I, J, yields:<sup>35</sup>

$$\hat{\mathbf{H}}\Psi = \left(-\sum_{I} \frac{\hbar^{2}}{2M_{I}} \nabla_{I}^{2} - \sum_{i} \frac{\hbar^{2}}{2m_{e}} \nabla_{i}^{2} + \frac{1}{2} \sum_{I \neq J} \frac{e^{2}}{4\pi\epsilon_{0}} \frac{Z_{I}Z_{J}}{|\mathbf{R}_{I} - \mathbf{R}_{J}|} - \sum_{i,I} \frac{e^{2}}{4\pi\epsilon_{0}} \frac{Z_{I}}{|\mathbf{r}_{i} - \mathbf{R}_{I}|} + \frac{1}{2} \sum_{i \neq j} \frac{e^{2}}{4\pi\epsilon_{0}} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} \right) \Psi = E_{tot} \Psi \quad (5)$$

Applying the Born-Oppenheimer approximation, which will be discussed later, we assume no ionic motion such that  $T_n = 0$ . Additionally, considering a single electron instead of the entire system such that we neglect  $U_{nn}$ , we obtain the Hartree equations:<sup>36</sup>

$$\hat{\mathbf{H}}\psi_{i}(\mathbf{r}) = -\sum_{i} \frac{\hbar^{2}}{2m_{e}} \nabla_{i}^{2} \psi_{i}(\mathbf{r}) + \sum_{\mathbf{R}} \frac{Ze^{2}}{|\mathbf{r} - \mathbf{R}|} \psi_{i}(\mathbf{r}) + \sum_{j} \int d\mathbf{r}' \left| \psi_{j}(\mathbf{r}') \right|^{2} \frac{e^{2}}{|\mathbf{r} - \mathbf{r}'|} \psi_{i}(\mathbf{r}) = \epsilon_{i} \psi_{i}(\mathbf{r}) \quad (6)$$

However, as pointed out by Slater, these expressions only evaluate the coulombic interaction between electrons, and do not consider the antisymmetry constraint of the wavefunctions imposed by the Pauli exclusion principle. This is treated through the use of a Slater determinant between two particles with orthogonal wavefunctions of the form:<sup>37</sup>

$$\Psi(\mathbf{r}_{1},\mathbf{r}_{2}) = \psi_{1}(\mathbf{r}_{1})\psi_{2}(\mathbf{r}_{2}) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1}(\mathbf{r}_{1}) & \psi_{2}(\mathbf{r}_{1}) \\ \psi_{1}(\mathbf{r}_{2}) & \psi_{2}(\mathbf{r}_{2}) \end{vmatrix}$$
(7)

The Pauli exclusion principle is then incorporated into a new exchange-correlation term  $U_{XC}$ , such that we obtain the new and improved Hartree-Fock equations of the form:<sup>38</sup>

$$\epsilon_i \psi_i(\mathbf{r}) = [T_e + U_{en} + U_{ee} + U_{XC}]\psi_i(\mathbf{r}) \tag{8}$$

$$\epsilon_{i}\psi_{i}(\mathbf{r}) = -\frac{\hbar^{2}}{2m_{e}}\nabla^{2}\psi_{i}(\mathbf{r}) + \sum_{\mathbf{R}}\frac{Ze^{2}}{|\mathbf{r}-\mathbf{R}|}\psi_{i}(\mathbf{r}) + \sum_{j}\int d\mathbf{r}' \left|\psi_{j}(\mathbf{r}')\right|^{2}\frac{e^{2}}{|\mathbf{r}-\mathbf{r}'|}\psi_{i}(\mathbf{r}) - \sum_{j}\int d\mathbf{r}' \frac{e^{2}}{|\mathbf{r}-\mathbf{r}'|}\psi_{j}^{*}(\mathbf{r}')\psi_{i}(\mathbf{r}')\psi_{j}(\mathbf{r})\delta_{s_{i}s_{j}}$$
(9)

Which comes out of the exact solution of the crystal Hamiltonian when incorporating spin-states.<sup>36,39</sup> However, when using these expressions for large systems where  $N \ge 10$  this becomes too computationally expensive to use primarily due to the exchange-correlation term of the electron-electron interaction  $U_{XC}$  as previously stated.

#### 2.2 Hohenberg-Kohn Theorems and Kohn-Sham Equations

In order to treat this, 'Schrödinger-like' Kohn-Sham equations are used in place of the original wave-functions allowing the use of a functional in order to approximate the exchange-correlation term.<sup>40–42</sup>

Through the Rayleigh-Ritz variational principle<sup>43</sup>, Hohenberg and Kohn prove two theorems they put forth that allow for this approximation to work. The first, is that given an electron density  $n(\mathbf{r})$  one is able to obtain a value for the potential energy of the ground state with the use of a functional, i.e. that  $U_{XC}$  can be evaluated with a functional provided the electron density is known. The second is that for the ground state of the system there is only one unique electron density that corresponds to this state.<sup>40</sup>.

In the context of DFT, this idea is used to iteratively evaluate the energy of the system in a self-consistent process in order to try to minimize the energy of the ground state. An initial electron density is formulated from the crystal structure and atomic data provided by the user, some parameter is varied such as atomic and/or electron position, the new electron density is evaluated, and through the use of a functional the energy of the new state and previous state is compared. If the new state resulted in a lower energy it is carried forward and used to evaluate the next step as the new 'initial' density. If the new state resulted in a higher energy, it is discarded and another variation is attempted and compared to the initial density once more. This process continues until the difference in energy between steps meets a tolerance set by the user, at which case the self-consistent loop exits, data for the resolved system is provided, and the calculation is declared complete.

#### 2.3 Exchange Correlation Functionals

Which functional is used in this iterative process can have a drastic effect on the converged solution from the calculation depending on the approximations made and how energy is resolved from the electron density. While there are several to chose from, each incorporates some sort of approximation due to the computational cost previously discussed.

The most basic of these functionals is the local-density approximation (LDA)<sup>41,44</sup> which models the exchange-correlation interaction in equation (9) by assuming the density is the same everywhere and neglects other contributions of the form:<sup>39,45</sup>

$$E_{XC}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r}) \left(\frac{1}{2} \int \frac{n(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \,\mathrm{d}\mathbf{r}'\right) n(\mathbf{r}) \,\mathrm{d}^{3}\mathbf{r}$$
(10)

This leads to the trend that DFT often underestimates the band gap. A step up from this is the generalized gradient approximation (GGA) in which the LDA contribution is taken into account along with a gradient term for the charge density, discarding the assumption of uniform density:<sup>15,45–47</sup>

$$E_{XC}^{GGA}[n(\mathbf{r})] = \int A_{XC}[n(\mathbf{r})]n(\mathbf{r})^{4/3} \,\mathrm{d}\mathbf{r}^3 + \int \frac{C_{XC}[n(\mathbf{r})]|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})^{4/3}} \,\mathrm{d}^3\mathbf{r}$$
(11)

Where  $A_{XC}$  and  $C_{XC}$  are the first and third order coefficients to the gradient expansion correction functional  $F_{XC}$ . GGA is an improvement over LDA, but still tends to underestimate the band gap for the same reason. There are also a variety of forms for this gradient, but the default implementation is generally that of Perdue, Burke, Ernzerhof (PBE)<sup>48,49</sup> and is a good approximation for most systems and calculations. In the PBE form, we break the exchange-correlation term into two separate exchange and correlation terms respectively such that  $E_{XC} = E_X + E_C$ .<sup>15,45,47</sup> Firstly, we have the exchange term:

$$E_X^{GGA_{PBE}}[n(\mathbf{r}), s] = \int n(\mathbf{r}) \left(\frac{1}{2} \int \frac{n(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \,\mathrm{d}\mathbf{r}'\right) n(\mathbf{r}) F_X(s) \,\mathrm{d}^3\mathbf{r}$$
(12)

Where:

$$F_X(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}$$
(13)

s is the dimensionless density gradient:

$$s = \frac{|\nabla n(\mathbf{r})|}{2k_F n(\mathbf{r})} \tag{14}$$

with  $\mu = 0.21951$ , and  $\kappa = 0.804$ .

Secondly, we have the correlation term:

$$E_C^{GGA_{PBE}} = [n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] = \int n(\mathbf{r}) \left( E_C^{LDA}(r_s, \zeta) + H(r_s, \zeta, t) \right) \mathrm{d}^3 \mathbf{r}$$
(15)

Where  $r_s$  is the Wigner-Seits radius:

$$r_s = \left(\frac{3}{4\pi n(\mathbf{r})}\right)^{1/3} \tag{16}$$

 $\zeta$  corresponds to the net spin polarization where  $n \uparrow$  and  $n \downarrow$  correspond to the number of n total electrons that are spin up or spin down respectively:

$$\zeta = \frac{n_{\uparrow} - n_{\downarrow}}{n} \tag{17}$$

$$t = \frac{|\nabla n(\mathbf{r})|}{2\varphi(\zeta)k_s n(\mathbf{r})} \tag{18}$$

with spin-scaling factor  $\varphi(\zeta)$ :

$$\varphi(\zeta) = \frac{(1+\zeta)^{2/3} + (1-\zeta)^{2/3}}{2}$$
(19)

the Thomas-Fermi screening wave number, which incorporates the effects of electric field screening by electrons in a solid:<sup>50,51</sup>

$$k_s = \sqrt{\frac{4k_F}{\pi}} \tag{20}$$

and our Fermi radius, or radius of a sphere in k-space:

$$k_F = (3\pi^2 n(\mathbf{r}))^{1/3} \tag{21}$$

In continuing to improve the description of the system, a corrective term may be introduced in order to account for the missing contribution from this approximation, particularly for localized d- and f-orbitals in strongly correlated materials like NiO.<sup>52</sup> Known as the Hubbard Potential,<sup>53,54</sup> a constant energy value U is imposed on one or several orbitals in order to better describe localized atomic orbitals at the top of the valence band. Referred to as LDA+U or GGA+U, the selection of U value and orbital can heavily influence the result of the calculation and should be selected carefully.<sup>55</sup> In the case of GGA+U, our functional for exchange and correlation becomes:<sup>15</sup>

$$E_{XC}^{GGA+U} = E_{XC}^{GGA} + \frac{U}{2} \sum_{i,j,\sigma} \rho_{ij}^{\sigma} \rho_{ji}^{\sigma}$$
(22)

Where  $\rho$  is the density matrix of the electrons in the orbital the Hubbard potential is applied to and  $\sigma$  is the spin quantum number. For additional details on the Dudarev approach to the Hubbard potential energy and its implementation in DFT, see Reference<sup>52</sup>. When doing calculations, U is a constant supplied by the user and chosen or optimized for agreement with known experimental physical properties.<sup>56</sup> In this work we do not uniquely determine the Hubbard potential used, but instead use a well-known U value previously optimized for NiO in other work<sup>2,15,27</sup> and compare these results to those of the following approach. Finally, these systems may be evaluated using some sort of hybrid functional which mixes contributions from the GGA approximate solution and from the exact solution via the Hartree-Fock equations previously discussed given by:<sup>57</sup>

$$E_{XC}^{hybrid} = \alpha E_X^{HF} + (1 - \alpha) E_X^{GGA} + E_C^{GGA}$$
(23)

Where  $\alpha$  is a mixing parameter that determines the weight each contribution has to the total energy. In this work the hybrid functional HSE06 is used and mixes a 75% GGA contribution with a 25% exact contribution, which corresponds to an  $\alpha$  value of 0.25.

In this work we adopt the GGA+U approach with the previously stated +U of 5.3 eV applied to the d-orbital of Ni and the transition metal impurities, which has been previously tested and used in the literature to correctly reproduce important features such as band gap and density of states for the pristine and Fe-doped systems,<sup>2,15,27</sup> alongside the HSE06 approach and draw comparisons between the two.

#### 2.4 VASP

DFT calculations were done using the The Vienna Ab Initio Simulation Package (VASP).<sup>58–62</sup> In addition to the theory described above, VASP implements the Born-Oppenheimer approximation where ionic motion is neglected, the non-valence core states are considered 'frozen', and the contribution of those electrons and the atom itself are modeled using a pseudopotential while leaving the valence electrons explicitly able to interact and are treated in the self-consistent calculation. While this is not strictly necessary for convergence, and codes such as WIEN2k<sup>63</sup> do not use this idea and instead explicitly evaluate the contribution of the core electrons, the idea of pseudopotentials is implemented in VASP in the form of the POTCAR file.<sup>61</sup> The pseudopotentials used in this work were implemented using the projected augmented plane wave (PAW) method<sup>62,64,65</sup> and are generally available to the user as a repository. Additionally, since

NiO is well-known to be an anti-ferromagnetic (AFM) material,<sup>2,8,10</sup> calculations were done using spin polarization in order to account for this important feature.

In order to study the effect intrinsic defects and impurities have on the material within this framework a supercell was constructed and used. For a 4 atom unit cell which may be referred to as a 1x1x1 cell, a 32 atom 2x2x2 cell may be constructed by repeating the principal unit cell along each lattice vector resulting in a larger conventional cell to be treated when VASP replicates the lattice. The advantage of such an approach is that it allows for greater granularity when studying various concentrations, where a 2x2x2 32atom supercell allows for doping concentration to be evaluated in steps of 6.25% for a single species (1 of 16 Ni or O), as opposed to 50% in the original 4 atom cell. Unfortunately, as the system increases in size there is an exponential growth in the time needed to converge the system as well. Thus it is up to the researcher how much granularity they need and are able to obtain with the resources available to them, and how long they are willing to wait for each individual calculation to finish. For the systems described later on in this work, a typical runtime for NiO in a 32 atom 2x2x2 supercell with spin polarization and some sort of defect or impurity would take about 3 hours to converge with GGA+U, and about 1-2 days with HSE06 on the LEAP cluster here at Texas State University.

As input, VASP generally takes the requires parameters in the form of 4 files. The INCAR file, in which the technical parameters of the calculation such as convergence criteria and functional are declared through the use of various 'tags'; the KPOINTS file, in which the user defines their k-point mesh they wish to sample the crystal with; the POSCAR file, in which the crystal structure and number of atoms in the unit or conventional cell you wish to evaluate; and the POTCAR file, which contains the pseudopotential data previously described. As output, the files of note are the CHGCAR file, which contains the converged charge density of the system; the CONTCAR file, which contains the new atomic positions if atoms were moved from their initial POSCAR

positions during a calculation with ionic relaxation; the EIGENVAL file, which contains the list of energy eigenstates as a function of k-point and band number; the OUTCAR which contains an overview of the calculation and the complex components of the dielectric function for an optical calculation; and the WAVECAR file, which contains the converged electron wavefunctions. Graphical representations of crystal structures and charge densities were done with the use of the VESTA software.<sup>66</sup> The inclusion of relativistic effects was examined using spin-orbit coupling (SOC) for the pristine material and systems with transition metal impurities using the GGA+U approach. Aside from slightly shifting the band gap by less than 0.1 eV, which is a well-known feature of SOC,<sup>67</sup> it was found that SOC had a negligible effect on the result of these calculations. Thus calculations shown here and compared to the HSE06 approach do not include SOC. Forces on the ions for each converged calculation were minimized to the order of 10 meV/Å or less.<sup>2</sup>

#### **2.5 Optical Properties**

In order to evaluate the frequency dependent complex dielectric function and subsequent optical properties of a system, one needs to use the INCAR tag LOPTICS. This yields a 2nd rank symmetric tensor of size 3x3 with 3 unique diagonal and 3 unique off-diagonal elements in the form of X, Y, Z, XY, YZ, and ZX respectively for both the real and imaginary components of the dielectric function.<sup>68</sup> These elements are tabulated as a function of energy at the discrete points calculated by VASP and written to the OUTCAR file of the calculation. Explicitly, VASP first finds the imaginary component  $\epsilon_2$  and uses this to find the real component  $\epsilon_1$  using the Kramers-Kronig transformation:<sup>69,70</sup>

$$\epsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2 \omega^2}\right) \sum_{i,j} \int \langle i | M | j \rangle^2 f_i(1 - f_i) \delta(E_f - E_i - \omega) \,\mathrm{d}^3k \tag{24}$$

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'$$
(25)

Where M is the dipole matrix, i and j are initial and final states respectively,  $f_i$  is the Fermi distribution function for the  $i^{th}$  state,  $E_i$  is the energy of the electron in the  $i^{th}$  state,  $\omega$  is the frequency of the incident photon and P stands for the principal value of the integral. Once the complex dielectric function has been obtained, the following expressions may be used to derive the optical properties of the material where  $\epsilon_1$  and  $\epsilon_2$  are the real and imaginary components of the function respectively.<sup>69,70</sup>

For the refractive index n:

$$n(\omega) = \frac{\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} + \epsilon_1(\omega)^{1/2}}{\sqrt{2}}$$
(26)

For the extinction coefficient k:

$$k(\omega) = \frac{\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} - \epsilon_1(\omega)^{1/2}}{\sqrt{2}}$$
(27)

For the reflectivity *R*:

$$R(\omega) = \frac{[n(\omega) - 1]^2 + k^2(\omega)}{[n(\omega) + 1]^2 + k^2(\omega)}$$
(28)

For the absorption coefficient  $\alpha$ :

$$\alpha(\omega) = \frac{2\omega k(\omega)}{c} \tag{29}$$

For the optical conductivity  $\sigma$ :

$$\sigma(\omega) = \frac{\omega}{4\pi} \epsilon_2(\omega) \tag{30}$$

For the energy loss function *L*:

$$L(\omega) = \frac{\epsilon_2(\omega)}{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)}$$
(31)

Where each property also has an associated 3x3 2nd rank tensor with diagonal and off-diagonal elements as with the original dielectric functions.

#### 2.6 Formation Energies

The calculation of formation energies of a defect D in a crystalline solid in a charge state q was done using the following expression:<sup>71</sup>

$$E_f[D^q] = E_{tot}[D^q] - E_{tot}[\text{bulk}] - \sum_i n_i \mu_i + (\epsilon_f + E_v)q$$
(32)

Since we have a few terms that need more description than is typical, let us list them where for each term we have:

- $E_f[D^q]$ : The formation energy of the system under consideration.
- $E_{tot}[D^q]$ : The total energy of the system under consideration. Available in the OUTCAR file output of a VASP calculation labeled as TOTEN.
- *E<sub>tot</sub>*[bulk]: The total energy of the 'ideal' version of system being considered, i.e. without any defects. Available in the OUTCAR file output of a VASP calculation labeled as TOTEN.
- $n_i$ : The number of atoms of element *i* being added (+) or removed (-) where the negative in front of the sum preserves the sign of this quantity.
- $\mu_i$ : The chemical potential of element *i*.
- $\epsilon_f$ : The Fermi level for the defect or impurity being calculated. This value is typically the highest occupied state and assigned as the valence band maximum (VBM), however when calculating formation energy we may consider not only the VBM, but also values within the band gap by incrementing this value from the VBM to the conduction band minimum (CBM) resulting in the slope typical of formation energy plots.<sup>16</sup>

- $E_v$ : The valance band maximum (VBM) of the system under consideration.
- q: The charged state of the system under consideration.

In the case where only the neutral charge states are considered such that q = 0, expression (32) then becomes:

$$E_f[D] = E_{tot}[D] - E_{tot}[\text{bulk}] - \sum_i n_i \mu_i$$
(33)

Upfront this appears fairly simple, just calculate the value for each term and plug it in, however the values for the chemical potential terms  $\mu_i$  require a little more consideration. How these chemical potentials were determined in the context of NiO is discussed in the beginning of Chapter 4.

#### **3. RESULTS OF ELECTRONIC AND OPTICAL CALCULATIONS**

All the crystal structures and charge density plots shown in this work were produced using VESTA.66 First, the electronic band structure, density of states, and optical properties are all shown for pristine NiO. Subsequently, each of the defects and impurities mentioned previously in Chapter 1 are studied in the same manner and compared to the pristine material and each other. Here we use the notation of  $n A_B$  to denote a number of n atoms of species A replacing n atoms of species B in the lattice. Crystal structures and charge planes for each system are shown for the HSE06 case since there was no significant difference between the GGA+U and HSE06 functional in terms of ionic relaxation. Charge planes shown are defined by [-1,2,-1] and contain the [111] direction, where the charge density is normalized by the highest absolute value and displayed on a scale from 0 to 1. Electronic band structures are plotted along the high symmetry lines of the 1<sup>st</sup> Brillouin Zone with the Fermi Energy taken as the zero of energy. Lastly, with the exception of the C<sub>o</sub> case, optical properties shown here are all the X contribution of the tensor described in Chapter 2 as the contribution of all diagonal elements were all within 5% of each other and considered isotropic, with off-diagonal elements of around 5 orders of magnitude less and considered negligible in every case. In the case of Co the X contribution was anisotropic to both Y and Z, which were isotropic to each other, and thus the X and Y directions are both plotted for this system. Each optical plot has dotted reference lines for the lower and upper bounds of the visible range at 1.77 eV and 3.10 eV (700 nm and 400 nm) respectively in order to facilitate the examination of features within the visible and UV regimes, which are of particular interest for solar cell applications. It is also worth noting that optical properties shown are only for direct transitions in the band structure due to the Born-Oppenheimer approximation.

#### **3.1 Pristine NiO**

In order to examine what effect the defects and impurities in question have on NiO, we need to first establish what the crystal structure and behavior of the pristine material looks like for each of the functionals we want to evaluate these systems with. First building our unit cell and subsequent 2x2x2 supercell, electronic and optical properties are shown for the pristine material within the GGA+U and HSE06 approaches.

#### 3.1.1 Comparison of Functionals and Configurations

When building a unit cell for a material is it desirable to have the smallest possible unit cell in order to mitigate the amount of computational resources needed to evaluate it. In the case of NiO, the most important feature that needs to be maintained in this cell is the AFM configuration of the Ni atoms along the [111] direction. Thus at the bare minimum we need 2 Ni atoms and 2 O atoms along the 1x1x1 direction in a rock-salt structure in order to describe this behavior as shown in Figures 1 and 2, where Ni 1 and Ni 2 are spin up and spin down respectively.



Figure 1. NiO Unit Cell Crystal Structure.



Figure 2. NiO Unit Cell Crystal Structure with Charge Density Plane.

This lattice structure is not unique to this work and has been used in other studies as well and is comprised of the following lattice vectors with a previously relaxed lattice constant of a = 4.19 Å.<sup>15</sup>

$$\mathbf{a_1} = a(\hat{\mathbf{x}} + \frac{1}{2}\hat{\mathbf{y}} + \frac{1}{2}\hat{\mathbf{z}})$$
  

$$\mathbf{a_2} = a(\frac{1}{2}\hat{\mathbf{x}} + \hat{\mathbf{y}} + \frac{1}{2}\hat{\mathbf{z}})$$
  

$$\mathbf{a_3} = a(\frac{1}{2}\hat{\mathbf{x}} + \frac{1}{2}\hat{\mathbf{y}} + \hat{\mathbf{z}})$$
(34)

Although cells in different magnetic configurations with the same structure were tested, namely a ferromagnetic system in which both Ni 1 and Ni 2 were spin up and a non-magnetic system in which no spin was considered, the AFM case resulted in the lowest minimized ground state energy for the system by about 3.2 eV with GGA+U, agreeing with the experimental behavior. Following this, different functional approaches were applied to the AFM system whose resulting band structures are compared in Figure 3.



**Figure 3. Comparison of Functionals for the NiO Unit Cell Band Structure.** With the zero of energy as the Fermi Level.

An indirect band gap from T to K is observed for NiO, in agreement with experiment.<sup>14</sup> Comparing these results to the experimental band gap of 3.4 - 4.3 eV, where this range is the result of differing concentrations of native defects commonly seen during the fabrication of NiO,<sup>17</sup> we immediately see that the GGA functional alone tremendously underestimates this value. Following this, we have GGA+U showing improvement over GGA but still underestimating band gap by about 0.2 eV with HSE06 on the higher end of the quoted experimental range. This discrepancy is attributed to the hybridization of O-p with Ni-d, resulting in the Ni-d related conduction band being evaluated at a significantly lower energy than it should, where this issue is addressed within the GGA+U approach by the application of the previously described Hubbard potential to Ni-d.<sup>15</sup> Thus the GGA approach is shown to be insufficient in the case of even pristine NiO and is subsequently neglected.

#### 3.1.2 The Supercell Method

In order to allow for more granularity in concentration when considering a defect or impurity this initial 1x1x1 unit cell is repeated along each lattice vector in order to define a new larger 2x2x2 conventional cell used in the calculation referred to as a 2x2x2 supercell. With 4 atoms initially, this new supercell now contains 32 atoms with the AFM behavior maintained along the [111] direction as shown in Figures 4 and 5.



Figure 4. NiO 2x2x2 Supercell Crystal Structure.



Figure 5. NiO 2x2x2 Supercell Crystal Structure with Charge Density Plane.

Looking now to the electronic character of pristine NiO, we have for GGA+U and HSE06 respectively the band structures in Figures 6 and 7 followed by the density of states in Figures 8 and 9.


Figure 6. NiO GGA+U Band Structure. With the zero of energy as the Fermi Level.



Figure 7. NiO HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 8. NiO GGA+U Density of States.



Figure 9. NiO HSE06 Density of States.

There are a couple important features to keep in mind going forward as we examine how this behavior changes for each of the following systems. For the band structures of both functionals we see an indirect band gap from  $\Gamma$  towards F, which is different from the T to K band gap seen in the unit. This is due to the shrinking of the cell size in reciprocal space in response to the increased cell size, resulting in this feature moving towards the  $\Gamma$ point and is a known effect of the supercell method.<sup>45</sup> Additionally, the density of states describes the VBM as being mainly O-p related but with a considerable Ni-d contribution with the CBM being almost entirely described by Ni-d. The difference in the magnitude of the band gap is attributed to less hybridization of Ni-d and O-p within the HSE06 approach, particularly at the top of the valence band. These features are in agreement with previous theoretical calculations and with experiment.<sup>4,15,16</sup> Lastly, we have in Figure 10 the optical properties for each functional plotted and compared to each other.



**Figure 10. Comparison of NiO GGA+U and HSE06 Optical Properties.** According to the expressions presented in section 2.5.

Although the energy position of the peaks are consistently blue-shifted in the case of HSE06 due to the higher evaluated band gap, the features themselves are extremely similar. Most notably, we see that pristine NiO has very low absorption and optical conductivity in the visible and IR range due to its higher band gap. For subsequent systems, the optical properties will be plotted against those of the pristine material of the same functional to allow for more direct and easier comparison.

### 3.1.3 Pristine NiO Summary

After establishing a 1x1x1 unit cell for pristine NiO in the AFM configuration, a larger 2x2x2 supercell was constructed and examined. All defects and impurities studied in this work were done using the 32 atom 2x2x2 supercell method described and thus each atom added, replaced, or removed in the following systems represents a concentration of 6.25% for the defect or impurity in question.

## **3.2 Native Defects**

Without adding a foreign impurity into the pristine system, there are four major defects to consider for NiO. Either a vacancy of either Ni or O somewhere in the lattice, or an interstitial atom of Ni or O added into the lattice somewhere that is not already a valid lattice position. In the following sections we examine each case respectively along with consideration of the O vacancy in a 2+ charged state.

### 3.2.1 Ni Vacancy

The experimentally observed p-type behavior of NiO is attributed to Ni vacancy defects in the lattice,<sup>13,16</sup> giving rise to the TCO classification of the material. Starting with the removal of a Ni from the lattice, the resulting crystal structure is shown in Figures 11 and 12.



**Figure 11. Ni Vacancy Crystal Structure.** Simulated with the removal of atom Ni 1 from the pristine supercell of Figure 4.



Figure 12. Ni Vacancy Crystal Structure with Charge Density Plane.

The resulting electronic character is described by the band structures in Figures 13 and 14 followed by the density of states in Figures 15 and 16 for GGA+U and HSE06 respectively.



Figure 13. Ni Vacancy GGA+U Band Structure. With the zero of energy as the Fermi Level.



Figure 14. Ni Vacancy HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 15. Ni Vacancy GGA+U Density of States.



Figure 16. Ni Vacancy HSE06 Density of States.

The removal of an Ni atom results in the introduction of unoccupied acceptor states into the band gap due to the O dangling bonds left behind by the removed Ni atom. GGA+U finds this mid-gap state to be only 0.169 eV above the VBM, while HSE06 places this at a much higher 1.987 eV closer to the CBM. While both functionals attribute this state to both Ni-d and O-p, HSE06 shows the contribution of Ni-d to be more significant. Figures 17 and 18 show the resulting optical properties.



**Figure 17. Ni Vacancy GGA+U Optical Properties.** According to the expressions presented in section 2.5.



**Figure 18. Ni Vacancy HSE06 Optical Properties.** According to the expressions presented in section 2.5.

In both cases we see increased absorption in the visible and near-UV range with less absorption a little deeper into the UV regime with this Ni vacancy concentration. GGA+U predicts this increased absorption to be significantly higher than HSE06 with less of a decrease in the UV range, likely due to the lower predicted energy of the mid-gap state introduced by the Ni vacancy. It is worth noting here that this result did not change as a function of which Ni atom was removed, only as a function of the concentration of Ni vacancies in the lattice. The same is true of all defects and impurities studied in this work.

# 3.2.2 O Vacancy

Next we examine the removal of an O atom from its lattice site for both the neutral and 2+ charge state.

# 3.2.2.1 O Vacancy in the Neutral State

For the neutral case the resulting structure is shown in Figures 19 and 20.



**Figure 19. O Vacancy Crystal Structure.** Simulated with the removal of atom O 16 from the pristine supercell of Figure 4.



Figure 20. O Vacancy Crystal Structure with Charge Density Plane.

The primary effect of which is the three neighboring Ni atoms that now lack bonds. The effect this has on the electronic character of the system is shown in the band structures in Figures 21 and 22 followed by the density of states in Figures 23 and 24 for GGA+U and HSE06 respectively.



**Figure 21. O Vacancy GGA+U Band Structure.** With the zero of energy as the Fermi Level.



**Figure 22. O Vacancy HSE06 Band Structure.** With the zero of energy as the Fermi Level.



Figure 23. O Vacancy GGA+U Density of States.



Figure 24. O Vacancy HSE06 Density of States.

These dangling bonds result in an donor occupied state that is above and completely detached from the previous VBM, primarily Ni-d in character, and results in a shrinkage of the band gap by 1.311 eV for GGA+U and 1.539 eV for HSE06; a considerable amount for both functionals. This is not entirely unexpected, since the removal of O from the lattice represents a shift towards the metallic behavior of Ni as well. Ignoring the donor state, the VBM and CBM are in relatively the same positions as in the pristine material, showing less of an effect on these features than in the Ni vacancy case likely due to how strongly correlated the conduction band is with the Ni-d and the effect the removal of an Ni atom has on it as previously shown. The resulting change the removal of an O atom has on the optical properties is seen in Figures 25 and 26.



**Figure 25. O Vacancy GGA+U Optical Properties.** According to the expressions presented in section 2.5.



**Figure 26. O Vacancy HSE06 Optical Properties.** According to the expressions presented in section 2.5.

With the shrinking of the band gap we once more see an increase of the absorption in the visible and the near-UV region with decreased absorption as we move higher in energy before we once again see an increased response in the far-UV region. These results also agree with experiment, where a similar peak was observed in a temperature-dependent study that was attributed to the reduction of O in the lattice.<sup>72</sup> Given that O<sub>2</sub> flow into the chamber is an easily controlled quantity during device fabrication, decreasing this in order to increase the number of O vacancies may be done intentionally if these properties are desired for a particular device.

# **3.2.2.2 O Vacancy in the 2+ Charge State**

Now considering the same initial system but removing two electrons to simulate a 2+ charge for the O vacancy, we obtain the new structure shown in Figures 27 and 28.



Figure 27.  $O^{2+}$  Vacancy Crystal Structure. Simulated by the removal of two electrons in addition to atom O 16 from the pristine supercell of Figure 4.



Figure 28. O<sup>2+</sup> Vacancy Crystal Structure with Charge Density Plane.

As opposed to the neutral state, the 2+ charge state results in a significant perturbation of the lattice, supporting the model of  $O^{2+}$  vacancy movement as the primary driver of the resistive switching mechanism. The subsequent result of this on the electronic properties is seen in the band structures in Figures 29 and 30 followed by the density of states in Figures 31 and 32 for GGA+U and HSE06 respectively.



**Figure 29.** O<sup>2+</sup> Vacancy GGA+U Band Structure. With the zero of energy as the Fermi Level.



Figure 30. O<sup>2+</sup> Vacancy HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 31. O<sup>2+</sup> Vacancy GGA+U Density of States.



Figure 32. O<sup>2+</sup> Vacancy HSE06 Density of States.

Similar to the neutral O vacancy, the 2+ charge state introduces a state above the VBM that is primarily Ni-d related. However, with the removal of these two electrons this state is now unoccupied and found deeper in the band gap. The effect this has on the optical properties is seen in Figures 33 and 34.



**Figure 33.** O<sup>2+</sup> Vacancy GGA+U Optical Properties. According to the expressions presented in section 2.5.



**Figure 34.** O<sup>2+</sup> **Vacancy HSE06 Optical Properties.** According to the expressions presented in section 2.5.

With the introduction of the gap state we see a more drastic variant of the changes observed for the neutral case, with visible, near-, and far-UV having increased response while decreasing around the band gap for the pristine material when looking to the optical absorption and conductivity. We also see slight red-shifting for the 2+ state as compared to the neutral state.

### 3.2.3 Ni Interstitial

Moving on from the removal of intrinsic species, we begin our examination of the addition of an atom into a non-lattice site with the Ni Interstitial case. The resulting structure after many steps of ionic relaxation is shown in Figures 35 and 36.



**Figure 35. Ni Interstitial Crystal Structure.** Simulated by the addition of atom Ni 17 to the pristine supercell of Figure 4.



Figure 36. Ni Interstitial Crystal Structure with Charge Density Plane.

From this we see significant perturbation of the previous lattice structure around the interstitial atom. It is worth noting here that this system was relaxed after 200 steps of ionic relaxation and that fewer steps failed to converge to a solution that did not result in excessive forces or partial occupancies, where most other systems typically required less than 100 ionic steps for the same result. Moving on to the band structures in Figures 37 and 38 followed by the density of states in Figures 39 and 40 for GGA+U and HSE06 respectively, we see the effect this perturbation has on the electronic character of NiO.



**Figure 37. Ni Interstitial GGA+U Band Structure.** With the zero of energy as the Fermi Level.



Figure 38. Ni Interstitial HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 39. Ni Interstitial GGA+U Density of States.



Figure 40. Ni Interstitial HSE06 Density of States.

Along with this perturbation to the structure we see the introduction of an occupied state at the top of the valence band and an unoccupied state close to but detached from the conduction band, with HSE06 showing this separation as significantly higher than GGA+U. This indicates that the Ni interstitial behaves both as a donor and acceptor defect. The resulting optical properties are shown in Figures 41 and 42.



**Figure 41. Ni Interstitial GGA+U Optical Properties.** According to the expressions presented in section 2.5.



**Figure 42. Ni Interstitial HSE06 Optical Properties.** According to the expressions presented in section 2.5.

Similar behavior is seen here as with the Ni vacancy case, albeit with less effect on the response of the system in the visible range but slightly increased response as we move into the UV region apart from the band gap. Despite the bending of the lattice, symmetry with regards to the optical properties is still maintained here with the diagonal elements remaining within the previously stated 5%.

## 3.2.4 O Interstitial

To conclude our series of intrinsic defects, we now consider the case where an O atom is inserted somewhere in the crystal that is not a valid lattice site. The result this has on the structure is shown in Figures 43 and 44.



**Figure 43. O Interstitial Crystal Structure.** Simulated by the addition of atom O 17 to the pristine supercell of Figure 4.



Figure 44. O Interstitial Crystal Structure with Charge Density Plane.

Unlike the Ni interstitial case, the O interstitial does not result in a significant change in the crystal structure likely due to the relative size of O with respect to Ni. Additionally, this interstitial O atom appears to bond with some of the neighboring Ni atoms and blocking some of the bonds of its neighboring O atom, leaving it and the adjacent atoms with dangling bonds. The band structures in Figures 45 and 46 followed by the density of states in Figures 47 and 48 are shown for this system for GGA+U and HSE06 respectively



Figure 45. O Interstitial GGA+U Band Structure. With the zero of energy as the Fermi Level.



Figure 46. O Interstitial HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 47. O Interstitial GGA+U Density of States.


Figure 48. O Interstitial HSE06 Density of States.

These dangling bonds introduce an occupied state at the top of the valance band that is not detached from it as we saw with the neutral O vacancy. This shrinks the calculated band gap by less than 1 eV for either functional with GGA+U being significantly more affected, but otherwise maintains the electronic character of the pristine material. Let us now look to the optical properties in Figures 49 and 50.



**Figure 49. O Interstitial GGA+U Optical Properties.** According to the expressions presented in section 2.5.



**Figure 50. O Interstitial HSE06 Optical Properties.** According to the expressions presented in section 2.5.

The insertion of an O interstitial has little effect on the optical properties in the visible and near-UV ranges, with the flattening of curve the around the band gap and beyond seen previously. In general, O interstitial is shown to have a marginal effect on the electronic and optical character of NiO in small concentrations.

#### **3.2.5 Native Defects Summary**

In particular, the Ni interstitial and O<sup>2+</sup> vacancy resulted in a perturbation of the lattice structure, the former due to the size of an Ni atom being injected into a non-lattice size, and the latter due to the role of this state in the resistive switching mechanism commonly modeled as the mobility of these defects and formation of filaments in the lattice.<sup>16</sup> Intrinsic defects were also shown to decrease the band gap of NiO with the introduction of the Ni vacancy unoccupied acceptor states, O vacancy fully occupied donor states near the top of the valence band, Ni interstitial donor and acceptor states at the top of the valence band and bottom of the conduction band respectively, and O interstitial donor states at the top of the valence band. In every case studied intrinsic defects slightly increased optical absorption and conductivity in the visible and near-UV ranges while decreasing these same properties further into the UV regime as compared to the pristine material, however the O interstitial case observed the smallest of these changes as compared to the other systems studied.

#### **3.3 Impurities**

Now that we have covered the possible single defects intrinsic to NiO, we move on to examine the effects the introduction of a foreign species has on the character of the material. In particular, we examine Cu replacing Ni ( $Cu_{Ni}$ ), Ag replacing Ni ( $Ag_{Ni}$ ), Fe replacing Ni ( $Fe_{Ni}$ ), and C replacing Ni and O ( $C_{Ni}$ ,  $C_O$ ) respectively.

#### 3.3.1 Cu Doping

Looking to Cu as the first substitutional dopant studied, we have 1 and 2 Cu atoms replacing as many Ni atoms representing a doping concentration of 6.25% and 12.5% respectively.

# 3.3.1.1 1 Cu<sub>Ni</sub>

Replacing one Ni atom in the pristine lattice with a Cu atom results in the structure seen in Figures 51 and 52.



Figure 51. 1 Cu<sub>Ni</sub> Crystal Structure. Simulated by the replacement of Ni 1 with Cu 1 in the pristine supercell of Figure 4.



Figure 52. 1 Cu<sub>Ni</sub> Crystal Structure with Charge Density Plane.

Cu appears to cause no significant change in the lattice when replacing Ni, resulting in the same crystal structure as the pristine material. Following this we have the band structures in Figures 53 and 54 followed by the density of states in Figures 55 and 56 for GGA+U and HSE06 respectively.



Figure 53. 1 Cu<sub>Ni</sub> GGA+U Band Structure. With the zero of energy as the Fermi Level.



Figure 54. 1  $Cu_{Ni}$  HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 55. 1 Cu<sub>Ni</sub> GGA+U Density of States.



Figure 56. 1 Cu<sub>Ni</sub> HSE06 Density of States.

For both functionals we see the introduction of vacant states into the band gap acting as acceptor states that are almost entirely related to Cu-d, showing the p-type character of Cu doping described in experiment.<sup>20</sup> The expected behavior of Cu in NiO would likely be that of an n-type dopant given that it is just to the right of Ni in the periodic table with an extra electron. However unlike Ni with a valency of 4s<sup>2</sup>3d<sup>8</sup>, Cu with a valency of 4s<sup>1</sup>3d<sup>10</sup> has an incomplete s-orbital such that when Cu bonds with O in place of Ni we end up with unoccupied states in Cu-d, which is what the mid-gap state is attributed to in Figures 55 and 56. The resulting optical properties are shown in Figures 57 and 58.



Figure 57. 1 Cu<sub>Ni</sub> GGA+U Optical Properties. According to the expressions presented in section 2.5.



Figure 58. 1  $Cu_{Ni}$  HSE06 Optical Properties. According to the expressions presented in section 2.5.

Where we see an increase to the optical absorption and conductivity in the visible and near-UV range, but without nearly as much flattening of features found at higher energies as seen when looking at the native defects. This increase agrees with measured experimental absorption of Cu-doped NiO films as compared to the un-doped material.<sup>5</sup> Calculations done with GGA+U show higher absorption in the visible range than HSE06, however HSE06 predicts a higher contribution in the near-UV range over. This discrepancy stems from the difference in band gap energies in Figures 53 and 54, where HSE06 continues to evaluate systems at a higher energy than GGA+U.

## 3.3.1.2 2 Cu<sub>Ni</sub>

Subsequently with two Cu atoms replacing two Ni atoms we have in Figures 59 and 60 the resulting structure.



Figure 59. 2  $Cu_{Ni}$  Crystal Structure. Simulated by the replacement of Ni 1 with Cu 1 and Ni 2 with Cu 2 respectively in the pristine supercell of Figure 4.



Figure 60. 2  $Cu_{Ni}$  Structure with Charge Density Plane.

We once more see the rock-salt structure maintained without significant perturbation, even though here at 12.5% we are slightly above upper bound of the typical experimental range of  $0-10\%^{6,18}$ . Subsequently, band structures are shown in Figures 61 and 62 followed by the density of states in Figures 63 and 64 for GGA+U and HSE06 respectively.



Figure 61. 2 Cu<sub>Ni</sub> GGA+U Band Structure. With the zero of energy as the Fermi Level.



Figure 62. 2 Cu<sub>Ni</sub> HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 63. 2 Cu<sub>Ni</sub> GGA+U Density of States.



Figure 64. 2 Cu<sub>Ni</sub> HSE06 Density of States.

Once more we see unoccupied mid-gap states appear in all four figures and still Cu-d in nature, now spin-symmetric as shown in Figures 63 and 64 showing that at smaller concentrations of Cu doping the AFM character of NiO is preserved. Optical properties as a result of this are shown in Figures 65 and 66 for both functionals.



Figure 65. 2  $Cu_{Ni}$  GGA+U Optical Properties. According to the expressions presented in section 2.5.



Figure 66. 2  $Cu_{Ni}$  HSE06 Optical Properties. According to the expressions presented in section 2.5.

Increasing the concentration of Cu in NiO results in a continuation of the same trends seen in the previous case. However, we do see a massive discrepancy between functionals in energies up to the upper bound of the visible range, owing to a difference in about 1.2 eV for both the mid-gap state and the CBM between the two functionals. This shrinkage may be due to remaining hybridization effects between either O-p and the d orbital of the dopants or between the d-orbital of the dopants themselves, even after the implementation of the Hubbard potential.

#### **3.3.1.3 Cu Doping Summary**

Substitution of Ni with Cu in NiO results in a rock-salt crystal with no observed lattice distortion for the concentrations studied. The experimentally observed p-type character of Cu doping was confirmed by the emergence of a mid-gap acceptor state in both the band structure and density of state calculations in every case. This results in an increase of optical response in the near-UV range, with GGA+U predicting additional response in the visible range and lower in disagreement with HSE06, particularly for the 2  $Cu_{Ni}$  system. This increased optical response leads to the lower efficiency of solar cells using Cu-doped NiO as a hole extraction layer at higher concentrations as compared to lower concentrations.<sup>6</sup>

### 3.3.2 Ag Doping

Moving down a row in the periodic table, Ag doping is examined as an alternative to Cu doping to improve the electronic and optical character of NiO for solar cell applications.

## 3.3.2.1 1 Ag<sub>Ni</sub>

Replacing one Ni atom with one Ag atom in the pristine lattice results in the new structure shown in Figures 67 and 68.



Figure 67. 1 Ag<sub>Ni</sub> Crystal Structure. Simulated by the replacement of Ni 1 with Ag 1 in the pristine supercell of Figure 4.



Figure 68. 1 Ag<sub>Ni</sub> Crystal Structure with Charge Density Plane.

Where we see that the rock-salt structure is once more maintained. Following this we have the band structures in Figures 69 and 70 along with the density of states in Figures 71 and 72 for GGA+U and HSE06 respectively.



Figure 69. 1 Ag<sub>Ni</sub> GGA+U Band Structure. With the zero of energy as the Fermi Level.



Figure 70. 1 Ag<sub>Ni</sub> HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 71. 1 Ag<sub>Ni</sub> GGA+U Density of States.



Figure 72. 1 Ag<sub>Ni</sub> HSE06 Density of States.

For both functionals we see an unoccupied state added close to the top of the valence band that is only slightly detached if considering a direct transition, and essentially metallic in nature if considering an indirect transition in addition to a reduced band gap overall. Additionally, this behavior also shows Ag to behave as a p-type dopant in NiO as seen for Cu doping with the same reasoning as to why given that Ag also contains an incomplete s orbital. The top of the valence band now becomes primarily O-p and Ag-d related, with results in the optical properties seen in Figures 73 and 74.



**Figure 73. 1 Ag<sub>Ni</sub> GGA+U Optical Properties.** According to the expressions presented in section 2.5.



Figure 74. 1 Ag<sub>Ni</sub> HSE06 Optical Properties. According to the expressions presented in section 2.5.

The introduction of this unoccupied state increases optical absorption and mobility below the band gap while maintaining most of the character of the pristine material at higher energies. GGA+U predicts this increace to take place in the IR and lower visible range while HSE06 shows this to sit within the visible domain, showing a slight red-shift due to the lower calculated bang gap found in the GGA+U approach.

## 3.3.2.2 2 Ag<sub>Ni</sub>

Subsequently with two Ag atoms replacing two Ni atoms we have in Figures 75 and 76:



Figure 75. 2  $Ag_{Ni}$  Crystal Structure. Simulated by the replacement of Ni 1 with Ag 1 and Ni 2 with Ag 2 respectively in the pristine supercell of Figure 4.



Figure 76. 2 Ag<sub>Ni</sub> Crystal Structure with Charge Density Plane.

With the structure once more maintained with the addition of another Ag into the lattice, we move on to the band structures in Figures 77 and 78 followed by the density of states in Figures 79 and 80 for GGA+U and HSE06 respectively.



Figure 77. 2 Ag<sub>Ni</sub> GGA+U Band Structure. With the zero of energy as the Fermi Level.



Figure 78. 2 Ag<sub>Ni</sub> HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 79. 2 Ag<sub>Ni</sub> GGA+U Density of States.



Figure 80. 2  $Ag_{Ni}$  HSE06 Density of States.

From these figures we see a significant and glaring difference in the predicted behavior between the functionals. GGA+U once more places the unoccupied state at the top of the valence band, while HSE06 places this state 0.67 eV above the VBM, introducing a mid-gap state. Figures 81 and 82 show the effect this has on the optical properties.



**Figure 81. 2** Ag<sub>Ni</sub> GGA+U Optical Properties. According to the expressions presented in section 2.5.



Figure 82. 2  $Ag_{Ni}$  HSE06 Optical Properties. According to the expressions presented in section 2.5.

The unoccupied state at the top of the valence band in the GGA+U calculation yields an exaggeration of the behavior seen in the previous 1 Ag<sub>Ni</sub> case, while the HSE06 calculation blue-shifts and shows increased absorption closer to the upper edge of the visible and near-UV range. This large discrepancy between functionals is attributed to the U parameter used, where the more exact solution offered by the HSE06 functional is likely closer to the actual material behavior, where higher concentrations of Ag doping are experimentally shown to decrease conductivity.<sup>7</sup>

#### 3.3.2.3 Ag Doping Summary

Similar to what was seen for Cu, Ag introduces acceptor states into the band gap that contribute to optical absorption. As we move from one Ag to two Ag atoms, we see this acceptor state shift up into the band gap, with GGA+U showing these states to sit at the top of the valence band in both cases, predicting an almost metallic behavior most likely due hybridization issues described in the Cu doping system. HSE06 however predicts this state to detach from the top of the valance band and form a mid-gap state in the band gap. Optical response is once more shown to increase in the region of interest for solar cells with increasing Ag concentration, appearing to blue-shift the peak position for these optical properties potentially allowing for Ag doped NiO to be tuned to a particular energy regime through variance of the doping concentration. For applications as a hole-transport layer however, this heightened absorption is not desirable, and thus Ag-doped NiO works better for this function at lower doping concentrations where the introduced acceptor state may help with conductivity with less optical response than at higher concentrations. This result agrees with measured experimental performance.<sup>7</sup>

#### 3.3.3 Fe Doping

The last of the transition metal impurities studied, Fe doping is of particular interest due to its observed magnetic character and high solubility in NiO at the low pressures these devices are typically fabricated at.<sup>25,28</sup>

# 3.3.3.1 1 Fe<sub>Ni</sub>

Now replacing one Ni atom with an Fe atom, we obtain the resulting structures in Figures 83 and 84.



Figure 83. 1 Fe<sub>Ni</sub> Crystal Structure. Simulated by the replacement of Ni 1 with Fe 1 in the pristine supercell of Figure 4.



Figure 84. 1 Fe<sub>Ni</sub> Crystal Structure with Charge Density Plane.

Satisfied that and the solubility of Fe in NiO is demonstrated and our rock-salt lattice maintained, the band structures for this system is shown in Figures 85 and 86 followed by the density of states in Figures 87 and 88 for GGA+U and HSE06 respectively.



Figure 85. 1 Fe<sub>Ni</sub> GGA+U Band Structure. With the zero of energy as the Fermi Level.



Figure 86. 1 Fe<sub>Ni</sub> HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 87. 1 Fe<sub>Ni</sub> GGA+U Density of States.



Figure 88. 1 Fe<sub>Ni</sub> HSE06 Density of States.

Here we see the introduction of an occupied state at the top of the valence band, shrinking the band gap without the addition of a mid-gap or detached state into the band structure and showing Fe to behave as an n-type dopant in NiO. The effect of this reduced band gap on the optical properties is shown in Figures 89 and 90.



Figure 89. 1 Fe<sub>Ni</sub> GGA+U Optical Properties. According to the expressions presented in section 2.5.



Figure 90. 1 Fe<sub>Ni</sub> HSE06 Optical Properties. According to the expressions presented in section 2.5.

Fe doping is shown to negatively impact the optical absorption and reflectivity of the material until we reach higher energies further into the UV region. In the visible and lower UV region around the band gap, Fe doping in NiO reduced both of these properties, leading to increased transmittance and with about the same optical conductivity as the pristine material. This behavior has been previously predicted by Petersen et al. using GGA+U.<sup>15</sup>
# 3.3.3.2 2 Fe<sub>Ni</sub>

Subsequently with two Fe atoms replacing two Ni atoms we have in Figures 91 and 92 the resulting crystal lattice:



Figure 91. 2 Fe<sub>Ni</sub> Crystal Structure. Simulated by the replacement of Ni 1 with Fe 1 and Ni 2 with Fe 2 respectively in the pristine supercell of Figure 4.



Figure 92. 2 Fe<sub>Ni</sub> Crystal Structure with Charge Density Plane.

The increased concentration of Fe in NiO is shown to maintain the rock-salt structure of the material. This new lattice results in the band structures of Figures 93 and 94 followed by the density of states of Figures 95 and 96 for GGA+U and HSE06 respectively.



Figure 93. 2 Fe<sub>Ni</sub> GGA+U Band Structure. With the zero of energy as the Fermi Level.



Figure 94. 2 Fe<sub>Ni</sub> HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 95. 2 Fe<sub>Ni</sub> GGA+U Density of States.



Figure 96. 2 Fe<sub>Ni</sub> HSE06 Density of States.

With the addition of another Fe atom into the lattice we once more see the n-type character of Fe doping in NiO with the addition of occupied states to the top of the valence band. Additionally, we see that the density of states in both cases is spin-symmetric, confirming that the AFM character is maintained at this higher concentration of Fe. Finally, we have the optical properties for this system as shown in Figures 97 and 98.



Figure 97. 2 Fe<sub>Ni</sub> GGA+U Optical Properties. According to the expressions presented in section 2.5.



Figure 98. 2 Fe<sub>Ni</sub> HSE06 Optical Properties. According to the expressions presented in section 2.5.

In which we see very little change as compared to pristine NiO once more. What change we do see is a decrease in every property up until after the band gap, especially around the band-gap. Given that both optical reflectivity and absorption are continuing to decrease with the addition of more Fe into the lattice, Fe-doped NiO is shown to be more a more transparent TCO than the pristine material.

# 3.3.3.3 Fe Doping Summary

Fe doping in NiO results in a consistent change in the band gap by adding occupied states to the top of the valence band that is not detached from it. This behavior allows for a tunable and reduced band gap as compared to the pristine material without changing the overall character of the material, making Fe doping a strong candidate for treating NiO for different memristor and RRAM applications. In terms of optical performance, Fe doping is also shown to increase the transparency of the material and reduce optical conductivity. However, lack of an acceptor state due to the n-type behavior of Fe doping may hinder performance as a hole transport layer for solar cell applications as compared to a p-type dopant.

# 3.3.4 C Doping

Lastly we look to the effect C replacing either Ni or O in the lattice has on the material behavior. Starting with the  $C_{Ni}$  case and then to the  $C_O$  case, we first compare the GGA+U and HSE06 approach for each before comparing them to each other.

# 3.3.4.1 1 C<sub>Ni</sub>

Replacing one Ni atom with a C atom in the lattice results in the crystal structure seen in Figures 99 and 100.



Figure 99. 1  $C_{Ni}$  Crystal Structure. Simulated by the replacement of Ni 1 with C 1 in the pristine supercell of Figure 4.



Figure 100. 1 C<sub>Ni</sub> Crystal Structure with Charge Density Plane.

From this lattice we see C taking over the bonds the previous Ni atom had with O as seen with the transition metal dopants, slightly bending the lattice due to a shorter bond length but appearing to still maintain the overall rock-salt structure at this concentration. Following this, the band structures are shown in Figures 101 and 102 followed by the density of states in Figures 103 and 104 for GGA+U and HSE06 respectively.



Figure 101. 1 C<sub>Ni</sub> GGA+U Band Structure. With the zero of energy as the Fermi Level.



Figure 102. 1  $C_{\rm Ni}$  HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 103. 1 C<sub>Ni</sub> GGA+U Density of States.



Figure 104. 1 C<sub>Ni</sub> HSE06 Density of States.

The introduction of C into the lattice adds occupied states at the top of the valence band. Thus we see C behaving as an n-type dopant when replacing Ni in NiO. The consequent optical properties are shown in Figures 105 and 106.



Figure 105. 1  $C_{Ni}$  GGA+U Optical Properties. According to the expressions presented in section 2.5.



Figure 106. 1  $C_{Ni}$  HSE06 Optical Properties. According to the expressions presented in section 2.5.

In this case we see a significant changes of the optical absorption and conductivity in the visible and near-UV range with decrease in these same properties at slightly higher energies. GGA+U predicts this increase to be significantly larger than the HSE06 result however, with far less effect in the UV from this dopant.

# 3.3.4.2 1 Co

Following this, we have the last of the impurity systems studied with one C atom replacing one O atom yielding the structures seen in Figures 107 and 108.



**Figure 107. 1** C<sub>0</sub> Crystal Structure. Simulated by the replacement of O 1 with C 1 in the pristine supercell of Figure 4.



Figure 108. 1 Co Crystal Structure with Charge Density Plane.

Where we see the C atom shifts inward along the [111] direction slightly as compared to the O atom it replaces in the pristine material. Additionally, we see in Figure 108 that the introduction of  $C_0$  results in a lack of bonds with the neighboring Ni atoms as compared to the O that previously occupied this lattice site. The fact that C gas two less valence electrons than O (C:  $2s^22p^2$ , O:  $2s^22p^4$ ) pushes an unoccupied state up into the band gap region, found above the top of the valance band at 0.186 eV for GGA+U and 1.307 eV for HSE06. This produces the band structures in Figures 109 and 110 followed by the density of states in Figures 111 and 112 for GGA+U and HSE06 respectively.



Figure 109. 1 Co GGA+U Band Structure. With the zero of energy as the Fermi Level.



Figure 110. 1  $C_0$  HSE06 Band Structure. With the zero of energy as the Fermi Level.



Figure 111. 1 Co GGA+U Density of States.



Figure 112. 1 Co HSE06 Density of States.

The introduction of an unoccupied mid-gap state indicates an acceptor character showing  $C_0$  to behave as a p-type dopant contrary to the previous case,  $C_{Ni}$ , where we had n-type behavior. For the other p-type dopants studied in this work the mid gap state is attributed to the impurity itself, but for  $C_0$  this state is mostly Ni-3d related. An explanation for this behavior can be seen in Figure 108, where unlike the  $C_{Ni}$  case where C took over the bonds with O of the replaced Ni atom we instead see  $C_0$  act like an interstitial impurity and not bonded to any of the neighboring Ni atoms. The resulting incomplete Ni-d orbital gives rise to the mid-gap state seen in Figures 111 and 112. The effect this has on the optical properties is seen in Figures 113 and 114.



**Figure 113. 1 Co GGA+U Optical Properties.** According to the expressions presented in section 2.5.



**Figure 114. 1 Co HSE06 Optical Properties.** According to the expressions presented in section 2.5.

Looking to the optical properties, increase is seen in the absorption of the C<sub>O</sub> system over pristine NiO particularly in the visible and UV range once more with a reduction around the band gap of the pristine material. Unique to this system, we see that the difference between diagonal elements of the tensor that comprises each of these properties falls outside the previously stated 5% tolerance. Not only are these the regimes of interest for solar cells, but the anisotropy observed may lead to preferred crystal orientations for different applications depending on the energy range of interest. This increased optical response is likely due to the introduction of the acceptor state seen in Figures 111 and 112.

#### **3.3.4.3 C Doping Summary**

The character of C doping is shown to vary drastically depending on which intrinsic species it is replacing, with  $C_{Ni}$  acting as an n-type dopant and  $C_O$  behaving as a p-type dopant. From crystal structure plots, this difference is attributed to how C interacts with the neighboring species after it is inserted, with C bonding to O when replacing Ni and sitting in the lattice without bonds when replacing O. Both cases show increased optical response in the region of interest to solar cell applications, with both directions for the  $C_O$  case having higher absorption and reflectivity than  $C_{Ni}$ .

#### **3.3.5 Impurities Summary**

Cu and Ag are shown to both introduce unoccupied states into the band gap and behave as p-type dopants in NiO, where Ag doping yields shallow acceptor states near the VBM and Cu doping placing these states closer to the CBM. In both cases GGA+U is shown to have discrepancies with HSE06, indicating that the U value from the literature used did not accurately describe the valence band edge for these impurities leading to hybridization issues between orbitals. Looking to the HSE06 results then, doping in both cases resulted in increased optical performance in the visible and near-UV ranges of interest for solar cell applications. In particular, Ag doping shows significant increase over the pristine material as compared Cu doping at the same concentrations. However, the conductivity of the material should benefit much more from the shallow acceptor state introduced by Ag doping, and low concentrations of Ag doping may lead to better performance as a hole-transport layer than Cu doping. Therefore, these devices may benefit from additional experimentation with Ag-doped NiO as opposed to Cu-doped NiO which is far more prominent in the literature.

Fe doping is shown to behave as an n-type dopant as observed with experiment<sup>24</sup> and previous calculations,<sup>15</sup> adding occupied states to the top of the valence band and shrinking the band gap while maintaining the AFM behavior. This allows for a tunable

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band gap with a dopant observed to be highly soluble at low pressures<sup>28</sup> in order to help tailor devices for memristor and RRAM applications. Additionally, Fe doping is shown to decrease optical absorption and reflectivity at higher energies while not increasing either property at lower energies, making the resulting material more transparent than pristine NiO.

Both cases considered for C doping showed similar effects, with  $C_{Ni}$  having a similar amount of increased optical response in the visible and near-UV range as Cu doping with both directions of  $C_0$  behaving more similar to Ag doping. However both cases negatively affect optical absorption at higher energies similar to what was seen with the native defects. If these regions are not of interest for the device application in question,  $C_0$  may offer a cheaper alternative to Ag doping in order to obtain similar optical properties and possibly contributes to or even explains observed performance of NiO/graphene heterostructures.<sup>30</sup>

#### 4. FORMATION ENERGY CALCULATIONS

As described in expression (32) in Chapter 2, the energy cost of a particular defect or impurity forming with the NiO lattice may be evaluated once we have the chemical potentials of the elements involved and the total energy of both the pristine and altered system. While what one calls the total energy of anything is somewhat arbitrary and within this context changes depending on the functional the system is being evaluated with, the quantity used is the difference between the pristine and altered system rather than the absolute value of either.

# 4.1 Chemical Potentials

Looking to the last term in expression (33), we need to determine  $n_i$  and  $\mu_i$  for each case, where i is the atomic element being considered.  $n_i$  is simply the number of that element being added or removed such that sign in preserved. Thus in the case of 2 Cu replacing 2 Ni, one would have  $n_{Cu} = 2$  and  $n_{Ni} = -2$ . The chemical potentials of these elements,  $\mu_i$ , may be calculated from the total energy of one atom an 'ideal' system of that element. For the calculations done here, these systems consist of Ni, Cu, Ag, and Fe in their respective metallic configurations; O in an O<sub>2</sub> molecule that was isolated by defining an arbitrarily large unit cell such that when this cell is repeated throughout space for our periodic boundary conditions neighboring O<sub>2</sub> molecules do not interfere with each other; and C within a graphene structure due to the experimental motivation.<sup>30</sup> Additionally, in the case of the O<sub>2</sub> molecule the total energy of the converged system is divided by two, since the system is composed of two O atoms and the desired value is in units of eV per atom.

For NiO there are two conditions from the intrinsic material that need to be examined, O-Poor and O-Rich. These may be described as Ni-Rich and Ni-Poor respectively, but they are most commonly referred to in the literature in terms of O since when NiO films (or transition metal oxides in general) are fabricated  $O_2$  flow into the chamber is easily controlled and an integral quantity for analyzing the resulting film. These O-Poor or O-Rich conditions change the values for the chemical potential of O and Ni since they are intrinsic to the system, but do not affect external dopants and one may simply use the values obtained from the ideal system. In order to find our potentials for Ni and O within the NiO system, we need to look to the heat of formation of NiO given by:<sup>71</sup>

$$\Delta_f \text{NiO} = \mu_{NiO}^* - \mu_{Ni}^* - \mu_O^*$$
(35)

Where  $\mu_{\text{NiO}}^* = -10.25065 \text{ eV/molecule}$  from the 1x1x1 unit cell of the pristine system. Since the unit cell used has 4 atoms, 2 Ni and 2 O, this value is half of the total energy from that calculation. Combining this value along with the relevant values from table 1 below gives  $\Delta_f \text{NiO} = -2.4941$ . This value for heat of formation was then compared to the experimental value of -2.4849 eV/molecule.<sup>11</sup> Thus, the calculated value was found to be within 0.01 eV/molecule, verifying that the chemical potentials calculated within the context of the NiO system were accurate. With this value now in hand, we can find our potential such that:

$$\mu_{Ni} = \mu_{Ni}^* + (1 - \gamma) \Delta_f \text{NiO}$$
(36)

$$\mu_O = \mu_O^* + \gamma \Delta_f \text{NiO} \tag{37}$$

Where  $\gamma = 0$  denotes the O-Rich condition and  $\gamma = 1$  denotes the O-Poor condition. These results, along with the chemical potentials for the elements of interest may be found in Table 1. **Table 1. Chemical Potentials.** Calculated chemical potentials in eV/atom for the studied elements within the NiO system where the \* denotes that these values are for an ideal system.

Element:	Calculated Potential:	
$\mu^*_{ m Ni}$	-5.52760	
$\mu^*_{ m O}$	-2.22895	
$\mu_{ m Ni_{O-Rich}}$	-5.52760	
$\mu_{ m Ni_{O-Poor}}$	-8.02380	
$\mu_{ ext{O}_{ ext{O-Rich}}}$	-4.72305	
$\mu_{ ext{O}_{ ext{O} ext{-Poor}}}$	-2.22895	
$\mu^*_{\mathrm{Cu}}$	-3.55024	
$\mu^*_{ m Ag}$	-2.52020	
$\mu^*_{ ext{Fe}}$	-8.21125	
$\mu^*_{ m C}$	-9.24880	

It is worth noting that when these defects are formed or impurities introduced during device fabrication, the structure is most likely in the O-Rich/Ni-Poor condition depending on  $O_2$  flow into the chamber. When operating after fabrication however, the device is most likely in the O-Poor/Ni-Rich condition.

# 4.2 Comparison of Defects and Impurities

For each of the systems studied the converged total energy was collected and is shown in Tables 2 and 3 for GGA+U and HSE06 respectively.

 Table 2. GGA+U Total Energies. Total system energy in eV of the studied defects and impurities in NiO using GGA+U.

System (GGA+U):	Total Energy (TOTEN)
Pristine NiO	-164.066
Ni Vacancy	-157.616
O Vacancy	-154.883
O <sup>2+</sup> Vacancy	-169.302
Ni Interstitial	-160.174
O Interstitial	-165.712
1 Cu <sub>Ni</sub>	-161.583
2 Cu <sub>Ni</sub>	-159.606
1 Ag <sub>Ni</sub>	-158.964
2 Ag <sub>Ni</sub>	-153.482
1 Fe <sub>Ni</sub>	-167.153
2 Fe <sub>Ni</sub>	-170.170
C <sub>Ni</sub>	-162.753
Co	-161.137

**Table 3. HSE06 Total Energies.** Total system energy in eV of the studied defects andimpurities in NiO using HSE06.

System (HSE06):	Total Energy (TOTEN)		
Pristine NiO	-259.321		
Ni Vacancy	-248.682		
O Vacancy	-248.267		
O <sup>2+</sup> Vacancy	-256.357		
Ni Interstitial	-255.039		
O Interstitial	-263.818		
1 Cu <sub>Ni</sub>	-254.763		
$2 \ Cu_{Ni}$	-250.314		
1 Ag <sub>Ni</sub>	-251.734		
$2 \mathrm{Ag}_{\mathrm{Ni}}$	-243.657		
1 Fe <sub>Ni</sub>	-265.867		
2 Fe <sub>Ni</sub>	-272.703		
C <sub>Ni</sub>	-257.399		
Co	-255.724		

Then, using the method and values previously described, the formation energies of each defect and impurity was evaluated using expressions (32, 33) and are shown in Tables 4 and 5 for GGA+U and HSE06 respectively. It is worth noting that the  $O^{2+}$  vacancy state formation energy was calculated with expression (32) assuming  $\epsilon_f = 0$ .

**Table 4. GGA+U Formation Energies.** Formation energies in eV of the studied defectsand impurities in NiO using GGA+U.

System (GGA+U):	O-Rich/Ni-Poor	O-Poor/Ni-Rich
Ni Vacancy	-1.575	0.920
O Vacancy	6.954	4.460
O <sup>2+</sup> Vacancy	-7.645	-9.959
Ni Interstitial	11.915	9.421
O Interstitial	0.583	3.077
1 Cu <sub>Ni</sub>	-1.991	0.503
2 Cu <sub>Ni</sub>	-4.488	0.501
1 Ag <sub>Ni</sub>	-0.402	-2.092
2 Ag <sub>Ni</sub>	-0.424	4.564
1 Fe <sub>Ni</sub>	-2.900	-0.406
2 Fe <sub>Ni</sub>	-5.730	-0.742
C <sub>Ni</sub>	2.538	5.032
Co	9.948	7.454

 Table 5. HSE06 Formation Energies. Formation energies in eV of the studied defects

 and impurities in NiO using HSE06.

System (HSE06):	O-Rich/Ni-Poor	O-Poor/Ni-Rich
Ni Vacancy	2.615	5.109
O Vacancy	8.825	6.331
O <sup>2+</sup> Vacancy	0.735	-1.759
Ni Interstitial	12.306	9.812
O Interstitial	-2.268	0.226
1 Cu <sub>Ni</sub>	0.084	2.579
2 Cu <sub>Ni</sub>	0.060	5.048
1 Ag <sub>Ni</sub>	2.083	4.577
$2 \text{ Ag}_{\text{Ni}}$	4.656	9.644
1 Fe <sub>Ni</sub>	-6.358	-3.864
2 Fe <sub>Ni</sub>	-13.007	-8.019
C <sub>Ni</sub>	3.147	5.641
Co	10.616	8.122

Comparing these functionals, we see a difference in every value listed for the same system between the two due to the difference in how the total energy is evaluated as shown in Tables 2 and 3 and discussed in Chapter 2. What is more important when analyzing these results then is less the absolute value obtained, but rather the relative trends between systems evaluated with the same functional. With this in mind, many of the trends seen and described below are demonstrated in both Table 4 with GGA+U and Table 5 with HSE06, with exceptions explicitly mentioned below.

Between the intrinsic defects in the neutral charge state the neutral O vacancy and Ni interstitial are the most energetically expensive defects of the four systems with Ni interstitials being the most expensive defect of all systems studied. A discrepancy is seen between the more favorable of these four, with Ni vacancy shown to be the most stable for GGA+U and O interstitials for HSE06. This is likely due to hybridization between Ni-d and O-p even after the U correction, bringing the energy cost and subsequent total energy of the Ni vacancy system down. In both cases however, the  $O^{2+}$  vacancy is shown to be more stable than any of the neutral defects within the O-Poor/Ni-Rich condition, with O interstitial becoming more favorable in the O-Rich/Ni-Poor condition with HSE06. While fabrication conditions vary based off of  $O_2$  flow to the chamber itself it is generally assumed that they fall within the O-Rich/Ni-Poor regime, while the finished device is within the O-Poor/Ni-Rich condition where filament formation is often modeled with O vacancies within the 2<sup>+</sup> charged state.<sup>3,15,16</sup>. Thus the energetic favorability of the  $O^{2+}$  vacancy in this condition across both functionals is of particular interest as it helps support this model.

Cu doping in NiO is shown to be less favorable than some of the intrinsic defects but still more stable than several other systems, particularly within the O-Rich/Ni-Poor condition. Similarly, Ag doping follows a similar trend but is slightly more energetically expensive than Cu doping, likely due to the increased size of the atom itself.

Both functionals show Fe replacing Ni as being the most energetically favorable impurity, with HSE06 predicting favorability over even the  $O^{2+}$  vacancy. This stability is likely a contributing factor to the high degree of solubility of Fe in NiO as compared to Cu and Ag, with devices being routinely fabricated with concentrations as high as 20% Fe at low pressures<sup>24,28</sup> as opposed to around 10% for Cu and Ag<sup>6,7,18,23</sup>

In the case of C doping, we see that the C replacing Ni case is favorable over C replacing O in both conditions. This result is corroborated by other work in the literature where C replacing O in NiO was shown to not be energetically favorable even when compared to N replacing O.<sup>31,33</sup>

This combined with other work investigating Ni replacing C in graphene indicates that at the boundary of NiO/graphene layers there is a strong possibility of C and Ni atoms swapping lattice sites between structures and acting as substitutional defects in their new positions, creating a heterostructure of sorts.<sup>32</sup> Additionally, this mixing may be a large contributor to measured device properties and could be desirable depending on the application.<sup>30</sup> Lastly, there is less difference between GGA+U and HSE06 seen on the C systems as compared to the transition metal systems since the U value applied to the d orbital of the transition metals is not a factor between the C systems.

#### **5. CONCLUSIONS AND FUTURE WORK**

In this last chapter we present conclusions about the overall work and examine how various results relate to one another. Following this, suggestions and comments on the continuation of this work or possibilities for new directions to pursue with the same methodology are discussed.

# **5.1 Conclusions**

Consistently, a blue-shift was seen when drawing comparisons between GGA+U and HSE06 results, with HSE06 evaluating the band gap and any mid-gap states as being at a higher energy than the GGA+U counterpart in every case. This behavior is expected, as HSE06 considers an HF-like contribution that is neglected within the GGA+U formalism and only partially treated with the Hubbard potential correction U. Particularly, in the 2 Ag<sub>Ni</sub> case the U value of 5.3 eV used was shown to completely disagree with the HSE06 result and be insufficient to accurately describe the behavior of the system. In terms of solar cell applications, Ag-doping in NiO was shown to potentially be more beneficial to performance as a hole transport layer than Cu doping, albeit possibly at an increased cost depending on the concentrations. Particularly, Ag-doped NiO shows the most promising results of the systems studied due to the introduction of a shallow acceptor state at lower concentrations, with higher concentrations to be avoided due to the acceptor state detaching from the top of the valence band along with significantly increased optical absorption and reflectivity in the visible and near-UV range. C doping in NiO may also play a strong role in the measured performance of NiO/graphene heterostructures,<sup>30</sup> and these devices may benefit from intentionally promoting Ni and C doping along the layer boundary during fabrication.

## 5.2 Future Work

It may be of interest to revisit some of these systems, in particular the Cu and Ag doping cases, and re-evaluate the GGA+U calculations with either a higher Hubbard potential on both atoms or different corrections applied to Ni and the impurity. This new U value could then be used in the evaluation of larger supercells for increased granularity in doping concentration that may prove too computationally expensive for the HSE06 approach. The electronic and optical character of the various charge states of the native defects could also be investigated and their descriptions improved. Co-doping between various defects and impurities studied in this work would also be worth investigating. In fabricated films, native defects and foreign impurities are both present in the material and the way these interact with each other may produce some interesting behavior.

In continuing to improve the description of NiO and explore more options available to this versatile material, there are several projects that may be of interest. First is the study of Ta doping and the effect it may have on the character of the NiO film, particularly as it pertains to the resistive switching mechanism, with recent experimental work investigating the introduction of a layer of Ta between NiO films.<sup>73</sup> Such a study may benefit from the use of the hybrid functional HSE06 along with the introduction of SOC to account for relativistic effects due to the significant difference in size of Ta relative to the impurities previously studied. Another potential project would be to continue work in studying the effect of C in NiO, and model an NiO/graphene interface and examine the heterostructure after ionic relaxation along with resulting electronic and optical properties. Additionally, thermal properties for these systems may be examined through the use of an external code such as Gibbs2,<sup>74</sup> which builds off of information from previously converged DFT calculations, and compared to the behavior of the pristine material.

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