Role of O defects at the BiMnO₃/SrTiO₃ interface

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Abstract

We use first principles calculations to study ideal and O deficient BiMnO₃/SrTiO₃ superlattices. The ideal superlattice is characterized by parallel alignment of the Mn and Ti magnetic moments at the n-interface, while an antiparallel alignment has been reported experimentally. O defects at the n-interface are found to favor the MnO₂ and BiO layers over the TiO₂ layer. The band gap of the superlattice is strongly reduced when the MnO₂ layer is O deficient and d₃z²−r² states are observed at the Fermi energy when the BiO layer is O deficient. Only in the latter case the Mn and Ti magnetic moments at the n-interface align antiparallel. Therefore, O defects in the BiO layer turn out to be essential for reproducing the experimental interface magnetism and for understanding its mechanism.

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 CaRuO₃/CaMnO₃, BiMnO₃/SrTiO₃, and LaAlO₃/SrTiO₃ interfaces [1, 2] and metallicity/superconductivity at the LaAlO₃/SrTiO₃ interface [3, 4]. Interfacial magnetism is of particular interest due to potential applications in magnetic sensors [5] and tunnel junctions [6], for example. The class of perovskite manganites [7, 8] hosts interesting properties such as colossal magnetoresistance [9] and electronic phase separation [10]. BiMnO₃ has been reported to show ferromagnetism as well as ferroelectricity in the bulk [11], the latter being debated in the literature since the discovery of a centrosymmetric C2/c space group [12–14] instead of the previously proposed non-centrosymmetric C2 space group [15, 16]. The situation is involved, because the question about ferroelectricity is closely connected to those about orbital ordering and magnetism [16, 17]. In addition, the stoichiometry of the samples plays a significant role [18, 19]. The authors of reference [20] have demonstrated the effect of strain on the orbital reconstruction at the n-interface of the LaMnO₃/SrTiO₃ superlattice, which in turn modifies the exchange interaction. The interface between the polar insulator BiMnO₃ and the non-polar insulator SrTiO₃ can become metallic by means of a polar catastrophe, O defects, and intersite chemical disorder [21], all being related to interfacial magnetism. For thin films of BiMnO₃ on SrTiO₃ ferroelectricity has been reported in [22]. In addition, spin polarization is found for the Ti atoms at the (Bi³⁺O²⁻)⁺/(Ti⁴⁺O₂⁻)⁰ interface, with antiparallel orientation of the Mn and Ti spins [2]. 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.

2. Computational details

We model the (Bi³⁺O²⁻)⁺/(Ti⁴⁺O₂⁻)⁰ and (Sr²⁺O⁻)⁰/(Mn³⁺O²⁻)⁻ interfaces (which we denote as n and p-interfaces, respectively, referring to the compensating interface charges) simultaneously by building a BiMnO₃/SrTiO₃ superlattice. The fact that 3 unit cells of BiMnO₃ alternate with 3 unit cells of SrTiO₃ excludes interaction between the interfaces and makes it possible to compare to the results of [2] (thin film, no 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 [23]. For the exchange correlation functional we employ the generalized gradient approximation and include an onsite correction for the localized $d$ states [24]. The values of the onsite repulsion and exchange parameters are adopted from previous works (4 and 1 eV for the Mn 3$d$ states, 5 eV and 0.5 eV for the Ti 3$d$ states [25, 26]). 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 in the following 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$_3$ ferromagnetic 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 figure 1. While an optimization of the in-plane and out-of-plane lattice constants of BiMnO$_3$ leads to values of 3.97 Å and 3.94 Å, respectively, 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 figure 1. We note that the strain in our superlattice is smaller than the experimental strain, since the experimental lattice constant of 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. 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 $-5\text{ eV Å}^{-1}$) is used to evaluate the ability of the O defects to migrate [27].

### 3. Results and discussion

The structure of the (BiMnO$_3$)$_3$/SrTiO$_3$ superlattice is illustrated schematically in figure 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 figure 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 tiltings 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.

| Table 1. Bond angles, bond lengths, and magnetic moments next to the n and p-interfaces. |
|---------------------------------------------------------------|
|                      | ideal superlattice | O deficient MnO$_2$ layer | O deficient BiO layer |
| Mn–O                 | 2.02 Å             | 2.02 Å                     | 2.03 Å               | 1.94 Å               | 1.95 Å               |
| Ti–O                 | 2.07 Å             | 1.95 Å                     | 2.02 Å               | 2.04 Å               | 2.12 Å               |
| Mn–O                 | 3.79 µ$_B$         | 3.79 µ$_B$                 | 4.23/4.35 µ$_B$      | 3.86/3.89 µ$_B$      | 3.76/4.47 µ$_B$      |
| Ti–O                 | 0.01 µ$_B$         | 0.02 µ$_B$                 | 0.02 µ$_B$           | 0.02/−0.03 µ$_B$     | 0.03 µ$_B$           |
| Ti                   | 0.01 µ$_B$         | 0.02 µ$_B$                 | 0.02 µ$_B$           | 0.02/−0.03 µ$_B$     | 0.03 µ$_B$           |
| Mn                   | 3.79 µ$_B$         | 3.79 µ$_B$                 | 4.23/4.35 µ$_B$      | 3.86/3.89 µ$_B$      | 3.76/4.47 µ$_B$      |

**Figure 3.** Densities of states of (BiMnO$_3$)$_3$/SrTiO$_3$ superlattices with and without O defect. Red color refers to the BiMnO$_3$ part and blue color to the SrTiO$_3$ part.
from 180° to 161°–167°. Additionally, the O–Ti–O bond angles along the z-axis are reduced to about 172° 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 [26, 28], 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 [29]. Table 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$_3$ when the involved O atoms belong to the BiO and SrO layers, respectively, see the right-hand side of figure 2. Adjacent to an O defect in the MnO$_2$/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 figure 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 LaMnO$_3$/SrMnO$_3$ superlattice for which a half-metallic character is found though both component materials are insulators [30]. 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. When it is located in the BiO layer 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.

Figure 4. Orbitally projected densities of states of the Mn atom next to the n-interface.
We address orbitally projected densities of states of the Mn atom next to the n-interface in figure 4. We find that the $e_g$ ($d_{x^2-y^2}$ and $d_{z^2}$) states dominate around the Fermi energy and that in the case of the O deficient BiO layer the $d_{z^2-\tau_1}$ orbitals are partially occupied. Turning to the orbitally projected Ti densities of states in figure 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 [31–33]. O deficiency in the BiO layer also results in an energetical downshift of all states, but additionally the $d_{z^2-\tau_1}$ orbitals become partially occupied. In principle, orbital reconstructions similar to those dominating the properties of the O deficient LaAlO$_3$/SrTiO$_3$ interface [34] can be expected to appear also in our case. However, figure 5 demonstrates that the spin polarization of the Ti atoms at the interface is mostly carried by the $d_{x^2-y^2}$ states, whereas at the LaMnO$_3$/SrTiO$_3$ interface the induced Ti magnetic moments are always due to the $d_{xy}$ states [32, 33].

Table 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 [2]. 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 $\mu_B$ [35]). 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 $d_{z^2-\tau_1}$ 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$_{0.2}$Sr$_{0.8}$MnO$_3$/SrTiO$_3$ superlattice, but the authors rule out relevant effects of O defects due to a small concentration [36].

Since the Ti atom with inverted spin always is located directly next to an O defect, see the X in figure 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 figure 6. The Mn and Ti atoms next to the O defect along the z-direction experience approximately a square pyramidal instead of an octahedral crystal field. As a consequence, the $d_{z^2-\tau_1}$ states should shift down in energy relative to the $d_{x^2-y^2}$ states and the $d_{jz,xx}$ states relative to the $d_{xy}$

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**Figure 5.** Orbitally projected densities of states of the Ti atom next to the n-interface.
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 figures 4 and 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 in between 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. The orbital overlap between Mn and Ti modifies the level hierarchy by shifting the $d_{3z^2-r^2}$ states to the Fermi energy, which makes them susceptible to spin polarization.

4. Conclusions

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 analyzed. 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.

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