Ordering and multiple phase transitions in ultra-thin nickelate superlattices

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We interpret via advanced ab initio calculations the multiple phase transitions observed recently in ultra-thin \( \text{LaNiO}_3/\text{LaAlO}_3 \) superlattices. The ground state is insulating, charge-ordered, and antiferromagnetic due to concurrent structural distortion and weak valency disproportionation. We infer distinct transitions around 50 and 110 K, respectively, from antiferromagnetic order to moment disorder, and from structurally-dimerized insulator to an undistorted metallic Pauli paramagnet (exhibiting a cuprate-like Fermi surface). The results are in satisfactory agreement with experiment.

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Incipient or actual instabilities towards collective ordered states are typical of many correlated materials. Recent experiments \cite{1, 2} have investigated, via elegant nanostructuring manipulations of materials properties, the phase transitions playing out when \( \text{LaNiO}_3 \) (LNO henceforth – in the bulk the only metallic Pauli-paramagnetic (PM) rare-earth nickelate) is placed in an intentionally perturbed environment, namely epitaxially-strained ultra-thin superlattice (SL) of alternating layers of LNO and of the band insulator \( \text{LaAlO}_3 \) (LAO). For sufficiently thin LNO (2-3 layers at most), multiple transitions from a non-magnetic normal metal to a long-range-ordered magnetic, insulating, charge-ordered state were revealed by a crossover in conductivity temperature \((\text{T})\) dependence, muon spin rotation \((\mu\text{SR})\), spectral weight transfer in optical conductivity \cite{1}, and XAS (x-ray absorption spectroscopy) line splitting \cite{2}. Magnetometry and \(\mu\text{SR}\) strongly support long-range antiferromagnetic (AF) order \cite{1}.

The precise nature of the low-\(\text{T}\) state of the LNO/LAO SL and the transitions it undergoes is unclear. Here we address the problem from first principles studying a strained ultra-thin LNO/LAO SL using variational self-interaction-corrected local density functional theory (VPSIC) \cite{3} \cite{4}, a parameter-free method providing an improved description of correlated and magnetic materials compared to semi-local approaches. So far, ab initio calculations have neither been able to identify an AF ground state as observed for these SLs, nor, a fortiori, to provide a general picture of the rich experimental situation. Local (LDA) or gradient-corrected (GGA) density functionals find neither a stable AF phase nor distorted structures. LDA/GGA\(+U\) predicts ferromagnetic ground states not seen in experiment, apparently irrespective of \(U\) \cite{5}. The satisfactory agreement of VPSIC with experiment demonstrated below suggests an improved account for on-site correlations, also indicated by points of agreement with dynamical mean field theory (DMFT) \cite{6} \cite{7}, especially with the interpretation proposed in \cite{9} during the review of the present work.

The ground state, labeled AFD henceforth, is structurally dimerized, weakly charge-ordered, insulating, and AF with in-plane modulation similar to bulk rare-earth nickelates \cite{10}. From calculated energies, we infer magnetic-ordering and metal-insulator transitions at two distinct critical temperatures of around 50 K and 110-150 K respectively. The transitions are driven by cooperative structural distortion and partial valency disproportionation of Ni atoms at low T, inducing magnetic superexchange and Mott localization. In addition, we calculate the \(T\)-dependent SL conductivity within Bloch-Boltzmann theory \cite{11} and discuss a possible concurrent metal-insulator-transition mechanism. The results are consistent with the data of Ref.\cite{1}. We find that the high-\(T\) metallic Pauli-PM phase has a Fermi surface geometrically (though not orbitally) akin to optimally-doped cuprates, as suggested earlier \cite{2} \cite{12}.

**Method** – Total energy, force, and bands calculations are performed by VPSIC \cite{3} using the plane-wave ultrasoft pseudopotential method (energy cutoff 30 Ryd, \(4 \times 4 \times 4\) \text{k-mesh}, Gaussian smearing of 20 mRyd for the metal phases) in an 80-atom \(2\sqrt{2}\times2\sqrt{2}\times2\) perovskite supercell (40-atom \(2\sqrt{2}\times2\sqrt{2}\times4\) only for the calculation of vertical magnetic coupling). The \(\text{LNO}/\text{LAO} (1+1)\) SL is simulated at the in-plane lattice constant 4.02 Å, corresponding to a tensile planar strain of about 4% relative to the LNO bulk lattice constant. The LNO layer contains four Ni atoms to simulate AF structures. We optimize the cell length, and atomic positions via quantum forces \cite{3}. The \textit{dc} conductivity is calculated in Bloch-Boltzmann theory \cite{11} with a relaxation time approximation using ab initio band energies on dense \text{k} grids (over 2000 points).

**Structure and charge ordering** – In the AFD ground state the nominally trivalent \(\text{Ni}^{III}\) atoms of LNO are actually inequivalent in pairs due to a strong cooperative “checkerboard” dimerization of the Ni-centered octahedra (Fig.\cite{1}). Ni-O bonds alternatively expand and contract from 2 Å to 2.19 Å or respectively 1.83 Å in a predominantly breathing mode. Calculated octahedra rotations are minor (~1-2°). The short and long bonds match those, respectively, in peroxonickel complexes with non-
inally tetravalent Ni_{IV} and NiO with nominally divalent Ni_{II}. Although the charge transfer is small, we adopt this labeling convention for clarity. The distortion is indeed accompanied by charge transfer from Ni_{IV} to Ni_{II}, which we quantify by VPSIC occupations [3]. The total transfer is 0.07 |e|, in fair agreement with 0.03 |e| estimated in [1]. This charge-ordered bond-dimerized phase is quite compatible with the splitting in the SL XAS spectra, analogous to insulating nickelates [2], although we cannot provide a quantitative estimate of that splitting from our calculation. The magnetic order and insulating character of this state tend to confirm this conclusion, as discussed below.

**FIG. 1.** (Color on line) Magnetic pattern of the LNO layer of LNO/LAO (1+1). Expanded and contracted octahedra around Ni_{II} and Ni_{IV}, respectively, are red (filled) and blue (shaded). Oxygens (not shown) sit at the shared vertexes of the octahedra. Dashed: supercell lattice vectors. Drawing is approximately to scale.

**Magnetism** – The structural and valency dimerization are associated with the magnetic pattern in Fig.1. Our single-LNO-layer cell has no vertical modulation by construction; the planar modulation q=(0,1/2) in the reciprocal basis of the supercell (Fig.1) is the same as in bulk monoxides [3], and it is analogous to insulating nickelates. The main difference is that Ni_{IV} is entirely non-magnetic here, while the homologous “Ni(3–δ)” are still polarized in e.g. NdNiO_{3} [10]. Indeed, Ni_{II}’s [circles in the Figure] carry a moment μ_{Ni_{II}}=±1.44 μ_{B}, while Ni_{IV}’s [crosses in the Figure] have zero moment, confirming a qualitative picture of Ni_{II} disproportionation into unpolarized Ni_{IV} \( \mu^0_{2g} \) and polarized Ni_{IV} \( \mu^0_{2g} \). Overall, our charge-spin order pattern matches closely the mechanism sketched in Fig.1b of Ref.[13], on-site exchange and structural energy gains overrule the effective on-site repulsion, quite screened due to the \( e_g \) states delocalization (which is, in turn, coherent with LNO being paramagnetic, and with a weakened Jahn-Teller effect). Our result clearly agrees with the AF long-range order suggested by magnetometry and μSR.

The AFD phase is governed by the in-plane couplings \( J_L \) and \( J_S \) (Fig.1), and vertical coupling \( J_{\perp} \) across the LAO layer. An AF \( J_L \) is expected due to superexchange between partially-filled \( e_g \) states. \( J_S \) would be AF for purely \( x^2–y^2 \) hopping, but as \( e_g \) states are mixed \( J_S \) may well be FM and small. Using the energies of the AFD, FM, and AF-G phases in the expressions

\[
E_D - E_F = (16J_L + 8J_S) \mu_{Ni_{II}}^2, \quad E_G - E_F = 16J_{\perp} \mu_{Ni_{II}}^2,
\]

we extract \( J_S=-4.1 \) meV and a small FM \( J_S=0.9 \) meV. The energy difference \( E_{AF} - E_{FM} = 8J_{\perp} \mu_{Ni_{II}}^2 \) of the AF-A (LAO-separated AF-stacked FM LNO planes) and double-FM (the same stacked FM) phases yields a tiny \( J_{\perp} \approx -0.05 \) meV, as expected due to suppressed hopping through LAO’s Al \( p \) states very far from the Fermi energy. The large coupling anisotropy \( \alpha=J_L/J_{\perp} \approx 100 \) and the fact that \( J_S \) does not contribute to the magnetic energy of the AFD phase (see Fig.1) suggest using the Neel temperature \( T_N=4\pi J_L S^2/\alpha \) of the 3D anisotropic AF Heisenberg model [14] as estimate of the critical temperature: we find \( T_N \approx 50 \) K, in good agreement with 40 K experimentally. (As \( \alpha \) only affects \( T_N \) logarithmically, its exact value is not essential as long as it is large.) This interpretation of the magnetic transition as spin order–disorder implicitly assumes that disordered spins fluctuate rapidly enough (say, frequency \( \geq 1 \) MHz) above \( T_N \) so as not to be revealed by μSR.

We note in passing that FM and AF-G are also insulating and have structure, charge, and magnetic pattern largely similar to AFD; the main difference is that in the FM, \( \mu_{Ni_{IV}}=0.07 \mu_{B}, \) which we can neglect compared to \( \mu_{Ni_{II}} \) for our present estimate.

**FIG. 2.** (Color on line) Right panel: Total density of states of the AFD (orange, shaded) and Pauli-PM (solid line) states (zero is the Fermi energy). Left panel: Fermi surface of the Pauli-PM phase in the 1×1 Brillouin zone.

**Electronic structure and metal-insulator transition** – We now address electronic properties and discuss me-
mechanisms of metal-insulator transition. Fig 2 reports the total density of states (DOS), of AFD and Pauli-PM, right panel, and the Fermi surface of the latter (see below), left panel. The concurrent structural dimerization and magnetic superstructure open a 1.3-eV indirect electronic gap. The key point is that the octahedra distortion is essential to obtain a gap: all undistorted phases are metallic and show no charge transfer. Further, only the Pauli-PM metal is stable among these, while the AF or FM states dimerize spontaneously. This suggests that the transition be associated to the structural dimerization, and that the transition temperature $T_{MI}$ be identified as that at which the structure un-dimerizes thermally, with attendant gap closure. Using a stripped-down version of Vineyard’s transition-state theory, we describe the initially full population $N_0 \equiv N(t=0)$ of distorted structural units (contracted and expanded Ni-octahedron pairs) as undergoing thermal activation out of the low-T ground state. The population $N(t)=N_0 \exp (-Rt)$ is abruptly depleted, i.e. the system removes the distortion and hence the insulating character, for a sufficient Arrhenius activation rate $R=\nu_0 \exp (-\Delta E/k_B T)$. Since the Pauli-PM is the only stable undimerized state, we envisage an AFD-PM transition, and therefore use the AFD-PM energy difference $\Delta E=0.40$ eV per Ni pair. With a plausible effective vibrational prefactor $\nu_0=5$ THz [15], an activation rate $R$ between $10^{-6}$ and 1 Hz (i.e., lifetimes between 280 hrs and 1 sec) corresponds to

$$T_{MI} = -\Delta E/[k_B (\ln R - \ln \nu_0)] = 110 \pm 150 \text{ K}$$

in good agreement with 110 K experimentally [1]. In closing this section we note that the Ni_{IV}-Ni_{II} charge transfer is associated in optical experiments to a spectral weight depletion below 0.4 eV, identified as a “charge gap” [1]: our best shot at it is the (indeed somewhat larger) electronic gap, originating from the combined structure, charge and magnetic ordering.

We note that in the AFD state the valence top states mostly project on polarized Ni_{III}, while conduction states do so on unpolarized Ni_{IV}. This “site-discriminated” gap opening is quite consistent with the “site selective Mott transition” proposed by DMFT calculations [9], further suggesting that our method can produce, in specific instances, predictions matching those of sophisticated many-body methods.

Fermi surface – Confirming earlier theoretical suggestions [7, 12], the Pauli-PM phase has a single-sheet hole-like Fermi surface (Fig 2, left panel) centered at the 1x1 Brillouin zone corner and analogous to optimally-doped cuprates. The states character is, however, mixed $e_g$ rather than pure $x^2-y^2$, as also found by recent dynamical mean field calculations [13]. The nearly two-dimensional pockets in Fig. 2 should give rise to quantum oscillation as function of inverse magnetic field, with potentially observable frequencies of about 20 kTesla (compare the 30 kTesla in e.g. metallic In [17]).

Transport – Since we cannot calculate the T dependence of dielectric response measured in [1], we use Bloch-Boltzmann theory to calculate the dc conductivity, with the goal of associating the transition T with the zero of $d\sigma/dT$ as suggested in [1]. We tuned the energy dependence of the relaxation-time model [11] to reproduce the T-dependence (not the value) of $\sigma$ in the metal phase using the Pauli-PM bands. The model was then fed the AFD ground-state bands to obtain its conductivity vs T.

![Fig. 3. Calculated conductivity vs. T for the metallic PM phase (dashed) and n-doped AFD phase (dash-dot); solid line: linear interpolation of the metal and insulator curves. The value of $\mu$ is fixed at the vertical dashed line in Fig 4.](image-url)

We conjecture that the un-dimerization metal-insulator transition will cause the conductivity to cross over smoothly from the insulator to the metal. This can only be assessed qualitatively in the present context. First, our method cannot describe the “dirty” metal phase, which exhibits an unusually low experimental conductivity; to account for this, we rescale the calculated metal $\sigma$ by a factor 1/15, the ratio of the relaxation time [11] for the SL metal phase to that of a normal metal (Al). Second, the insulating phase’s experimental conductivity is much higher than that of our undoped insulator at the relevant temperatures. We assume that this is due to a background impurity of unidentified origin, and thus calculate $\sigma$ in the insulating phase for the chemical potential $\mu$ set to n-type. In Fig 3 we interpolate linearly the two $\sigma$’s just discussed (dashed and dash-dotted lines) vs T, obtaining a result (solid line) qualitatively similar to experiment [11], Fig. S8B of supporting material) and with $d\sigma/dT=0$ around 150 K, fairly consistent with undimerization. We note in passing that log $\sigma$ in the insulator phase is linear in 1/T as in [11]. Hopping behavior [2] may be due to local disorder [18], which we cannot assess.

Conductivity calculations as a function of $\mu$, and specifically in n-type conditions, suggest a further possible, concurrent transition mechanism. $\sigma(\mu,T)$ in Fig 4 exhibits three distinct transition mechanism. $\sigma(\mu,T)$ in Fig 4 exhibits three distinct transition mechanism. $\sigma(\mu,T)$ in Fig 4 exhibits three distinct transition mechanism. $\sigma(\mu,T)$ in Fig 4 exhibits three distinct transition mechanism.
high $T$ for fixed $\mu$; then, for $\mu$ just below the conduction edge, $\sigma$ is insulator-like at low $T$, and crosses over at higher $T$ to a normal-metal-like linear decrease; finally, at larger $\mu$, $\sigma$ decreases with $T$ (and grows with $\mu$) linearly as in a normal metal. This behavior is related to the slope change of the AFD near-conduction DOS (inset of Fig.4), with the crossover to metallic conduction occurring for $\mu$ above the DOS cusp (vertical solid line). The insulator $\sigma(T)$ in Fig.3 is obtained for $\mu$ just below the conduction edge (dashed vertical line in Fig.4), and has $d\sigma/dT=0$ at about 250 K. This calculation thus shows that an insulator-metal crossover can also be legitimately associated to a conduction-band-edge Fermi level pinning (e.g. by shallow-donor defects). Clearly, this mechanism would be preempted by, or at most concurrent with, the un-dimerization transition discussed earlier, which is robustly rooted in the structural and magnetic energetics.

Summary – LNO/LAO ultra-short-period SLs have a magnetic charge-ordered insulator ground state, making magnetic and metal-insulator transitions at temperatures we estimate in 50-70 K and 110-150 K respectively to a metal phase with a cuprate-like Fermi level surface. This interpretation is in good agreement with available experimental data. While resulting from several cooperative effects, this state is basically produced by an instability of a "checkerboard" breathing mode (induced in turn, from a chemical viewpoint, by a valency instability). This is indirectly supported by recent experimental evidence of the inverse effect, i.e. the destabilization and metallization of insulating NdNiO$_3$ via phonon injection from the LAO substrate [19].

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FIG. 4. (Color on line) Conductivity vs. chemical potential and $T$ from 10 K, thickest blue (black) line to 290 K, thickest red (gray) line (20-K steps). Inset: DOS near conduction edge. Dashed (solid) vertical line marks intermediate regime (metallic crossover). Chemical potential zero at midgap.
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