JCRS

Journal of Chemical Reactivity and Synthesis 2022: 12(3) 222-231

Research Article

Investigating the magnetic configuration of $(LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ Superlattices using the Stoner-Wolfarth model

Fatemeh Pirvand boori, Azadehe Aezami*

Department of Chemistry, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran

ARTICLE INFO:

Received:
24 August 2022

Accepted:
27 September 2022

Available online:
29 September 2020

✉: A. Aezami
a.aezami@gmail.com

ABSTRACT

In this study, we survey electronic and magnetic configuration of $(LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices based on density functional calculations (DFT+U) using Quantum-Espresso open source code. The Hubbard parameter has been calculated for the Mn and Ti atoms using a linear response approach. This parameter is 3.5 eV for $LaMnO_3$ and it is 4.98 eV for $SrTiO_3$, are in good agreement with the experimental results. The results of total and partial density of states calculations of the $LaMnO_3$ and $SrTiO_3$ compounds show that $LaMnO_3$ and $SrTiO_3$ compounds are insulator and antiferromagnetic and paramagnetic, respectively, but The 2DEG half-metallic observed in $(LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices by inclusion of electron-electron correlations with U_{Ti}=4.98 eV and U_{Mn}=3.5 eV. We used Stoner-Wolfarth model to investigate the magnetic configuration of $(LaMnO_3)_1/(SrTiO_3)_8$, $(LaMnO_3)_2/(SrTiO_3)_8$, $(LaMnO_3)_3/(SrTiO_3)_8$ superlattices . The results of density of states show that $(LaMnO_3)_1/(SrTiO_3)_8$, $(LaMnO_3)_2/(SrTiO_3)_8$, $(LaMnO_3)_3/(SrTiO_3)_8$ superlattices are ferromagnetic and half-metallic that are in good agreement with the Stoner-Wolfarth results.

Keywords: $(LaMnO_3)$ /$(SrTiO_3)$; SuperLattice; DFT+U; Stoner-Wolfarth model

1. Introduction

Super lattices composed of strongly correlated transition metal oxide layers have versatile physical properties such as new electronic and magnetic phases at the vicinity of the interface, which are qualitatively different from the parent compounds [1].

New advances in designing interfaces between dissimilar transition metal oxides have revealed the formation of with their parent compounds and are interesting for spintronic applications [2]. The interfacial properties show various magnetic and electronic structures due to the coupling between degrees of freedom such as charge, spin and orbital. For example, the magnetic configuration at the interface between the two insulators $LaMnO_3$ (antiferromagnetic-Atype) and $SrTiO_3$ (paramagnetic) could be ferromagnetic [3-4]. These changes could be depending on the epitaxial strain on the interface.

The relative alignment and possible magnetic coupling between Mn and Ti moments has been observed in $(LaMnO_3)_3/(SrTiO_3)_2$ superlattice to be ferromagnetic but in $(LaMnO_3)_{17}/(SrTiO_3)_2$ superlattice is antiferromagnetic. The different magnetic couplings between Ti-Mn magnetic moments may be caused by different Mn eg orbital reconstructions promoted by the different strain or thickness patterns, reported by J. G. Barriocanal et al [5].

In this work, we have considered the effects of atomic layer thickness of **(**$LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices on the interfacial magnetic configurations. We use first principle calculation based on density functional theory (DFT+U) by Stoner-Wolfarth model. We have schematically shown periodic layer in our superlattices in Fig. 1.

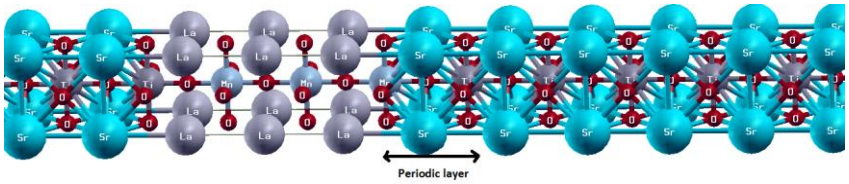

Fig. 1. Structure schemas of periodic atomic layer in our superlattices along z axiz.

2. Structural and Method

In this investigation, we have grown **(**$LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices from first principle calculation using the Quantom-Espresso within LDA+U approaches [6-7]. We have applied a strong coulomb repulsion U on the Mn and Ti atoms with moderate value of 3.5 eV and 4.98 eV, respectively, in our superlattices. We have calculated Hubbard U with linear response approach [8-13] using the wave pseudo potential method implemented in Quantum-Espresso code for Mn and Ti in the $LaMnO_3$ and $SrTiO_3$, respectively, and it is in accordance with other reported calculations. A linear response approach is proposed that in internally consistent with the chosen definition for the occupation matrix of the relevant localized orbitals. The unit cell of **(**$LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices are created on the basis the relaxed cubic provskite structures of the $LaMnO_3$ and $SrTiO_3$, with lattice parameters of 3.879 $\mathring{A}$ and 3.911 $\mathring{A}$, respectively [4]. In the bulk calculations, we have used an energy cutoff of 30 Ry for the plane wave expansion for $LaMnO_3$ and $SrTiO_3$, respectively and a 6×6×6 grid for both of compounds. We have used these theoretically determined geometries in all our calculations. The band structure and density of state calculations of $SrTiO_3$ show that has the same perovskite structure as $LaMnO_3$. We have grown **(**$LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices on the $SrTiO_3$ substrate. In all calculations of the superlattices, the energy cutoff of 60 Ry was set for the plane wave expansion. We have taken the xy-plane lattice parameters of**(**$LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices coinciding with the experimental lattice constants of the substrate ($SrTiO_3$) and the out-of-plane (along z axis) lattice parameters (c) are taken to be 3.919 $\mathring{A}$ and 3.787 $\mathring{A}$ for $SrTiO_3$ and $LaMnO_3$ respectively, with preserving the unit cell volumes [1].

3. Results and discussion

In this investigation, first, we calculate the electronic structure of $LaMnO_3$ and $SrTiO_3$ unit-cells. Despite of their common perovskite structure, $SrTiO_3$ and $LaMnO_3$ are electronically very different. $LaMnO_3$ exhibits rich and interesting physical properties related to a strong interplay between lattice distortions, transport properties and magnetic configuration. In stoichiometric $LaMnO_3$, electronic configuration of Mn^{3+} is postulated as $t_{2g}^{3\uparrow}$ $e_g^{1\uparrow}$. This electronic configuration is susceptible to a strong Jahn-Teller (JT) distortion [14, 15]. The JT distortion can be looked upon as a cooperative shifting of the oxygen atoms within the ab plane away from one of its two nearest neighboring manganese atoms toward the others, thereby creating long and short Mn-O bond lengths. The bond lengths are modified from 1.97 $\mathring{A}$ for the cubic lattice to 1.91 $\mathring{A}$, 1.96 $\mathring{A}$ and 2.18 $\mathring{A}$ for the orthorhombic system [16]. It is observed in Fig. 2 that the electrons of e_g level lie widely near Fermi level in conduction band that $d_{x^2-y^2}$ and d_{3z^2-1} orbitals are predominant in majority and minority spin states, respectively. The maximum stability occurs when axial orbitals of e_g level located along z axis has been more stable and lie in lower with respect to $d_{x^2-y^2}$ axial orbitals.

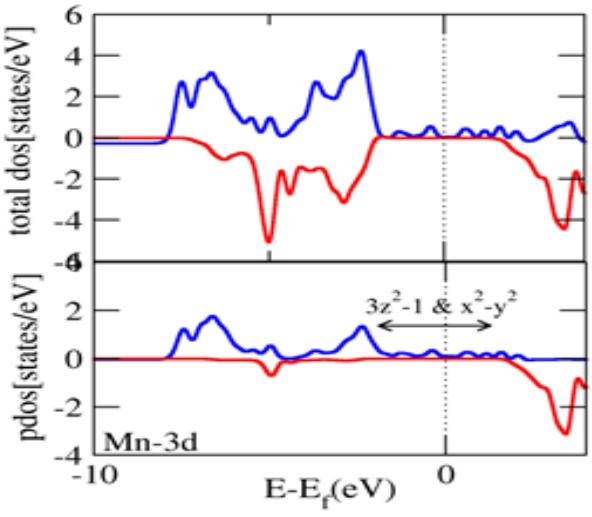

Fig. 2. Show the total DOS and Partial DOSs of the $LaMnO_3$ bulk. The Fermi energy is denoted by the vertical dotted line.

In bulk $SrTiO_3$, we used the cubic unit cell of the perovskite structure, containing one Sr, one Ti and three oxygen atoms. The ionic charges contain Sr^{2+}, Ti^{4+} and O^{2-}. The conduction band in $SrTiO_3$ correspond to the bands composed of mainly Ti 3d t_{2g} and e_g states, followed at higher energies by the bands of Sr 4d t_{2g} and e_g states [17]. $SrTiO_3$, with alternating ($Sr^{2+}O$) and ($Ti^{4+}O$) atomic planes, is a band-insulating compound characterized by an empty t_{2g} valence band and has paramagnetic ordering.

Perovskite oxides indicate a wide different of valence states that can be explained with the expression $A^{x+}B^{y+}O_3^{2-}$ where x+y=6 [18]. For the $LaMnO_3/SrTiO_3$ superlattice where $La^{2+}Mn^{3+}O_3^{2-}$ comprises of periodic $(LaO)^+$ and $(MnO_2)^-$ planes and $Sr^{2+}Ti^{4+}O_3^{2-}$ comprises of periodic $(SrO)^0$ and $(TiO_2)^0$ planes. Polar discontinuities at the interface between two different oxides can lead to interface reconstruction. It is showed in Fig. 3 that the electrons of t_{2g} level lie widely near Fermi level.

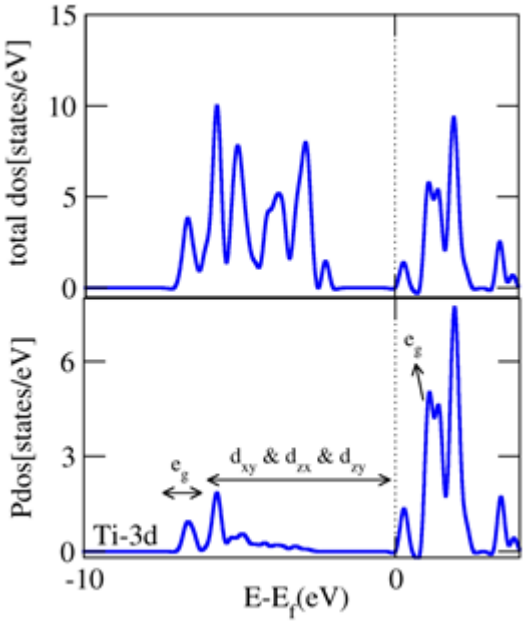

Fig. 3. Show the total DOS and Partial DOSs of the $SrTiO_3$ bulk. The Fermi energy is denoted by the vertical dotted line.

The calculation of partial and total density of states of $LaMnO_3$ and $SrTiO_3$ compounds under the influence of Hubbard parameter shows that $LaMnO_3$ compounds have insulator and

antiferromagnetic configuration and $SrTiO_3$ compounds have insulator and paramagnetic (Fig2 ana 3), which is in good agreement with experimental results.

We use the Stoner criterion to identify the magnetic ordering of interfacial atoms (ferro or anti ferromagnetic). Stoner model is based on a criterion for magnetism that is ascribed to the localized *d* electrons and is directly applicable to transition metals. By minimizing the energy a condition for magnetism analogous to the stoner criterion arises, $U\rho(E_f)>1$. Where $\rho(E_f)$ is the density of states of a paramagnetic state at the Fermi energy. So, the spin↑ and spin↓ bands are split by an energy which is proportional to the magnetization. This so called exchange splitting (Δ) is an important concept in theories of band ferromagnetism [19]. Note that, in absent Hubbard model (with U=0), the formation of spontaneous magnetic moment changes and leads to the gain in the exchange energy $E_{ex}=-\frac{1}{2}\mathrm{Im}^2$, where I is the Stoner parameter in absent Hubbard model. Thus, the condition that has to be satisfied for the appearance of ferromagnetism is the Stoner criterion, $I\rho(E_f)>1$.

Generally, if the Stoner criterion is satisfied, then the ferromagnetic state is favorable [19, 20]. By the assumption of being symmetric around E_f in energy interval Δ, it is easy to find by minimizing the total energy that the Stoner parameter is related to the exchange splitting by $I=\frac{\Delta}{m}$. In Table1 the values of Δ and $\rho(E_f)$ obtained from first principles calculation for **(**$LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices with U=0 eV and U=4.98 eV for Ti interfacial atoms and U=0 & 3.5 eV for Mn interfacial atoms are gathered.

Table 1. The exchange splitting (Δ) and the parameter relating to Stoner criterion on the interface Ti atoms with U=0 eV & U=4.98 eV and for Mn atoms with U=0 eV & U=3.5 eV for **(**$LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices.

	Δ (eV) U_{Ti}=0	Iρ (E_f) U=0	Δ (eV) U_{Mn}=0	Uρ (E_f) U_{Mn}=3.5 eV	Δ (eV) U_{Ti}=5 eV	Uρ (E_f) U_{Ti}=5 eV
($LaMnO_3)_1/(SrTiO_3)_4$	0.38	0.98	2.01	11.23	0.56	2.31
$(LaMnO_3)_2/(SrTiO_3)_4$	0.24	0.85	1.98	13.22	0.48	1.99
$(LaMnO_3)_3/(SrTiO_3)_4$	0.45	0.76	2.46	12.25	0.11	1.36

As it is evident from Table1 when U_{Ti}=0 and U_{Mn}=0 for Ti & Mn (interfacial atom) the Stoner criterion are not satisfied for **(**$LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices but it is satisfied for **(**$LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices which justifies the ferromagnetic configuration for Mn and Ti atoms in the interfacial layers. Then, we have applied a strong Coulomb Repulsion U on the Ti and Mn atoms in our superlattices. Seventh column in Table1 shows that the stoner criterion is also satisfied for all of the superlattoces for Ti and Mn atoms in the interfacial layers. The results show that by taking into account electron-electron correlations on Ti and Mn atoms, the ferromagnetic ordering is observed in all of our superlattices at interfacial layers. It has been found that the inclusion of the on-site Coulomb interaction with moderate value of U_{Ti}=4.98 eV and U_{Mn}=3.5 eV leads to half-metallic of the two dimensional electron gas (2DEG) and enhances the stabilities of the interface magnetization in our superlattices. The results are shown in Fig. 4.

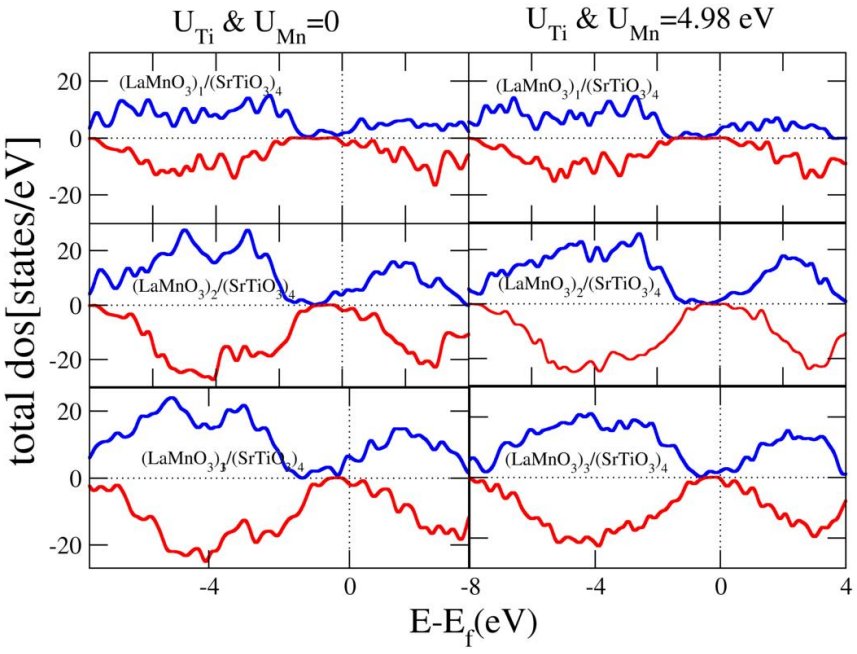

Fig. 4. Show the total Dos of majority and minority spin for **(**$LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices for U=0 and U≠0. The Fermi energy is denoted by the vertical dotted line.

The electronic structure of Mn atom in $LaMnO_3$ bulk is $t_{2g}^{3\uparrow}$ $e_g^{1\uparrow}$ but the electronic structure of Mn atom in the interfacial layer is $t_{2g}^{3\uparrow}$ $e_g^{0.5\uparrow}$. Also Ti atoms in $SrTiO_3$ bulk are Ti^{+4} ions and t_{2g} states are empty but in the interfacial layers, Mn $e_g^{1\uparrow}$ electron have been transferred to Ti atoms and consequently, Ti^{+4} ions are converted to Ti^{+3} ions. The results of the total density of states calculations show that **(**$LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices have half-metallic properties and have a ferromagnetic configuration. The results were confirmed by the Stoner model in Table1.

4. Conclusion

In summary, we have studied electronic and magnetic configuration of **(**$LaMnO_3)_1/(SrTiO_3)_4$, $(LaMnO_3)_2/(SrTiO_3)_4$, $(LaMnO_3)_3/(SrTiO_3)_4$ superlattices based on density functional calculations (DFT+U) using Quantum-Espresso open source code. The Hubbard parameter has been calculated for the Mn and Ti atoms using a linear response

approach. This parameter is 3.5 eV for $LaMnO_3$ and it is 4.98 eV for $SrTiO_3$. We have calculated exchange splitting (Δ) and magnetic configurations at the interfaces atoms, we have used the Stoner-Wolfarth model for all of **(**$LaMnO_3)_1/(SrTiO_3)_8$, $(LaMnO_3)_2/(SrTiO_3)_8$, $(LaMnO_3)_3/(SrTiO_3)_8$ superlattices . The 2DEG half metallic have been observed in these superlattices by inclusion of electron-electron correlations with U_{Ti}=4.98 eV and U_{Mn}=3.5 eV. The results of the density of states calculations show that the super lattices have a ferromagnetic configuration. The results were confirmed by the Stoner criterion.

Acknowledgements

We thank departments of Physics, Ahvaz Branch, Islamic Azad University for support.

References

[1] R. B. K. Nada, S. Satpathy, *Phys. Rev. B.* 79 (2009) 0544281-0544286.

[2] B. Chen, Z, Jovanovic, et al., *J. Am. Chem. Soc*. 38 (2020) 42925-42932.

[3] B. Chen, N. Gauquelin, et al., *Phys. Chem. Chem. Phys*. 9 (2021) 6981541-7.

[4] F. Cossu, et al., *Appl. Phys. Lett*. 102 (2013) 042401 (1-4).

[5] J. G. Barriocanal, et al., *Nature. Commun.* 1 (2010) 82 (1-7).

[6] A. Aezami, et al., *J. Alloys and Compounds*. 587 (2014) 778-782.

[7] M. Li, C. Tang, et al., *Adv. Mat.* 31 (2019) 1901366 (1-6).

[8] http://www.quantum-espresso.org/

[9] P. Giannozzi, et al., *J. phys. Condens. Matter*. 21 (2009) 395502.

[10] M. Cococcioni, et al., *Phys. Rev. B.* 71 (2005) 035105 (1-16).

[11] V. I. Anisimov, et al., *J. Phys: Condens. Matter*. 9 (1997) 767-808.

[12] V. I. Anisimov, et al., *Phys. Rev. B.* 48 (1993) 16929-16934.

[13] I. V. Solovyev, et al., *Phys. Rev. B.* 50 (1994) 16861-16871.

[14] A. I. Liechtenstein, et al., *Phys. Rev. B.* 52 (1995) R5467-R5470.

[15] W. E. Pickett, et al., *Phys. Rev. B*. 58 (1998) 1201-1209.

[16] L. Sheng, et al., *Phys. Rev. Lett*. 79 (1997) 1710-1713.

[17] W. E. Pickett and D. J. Singh, *Phys. Rev. B*. 53 (1996) 11461-11467.

[18] P. Ravindran, et al., *Phys. Rev. B*. 65 (2002) 064445 (1-5).

[19] K. V. Benthem and C. Elsasser, *J. Appl. Phys*. 90 (2001) 6156-6164.

[20] K. Janicka, J. P. Velev, and E. Y. Tsymbal, *J. Appl. Phys*. 103 (2008) 07B508 (1-3).

[21] P. Fazekas, Lecture Notes on Electron Correlation and magnetism (world Scientific, Singapore) (1999).