Massive symmetry breaking in LaAlO$_3$/SrTiO$_3$(111) quantum wells: a three-orbital, strongly correlated generalization of graphene

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Density functional theory calculations with an on-site Coulomb repulsion term (GGA+$U$ method) reveal competing ground states in (111) oriented (LaAlO$_3$)$_N$/SrTiO$_3$ superlattices with n-type interfaces, ranging from spin, orbital polarized, Dirac point Fermi surface to charge ordered flat band phases. These are steered by the interplay of (i) Hubbard $U$, (ii) SrTiO$_3$ quantum well thickness and (iii) crystal field splitting tied to in-plane strain. In the honeycomb lattice bilayer case $N=2$ under tensile strain inversion symmetry breaking drives the system from a ferromagnetic Dirac point (massless Weyl semimetal) to a charge ordered multiferroic (ferromagnetic and ferroelectric) flat band massive (insulating) phase. With increasing SrTiO$_3$ quantum well thickness an insulator-to-metal transition occurs.

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Remarkably rich electronic behavior has been discovered at oxide interfaces ranging from two-dimensional conductivity, superconductivity and magnetism to both confinement induced and gate controlled metal-to-insulator transitions. Most of the interest so far has been directed at (001) oriented interfaces as, e.g., the ones between the two band insulators LaAlO$_3$ (LAO) and SrTiO$_3$ (STO). Recently the growth and initial characterization, including finding of a high mobility electron gas, of LAO films on STO(111) has been reported. In contrast to the (001) direction where in the perovskite structure AO and BO$_2$ layers alternate, the (111) orientation comprises alternating stacking of AO$_3$ and B layers which can be highly charged: for example (LaO$_3$)$_{3-}/Al^{3+}$ for LAO, (SrO$_3$)$_{4-}/Ti^{4+}$ for STO, as illustrated in Fig. 1h. Despite the difference in stacking and charge of the individual layers, a polar discontinuity arises for both orientations, with a mismatch of $e/2$ per B cation for the n-type interfaces. For the (001) orientation this polar discontinuity is considered to be the origin of the rich spectrum of functional properties mentioned above, albeit the latter can also be influenced by defects. It is timely to investigate whether similar electronic reconstructions and exotic phases arise for the (111) orientation.

Perovskite (111) layers have distinctive real space topology: each BO$_6$ layer constitutes a triangular lattice where the B cations are second neighbors. Combining two such layers in a bilayer forms a buckled honeycomb lattice, topologically equivalent to that of graphene (Fig. 1a): three layers form the also distinctive dice lattice. The possibility for nontrivial topology of electrons hopping on a honeycomb lattice proposed by Haldane has spurred model Hamiltonians studies of topologically nontrivial states for (111)-oriented perovskite superlattices, where the focus was on the LaNiO$_3$ (LNO) $e_g$ system confined within LAO with quadratic band touching points, and a Dirac point at higher band filling. This two-orbital honeycomb lattice is beginning to be grown and characterized.

The corresponding three-orbital $t_{2g}$ system is realized for STO confined in LAO, where $e/2$ charge from each n-type “interface” (IF) will force one electron into 12 Ti conduction states (2 atoms, 3 orbitals, 2 spins), initially with P321 symmetry with two generators (3-fold rotation, mirror, and gauge symmetry; our methods do not address the latter. The corresponding model Hamiltonian would include the symme-

![Fig. 1: a) Side view of (LAO)$_3$/SrTiO$_3$(111) SL with an n-profile interface. b) Top view of the STO bilayer forming a buckled honeycomb lattice out of the two triangular lattices of Ti cations at each interface where Ti are second nearest neighbors. c) splitting of the $t_{2g}$ orbitals in $e_g$ and $e'_g$ due to trigonal symmetry, for one sign of the strain.](cond-mat.str-el)
try group $\text{SU}(2)_{\text{spin}} \times \text{SU}(2)_{\text{orb}} \times P_3 \times \mathcal{T} \times U(1)_{\text{gauge}}$.

A key question is that of orbital polarization, which is a primary factor in magnetic, transport, and optical properties. The geometry of the 111-superlattice breaks orbital 3-fold ($t_{2g}$) symmetry into trigonal $t_{2g} \rightarrow e'_g + a_{1g}$ as shown schematically in Fig. 1. For the (001) IF, previous DFT studies predicted,[15–18] and XAS data[19] demonstrated, that the $t_{2g}$ degeneracy is lifted such that the $d_{xy}$ orbital at the interface lies lower in energy. Including static local correlation effects within GGA+$U$ stabilizes a charge ordered and orbitally polarized layer with alternating Ti$^{3+}$ and Ti$^{4+}$ in the interface layer and a $d_{xy}$ orbital occupied at the Ti$^{3+}$ sites.[15, 16] It will be instructive to compare this scenario with the behavior for (111) orientation.

A mathematically symmetric expression adapted to trigonal symmetry for $t_{2g}$ orbitals is

$$\psi_m = (\zeta_m^{+}|d_{xy}) + \zeta_m^{-}|d_{yz}) + \zeta_m^0|d_{xz})|\sqrt{3},$$

where $\zeta_m = e^{2\pi i m/3}$. One issue is whether complex $e'_g$ orbitals $m=1,2$ ($m=0$ is the $a_{1g}$ orbital) assert themselves, inviting anomalously large response to spin-orbit coupling in $t_{2g}$ systems,[20] or whether real combinations of the $e'_g$ orbitals persist. Complex orbitals in the $e_g$ bilayer have been predicted to encourage topological phases.[12]

In this paper we find that trigonal level splitting, which is directly connected to strain, determines the orbital occupation that vastly influences the electronic structure in (111) oriented STO quantum well (QW).

DFT calculations have been performed on (LAO)$_M$/STO)$_N$ superlattices with varying thickness $M$, $N$ of both constituents, using the all-electron full-potential linearized augmented plane wave (FP-LAPW) method, as implemented in the WIEN2k code[21, 22]. The LAO thickness $M$ is always large enough to confine the carriers to STO. For the exchange-correlation potential we used the generalized gradient approximation (GGA).[23] Static local electronic correlations were taken into account in the GGA+$U$ method[24] with $U = 5$ eV, $J = 0.7$ eV (Ti 3$d$), $U = 8$ eV (La 4$f$). As discussed in the Suppl. Material[25], the obtained solutions are found to be robust with respect to variations of the on-site Coulomb repulsion parameter. The influence of strain was investigated by choosing the lateral lattice parameter of either LAO ($a_{\text{LAO}}=3.79$ Å) or STO ($a_{\text{STO}}=3.92$ Å), which correspond to superlattices grown either on a LAO(111) or STO(111) substrates. We note that these lateral lattice constants impose different strain states in the two parts of the superlattice. Octahedral tilts and distortions were fully taken into account when relaxing atomic positions, whether constrained to P321 symmetry (3-fold rotation plus $\mathcal{T}$) or fully released to P1 symmetry (in most cases solutions retained the higher P3 symmetry).

Results for $a_{\text{LAO}}$, corresponding to an underlying LAO(111) substrate. Fig. 2 presents results for $n$-type (111) oriented (LAO)$_M$/STO)$_N$ superlattices with
thickeneses $N=2,3,4$ of the STO quantum well, each of which is ferromagnetic (FM). The bilayer at $a_{\text{LAO}}$ (Fig. 2a) is a charge ordered FM insulator with two distinct interfaces with Ti$^{3+} (0.60\mu_B)$ and Ti$^{4+} (0.10\mu_B)$, respectively, and due to broken inversion symmetry it is also ferroelectric (FE). The occupied orbital assumes local $d_{xy}$ orientation (similar to the (001) superlattices [15–19]). This state (P1 symmetry) is preferred by 42 meV/Ti over the inversion symmetric case (P321 symmetry, Fig. 2a), where in contrast $e'_{g}$ orbitals become preferentially occupied, indicating strong competition of electronic states with distinct orbital occupation, with very different symmetries, and electronic properties (ungapped versus gapped). $e'_{g}$ orbital occupation is preferred also for $N=3$ and 4 (Fig. 2c–d) [20]. The difference $N \to 2-4$ (Fig. 2c–d) in electronic structure seems minor: the flattish lower conduction band is mostly occupied, leaving a hole Fermi surface (FS) surrounding the zone corner point K, with charge being balanced by one or two electron FS pockets centered at $\Gamma$. For the thicker $N=3, 4$ STO QWs, the extra $e/2$ charge from each interface is distributed preferentially towards the central layers, related to the different chemical environment of interface vs. central Ti ions.

Results for $a_{\text{STO}}$, corresponding to an underlying STO(111) substrate. Using the in-plane STO lattice constant strains the LAO layer but leaves STO cubic (subject to relaxation), it reverses the orbital polarization – a remarkably strong strain effect – and produces richer behavior: the symmetric $a_{1g}$ orbital becomes occupied independently of the $N_{\text{STO}}$ thickness, as shown in Fig. 3 (only for $N=4$ the shape is distorted). Similar to the compressive case, the charge is shifted from the interface towards the central layers with increasing STO thickness. For the FM CO insulating $N=2$ case, the top of the gap is bounded by a remarkably flat band. For the dice lattice (3/3) case the Ti$^{3+}$ central layer (0.50 $\mu_B$) is sandwiched by Ti$^{4+}$ interface layers, a confinement effect resulting in a FM insulating ground state. An insulator-to-metal transition occurs at $N=4$, always retaining FM order, although the exchange splitting is reduced with increasing STO QW width. For LAO layers grown on STO(111), Herranz et al. found a critical thickness of $\sim 10-12$ LAO layers for the onset of conductivity, but their setup [7] is not comparable to our QW system. We note from both Figs. 2 and 3 the proclivity of linear “Dirac” bands to occur at K, but when such points are not pinned to $E_F$ they have no consequence.

As mentioned, the case $N=2$ is special because the Ti bilayer forms a buckled honeycomb lattice, prompting us to study this system in more detail. The single electron can be shared equally and symmetrically by the two Ti ions, or it can tip the balance to charge order, which requires symmetry breaking from P321 to P3 or possibly P1. Both CO and non-CO scenarios can be handled with or without other broken symmetries. We remind that in this $t_{2g}$ system we always find the spin symmetry is broken to FM order, regardless of in-plane strain,
restriction of symmetry, and starting configuration. Similarly, in their model studies of an $e_g$ bilayer honeycomb lattice (LNO superlattices), Rüegg et al. [12] found FM ordering for broad ranges of model parameters. Constraining to P321 symmetry, a graphene-like Dirac point emerges at the zone corner point K that is pinned to the Fermi level and protected by the equivalence of the Ti sites, see Fig. 3. True particle-hole symmetry is restricted to relatively low energy due to coupling of the upper band to high-lying bands. The occupied bandwidth corresponds to hopping $t_{\text{xy}}a_{1g} = 0.28$ eV. Having a single electron shared symmetrically by two Ti sites is potentially unstable. Allowing breaking of this $I$ symmetry results again, as for compressive strain, in a CO state for compressive strain, which has d polarization, which is pure (being 1.94˚A in the symmetric case). The orbital polar-tensile case the Ti-Ti interlayer distance is 2.1 ˚A, with the system. The complex occupied orbitals that arise in QWs touching point at Γ [11, 12]. In contrast, for this $t_{2g}$ system at low filling there are only two relevant bands, and inversion symmetry breaking gaps the two linearly crossing bands into two relativistically flat bands. The very flat conduction band we find occurs only for the CO states (which are the ground states) that involve either $a_{1g}$ and $d_{xy}$ orbital occupation, depending on strain. Its origin therefore is not as straightforward as for the above mentioned models.

Allowing a difference in on-site 3$d$ energies will be an essential part of breaking $I$ symmetry when modeling the transition from massless Dirac pair into massive (gapped) bands, see Fig. 3a,b. This difference in Ti$^{4+}$ and Ti$^{3+}$ 3$d$ energies will be similar to the 2$p$ core level difference arising from different Ti-oxygen bond lengths, which at 1.7 eV is twice the occupied bandwidth of the Dirac band structure. Focusing on the majority (blue) bands of the CO state, a regularity can be seen: there is a parallel pair of bands of the same shape as the occupied band, but lying 1.3 eV higher, which is the pair of Ti$^{3+}$ $e'_g$ bands. Mirroring the flat band and again 1.3 eV higher are two more (no longer precisely) flat bands; these are the Ti$^{4+}$ $a_{1g}$ and $e'_g$ bands.

As our analysis shows [25], both the Dirac point and the charge ordered state result from on-site correlation. Both solutions emerge at relatively small $U$ values (1-2 eV) and are robust with respect to further increase of $U$. In the CO case, the primary effect of $U$ is to encourage integer orbital occupations, i.e., a Mott insulating state: four quarter-filled spin-orbitals (two sites, two orbitals) convert by CO to one empty sublattice and one half-filled sublattice, which then becomes Mott insulating. This CO-Mott transition is driven by a combination of Hubbard $U$ and symmetry breaking (accompanied by a substantial oxygen relaxation), and may be aided by intersite repulsion.

Bands on the same graphene lattice, displaying the topology that we find for the Dirac bilayer, have been related to topological character. Typically topological phases are protected by time reversal symmetry coupled with additional symmetries. Fu and others [37] have noted that SOC is not required, demonstrating that topological band insulators can also be protected by crystalline symmetry rather than $I$ symmetry.

Now we summarize. Unexpected richness has been uncovered in (111)-oriented STO/LAO heterostructures, where carriers must reside in Ti $t_{2g}$ states. The competing ground states are ferromagnetic, with strain-controlled crystal field splitting $t_{2g} \to a_{1g} + e'_g$, promoting strain engineering of orbital polarization. For the system under tensile strain, a graphene-like Dirac point degeneracy survives as long as inversion symmetry of the bilayer is preserved. Allowing breaking of this symmetry, charge ordering with a flat conduction band and multi-ferroic properties results, again with orbital polarization dependent on strain. Melting of the CO phase as temperature is raised, where several symmetries (and conductivity) are restored, should reveal very rich behavior.

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