Finite-temperature phase diagram of (111) nickelate bilayers

Oleg Janson* and Karsten Held
Institut für Festkörperphysik, TU Wien, Wiedner Hauptstraße 8-10, 1040 Vienna, Austria
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We report a density functional theory plus dynamical mean field theory (DFT+DMFT) study of an oxide heterostructure of LaNiO$_3$ (LNO) bilayers in [111] direction interleaved with four atomic monolayers of LaAlO$_3$. DFT+U optimizations yield two stable solutions: a uniform structure with equivalent NiO$_6$ octahedra, as well as a bond-disproportionated (BD) structure featuring a breathing distortion. For both structures, we construct the low-energy models describing the Ni $e_g$ states by means of Wannier projections supplemented by the Kanamori interaction, and solve them by DMFT. Using the continuous-time quantum Monte Carlo algorithm in the hybridization expansion, we study the temperature range between 145 and 450 K. For the uniform and the BD structure, we find similar phase diagrams that comprise four phases: a ferromagnetic metal (FM), a paramagnetic metal (PM), an antiferro-orbitally-ordered insulator (AOI), as well as a paramagnetic insulator (PI). By calculating momentum-resolved spectral functions on a torus and a cylinder, we demonstrate that the FM phase is not a Dirac metal, while both insulating phases are topologically trivial. By a comparison with available experimental data, we suggest that (LNO) bilayers are in the AOI phase at room temperature.

I. INTRODUCTION

Transition metal oxides (TMO) exhibit a plethora of fascinating physical behaviors, such as metal-insulator transitions [1], multiferroicity [2–4], colossal magnetoresistance [5, 6], and high-temperature superconductivity [7, 8]. The ongoing progress in fabricating high-quality TMO thin films led to the emergence of a new class of artificial materials: oxide heterostructures. Their properties are often markedly different from their TMO constituents. An archetypical example are heterostructures of two band insulators, SrTiO$_3$ (STO) and LaAlO$_3$ (LAO): if the latter component reaches the critical thickness of four atomic monolayers, a two-dimensional (2D) electron gas emerges at the interface [9]. Even more striking effects are observed for TMO with a partly filled $d$ shell. Here, electronic correlations become essential. For example, the emergence of a ferromagnetic metal at LaMnO$_3$/SrMnO$_3$ interfaces was reported [10], where both constituents are bulk antiferromagnetic insulators; or the polar field and the Mott insulating gap of STO/LaVO$_3$ can be employed as a solar cell [11, 12].

Although the variety of TMO gives rise to a very large number of possible binary combinations, the count of studied oxide heterostructures grows slowly. Following the pioneering works of Hwang and Ohtomo [9, 13], the research has been largely focused on superlattices whose constituents have a (possibly distorted) perovskite structure in the bulk, and the direction of growth was typically chosen to be along the (pseudo)cubic [001] direction. Against this backdrop, Xiao et al. [14] argued that bilayers grown along the trigonal axis, i.e. in the [111] direction, form a honeycomb lattice, with an excellent potential to create correlated analogs of graphene [14]. By employing the tight-binding (TB) approximation, they studied different fillings of the correlated $d$ shell in the presence of the spin-orbit coupling (SOC), and demonstrated that such (111) bilayers can host various topologically nontrivial phases. Also Haldane’s [15] quantum anomalous Hall state can be realized in (111) bilayers of SrRuO$_3$ on STO [16].

The ensuing numerical studies extended the TB analysis by including electronic interactions effects on a mean-field level [17, 18], and identified LaNiO$_3$ bilayers (2LNO) in an LAO matrix as a promising candidate for the realization of topological states [17, 19]. In the simplest ionic approximation, Ni$^{3+}$ has the $d^7$ electronic configuration, whereby six electrons fully occupy the low-lying $t_{2g}$ states and render them inactive. Hence, all change, orbital, and spin degrees of freedom in the 2LNO/3LAO
superlattices (Fig. 1, a) pertain to the single electron in the $e_g$ orbitals that remain degenerate due to the trigonal symmetry. This resilient degeneracy, in contrast to (001) superlattices [20], gives room for spontaneous ordering of complex orbitals and thus topologically nontrivial states emerge despite the small SOC [18]. While first analyses involving realistic tight-binding Hamiltonians evaluated by means of density functional theory (DFT) [19] as well as DFT+$U$ calculations [19, 21] suggested the stability of a Dirac semimetal state, later DFT+$U$ studies established a key role of a breathing distortion of NiO$_6$ octahedra (Fig. 1 b, c) which opens a gap and competes with the topological states [21, 22]. The breathing distortion is accompanied by a polarization, rendering (111) LNO bilayers a prospective multiferroic with a sizable spin polarization [22].

On the experimental side, first transport measurements indicated a semiconducting behavior, with the gap showing a sizable dependence on the thickness of the LAO layer [23]. Recently, both the activated behavior and the sensitivity of the gap size were corroborated by an independent study, which reported gaps between 17 and 162 meV for different LAO thicknesses [24]. The nature of the gap, in particular whether it is topological or related to a breathing distortion, remains an open question.

Here, we employ a combination of DFT and dynamical mean-field theory (DMFT) [25–29] to explore the phase diagram of 2LNO/4LAO heterostructures (Fig. 1, a). By performing detailed structural relaxations, we demonstrate that the presence of a breathing distortion can be neither proved, nor disproved: both structure types feature the same DFT+$U$ total energies within the error bars. Hence, we carry out DFT+DMFT calculations for the uniform as well as the bond-disproportionated structure. Both show, despite the symmetry breaking associated with the distortion, actually quite similar physics.

This paper is organized as follows. The methods employed, including the structure optimization, DMFT, and the evaluation of spectral functions, are described in Sec. II. DFT+DMFT results for the uniform and the bond-disproportionated structures are presented in Sec. III. A discussion of the topological properties as well as comparison of our numerical results with the available experimental data are given in Sec. IV. We conclude our paper and provide a brief outlook in Sec. V.

II. METHOD

A. Optimization of the crystal structure

DFT+DMFT results generally depend on the structural input from DFT calculations. Hence, accurate information on the crystal structure is of crucial importance. This is particularly challenging for superlattices that are not amenable to standard x-ray or neutron diffraction measurements. A common approach is to evaluate the structural input computationally, by allowing for a relaxation of the atomic coordinates, but keeping the lattice constants fixed to that of the substrate and minimizing the total energy [29]. In contrast, for correlated materials, the underestimation of electronic correlations can have drastic impact on the crystal structure. A prominent example is KCuF$_3$, where orbital ordering can give rise to a distortion of the lattice, known as the cooperative Jahn-Teller effect. This can be assisted by lattice effects, which may also be a driving force. While conventional DFT functionals yield a spurious undistorted structure, DFT+$U$ captures the underlying physics and reproduce the experimentally observed distortion [30].

A distinct trait of bulk nickelates is their tendency towards bond disproportionation, i.e. developing a breathing distortion of NiO$_6$ octahedra (e.g., [31–33]). Although it is not the case for bulk LaNiO$_3$, the compressive strain exerted by the LaAlO$_3$ substrate can stabilize the respective distortion. Similarly to KCuF$_3$, this physics is not captured by DFT, and conventional functionals favor such a bond disproportionation [21]. Hence, structural optimizations of nickelate superlattices performed using a conventional DFT functional can possibly lead to spurious results, and correlations have to be accounted for in the course of a structural optimization. The optimal solution would be a self-consistent DFT+DMFT scheme with an atomic force calculation at every step, but such calculations require enormous computational efforts and remain unfeasible for multisite and multi-orbital systems such as nickelate heterostructures. Therefore, in this work, we restrict ourselves to DFT+$U$ structural optimizations that generally capture the structural details in the rare earth nickelates [34].

We employ the generalized gradient approximation (GGA) +$U$ functional with $U$ in the range 4.0 to 6.0 eV and $J = 1.0$ eV as implemented in vasp-5.3 [35]. Ionic relaxations are performed until all forces are below 0.005 eV/Å. The in-plane unit cell parameters are fixed to that of bulk LAO. To optimize the $c$ parameter, we construct cells with different $c$ and subsequently optimize the atomic coordinates. In this way, we find that $c = 13.30$ Å yields the lowest total energy independent of the $U$ value. Next, we consider two trial structures as a starting point — a uniform structure and a structure with a breathing distortion (BD), see Fig. 1 b,c — and relax the atomic coordinates by keeping the unit cell parameters fixed. Despite the general trend that the uniform structure has a lower energy for smaller $U_d$, the energy differences are of the order of several K per cell, i.e. on a par with the accuracy of DFT total energies. We conclude that the elastic energy due to BD and the concomitant change in the electric potential are well-balanced, so that DFT+$U$ calculations cannot provide an unambiguous answer, which of the two structure types is realized in 2LNO/4LAO. We therefore perform DFT+DMFT calculations for both, the uniform as well as the BD structure.
B. DFT+DMFT

Subsequently, self-consistent DFT calculations for the optimized structures were performed using WIEN2K [36], the maximally localized Wannier functions (WF) were evaluated using WANNIER90 [37] via the WIEN2WANNIER interface [38]. The non-interacting Hamiltonian $H(k)$ for DMFT was obtained by Fourier transforming the Wannier functions on a $48 \times 48 \times 1$ $k$-mesh with two Ni sites in the cell, see Fig. 1 (a,d). DMFT calculations were performed using the continuous-time quantum Monte Carlo in the hybridization expansion (CT-HYB) as implemented in W2DYNAMICS [39, 40]. We used the rotationally invariant Kanamori interaction $U' = U - 2J$, which accounts for the spin flip and pair hopping terms. By fixing the Hund’s exchange $J$ to 0.75 eV [41], we varied the inter-orbital Coulomb repulsion $U'$ from 2 to 5 eV [42] and scanned the temperature range between 115 and 580 K (100 $\geq \beta \geq 20$ eV$^{-1}$). The quasiparticle renormalization is estimated from the slope of the imaginary part of the self-energy $\text{Im} \Sigma(\omega_n)$ which depends on $\omega_n$ linearly at low Matsubara frequencies:

$$Z \simeq \left(1 - \frac{\partial \text{Im} \Sigma(\omega_n)}{\partial \omega_n}\right)^{-1}. \quad (1)$$

For each DMFT calculation, we considered only those $\text{Im} \Sigma(\omega_n)$ that still lie on a straight line according to a $\chi^2$ fit.

C. Spectral functions

For selected values of $\beta$ and $U$, we present spectral functions. For these we used self-energies $\Sigma(\omega)$ computed with the worm algorithm [43], and analytically continued to the real axis using MAXENT [44] which employs the maximum entropy method [45]. The resulting self-energies $\Sigma(\omega)$ are used to calculate the interacting Green’s function on the real frequency axis:

$$G^{-1}(\vec{k}, \omega) = (\omega + i\delta + \mu) I - H(\vec{k}) - \Sigma(\omega) - \Sigma_{dc}, \quad (2)$$

where matrices in terms of orbitals and sites of the cell are denoted bold, $\Sigma_{dc}$ is the double-counting correction in the fully localized limit [46] and $I$ the identity matrix. The $\vec{k}$-resolved spectral function can be obtained as

$$A(\vec{k}, \omega) = -\frac{1}{\pi} \left( \frac{1}{m} \right) \text{Tr} \left( \text{Im} G(\vec{k}, \omega) \right), \quad (3)$$

where $m$ is the dimension of the $H(\vec{k})$ matrix. These spectral functions are based on $H(\vec{k})$ with the periodic boundary conditions along both in-plane directions, i.e. the Hamiltonian is defined on a torus. To address the edge states, we resort to mixed boundary conditions of a cylinder, which is periodic along $x$ and open along $y$ [47]. The respective Hamiltonian $H(k_x)$ is now a $n_y m \times n_y m$ matrix, where $n_y$ is the number of unit cells along the open direction, and the Green’s function is

$$G^{-1}(k_x, \omega) = (\omega + i\delta + \mu) \mathbf{I} - H(k_x) - \Sigma(\omega) + \Sigma_{dc}. \quad (4)$$

The respective spectral function is

$$A(k_x, \omega) = -\frac{1}{\pi} \left( \frac{1}{n_y m} \right) \text{Tr} \left\{ \text{Im} \left[ G(k_x, \omega) \right] \right\}. \quad (5)$$

Since we are primarily interested in the edge states, we also explicitly calculate their contribution to the spectral weight as:

$$A_{\text{edge}}(k_x, \omega) = -\frac{1}{\pi} \left( \frac{1}{2m} \right) \text{Tr} \left\{ \text{Im} \left[ G_{TT}(k_x, \omega) + G_{BB}(k_x, \omega) \right] \right\}, \quad (6)$$

where $G_{TT}$ ($G_{BB}$) denotes the Green’s function projected onto the top (bottom) cell.

D. Choice of the model

Before turning to the DMFT results, we address a controversially discussed issue of the minimal model for nickelates. The hybridization of $Ni$ $e_g$ states and the $\sigma$-bonded $O$ $p$ states gives rise to molecular-like $dp_\sigma$ orbitals. In a unit cell of $n$ Ni atoms, the antibonding states form an isolated $\frac{7}{2}$-filled manifold of $2n$ bands at the Fermi energy. For low-energy excitations, it is seemingly natural to restrict the analysis to these states and use the respective antibonding $dp_\sigma$ orbitals as a basis in real space. This minimal two-orbital model, known as the $d$-only model, has been employed in early DMFT studies [20, 48].

On the other hand, the high oxidation state of $Ni^{3+}$ can possibly lead to a very small, possibly even negative charge transfer gap. In this case, the low-energy physics will be largely affected by charge transfer processes between $d$ and $p$ states. Indeed, DMFT calculations for such $d + p$ models yielded qualitatively different results [49], mainly because the $e_g^2$ oxygen ligand hole (L) configuration resulting from the negative charge transfer forms a spin $S = 1$ on the Ni sites [50]. It has been further suggested that every second Ni site forms a spin singlet with two ligand holes [51–53], leaving only localized $S = 1$ states on the other half of the Ni sites. One should carefully note however that whether one has a negative charge transfer ($d^8$) or not ($d^7$) very sensitively depends on the relative position of oxygen and Ni $e_g$ states. In DFT, the oxygen bands are too close to the Fermi level, which would favor the negative charge transfer $d^8L$ picture. On top of this, the DFT+DMFT double counting and possible inclusion of the $d$-$p$ interaction make a theoretical prediction unreliable. Hence, in our view, this
question has to be answered by experiment eventually. In this respect, there are indications of a $d^6L$ configuration from x-ray absorption spectroscopy for smaller rare earth cations such as NdNiO$_3$ [54], but not for bulk LaNiO$_3$: very recent single-crystal experiments [55] yield the ordered magnetic moment of $\sim 0.3 \mu_B$, which is far too low for $S = 1$.

In fact a BD scenario can be realized also in a $d$-only model as has been acknowledged long ago [56]. Recent DFT+DMFT calculations by Subedi et al. showed that the BD phase sets in if $(U_d - 3J_d)$ is smaller than the difference between the on-site energies of the $e_g$ orbitals [57], which in our case is zero (degenerate $e_g$ orbitals). This result demonstrates that the emergence of the BD phase, and hence, the nature of the metal-insulator transition in bulk nickelates are reproduced by a $d$-only model, albeit with a strongly reduced Coulomb interaction $U_d$.

In view of this and the unclear experimental situation, we restrict ourselves to the $d$-only model. It features a considerably smaller number of free (and prospectively very sensitive) parameters; and because the effective Coulomb repulsion in the $d$-model can be strongly reduced [57], we scan a broad range of $U_d$.

### III. DFT+DMFT RESULTS

#### A. Uniform structure

We start with the uniform structure, for which DFT+$U$ calculations yield a FM Dirac metal, nearly independent of the $U$ value. Our DMFT ($U'$,$T$) phase diagram (Fig. 2, left) reveals a much more involved picture, with four different phases: a ferromagnetic metal (FM) at low $U'$, a paramagnetic metal (PM), an antiferro-orbital insulator (AOI), and a paramagnetic insulator (PI). The long-range ferromagnetic ordering transition temperature $T_C$ depends on the onsite Coulomb repulsion: while $U' \leq 3$ eV yield a ferromagnetic state at room temperature, larger $U' \geq 3.5$ eV strongly disfavor spin polarization in the studied temperature range. In contrast, the metal-insulator transition (the thick line in Fig. 2) occurs at the critical $U'$ which is slightly smaller than 4 eV. The nearly vertical line separating PM and insulating phases indicates thermal fluctuations play a minor role in the metal-insulator transition. In the insulating part of the phase diagram, the high-temperature paramagnetic phase (PI) develops an orbital polarization upon cooling, with a gradual crossover to the AOI phase.

**a. FM phase** The existence of a FM phase is seemingly in agreement with the DFT+$U$ results that yield a Dirac metal state for the uniform structure. However, the spin-resolved spectral function $A(\vec{k}, \omega)$ (Fig. 3, top) reveals that our FM phase is not a Dirac metal: the band crossing at the K point lies $\sim 0.1$ eV above the Fermi level. Instead, the majority states at the Fermi surface form a loop around the K point (Fig. 4, middle).

**b. PM phase** Above $T_C$, the LNO bilayer is a paramagnetic metal, where both Ni sites, both orbitals and both spin channels are equally occupied with 0.25 electrons per site and orbital. Correlation effects manifest
emerging phases are analogous to those of the uniform structure. The four phase diagram for the BD structure (Fig. 2, right) is largely broadened by the enhanced \( \text{Im} \Sigma(0) \). As a result, the Fermi surface plot lacks any sharp features (Fig. 4, right).

c. PI and AOI phases Similar to the PM phase, both orbitals and both spin channels are equally populated also in the PI phase, but the spectral function has a gap which grows with \( U' \). There is an orbital disproportionation between the two \( e_g \) orbitals setting in at \( \sim 350 \) K, and already at room temperature, a sizable orbital polarization develops. The two neighboring NiO\(_6\) octahedra have different predominantly occupied orbitals, giving rise to an antiferro-orbital order (AOI). Interestingly, this spontaneous symmetry breaking occurs despite the degeneracy of the \( e_g \) orbitals, and hence is of a purely electronic origin. The spectral function (Fig. 3, bottom) shows a wide gap between two incoherent continua — the lower and the upper Hubbard bands.

The degree of the orbital polarization \( p \) in nickelates is typically defined [58, 59] as

\[
p = \frac{n_{3z^2-r^2} - n_{x^2-y^2}}{n_{3z^2-r^2} + n_{x^2-y^2}},
\]

where \( n_{3z^2-r^2} \) and \( n_{x^2-y^2} \) are orbital occupations (a summation over both spin channels is implied). The polarization \( p \) is shown in Fig. 5 (left) as a function of temperature for \( U' = 4 \) eV. A sharp increase of orbital polarization is seen below \( \sim 350 \) K, signaling the phase transition from the PI to the AOI phase.

B. Bond-disproportionated structure

For the BD structure, DFT+\( U \) calculations with \( U \) from a reasonable range yield a semiconductor with a gap of about 0.05 eV [22], in contrast to the Dirac metal state of the uniform structure. Surprisingly, our DFT+DMFT phase diagram for the BD structure (Fig. 2, right) is very similar to that of the uniform structure. The four emerging phases are analogous to those of the uniform structure, expect for the slight charge disproportionation between the Ni sites that naturally occurs for a BD structure [49, 51]. Two noticeable differences are i) the shift of boundaries of both phase transitions (PM→PM and PM→PI/AOI) towards larger \( U' \) values and ii) the crossover between the AOI and PI phases showing an even weaker dependence on \( U' \) than in the uniform case. Please note that the charge disproportionation of the starting BD Hamiltonian is very small and hardly affected by the DMFT correlations. Instead, DMFT correlations support again the orbital polarization, see Fig. 5 (right), which is not present in the DFT-derived BD Wannier Hamiltonian.

IV. DISCUSSION

A. Topological properties

The honeycomb lattice has an excellent potential for the formation of topological edge states. The emergence of topological states in (111) bilayers of \( e_g \) electrons has been addressed on the model level [14, 18] and in the context of nickelate heterostructures [17, 19, 21]. Hartree-Fock calculations [17–19] yield a rich phase diagram with orbitally ordered and topologically nontrivial phases, but direct DFT+\( U \) calculations favor a conventional ferromagnetic phase [19]. Lattice distortions, and in particular, the breathing distortion can drive the system away from a topological phase [21], as confirmed by direct DFT+\( U \) calculations for LNO bilayers [22]. But in the absence of lattice distortions, DFT+\( U \) yields a Dirac metal state.

In all the above studies, electronic correlations were either neglected or taken into account at the Hartree-Fock level. DMFT accounts for all local Feynman diagrams, and in this way represents a systematic and substantial improvement over the Hartree-Fock method. On the DMFT level, the electronic correlations are described by the frequency-dependent self-energy. In general, the self-energy is a matrix with nonzero orbital offdiagonal elements. However, for LNO bilayers, the proximity of the Ni–O–Ni angles (165.81 and 165.58°) in the uniform and the BD structure, respectively to 180° leads to vanishingly small offdiagonal elements between \( 3z^2-r^2 \) and \( x^2-y^2 \).
As a result, we can safely neglect off-diagonal elements of the hybridization function $F(i\omega_n)$ in our impurity problems, leading to the self-energies $\Sigma(i\omega_n)$ that are diagonal in the site-orbital-spin basis.

The resulting DMFT self-energies are used to calculate the interacting Greens function using Eq. (4) and subsequently, the spectral functions using Eqs. (5) and (6). To this end, we use the DMFT self-energy of our bulk calculation for all sites and consider periodic boundary conditions along the $x$ axis and open boundary conditions for the $y$ axis, leading to the cylinder geometry. The spectral functions for the FM, PM, and AOI states are shown in Fig. 6. Only the FM state shows a distinct edge state, which however lies entirely in the unoccupied part of the spectrum, $\sim 0.1$–$0.2$ eV above the Fermi energy. This agrees with the position of the Dirac point in Fig. 3 (top). Both PM and AOI phases yield very incoherent features, without any distinct edge states. We therefore conclude that the emergence of topological states in (111) LNO bilayers is unlikely.

B. Comparison with experiments

Recent transport measurements on 2LNO/4LAO heterostructures yield a band gap of $120$ meV [24], which grows if the thickness of the LAO layer increases, which has been argued to stem from the accumulation of defects in thicker layers. Nevertheless, the insulating nature of the LNO bilayers can be regarded as a sound experimental result as it also concurs with the earlier report [23]. Thus, we infer that the inter-orbital repulsion $U'$ in LNO bilayers exceeds $4$ eV, as only such high values yield an insulating phase (Fig. 2). We cannot say, however, whether the breathing distortion occurs or not, as the respective part of the phase diagram is similar for both structures, and the DFT+$U$ energies are essentially degenerate.

Magnetic properties of LNO bilayers remain hitherto unexplored, but the recent study of NdNiO$_3$ bilayers on LAO, reporting antiferromagnetic correlations and orbital order [60], demonstrates that such an experimental insight is feasible. According to our DFT+DMFT results, the insulating phases, PI and AOI, do not show any magnetic order above $\sim 150$ K, and it would be interesting to verify this result experimentally. Conversely, the ferromagnetism is stable only in the metallic state.

According to our DFT+DMFT calculations, both the uniform and the BD structure show a very strong orbital polarization $p$ at room temperature and $U' > 4$ eV (Fig. 5). Nickelate heterostructures with a sizable orbital polarization do exist for the (001) case [61]. In contrast to the (001) case, the AOI state in (111) LNO bilayers is an insulating state, and a large orbital polarization is easier to achieve. In several cases, the Mott-Hubbard metal-insulator transition is indeed accompanied by an orbital polarization, e.g. in V$_2$O$_3$ [62] and SrVO$_3$ films [63].

V. SUMMARY AND OUTLOOK

Using DFT+DMFT calculations, we evaluated the phase diagram of a (111) oxide heterostructure formed by LaNiO$_3$ bilayers interleaved with four layers of LaAlO$_3$, in a wide range of temperatures and the values of the inter-orbital Coulomb repulsion $U'$. Independent of the presence or absence of breathing distortions that are typical for bulk nickelates, we find four phases: a ferromagnetic and a paramagnetic metal, a paramagnetic insulator, as well as an antiferro-orbitally-ordered insulator. Spectral functions calculated on cylinders feature edge states in the ferromagnetic metallic state, whereas both insulating phases are topologically trivial. Taking the experimentally observed activated behavior as an indication for a insulating state, we argue that LaNiO$_3$ bilayers can develop sizable orbital polarization at room temperature.

Compared to DFT+$U$, DFT+DMFT provides a more realistic treatment of electronic correlations and gives access to finite temperature properties. However, DMFT is by construction restricted to local correlations. For a
quasi-2D system with the low coordination number such as nickelate (111) bilayers, nonlocal correlation effect can play an important role. A natural extension of our study would be the application of cluster [64, 65] or diagrammatic [66] extensions of DMFT to the phase diagram of 2LNO/4LAO.

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