Orbital order and possible superconductivity in LaNiO$_3$/LaMO$_3$ superlattices

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A hypothetical layered oxide La$_2$NiMO$_6$ where NiO$_2$ and MO$_2$ planes alternate along the c-axis of ABO$_3$ perovskite ladder is considered theoretically. Here, M denotes a trivalent cation Al, Ga... such that MO$_2$ planes are insulating and suppress the c-axis charge transfer. We predict that correlated $e_g$ electrons in the NiO$_2$ planes develop a planar $x^2 - y^2$ orbital order driven by the reduced dimensionality and further supported by epitaxial strain from the substrate. Low energy electronic states can be mapped to a single-band $t-t' - J$ model, suggesting favorable conditions for high-$T_c$ superconductivity.

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Despite decades of extensive research, cuprates remain the only compounds to date hosting the high-temperature superconductivity (SC). On empirical grounds, the key electronic and structural elements that support high $T_c$ values are well known – no orbital degeneracy, spin one-half, quasi two-dimensionality (2D), strong antiferromagnetic (AF) correlations. While these properties are partially realized in various materials (e.g., layered cobaltates), only cuprates do possess all of them.

A unique feature of the high-$T_c$ cuprates is the presence of an extended doping interval 0.05 ≲ $\delta$ ≲ 0.20 where the correlated electron maintains its (plane-wave/localized-particle) duality, and both fermionic and spin statistics may operate in physically relevant energy scales. Multifaceted behavior of electrons results in an exotic “normal” state of the cuprates with ill-defined quasiparticles, pseudogap etc, which condenses into the superconducting state below $T_c$. There are a number of strongly correlated metallic oxides $^1$ based on $S = 1/2$ 3d-ions as Ti$^{3+}$ and V$^{4+}$ (both with a single $t_{2g}$ electron), Co$^{4+}$ (a $t_{2g}$ hole) and Ni$^{3+}$ (closed $t_{2g}$ shell plus one $e_g$ electron) that possess a low-spin state in octahedral environment. These compounds show a great diversity of physical properties $^1$; however, the mysterious strange-metal phase from which anomalous SC may emerge is missing.

Apart from dimensionality, the orbital degeneracy is “to blame” here. Originating from high symmetry of the MeO$_6$ octahedron – a common building block of both pseudocubic and layered perovskites, – the orbital degeneracy enlarges the Hilbert space and relaxes kinematical constraints on the electron motion. Consequently, a fermionic coherence is enhanced and doping induced insulator-metal transitions occur without a reference to the pseudogap phase. E.g., in La$_{1-x}$Sr$_x$TiO$_3$ the formation of a three-band, correlated Fermi-liquid completes within just a few percent doping range near $x \sim 0.05$ $^2$.

The orbital degeneracy strongly reduces AF correlations (believed to be crucial in cuprate physics), as electrons are allowed to have parallel spins residing on the different orbitals. This leads to competing Ferro- and AF-interactions that result in a rich variety of magnetic states in $S = 1/2$ oxides RTIO$_3$, Na$_x$CoO$_2$, Sr$_2$CoO$_4$, RNiO$_3$, NaNiO$_2$, etc. In contrast, spin correlations in single-band cuprates are of AF nature exclusively and hence strong.

How to suppress the orbital degeneracy and promote cuprate-like physics in other $S = 1/2$ oxides? In this Letter, we suggest and argue theoretically that this goal can be achieved in oxide superlattices. Specifically, we focus on Ni-based superlattices (see Fig. 1) which can be fabricated using recent advances in oxide heterostructure technology ($^3$ and references therein). While the proposed compound has a pseudocubic ABO$_3$ structure, its low-energy electronic states are confined to the NiO$_2$ planes hence are of quasi-2D nature. A substrate induced compression of the NiO$_6$ octahedra further stabilizes the $x^2 - y^2$ orbital. Net effect is a strong enhancement of AF correlations among spin one-half electrons residing predominantly on a single band of $x^2 - y^2$ symmetry. Thus, all the “high-$T_c$ conditions” are perfectly met. Moreover, the presence of a virtual $3z^2 - r^2$ orbital deforms the band dispersion compared to cuprates, leading to an enhanced next-neighbor hopping $t'$ which is known to support higher $T_c$ values $^6$.

The proposed superlattices can be viewed as a layer-by-layer “mixture” of a correlated $e_g$-band metal LaNiO$_3$ and a band insulator LaMO$_3$. The MO$_2$ planes with a trivalent M=Al or Ga serve here as block layers suppressing the c-axis hopping. The lattice parameters of LaAlO$_3$ ($\sim 3.79\text{Å}$) and LaGaO$_3$ ($\sim 3.89\text{Å}$) are close to that of LaNiO$_3$ ($\sim 3.83\text{Å}$); further, NiO$_2$ and MO$_2$ planes have the same nominal charges. These factors should result in a minimal only structural and electronic mismatch, suggesting a stability of La$_2$NiMO$_6$ compounds. Yet another intriguing option is the case of M=Ti (the lattice parameter of LaTiO$_3$ $\sim 3.96\text{Å}$), where TiO$_2$ planes would themselves have a spin one-half residing on the $t_{2g}$ orbital. As the $t_{2g}$ shell of Ni$^{3+}$ is full while $e_g$ level of Ti$^{3+}$ is located well above the Fermi energy (roughly at $10Dq \sim 2\text{ eV}$), the c-axis hoppings will be strongly sup-
pressed again; therefore, NiO$_2$ and TiO$_2$ planes both develop quasi-2D electronic states of $e_g$ and $t_{2g}$ symmetry, respectively. While these states are not mixed by symmetry, the exchange of AF spin fluctuations will lead to a sizable interplane coupling, having interesting implications for magnetism and possible SC in La$_2$NiTiO$_6$.

The $c$-axis compression of the NiO$_6$ octahedra favoring $x^2-y^2$ orbital can be imposed by epitaxial strain from the substrate with a lattice parameter larger than that of LaNiO$_3$, e.g., on LaGaO$_3$ or SrTiO$_3$ ($\approx 3.90\AA$). The orbital selection by tuning epitaxial strain has been demonstrated in Ref. [3]; it is based on strong Jahn-Teller response of the $e_g$ orbital on volume conserving distortions of the oxygen octahedron [3]. In superlattices of alternating NiO$_2$ and GaO$_2$ planes (Fig. 1), strain effect should be more efficient as the lattice constants of LaGaO$_3$ and SrTiO$_3$ nearly match. Hence, lattice relaxation is reduced and thicker superlattices La$_2$NiGaO$_6$ can be grown. Further, using the LaGaO$_3$ substrate (instead of SrTiO$_3$) may help to disentangle the intrinsic physics within the bulk of La$_2$NiMO$_6$ superlattice from the charge-transfer effects at the interface between La$_2$NiMO$_6$ and the SrTiO$_3$ substrate, induced by different valences of Sr and La [6, 8].

Now, we turn to the theoretical examination of our proposal. The formal valence state in undoped case is Ni$^{3+}$ in a low-spin configuration $t_{2g}^6e_g^1$, and its 4-fold degeneracy is specified by spin $S=1/2$ and orbital pseudospin $\tau=0, 1$. Because of strong pd-covalency, wave functions are composed of the Ni $e_g$ states and a proper combination of the oxygen $p$ holes of the same $e_g$ symmetry. In other words, the Ni$^{3+}$ is shorthand notation for the (NiO$_6/2$)$^{3−}$ complex with the same spin doublet orbital doublet − quantum numbers. Nearest-neighbor (NN) hopping matrix within the NiO$_2$ plane, as dictated by symmetry, is:

$$t_{\alpha\beta} = t_0 \left( \frac{3}{\sqrt{3}} \mp \sqrt{3} \right), \quad \alpha, \beta \in \{x, z\}.$$  (1)

Here, $\{x \equiv x^2-y^2, z \equiv 3z^2-r^2\}$ basis is used, $\mp$ sign is valid for the $a$ and $b$ bond respectively. We assume small $c$-axis hopping $\eta t_0 \ll t_0$ through the block MO$_2$ layers.

The tensile strain effect is modeled by orbital splitting $\Delta = \epsilon_c - \epsilon_e$. The (volume conserving) strain from SrTiO$_3$ substrate may provide $\approx 5\%$ difference between the long/short axes of NiO$_6$ octahedron, nearly half of that in LaNiO$_3$ where this leads $0.5 - 1.0$ eV orbital splitting. Thus, $\Delta \sim 0.2 - 0.4$ eV might be realistic.

The 3D nickelate LaNiO$_3$ is a correlated two-band metal. Nickelates of a smaller-radii rare-earth ions, where the bandwidth is reduced due to a stronger GdFeO$_3$-type distortion, undergo the insulating state at low temperature [312] and show a peculiar AF order [13]. Whether the 2D NiO$_2$ planes of La$_2$NiMO$_6$ are insulating or not has to be decided by experiment. Physically, the reduction of $c$-axis hopping and crystal-field splitting both should support the insulating state via the orbital disproportionation phenomenon in correlated systems [14]. In other words, correlations are effectively enhanced when the orbital degeneracy is lifted [13]. Based on these arguments, we consider below the insulating ground state.

We derived the superexchange Hamiltonian, including both intersite ($dd$) Ni$^{3+}$–Ni$^{3+}$ → Ni$^{4+}$–Ni$^{2+}$ and charge-transfer (CT) Ni$^{3+}$–O$^{2−}$–Ni$^{3+}$ → Ni$^{2+}$–O–Ni$^{2+}$ processes, along the lines of Ref. [17]. The result for a bond $ij \parallel \gamma$ in the NiO$_2$ plane can be written as

$$H_{ij}^{(\gamma)} = J_0 (K^{dd}_{\sigma,\sigma,\pm,\pm} + K^{CT}_{\sigma,\sigma,\pm,\pm} (1) \left( \frac{1}{2} \pm t_i^{(\gamma)} (\frac{1}{2} \pm t_j^{(\gamma)} (1) \right) \right) \hat{P}_{ij}^{(\gamma)}$$  (2)

with an implied sum over $\sigma = 0, 1$ and all combinations of $\pm, \pm$. Here, $J_0 = 4t_0^2/U$, and $U$ stands for the Coulomb repulsion on the same orbital. In the $c$-axis, CT part of (2) drops out and the rest is multiplied by small $\eta^2$. We have used projectors to a singlet and triplet state of two Ni$^{3+}$ $S = 1/2$ spins: $P_{iji} = \frac{1}{2} - S_i S_j$, and $P_{iji} = \frac{3}{4} + S_i S_j$ respectively, and orbital projectors $\frac{1}{\gamma} ± t_i^{(\gamma)}$ and $\frac{1}{\gamma} ± t_j^{(\gamma)}$ selecting the planar orbital in the plane perpendicular to the $\gamma$-axis and the directional orbital along this axis, e.g. $x^2-y^2$ and $3z^2-r^2$ orbitals, respectively, when $\gamma = c$. While the form (2) is determined by symmetry, the coefficients $K^{dd,CT}_{\gamma}$ are sensitive to the multiplet structure of excited states, as usual. Namely, they depend on two parameters $J_y/U$ and $2U/(2\Delta pd + U_p)$ characterizing the strength of the Hund coupling and the strength of CT processes [16,17], respectively (explicit expressions will be given elsewhere [18]). In the following, we study the mean-field phase diagram depending on these two parameters.
FIG. 2: Phase diagram of the spin-orbital Hamiltonian \( \rho \). The c-axis hopping is 0.3\( t_0 \). The labels AAA etc indicate the magnetic order, with F (A) denoting parallel (antiparallel) orientations of the NN spins in the a, b and c directions, respectively. Representative orbital states are sketched. In the pure planar-orbital phase (left-bottom), a weak A-coupling between the layers is due to the higher order hoppings. Upper right panel: the phase diagram for \( \Delta = \epsilon_a - \epsilon_x = 0.5t_0 \), the gray area indicates the planar-orbital/spin-AAA phase. Lower right panel: the phase diagram at 5% hole doping (\( \Delta = 0, J = 0.3t_0 \)) shows that charge carriers strongly favor the planar orbital phase.

The orbital state \( |3z^2 - r^2\rangle \cos \frac{1}{3} \theta_i + |x^2 - y^2\rangle \sin \frac{1}{3} \theta_i \) is specified by the site-dependent orbital angle \( \theta_i \). We assume two sublattices with \( \theta_A \) and \( \theta_B \) in each NiO\(_2\) plane and different spin arrangements and minimize superexchange (H) in this state. The result is the phase diagram in Fig. 2. The antiferromagnetic phase in the lower left part consists of pure \( x^2 - y^2 \) planar orbitals (as in cuprates). At higher strength of CT processes, this phase changes to the mixed orbital phases AAF, AAA, and AFA (\( \theta_A = \theta_B \) evolve gradually from 0 to \( \pi/2 \)) with strongly anisotropic spin couplings. Upper in-plane ferromagnetic phases have staggered orbital order \( \theta_A = 2\pi - \theta_B \approx \pi/2 \).

Effect of the strain-induced field \( \Delta \) on phase diagram is dramatic. Even a very modest splitting \( \Delta \) makes the planar orbital phase a dominant one (Fig. 2).

Next, we address the effect of mobile holes (introduced either by an oxygen-excess or by Sr doping). Evaluating (1) in our orbital state specified by \( \{\theta_i\} \), we arrive at the effective NN hopping \( \langle t_{\alpha\beta}\rangle \rangle = t_0 \left( 2 \cos \theta_\alpha - \cos \theta_\beta \mp \sqrt{3} \sin \theta_\alpha \right) / 4 \), where \( \theta_\pm = (\theta_i \pm \theta_j) / 2 \). (E.g., in the planar orbital phase with \( \theta = \pi \), one finds \( \langle t \rangle = 3t_0 / 4 \) as in cuprates.) For a simple estimate, we add kinetic energy \(-2|\langle t’\rangle| - 2|\langle t\rangle|\) per hole to the superexchange energy. The modified phase diagram in Fig. 2 shows that the planar-orbital phase gains the largest kinetic energy \[12\] and quickly spreads with \( \delta \).

The spin-exchange constant in the planar orbital phase takes the familiar form (at \( J_H / U = 0 \) \[16\]): \( J = (9t_0^2 / 4) [1 / U + 2 / (2\Delta_{pd} + U_H)] \). With \( t = 3t_0 / 4 \) (hopping between the planar orbitals), the prefactor reads \( 4t^2 \) as in cuprates. The value of \( J \) is not much sensitive to the strength of the Hund coupling, it is about 10% smaller at finite \( J_H / U = 0.15 \).

At larger doping, the kinetic energy dominates and the spin order is lost. We show in the following that the orbital degeneracy is lifted again and the planar orbital is selected by correlated motion of holes. To address this regime, we adopt the multiorbital Gutzwiller approximation as described, e.g., in Ref. [20]. The hopping matrix elements are renormalized \( t_{\alpha\beta} \rightarrow g_{\alpha\beta}t_{\alpha\beta} \) according to the orbital occupations via \( g_{\alpha\beta} = 25/\sqrt{(2 - n_\alpha)(2 - n_\beta)} \) (where \( \alpha, \beta \in \{x, y\} \) and orbital splitting is adjusted \( \Delta \rightarrow \Delta \) to minimize energy. The renormalized dispersion \( \varepsilon_k \) is then

\[
\frac{2\varepsilon_k}{t_0} = -\gamma_+ \pm \sqrt{\left(g_+ - \gamma_+ + \Delta / t_0\right)^2 + 12g_+^2 \gamma_-^2}
\]

(3)
apart from a \( k \)-independent constant. Here \( g_\pm = 3g_{xx} \pm g_{zz} \), and \( \gamma_\pm = 2/3 (\cos k_x \pm \cos k_y) \).

Fig. 3 shows bands \((\varepsilon_k - \mu) / t_0\) and density of states for different dopings at bare orbital splitting \( \Delta = 0.25t_0 \). Correlations separate the bands and suppress the orbital mixing, such that the lower band is dominated by \( x^2 - y^2 \) orbital and contains only a negligible \( 3z^2 - r^2 \) fraction. Correlation-induced increase in orbital splitting (see Fig. 4b) and a reduced mobility of the \( 3z^2 - r^2 \) orbital cooperate to lift the orbital degeneracy. The re-

FIG. 3: The band structure and density of states for the \( \epsilon_g \) orbital splitting \( \epsilon_x - \epsilon_z = 0.25t_0 \) at doping levels (a) 100% (bare bands), (b) 20%, and (c) 5%. The dotted curves show the density of states projected onto the \( 3z^2 - r^2 \) orbital. The gray areas indicate the occupied states at given \( \delta \).
main effect of the initially degenerate $3z^2 - r^2$ orbital is a deformation of the lower band of $x^2 - y^2$ symmetry, so that the van Hove singularity stays close to the Fermi level. The Fermi surface shape can exactly be reproduced as function of doping $\delta$ for different $\epsilon_z - \epsilon_\xi$. (c) The mean-field $T_c$ [22] at various levels of $\epsilon_y$ orbital splitting. The dashed-dotted line ($\epsilon_z - \epsilon_y = 5t_0$) corresponds to the “cuprate” situation with inactive $3z^2 - r^2$ state.

To conclude, we pointed out that the orbitally-nondegenerate spin one-half electronic structure – as in cuprates – is expected in the Ni-based superlattices. This suggests that artificially tailored superlattices may open new perspectives for the high-$T_c$ superconductivity. We hope that the theoretical expectations for our particular proposal – “the double perovskite” La$_2$NiMnO$_6$ – are encouraging enough to motivate experimental efforts.

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[23] At a first glance, La$_2$NiMnO$_6$ superlattice might seem as an analog of layered perovskite La$_2$–Sr$_{2}$NiO$_4$ at $x \approx 0$ compositions [R.J. Cava et al., Phys. Rev. B 43, 1229 (1991)], where an average valence state is Ni$^{3+}$. However, there are two crucial differences. First, LaSrNiO$_4$ is a solid solution of La and Sr where large local variations of the ratio La/Sr (forming perhaps some patterns) are possible. This should lead to mixed valence states Ni$^{2.5+,3+}$ and strong disorder effects. Second, there is no compression of NiO$_6$ octahedra in La$_2$–Sr$_{2}$NiO$_4$, which are rather elongated at small $x$ and become of a regular shape at $x \approx 1$. For these reasons, we expect that La$_2$NiMnO$_6$ superlattice and La$_2$–Sr$_{2}$NiO$_4$ solid solution should have different properties.