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Magnetic Properties of $LaAlO_3/SrTiO_3$ Heterostructure Modelled on a Supercomputer

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The oxide heterostructure composed of $LaAlO_3$ (LAO) thin film on top of $SrTiO_3$ (STO) substrate is the best known example of a system where a metallic state is formed in the STO layers next to the interface [1]. In the frame of present work we analyze an impact of oxygen vacancies and hydrogen dopants located in the AlO_2 surface layer and in the TiO_2 interfacial plane of LAO/STO heterostructure onto the magnetic properties by performing spin-polarized calculations based on density functional theory (DFT). We found stable local magnetic moments formed within atomically thin magnetic layers at the interface. We confirmed that magnetism can be generated by oxygen vacancies located either at the surface or at the interface. In addition, we demonstrate magnetic moments formation by hydrogen dopants located at the interface. Finally, the case of two defects combination was investigated, when negligibly small magnetic moment induction was found to take place.

Keywords: DFT, $LaAlO_3/SrTiO_3$ heterostructure, defects, magnetic properties.

Introduction

The arising magnetic order in the LAO/STO system is a matter of intensive discussion [2, 3]. It was found from *ab initio* calculations that the bare heterostructure is non-magnetic, and magnetic ordering was related to defects formation, in particular to oxygen vacancies at the interface and/or the surface [2]. Other scenarios were also suggested, for instance, the formation of Ti^{3+}-on-Al^{3+} defects in LAO near the interface or the Zener exchange between an insulating interface layer and the nearest TiO_2 plane [3]. No doubt, that defect states play an important role in structural, electronic and magnetic properties, especially if they are electron donor states. In spite of the fact that experimentalists seek to get rid of any impurities and defects, especially dealing with electronic devices, it is almost impossible to avoid any possible contaminations. Obviously, defects affect the functionalization of devises based on oxide heterostructures. The facts that oxygen vacancies and hydrogen dopants have relative low defect formation energies, that they are omnipresent in experiments, and both are electron-donor defects motivate us to investigate their impact on magnetic properties.

1. Results

The *ab initio* calculations were based on DFT [4] in the framework of the GGA+U method, with additional local correlations of $U = 2\,\text{eV}$ to the Ti $3d$ orbitals and $U = 8\,\text{eV}$ to the La $4f$ orbitals [5]. We used Vienna Ab-Initio Simulation Package (VASP) [6], which is part of the MedeA® software of Materials Design. To study the heterostructure with defects, we used 2×2 in-plane supercells of the bare heterostructures [7] with introduced oxygen vacancies and hydrogen dopants at the surface, or in an interfacial layer on both sides while preserving the inversion symmetry of the slabs. More details about computation parameters and slab geometry can be found in [5, 7, 8].

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While investigating defects profile in the LAO/STO heterostructure we have found that for sufficiently large concentrations of oxygen vacancies the formation energy drops at the interface [8]. We started with a bare insulative and non-magnetic heterostructure containing three LAO overlayers. The presence of an oxygen vacancy caused an upshift of the Fermi energy and magnetic moment induction. We considered two cases of oxygen vacancy location: either in the surface AlO_2 layer or in the interfacial TiO_2 layer. Quantitative and qualitative comparison of obtained magnetic moments are presented in Fig. 1 and Tab. 1, respectively. Both cases of a surface and interface oxygen vacancy show that about 85% of the total magnetization corresponds to the layer comprising the vacancy.

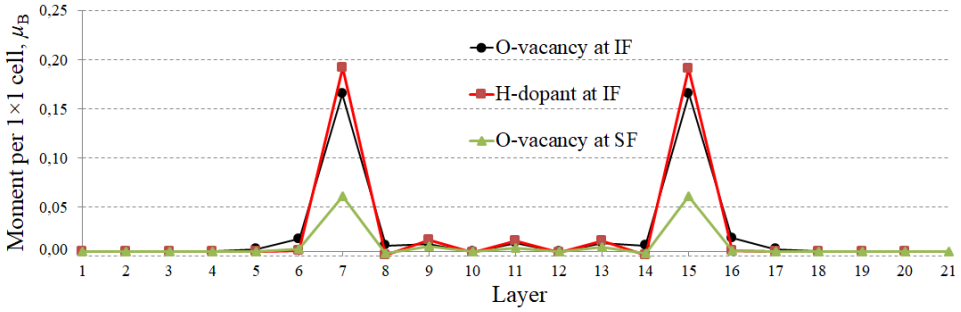


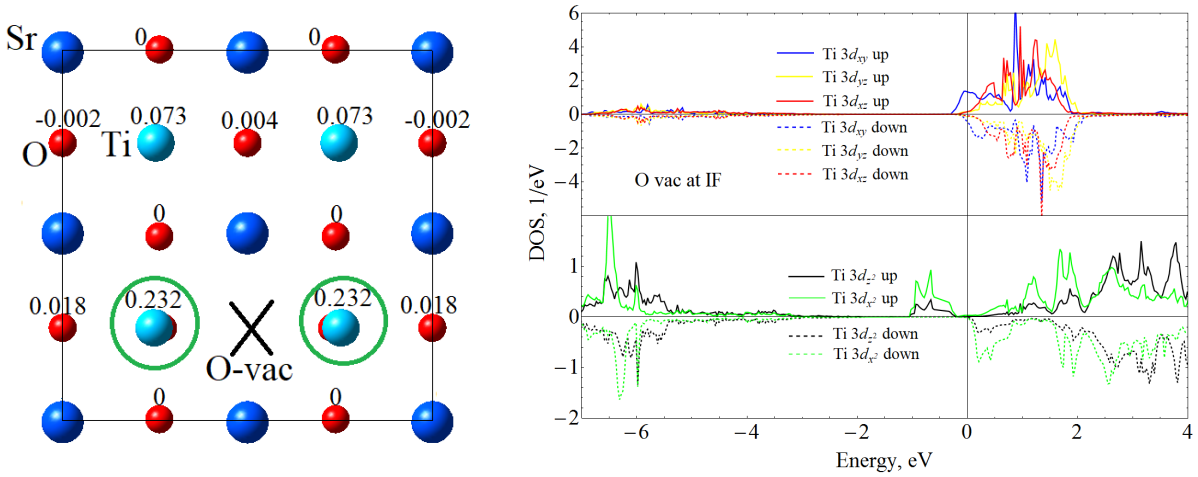
Figure 1. Magnetic moments per 1×1 cell of the 3 LAO/4.5 STO/3 LAO heterostructures with hydrogen dopant atom located at the interface, oxygen vacancy at the interface and surface

Table 1. Total and per interface (total/per IF) magnetic moments in Bohr magnetons per 1×1 cell of heterostructure with defects located whether at the surface (SF) or at the interface (IF)

Defect location	O-vacancy	H-dopant	O-vac and H-dop
at SF	0.12/0.06	0/0	0/0
at IF	0.38/0.16	0.41/0.19	0/0

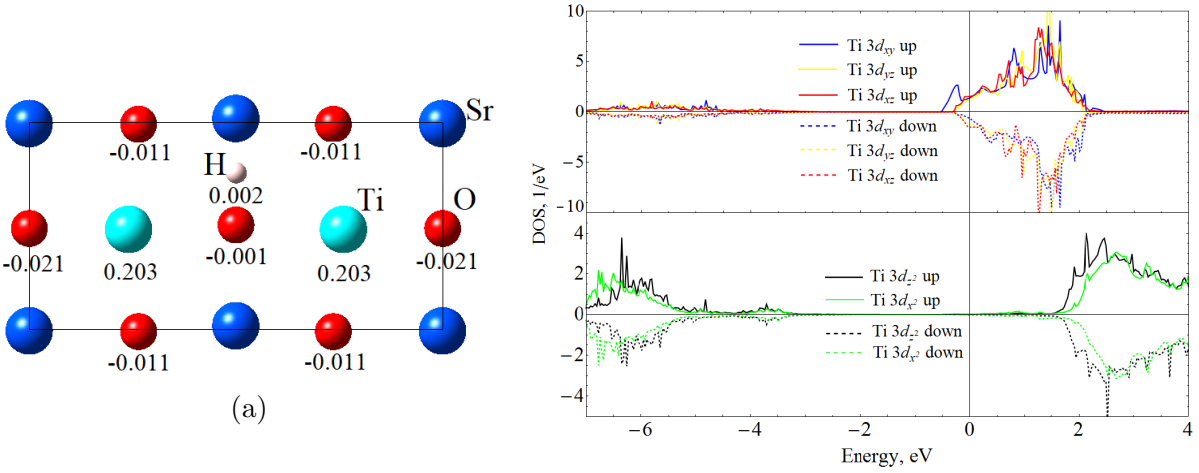
The most astounding result was found considering the densities of states (DOS) of interfacial Ti atoms. The contribution from a distant Ti atom and a Ti atom next to the vacancy differ significantly. In particular, we found the downshift of the e_g states of the latter atom as compared to those of the former by about 2 eV [8], which leads to a finite occupation of these orbitals as well as a finite contribution to the local magnetic moment, which even exceeds that of the t_{2g} states (Fig. 2 b)). In contrast, the t_{2g} partial DOS of both atoms are very similar. The calculated local magnetic moments per interface atom are given in Fig. 2 a). Thus, oxygen vacancies at the interface induce atomically thin magnetic layers with a rather uniform background of magnetic moments generated by the Ti $3d$ t_{2g} states, which are complemented by well localized magnetic moments due to e_g states of the Ti atoms neighboring the vacancy [8].

Spin-polarized calculations were also performed for a 2×1 supercell of the 3LAO/4.5STO/3LAO heterostructure with one hydrogen dopant located either in the AlO_2 surface layer or in the TiO_2 interface layer. These cases lead to the same electrons concentrations as the case of one vacancy per 2×2 cell. We found that hydrogen dopants located at the surface do not produce magnetization, whereas located in the interfacial layer induce sizable magnetization. The calculated local magnetic moments per interfacial atom are given in Fig. 3 a).



(a) (b)

Figure 2. (a) Local moments and (b) spin-resolved Ti $3d$ partial DOS of a 2×2 3 LAO/4.5 STO/3 LAO heterostructure with one oxygen vacancy



(a) (b)

Figure 3. (a) Local moments and (b) spin-resolved Ti $3d$ partial DOS of a 2×1 3 LAO/4.5 STO/3 LAO heterostructure with one hydrogen dopant

Generated total and per 1×1 interface layer magnetic moments amplitudes are listed in Tab. 1. Layer-distribution is shown in Fig. 1. As in the previous case we found strong confinement of magnetization within interface layers. Hydrogen dopants located in the interface plane produce even larger magnetic moment, however, the formation energy does not have a minimum at the interface as in the case of oxygen vacancy [8]. The spin-resolved Ti $3d$ partial DOS are shown in Fig. 3 (b). Here, no downshift of the Ti $3d$ e_g orbitals is observed since the octahedral environment of the metal atoms is not affected in contrast to the case of oxygen vacancy. Moreover, in Fig. 3 (a), the hydrogen dopant forms an almost rectangular triangle with the neighboring Ti atoms in the same plane, its s-orbital hybridizes mainly with the Ti d_{xy} orbitals. As a consequence, electron transfer from the H $1s$ orbital is predominantly to the d_{xy} orbitals of the $3d$ t_{2g} manifolds centered at the neighboring Ti ions, which thus hold the large part of the local magnetic moment.

Conclusions

In the present work, first principles electronic structure calculations as based on DFT and including local electronic correlations within the GGA+U approach have been employed to study the impact of oxygen vacancies and hydrogen dopant atoms on the magnetic properties of insulating 3LAO/STO/3LAO heterostructure slabs. We confirmed the local-moment formation induced by vacancies located either at the surface or in the TiO_2 interface layer and found strong confinement of the magnetization within these layers. Hydrogen dopant atoms in the TiO_2 interface layer of the LAO/STO heterostructure give rise to magnetism with even larger magnetic moments, which are mainly carried by the Ti $3d_{xy}$ states and again confined within the interface layer.

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