Zoology of spin and orbital fluctuations in ultrathin oxide films

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Many metallic transition-metal oxides turn insulating when grown as films that are only a few unit-cells thick. The microscopic origins of these thickness induced metal-to-insulator transitions however remain under dispute. Here, we simulate the extreme case of a monolayer of an inconspicuous correlated metal—the strontium vanadate SrVO3—deposited on a SrTiO3 substrate. Crucially, our system can have a termination to vacuum consisting of either a SrO or a VO2 top layer. While we find that both lead to Mott insulating behavior at nominal stoichiometry, the phase diagram emerging upon doping—chemically or through an applied gate voltage—is qualitatively different. Indeed, our many-body calculations reveal a cornucopia of nonlocal fluctuations associated with (in)commensurate antiferromagnetic, ferromagnetic, as well as stripe and checkerboard orbital ordering instabilities. Identifying that the two geometries yield crystal-field splittings of opposite signs, we elucidate the ensuing phases through the lens of the orbital degrees of freedom. Quite generally, our work highlights that interface and surface reconstruction and the deformation or severing of coordination polyhedra in ultra-thin films drive rich properties that are radically different from the material’s bulk physics.

I. INTRODUCTION

In strongly correlated materials\cite{1,2} various energy scales compete in defining the ground state. Perturbing their balance, e.g., through pressure or doping, may induce a multitude of different long-range orders or trigger metal-insulator transitions.\cite{3} Particularly rich are phenomena involving the orbital degrees of freedom.\cite{4,5} Their behavior is extremely sensitive to the local atomic environment that controls hybridizations,\cite{6} crystal-fields,\cite{7} and their degeneracy. Therefore, the advent of epitaxial growth of ultra-thin films and hetero-structures has unlocked vast possibilities\cite{8,9} to explore orbital physics and electronic anisotropies\cite{10} in general. Indeed, substrate strain, interfacial or surface reconstruction, and varying surface terminations cause distortions, rotations, or even the severing of coordination polyhedra. These structural changes invariably affect the electronic, magnetic, and orbital state, often leading to properties absent in bulk samples of the same material.

Here, we study the extreme case of a monolayer of the perovskite transition-metal oxide SrVO3 deposited on a SrTiO3 substrate. A moderately correlated paramagnetic metal in the bulk,\cite{11,12} SrVO3 is known to undergo a metal-to-insulator transition (MIT) in ultra-thin films on SrTiO3 below a critical thickness of 2-3 unit-cells.\cite{13,14} This Mott insulator,\cite{13,15} has further been suggested\cite{15} as active material in a Mott transistor,\cite{16} where a gate voltage is used to switch between the insulator (OFF) and a metallic (ON) state. Besides the characterization of the charge state, however, little is known about ordered phases or long-range fluctuations in ultra-thin films. Bulk Mott insulators typically order antiferromagnetically (AF) at low enough temperatures, while doping them may lead to various types of fluctuations and symmetry-broken phases, e.g., superconductivity or charge-order. Here, we find that the SrVO3 monolayer realizes more than five distinct phases, see Fig. 1, including (in)commensurate antiferromagnetism (AF), ferromagnetism (FM), as well as stripe (s) and checkerboard (c) orbital-order (OO). Some of these regimes can be explored by chemical doping or an applied gate voltage. Additionally, we evidence a qualitatively different phase diagram for the two possible choices of surface termination, in which the top is formed by either a VO2, or a SrO layer (Fig. 1a, 1b, respectively). Ultimately, we link the character of dominant fluctuations to the orbital degrees of freedom, that are tuned through the (total) filling n and the crystal-field splitting Δ_cfs between the two-fold degenerate d_{xz}, d_{yz} orbitals and the d_{xy} orbital residing in the film’s plane. With these key ingredients being common to a multitude of correlated oxides, our study of the SrVO3 monolayer anticipates rich phase diagrams in transition-metal oxide ultra-thin films.

The outline of the paper is as follows: Section II briefly discusses the methods employed: density functional theory (DFT) and dynamical mean-field theory (DMFT). Section III A presents the quantitative differences between the two different surface terminations on the one-particle level. Section III B presents a many-body discussion of the Mott insulating state found in the stoichiometric systems, while Section III C presents the electronic structure trends upon doping the SrVO3 monolayers. Section III D characterizes magnetic and orbital fluctuations and associated ordering instabilities on the basis of DMFT susceptibilities. Section IV puts our findings in perspective. Finally, Section V summarizes the results and provides an outlook.

II. METHOD

DFT calculations are performed with the WIEN2k package\cite{17,18} using the PBE\cite{19} exchange-correlation potential. We construct systems with one half of a unit cell of SrVO3 (VO2 termination) and one unit cell of
SrVO₃ (SrO termination) on top of a substrate of six unit cells of SrTiO₃ surrounded by sufficient vacuum of around 10Å in z-direction (see insets in Fig. 1). In both setups the transition between SrTiO₃ and SrVO₃ consists of a TiO₂ - SrO - VO₂ interface, consistent with experiment, while at the bottom the SrTiO₃ substrate is terminated via SrO to vacuum. Since experimentally SrVO₃ is locked to the SrTiO₃ substrate we initialize the in-plane lattice constant with the PBE-optimized value for bulk SrTiO₃ $a_{\text{SrTiO}_3} = 3.95\text{Å}$. To treat the surface properly the two unit cells of SrTiO₃ furthest away from SrVO₃ are then constrained to $a_{\text{SrTiO}_3}$, simulating the transition to the SrTiO₃ bulk, while all other internal atomic positions are fully relaxed.

We then perform Wannier projections onto maximally localized V-$t_{2g}$ orbitals, using the WIEN2Wannier interface to Wannier90, see Fig. 2. These Wannier Hamiltonians are supplemented with an effective SU(2)-symmetric Kanamori interaction of $U = 5\text{eV}$, $J = 0.75\text{eV}$, $U' = 3.5\text{eV}$ (similar to Ref. 15), for which we perform dynamical mean-field theory (DMFT) calculations at various temperatures. For the undoped bulk, this setup yields the correct mass enhancement and spectra qualitatively congruent with photoemission spectroscopy. These values can be thought of as a lower boundary since in ultrathin films, interaction parameters increase slightly with respect to their bulk values. The Hamiltonians are kept constant under doping. The analytic continuations to real frequencies are performed with the maximum entropy method used in the ana_cont library.

The DMFT self-consistency cycle as well as the sampling of the two-particle Green’s function is done by continuous-time quantum Monte Carlo simulations in the hybridization expansion using w2dynamics with worm sampling. Momentum-dependent DMFT susceptibilities are calculated from the local vertex, using the AbinitioDΓA program package.

III. RESULTS

A. Surface termination, band structure and density of states

Both, SrO and VO₂-terminated films result in similarly looking DFT band structures whose relevant orbitals around the Fermi level are of vanadium $t_{2g}$ character, see Fig. 2. The densities of states (DOS) of these orbitals showcase the abrupt surface termination of the sample: While the $xy$-projection (blue line) keeps its two-dimensional character (as in bulk SrVO₃) the (locally degenerate) $xz$- and $yz$-projections (green lines) now become one-dimensional and, concomitantly, display a strongly reduced bandwidth. Consequently a van-Hove singularity emerges, which, at zero doping, is in close proximity to the Fermi level. Indeed, in the VO₂ (SrO) terminated system this singularity is situated slightly below (above) the Fermi level. On top of this dimensionality reduction we find the crystal-field splitting (cfs) of the two-particle Green’s function is done by continuous-time quantum Monte Carlo simulations in the hybridization expansion using w2dynamics with worm sampling. Momentum-dependent DMFT susceptibilities are calculated from the local vertex, using the AbinitioDΓA program package.

$$\Delta_{\text{cfs}} = E_{xz/yz} - E_{xy}$$

(1)

to have opposite signs for the two different setups: The positive cfs of the SrO terminated monolayer, $\Delta_{\text{cfs}} =$
Recent experiments\(^1\)\(^{10}\)\(^{14}\)\(^{30}\)\(^{40}\)\(^{41}\) suggest ultra-thin SrVO\(_3\) films to be VO\(_2\)-terminated. However, for reasons of stability (surface oxidization, surface protection, etc.), a SrO-boundary could be preferable. This might be achievable either implicitly via a SrTiO\(_3\) capping-layer (see Sec. V) or explicitly via deposition of SrO on top of the VO\(_2\) surface. The latter has in fact been achieved for LaNiO\(_3\) films on LaAlO\(_3\) substrate, where both LaO and NiO terminations are possible through an ablation of La\(_2\)O\(_3\) and NiO, respectively\(^{40}\).

**B. Stoichiometric Mott insulator**

Next, we analyze the electronic structure for the stoichiometric samples (\(n = 1\)) on the many-body level, using DMFT at room temperature \(T = 290\)K: While in the VO\(_2\)-terminated monolayer (Fig. 3a) the out-of-plane \(xz/yz\)-orbitals realize a *quarter-filled* Mott insulator with a gap of 0.5eV, in the SrO terminated monolayer (Fig. 3c) the in-plane \(xy\)-orbital hosts an essentially *half-filled* canonical Mott insulator with a gap of 1.2eV. This difference can be traced back to the bare crystal-fields. Indeed, DMFT amplifies the effect of the DFT cfs for both terminations, leading to the depletion of the energetically higher lying orbital(s), i.e., the \(xy\) and the \(xz/yz\) orbital(s) for the VO\(_2\) and SrO termination, respectively.

This correlation-enhanced orbital polarization\(^41\) leads to an effectively reduced orbital-degeneracy. As a consequence, charge (inter-orbital) fluctuations are suppressed and the critical interaction for reaching the Mott state diminishes\(^{27,42,43}\). The Coulomb interaction is large enough to open a Mott gap in the SrO (VO\(_2\)) terminated monolayer with a single (two-fold) degenerate lowest orbital, while three-fold orbitally degenerate bulk SrVO\(_3\) is a stable metal. Let us note that the evidenced orbital polarization persists when including charge self-consistency, which only yields minor corrections because charge is only redistributed between orbitals, not between sites\(^{44}\).
However, for both terminations the insulating behavior is actually driven by a combination of the crystal-field splitting\textsuperscript{15} and the reduced band-widths\textsuperscript{13}. Whereas the crystal-field splitting is essential for the bilayer system\textsuperscript{15}, we find that the bandwidth reduction alone is sufficient to drive the monolayers insulating. We illustrate this in Fig. 3b and Fig. 3d where we take the original Hamiltonians and set the cfs artificially to zero by shifting the local orbital energies. Both systems remain insulating in DMFT. Unswayed by the cfs, however, the Mott gaps turn out smaller and orbital occupations (in both cases: $n_{xz/yz}\sigma > n_{xy}\sigma$) only reflect the asymmetry of the orbitals’ DOS. Let us note here that if we instead keep the cfs unchanged and adjust the $xz/yz$-bands such that $W_{xz/yz} = W_{xy}$ both systems remain firmly metallic.

To investigate the stability of the insulating state further, we perform DMFT calculations for various intra-orbital interaction strengths $U$. While keeping the Hund’s coupling $J$ fixed to 0.75eV\textsuperscript{45} we adjust the inter-orbital interaction strength $U'$ according to spherical symmetry ($U' = U - 2J$)\textsuperscript{46}. Fig. 4 shows the orbital occupations depending on the interaction $U$. Starting from our standard value $U = 5eV$ (vertical dashed line), going to larger interaction strengths simply stabilizes the insulating solution further, while also increasing the orbital polarization slightly. Smaller interaction strengths on the other hand, reduce the orbital polarization until, eventually, the insulating solution can no longer be stabilized. This metal-to-insulator transition is, as expected within DMFT, of first order (hysteresis or coexistence regime marked in gray in Fig. 4) and manifests itself by a sudden drop of the orbital polarization. The Mott insulating state is stable down to $U = 4.5eV$ ($U = 4.1eV$) for the VO\textsubscript{2} (SrO) terminated monolayer.

The stability of the stoichiometric Mott insulating solution is in particular important when doping away from it, see Sec. III C. As long as the stoichiometric sample is insulating, we expect that any variation of the interaction will have no qualitative impact on the DMFT phase diagram. A smaller on-site repulsion will merely lead to weaker orbital polarizations and shifted boundaries in the phase diagrams, Fig. 1a,b.

On top of the Mott physics discussed here, weak localization through disorder may play an additional role in the insulating behavior of transport properties\textsuperscript{21}. However, the suppression of the one-particle spectra for thin films\textsuperscript{13}, magneto-transport results for SrVO\textsubscript{3} thin films on an LSAT substrate\textsuperscript{47} as well as SrVO\textsubscript{3}/SrTiO\textsubscript{3} superlattices\textsuperscript{48} argue against a dominant weak localization scenario for the insulator. Similar observations have been made for CaVO\textsubscript{3} thin films on SrTiO\textsubscript{3} substrate\textsuperscript{49}.

### C. Behavior under doping

We now discuss the electronic structure of the doped monolayers in their non-symmetry broken phases. From the information of orbital occupations and degeneracies, we motivate possible ordering instabilities (that will then be quantitatively assessed in Sec. III D). First, the stoichiometric insulating state in Fig. 3 and the various orbital occupations in Fig. 5, indicate that our systems

![FIG. 3. Mott insulating ground state.](image)

![FIG. 4. Stability of Mott insulating state.](image)
particular filling of the so far auxiliary vector changes to stripe orbital ordering (sOO) above a OO is fully suppressed upon hole doping the ordering ntron doping on the other hand maintains the quarter-
xy into the filling by redistributing electrons from the xz/yz terminated monolayer quickly moves away from quarter-
U of (virtual) hopping process costs only in a state where different orbitals are occupied so that a favorable, since a nearest-neighbor hopping then results (cOO) (Fig. 5a) somewhat upholds its orbital polarization 3 temper at and below nominal filling can effectively be described (xz/yz) orbitals. (b) The SrO terminated sys-
terminated monolayer, such degenerate quarter-filled orbitals may lead again to orbital ordering.

D. DMFT susceptibilities

We now put the above analysis of potential ordered phases on firm footing: For the prevailing magnetic and orbital orders, Fig. 6a and Fig. 6b displays the relevant DMFT susceptibilities at temperatures above the respective instabilities. Maxima in the shown susceptibilities indicate type and Q-vector of the dominant fluctuations. Fig. 6c illustrates, for selected examples, the critical behavior of the (inverse) susceptibilities and (inverse) correlation lengths emerging when said maxima turn into instabilities. Magnetic instabilities occur where the static susceptibility in the magnetic channel

\[ \chi_m(Q) = g^2 \sum_{ij,il} e^{iQ(R_i-R_l)} \int d\tau \langle T_\tau S^z_{il}(\tau)S^z_{jal}(0) \rangle \]

diverges at a critical temperature, indicated by the intercept of \( \chi^{-1}(Q) \) with the temperature axis in Fig. 6c. In Eq. (2), g is the Landé factor; i, j are indices for the lattice sites \( R_{il} \); l, l’ are orbital indices. The z-component of the spin operator \( S^z_{il} = (n_{il\uparrow} - n_{il\downarrow})/2 \) is expressed in terms of the number operator \( n_{il\sigma} \) for an electron on site i in orbital l with spin \( \sigma \). Ferromagnetism (FM) and antiferromagnetism (AF) correspond to the usual order-
ing vectors \( Q = (0,0) \) and \( Q = (\pi, \pi) \), respectively. The incommensurate magnetism (iM), that we find for the VO2-termination, corresponds to an ordering vector \( Q \) with fixed length \( |Q| = \delta \geq 0 \), see Fig. 6a and Fig. 7.

We now assess the instabilities resulting in the phase diagrams, Fig. 1a,b. Antiferromagnetic (AF) order from super-exchange is facilitated by effectively half-filled orbitals. For the d^3 configuration of SrVO₃, only the SrO-terminated monolayer provides this favorable condition. Indeed, there, the positive crystal-field realize
a half-filled, Mott insulating $xy$-orbital that then hosts AF order, see the diverging susceptibility in Fig. 6(c). Note that AF order was also predicted for a SrO-terminated SrRuO$_3$ monolayer on SrTiO$_3$ around nominal stoichiometry.\textsuperscript{55} There, the $d^4$ configuration results in an essentially fully occupied $xy$-orbital, and the staggered moment is instead carried by half-filled $xz/yz$ orbitals. In both cases, doping with either electrons or holes suppresses the AF state.

Doping the SrVO$_3$ monolayer with either termination towards their respective van-Hove singularities, i.e., hole (electron) doping for the VO$_2$ (SrO) terminated sample (see Fig. 2) results in a strongly increased spectral density around the Fermi level within DMFT. Concomitantly doping generates an orbital configuration where all involved orbitals are close to equally filled, promoting energy minimization through Hund’s exchange $J$ and therefore a parallel alignment of the involved spins. This situation, leading to ferromagnetism (FM), is found around $n=0.7$ in the VO$_2$-terminated and near $n=1.3$ in the SrO-terminated sample. In both cases, ferromagnetism is hosted by the degenerate $xz$ and $yz$-orbitals. Subleading non-local AF fluctuations are, however, still present in the $xy$-orbital of the SrO-terminated system. Indeed, an antiferromagnetic stripe pattern, $Q=(0,\pi)$, and symmetrically related at $Q=(\pi,0)$, appears, indicated by additional local maxima in the susceptibility, see Fig. 6b. Quite notably, in the absence of Hund’s rule coupling FM fluctuations are strongly suppressed and said frustrated AF spin-fluctuations would be on par with them (additional data, not shown). Moreover, we also find incommensurate magnetic order in the VO$_2$-terminated system around $n=1.3$ in the $xz/yz$-orbitals (iM at $n=1.3$ in Fig. 6a). There, instead of a specific ordering vector $Q$ the magnetic susceptibility is maximal for all vectors $Q$ with origin $(0,0)$ and a length of $\delta=|Q|\geq 0$, i.e., roughly a circle in the $q$-plane. Upon lowering temperature, $\delta$ increases and in close vicinity to the ordered phase anisotropy develops; the maximum susceptibility within the circle is found at $Q=(\pm\delta,\pm\delta)$, see Fig. 7. These clear maxima suggest that a kind of frustrated ferromagnetism develops where the $xy$-orbital disturbs the alignment of the $xz/yz$-orbitals. Doping beyond $n=1.3$ further increases $\delta$ (data not shown). Let us note here that throughout the phase diagram we did not find any magnetic instabilities supported by Fermi surface nesting.

The other prevalent type of instabilities we find are of orbital-ordering type between the degenerate $xz/yz$ orbitals and can be monitored in the density channel

$$\chi_d(Q) = \sum_{ij\sigma\sigma'} e^{iQ(R_i-R_j)} \int d\tau \times$$

$$\times \langle T_\tau(n_{i,x\sigma}-n_{i,y\sigma})(n_{j,x\sigma'}-n_{j,y\sigma'})(0) \rangle.$$

Towards quarter-filling ($n_{i,\sigma}=0.25$) of the $xz/yz$-orbitals, i.e., at and around stoichiometric filling in the VO$_2$-terminated monolayer and around $n \sim 1.5$ in the SrO-terminated sample, the wave-vector of critical fluctuations is firmly $Q=(\pi,\pi)$. As previously alluded to, this leads to a checker-board orbital-order (cOO), consistent with model expectations.\textsuperscript{50,51} We note that the $xy$-orbital does not participate in the ordering, as signaled by susceptibility enhancements being confined to components of the other two orbitals. The $xy$ orbital can also be passive at larger fillings or valencies: With one electron more, at $n=1$ the $t_{2g}$-orbitals are partially replaced by Ca (Sr)	extsuperscript{56}, cf. Refs. 57 and 58. An OO with all three $t_{2g}$-orbitals participating on the other hand is highly frustrated for a cubic lattice.\textsuperscript{59}

Due to the strong asymmetry around nominal filling in our monolayers, we also find a strong asymmetry of the

![FIG. 6. DMFT susceptibilities and criticality.](image-url)
corresponding cOO-dome in Fig. 1a, where the cOO transition temperature even increases upon electron-doping. If we move too far away from ideal quarter-filling, the ordering temperature is suppressed rapidly. Despite this suppression of cOO we find an additional emerging ordering for $n \sim 0.9$ in Fig. 1a. The corresponding ordering can again be described via Eq. (3) with, however, a characteristic vector $\mathbf{Q} = (0, \pi)$ (and $\mathbf{Q} = (\pi, 0)$ related via symmetry), describing stripe orbital-ordering (sOO). The cOO-to-sOO transition under hole-doping is not realized by a continuous move of the ordering vector from $\mathbf{Q} = (\pi, \pi)$ to $\mathbf{Q} = (0, \pi)$. Instead, increased hole-doping suppresses cOO while simultaneously promoting sOO. We conjecture that this transition can be ascribed to the ‘auxiliary’ $xy$-orbital, that does not contribute to the susceptibility enhancements of either fluctuations. Illustrated in the inset of Fig. 5 we find a semi-empirical condition that links the preference for stripe over checkerboard orbital order to the filling of the $xy$-orbital: $n_{xy,\sigma} = (0.25 - n_{xz,yz,\sigma})/2$ below which checkerboard ordering and above which stripe ordering is preferred by the system. Effectively, enough $d_{xy}$ occupation frustrates the local site enough for stripe ordering to be energetically favorable. As for the electron-doped side, the orbital-ordering domes in both systems disappear when doping too far away from quarter-filling.

IV. DISCUSSION

Mapping out all these different magnetic and orbital-ordering instabilities and their corresponding critical temperatures yields the phase diagrams in Fig. 1. Naturally, the DMFT long-range order exhibits mean-field criticality (Gaussian fluctuations), i.e., the critical exponents are $\gamma = 1$ for the susceptibility $\chi$, and $\nu = 0.5 = \gamma/2$ for the correlation length $\xi$, see Fig. 6. We note that in strictly two dimensions, due to the Mermin-Wagner theorem, long-range order can only set in at $T = 0$. As a spatial mean-field theory, DMFT does not verify this constraint, while it is captured in, e.g., DPA$^{61,62}$. In an experimental setting, however, perturbations by disorder (oxygen vacancies, etc.), spin-orbit coupling, single-ion anisotropy, surface adatoms, as well as tunneling into the substrate render strict 2Dness obsolete. This allows for phase transitions at finite temperatures. Still, non-local correlations beyond DMFT$^{63,64}$ are expected to attenuate the tendency for long-range order with respect to our DMFT solution. Non-local fluctuations may even drive pseudogaps, as shown for antiferromagnetic fluctuations in the one-band Hubbard model$^{62,65-67}$.

In Fig. 1 we further indicate that instead of chemical doping, the phase diagram can be perused by applying a gate voltage $V_G$. We note that the estimated values of $V_G$ measure the necessary potential directly in the monolayer, not the truly external one applied at a certain distance through a dielectric medium. Realizing the whole phase diagram with a sheet carrier change of 0.5 electrons/unit cell ($3 \cdot 10^{14}$ electrons/cm$^2$) in a single device might be challenging$^{68}$. Ionic electrolytes as dielectrics, however, allow for such a large amount of induced charges thanks to the large capacitance of polarized ions$^{69}$. Experimentally, the phase diagram Fig. 1 can hence be realized either by doping or via gate voltage, or a combination of both.

Finally, let us comment on an important difference between our semi-\textit{ab initio} calculations and typical model setups. In multi-orbital (Hubbard) models, orbital complexity is often simplified, in the sense that the hopping of each orbital is considered to be isotropic vis-à-vis all neighboring atoms. Many model studies even employ semi-circular densities of states, corresponding to the Bethe lattice with infinite coordination number. Such simplifications allowed distilling essential behaviors of, e.g., correlation enhancements of crystal-fields$^{70}$, the influence of Hund’s physics on the Mott transition$^{71}$, or correlations in band-insulators$^{72,73}$. Indeed, qualitative spectral properties of 3D systems without broken symmetries, are mainly controlled by the orbitals’ filling and the kinetic energy they mediate. Near symmetry-broken phases, however, the associated fluctuations in physical susceptibilities are strongly dependent on electronic-structure details. In fact, van-Hove singularities, nesting, or Kohn points may well be the cause of an instability. In our context, besides anisotropies, e.g., induced by the tetragonal distortion$^{10}$ and the obvious geometric restriction, a crucial ingredient is the \textit{per se} 2D nature of the $t_{2g}$-orbitals: In perfectly 3D cubic perovskites (e.g., bulk SrVO$_3$) each transition-metal $t_{2g}$ orbital only hybridizes with four of the six oxygen ions of the coordination octahedron. Therefore, both in bulk and ultra thin films, the in-plane $d_{xy}$ DOS is 2D-like. The loss of hopping along the z-direction in ultra-thin films further reduces the effective dimensionality, leading to the 1D-like DOS of the $d_{xz,yz}$ orbitals, see Fig. 2. Our analysis suggests, that even for qualitative phase diagrams of ultra-thin oxide
FIG. 8. Global phase diagram of SrVO$_3$ monolayers on SrTiO$_3$. DMFT orbital occupations of each setup are mapped into a $n_{xy}$ vs. $n_{xz} + n_{yz}$ graph. Due to the reduced bandwidth in the monolayer on a SrTiO$_3$ substrate, any orbital occupation repartitioning of the nominal $n=1$ filling (orange line) realizes a Mott insulator. SrO-terminated (black) and VO$_2$-terminated (gray) monolayers and their dominant non-local fluctuations (shaded background; colors identical to Fig. 1, but lighter) are discussed in this publication. As an outlook we showcase the effect of embedding a SrVO$_3$ monolayer in a SrTiO$_3$ sandwich (navy blue, dashed): The crystal-field and orbital structure is somewhat intermediate to the two uncapped monolayers. The computation of respective instabilities is left for future work.

V. CONCLUSION AND OUTLOOK

We have studied a single layer of SrVO$_3$ on a SrTiO$_3$ substrate, using DFT and DMFT, considering both possible surface terminations, VO$_2$ and SrO, to vacuum. We demonstrated that stoichiometric samples ($n=1$) are bandwidth-controlled Mott insulators: Depending on the surface termination, SrO or VO$_2$, the monolayer is an effectively half-filled one-orbital or a quarter-filled two-orbital Mott insulator. We showed this orbital polarization to derive from the crystal-field splitting having opposite signs for the two terminations and to be significantly enhanced by electronic correlations. Electron or hole-doping reveals multi-orbital effects: For the SrO-termination, AF-fluctuation are dominant around nominal filling. Doping with electrons populates the $xz/yz$-orbitals; they order ferromagnetically ($n \sim 1.3$) or realize checkerboard orbital orbital order ($n \sim 1.5$). For the VO$_2$ termination checkerboard $xz/yz$ orbital-order already dominates around nominal filling. Doping then instead promotes the $xy$-orbital which acts as a mediator for ferromagnetism and stripe orbital-order on the hole-doped side and incommensurate magnetism on the electron-doped side. While the change in magnetic fluctuations and orders could be observed in neutron experiments, experimentally evidencing the orbital fluctuations is only possible indirectly: the staggered pattern of $xz$ and $yz$-orbitals will result in a dynamic (potentially static) alternation of the bond-length in the $x$ and $y$ direction, possibly detectable in future x-ray measurements.

In all, the orbital polarization is the essential driver of the phase diagram of the SrVO$_3$ monolayer on SrTiO$_3$. We therefore summarize our results in Fig. 8 in form of an orbital occupation map. The considered surface terminations each realize, under doping, a characteristic trajectory in the $n_{xy}$ vs. $n_{xz} + n_{yz}$ space. As an outlook, we include a third possibility—a SrVO$_3$ monolayer with SrTiO$_3$ on both sides: At nominal filling this sandwich is, again, a Mott insulator. However, owing to the symmetric embedding, the crystal-field is minute (but positive). The computation of ordering instabilities of capped ultra-thin films, in which quantum confinement effects could be studied in a more controlled fashion, is left for future work.

A different future avenue are even more realistic setups of the current geometries, e.g., atomic position relaxation with the inclusion of correlation effects and recent advances$^{74,75}$ which allow for calculations of forces and phonons within DFT+DMFT to test the dynamical stability against superstructure formations.

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