Using spin-assisted ab initio random structure searches, we explore an exhaustive quantum phase diagram of archetypal interfaced Mott insulators, i.e. lanthanum-iron and lanthanum-titanium oxides. In particular, we report that the charge transfer induced by the interfacial electronic reconstruction stabilises a high-spin ferrous Fe\(^{2+}\) state. We provide a pathway to control the strength of correlation in this electronic state by tuning the epitaxial strain, yielding a manifold of quantum electronic phases, i.e. Mott-Hubbard, charge transfer and Slater insulating states. Furthermore, we report that the electronic correlations are closely related to the structural oxygen octahedral rotations, whose control is able to stabilise the low-spin state of Fe\(^{2+}\) at low pressure previously observed only under the extreme high pressure conditions in the Earth’s lower mantle. Thus, we provide avenues for magnetic switching via THz radiations which have crucial implications for next generation of spintronics technologies.

RESULTS

Epitaxial engineering of robust high-spin ferrous oxides

In Fig. 1a, we show a schematic band diagram of the electronic reconstruction at the LaTiO\(_3\)/LaFeO\(_3\) interface. Considering only the bulk counterparts, we note that Ti and Fe are both Ti\(^{3+}\) and HS configuration, with \(d^1\) and \(d^5\) filling, respectively. When the LaTiO\(_3\)/LaFeO\(_3\) interface is formed, band alignment of the oxygen states leads to an effective CT of one electron from Ti (3d) to Fe (3d) states. Thus, the CT fixes Ti\(^{4+}\) and Fe\(^{2+}\) oxidation states in the superlattice, where the ferrous iron has the freedom to occupy either a high- or low-spin configuration.

Using spin-assisted random structure searches we can explore the phase space of the accessible (ground and metastable) magnetic states. We use the AIRRSS package interfaced with Quantum Espresso to execute the search whose primary constraint is the starting spin configuration. As shown in Fig. 1b, we obtained a classification of the possible spin-states into four categories. The most likely candidates found have an antiferromagnetic ordering, occurring in 57\% of cases and are followed by the ferromagnetic structures at 0.07 eV higher in energy, which
occur in 20% of the instances. The remaining 23% intermediate spin states are characterised by strong spin and charge disproportions, where a manifold of $M_{mm}$ and $M_{pp}$ like spin-density waves (SDW) emerge at 0.2 eV. We emphasise that such SDW metastable configurations, as revealed by our statistical analysis, are not often mentioned in the literature, where the usually studied phases are AFM C, G, A-types. Finally, at 0.7 eV the phase space is dominated by states with only a PCT occurring, wherein residual moments on one of the Ti ions give rise to a more intricate magnetic ordering. Thus, the spin-assisted random structure search outlines the ground state of the parent LaFeO$_3$ constituent, as the in-plane super-exchange coupling is protected upon the formation of the (1/1) interface. We emphasise that these features persist also in a (2/2) interface (see Supplementary Fig. S11). We obtain the energy difference between the low and HS configuration: \( \Delta E = E_{\text{HS}} - E_{\text{LS}} = -8J + 2\Delta - t^2/U \). Using typical values of, e.g., $\Delta \sim 2$ eV, $J \sim 0.45$ eV, $U \sim 4.8$ eV and $t \sim 2$ eV, the balance between magnetic interactions and crystal field splitting stabilises the high-spin configuration. Thus, the superlattice inherits the magnetic ground state of the parent LaFeO$_3$ constituent, as the in-plane super-exchange coupling is protected upon the formation of the (1/1) interface. We emphasise that these features persist also in a (2/2) interface (see Supplementary Fig. S11).

We demonstrate in Fig. 1d that through the process of epitaxial engineering the Fe$^{2+}$ HS configuration is particularly robust to in-plane strain. Throughout a range of realistic epitaxial strain amounts (from $-5\%$ to $+5\%$), there is a consistent $\approx 1$–3 eV energy difference between magnetic and nonmagnetic configurations. Using a spin-assisted random structure search (see Supplementary Fig. S5) several new phases are discovered, the majority being ferromagnetic that lie between 1 and 10 meV above the antiferromagnetic phase, as shown in Fig. 1d. We notice that, as the in-plane states are increasingly localised through tensile strain, then the relative energy difference between the ferromagnetic and antiferromagnetic configurations becomes smaller, which is typical of the onset of a Mott transition. In the opposite limit,
where the in-plane states are compressed, the states are far in energy, indicative of itinerant magnetism (see Supplementary Fig. S6c). Additionally, two new phases are predicted and illustrated in Fig. 1c, the first with no charge transfer (NCT) and the other with a partial charge transfer (PCT), both lying about 1 eV above the ground state. We note that the spin-assisted random structure search always finds structures with a final configuration that is HS thus verifying the robustness of the antiferromagnetic ground state, finding that it comprises ~74% of all predicted structures.

**Ionic radii and correlation strength**

We further extend the analysis of the phenomena stemming from the epitaxial strain, focusing on the strong coupling between electronic and lattice degrees of freedom. We study as a key structural parameter the ionic radii. We estimate the atomic radii by averaging over the equatorial and apical bonds of the TiO$_2$ and FeO$_6$ octahedra of all the compounds shown in Fig. 1d. Note that we investigate both the ground state and the metastable configurations. Interestingly we notice in Fig. 2a that the obtained ionic radii group together following phase boundaries defined by the charge and magnetic configurations, e.g. CT or NCT, low-spin (LS) or HS. For comparison, we include in the diagram the atomic ionic radii obtained in vacuum configurations as in ref. 10, corresponding to the nominal valence and spin states of Ti and Fe ions (black crosses). The resulting scenario unveils that the latter ionic radii play the role of basins of attraction for the different phases which extend around them. For instance, the values of ionic radii computed for the ground state of the heterostructure (up triangle) are close to the ionic radii obtained in vacuum configurations which are 92 and 74.5 pm, respectively, for Fe$^{3+}$ and Ti$^{4+}$ (CT HS). Similarly all the structures fall close to their nominal atomic configuration.

Outlier cases emerge in the limits of epitaxial compression (YAlO$_3$, LuAlO$_3$) and expansion (LaLuO$_3$) in the CT HS configuration, where the ionic radius for Fe has a large effective value for YAlO$_3$ and LuAlO$_3$, whereas the ionic radius of Ti increases for LaLuO$_3$. Since the obtained ionic radii are related to the volumes, in Fig. 2b we analyse its trend as a function of the selected substrates. We notice that a decrease of the lattice constant is coupled to a volume collapse of LaTiO$_3$/LaFeO$_3$ with CT HS. However, if $a < 3.79$ Å, the ground state volume does not follow the expected trend (dashed line) but instead expands abruptly, albeit within the stability range of the perovskites (see Supplementary Fig. S8a). A close comparison between the energies of the relaxed configurations and the unrelaxed structure corresponding to the extrapolated volume reveals that volume expansion together with increasing of octahedral rotations (see Supplementary Fig. S8c) favour the lowest energy configurations for LaTiO$_3$/LaFeO$_3$ constrained on LuAlO$_3$ and YAlO$_3$. In the opposite limit of strain, when the structure is clamped on LaLuO$_3$ the large tensile strain triggers an asymmetric in-plane extension of the Ti–O bonds, which allows the positively charged Ti to effectively screen its neighbouring oxygen anions. Further analysis of the O–Ti–O angles (see Supplementary Fig. S8b) reveals that for substrates with $a > 3.905$ Å, Ti prefers a tetrahedral coordination.

We extend the analysis by considering their density of states. The fractional density of states in Fig. 2c shows that if the heterostructure is clamped on LaLuO$_3$, the insulating gap is between d(Ti) and d(Fe), hence the configuration is Mott-Hubbard type. As the in-plane lattice constant is reduced to the LaAlO$_3$ one, the band distribution at the Fermi level changes. The Fe (3d) bands, albeit keeping the localised character as in LuAlO$_3$, are more hybridised with the O (2p), resulting in an overall CT Mott insulator. As the in-plane parameter is further reduced (up to LuAlO$_3$ substrate), the Fe (3d) states show a broader distribution and a larger hybridisation with the oxygen states. A further clarification on the nature of the heterostructure clamped on LuAlO$_3$ is provided by looking at the fractional density of states (Fig. 2d). The resulting scenario unveils that the latter ionic radii play the role of basins of attraction for the different phases which extend around them. For instance, the values of ionic radii computed for the ground state of the heterostructure (up triangle) are close to the ionic radii obtained in vacuum configurations which are 92 and 74.5 pm, respectively, for Fe$^{3+}$ and Ti$^{4+}$ (CT HS). Similarly all the structures fall close to their nominal atomic configuration.
deformation (volume expansion, increased octahedral rotation and enhanced La polarisation) to lower the energy and stabilise an insulator with itinerant magnetism, bearing similarities with the characteristic features of a Slater insulator. Therefore, the CT HS region in the ionic radii phase diagram is characterised by the transition between three different magnetic configurations: from the Slater insulator-like behaviour stemming from the itinerant magnetism to a more localised Mott CT insulator with an O(2p)–Ti (3d) bond gap and finally up to a Mott-Hubbard insulating d–d gap. Our results confirm the expected trend that the effect of correlation increases as we go from compressive to tensile epitaxial strain, due to the reduction of the bandwidth. Notably, there is also a simultaneous structural deformation associated with the local coordination of both La and Ti (see Supplementary Fig. S8). Moreover, we find that in the Mott phase at room temperature, via paramagnetic dynamical mean-field theory (DMFT) calculations, the CT, local magnetic moment, and spectral weight remain consistent with the zero temperature DFT magnetic calculations (see Supplementary Figs. S9 and S10).

**Pressure induced spin-state crossover**

We have highlighted that the ground state has a Fe$^{2+}$ HS configuration, while the LS one represents a metastable state for all of the structures analysed. An unexplored question that naturally follows is whether a volume-induced spin crossover can be observed in the heterostructure at hand. The spin crossover in iron has been widely studied in the context of geochemical modelling of the Earth’s deep interior. In particular, crystal field theory and band theory predicted for ferropericlase and iron-bearing magnesium silicate perovskites that a HS to LS transition occurs as a result of compression. Although the latter transition has been widely studied in minerals, a realisation of such a transition in deposited compounds remains unclear. Based on similar studies of the structural-induced switching of spin-state ordering, we analyse first the stability of the HS state in absence of substrate under the uniaxial compressive strain along the c-axis.

For the current analysis, there are significant changes in the volume and pressure of the structures studied and energy no longer becomes the thermodynamical quantity of choice, but instead the enthalpy. Thus, in Fig. 3a we show the enthalpies associated with the configurations obtained under the uniaxial strain. We predict for increased compression and consequent volume reduction that the enthalpy difference between the LS and the HS configuration decreases, which suggests the progressive destabilization of the latter. In particular, we report that the HS state remains robust until very large pressure. At a pressure of 60 GPa, the system undergoes a transition towards the LS configuration, as the HS state accommodates smaller volumes. Furthermore, as a consequence of the uniaxial compression, the octahedral distortions change and we notice that the high to LS transition occurs as a result of compression. Although the latter transition has been widely studied in minerals, a realisation of such a transition in deposited compounds remains unclear.

**Terahertz-induced spin-state transition mediated by octahedral distortions**

Our results so far indicate that the spin transition is weakly affected by the c-axis compression, albeit particularly sensitive to octahedral tilts. We now focus on probing the spin-state dependence on octahedral rotations only, in a manner that is independent of strain or pressure and accessible with THz light pumps. Our motivation is linked to advances in state-of-the-art epitaxial growth techniques which have allowed for the atomic manipulation of octahedral rotations, particularly in their capabilities to suppress them. Supplementary to these advances, ultrafast optical spectroscopy can now probe selective low-energy phonon modes by a THz pump. We demonstrate that through the manipulation of octahedral rotations in the LaTiO$_3$/LaFeO$_3$ superlattice, a spin-state transition can be achieved on the LaAlO$_3$ substrate. We analyse the effect of octahedral rotations by constructing a linearly interpolated isovolumetric pathway between the high symmetry undistorted superlattice and low symmetry distorted structures, with in-plane lattice parameters constrained to $a = 3.79$ Å. At each point along the path, the lowest energy spin-state configuration is chosen such that the energy is given relative to the high-spin distorted structure, as shown in Fig. 4a. $a$ is the Fe–O–Fe angle and is a measure of octahedral rotation in the superlattice where for an induced tilt of $\pm 6^\circ$ the spin-state transition occurs. A high energy THz pump can induce lattice vibrations on scales of fractions of an Angstrom and this corresponds to the appropriate range defined by $a$. With this in mind, we explore the phonon spectrum, achieved by doing Γ point DFPT calculations, to identify vibrational modes within the THz regime that are compatible with octahedral distortions. The phonon density of states, shown in Fig. 4b, is distinctly split between the strongly coupled heavier anions and cations and lighter oxygen ions with a phase boundary at 6 THz. We identify a representative $A_g$ phonon candidate present at 7.42 THz, illustrated in Fig. 4c, that is similar to the tilts induced in Fig. 4a.

Fig. 3 Pressure induced spin-state crossover. Enthalpy difference between the low-spin and high-spin configurations obtained under the compressive strain along the c-axis for LaTiO$_3$/LaFeO$_3$ a bulk and b clamped on the LaAlO$_3$ substrate both with (triangles) and without (stars) octahedral distortions. In a the value of the angle $a = Fe_1-O-Fe_2$ is also shown along the z-axis. The configuration with LS is the most stable structure even at small pressure values.
and of primarily oxygen character only. Moreover, there are additional modes beyond 7.42 THz that extend into the Raman spectrum and beyond the range of THz spectroscopy. In summary, while the spin-state crossover is hard to achieve through uniaxial pressure, it is much more accessible by manipulating the c-axis of the heterostructure unit cell and allowing for internal relaxation. Regarding the latter, we focus on epitaxial strain constraining the orthorhombic in-plane lattice a and b to the pseudocubic parameter $a_{sub}$ of a set of different substrates, while the out-of-plane lattice parameter $c$ is free to relax. Therefore, the initial structure for all the simulations with different substrates, characterised by in-plane lattice constant $a_{sub}$, is represented by a 20 atoms unit cell (with 12 oxygen, 2 Fe, 2 Ti and 4 La ions) with the Gd-orthoferrite distortions inherited from the bulk counterparts (LaTiO3 and LaFeO3) and in-plane lattice constants constrained to $\sqrt{2}a_{sub} \times \sqrt{2}a_{sub}$. The allowed relaxations involve internal coordinates of the atoms and the lattice vector along c-axis. We clarify that we did not directly include the substrates in the calculations and as a result, we are dealing with only a single interface between two perovskites. Structural degrees of freedom are relaxed until all forces are smaller than 1 mRyd/a.u. In our calculation we consider different initial magnetic conditions for the superlattice in the DMFT approximation and neglect the effect of charge self-consistency.

**DISCUSSION**

We have shown that a remarkably robust HS antiferromagnetic ferrous oxide emerges in heterostructure due to interfacial electronic reconstruction. In particular, we illustrate that through epitaxial engineering the electronic correlation strength is tunable and causes a rich phase diagram to arise, with a Mott- to Slater-like transition, predicted to remain stable at room temperature. The realisation of this effect has direct technology relevance for switchable oxide devices at the nanoscale. Moreover, we show that a magnetic phase transition in the superlattice can be triggered by octahedral rotations for which geological scales of pressure are not required. As such, we identify a series of compatible phonon modes at the THz scale in the vibrational spectra that can excite these rotations that are capable of activating the magnetic phase transition. From our results, it is clear that a plethora of fascinating properties emerge beyond what can be attributed solely to electronic interfacial reconstruction alone when additional tunable degrees of freedom are manipulated at the interface of two Mott insulators.

**METHODS**

**Calculation details**

All DFT calculations were performed using the plane wave code Quantum Espresso\(^\text{14}\), version 6.4.1, together with the GGA-PBE exchange-correlation functional\(^\text{14}\). Atomic cores were treated within the ultrasoft, nonlinear core correction approach\(^\text{15}\) with valence configurations La(4f5s 5p5d6s6p), Ti (3s3p3d4s), Fe(4p4s3d3p3s) and O(2s2p). The plane wave basis representation is used for the wavefunctions, with a cutoff of 800 eV. Results are converged by sampling a 6 x 6 x 4$\Gamma$-centred k-point mesh in the Brillouin zone. We apply $U = 4.8$ eV on Fe and $U = 3.0$ eV on Ti within the DFT + U approximation, where we specify the effective value of the Coulomb interaction $U_{eff} = U - J$\(^\text{18}\) as implemented in the QUANTUM Espresso package\(^\text{17}\). Our values reflect those commonly used in the literature for the study of a similar system\(^\text{12}\). Both LaTiO3 and LaFeO3 belong to the Pbnm spacegroup, with $a\ a\ c$ octahedral distortions in Glazer notation. We therefore constructed the (1/1) heterostructure starting from unit cell of LaTiO3 with 20 atoms which has $\sqrt{2}a_{sub} \times \sqrt{2}a_{sub} \times c_{sub}$ and then substituting two in-plane Ti ions with two Fe. The heterostructure is then fully relaxed into its (1/1) ground state configuration. We further investigated the stability of the ground state obtained for the unstrained heterostructure, extending the calculation where we apply both uniaxial and epitaxial strain. The former is achieved by varying the $a$ lattice parameter and causes a rich phase diagram to arise, with a Mott- to Slater-like electronic reconstruction. In particular, we illustrate that through octahedral distortions which involves transitions at a lower energy scale.

**REFERENCES**

1. Li, J. et al. Electronic spin state of iron in lower mantle perovskite. Proc. Natl Acad. Sci. USA 101, 14027–14030 (2004).
Li, J. et al. Dramatically enhanced polarization in (001), (101), and (111) BiFeO3 thin films due to epitaxial-induced transitions. Phys. Rev. B 87, 100101 (2006).

Lin, J.-F. et al. Spin transition of iron in magnesiowüstite in the Earth’s lower mantle. Nature 436, 377–380 (2005).

Tsuchiya, T., Wentzcovitch, R. M., da Silva, C. R. S. & de Gironcoli, S. Spin transition in magnesiowüstite in Earth’s lower mantle. Phys. Rev. Lett. 96, 198501 (2006).

Park, S.-E. & Shrout, T. R. Ultrahigh strain and piezoelectric behavior in relaxor-based ferroelectric single crystals. J. Phys. Condens. Matter 100, 2526–268 (2010).

Vrejoiu, I. et al. Intrinsic ferroelectric properties of strained tetragonal PbZr0.2Ti0.8O3 obtained on layer-by-layer grown, defect-free single-crystalline films. Adv. Mater. 18, 1657–1661 (2006).

Chen, H. & Millis, A. Charge transfer driven emergent phenomena in oxide heterostructures. J. Phys. Cond. Mat. 29, 243001 (2017).

Zhong, Z. & Hansmann, P. Band alignment and charge transfer in complex oxide heterostructures. Phys. Rev. Lett. 111, 116403 (2013).

Beck, S. & Ederer, C. Charge transfer in LaVO3-LaTiO3 multilayers: Strain-controlled dimensional intensity of interface metallicity between two Mott insulators. Phys. Rev. Mater. 3, 095001 (2019).

Zaanen, J., Sawatzky, G. A. & Allen, J. W. Band gaps and electronic structure of transition-metal compounds. Phys. Rev. Lett. 55, 418–421 (1985).

Pickard, C. J. & Needs, R. J. High-pressure phases of silane. Phys. Rev. Lett. 97, 045504 (2006).

Pickard, C. J. & Needs, R. J. Ab initio random structure searching. J. Phys.: Condens. Matter 23, 053201 (2011).

Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crys. Sect. A 32, 751–767 (1976).

Rondinelli, J. M. & Spaldin, N. A. Structural effects on the spin-state transition in epitaxially strained LaCoO3 films. Phys. Rev. B 79, 054409 (2009).

Arabi-Kanoutas, G. et al. Co valence transformation in isopolar LaCoO3/LaTiO3 perovskite heterostructures via interfacial engineering. Phys. Rev. Mat. 4, 026001 (2020).

Wang, R. et al. Low-energy orbital excitations in strained LaCoO3 films. Phys. Rev. B 100, 165148 (2019).

Lin, Z. et al. Controlled lateral anisotropy in correlated manganese heterostructures by interface-engineered oxygen octahedral coupling. Nat. Mater. 15, 425–431 (2016).

Huibjorn, M., Koster, G., Liao, Z. L. & Rijnders, G. Interface-engineered oxygen octahedral coupling in manganese heterostructures. Appl. Phys. Rev. 4, 041103 (2017).

Li, X. et al. Terahertz field-induced ferroelectricity in quantum paraelectric SrTiO3. Science 364, 1079–1082 (2019).

Giannozzi, P. et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J. Phys.: Condens. Matter 21, 395502 (2009).

Perdew, J., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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