**Persistent half-metallic ferromagnetism in a (111)-oriented manganite superlattice**

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We employ electronic structure calculations to show that a (111)-oriented (LaMnO3)12|(SrMnO3)6 superlattice retains a half-metallic ferromagnetic character despite its large thickness. We link this behaviour to the strain and the octahedral connectivity between the layers. This also gives rise to breathing modes, which are coupled to charge and spin oscillations, whose components have a pure $e_g$ character. Most interestingly, the magnetisation reaches its maximum value inside the LaMnO3 region and not at the interface, which is fundamentally different from what observed for the (001) orientation. The inter-atomic exchange coupling shows that the magnetic order arises from the double-exchange mechanism, despite competing interactions inside the SrMnO3 region. Finally, the van Vleck distortions and the spin oscillations are crucially affected by the variation of Hund’s exchange and charge doping, which allows us to speculate that our system behaves as a Hund’s metal, creating an interesting connection between manganites and nickelates.

**RESULTS AND DISCUSSION**

**Ground-state structure and spectral properties**

The (LaMnO3)12|(SrMnO3)6 superlattice is investigated via density functional theory (DFT) plus Hubbard U approach, labelled as sDFT+U. While tilting systems and angles are known for many perovskites in the bulk, their determination at surfaces and interfaces is not trivial. A previous ab-initio study54 predicted that (111)-oriented manganite superlattices should adopt the $a^-a^-a^+$ tilting system instead of the native $a^-a^-c^+$ tilting system, as expressed in Glazer notation58, used throughout this paper. The energy difference between these two structures depends on the lattice parameters. With a lattice constant of 3.860 Å (hereby denoted as equilibrium or 0% strain), the $a^-a^-c^+$ tilting system is favoured by 7.6 meV per formula unit (f.u., i.e., a AMnO3 unit, where A may be La or Sr) with respect to the $a^-a^-a^+$ tilting system. A reasonably small compressive strain may change this structural order, as recently

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Fig. 1 Overview of the superlattice and its properties. 

(a) Crystal structure of the superlattice. The interfacial layers are #0 and #12. 

(b) Curve total energy vs strain for FM solutions with $\sigma^{-} \sigma^{-} \sigma^{+}$ (black) and $\sigma^{-} \sigma^{-} \sigma^{-}$ (red); 'zero' strain means that the pseudo-cubic lattice constant is 3.860 Å. 

(c) Projected DOS for Mn-$t_{2g}$ and Mn-$e_{g}$ states for selected layers; additional information, covering all Mn and O layers, is provided in the Supplemental Material. 

(d) Total, Mn-$d$ projected and O-$p$ projected DOS for the FM solution.
reported for nickelates. As shown in Fig. 1(b), we predict a transition to the a’a’-tilting system for a compressive strain of ~1.5%, corresponding to epitaxial growth on SrMnO$_3$ (on LaMnO$_3$ the strain is ~2%). The energy difference between the two tilting systems remains below 7 meV (~80 K) at all simulated strain values, whereas that between the ground state FM and anti-ferromagnetic (AFM) orders are larger than 25 meV (~290 K), see Table 1. Therefore, phase transitions and coexistence are more likely to occur in the structure than in the magnetic order.

The two tilting systems do not lead to qualitatively different results in terms of distribution of charges and magnetic moments, but the a’a’-c’ requires a large supercell, which may hinder a thorough analysis of the layer-resolved properties. Therefore, we focus on the a’a’a’-tilting system at the equilibrium lattice constant, for simplicity.

The superlattice analysed has a half-metallic character, as inferred from the total density of electronic states (DOS) in Fig. 1(d), with a band-gap in the minority-spin channel between Mn-d and O-p of ~2.0 eV. The site-projected DOS in Fig. 1(c) reveals that the half-metallicity persists across all the layers. The curves show that the deeper the Mn inside the LaMnO$_3$ region, the lower the onset half-metallicity persists across all the layers. The curves show that the deeper the Mn inside the LaMnO$_3$ region, the lower the onset half-metallicity persists across all the layers.

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Table 1. Energy difference per formula unit relative to the ground state structure – i.e., the FM phase with the a’a’-c’-tilting system – of various magnetic orders and tilting systems. The energies are computed for the same in-plane lattice parameters, corresponding to 0% strain.

|       | a’a’-c’ | a’a’a’ |
|-------|---------|--------|
| FM    | G. S.   | 7.6    |
| A-type AFM | 26.5   | 37.5   |
| C-type AFM | 43.7   | 53.8   |
| G-type AFM | 71.8   | 95.6   |

As for most perovskites, the structural features are linked to the electronic and magnetic properties. In agreement with leading literature, we introduce the Jahn-Teller distortions and breathing distortions in terms of the variations of the octahedral lengths $x$, $y$, and $z$ (with respect to their average values). Breathing distortions are defined as $Q_{\text{breathing}} = (\Delta x + \Delta y + \Delta z)/\sqrt{3}$, whereas the Jahn-Teller distortions are $Q_{\text{JT}} = (\Delta x + \Delta y)/\sqrt{2}$ and $Q_{\text{JT}}' = (-\Delta x - \Delta y + 2\Delta z)/\sqrt{6}$. Breathing distortions are seldom found in manganites, which host orbital order and Jahn-Teller distortions (also defined in the Methods) instead. A recent study highlighted that Jahn-Teller modes arise from a steric effect that affects the electron-lattice coupling and are therefore dependent on the tilting system. In the bulk, the constraint imposed by the R$_3$C$_4$ phase should lead to a total quenching of these (pseudo) Jahn-Teller modes. The Jahn-Teller distortions are shown in Fig. 2 (a) and are quenched in agreement with the aforementioned literature. The quenching is not full because the relaxation of the superlattice modifies the pristine a’a’a’-tilting pattern.

Breathing distortions and spin-charge oscillations

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The quenching of the Jahn-Teller modes is accompanied by the presence of the breathing modes. The latter are lessened by a factor 4 in the structure without tilts (data not shown). A similar relation between octahedral tilts and breathing distortions was recently found in rare-earth nickelates, where it leads to a structurally triggered metal-insulator transition. In addition, LaMnO$_3$ is mentioned as a case where a close competition between charge and orbital order is driven by a similar mechanism (in line with refs. and). In the superlattice analysis, this mechanism has to compete with the high stability of the FM half-metallic phase, associated to the strained structure, and with the uniform shift of the band-edge, induced by the charge transfer – see again Fig. 1(b). Therefore, it becomes unfavourable to induce a transition to an AFM insulator with orbital order. The site-projected charge and magnetic moment distributions, as computed ‘a la Bade’, is presented in Fig. 2(b) and shows a hint of charge order, leading to oscillations in the LaMnO$_3$ region and a smooth behaviour in the SrMnO$_3$ region.

The smooth variation of the Mn-O-Mn angles across the superlattice (which take approximately the same values for all
clearly visible in Fig. 2(b), where the largest magnetisation is found and strain, we do not expect it to be interfacially driven. This is Exchange couplings and ferromagnetic order

Fig. 3(a). Where the Mn-O-Mn bond are closer to a atom to its

(layers in the central LaMnO3 region) mirrors the uniform shift of the band-edge, compare Figs. 3(b) and 1(b), whereas the Mn-O distances appear with oscillations in the inner LaMnO3 region, see Fig. 3(a). Where the Mn-O-Mn bond are closer to a flat angle (the SrMnO3 region) the structure presents larger splitting in the Mn-O distances between increasing z and decreasing z, and where the Mn-O-Mn bonds are more bent (the LaMnO3 region) the structure presents oscillating Mn-O distances and breathing modes, see Figs. 2, 3. In fact, the connection between breathing distortions and angles is even more apparent in the inset of Fig. 3(b), where flat angles correspond to single values for the MnO6 volumes (breathing distortion) and bent angles – in the LaMnO3 region – correspond to large variance of the MnO6 volumes distribution, in line with the above mentioned literature.67 The large Mn-O distance splitting, occurring in the SrMnO3 region, reveals a typical tendency for SrMnO2 to ferroelasticity, avoided by the symmetry with respect to the interface.

Exchange couplings and ferromagnetic order

As we argued, the magnetism is a consequence of structure and strain, we do not expect it to be interfacially driven. This is clearly visible in Fig. 2(b), where the largest magnetisation is found in the innermost layers of the LaMnO3 region. For a better insight into the magnetic properties, we analyse the inter-atomic exchange coupling, computed for a lattice constant of 3.892 Å (which corresponds to a tensile strain below 1%). The largest contributions in the Mn sublattice are those connecting a Mn atom to its first nearest neighbours or fourth-nearest neighbours. The latter correspond to the second-nearest neighbours along Mn-O-Mn-... lines, consistently with the double-exchange mechanism.68,69 The relevant exchange couplings across the superlattice are illustrated in Fig. 4. In the LaMnO3 region, the magnetic order is driven by the FM nearest neighbour coupling, which in the innermost layer takes the value of 17.7 meV and sharply decreases at the interface, exhibiting oscillations in phase with the magnetic moments. Interestingly, the maximum value is not reached at the innermost layer, but at intermediate layers, and amounts to 18.4 meV, which is 30% smaller than in the isostochiometric La2/3Sr1/3MnO3.75 This behaviour reflects a competition between the trend of the magnetisation – see Fig. 2(b) – and the potential induced by the charge transfer across the interface – see Fig. 1(b). Such relatively strong ferromagnetism is even more surprising if compared to the behaviour of (001)-oriented supercells, whose nearest neighbour exchange becomes bulk-like AFM for LaMnO3 regions thicker than 2 unit cells.60,69 A smaller contribution to the magnetic order is given by the fourth-nearest neighbour exchange, whose values are noticeable at the interface (1.36 meV), but are totally quenched in the innermost layers of the LaMnO3 region.

The situation is even more complicated in the SrMnO3 region. In the innermost layers, the nearest neighbour exchange is AFM, as in the bulk.76 However, The strength of the coupling is much weaker than in the bulk, i.e., -1.6 meV versus -7.5 meV, due to the combined effect of charge transfer and epitaxial strain (about 1%). Strain alone was shown to induce an AFM-FM transition at about 3% in bulk cubic SrMnO3 – while here the strain is virtually null on SrMnO3. Interestingly, the FM order inside the SrMnO3 region is stabilised by the fourth-nearest neighbour coupling, which becomes even larger (1.8 meV) than the nearest neighbour one. This frustration due to competing FM and AFM interactions is likely to lead to a more complex magnetic structure, probably accompanied by non-collinearity. Exploring the magnetic phase diagram may be an interesting project, but outside the scope of the present work. We prefer, instead, to focus on the origin of the oscillations of charge, magnetic moments, exchange couplings and breathing distortions.

We can summarise what leads to the half-metallic FM state with the help of Fig. 5. In the bulk, LaMnO3 and SrMnO3 behave as an AFM Mott insulator with Mn3+ ions and an AFM band insulator with Mn4+ ions, respectively. In the superlattice, the local strain in the LaMnO3 region induces the delocalisation of the Mn-3d states, which in turn suppresses the AFM super-exchange and favours the FM double-exchange.60,61 This effect is further enhanced by the charge transfer across the interface, which penalises the ionic picture and promotes the hopping between Mn sites. In (001)-oriented superlattices, the local strain is imposed in-plane – hence along two crystallographic directions – and allows different relaxations in different regions: SrMnO3 recovers its G-type AFM order, blocking the tunnelling of eg electrons from LaMnO3 and imposing a strong penalty on the double-exchange mechanism. For the (111) orientation, the strain acts on the same footing for all octahedral axes, and therefore the aforementioned phase separation is forbidden, the eg tunnelling survives and the FM coupling prevails. In summary, geometrical degrees of freedom affect the electronic ones, governing the magnetic and metallic properties of the superlattice. Further information can be inferred by the analysis of the bond angles, shown in Fig. 3. In the LaMnO3 region, the Mn-O-Mn angles vary from 160° to 165°. These values are higher than the bulk LaMnO3 value76 of 155° and close to the La2/3Sr1/3MnO3 value79 of 165°. The analysis of the Mn-O bond lengths, see Fig. 3, is in line with the presence of breathing modes in the LaMnO3, but also with a tendency to ferroelasticity in SrMnO3, avoided by the equivalence of the interfaces. Such behaviour is typical of SrMnO3.76 Charge doping and metallicity would anyway prevent the transition to a ferroelectric phase.

Role of Hund’s coupling

The suppression of Jahn-Teller order in favour of breathing distortions was predicted a decade ago in nickelates as a consequence of Hund’s coupling and was pointed out to be persistent well into the metallic side of the Mott transition.60.
Later studies\(^6^7\) pointed to structural distortions as the driving mechanism. In the present case, we observe an intermediate situation. On one hand, the structure has a primary importance, forbidding certain distortions, such as Jahn-Teller, and preserving metallicity. On the other hand, the breathing distortions are not large enough to induce a metal-insulator transition, but we still observe signs of charge order. The dependence of our results on the strength of Hund’s exchange \(J\) is investigated via charge density functional plus \(U\) scheme (denoted as cDFT+\(U\)) hereafter\(^8^1,8^2\) for a lattice constant of 3.892 Å. It suggests to what extent Hund’s coupling affects the properties of our system. The oscillations of the magnetic moments across the superlattice depend crucially on the value of Hund’s coupling, see Fig. 6(b). When \(J\) becomes as small as 0.6 eV, the magnetism is no longer pinned at the innermost layers of the LaMnO\(_3\) region. Instead, it becomes pinned at the interface, similarly to what happens in (001)-oriented superlattices. The change in the trend of the magnetic moments across the superlattice is accompanied by an analogous change of the breathing distortions, emphasising that the former drives the latter, to a large extent. Furthermore, electron/hole doping may lead to the disappearance of the breathing distortions as well as the magnetic moments oscillations (data not shown). Such a drastic change is surprising, considering the shape of the density of states in the corresponding doping range (±0.1 eV), and suggests that strong electronic correlations play an important role. Overall, the metallic character with spin and charge oscillations, the presence of strong correlation effects, and the key role of the Hund’s exchange \(J\) suggest that our superlattice behaves as a Hund’s metal\(^8^3,8^4\). Using our parameters \(U\) and \(J\), as well as the effective bandwidth extracted from the DOS, we can obtain some information from existing phase diagrams of the Hubbard model\(^8^5-8^7\). The most accurate comparison is offered by ref. \(^8^7\), where Merkel et al. investigated a 5 orbital system with a \(d^4\) occupation, including the level splittings associated to the presence of breathing modes (representative of CaFeO\(_3\)). Using their phase diagram, we can confirm the regime of (homogeneous) Hund’s metallicity, with an
estimated quasiparticle weight between 0.4 and 0.6. By increasing J, we expect to get closer to a valence skipping metal phase, which finds correspondence in an increasing amplitude of charge and spin oscillations (see inset of Fig. 6(b)). A further increase of J would lead to a charge disproportionated insulator, which in ref. 87 is predicted to happen for values larger than 2.3 eV. Despite signs of “Hundness” have been found in a variety of systems during the last decade83,84, they had never been reported for a manganite superlattice. For a more quantitative analysis allowing for more precise conclusions, one would need to perform calculations beyond DFT, e.g. in combination with the dynamical mean-field theory (DMFT), including the structural response. Considering the size of the system as well as the very high number of degrees of freedom, such an analysis would be beyond the scope of the present study.

**Outlook**

In summary, we have investigated the electronic and magnetic properties of the (111)-oriented (LaMnO₃⁾₁₂⁺Sr₂MnO₃ superlattice using DFT+U. A half-metallic FM state is supported by the cooperation of charge, spin, orbital and lattice degrees of freedom, and is favoured with respect to an AFM state. The half-metallic FM character is found to persist across the entire superlattice, while the innermost layers of its (001)-oriented counterpart become AFM insulators for a thickness larger than 3 layers. The atomic volumes, charges and magnetic moments are correlated across the superlattice, in particular in the LaMnO₃ region, where adjacent sites display charge, spin, and volume oscillations. Breathing distortions arise and may be accompanied by the quenching of Jahn-Teller distortions in the presence of a a a "tilting of MnO₆ octahedra while may coexist with the Jahn-Teller distortions in other tilting systems such as a a c". Overall, the present results suggest that the [111] epitaxial strain associated to the superlattice formation is a viable pathway to engineer a system analogous to La₂/₃Sr₁/₃MnO₃ without introducing doping-induced disorder. This is not only an advantage for avoiding alloy-related problems, as e.g. cation disorder, but does also widen the potential of interfacial engineering in oxide heterostructures. Finally, we also speculate that the fascinating physics exhibited by this superlattice may arise from Hundness, alongside with structural aspects, similarly to what happens in nickelates. Therefore, the system addressed here can provide further theoretical ground for the development of heterostructures hosting exotic magnetic phases and topological states.

**METHODS**

**Framework and parameters**

The superlattice is fully relaxed with an optimised lattice constant of 3.860 Å (denoted as equilibrium or 0 % strain). Calculations are performed in density functional theory (DFT) using the projector-augmented wave method as implemented in the Vienna Ab-initio Simulation Package (VASP)88,89. The exchange-correlation functional is treated in the generalized gradient approximation (GGA) by Perdew-Burke-Ernzerhof90,91. To improve the description of the Mn-3d states92, we make use of on-site corrections for static correlation effects in the rotational invariant DFT+U approach by Liechtenstein et al.93, denoted as SDFT+U. Further calculations to analyse Hund’s coupling are performed by following the approach discussed in ref. 88, which we label as cDFT+U. The Coulomb interaction parameters are chosen as U = 3.8 eV and J = 1.0 eV, in accordance with works on similar systems95,96. A deeper analysis of the magnetic properties is then performed via the full-potential linear muffin-tin orbital (FP-LMTO) method as implemented in the RSPt code97. We used also the SCAN parameter-free functional98: results (shown in the Supplemental Material) confirm the core results obtained with DFT+U. The inter-atomic exchange interactions J are calculated by mapping the exchange-correlation functional onto an effective Heisenberg Hamiltonian $H = -\sum_{\alpha,\beta} J_{\alpha,\beta} \cdot (\vec{\Sigma}_{\alpha} \cdot \vec{\Sigma}_{\beta})$, where i, j are atomic sites and $\vec{\Sigma}_{\alpha}$, $\vec{\Sigma}_{\beta}$ are unit vectors along the local magnetisation direction. This calculation is performed via the magnetic force theorem, using the implementation of ref. 99, which was also successfully applied to CaMnO₃100. Due to the better accuracy of all-electron methods102, these calculations also serve to confirm the validity of VASP results.

**General considerations on the modelled system**

The supercells used for the calculations consist of two types: the R3C cell was used for the results presented throughout this work, whereas an orthorhombic cell was used for calculations to compare total energies and results on the charge and spin distributions. The two interfaces have the same stacking sequence (i.e. La₂O₃/MnO, or Sr₂O₃/MnO₂), thus they are equivalent; furthermore, the superlattice possess inversion symmetry with respect to the Mn atom at the interface and therefore there is no built-in electric field generated. Further details on the cells and the sampling of the Brillouin zones are given in the Supplemental Material.

The analysis on the on-site charges and magnetic moments is carried on by in agreement with state-of-the-art methods92–95. The analysis of the electronic properties is performed with the aid of the post-processing code VASPKIT103. Finally, images of structures and charge/spin distributions are produced with VESTA JP-Minerals104. Further details on the calculations are given in the Supplemental Material.

**DATA AVAILABILITY**

The datasets generated during and/or analysed during the current study are available from the first author on reasonable request.

**CODE AVAILABILITY**

The calculations for this work have been performed with VASP and RSPt. The former is a licence product from the University of Vienna; the licence can be obtained upon submitting an application through the vasp portal (http://www.vasp.at). The latter is a free software distributed under GPL license after registration to a mailing list. More information about RSPt can be found at http://fpitombo-rsp.org/98.

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AUTHOR CONTRIBUTIONS

F. C. planned the project and performed all the VASP calculations. I. D. M. performed all the RSPt calculations. F. C. and I. D. M. wrote the initial paper. All authors contributed to analysing the data, revising the paper and drawing the conclusions.

COMPETING INTERESTS

The authors declare no competing interests.

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