Emergence of a ferromagnetic insulating state in LaMnO$_3$/SrTiO$_3$ heterostructures: The role of strong electronic correlations and strain

Hrishit Banerjee$^1$ and Markus Aichhorn$^{1,}$

$^1$Institute of Theoretical and Computational Physics, Graz University of Technology, NAWI Graz, Petersgasse 16, Graz, 8010, Austria.

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Inspired by the experimental findings of an exotic ferromagnetic insulating state in LaMnO$_3$/SrTiO$_3$ heterostructures, we calculate the electronic and magnetic state of LaMnO$_3$/SrTiO$_3$ superlattices with comparable thicknesses employing ab-initio dynamical mean-field theory. Projecting on the low-energy subspace of Mn 3$d$ and Ti 3$d$ states, and solving a multi-impurity problem, our approach emphasizes on local correlations at Mn and Ti sites. We find that a ferromagnetic insulating state emerges due to intrinsic effects of strong correlations in the system, in agreement with experimental studies. We also predict that, due to electronic correlations, the emerging 2D electron gas is located at the LMO side of the interface. This is in contrast to DFT results that locate the electron gas on the STO side. We estimate the transition temperature for the paramagnetic to ferromagnetic phase transition, which may be verified experimentally. Importantly, we also clarify that the epitaxial strain is a key ingredient for the emergence of the exotic ferromagnetic insulating state. This becomes clear from calculations on a strained LaMnO$_3$ system, also showing ferromagnetism which is not seen in the unstrained bulk material.

Introduction

Since the first report of a highly conducting and mobile 2-dimensional electron gas (2DEG) occurring at the interface of oxide insulators $[1]$, the study of hetero-interfaces formed between perovskite oxides has made a serious impact on the scientific community engaged in experimental and computational condensed matter research. It has paved the way to many different prospective device applications, and garnered considerable interest in the field of oxide electronics. Interfaces have been formed between band insulators, for example between SrTiO$_3$ (STO) and LaAlO$_3$ (LAO) $[1,2]$, and between band insulators and Mott insulators, as in the case of SrTiO$_3$ and GdTiO$_3$ (GTO) $[3,4]$, with qualitatively different behaviour from that of LAO/STO interface. This is due to the fact that GdTiO$_3$, being a Mott insulator, has a very different band structure compared to LAO which is a band insulator, which in turn has a deep influence on the band alignment of the two oxides making up the interface $[5]$.

Experimental studies on interfaces between cooperative Jahn-Teller (JT) distortion driven insulators like LaMnO$_3$ (LMO), in which strong correlations have a significant effect, with band insulators like SrTiO$_3$ have been carried out in the recent past. In these systems, the interplay of structural distortions and strong electronic correlations are expected to lead to a variety of different phases. Indeed, a large and diverse number of magnetic and electronic phases of the LMO/STO interfaces have been observed, depending on the relative thickness of STO and LMO and their geometry $[6,12]$. Amongst these varied number of electronic and magnetic states, the most intriguing is the observation of ferromagnetic insulating behavior, which has been reported for both LMO/STO superlattices and thin-film/substrate geometries when LMO and STO have comparable thicknesses $[10,12]$. Since ferromagnetism is generally associated with metallicity, and antiferromagnetism is typically seen in case of insulators, this happens to be a counter-intuitive observation.

Ferromagnetic insulators are essential for many new magnetic devices, such as dissipation-less quantum-spintronic devices, magnetic tunneling junctions, etc. Ferromagnetic insulators with a high $T_C$ and a high-symmetry crystal structure are critical for integration with common single-crystalline oxide films or substrates. The few known high-symmetry materials either have extremely low Curie temperatures ($\leq 16$ K) $[13,14]$, or require chemical doping of an otherwise antiferromagnetic material. Thus, it is imperative to theoretically understand the origin of intrinsic ferromagnetic insulating behaviour in heterostructures.

Few attempts have been made in case of LMO/STO to theoretically justify the observed coexistence of ferromagnetism and insulating properties. Most of these attempts depend on either symmetry lowering or on orbital polarisation effects. However, symmetry lowering in the geometry of strained LMO $[15]$ seems unlikely in superlattices because LMO is sandwiched between cubic STO. Concerning orbital polarisation, experiments show a significant suppression of the JT distortion, further supported by DFT+U studies $[16,17]$, which in turn reduces orbital polarisation $[12]$ in the superlattice geometry that hosts the ferromagnetic insulating behavior. A further attempt suggests electronic phase separation leading to the nucleation of metallic nanoscale ferromagnetic islands embedded in an insulating antiferromagnetic matrix. This, however, is not the case of intrinsic ferromagnetic insulating behaviour $[10]$. The observed coexistence of ferromagnetism and insulating behavior in the LMO/STO heterostructure thus remains a mystery.
Saha-Dasgupta et al. studied the problem considering bulk LMO, but epitaxially strained to the lattice constants of a square substrate of STO [17]. They consider the general framework of DFT, which is expected to capture the structural changes that happen upon epitaxial straining of LMO correctly, supplemented with Hartree-Fock based hybrid functional calculations. They find a ferromagnetic ground state driven by the marked reduction of orthorhombic distortion in the optimized LMO structure, when epitaxially strained to the square substrate of STO, resulting in a strong suppression of the JT distortion. The suppression of the JT distortion and modification of the octahedral rotation, as captured in this study, is in agreement with structural characterization of LMO/STO superlattices [12]. The treatment of exact exchange within a hybrid functional resulted in an insulating solution. This result was attributed to originate from electronically driven charge disproportionation within the Mn sublattice that arises due to a strain-driven enhanced covalency between Mn and O. Calculations using hybrid functionals on a heterostructure geometry confirmed the ferromagnetic insulating result. However, charge disproportionation has not been confirmed experimentally.

The questions that we intend to address in this letter are, thus, well defined. We are interested in looking at how strong correlations affect these oxide LMO/STO heterostructure systems. In particular, we intend to examine the fate of the 2D electron gas. We carry out paramagnetic density-functional theory (DFT) plus dynamical mean-field theory (DMFT) calculations on (LMO)$_{2.5}/$(STO)$_{2.5}$ and (LMO)$_{3.5}/$(STO)$_{2.5}$ which are multi-impurity calculations including both Ti-3d and Mn-3d, and observe a metal-to-insulator phase transition by varying the interaction strength. Furthermore, we also find a ferromagnetic insulating solution which is stable at low enough temperatures. Given the overestimation of $T_C$ in DMFT studies, we estimate the transition temperature to be in the range of $\approx 100$ K. Both the heterostructures, (LMO)$_{2.5}/$(STO)$_{2.5}$ and (LMO)$_{3.5}/$(STO)$_{2.5}$, yield qualitatively similar results. In contrast to previous studies, we find that the 2D electron gas generated due to the polar catastrophe moves to the LMO side of the interface and effectively dopes the Mn 3d orbitals.

An important result of our study is that an exotic ferromagnetic insulating state emerges also in a calculation of a bulk LaMnO$_3$ system, which is strained by matching to a square STO substrate. As LaMnO$_3$ under ambient pressure conditions is antiferromagnetic, this opens up a way to induce phase transitions between different magnetic states as function of strain. This may be realised by modern experimental techniques of stress generation.

**Computational Details** Our DFT calculations for structural relaxation were carried out in a plane-wave basis with projector-augmented wave (PAW) potentials [18] as implemented in the Vienna Ab-initio Simulation Pack-
effective $U$ is generally required to match the experimental values of the band gap.

**LMO/STO Superlattice** We investigate the electronic structure of LMO on STO in the experimental set-up, i.e., we consider an actual heterostructure consisting of LMO and STO layers. In addition to the square epitaxial strain generated due to the mismatch between the LMO and STO unit cells, the superlattices in particular involve the polar discontinuity formed between LMO consisting of alternating layers of LaO and MnO$_2$ of +1 and -1 charges, resp., and STO consisting of alternating charge neutral layers of SrO and TiO$_2$. The latter would cause half a charge to be transferred between the layers at the interface. Neither the direction nor extent of this charge transfer has been clarified. We consider superlattice geometries of LMO/STO, with an alternate repetition of LMO and STO layers of comparable thickness, stacked along the [001] direction. This creates two symmetric n-type interfaces between the LaO layer of LMO and the TiO$_2$ layer of STO [5, 12]. The structure of the superlattice for the case of (LMO)$_{3.5}/$(STO)$_{2.5}$ has been shown in the top panel of Fig. 1. Comparable thicknesses are chosen since the FM insulating state has been experimentally observed for superlattice geometries with nearly equal thickness of LMO and STO layers [12]. In this letter we show multi-impurity calculations for heterostructure systems, which are not very common in existing literature.

For the structural relaxation, we place LMO in an orthorhombic geometry matching to the square plane of STO layers (in the [100] and [010] directions). Here a $\sqrt{2} \times \sqrt{2} \times c$ supercell of both LMO and STO was allowed to tilt and rotate. This results in four Mn and Ti atoms in each MnO$_2$ and TiO$_2$ layer, respectively. The ionic positions and $c$ lattice parameters are allowed to relax, keeping the constraint on the planar lattice constants of $a = b$. This generates a square-matched epitaxial strain of -1.8%. The optimized structure shows a significant decrease in JT distortion, and modification of tilt and rotation angles in LMO, while some JT distortion, and tilt and rotation is introduced in the STO due to its proximity to the distorted LMO block. This is very similar to other heterostructures such as GTO/STO [5].

Our paramagnetic DFT calculations reveal a metallic solution with Ti $t'_{2g}$ and Mn $t'_{2g}$ states at Fermi level. We first carry out paramagnetic DMFT calculations at $\beta = 40$ eV$^{-1}$, including Ti $t_{2g}$ and Mn $t_{2g}$ orbitals. We use $U = 6$ eV and $J = 0.75$ eV on Ti $t_{2g}$, and $U = 8$ eV.
and $J = 0.75\text{eV}$ on Mn $t_{2g}$. This gives an insulating solution with a band gap of $\sim 2\text{eV}$ seen in the spectral function, as shown in Fig. 2. The insulating state may be driven to a metallic state by reducing the value of $U$ on Mn to below $U = 6\text{eV}$.

In the next step, in order to account for a spin-polarized solution, we first extend the Wannier basis set to include all 3$d$ orbitals of Mn to allow for the high-spin state of Mn with magnetic moment of $4\mu_B$. Starting from the paramagnetic solutions, we introduce a spin splitting in the real part of the self energies and let the DMFT iterative cycle converge to a possibly spin-split solution. We carry out the calculations at various values of $\beta$ between 40 to $80\text{eV}^{-1}$. At $\beta = 40\text{eV}^{-1}$, the calculation converges still to a paramagnetic state, but when reducing the temperature we find a transition to a ferromagnetic ground state. The spectral function at $\beta = 60\text{eV}^{-1}$ is shown in Fig. 3. We see a clear splitting between the up and down spin channels, and a reasonably large band gap.

What is very interesting to note is that the Ti $t_{2g}$ orbitals are now completely emptied out; the occupancies of the Ti $t_{2g}$ orbitals are negligible, whereas the occupancies of the Mn $d$ orbitals are $\sim 4.5$ each. This indicates that the electron gas is located at the the LMO side of the interface when correlations are included and properly taken care of. In contrast, previous studies using DFT+U and hybrid functionals put the electron gas at the STO side and explain the insulating behavior of Ti electrons by a high-spin polarisation [17]. However, those approaches are inadequate when it comes to capturing the correct nature of correlations. From our calculations, however, we can show from an actual first-principles calculation that indeed the electron generated due to polar catastrophe moves to the LMO side of the interface and dopes the Mn atoms instead of the Ti atoms.

Next, we look at the temperature dependence of the ferromagnetic solution. For this purpose a larger number of calculations at different temperatures are required, we are doing calculations for a (LMO)$_{2.5}/$(STO)$_{2.5}$ heterostructure. This structure is obtained from (LMO)$_{3.5}/$(STO)$_{2.5}$ as shown in Fig. 1 by removing one LMO layer. Hence, this reduces the number of inequivalent Mn atoms from two to one, leading to a three-impurity DMFT problem and, hence, makes calculations cheaper. Importantly, (LMO)$_{2.5}/$(STO)$_{2.5}$ shows essentially the same qualitative electronic structure as (LMO)$_{3.5}/$(STO)$_{2.5}$.

We plot the Wannier magnetic moments on Mn, obtained from the density matrix of the spin-split DMFT solution, in Fig. 4. It is obvious that a transition from a paramagnetic to a ferromagnetic state occurs at around $\beta = 60\text{eV}^{-1}$, which corresponds roughly to a temperature of $200\text{K}$. Given the fact that DMFT overestimates strongly the magnetic transition temperatures [38], we would give a rough estimate for the transition temperature $T_C$ to be around $50$-$100\text{K}$. A more precise prediction is beyond the capabilities of single-site DMFT calculations. We note that the Néel temperature for bulk unstrained LMO has been measured experimentally and found to be $\sim 177\text{K}$. We also note that our saturated magnetic moment is enhanced to $\sim 4.9\mu_B$, instead of $4\mu_B$ as expected for Mn with a $d^4$ configuration. This enhancement comes from the two symmetric $n$-type interfaces giving $0.5e$ each to the 2DEG. This again confirms that indeed the electron generated due to polar catastrophe moves to the LMO side of the interface and dopes the Mn atoms instead of the Ti atoms.

Finally, to further re-affirm our results, we carry out spin-polarised DFT calculations and then look at the DMFT solution to see how correlations affect the already spin-polarised system. Our spin-polarised DFT results
show Ti $d$, specifically the $d_{xy}$ states, and the Mn $t_{2g}$ states at the Fermi level. We carry out DMFT calculations at $\beta = 60 \text{ eV}^{-1}$, within a basis set of Ti $t_{2g}$ and Mn $d$. We use the same interaction parameters as before. We find again a ferromagnetic insulating solution with a reasonable band gap as shown in Fig. 5. Our calculations further show that also here the Ti $t_{2g}$ states empty out and the 2DEG moves to the LMO side and dopes the Mn $d$ states which become insulating. The spectral function in Fig. 6 itself looks similar to the previous case, Fig. 3, where we see a clear separation between Mn $t_{2g}$ and $e_g$ states, and empty Ti $t_{2g}$ states. We thus confirm that our results are robust and independent of initial conditions.

All our calculations confirm the presence of an intrinsic ferromagnetic insulating state, arising due to electronic correlations, and clarify the location of the extra charge due to the polar catastrophe.

**Epitaxially strained LMO** In this final part, we want to clarify the role of strain on the magnetic state, and whether the heterostructure geometry is necessary for it. This we do by looking at bulk LMO samples.

Bulk unstrained LMO crystallizes in the orthorhombic $Pbmn$ crystal structure, and is an A-type antiferromagnetic insulator. In order to mimic the effect of epitaxial strain, we carry out “strained-bulk” calculations. The structural parameters ($c$ lattice parameter and ionic positions) of the orthorhombic perovskite unit cells are optimized under the constraint that the two in-plane lattice vectors, defining the epitaxial substrate, are kept fixed to produce the specific square lattice corresponding to the substrate, in our case that of STO. The lower panel of Fig. 5 shows the structure of unstrained and strained LMO, viewed along the $c$ direction. We find a rather strong influence of strain on the structural parameters of LMO, particularly on the JT distortion, which becomes negligibly small in case of a compressive strain of 1.8% generated by an STO substrate with $a_c = 3.905 \text{ Å}$. A strong reduction of tilt and rotation of the octahedra is also seen due to the epitaxial strain of the square substrate.

Paramagnetic DFT+DMFT calculations with interaction values $U = 6 \text{ eV}$ and $J = 0.75 \text{ eV}$ yield an insulating ground state at $\beta = 40 \text{ eV}^{-1}$ as seen in left panel of Fig. 6. As for the heterstructure calculations, we then try to find a spin-split solution by introducing a spin-splitting to the paramagnetic solution. Doing so, we find a ferromagnetic insulator with a net magnetization of $M = 3.96$ at $\beta = 60 \text{ eV}^{-1}$. The spectral function for this ferromagnet is shown in the right panel of Fig. 6. If we decrease $\beta$ slightly, there is a phase transition to a $M = 0$ paramagnetic insulating phase at $\beta = 50 \text{ eV}^{-1}$. Thus, we obtain here a very similar $T_C$ as in the previous case of the LMO/STO heterostructures.

We thus conclude that our DFT+DMFT calculations based on a five-orbital $d$ model yield a ferromagnetic insulator within a reasonable range of interaction parameters for epitaxially strained LMO as well, a phase which is not seen in the bulk unstrained condition of LMO. The necessary strain may be generated experimentally very easily by modern piezoelectric methods of strain generation as recently demonstrated by Hicks et al. [39].

**Summary and Discussion** With the aim to provide an understanding for the ferromagnetic insulating state in LMO/STO heterostructures, we apply *ab initio* DFT+DMFT methods to both superlattices of LMO/STO and strained-bulk LMO structures.

We investigated the case of LMO/STO superlattice structures with comparable thicknesses of LMO and STO. The ground state was found to be insulating in both paramagnetic and ferromagnetic DFT+DMFT calculations. In all heterostructure geometries that we considered, the 2DEG was found to reside on the LMO side of the interface, contrary to DFT results. Though this has been suggested before, this is the first time that an actual first-principles calculation shows the doping of Mn due to the 2DEG. We also showed that the transition
temperature from paramagnetic to ferromagnetic phase is high enough to be of practical relevance and accessible to experimental studies.

Finally, we showed that epitaxial straining of LMO to the square substrate of STO is key for the ferromagnetic ground state. This primarily results from a strong suppression of the JT distortion, which quenches the orbital polarization and hence antiferromagnetism in turn. For the “strained-bulk” structure, it was found that DFT+DMFT yields a ferromagnetic insulating solution for small enough temperature. The critical temperature $T_c$ here is similar to the case of the heterostructures. Since the exotic ferromagnetic insulating state does exist in case of strained LMO, it may even be realised by using modern piezoelectric experimental techniques for generating uni/biaxial strain. Our study shows from the perspective of correlation and dynamics, the emergence of the exotic ferromagnetic insulating state, which has been touted to be immensely important in case of many spintronics applications.

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* Electronic address: aichhorn@tugraz.at

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