Stripe Phases in Layered Nickelates

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To describe quasi two-dimensional nickelates we introduce an effective Hamiltonian for $e_g$ electrons which includes the kinetic energy, on-site Coulomb interactions, spin-spin and Jahn-Teller (static) terms. The experimental stripe phases are correctly reproduced by the model. The mechanisms responsible for stripe formation are different than those reported in cuprates and manganites. Published in: Acta Phys. Polon. A 121, 1048 (2012).

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Strong electron correlations are responsible for numerous interesting properties of doped transition metal oxides. In these systems coexisting charge, magnetic and orbital order emerge from competition of different type of electronic energy and the coupling with the lattice\cite{1}. Among them the phenomenon of stripes is common — it plays an important role in cuprates\cite{2} and occurs also in nickelates\cite{3} and manganites\cite{4}. The stripes in cuprates arise from the competition between kinetic energy of doped holes and magnetic energy of ordered spins\cite{5}. The evolution of metallic stripes under increasing hole doping and their spectral properties could be described within a purely electronic model\cite{6}.

In contrast, the origin of stripe phases which involve orbital order is more subtle. The kinetic energy is here anisotropic and the orbital states easily couple to the lattice. The extension by Jahn-Teller (JT) interactions is necessary in the models describing doped manganites\cite{6} and nickelates\cite{7}. The stripes in monolayer nickelates La$_{2-x}$Sr$_x$NiO$_4$ were observed in a range of doping 0.289 < $x$ < 0.5\cite{8}. They occur as charge walls in an antiferromagnetic (AF) phase and were described within the electronic model in a broad range of doping $x < 0.4$\cite{9}, while the electronic structure calculations reproduced them at $x = 1/3$ and 1/2\cite{8,10}. Here we describe stripe phases within an effective model featuring only $e_g$ electrons at Ni sites renormalized by oxygen ions. At each site the local basis is given by two $e_g$ orbitals symmetry, i.e., $x = x^2 - y^2$ and $z = 3z^2 - r^2$ orbitals.

The degenerate Hubbard Hamiltonian $\mathcal{H}$ for two $e_g$ orbital states contains several terms,

$$\mathcal{H} = H_{\text{kin}} + H_{\text{cr}} + H_{\text{int}} + H_{\text{JT}}.$$  \hspace{1cm} (1)

The kinetic part $H_{\text{kin}}$ is given by $(dd\sigma)$ element $t$,

$$H_{\text{kin}} = -\frac{1}{4} \sum_{\{ij\}} \left\{ (3d_{i\sigma}^\dagger d_{j\sigma} + d_{i\sigma}^\dagger d_{j\sigma} + d_{i\sigma}^\dagger d_{j\sigma} + d_{i\sigma}^\dagger d_{j\sigma}) \right\}, \hspace{1cm} (2)$$

and contains the hopping between $x$ and $z$ orbitals at neighboring sites $\{ij\}$ which changes sign between bonds along $a$ and $b$ axis. The creation operators $d_{i\sigma}^\dagger$ correspond to electron in orbital $\mu = x, z$, with spin $\sigma = \uparrow, \downarrow$ located at the site $i$. The kinetic energy is supplemented by orbital splitting $E_z > 0$ due to crystal field

$$H_{\text{cr}} = -\frac{1}{2} \sum_{\{ij\}} (n_{i\sigma} - n_{i\sigma}) = -E_z \sum_i \tau_i^z. \hspace{1cm} (3)$$

$H_{\text{int}}$ stands for on-site Coulomb interactions between $e_g$ electrons and was used before for monolayer, bilayer and cubic manganites\cite{6} and does not need to be reproduced here; it is parametrized by intraorbital Coulomb element $U$ and Hund’s exchange $J_H$.

The simplified JT interaction $H_{\text{JT}}$ is:

$$H_{\text{JT}} = 2g_{\text{JT}} \sum_i \left\{ \left( \frac{1}{2} Q_{1i}(2 - n_{i}) + Q_{2i} \tau_i^x + Q_{3i} \tau_i^z \right) \right\} + \frac{1}{2} K \sum_i \left\{ 2Q_{1i}^2 + Q_{2i}^2 + Q_{3i}^2 \right\}, \hspace{1cm} (4)$$

where $n_{i} = \sum_{\alpha\sigma} n_{i\alpha\sigma}$ is $e_g$ electron density operator and the pseudospin $\tau = 1/2$ operators are defined as follows:

$$\tau_i^x = \frac{1}{2} \sum_{\sigma} (d_{i\sigma}^\dagger d_{i\sigma} + d_{i\sigma}^\dagger d_{i\sigma}), \hspace{1cm} \tau_i^z = \frac{1}{2} (n_{ix} - n_{iz}). \hspace{1cm} (5)$$

The JT term includes three modes, $\{Q_{1i}, Q_{2i}, Q_{3i}\}$ which denote standard $e_g$ static deformations of the octahedron around site $i$. Note that for dynamic JT effect each two neighboring Ni$^{2+}$ ions share one oxygen and thus the JT distortions around them are not independent.

We performed Hartree-Fock (HF) computations on a finite $6 \times 6$ cluster (with periodic boundary conditions) filled by $N$ electrons and determined the ground state by comparing energies of several converged HF states. Following them the electron correlations were studied using Local Ansatz (LA) method which implements the leading on-site electron correlations\cite{11}. Due to high density of $e_g$ electrons per site $n = 2 - x$ the correlation energies were found to be much larger here than those reported before for cuprates\cite{12} or manganites\cite{6}, but they do not modify the stability of the HF ground state.
FIG. 1: The antiferromagnetic ground state obtained for La$_2$NiO$_4$ (at $x = 0$). Each circle represents $e_g$ electron density with its diameter corresponding to one-half of density; the arrow length — one-half of the $e_g$ spin; the horizontal bar length (here absent) — charge density difference between $x$ and $z$ orbitals (longest bar to the right/left corresponds to pure $x/z$ orbital state). Parameters (in eV): $t = 0.6$, $J_H = 0.9$, $E_z = -0.6$; $U = 8t_0$, $g_{JT} = 3.0$ eV/Å, $K = eV/Å^2$.

In the undoped La$_2$NiO$_4$ ($N = 2 \times 6^2$ corresponds to $n = 2$ electrons per site) we found a uniform charge distribution in the ground state, with equal orbital electron densities $n_x = n_z = 1$, corresponding to a high-spin $S = 1$ state at each Ni$^{2+}$ ion. The ionic spins $S = 1$ are coupled by the AF interaction which follows from the Hamiltonian $H$ Eq. (1) in a similar way as it does for $s = 1/2$ spins in cuprates. This explains the origin of $G$-type AF order ($G$-AF) shown in Fig. 1.

Next we investigate the ground states for decreasing electron number per site $n = 2 - x$. At low doping $0.1 < x < 0.3$ we obtained within the present approach isolated polaronic states (not shown). Diagonal stripe phases are found for doping $x = 1/3$ and $x = 1/2$, in agreement with experimental observations [3] — they are shown in Figs. 2 and 3. They are not like the stripes in cuprates or manganites. In cuprates charge order coexists with the modulation of AF order between alternating AF domains, separated by nonmagnetic and half-filled domain walls. The JT coupling does not contribute here as the hole sites are inactive. In contrast to cuprates, Ni ions always carry magnetic moments and contribute to the magnetic order within a single domain of the C-AF phase. Note also that the present stripe phases are insulating, while the ones in cuprates are metallic [6].

In manganites the situation is more complex due to possible presence of orbital order and due to extra Hund’s exchange coupling of $e_g$ electrons with $t_{2g}$ core spins $S = 3/2$ [4]. Here several competing mechanisms enter on equal footing and distinct stripe patterns with the true long range order are not a rule. As a result, the magnetic order of the ground state was found to be very sensitive to the precise values of the model parameters [13]. However, at $x = 1/2$ doping one finds a robust instability for monolayer manganites toward two sublattices with charge majority and minority sites, see also [8a] The JT effect stabilizes here the CE magnetic order accompanied by checkerboard charge order, with the JT distortions contributing only on charge majority sites.

In monolayer nickelates one finds the opposite situation: The main difference in the ionic picture is that in the undoped substance there are two $e_g$ electrons per site, and hole doping generates JT active sites, where a single electron couples to JT distortions $Q_2$ and $Q_3$, see Fig. 3. This coupling is crucial for stabilizing ordered stripe structures at $x = 1/3$ and $x = 1/2$ doping, shown in Fig. 2. In effect one can say that the kinetic energy of doped holes is suppressed and the competition between magnetic and kinetic energy along the charge minority walls is quenched, in agreement with double exchange [4].

The above ionic picture used to interpret both stripe
quantum fluctuations are suppressed in the HF method, majority/minority sites at the magnetic moments are suppressed. The density in cases. For this charge distribution both z-doping, while density in n-obtained in the present computations. We have found phases is not far from the actual charge distribution obtained in the present computations. We have found n₁ = 1.82, n₂ = 1.37 (n₁ = 1.66, n₂ = 1.34) at charge majority/minority sites at x = 1/3 (x = 1/2) doping. As quantum fluctuations are suppressed in the HF method, this corresponds to magnetic moments m₁ = ±0.89, m₂ = ±0.67 (m₁ = ±0.81, m₂ = ±0.62) in both phases. Doping occurs predominantly in x orbitals, where also the magnetic moments are suppressed. The density in x orbitals varies between nₓ = 0.47(0.85) and nₓ = 0.45(0.73) for the stripe phases at x = 1/3 and x = 1/2 doping, while density in z orbitals is nₓ ≥ 0.89 in all cases. For this charge distribution both Q₂ₓ and Q₃ₓ JT modes are active at charge minority sites, see Fig. 3. We suggest that JT distortions govern the stripe formation in monolayer nickelates, and stabilize the obtained charge alternation accompanied by large JT distortions at charge minority sites. We have found that the doped sites can order at doping x = 1/3 and appear as diagonal stripes (each third line). Similarly, they give diagonal stripes (each second line) for x = 1/2 doping stabilized by the JT distortions. Indeed, when the JT coupling is turned off (at g_JT = 0), the stripes do not form. Strong electron correlations are also important and we have verified that similar stripe phases to those shown in Figs. 2 and 3 occur for a stronger on-site Coulomb repulsion U = 12t in the present model Eq. (1), only the charge modulation is somewhat enhanced.

In summary, we identified the coupling of eₜ electrons at sites doped by holes to local Jahn-Teller distortions as the microscopic origin of diagonal stripe phases in monolayer nickelates. The presented results elucidate fundamental difference between stripe phases in doped nickelates, cuprates and manganites, as the ions active for the Jahn-Teller effect play a different role in each case.

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