Manganites in Perovskite Superlattices: Structural and Electronic Properties

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ABSTRACT

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Perovskite oxides have the general chemical formula ABO$_3$, where A is a rare-earth or alkali-metal cation and B is a transition metal cation. Perovskite oxides can be formed with a variety of constituent elements and exhibit a wide range of properties ranging from insulators, metals to even superconductors. With the development of growth and characterization techniques, more information on their physical and chemical properties has been revealed, which diversified their technological applications.

Perovskite manganites are widely investigated compounds due to the discovery of the colossal magnetoresistance effect in 1994. They have a broad range of structural, electronic, magnetic properties and potential device applications in sensors and spintronics. There is not only the technological importance but also the need to understand the fundamental mechanisms of the unusual magnetic and transport properties that drive enormous attention. Manganites combined with other perovskite oxides are gaining interest due to novel properties especially at the interface, such as interfacial ferromagnetism, exchange bias, interfacial conductivity. Doped manganites exhibit diverse electrical properties as compared to the parent compounds. For instance, hole doped La$_{0.7}$Sr$_{0.3}$MnO$_3$ is a ferromagnetic metal, whereas LaMnO$_3$ is
an antiferromagnetic insulator. Since manganites are strongly correlated systems, heterojunctions composed of manganites and other perovskite oxides are subject to complex coupling of the spin, orbit, charge, and lattice degrees of freedom and exhibit unique electronic, magnetic, and transport properties. Electronic reconstructions, O defects, doping, intersite disorder, magnetic proximity, magnetic exchange, and polar catastrophe are some effects to explain these interfacial phenomena.

In our work we use first-principles calculations to study the structural, electronic, and magnetic properties of manganite based superlattices. Firstly, we investigate the electronic structure of bulk CaMnO$_3$ and LaNiO$_3$. An onsite Coulomb interaction term $U$ is tested for both the Mn and Ni atoms. G-type antiferromagnetism and insulating properties of CaMnO$_3$ are reproduced with $U = 3$ eV and ferromagnetic ordering is favorable when CaMnO$_3$ is strained to the substrate lattice constant. This implies that the CaMnO$_3$ magnetism is sensitive to both strain and the $U$ parameter.

Antiparallel orientation of the Mn and Ti moments has been found experimentally in the BiMnO$_3$/SrTiO$_3$ superlattice. By introducing O defects at different layers, we find similar patterns when the defect is located in the BiO layer. The structural, electronic and magnetic properties are analysed. Strong hybridization between the $d_{3z^2-r^2}$ orbitals of the Mn and Ti atoms near the O defect is found.

The effect of uniaxial strain for the formation of a two-dimensional electron gas and the interfacial Ti magnetic moments of the (LaMnO$_3$)$_2$/(SrTiO$_3$)$_2$ superlattice are investigated. By tuning the strain state from compressive to tensile, we predict under which conditions the spin-polarization of the electron gas is enhanced. Since the thickness ratio of the superlattice correlates with the strain state, we also study the structural, electronic and magnetism trends of (LaMnO$_3$)$_n$/(SrTiO$_3$)$_m$ superlattices with varying layer thicknesses. The main finding is that half-metallicity will vanish for $n, m > 8$. Reduction of the minority band gaps with increasing $n$ and $m$ originates mainly from an energetic downshift of the Ti $d_{xy}$ states.
Along with these, the interrelation between the interface geometry and the electronic properties of the antiferromagnetic/ferromagnetic superlattice BiFeO$_3$/La$_{0.7}$Sr$_{0.3}$MnO$_3$ is investigated. The magnetic and optical properties are also analysed by first principles calculations. The half-metallic character of bulk La$_{0.7}$Sr$_{0.3}$MnO$_3$ is maintained in the superlattice, which implies potential applications on spintronics and memory devices.
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Chapter 1

Introduction

Combining two or more compounds in order to investigate their new possible functions and properties (for electronic device applications) is nowadays a common trend in research and industry. Among these, the transition metal oxide heterostructures play a major role, especially concerning the emergence of new states of matter at artificially constructed heterointerfaces [1]. The complex interactions between oxide films generate various electronic and magnetic properties, such as two dimensional electron gas, superconductivity, colossal magnetoresistance, ferroelectricity, piezoelectricity, interfacial magnetism, exchange bias, etc. From the growth point of view, pulsed laser deposition [2] and molecular beam epitaxy [3] have been the most commonly employed methods for fabricating nanoscale composites.

Among the transition metal oxides, perovskite oxides with the common chemical formula ABO$_3$ have been a popular subject, since for different elements on the A and B sites they give rise to many diverse physical phenomena. Interestingly, more than half of the elements in the periodic table can be placed either on the A site or B site to form a perovskite compound. In the ideal perovskite arrangement the A site cation (large rare-earth or alkali-metal cation) sits in the corner of the cubic unit cell while the B site cation (transition metal cation) sits at the center of the cell surrounded by six O atoms located at the centers of the six surfaces forming a corner sharing BO$_6$ octahedron. Figures 1.1, 1.2 and 1.3 give the schematic views of the cubic perovskite
Figure 1.1: Schematic view of the cubic perovskite structure $\text{ABO}_3$. Green and blue balls represent the A and B site cations, red balls represent the O atoms.

structure, $\sqrt{2} \times \sqrt{2}$ in-plane supercell of the cubic perovskite structure, and top view of the $\sqrt{2} \times \sqrt{2}$ supercell with O octahedra highlighted. In our work, we construct a $\sqrt{2} \times \sqrt{2}$ supercell in order to take into account possible tiltings and rotations of the O octahedra as well as different magnetic orderings (since in the perovskite unit cell antiferromagnetic orderings, such as G and C-types, cannot be modeled for further stability evaluation).

Figure 1.2: Schematic view of the $\sqrt{2} \times \sqrt{2}$ in-plane supercell of the cubic perovskite structure.
The best known cubic perovskite oxide is SrTiO$_3$. However, in reality perovskite oxides often are not in perfect cubic structures but show certain distortions. The relation between the ionic radii of the A, B, and O atoms (described by the tolerance factor $t$) as well as the Jahn-Teller effect are main factors to the structural stability and the degree of distortion in perovskite oxides. Different types such as thin films, superlattices, and heterojunctions have been fabricated with perovskite oxides using methods such as pulsed laser deposition [5], molecular beam epitaxy [6], chemical vapor deposition, and sol-gel spin-coating [7]. The characterization methods include X-ray/ultraviolet photoelectron spectroscopy (XPS/UPS), low energy electron diffraction (LEED), X-ray/neutron diffraction, atomic-force microscopy (AFM), transmission electron microscopy (TEM), scanning tunneling microscopy/spectroscopy (STM/STS), X-ray absorption fine structure (XAFS), inductively coupled plasma mass spectrometry (ICP-MS), etc. Although we have advanced experimental tools and methods available for analysing different properties at the nanoscale, factors such as temperature, pressure, environment, might inaccuracies, for example, when measuring local magnetic moments of atoms. Numerical methods on the other hand can provide detailed information on the material’s electronic proper-
ties. The results only depend on the calculation method, and often can be produced faster as compared to experiments. With the development of supercomputing techniques and calculation methods, more and more materials can be analysed numerically (quantum mechanical calculation) for understanding and predicting the underlying physics. Experimental and theoretical results seem to rely on each other gradually.

There are various types of transition metal perovskite oxides, including manganites, titanates, ferrites, nickelates, cuprates, ruthenates, iridates, etc. In our work, we focus on perovskite superlattices (which are a periodically repeated heterostructure) due to intriguing novel functionalities [8, 9, 10]. In particular we deal with the heterointerfaces between manganites and other perovskite oxides.

Manganites belong to the most commonly investigated perovskite oxides. For instance, in 1994, Jin et al. discovered the colossal magnetoresistance effect (CMR) on epitaxially grown La$_{1-x}$Ca$_x$MnO$_3$ thin films with a magnetoresistance ratio of up to $1.27 \cdot 10^{-5}$ [11]. Since then, many theoretical and experimental investigations on manganites have been conducted. Perovskite manganites not only have potential applications in information storage (magnetic recording), and magnetic sensors but also show rich physical phenomena (Jahn-Teller effect, double exchange, spin/charge/orbital ordering, magnetic coupling, metal-insulator transition). Superlattices obtained by combining manganites with other perovskite oxides yield many novel properties. For instance, interfacial metallicity, exchange bias, two-dimensional electron gas, interfacial ferromagnetism, metal-insulator transition, etc.

Interfacial magnetism and metallicity of transition metal oxides have been attracting considerable interest due to potential applications in spin based technologies. Many investigations of the interfacial properties of new combinations of perovskite oxide heterostructures have been reported [12, 13, 14, 15, 16, 17] and different possible origins are proposed. For instance, electronic reconstructions, polar catastrophe, O defects, intersite disorder, etc can explain the interfacial metallicity to some extent.
For the interfacial magnetism, point defects, magnetic proximity, double exchange interaction, interdiffusion, etc can be main factors. Apparently interfacial magnetism and metallicity correlate to a certain degree and one property can possibly be tuned by the other one.

CaMnO$_3$ is a parent compound of La$_{1-x}$Ca$_x$MnO$_3$. Slight doping of CaMnO$_3$ with Mo, Ru, Fe, or Ti can modify its magnetic, electrical properties and even induce interfacial ferromagnetism \[18\]. Suzuki’s group in 2012 has found interfacial ferromagnetism in CaRuO$_3$/CaMnO$_3$ superlattices and attributed it to double exchange interaction \[16\]. They used exchange bias, polarized neutron reflectivity, scanning transmission electron microscopy, and electron energy loss spectroscopy measurements to analyse the interfacial properties and excluded possible factors for inducing interfacial magnetism such as substrate strain and alloying at the interface. A year later they found similar results in LaNiO$_3$/CaMnO$_3$ superlattices and from comparing the ferromagnetism for different LaNiO$_3$ layer thickness they concluded that only metallic LaNiO$_3$ yields interfacial ferromagnetism \[17\]. Understanding the fundamental physics of this compound on the nanoscale is important for designing future CaMnO$_3$ based heterostructures. In Chapter 3, we study the structural, electronic, and magnetic properties of the LaNiO$_3$ and CaMnO$_3$ perovskites and give insights in the magnetic properties of the combined system. The onsite Coulomb interaction term U turns out to be critical in determining the bulk as well as superlattice magnetism. Additionally, induced Ni magnetic moments at the interface indicate that LaNiO$_3$ at least partially contributes to the interfacial magnetism.

Heterojunctions composed of polar and non-polar perovskite oxides are gaining more attention due to the discovery of two-dimensional electron gases \[19\ 20\ 21\ 22\]. Many factors such as temperature, doping level, defects, external magnetic, electric fields, and strain, etc can affect the coupling of the spin, charge, lattice and orbital degrees of freedom, which in turn may result in different electrical properties. BiMnO$_3$
is a ferromagnetic insulator which has been of much interest due to its multiferroic property [23, 24, 25]. However, the ferroelectricity of BiMnO$_3$ is strongly debated due to the finding of a centrosymmetric C2/c space group [26, 27, 28] instead of the previously proposed non-centrosymmetric monoclinic C2 structure [29, 30]. Orbital ordering closely is connected with ferroelectricity [29]. Magnetic ordering of the system [31] and the stoichiometry of BiMnO$_3$ films [25] are important in determining the ferroelectricity as well. The O stoichiometry plays a crucial role in determining the structural and magnetic properties, too [32]. Interfacial Ti magnetic moments have been found in BiMnO$_3$/SrTiO$_3$ thin films, with antiparallelly aligned Mn and Ti spins [15], where it was suggested that the superexchange interaction between the transferred electrons at the interface and local magnetic moments provided by interfacial Mn ions contribute to the interfacial Ti magnetism. In Chapter 4, we discuss the role of O defects for the structural, electronic, and magnetic properties of the BiMnO$_3$/SrTiO$_3$ interface and propose a possible origin of the interfacial magnetism. O defects in different layers show dramatically different electronic structures. For instance, when the O defect is located in the MnO$_2$ layer the system is an insulator with reduced band gap as compared to the ideal superlattice. When the O defect is located in the BiO layer the system exhibits states at the Fermi. Antiparallelly aligned Ti and Mn magnetic moments are observed similar to the experiment.

Ti interfacial magnetism has also been found at the LaMnO$_3$/SrTiO$_3$ interface [33] showing the importance of strain for the magnetic and electrical properties. The authors in Ref. [34] suggest that uniaxial strain alone without chemical doping can modify the magnetic and electric ordering in manganites. Extensive studies demonstrate that both octahedral deformations and octahedral rotations can be manipulated by strain which in turn allow to control properties such as ferroelectricity, magnetic anisotropy, metal-insulator transition and superconductivity [35]. Uniaxial strains induced by different substrates can alter the structural, magnetic coupling,
and transport properties [36]. It can also modify the magnetic and orbital ordering in LaMnO$_3$ and enhanced the ferroelectricity SrTiO$_3$ [37, 38]. In order to explore the conditions that induce a spin-polarization of Ti atoms and a two dimensional electron gas at the interface, in Chapter 5 we analyse the effect of uniaxial strain (compressive and tensile strain, by decreasing and increasing the out of plane lattice constant) on the structural, electronic and magnetic properties of the (LaMnO$_3$)$_2$/(SrTiO$_3$)$_2$ superlattice. The analyse shows that it is possible to modify the interfacial Ti magnetic moments by tuning the uniaxial strain. In addition, a two dimensional electron gas can be generated by applying compressive strain.

One important factor that controls the state of the superlattice is the thickness ratio. For instance, the strain state of La$_{0.7}$Sr$_{0.3}$MnO$_3$ films can be varied by varying the film thickness, which in turn modifies the electrical conductivity [39]. Similar works about the effect of the different thicknesses are reported in Refs. [40, 41, 42, 43]. Another important finding is the thickness dependence of the metal-insulator transition in the LaAlO$_3$/SrTiO$_3$ system, with a critical thickness of 4 unit cells of LaAlO$_3$ [20]. In Ref. [33] the authors have experimentally analysed the electronic and magnetic properties of epitaxially grown LaMnO$_3$/SrTiO$_3$ superlattices with thickness ratios using X-ray absorption spectroscopy, X-ray linear dichroism, magnetic circular dichroism, etc. They concluded that the orbital occupation of the Mn atoms depends on the layer thickness ratio, which results in different magnetic coupling, and pointed out the strong dependence between the magnetic signal and the thickness ratio of the superlattice. Magnetic and transport properties of the LaMnO$_3$/SrTiO$_3$ superlattice are also strongly influenced by the doping level at the interface with different component layer thicknesses [44]. Motivated by these works, in Chapter 6 we study the structural, electronic, and magnetic properties of (LaMnO$_3$)$_n$/(SrTiO$_3$)$_m$ superlattices and report trends with varying layer thicknesses. The subscripts $n$ and $m$ represent the number of unit cells in each component. All systems exhibit a
half-metallic character with reduced minority spin band gaps with increasing layer thicknesses. By analysing the projected densities of states of the Ti $d$ orbitals, we will conclude that the Ti $d_{xy}$ states contribute to the reduction of the minority band gaps. Interfacial Ti magnetic moments are observed as well.

La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) is a ferromagnetic manganite with rich phase diagram as a function of doping and temperature. At an optimal doping level of 0.33, the LSMO reaches the highest Curie temperature of 370 K with a half-metallic character and exhibits CMR. The ferromagnetic phase of LSMO is stabilized by double exchange. BiFeO$_3$ (BFO) is another type of Bi based multiferroic material (besides BiMnO$_3$) which exhibits simultaneous electric polarization (ferroelectric when $T_C < 1100K$) and long range magnetic order (antiferromagnetic when $T_N < 643K$).

Both compounds are well studied theoretically and experimentally. They have potential applications in spintronic devices, information storage and sensor applications mainly due to the fully spin polarized character of LSMO and strong electric polarization of BFO. The combination of a ferromagnetic half-metallic perovskite with an antiferromagnetic ferroelectric insulator can yield interesting phenomena such as CMR, magnetoelectric effects, exchange bias, etc. Exchange bias is a prominent effect between ferromagnetic and antiferromagnetic materials which arises from the exchange coupling. In Ref. the authors have found exchange bias with a strong electronic orbital reconstruction at the interface between BFO and LSMO as well as an interfacial ferromagnetic state of BFO, which implying the possibility to control the magnetization of the ferromagnet using an electric field. In order to understand the fundamental interfacial physics of the BFO/LSMO superlattice at the atomic scale, in Chapter 7 we investigate the structural, electronic, magnetic, and optical properties of this system. We propose the applications of this compound due to its half-metallic character. The maintained half-metallicity of LSMO in the superlattice implies that structural relaxation and charge transfer at both interfaces
are not strong enough to strongly modify the bulk character. Both the ferroelectric character of BFO and half-metallic character of LSMO can be manipulated which can be interesting for multifunctional device applications.
Chapter 2

The Basic Theory and Methodology of First Principles Calculations

2.1 Density Functional Theory

Theoretical modeling of systems such as molecules and condensed matter (solids) has to consider mainly two aspects: the chemical composition and the structure. Matter is a collection of a collection of nuclei and electrons. The interaction of these particles is mainly governed by quantum mechanics in which the behavior of the electrons is a key factor for determining the macroscopic physical properties of the system. A precise description of a piece of matter lies in its Hamiltonian:

\[ \hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{e-e} + \hat{V}_{N-N} + \hat{V}_{e-N}, \]  

(2.1)

where the first and second terms on the right hand side are the kinetic energies of the electrons and nuclei; the following terms are the potential energies of the electron-electron, nucleus-nucleus, and electron-nucleus interactions, respectively. However, the solution to of this equation is practically impossible due to the large number of
interacting particles. After the introduction of the Born-Oppenheimer approximation \cite{52} in which the motions of the electrons and nuclei are decoupled by considering the nuclei positions as fixed due to their larger mass as compared to the electrons, Eqn. \ref{eq:2.1} can be simplified as:

\[
\hat{H} = \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{e-N} \tag{2.2}
\]

In Eqn. \ref{eq:2.2} we have the many body (electrons and nuclei) interaction terms and the most sophisticated electron-electron interaction term (second term). Density functional theory (DFT) is a prominent and successful method for the calculation of the ground state of an electronic system at absolute zero temperature based on the Hohenberg and Kohn theorem \cite{53} and Kohn-Sham equations \cite{54}. The main idea is the realization of direct correspondence between the ground state electron charge density and total energy of the many particle system. The complexity of the interacting many particle system is reduced to a non-interacting single particle system by introducing DFT.

### 2.2 Exchange-Correlation Functional: GGA+U

In order to make DFT more practical, an approximation is needed for the exchange correlation functional which originates from the complex electron-electron interaction. The existence of an exchange-correlation functional is mathematically proved, however as the exact form is unknown yet, it is necessary to approximate it. The most common approximation methods for the exchange-correlation functional are the Local-Density Approximation (LDA) \cite{55} and Generalised Gradient Approximation (GGA) \cite{56, 57}. Concerning the LDA, the exchange-correlation functional of an inhomogeneous electron gas can be derived from the exchange-correlation energy density of a homogeneous electron gas with a constant local density. This approximation
works well in systems such as metals with slowly varying electron density, however it fails to describe the electronic properties of systems such as defect in semiconductors, surfaces, etc. Therefore, the GGA was introduced in which the exchange-correlation energy is expressed as a functional of the electron density $n(r)$ and its gradient $\nabla n(r)$. The GGA gives more accurate binding energies and structural information such as bond lengths, bond angles and lattice constants as compared to the LDA. The GGA also works well for describing the light elements (for instance, water molecules). When it comes to transition metal oxides, Mott-Hubbard insulators [58], and rare earth elements, both the LDA and GGA methods will not be able to reproduce the correct band gaps and magnetic properties. In order to account for strongly correlated $3d$ or $4f$ orbitals (localized orbitals), a modification to the conventional DFT approach is needed. Several approaches such as the Hubbard method [59], self-interaction correction [60], hybrid functional [61], dynamical mean field theory [62], were introduced. The Hubbard model is one of the simplest models for treating strongly correlated electronic states in which an on-site Coulomb repulsion term $U$ (also called Hubbard U parameter) is added to the total energy of the system. The selection of $U$ for the same element in different atomic surroundings can be different. Therefore, careful evaluation of the $U$ value is necessary to ensure the accuracy of the produced properties in different systems. By comparing with experimental findings on electronic properties (especially by checking the band gaps and magnetic moments) of a compound, one can test and approximate the $U$ value by matching with these data.

### 2.3 Bloch Theorem and Supercell Approach

The electrons in a crystal move in a periodically-repeating potential $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$, where $\mathbf{r}$ is position, $\mathbf{R}$ is the reciprocal lattice vector determining the periodicity of the lattice. According to the Bloch theorem the Kohn-Sham wavefunction can be
written as:
\[ \psi_n(r) = u_k(r)e^{i\mathbf{k}\cdot \mathbf{r}}, \]  
(2.3)

where \( u_k(r) \) is a function that is periodic in the same way as lattice, the \( \mathbf{k} \) is the wavevector of electron at which the Kohn-Sham equations are solved, \( e^{i\mathbf{k}\cdot \mathbf{r}} \) is the plane wave basis. Bloch theorem\cite{63} transformed an infinite electron problem to electrons in a unit cell problem with a finite number of \( \mathbf{k} \) points and largely reduced the computational complexity.

However it is only applicable in a periodic system, for non-periodic systems such as single molecule, thin films, (or randomly ordered alloys) where surface is involved, supercell slab approach by applying the periodic boundary conditions was introduced. In this model, the supercell is separated artificially by an empty space (also called vacuum space) and the empty space is required to be far enough to avoid any interaction between two supercells (also called images). For the selection of the finite \( \mathbf{k} \) points both for periodic and non-periodic systems, the most effective method is Monkhorst-Pack method \cite{64} which we used in all of our calculations. Typically it is harder to get the electronic and force convergence for superlattices or the large supercells with big spaces (empty spaces) since it might get stuck in some local minimum (for former case) or the memory of the hard drive can be an issue (for latter case). One way to get them converged is starting with a low energy (and/or force) criterium and then increase it stepwise (for superlattices). The other way can be to reduce the extra empty space in supercells (by avoiding self interaction between images) such as molecules and thin film modeling with spaces. For structural modeling, Visualization for Electronic and Structural Analysis (VESTA) and Atomic Simulation Environment (ASE) softwares can be useful tools. For instance, using these tools, the rhombohedral cell can be transformed to a tetragonal cell with almost same symmetry.
Chapter 3

The Modelling of LaNiO$_3$ and CaMnO$_3$ Perovskites

3.1 Introduction

The development of the layer-by-layer growth technique \cite{65} of perovskite oxides and their broad range of physical properties have created significant research interest. The common chemical formula of perovskite oxide is ABO$_3$. Importantly, properties of the perovskite oxide family can be drastically different ranging from insulators, semiconductors, metals to even superconductors. Recently, many exotic electronic properties have been observed in perovskite-based heterostructures and their interfaces. Many investigations of the interface properties of new combinations of perovskite oxide heterostructures have been reported. For instance, interfacial metallicity have been found in LaTiO$_3$/SrTiO$_3$ \cite{12} while both constituents are insulators. LaMnO$_3$/SrMnO$_3$ \cite{13}, CaRuO$_3$/CaMnO$_3$ \cite{14}, BiMnO$_3$/SrTiO$_3$ \cite{15} superlattices exhibit ferromagnetic property which is different from their bulk magnetic ordering. Exchange bias has been observed between a paramagnet LaNiO$_3$ and a ferromagnet LaMnO$_3$ \cite{66}.

Among different combinations of perovskite oxides, we are interested in LaNiO$_3$/CaMnO$_3$ superlattice. LaNiO$_3$ is a paramagnetic metal which is a popular electrode
material in oxide electronics. Compared to its bulk properties, thin films, and superlattices of LaNiO$_3$ show significantly different properties such as metal-insulator transition [67], and increased conductivity [68]. On the other hand, CaMnO$_3$ is a G-type antiferromagnetic insulator which has applications on spintronics since the discovery of colossal magneto-resistance effect in 1990s [11]. Combinations of these two may result in interesting interfacial properties.

Experimental work [17] has suggested the metal-insulator transition in the LaNiO$_3$ layers of the (LaNiO$_3$)$_n$/CaMnO$_3$$_m$ superlattices as well as the interfacial ferromagnetism. Specifically, authors found that when $n \geq 4$ unit cells (with thicker LaNiO$_3$), the samples are metallic with emergence of the interfacial ferromagnetism at one unit cell of CaMnO$_3$, when $n=2$, the samples are insulating and there is no interfacial ferromagnetism. In similar superlattices such as LaNiO$_3$/LaMnO$_3$, LaNiO$_3$/SrMnO$_3$, LaNiO$_3$/SrTiO$_3$, and LaNiO$_3$/LaAlO$_3$, authors also found a transition from metallic to insulating behavior as the thickness of the LaNiO$_3$ layer was reduced below three unit cells. In Ref. [74], authors found a metal-insulator transition in LaNiO$_3$ ultra-thin films when its thickness is down to five unit cells. Similar transition and interfacial ferromagnetism is expected from first-principles calculations in (LaNiO$_3$)$_n$/CaMnO$_3$$_m$ superlattices. First of all, the electronic and magnetic properties of bulk compounds should be well reproduced with optimal computational parameters. Therefore, we study the effect of the Hubbard U values as well as strain to the electronic and magnetic properties of bulk compounds.
3.2 Bulk Models and Computational Details

Bulk Components

The orthorhombic CaMnO$_3$ (CMO) and rhombohedral LaNiO$_3$ (LNO) was built according to the atomic positions and symmetry reported in the literature $^{[75, 76, 77]}$. Both components are optimized within our computational scheme. Tetragonal settings were illustrated in Fig. 3.2 (right). Tetragonal cells can be derived from the optimized bulk structures using VESTA software and Atomic Simulation Environment program. Tetragonal cells from optimized bulk structures with averaged in-plane lattice constants as well as the tetragonal cells from optimized bulk structures with substrate lattice constants have been built. Different U values and spin orderings have been tested, see Figs. 3.3 and 3.4 for CMO and LNO, respectively.

We performed our calculations using Vienna Ab-initio Simulation Package (VASP) $^{[78]}$ with projector augmented wave pseudopotentials and employed the generalized gradient approximation in the parametrization of Perdew, Burke, and Ernzerhof $^{[57]}$. 
Figure 3.2: Rhombohedral LaNiO$_3$ (left) and tetragonal setting of LaNiO$_3$ (right)

We added onsite Coulomb interaction term using the Dudarev scheme\cite{79} by considering the correlated nature of the transition metal $d$ orbitals. For the background on this subject see chapter 2. The values for the $U$ parameter have been tested for the Mn and Ni $d$ states. We set the energy tolerance to $10^{-5}$ eV with an energy cutoff of 400 eV. There are two types of interfaces, we denote them as $n$-type $(\text{La}^{3+}\text{O}^2^-)^+/(\text{Mn}^{4+}\text{O}^2^-)^0$ interface and the $p$-type $(\text{Ca}^{2+}\text{O}^2^-)^0/(\text{Ni}^{3+}\text{O}^2^-)^-$ interface, where they refer to the compensating charges formed at the corresponding interfaces.

### 3.3 The Effect of the Strain on Electronic and Magnetic Properties

Bulk orthorhombic CMO is a G-type antiferromagnetic insulator. The $U$ values ranging from 1 4 has been tested. The electronic and magnetic properties of CMO are well reproduced in orthorhombic, optimized orthorhombic (optimized the experimental orthorhombic structure within our computational scheme), and tetragonal cell from optimized orthorhombic CMO with $U = 3$ eV. However, when the in-plane lattice constants are strained to substrate LaAlO$_3$ lattice constant of 3.789 Å, U value
for reproducing the bulk magnetism (G type antiferromagnetism) should be less than 3 eV (around 2.5 eV). If we apply 3 eV, ferromagnetic ordering turns out to be favorable. At this point, the selection of the Hubbard U value is crucial. Since the ferromagnetism of strained CMO with $U = 3$ eV may be due to the nature of the material. To confirm whether it is indeed ferromagnetic under this strain would require experimental results for the in-plane strained bulk CMO magnetism. Another possibility is that this ferromagnetism may result from the computational artifact due to higher estimation of U value for Mn atom. Therefore it is difficult to determine the accuracy of U value for correctly describing the magnetism of bulk as well as the superlattice. Bulk rhombohedral LNO is a paramagnetic metal. When applying U value to Ni atom, we obtain a ferromagnetic ordering for LNO. When the tetragonal LNO is strained to substrate LaAlO$_3$ lattice constant, antiferromagnetic ordering has substantially lower energy than ferromagnetic ordering without U value. Above $U = 0.42$ eV LNO becomes ferromagnetic. No U values for Ni can be the optimal choice since the paramagnetic property can be well described without U value according to the small energy difference between ferromagnetic and antiferromagnetic spin ordering when U equals zero.

3.4 Discussion and Conclusion

The electronic and magnetic properties of CMO are reproduced with Hubbard U value of 3 eV per Mn atom in the orthorhombic (both bulk and optimized) and tetragonal setting of optimized orthorhombic CMO whereas ferromagnetism is found when the CaMnO$_3$ is strained to substrate lattice constant. This indicates that the CaMnO$_3$ magnetism is either sensitive to uniaxial strain or the selection of the optimal Hubbard U value in theoretical work. Paramagnetic property of LaNiO$_3$ can be well described without applying a U value to Ni since ferromagnetism is found
Figure 3.3: U values tests with different spin orderings for CaMnO$_3$.

with application of U values. Induced Ni magnetic moments at the interfaces have been observed in some test superlattice calculations with and without onsite Column interaction term which indirectly indicates the possible contribution from Ni atom to the interfacial magnetism. In summary, in-plane strain affects the choice of U value for Mn and modifies the magnetism in CaMnO$_3$. It is difficult to determine the interfacial magnetism accurately for the superlattice since it involves the effect of both strain as well as the computational parameters. Further experimental work on the magnetic properties of CaMnO$_3$ on LaAlO$_3$ substrate needs to be conducted to validate our findings. The analysis of the electronic and magnetic properties of their superlattices then would be more meaningful.
Figure 3.4: U values tests with different spin orderings for LaNiO$_3$.
Chapter 4

Role of O Defects at the BiMnO$_3$/SrTiO$_3$ Interface

4.1 Introduction

The possibility to grow perovskite oxides layer by layer has lead to the discovery of exotic electronic phenomena. For instance, magnetism has been found at the CaRuO$_3$/CaMnO$_3$, BiMnO$_3$/SrTiO$_3$, and LaAlO$_3$/SrTiO$_3$ interfaces [80, 15] and metallicity/superconductivity at the LaAlO$_3$/SrTiO$_3$ interface [19] [81]. Interfacial magnetism is of particular interest due to potential applications in magnetic sensors [82] and tunnel junctions [83], for example. The class of perovskite manganites [84, 85] hosts interesting properties such as colossal magnetoresistance [11] and electronic phase separation [86]. The authors of Ref. 33 have demonstrated the effect of strain on the orbital reconstruction at the $n$-interface of the LaMnO$_3$/SrTiO$_3$ superlattice, which in turn modifies the exchange interaction. The interface between the polar insulator BiMnO$_3$ (shows ferromagnetism as well as ferroelectricity in the bulk [24]) with the non-polar insulator SrTiO$_3$ can become metallic by means of a polar catastrophe, O defects, and intersite chemical disorder [87], all being related to interfacial magnetism. The importance of the oxygen stoichiometry have been shown in determining the structural and magnetic properties of BiMnO$_3$ [82]. Spin polariza-
tion has been found experimentally for the Ti atoms at the \((\text{Bi}^{3+}\text{O}^{2-})^+/\text{(Ti}^{4+}\text{O}_2^{2-})^0\)
interface of BiMnO$_3$/SrTiO$_3$ thin films, with antiparallel orientation of the Mn and
Ti spins \cite{15}. While it has been speculated that the Ti interfacial magnetism is due
to superexchange, we show in the following that O defects play a dominating role.

4.2 Superlattice Modeling and Computational Details

We model the \((\text{Bi}^{3+}\text{O}^{2-})^+/\text{(Ti}^{4+}\text{O}_2^{2-})^0\) and \((\text{Sr}^{2+}\text{O}^{2-})^0/(\text{Mn}^{3+}\text{O}_2^{2-})^-\) interfaces (which
we denote as \(n\)- and \(p\)-interfaces referring to the compensating interface charges,
respectively) simultaneously by building a \((\text{BiMnO}_3)_3/(\text{SrTiO}_3)_3\) superlattice. Our
work mainly focuses on the \(n\)-interface due to its experimental relevance. We perform
ab-initio calculations using the Vienna Ab-initio Simulation Package with projector
augmented wave pseudopotentials \cite{78}. For the exchange-correlation functional we
employ the generalized gradient approximation and include an onsite correction for
the localized \(d\) states \cite{79}. The values of the onsite repulsion and exchange parameters
are adopted from previous works (4 eV and 1 eV for the Mn 3\(d\) states, 5 eV and 0.5 eV
for the Ti 3\(d\) states) \cite{88, 89}. An energy tolerance of \(10^{-5}\) eV for the self-consistency
iteration and an energy cutoff of 400 eV for the plane wave basis functions are used.
For the structural relaxation we employ a \(5 \times 5 \times 1\) k-mesh and for calculating the
density of states a refined \(10 \times 10 \times 2\) k-mesh (Monkhorst-Pack scheme). All charge
evaluations refer to the atomic orbitals. Possible octahedral rotations are taken into
account by using a \(\sqrt{2} \times \sqrt{2}\) in-plane supercell of the cubic perovskite unit cell. Bulk
SrTiO$_3$ is non-magnetic with cubic perovskite structure and bulk BiMnO$_3$ ferromag-
netic with distorted perovskite structure. The relaxed lattice constant of bulk SrTiO$_3$
turns out to be 3.96 Å and we obtain a band gap of 2.33 eV, see Fig. \[4.3\]. While opti-
mization of the in-plane and out-of-plane lattice constants of BiMnO$_3$ leads to values
we fix the in-plane lattice constant to the SrTiO$_3$ value when building the superlattice, which results in a minor strain. Bulk BiMnO$_3$ under this strain shows a band gap of 0.58 eV, see Fig. 4.1. In order to determine the locations of the O defects, we remove one O atom from different atomic layers at the $n$-interface and compute the total energy. The nudged elastic band method (seven images, spring constant $-5$ eV/Å) is used to evaluate the ability of the O defects to migrate \cite{90}.

4.3 The Effect of the O Defect on BiMnO$_3$/SrTiO$_3$ Superlattice

4.3.1 The Ideal Superlattice vs O Defective Superlattice

The structure of the (BiMnO$_3$)$_3$/(SrTiO$_3$)$_3$ superlattice is illustrated schematically in Fig. 4.2. The total energy of an O defect in the MnO$_2$ layer at the $n$-interface is found to be 335 meV and 796 meV, respectively, lower than in the neighboring BiO and TiO$_2$ layers. Out of the four O atoms in the favorable MnO$_2$ layer those two located slightly closer to the $n$-interface have 243 meV higher total energies than the others. O migration barriers above 1 eV from the MnO$_2$ to the BiO layer and from the BiO to the TiO$_2$ layer indicate that O defects are unlikely to migrate. Ti
off-centerings along the z-axis (perpendicular to the interfaces, see Fig. 4.2) of up to 0.12 Å, 0.13 Å, and 0.23 Å, respectively, are observed in the ideal superlattice and in the superlattices with O defects in the MnO$_2$ and BiO layers. This effect is larger than the weak ferroelectric distortion of 0.03 Å found in bulk SrTiO$_3$. During the structure relaxation strong octahedral tilting develop in the SrTiO$_3$ region in the ideal as well as O deficient superlattices, as the Ti-O-Ti bond angles between adjacent TiO$_6$ octahedra along the z-axis decrease from $180^\circ$ to $161^\circ$-$167^\circ$. Additionally, the O-Ti-O bond angles along the z-axis are reduced to about $172^\circ$ at the n-interface only. Significant structural reconstruction previously also has been reported for the SrTiO$_3$ region of the LaTiO$_3$/SrTiO$_3$ and LaMnO$_3$/SrTiO$_3$ superlattices [89, 91], in contrast to the situation in LaAlO$_3$/SrTiO$_3$ thin films, which show (besides the large polar distortions in the LaAlO$_3$ region) little alterations in the SrTiO$_3$ region [92]. Table 4.1 summarizes the bond angles (Ti-O-Mn) and lengths (Mn-O and Ti-O) across the n- and p-interfaces as they play a key role for the magnetic coupling. The difference of the Ti-O-Mn bond angles between the two interfaces is more than 10°, which allows the superlattice to resemble the bulk bond angles of BiMnO$_3$ and SrTiO$_3$ where the involved O atoms belong to the BiO and SrO layers, respectively,
Table 4.1: Bond angles, bond lengths, and magnetic moments next to the \( n \)- and \( p \)-interfaces.

<table>
<thead>
<tr>
<th></th>
<th>ideal superlattice</th>
<th>( \text{MnO}_2 \text{(vac)} ) layer</th>
<th>BiO(vac) layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n )</td>
<td>( p )</td>
<td>( n )</td>
</tr>
<tr>
<td>Ti-O-Mn</td>
<td>( 153^\circ )</td>
<td>( 166^\circ )</td>
<td>( 148^\circ-151^\circ )</td>
</tr>
<tr>
<td>Mn-O (Å)</td>
<td>2.02</td>
<td>2.02</td>
<td>2.07</td>
</tr>
<tr>
<td>Ti-O (Å)</td>
<td>2.07</td>
<td>1.95</td>
<td>2.03</td>
</tr>
<tr>
<td>Ti (( \mu_B ))</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Mn (( \mu_B ))</td>
<td>3.79</td>
<td>3.79</td>
<td>4.23/4.35</td>
</tr>
</tbody>
</table>

see the right hand side of Fig. 4.2. Adjacent to an O defect in the \( \text{MnO}_2/\text{BiO} \) layer the Ti-O-Mn bond angles slightly decrease/increase. Most significantly, we find that the Mn-O bond lengths increase when O defects are introduced, while the Ti-O bond lengths decrease. This difference is more pronounced at the \( n \)-interface (as the O defect is close) but also persists at the \( p \)-interface.

O deficiency results not only in structural but also in electronic reconstructions, which turn out to be rather complex as the extra charge introduced into the system does not stay localized at the defect site. Densities of states are shown in Fig. 4.3 for the ideal and O deficient superlattices. Without O defect both regions of the superlattice maintain the insulating character of the respective bulk material. This is different from the \( \text{LaMnO}_3/\text{SrMnO}_3 \) superlattice for which a half-metallic character is found though both component materials are insulators [93]. Similar half-metallicity can be achieved by applying the experimental substrate in-plane lattice constant of 3.905 Å. We note that the strain in our superlattice is smaller than the experimental strain, since the experimental lattice constant of \( \text{SrTiO}_3 \) is only 3.905 Å. In order to check whether this fact plays a critical role, we have performed all calculations also using the latter value for the in-plane lattice constant of the superlattice. We observe only small quantitative differences, while all the trends reported in the following are maintained. See the appendix for the supplementary figures. Dramatic changes of the electronic properties are introduced by O defects. The band gap is reduced
substantially when the O defect is located in the MnO$_2$ layer and even a metallic character is observed when it is located in the BiO layer. In the latter case the majority spin states from the BiMnO$_3$ region (mainly the Mn $e_g$ and O $p$ states at the $p$-interface, not shown) and minority spin states from both regions appear at the Fermi energy. Large minority spin band gaps are found for the ideal superlattice and in the case that the O defect is located in the MnO$_2$ layer.

We address orbitally projected densities of states of the Mn atom next to the $n$-interface in Fig. 4.4. We find that the $e_g$ ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$) states dominate around the Fermi energy and that in the case of the O deficient BiO layer the $d_{3z^2-r^2}$ orbitals contribute to the metallicity. Turning to the orbitally projected Ti densities of states
in Fig. 4.5, we find for the ideal superlattice and the case that the O defect is located in the MnO$_2$ layer no states at the Fermi energy. In addition, the $d_{xy}$ states have the lowest energy, consistent with experimental observations for the LaAlO$_3$/SrTiO$_3$ interface [94, 95, 96]. O deficiency in the BiO layer also results in an energetical downshift of all states, but additionally the $d_{3z^2-r^2}$ orbitals become partially occupied. In principle, orbital reconstructions similar to those dominating the properties of the O deficient LaAlO$_3$/SrTiO$_3$ interface [97] can be expected to appear also in our case. However, Fig. 4.5 demonstrates that the spin polarization of the Ti atoms at the interface is mostly carried by the $d_{3z^2-r^2}$ states, whereas at the LaMnO$_3$/SrTiO$_3$ interface the induced Ti magnetic moments are always due to the $d_{xy}$ states [96, 95].

Table 4.1 demonstrates that only in the case that the O defect is located in the BiO layer the Ti spin is oriented antiparallel to the Mn spin, as it has been observed experimentally by X-ray magnetic circular dichroism [15]. The adjacent Mn atom shows a magnetic moment of 3.76 $\mu_B$, slightly less than in the ideal superlattice (3.79 $\mu_B$) and the other Mn atom in the same atomic layer an enhanced magnetic moment of 4.47 $\mu_B$ (bulk value: 3.60 $\mu_B$ [98]). These modifications come along with changes in the orbital occupations: In the former case 0.14 electrons shift mostly from the $d_{x^2-y^2}$ orbital to the $d_{3z^2-r^2}$ orbital and in the latter case these two orbitals together gain 0.20 electrons. We note that antiparallel alignment of the transition metal spins also has been found at the $n$-interface of the La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ superlattice, but the authors rule out relevant effects of O defects due to a small concentration [99]. Since the Ti atom with inverted spin always is located directly next to an O defect, see the X in Fig. 4.6 superexchange with Mn is not possible. We observe that the local structural distortions around the O defect are less pronounced than one may expect, compare Fig. 4.6. The Mn and Ti atoms neighbouring the O defect in the $z$-direction experience in good approximation a square pyramidal instead of an octahedral crystal field. As consequence, the $d_{3z^2-r^2}$ states should shift down in
energy relative to the $d_{x^2-y^2}$ states and the $d_{y^2,x^2}$ states relative to the $d_{xy}$ states. However, this effect cannot explain why the $d_{3z^2-r^2}$ orbitals of the Mn and Ti atoms become occupied, see the bottom panels of Figs. 4.4 and 4.5 as the $e_g$ states should still remain energetically above the $t_{2g}$ states. We note the very strong hybridization between the $d_{3z^2-r^2}$ states of the two atoms, which implies that there is direct overlap between these orbitals. Indeed, this is possible, because the O atom inbetween is missing, even though the Mn-Ti distance after relaxation is 4.08 Å. Direct interaction across the defect is further supported by the previously mentioned increase of the $d_{3z^2-r^2}$ occupation of the Mn atom next to the defect.

### 4.4 Summary

The structural, electronic, and magnetic properties of the (BiMnO$_3$)$_3$/(SrTiO$_3$)$_3$ superlattice have been investigated and the effects of O defects in the different atomic layers have been analysed. Strong structural distortions and systematic Ti off-centering in the SrTiO$_3$ region are observed as well as Ti magnetic moments at all interfaces. While total energy calculations point to a preference of O defects to be located in the MnO$_2$ layer, only O defects in the BiO layer can generate an antiparallel alignment of the Mn and Ti spins at the $n$-interface and thus can reproduce the experimental situation. It therefore must be conjectured that more O defects exist in the BiO layer than expected from total energy considerations, which can only be a consequence of the growth process, as the O migration barriers are found to be high. Strong hybridization between the $d_{3z^2-r^2}$ orbitals of the Mn and Ti atoms adjacent to an O defect, which are subject to a square pyramidal crystal field, points to direct Mn-Ti coupling.
Figure 4.4: Orbitally projected densities of states of the Mn atom next to the n-interface.
Figure 4.5: Orbitally projected densities of states of the Ti atom next to the $n$-interface.
Figure 4.6: Schematic structure of the relaxed $n$-interface with an O defect in the BiO layer. The X indicates the Ti atom with inverted spin.
Chapter 5

Uniaxial Strain on the LaMnO$_3$/SrTiO$_3$ Superlattice

5.1 Introduction

Since the discovery of a quasi two-dimensional electron gas at the LaAlO$_3$/SrTiO$_3$ interface [19], much recent research in the field of perovskites focuses on interfaces between polar and non-polar compounds, and on the production and testing of devices for new generation electronics [20]. Intense investigations have explained the mechanism underlying the formation of the electron gas [100, 94, 101, 102], identified spin-polarization [103, 104, 105] and superconductivity [81], and clarified the quantum nature [106, 22, 107]. The field of two-dimensional electron gases is extending more and more to new systems, such as organic/inorganic [108], perovskite/carbon-nanotube [109], and perovskite/spinel interfaces [110], as well as to (magnetic) tunnel junctions [111]. Lately, manganites and titanates are receiving particular attention [33, 112, 113, 114]. Bulk manganites have a rich magnetic phase diagram. LaMnO$_3$ and SrMnO$_3$ are antiferromagnetic (AF) insulators, but tend to ferromagnetic (FM) ordering in nanostructures [115], where they can also exhibit conducting states [116, 21, 93]. However, the two-dimensional character of the resulting electron gas is not clear yet. On the other hand, there is experimental evidence for
two-dimensional electron gases in SrTiO$_3$ at the interface with KTaO$_3$ [117], KNbO$_3$ [118], and La$_{0.7}$Sr$_{0.3}$MnO$_3$ [99].

A fully spin-polarized hole gas has been reported in Ref. [119] and Ti magnetism has been found at the La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ interface [99], whereas a fully spin-polarized two-dimensional electron gas so far has not been discovered at perovskite interfaces. The LaMnO$_3$/SrTiO$_3$ interface, combining the ferroelasticity of SrTiO$_3$ and the spin-polarization of LaMnO$_3$, constitutes a good candidate for such a system. Experimental studies have revealed FM ordering in (LaMnO$_3$)$_n$/SrTiO$_3$, $n = 1, 2, 8$, superlattices [113] as well as (orbital) Ti magnetism in (LaMnO$_3$)$_n$/SrTiO$_3$, superlattices with $n \gg m$ [33]. Aiming at an exploration of the conditions that induce a high degree of spin-polarization, we investigate the magnetic and electronic properties of the (LaMnO$_3$)$_2$/SrTiO$_3$ superlattice under uniaxial external strain, since such strain can enhance the effect of the SrTiO$_3$ ferroelectricity and can modify the magnetic and orbital ordering in LaMnO$_3$ [37, 38]. We will clarify how the strain influences the orbital reconstruction, the formation of the two-dimensional electron gas, and the magnitude of the Ti magnetic moments at the interface, and predict under which conditions the spin-polarization of the electron gas is enhanced.

5.2 Superlattice Modeling and Computational Details

The (LaMnO$_3$)$_2$/SrTiO$_3$ superlattice is modeled by a $\sqrt{2} \times \sqrt{2}$ in-plane supercell of the cubic perovskite structure, which allows us to account for tilting and rotations of the O octahedra as well as different magnetic orderings. The supercell has two interfaces, LaO/TiO$_2$ and MnO$_2$/SrO. By the nominal charge of the cations in the bulk compounds, the former interface is $n$-type and the latter $p$-type. However, note that the local environment affects the valency of the Mn atoms, suggesting that this
terminology might no longer apply in the case of charge transfer. It is intended solely as a convention. Because of the analogy with the well known LaAlO$_3$/SrTiO$_3$ interface, we employ this convention in the following.

For our calculations we use the Vienna Ab-initio Simulation Package (version 5.2.12) with projector augmented wave pseudopotentials [120][78], and we employ the generalized gradient approximation in the parametrization of Perdew, Burke, and Ernzerhof. The basis set consists of Sr 4s$^2$ 4p$^6$ 5s$^2$, Ti 3p$^6$ 4s$^2$ 3d$^4$, O 2s$^2$ 2p$^4$, Mn 3s$^2$ 3p$^6$ 4s$^2$ 3d$^5$, and La 4s$^2$ 4p$^6$ 5s$^2$ 6d$^1$ orbitals. Moreover, the atomic sphere radii are chosen to avoid overlap during the ionic relaxation, for which we set the energy tolerance to $10^{-3}$ eV, employ a $4 \times 4 \times 1$ k-mesh, a Gaussian smearing of 0.05 eV, and an energy cutoff of 500 eV. Concerning the calculation of the electronic properties, we set the energy tolerance to $10^{-5}$ eV, adopt a $6 \times 6 \times 2$ k-mesh, and employ a smearing of 0.01 eV within the tetrahedron method with Blöchl corrections [121]. In order to account for electronic correlations, we apply the GGA+U approach within the Lichtenstein scheme [122] using the following values for the onsite Coulomb interaction $U$ and exchange interaction $J$: 4 eV and 1 eV for the Mn 3d states, 5 eV and 0.5 eV for the Ti 3d states, and 9 eV and 1 eV for the La 4f states, compare Refs. [123][89].

5.3 Compressive and Tensile Strained LaMnO$_3$/SrTiO$_3$ Superlattice

5.3.1 Structure and Magnetic Competition

Total energy calculations are performed for systems belonging to the following point groups: $D_{4h}$ (tetragonal crystal system), $D_{2h}$ (orthorhombic crystal system), and $C_{2h}$ (monoclinic crystal system). We find that the $C_{2h}$ point group is favored by 1.02 eV
and 0.26 eV per supercell with respect to the $D_{4h}$ and $D_{2h}$ point groups, respectively. The results in the following thus refer to the $C_{2h}$ point group. Rotations and tilting of the O octahedra are essential for correctly predicting the magnetic and electronic properties of perovskite interfaces, as they are affected by strain.

The structurally relaxed supercells feature ferroelastic distortions, which consist of apical Ti-O/Mn-O bond elongation/contraction, Ti/Mn off-centering with respect to the basal plane of the O octahedra, and buckling of the SrO and LaO planes. Adopting the convention of positive/negative displacements towards/off the $p$-type interface, we obtain: For compressive strain, the apical O atoms at the $p/n$-type interface are displaced by $+0.08/+0.07$ Å off the Ti atoms and by $-0.01$ Å off the Mn atoms. Without strain they are displaced by $+0.08/0.10$ Å off the Ti atoms and by $-0.03/+0.05$ Å off the Mn atoms. Finally, for tensile strain, they are displaced by $+0.16/+0.23$ Å off the Ti atoms and by $-0.06/+0.05$ Å off the Mn atoms. While for compressive strain they always shift towards the $p$-type interface, for zero and tensile strain the Mn atoms shift towards the LaMnO$_3$ bulk region. This can be seen in Fig.
Figure 5.2: (Color online) Dependence of the total energy on the uniaxial strain for FM and AF A orderings. The dashed lines represent parabolic fits for small strain, for which FM ordering is favorable.

Figure 5.3: Sketch of the structure under compressive (left) and tensile strain (right). The structure without strain resembles that under tensile strain. Only the Mn and Ti cations together with their apical O atoms are drawn. The interfaces are represented by dashed lines, where the $p$-type interfaces are aligned vertically.

The number of Mn atoms and MnO$_2$ layers present in our supercell allows us to realize four magnetic orderings: FM, AF A-type, AF C-type, and AF G-type. The three AF orderings are close to each other in energy, so that we can restrict our
considerations to the AF A-type case for comparison with the FM ordering, which gives overall the lowest energy. Without strain ($c/a = 4.05$) the energy difference between FM and AF A-type ordering is 0.35 eV per supercell. For $\pm 2\%$ strain FM ordering is also favorable, whereas for a compressive strain of $\sim 5\%$ a crossover to AF A-type ordering occurs.

### 5.3.2 Electronic Properties

Figure 5.4 shows the total density of states (DOS) for relaxed superlattices with different lattice parameters. Curves for 0\% and 1.5\% in-plane strain are superimposed, while the out-of-plane strain ranges from 4\% compressive (bottom) to 4\% tensile (top). The main features, in particular the gap in the minority spin channel and a broad majority spin DOS, are identical, and resemble the DOS of the (LaMnO$_3$)$_2$/(SrTiO$_3$)$_8$ superlattice as reported in Ref. [124]. Going into more detail, we first address the case without in-plane strain. Concerning the onsets and widths of the valence bands of the two spin channels we note that compressive/tensile out-of-plane strain shifts the occupied electronic states down/up in energy. The band gap of the minority spin channel is enhanced from 1.8 eV to 2.4 eV under compressive strain and from 1.8 eV to 1.9 eV under tensile strain. Also, the onset of the conduction band is shifted up in energy under both tensile and compressive strain. The effect of the in-plane strain is much weaker, see the similarity of the DOS curves in every panel in Fig. 5.4. The curves for a 4\% in-plane compressive strain resemble those for zero strain and therefore are not shown. Clearly, the spin-polarization at the Fermi level can be

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<th>+4%</th>
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<tbody>
<tr>
<td>Mn</td>
<td>p-type</td>
<td>n-type</td>
<td>p-type</td>
</tr>
<tr>
<td>Ti</td>
<td>+0.02</td>
<td>+0.01</td>
<td>+0.03</td>
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<td>+0.03</td>
<td>+0.03</td>
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Figure 5.4: Total DOS for different strain conditions. The in-plane lattice constant grows from left to right and the out-of-plane lattice constant from bottom to top.

efficiently tuned by strain.

Under out-of-plane strain the total magnetic moment of the superlattice is essentially constant (15.02 $\mu_B$ for compressive, 15.03 $\mu_B$ for zero, and 15.01 $\mu_B$ for tensile strain), whereas the Mn and Ti magnetic moments at the $p$-type and $n$-type
Table 5.2: Magnetic moments (in $\mu_B$) and charge (in electrons) of the Mn and Ti atoms at the $n$- and $p$-type interfaces, for different values of the out-of-plane strain. A positive charge difference represents an excess of electrons at the $n$-type interface.

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<th>$+4%$</th>
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<tr>
<td></td>
<td>$p$-type</td>
<td>$n$-type</td>
<td>$p$-type</td>
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<tr>
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<td>3.60</td>
<td>3.63</td>
<td>3.76</td>
</tr>
<tr>
<td>Ti</td>
<td>0.04</td>
<td>0.14</td>
<td>0.04</td>
</tr>
</tbody>
</table>

interfaces are significantly affected. The Mn magnetic moments decrease at both interfaces under compressive strain, while under tensile strain they increase at the $p$-type interface and decrease at the $n$-type interface, see Table 5.2. In the SrTiO$_3$ region the Ti magnetic moments at the $n$-type interface increase remarkably under compressive strain and decrease slightly under tensile strain, whereas at the $p$-type interface the changes are negligible. A finite, although low, difference of charge at the two interfaces supports a mixed valency scenario, as expected. The $n$ and $p$-type interfaces exchange their roles when passing from zero to compressive strain, where we find an excess of electrons at the $n$-type rather than at the $p$-type interface. The charge difference under compressive strain is mirrored by a difference in the Ti magnetic moments, while for tensile strain there is no such difference. All of the above effects are essentially due to the respective $d$ orbitals.

A simplified scenario for the enhanced Ti magnetic moment under compressive strain would be that the Mn atoms move closer to the $p$-type interface, whereas they move away without and under tensile strain. Because of the charge of the Mn ions this induces a polarization, as the off-centering is oriented in the same direction in all atomic layers. The Ti atoms thus obtain additional charge. At the $n$-type interface they show spin-polarization, but not at the $p$-type interface (due to the higher local symmetry). In fact, the difference between the apical Ti-O bond lengths is lower at
the $n$-type than at the $p$-type interface. The decrease of the Mn magnetic moments therefore is due to orbital hybridization. Note that in-plane strain has hardly any effect on the magnetic moments.

The orbitally resolved Mn DOS in Fig. 5.5 shows a metallic majority spin channel and a wide band gap around the Fermi level for the minority spin channel. The $3d_{x^2}$...
and $3d_{x^2-y^2}$ orbitals are responsible for the metallicity. At the $p$-type interface they swap roles depending on the strain. For tensile strain the $3d_{x^2-y^2}$ orbital dominates at the Fermi level, while the $3d_{z^2}$ DOS almost vanishes there, having its main weight around $-1.5$ eV. Without strain the two orbitals contribute almost equally at the Fermi level, because the $3d_{x^2-y^2}$ shifts to lower energy, and the $3d_{z^2}$ peak smears out.
Figure 5.7: (Color Online) Band structure (a) without strain and (b) under compressive strain (magnified in order to show the strain effect on the bands near the Fermi level. The continuous (dashed) lines represent the majority (minority) spin channel. In (a) the fully occupied and the fully unoccupied bands are drawn in black, while spin majority (minority) bands crossing the Fermi level are drawn in red (blue). The bands most affected by compressive strain are highlighted by a thicker line. In (b) the same colors are maintained for comparison. (c) Brillouin zone with high symmetry lines.

and shifts to higher energy. For compressive strain the $3d_{z^2}$ DOS dominates at the Fermi level, while the $3d_{x^2−y^2}$ DOS shows gap between 0.0 and 0.2 eV. The main difference with the $n$-type interface is that for tensile and zero strain the occupation of the $3d_{z^2}$ orbital is substantially reduced. The orbital hybridization is higher at the
$n$-type than at the $p$-type interface, and tensile strain tends to lift it. The Ti DOS, shows a strong orbital ordering at both interfaces, in agreement with the results of Ref. [124]. At the $p$-type interface it always exhibits an insulating character, and thus is not shown, while the $n$-type interface is insulating under tensile and zero strain. Compressive strain, on the other hand, gives rise to a fully spin-polarized two-dimensional electron gas. The band structure in Fig. 5.7 shows that the highest partially occupied majority spin band is degenerate with a minority spin band around the $\Gamma$ point for zero strain, while there is a splitting by a few meV under strain. Tensile strain (not shown) mainly shifts the bands at the Fermi level by $\sim 0.3$ eV, whereas compressive strain considerably affects the band slopes.

### 5.3.3 Summary

We have analysed the LaMnO$_3$/SrTiO$_3$ superlattice concerning its structure, magnetism, and electronic properties. Considering three crystal systems, the C$_{2h}$ point group turned out to be energetically favorable, for which we have determined the electronic structure under different strain conditions. Our results demonstrate that uniaxial strain can induce half-metallicity. In particular, we find a fully spin polarized two-dimensional electron gas, tracing back to the Ti atoms, at the (nominal) $n$-type interface for 4% compressive out-of-plane strain. This fact, together with high Ti magnetic moments, indicates great potential of LaMnO$_3$/SrTiO$_3$ superlattices in the field of spintronics.
Chapter 6

Trends in \((\text{LaMnO}_3)_n/(\text{SrTiO}_3)_m\) Superlattices

6.1 Introduction

A zoo of extraordinary phenomena, such as two dimensional quantum gases \[110\], superconductivity \[125\], magnetism \[126\], magnetoresistance \[127\], exchange bias \[128, 129\], half-metallicity \[130\], and ferroelectricity \[131\], is hosted by perovskite oxide heterostructures. The lattice, charge, orbital, and spin degrees of freedom and their competition give rise to these properties \[132\]. In general, electrostatic and strain effects drive structural and electronic reconstructions at interfaces \[133\], which thus often behave distinctly different from their component materials. Nowadays the thickness of superlattices can be determined and controlled down to the atomic scale, where interface effects become more and more important. Thus, the thickness is a key factor for tailoring the electronic and transport properties. For example, Nanda and coworkers \[134\] have studied the magnetism in LaMnO$_3$/SrMnO$_3$ superlattices with varying layer thicknesses, concluding that the charge reconstruction is confined to two unit cells around the interfaces. Volume changes have been observed in NaNbO$_3$/SrTiO$_3$ superlattices \[135\], for example, and it has been demonstrated that the appearance of metallicity correlates with the layer thicknesses \[136\].
Manganites and titanates are popular perovskite oxides, displaying colossal magnetoresistance [137] and superconductivity [138]. Colossal magnetoresistance was first observed in 1994 in La$_{1-x}$Ca$_x$MnO$_3$ [11] and gained considerable attention thereafter. The parent compound, LaMnO$_3$, is an antiferromagnetic insulator, which becomes ferromagnetic under hole doping with Sr [139], Ca [140] and Ba [141]. Therefore, superlattices with SrTiO$_3$ can be expected to show an unusual magnetic behavior and accordingly are attracting interest both for fundamental and technological reasons. The authors of Ref. [113], for example, have reported significant doping effects in LaMnO$_3$/SrTiO$_3$ superlattices, which can extend over few unit cells [142], and have studied their origin. In LaSrMnO$_3$/SrTiO$_3$ superlattices with SrTiO$_3$ layers thinner than 1 nm an interfacial charge transfer leads to finite Ti magnetic moments [99]. In general, the thicknesses of the component layers in a LaMnO$_3$/SrTiO$_3$ superlattice seem to strongly influence the magnetic and transport properties [44]. This would be interesting, because the behavior of the system could be controlled by means of the layer thickness. However, it requires detailed understanding of the strong lattice distortions and their implications for the physics of this superlattice, which is the topic of the present study.

6.2 Superlattices Modeling and Computational Details

The atomic sphere radii are chosen such that overlap is avoided during the ionic relaxation, for which we set the energy tolerance to $10^{-3}$ eV, employ a $4 \times 4 \times 1$ k-mesh, a Gaussian smearing of 0.05 eV, and an energy cutoff of 500 eV. To obtain accurate electronic states, we set the energy tolerance to $10^{-5}$ eV and adopt dense k-meshes of $8 \times 8 \times 3$ for $n + m = 4$, $8 \times 8 \times 2$ for $n + m = 6$, and $8 \times 8 \times 1$ for $n + m = 8$ and 10.
6.3 LaMnO$_3$/SrTiO$_3$ with Varying Layer Thicknesses

6.3.1 Structural Properties

(LaMnO$_3$)$_n$/(SrTiO$_3$)$_m$ superlattices are modeled by a $\sqrt{2} \times \sqrt{2}$ in-plane supercell of the cubic perovskite structure for taking into account possible effects of octahedral rotations. We use the Vienna Ab-initio Simulation Package [78] with projector augmented wave pseudopotentials and employ the generalized gradient approximation in the parametrization of Perdew, Burke, and Ernzerhof (including spin polarization). The density of states is calculated by the tetrahedron method (smearing 0.01 eV) with Blöchl corrections [121]. Because of the correlated nature of the transition metal $d$ orbitals, we add an onsite Coulomb interaction using the Lichtenstein scheme [122]. The values for the $U$ and $J$ parameters are taken from Refs. [123, 89, 88] as 4 eV and 1 eV for the Mn $d$ states, 5 eV and 0.5 eV for the Ti $d$ states, and 9 eV and 1 eV for the La $f$ states. We have tested different $U$ parameters for Mn and Ti based on the literature values on 2:2 system and found out similar electronic properties as half-metallicity with slight differences in the minority band gaps. The optimized lattice constant of SrTiO$_3$ is 3.97 Å, with a band gap of 2.6 eV, and the optimized in-plane and out-of-plane lattice constants of LaMnO$_3$ are 3.95 Å and 4.01 Å. The total densities of states obtained for bulk SrTiO$_3$ and strained bulk LaMnO$_3$ (half-metallic)

![Figure 6.1: Total densities of states of bulk SrTiO$_3$ and strained bulk LaMnO$_3$.](image)
are shown in Figure 6.1.

Structural optimization of the superlattices with and without onsite interaction is found to yield substantial differences in the electronic structure, especially near the Fermi level. More specifically, the minority channel shows a metallic character without onsite interaction in the 2:2 case, whereas with onsite interaction we obtain a half-metallic character. The supercells have $C_{2h}$ point group symmetry (tetragonal perovskite structure) with a fixed in-plane lattice constant of 5.56 Å which is taken from the optimized lattice constant of 2:2 due to expected small differences. Starting from $n:m = 2:2$ (2 unit cells of LaMnO$_3$ alternate with 2 unit cells of SrTiO$_3$), we fix the LaMnO$_3$ thickness and increase the SrTiO$_3$ thickness (2:4, 2:6, 2:8) or fix the SrTiO$_3$ thickness and increase the LaMnO$_3$ thickness (4:2, 6:2, 8:2). The $n:m = 4:4$ system is also considered for comparison. Figure 6.2(left) illustrates the 2:4 system as an example. There are two types of interfaces, the $n$-type LaO/TiO$_2$ interface and the $p$-type MnO$_2$/SrO interface, denoted in the following as n-IF and p-IF, respectively. The nomenclature refers to the compensating charges formed at the $(La^{3+}O^{2-})^+/(Ti^{4+}O^{2-})^0$ and $(Sr^{2+}O^{2-})^0/(Mn^{3+}O^{2-})^-_{\sigma}$ contacts, respectively.

The Ti-O-Mn bond angle at the n-IF (where the MnO$_6$ and TiO$_6$ octahedra are connected) is found to be 159.4°, whereas at the p-IF it has a larger value of 164.8°, which corresponds to a reduced tilting. While substantial modifications of the structure are expected in the vicinity of an interface, strong effects are also observed for the O octahedra further apart. For instance, the Mn-O-Mn bond angles increase by up to 8.3° with respect to the bulk value (154.6°), which supports double exchange. On the other hand, the Ti-O-Ti bond angles strongly decrease throughout the SrTiO$_3$ layer, reflecting huge distortions as compared to the bulk cubic structure. In general, the Ti-O-Ti (Mn-O-Mn) bond angles near the p-IF (n-IF) are less modified, because the distance to the interface is larger. The tiltings of the O octahedra are found to vary distinctly for different thicknesses $n:m$, and so do the electronic properties.
Table 6.1: Bond distances (in Å) at the n-IF and p-IF for different $n:m$.

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<thead>
<tr>
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<th>$n$-IF</th>
<th>$p$-IF</th>
<th>$n$-IF</th>
<th>$p$-IF</th>
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<tbody>
<tr>
<td>Mn-O</td>
<td>2:2</td>
<td>2.12</td>
<td>2:4</td>
<td>2.17</td>
</tr>
<tr>
<td>Ti-O</td>
<td>2.04</td>
<td>1.91</td>
<td>2:01</td>
<td>1.90</td>
</tr>
<tr>
<td>Mn-O</td>
<td>2:4</td>
<td>2.17</td>
<td>4:2</td>
<td>2.14</td>
</tr>
<tr>
<td>Ti-O</td>
<td>2.00</td>
<td>1.93</td>
<td>2.04</td>
<td>1.88</td>
</tr>
<tr>
<td>Mn-O</td>
<td>2:6</td>
<td>2.12</td>
<td>6:2</td>
<td>2.14</td>
</tr>
<tr>
<td>Ti-O</td>
<td>1.95</td>
<td>1.96</td>
<td>2.04</td>
<td>1.91</td>
</tr>
<tr>
<td>Mn-O</td>
<td>2:8</td>
<td>2.12</td>
<td>8:2</td>
<td>2.13</td>
</tr>
<tr>
<td>Ti-O</td>
<td>1.95</td>
<td>1.97</td>
<td>2.08</td>
<td>1.87</td>
</tr>
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</table>

For increasing $m$ the Mn-O (Ti-O) bond length along the $z$ axis at the p-IF decreases (increases) from 2.13 Å to 1.99 Å (1.91 Å to 1.97 Å), while at the n-IF the Mn-O bond length stays close to 2.13 Å and the Ti-O bond length decreases from 2.04 Å to 1.95 Å, see Table 6.1. A schematic view of the Mn-O and Ti-O bonds is given in Figure 6.2(right). For increasing $n$ the Mn-O bond length at the p-IF maintains a value of 2.10 Å, while the Ti-O bond length decreases (bulk value 1.95 Å) from 1.91 Å in the 2:2 system to 1.87 Å in the 8:2 system. At the n-IF the Mn-O bond length shows no clear trend, while the Ti-O bond length grows significantly from 2.04 Å in the 2:2 system to 2.08 Å in the 8:2 system.

It is found that all Ti atoms shift systematically off the center of their O octahedron towards the p-IF by up to 0.1 Å (in all cases more at the p-IF than at the n-IF), implying a ferroelectric-like distortions, while bulk SrTiO$_3$ is not ferroelectric experimentally. Theoretical calculations usually predict ferroelectric bulk SrTiO3 due to lack of quantum nuclear effects implemented in the codes which is demonstrated in Refs. [143]. External factors such as doping may induce ferroelectric phase transition in SrTiO$_3$ [144, 145]. The off-centering is generally enhanced at the interfaces when $n$ increases and reduced when $m$ increases. It is known that the properties of SrTiO$_3$ are very sensitive to dopants and external perturbations [146] so that it cannot surprise that the superlattices react similarly [147].
Figure 6.2: Left: Structure of the \((\text{LaMnO}_3)_n/(\text{SrTiO}_3)_m\) superlattice for \(n:m = 2:4\). Right: Schematic view of the Mn-O and Ti-O bonds perpendicular to the interfaces.

### 6.3.2 Electronic Properties

Bulk LaMnO$_3$ is an A-type antiferromagnetic (AFM) Mott insulator, due to a combination of superexchange and Zener double exchange [148], whereas SrTiO$_3$ is a non-magnetic insulator (d$^0$ configuration of Ti). Figure 6.3 shows the total densities of states obtained for the superlattices with \(n:m = 2:2, 2:8, \) and \(8:2\). The general shape of the curves is similar, showing half-metallicity in each case. From \(-7\) to \(-2\) eV we find mainly Mn $d$, Ti $d$, and O $p$ states, from \(-2\) to \(2\) eV Mn $d$ and O $p$ states, and above \(2\) eV Ti $d$, La $f$, Sr $d$, and O $p$ states. Figure 6.4 demonstrates systematic changes for varying \(n\) and \(m\). The density of states at the Fermi energy remains similar for growing \(m\) but increases significantly for growing \(n\) due to the fact that these states mainly belong to the LaMnO$_3$ layer. Importantly, for increasing \(n\) as well
Figure 6.3: Total densities of states for thicknesses \( n:m = 2:2, 2:8, \) and \( 8:2 \).

as \( m \), the minority spin band gap is reduced substantially. Indeed, the band onsets in the 2:8 and 8:2 systems are close to the Fermi energy so that the half-metallicity will most likely vanish for \( n, m > 8 \).

The reduction of the minority spin band gap is explained by the projected densities of states of the Ti atoms at the n-IF in Fig. 6.5. The Ti 3\( d \) orbitals, being split into \( d_{xy}, d_{yz}, d_{xz} \) (\( t_{2g} \)) and \( d_{x^2-y^2}, d_{3z^2-r^2} \) (\( e_g \)) states due to the octahedral crystal field, systematically shift to lower energy, which is consistent with previous experimental observations for LaAlO\(_3\)/SrTiO\(_3\) interfaces \[96\]. The energetic lowering is strongest for the \( d_{xy} \) states, which thus govern the reduction of the minority spin band gap. The orbital ordering seen in Fig. 6.5 decreases for increasing \( m \), while it remains similar for increasing \( n \). In addition, it is always more pronounced at the n-IF than at the p-IF, and almost lost at the p-IF and in the bulk-like regions of the 2:8 system. Figure 6.6 gives projected densities of states of Ti atoms in layers with increasing distance from the 2:8 n-IF. As to be expected, away from the n-IF the states shift to higher energy. Projected densities of states of the Mn atoms at the p-IF are shown in Fig. 6.7. Note that the Mn \( d_{x^2-y^2} \) and \( d_{3z^2-r^2} \) orbitals contribute at the Fermi energy in the majority spin channel, though differently for the different systems. Since bulk LaMnO\(_3\) forced into \( C_{2h} \) symmetry becomes metallic, the conducting Mn states are a result of the in-plane strain. The metallicity at the p-IF is substantially reduced
for increasing $n$, especially in the 8:2 system, as the LaMnO$_3$ layer becomes more bulk-like. Figure 6.8 gives projected densities of states of the Mn atoms in layers with increasing distance from the 8:2 p-IF. The distinct difference between the $d_{x^2−y^2}$ and $d_{3z^2−r^2}$ states is reduced when the distance increases.

### 6.3.3 Magnetic Properties

In order to assess the magnetic ground state, we study the total energies for FM and A-type AFM spin ordering for strained bulk LaMnO$_3$ and the superlattices. Other spin orderings (such as C-type and G-type AFM) have much higher energies, as we have checked for the 2:2 system. FM spin ordering is found to be favorable, in agreement with previous experiments \[113, 44, 96\] and calculations \[124\] as well as reports on related perovskite oxide interfaces \[17, 15, 93\]. The energy difference
between FM and A-type AFM spin ordering per unit formula is 0.75 eV for strained bulk LaMnO$_3$, whereas in the case of the superlattices it slightly decreases from 0.27 eV to 0.20 eV for increasing $m$ and remarkably increases from 0.27 eV to 0.85 eV for increasing $n$, which shows that it can be attributed to the LaMnO$_3$ layer (the Ti magnetic moments are very small). Because of this, we normalize our results in the following with respect to the number of Mn atoms. The energy difference steadily decreases for increasing $n$ as well as $m$ though the FM ordering, which is due to Zener double exchange between partially filled Mn $e_g$ states [47], remains favorable. For $x = 0.3$ FM spin ordering is also established in La$_{1-x}$Ca$_x$MnO$_3$, see the neutron diffraction experiments in Ref. [149]. Moreover, X-ray magnetic circular dichroism and absorption spectroscopy on LaAlO$_3$/SrTiO$_3$ have given direct evidence of a FM interface state, originating from the Ti $d_{xy}$ orbitals [96]. Interestingly, induced Ti magnetic moments of 0.02 to 0.04 $\mu_B$ are observed at both interfaces in our systems, see Table 6.2 whereas far from the interfaces they are negligible ($<0.01$ $\mu_B$). For increasing $m$ they increase (decrease) at the n-IF (p-IF), while for increasing $n$ we obtain higher magnetic moments at the p-IF ($\sim0.04$ $\mu_B$) than at the n-IF ($\sim0.02$ $\mu_B$). We note that even small Ti magnetic moments at perovskite oxide interfaces can have important consequences for the magnetism [95, 96].

We find Mn magnetic moments of 3.72 to 4.03 $\mu_B$, with larger values at the n-IF than at the p-IF in all cases. When $m$ increases they increase (decrease) at the n-IF (p-IF), while the changes are not systematic under variation of $n$. The highest value appears in the 4:4 system at the n-IF. Concerning the charges in the atomic orbitals, we find small but finite differences from the corresponding bulk values at both interfaces, see Table 6.2 A detailed analysis shows that for increasing $n$ ($m$) the Mn atoms lose more (less) charge at the p-IF. Moreover, the Ti (Mn) atoms gain (lose) charge at the n-IF (p-IF) in all cases, while there is no clear trend at the p-IF (n-IF) because of the larger distances of the atoms from to the interface plane. The
Table 6.2: Magnetic moments (in $\mu_B$) and charge deviations with respect to the bulk (in electrons) of the interfacial Mn and Ti atoms for different $n:m$. Positive (negative) values represent gain (loss) of charge.

<table>
<thead>
<tr>
<th>$n:m$</th>
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<th>$p$-IF</th>
<th>Ti $n$-IF</th>
<th>$p$-IF</th>
<th>Mn $n$-IF</th>
<th>$p$-IF</th>
<th>Ti $n$-IF</th>
<th>$p$-IF</th>
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<td>−0.05</td>
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<tr>
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<td>3.76</td>
<td>0.02</td>
<td>0.02</td>
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<td>−0.02</td>
<td>+0.02</td>
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</tr>
<tr>
<td>2:6</td>
<td>3.96</td>
<td>3.74</td>
<td>0.02</td>
<td>0.02</td>
<td>+0.03</td>
<td>−0.02</td>
<td>+0.02</td>
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</tr>
<tr>
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<td>3.97</td>
<td>3.72</td>
<td>0.03</td>
<td>0.02</td>
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</tr>
<tr>
<td>4:4</td>
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<td>3.78</td>
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<td>+0.02</td>
<td>0.00</td>
</tr>
<tr>
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<td>0.00</td>
<td>−0.04</td>
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</tr>
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<td>6:2</td>
<td>4.01</td>
<td>3.88</td>
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</tr>
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<td>+0.01</td>
<td>−0.07</td>
<td>+0.04</td>
<td>+0.03</td>
</tr>
</tbody>
</table>

observed small charge transfers give rise to the mentioned Ti magnetic moments but cannot explain the ferroelectric distortions in the SrTiO$_3$ layer, which thus are likely direct consequences of the interface interaction.

6.3.4 Summary

The structural, electronic, and magnetic properties of (LaMnO$_3$)$_n$/SrTiO$_3$$_m$ superlattices have been investigated and compared for various thicknesses $n:m$. Both $n$ and $m$ are found to strongly affect the material properties. In general, the SrTiO$_3$ layers show heavy distortions of the O octahedra, which are not present in bulk SrTiO$_3$, consistent with recent experimental findings [150]. Since LaMnO$_3$ is polar along the [001] direction (with alternating (LaO)$^+$ and (MnO$_2$)$^-$ layers) and SrTiO$_3$ is non-polar, a compensation mechanism is required. As the strained LaMnO$_3$ is metallic, we could expect accumulation of charge carriers at the interfaces. However, this effect is much too small according to the charge deviations reported in Table 6.2 so that a second mechanism must play a role. The projected densities of states of the Ti atoms in layers of increasing distance from the 2:8 $n$-IF in Fig. 6.6 show an almost continuous shift of all curves to higher energy. This reflects the built up of an electric field, which in turn induces ferroelectric distortions in the SrTiO$_3$ region, as discussed before. The
ferroelectric distortions constitute the main compensation mechanism in the present superlattice. Similar distortions of the TiO$_6$ octahedra have been reported in Ref. [89].

All studied systems exhibit half-metallicity, though our results indicate that this property will vanish for $n, m > 8$. FM spin ordering is always energetically favorable over AFM spin ordering but the preference becomes smaller for increasing $n$, since the A-type AFM ordering of bulk LaMnO$_3$ starts to dominate. The Ti magnetic moments observed at the interfaces are small. The authors of Ref. [33] have found ferromagnetic and antiferromagnetic alignment of the Mn and Ti spins for $n:m$ ratios of 3:2 and 17:2, respectively, and have argued that Mn-O-Ti superexchange therefore must play a role. In general, defects and cation intermixing are important for the stabilization of perovskite superlattices. For instance, the high electrical conductivity of the LaAlO$_3$/SrTiO$_3$ interface is related to the formation of O vacancies during the deposition process due to the extra charges introduced into the system [151]. In addition, Sr/La intermixing leads to a metallic interface between the insulators LaTiO$_3$ and SrTiO$_3$, because mixed valent Ti states are created [152]. We expect that these factors are less important for the LaMnO$_3$/SrTiO$_3$ interface, as it was found to be rather sharp [150]. We find a systematic reduction of the minority spin band gaps with increasing $n$ and $m$, which originates mainly from an energetic downshift of the Ti $d_{xy}$ states.
Figure 6.5: Projected densities of states of the Ti atom next to the n-IF for thicknesses $n:m = 2:2, 2:4, 2:6, 2:8, 4:2, 6:2, \text{ and } 8:2.$
Figure 6.6: Projected densities of states of the Ti atoms in layers with increasing distance from the 2:8 n-IF.
Figure 6.7: Projected densities of states of the Mn atom next to the p-IF for thicknesses $n:m = 2:2$, 2:8, and 8:2.
Figure 6.8: Projected densities of states of the Mn atoms in layers with increasing distance from the 8:2 p-IF.
Chapter 7

Half-Metallicity in a BiFeO$_3$/La$_{0.7}$Sr$_{0.3}$MnO$_3$ Superlattice

7.1 Introduction

The control of material interfaces at the atomic level has led to novel interfacial properties and functionalities [153]. In material science, multiferroic materials are of interest because they show spontaneous electric and magnetic polarizations. Important examples of single phase multiferroic materials are BiFeO$_3$ (BFO), BiMnO$_3$, LuFe$_2$O$_4$, and BaNiF$_4$. Research on room temperature multiferroic materials has focused on BiFeO$_3$ and its derivatives [154] due to the strong electric polarization and potential applications in spintronics and memory devices. However, single phase multiferroic compounds in general suffer from weak magnetoelectric response [155] and low electrical resistivity [156]. Recently, new strategies for engineering multifunctional multiferroic materials based on composites have been introduced. In comparison to bulk compounds, nanostructured thin films provide more degrees of freedom, such as lattice strain and interlayer interaction, to modify the magnetoelectric behavior. They offer novel ways to investigate the physical mechanisms behind the magnetoelectric effect on the nanoscale [157]. Combining multiferroic and ferromagnetic (FM) materials in a thin film epitaxial heterostructure provides control of the elec-
tron spin polarization through the lattice polarization \cite{158}. Nanoscale composite thin films have been found to be capable of producing relatively large magnetoelectric coefficients \cite{159,160}. From the growth point of view, pulsed laser deposition \cite{5}, molecular beam epitaxy \cite{6} and sol-gel spin-coating \cite{7} have been employed for achieving nanoscale composites.

In recent years the multiferroic FM heterostructure BFO/La$_{1-x}$Sr$_x$MnO$_3$ has obtained increasing interest because of its high dielectric constant and excellent ferroelectric behaviour \cite{161}. In addition, a strong magnetoelectric coupling at the interface has been reported in Ref. \cite{155}. BFO/La$_{1-x}$Sr$_x$MnO$_3$ bilayers reveal a high and homogeneous resistive state for the BFO film that can be used as ferroelectric tunnel barrier \cite{5}. In addition, a significant exchange bias has been observed in this heterostructure \cite{50,162}. The electronic states of bulk BFO and La$_{1-x}$Sr$_x$MnO$_3$ have been widely studied experimentally and theoretically. However, research on the heterostructure of these two compounds has been emerging only in recent years, where very few investigations have dealt with ab-initio calculations using density functional theory. In this work, we therefore study BFO/La$_{0.7}$Sr$_{0.3}$MnO$_3$ (BFO/LSMO) superlattice by first principles calculations, in particular to address the interrelation between the interface geometry and the electronic properties.

### 7.2 Superlattice Modeling and Computational Details

In order to study the electronic structure and magnetic properties of the BFO/LSMO heterostructure, we apply the full-potential (linearized) augmented plane-wave method, as implemented in the WIEN2k package \cite{163}. This approach is based on density functional theory and is one of the most accurate schemes of solid state electronic structure calculations \cite{164}. The generalized gradient approximation with onsite Coulomb inter-
Table 7.1: Structural and technical parameters.

<table>
<thead>
<tr>
<th>Property</th>
<th>BiFeO$_3$</th>
<th>La$<em>{0.7}$Sr$</em>{0.3}$MnO$_3$</th>
<th>BFO/LSMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>AFM insulator</td>
<td>FM half-metal</td>
<td></td>
</tr>
<tr>
<td>Lattice parameters</td>
<td>$a = b = 5.57$ Å</td>
<td>$a = b = 5.49$ Å</td>
<td>$a = b = 5.54$ Å</td>
</tr>
<tr>
<td>$c$</td>
<td>$13.86$ Å</td>
<td>$13.37$ Å</td>
<td>$27.24$ Å</td>
</tr>
<tr>
<td>$\alpha = \beta = 90^\circ$</td>
<td>$\gamma = 120^\circ$</td>
<td>$\gamma = 120^\circ$</td>
<td>$\gamma = 120^\circ$</td>
</tr>
<tr>
<td>Space group</td>
<td>R3c</td>
<td>R3c</td>
<td>P3</td>
</tr>
<tr>
<td>Atoms</td>
<td>30 (6 BFO)</td>
<td>30 (6 LSMO)</td>
<td>60</td>
</tr>
<tr>
<td>Inequivalent</td>
<td>18</td>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td>Method</td>
<td>GGA+U (AFM)</td>
<td>GGA+U (FM)</td>
<td>GGA+U</td>
</tr>
<tr>
<td>Onsite interaction</td>
<td>$U = 7$ eV</td>
<td>$U = 5$ eV</td>
<td>$U = 7$ eV (Fe)</td>
</tr>
<tr>
<td></td>
<td>$J = 0$ eV</td>
<td>$J = 0$ eV</td>
<td>$U = 5$ eV (Mn)</td>
</tr>
</tbody>
</table>

action and self-interaction correction (GGA+U) is used for the exchange-correlation functional [165, 57, 166]. The Coulomb interaction parameter $U$ and exchange parameter $J$ are introduced to account for the onsite electron-electron interaction in the localized 3$d$ orbitals of the transition metals. We set $U = 5$ eV for Mn, $U = 7$ eV for Fe, and $J = 0$ eV for both Fe and Mn, based on previous electronic structural calculations of bulk BFO [167, 168] and LSMO [169].

Brillouin zone integrations are performed on a $6 \times 6 \times 2$ Monkhorst-Pack k-mesh [64] with 16 points in the irreducible wedge of the Brillouin zone. We have tested different meshes for BFO and LSMO to confirm that this mesh is sufficiently fine to guarantee converged results. The muffin-tin radii are set to 1.5, 1.95, 2.13, and 2.48 Bohr radii for O, Fe, Bi, and Sr, respectively, and to 1.93 for both La and Mn. Moreover, an energy cutoff given by $R_{mt}K_{max} = 7$ with $\ell_{max} = 10$ is employed. Self-consistency is achieved with an energy convergence of $10^{-3}$ Ry. In our calculations, the charge densities are represented by 24535, 6414, and 47521 plane waves for BFO, LSMO, and BFO/LSMO, respectively. Full relativistic effects are taken into account for the core states, while the scalar relativistic approximation is used for the valence states. The basis set consists of O 2$s^2$ 2$p^4$, Mn 3$s^2$ 3$p^6$ 3$d^5$ 4$s^2$, Fe 3$s^2$ 3$p^6$ 3$d^6$ 4$s^2$, ...
Sr $4s^2\ 4p^6\ 5s^2$, La $4d^{10}\ 5s^2\ 6s^2\ 5p^6\ 5d^1$, and Bi $5p^6\ 5d^{10}\ 6s^2\ 6p^3$ orbitals. In order to address the effect of the structural relaxation at the interfaces in the BFO/LSMO superlattice on the physical properties, the atomic positions are fully relaxed with a force tolerance of 2 mRy/Bohr. Moreover, the density of states (DOS) is calculated with a Gaussian broadening of 5 mRy. A summary of the employed structural and technical parameters is given in Table I.

Figure 7.1: Structure of bulk BiFeO$_3$, bulk La$_{0.7}$Sr$_{0.3}$MnO$_3$, and the BFO/LSMO superlattice. Small red spheres denote O atoms, while the other atoms are indicated in the figure. Arrows indicate the orientation of the magnetic moments, and AFM IF and FM IF denote, respectively, the locations of the antiferromagnetic and the ferromagnetic interface.
Figure 7.2: Total DOS of bulk BFO, bulk LSMO, and the BFO/LSMO superlattice.

7.3 Calculation Results

7.3.1 Structural and Electronic Properties

Bulk BFO and LSMO have a rhombohedrally distorted perovskite structures with hexagonal lattice parameters $a = 5.58 \, \text{Å}$, $c = 13.87 \, \text{Å}$ [170] and $a = 5.49 \, \text{Å}$, $c = 13.37 \, \text{Å}$ [171], respectively, as shown in Figs. 7.1(a) and (b). Moreover, BFO exhibits a ferroelectric transition at $T_C = 1100 \, \text{K}$ (from ferroelectricity to paraelectricity) and a magnetic transition at $T_N = 643 \, \text{K}$ [172] (from an antiferromagnet to a paramagnet). The antiferromagnetic (AFM) order in BFO is of G-type [173]. Hole-doped La$_{0.7}$Sr$_{0.3}$MnO$_3$ is a double-exchange ferromagnet with metallic conductivity below $T_C = 370 \, \text{K}$ [16]. Starting from the bulk materials, we set up a hexagonal supercell,
see Fig. 7.1 (c), by stacking the bulk unit cells along the [001]_{hex} direction. Figure 7.1 (c) shows two BFO unit cells in the center of the supercell sandwiched between LSMO layers, which both consist of one unit cell. Due to the periodic boundary conditions, we therefore have alternating BFO and LSMO layers of two unit cell thickness. Our supercell contains 36 inequivalent atomic sites and 60 atoms in total. The lattice constants parallel to the interfaces are chosen to assume the average value \(a = b = 5.54\,\text{Å}\), while the perpendicular length is \(c = 27.24\,\text{Å}\), i.e., the sum of the underlying BFO and LSMO bulk lattice constants. By construction, our supercell contains two interfaces, one FM and the other AFM, because BFO is subject to AFM order and LSMO to FM order. Thus, the Fe atoms at the two interfaces have the magnetic moments oriented in opposite direction and the coupling between BFO and LSMO is FM at one interface and AFM at the other one.

After the structural relaxation of the BFO/LSMO superlattice we find a significant modification of the structure in the LSMO region, specifically, the distortion of the MnO\(_6\) octahedra is extended to the BFO. In other words, the bond angles within the MnO\(_6\) octahedra change such that they resemble the FeO\(_6\) octahedra. For a deeper analysis, we compare the structure of our superlattice with the corresponding structural data of the bulk compounds. The O-Mn-O (Mn-O-Mn) bond angles decrease by up to 6° (10°) from their bulk value of 180° (173°). This alteration indicates that the O octahedra in our superlattice no longer maintain the almost perfect octahedral shape as found in bulk LSMO. The Mn-O bond length (1.94 Å in the bulk) at the AFM interface increases to 2.04 Å, whereas the Fe-O bond length (2.11 Å in the bulk) at the FM interface shrinks to 2.07 Å. These alterations are either due to the strain induced by the lattice mismatch or the broken translational symmetry at the interface. Importantly, the off-centering of the Fe atoms within the O octahedra shows significant modifications in the superlattice. While in bulk BFO there are three Fe-O bond lengths of 1.96 Å and three other of 2.11 Å, these values change to 2.00 Å and
2.03 Å, respectively, except for the FM interface, see above. This fact implies that the ferroelectric behavior is reduced due to the proximity of the LSMO. We note that this finding does not contradict the experimental situation of Ref. [161], because in that work the film thickness is much higher. We will discuss below how the structural distortions in the superlattice affect the orbital occupations and spin polarization at the two interfaces.

The total DOS is presented in Fig. 7.2 for bulk BFO (top left) and bulk LSMO (top right). The BFO DOS shows that in the low energy range between about −8 eV and −7 eV the Fe 3d states dominate. On the other hand, the region from −6 eV to the Fermi energy ($E_F$) is mainly due to the Bi 4p and O 2p states. There is a strong hybridization between Bi and O, which plays an important role for the ferroelectricity, because in BFO ferroelectricity results from the local distortion introduced by the stereo-chemically active 6s$^2$ lone pair of electrons of the Bi$^{3+}$ cation [174]. From 3 eV to 6.8 eV (the conduction band), the Fe 3d and Bi 4p states are dominant with small contributions from the O 2p states. We find that the Fe 3d states at the conduction band minimum are hybridized with O 2p states to some extent.

In general, BFO displays an insulating character with a band gap of 2.8 eV, which is determined by the energetical separation between strongly hybridized O 2p and Fe 3d valence states and the bottom of the conduction band. The calculated band gap is in reasonable agreement with the experimental results of 2.5 eV [175] and 2.7 eV [176]. In the LSMO DOS the majority spin metallicity results from the broad Mn 3d and O 2p hybridized states in the energy range from −7.2 eV to 2.6 eV, while $E_F$ is located in the minority spin band gap. The shape of the valence DOS with two broad peaks agrees well with results from x-ray photoemission spectroscopy [177]. Sharp peaks at 3.3 eV (3.8 eV) are mainly due to La f (Mn d) contributions. From about 6.5 eV to 8.3 eV the Sr d states are dominant. The LSMO DOS exhibits a half-metallic character with a spin minority band gap of 3.2 eV. This value is larger than reported
in previous studies, mainly because we use a higher Coulomb parameter of $U = 5$ eV. In fact, the GGA+$U$ approach with this $U$ value produces an increased band gap and a more consistent picture of the electronic structure for the two bulk compounds.

Importantly, the total DOS of the superlattice in Fig. 7.2 (bottom) clearly shows a half-metallic character with a minority spin band gap of 2.2 eV. This fact indicates that our superlattice preserves the half-metallic nature of bulk LSMO. We note that the Fe $d$, Sr $d$, La $f$, and Bi $p$ states do not contribute to the metallicity in the spin majority channel. Although the Fe $3d$ states at the conduction band minimum are slightly shifted to lower energy in the BFO/LSMO superlattice with respect to the bulk Fe states, due to differences in the electrostatic background, they are still far from $E_F$ and therefore do not contribute to the metallicity. The energetical shift implies that there is a transfer of charge in the superlattice, which mainly affects the states between $-2$ eV and 2 eV. In the vicinity of $E_F$ the DOS predominately can be traced back to hybridized Mn $3d$ and O $2p$ states. The band gap in the minority channel is reduced with respect to bulk LSMO because bulk BFO O $2p$ minority states appear between $-1$ eV and 0 eV. Strain effects, which also could modify the band gap, seem to play a subordinate role.

To distinguish the atoms near and far from the interface, we label the atoms as shown in Fig. 7.1 (c). The Fe $d$ (left) and O $p$ (right) DOSs are addressed in Fig. 7.3. The sites Fe1 and Fe6 are located near the FM interface, the sites Fe3 and Fe5 near the AFM interface, and the sites Fe2 and Fe4 close to the center of the BFO region. These pairs of atoms therefore exhibit similar DOSs but with opposite spins. We observe that Fe3 (located near the AFM interface) appears at lower energy than Fe1 (located near the FM interface), where Fe2 (located in a bulk-like environment) resembles the bulk DOS. A similar behavior is found for Sr, La, and Bi. In general, a more positive electrostatic background will lead to electronic states at lower energy. According to the above analysis, the FM interface thus is characterized by a less
positive electrostatic background. As a consequence, we should obtain less charge near the FM interface, while the more positive electrostatic background near the AFM interface should lead to higher orbital occupations. We will discuss this point in the next section. Finally Fig. 7.3 (right) shows DOSs for three selected O atoms from the LSMO region, the BFO region, and the AFM interface. We find that only O atoms in the LSMO region contribute to the metallicity of the BFO/LSMO superlattice, while the O atoms in the BFO region give essentially no contribution except for those located exactly at the AFM interface. Strong hybridization between the Mn and O states near $E_F$ is reflected by common peaks in the Mn and O DOSs.

In Fig. 7.4 we display the partial Mn 3$d$ DOS. The main contribution to the DOS at $E_F$ and thus to the metallicity is due to the spin majority Mn 3$d$ states. The sites
Mn2 and Mn3 (located near the AFM interface), Mn5 and Mn6 (located near the FM interface), and Mn1 and Mn4 (located in a bulk-like environment) exhibit similar DOSs; also the differences between these groups are not significant.

We first address the orbital occupations in our superlattice. As to be expected, the Bi and Mn atoms lose some charge, specifically atom Mn2 (Mn5) near the AFM (FM) interface loses 0.02 (0.07) electrons. Atom Bi6 (Bi2) near the AFM (FM) interface loses 0.01 (0.02) electrons. On the other hand, each La atom in the superlattice gains 0.02 electrons, while Sr2 near the AFM interface gains 0.02 electrons and Sr1 near the FM interface gains 0.03 electrons. Charge differences turn out to be negligible for the Fe atoms, except for Fe5 near the AFM interface which gains 0.01 electrons. All O atoms lose some charge (< 0.02 electrons) except for those at the FM interface. Comparing the atomic charges near the two interfaces, we find a bit less charge at the FM interface than at the AFM interface, which agrees with the above analysis of the DOSs and implies that the orbital reconstruction at the AFM interface is larger than at the FM interface.

So far we have investigated the change of the orbital occupations in the BFO/LSMO superlattice with respect to the bulk compounds. However, such changes have implications for the magnetic moments. The average Mn magnetic moment in the superlattice is found to be 3.54 $\mu_B$, which is slightly larger than the bulk value of 3.52 $\mu_B$, in reasonable agreement with the experimentally reported value of 3.67 $\mu_B$/Mn [178]. Interestingly, the Mn magnetic moment varies significantly near the interface to the BFO, which supports magnetoelectric coupling. In agreement with the DOS in Fig. 7.4, Mn2 (Mn5) gains (loses) a magnetic moment of 0.33 (0.38) $\mu_B$. The Mn magnetic moments are determined by the majority spin electrons while the minority spin contributions are negligible around $E_F$. The reduction of the magnetic moment near the FM interface thus is due to the loss of majority spin states.

The magnetic moments of all the Fe atoms almost keep their bulk values, except
for the slight decrease of $0.02 \mu_B$ for Fe1 near the FM interface. The average Fe magnetic moment is $4.2 \mu_B$, which is similar to the reported value of a previous GGA+$U$ calculation using the same $U$ parameter [168]. However, this value is slightly larger than the experimental magnetic moment of $3.7 \mu_B$ [179]. This observation confirms that the GGA+$U$ method slightly overestimates Fe magnetic moments [180].

According to the reported variations of the magnetic moment between the bulk and the superlattice, it can be concluded that the FM interface is subject to a reduced spin polarization, whereas the spin polarization is enhanced at the AFM interface. As a consequence, an AFM spin order across the interface is energetically favourable as compared to a FM spin order, in agreement with the findings reported in Ref. [181].

Yu and coworkers [182] also suggested that the coupling between the Mn bulk and Fe interfacial spins is anti-parallel according to the opposite signs observed in Mn and Fe x-ray magnetic circular dichroism.

In general, interaction between O atoms and magnetic ions plays an important role for the magnetic properties of transition metal oxides. For BFO, O vacancies have been found to result in a noticeable modification of the magnetism due to a transition of the Fe oxidation state from 3+ to 2+ [183]. Both experimentally and theoretically it has been suggested that O vacancies enhance the ferromagnetism because they alter the distance between the Fe ions and, therefore, the strength of the Dzyaloshinskii-Moriya interaction [184]. Similar effects can be expected for the BFO/LSMO superlattice.

### 7.3.2 Optical Properties

We next address the optical properties of the BFO/LSMO superlattice, in particular the imaginary part of the dielectric function, $\text{Im}(\epsilon)$, and the reflectivity, $R(\omega)$. Fig. 7.3 compares results for the superlattice to those of bulk BFO and LSMO, separately for the majority and minority spins. Since BFO is not subject to spin polarization,
Figure 7.5: Imaginary part of the dielectric function (xx component) and reflectivity of the BFO/LSMO superlattice. Top: majority spins, bottom: minority spins. While the xx and yy components of the dielectric function are obviously identical, we find that also the zz component is very similar.

The two spin channels are degenerate in this case. The results clearly reflect that bulk BFO is insulating with an optical band gap of about 2.5 eV. There appear mainly two peaks in \( R(\omega) \), with some additional subpeaks. The peak around 4 eV reflects transitions of O \( p \) electrons into unoccupied Fe \( d \) states, whereas the peak around 6 eV corresponds to transitions of O \( p \) electrons into the Bi \( p \) conduction bands. These findings match well with previous first principles calculations reported in Ref. [185]. Our results for \( \text{Im}(\epsilon) \) agree much better with the experimental situation [176] than the data obtained in Ref. [167], in particular, for the 4 eV peak, for which even the substructure reproduces the experimental spectrum. The better agreement is probably due to the different onsite interaction parameter applied in our study.

Bulk LSMO shows a high reflectivity in the low energy range for the majority spin states, the metallic Drude peak. For the minority spin states, both \( R(\omega) \) and \( \text{Im}(\epsilon) \) exhibit a band gap, reflecting the half-metallic character of LSMO. The spin majority
reflectivity peak at 2 eV is consistent with the experimental peak with respect to
energy and magnitude \[186, 187\]. It is due to transitions from the hybridized O \(p\)
and Mn \(d\) states into the Mn \(d\) states in the conduction band. At 3.3 eV we observe
the remainder of the dipole forbidden transition from the O \(p\) into the La \(f\) states.
Concerning the minority spin channel, the pronounced \(R(\omega)\) peak between 5 and
6 eV is due to transitions of O \(p\) electrons into Mn \(d\) conduction states. Previous
calculations on the optical properties of LSMO \[188\] have suggested transitions from
Mn \(d\) \(t_{2g}\) into Mn \(d\) \(e_g\) states in the majority spin channel, and from O \(2p\) into Mn \(d\)
\(t_{2g}\) and \(e_g\) states in the minority spin channel.

We find that the BFO/LSMO superlattice also shows a high reflectivity in the
low energy range for the majority spin states, and a band gap for the minority spin
states, thus merging the individual properties of bulk BFO and LSMO. The half-
metallic behavior discussed before for the DOS accordingly is reflected by the optical
spectrum. For the minority spin channel, \(\text{Im}(\epsilon)\) shows that the absorption begins
above 2 eV for the superlattice, whereas for bulk LSMO absorption occurs only above
3 eV. The required excitation energy thus is reduced, since the half-metallic band gap
is smaller in the case of the superlattice. The calculated optical band gaps match well
with the minority spin band gaps in the DOS, which amount to 2.2 and 3.2 eV in
the case of the BFO/LSMO superlattice and bulk LSMO, respectively. We note that
a reduced minority spin band gap opens potential applications in spintronic devices
and photocatalyst materials. As compared to the bulk compounds, we observe shifts
in the energetical positions of the \(R(\omega)\) peaks. In the energy range from 3 to 6 eV we
notice a shift towards lower energy, and above 8 eV a shift towards higher energy. This
behavior corresponds to the aforementioned modifications of the DOS, in particular,
the shift of states of atoms near the AFM (FM) interface to lower (higher) energy. In
general, the optical spectrum of the BFO/LSMO superlattice is well understood in
terms of merged bulk BFO and LSMO spectra. A clear optical anisotropy in neither
found for the two bulk compounds nor for the superlattice.

7.3.3 Summary

We have investigated the structural, magnetic, and optical properties of hexagonal (rhombohedral) BFO, LSMO, and a BFO/LSMO superlattice using the GGA+$U$ approach. As concerns the structural properties, our calculations are in good qualitative and quantitative agreement with the experimental situation. In addition, they reproduce the insulating and half-metallic natures of bulk BFO and LSMO, respectively. The Fe magnetic moments are found to slightly exceed the experimental values, which is a well-known phenomenon for GGA+$U$ calculations. On the other hand, the calculated band gap agrees well with experiment. Intriguingly, the BFO/LSMO superlattice maintains the half-metallic character of bulk LSMO. Structural relaxation and charge transfer are present at both interfaces, but are not strong enough to significantly modify the bulk properties.
Chapter 8

Conclusion

We have investigated the structural, electronic, and magnetic properties of the manganite based superlattices using first-principles calculations within the density functional theory framework. The bulk and interfacial properties are mainly studied. Our selected superlattices include LaNiO$_3$/CaMnO$_3$, BiMnO$_3$/SrTiO$_3$, LaMnO$_3$/SrTiO$_3$ and BiFeO$_3$/La$_{0.7}$Sr$_{0.3}$MnO$_3$. The aim of the investigation is to analyse and predict the electronic structure of the system and explain the experimental findings. Our results are found to be in good agreement with experimental findings.

The manganites we consider have highly distorted perovskite structures. We noticed strong structural distortions of strontium titanate SrTiO$_3$ in the combined superlattices as well, whereas its bulk structure is cubic. Importantly a systematic off-centering of Ti atoms in the TiO$_6$ octahedra has been observed which implies the possibility of induced ferroelectric behaviour in SrTiO$_3$ region. Since a superlattice is a periodically repeated heterostructure of at least two different components, they have two different connected interfaces. According to the polarity of layers, we denote them as $n$ and $p$ type interfaces. For instance, the $n$-type LaO/TiO$_2$ interface and the $p$-type MnO$_2$/SrO interface in the LaMnO$_3$/SrTiO$_3$. The nomenclature refers to the compensating charges formed at the $(\text{La}^{3+}/\text{O}^{2-})^+/(\text{Ti}^{4+}/\text{O}^{2-})^0$ and $(\text{Sr}^{2+}/\text{O}^{2-})^0/(\text{Mn}^{3+}/\text{O}^{2-})^-$ contacts, respectively. The interfacial electrical properties can be different with different strain state, defect location as well as the constituent
elements. The polarization and magnetism can be tuned by strain and O defect [189].

Regarding the computational scheme, the electronic structure turns out to be highly sensitive to the onsite Coulomb interaction term for the highly localized orbitals such as 3\textit{d} states in Mn atom. The detailed analysis of the selection of the correction term is needed (literature suggested values should be tested carefully). Induced interfacial Ni magnetic moments have been observed in some test superlattice calculations in LaNiO\textsubscript{3}/CaMnO\textsubscript{3} with and without onsite Column interaction term which indicates that Ni atoms at the interfaces may also contribute to the interfacial magnetism. The values of the magnetic moment are also sensitive to the selection of the pseudopotentials, therefore initial test calculations for reproducing the experimental values are strongly recommended.

The Oxygen defect plays an important role in determining the electronic and magnetic properties of the BiMnO\textsubscript{3}/SrTiO\textsubscript{3} superlattice. Especially density of states at the Fermi level at the interfaces or interfacial metallcity can be induced by introducing the O defect. O defect in the BiO layer turns out to be essential for reproducing the experimental interface magnetism and for understanding its mechanism.

We also investigate the effect of the uniaxial strain to the electronic structure of the (LaMnO\textsubscript{3})\textsubscript{2}/(SrTiO\textsubscript{3})\textsubscript{2} superlattice and we found that the observed two-dimensional electron gas and interfacial Ti magnetic moments can be tuned by applying uniaxial strain. This finding may guide experimental work on how to select substrates and tune the experimental parameters in order to obtain interfacial conductivity. We also investigate the thickness dependence of the properties of (LaMnO\textsubscript{3})\textsubscript{n}/(SrTiO\textsubscript{3})\textsubscript{m} superlattices. The systems favour ferromagnetic spin ordering rather than the antiferromagnetic spin ordering of bulk LaMnO\textsubscript{3} and all show half-metallicity, while a systematic reduction of the minority spin band gaps as a function of the LaMnO\textsubscript{3} and SrTiO\textsubscript{3} layer thicknesses originates from modifications of the Ti \textit{d}_{xy} states.

We turn our attention to the superlattice BiFeO\textsubscript{3}/La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3} (antiferromag-
netic/ferromagnetic) in which the multiferroic properties of BiFeO$_3$ and half-metallic, ferromagnetic properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ are of great interest for magnetic storage applications such as magnetic heads and sensors. The electronic states of the heterostructure are compared to those of the bulk compounds. Structural relaxation turns out to have only a minor impact on the chemical bonding, even though the Oxygen octahedra in La$_{0.7}$Sr$_{0.3}$MnO$_3$ develop some distortions due to the interface strain. While a small charge transfer affects the heterointerfaces, our results demonstrate that the half-metallic character of La$_{2/3}$Sr$_{1/3}$MnO$_3$ is fully maintained.

There are some important factors such as work function difference (or band bending) and valence mismatch (or polar discontinuity) of different types of perovskite oxides [182] that influence the interfacial electronic properties. The investigation of the effect of the cation intermixing and impurity concentration in superlattice and thin films can be important directions in future work since more and more experimental work suggests the importance of these factors to the electronic properties, besides the O defects and epitaxial strain. It is also fundamentally important to further explore the multiferroic properties of the superlattices especially switching the magnetization by tuning the electric field or vice versa (magnetoelectric property) and investigate the effect of the strain to magnetoelectric behaviour.
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Figure 8.1: Total densities of states of bulk SrTiO$_3$ and strained bulk BiMnO$_3$ with SrTiO$_3$ lattice constant.
Figure 8.2: Densities of states of (BiMnO$_3$)$_3$/SrTiO$_3$ superlattices with and without O defect (in plane lattice constant is strained to SrTiO$_3$ lattice constant). Red color refers to the BiMnO$_3$ part and blue color to the SrTiO$_3$ part.
Figure 8.3: Orbitally projected densities of states of the Mn atom next to the $n$-interface (in plane lattice constant is strained to SrTiO$_3$ lattice constant).
Figure 8.4: Orbitally projected densities of states of the Ti atom next to the n-interface (in plane lattice constant is strained to SrTiO₃ lattice constant).


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