Jahn–Teller mechanism of stripe formation in doped layered \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_4 \) nickelates

Krzysztof Rościszewski\(^1\) and Andrzej M Oleś\(^1,2\)

\(^1\) Marian Smoluchowski Institute of Physics, Jagellonian University, Reymonta 4, PL-30059 Kraków, Poland
\(^2\) Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

E-mail: krzysztof.rosciszewski@uj.edu.pl and a.m.oles@fkf.mpg.de

Received 11 March 2011, in final form 23 May 2011
Published 15 June 2011
Online at stacks.iop.org/JPhysCM/23/265601

Abstract

We introduce an effective model for \( e_g \) electrons to describe quasi-two-dimensional layered \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_4 \) nickelates and study it using correlated wavefunctions on \( 8 \times 8 \) and \( 6 \times 6 \) clusters. The effective Hamiltonian includes the kinetic energy, on-site Coulomb interactions for \( e_g \) electrons (intraorbital \( U \) and Hund’s exchange \( J_H \)) and the coupling between \( e_g \) electrons and Jahn–Teller distortions (static modes). The experimental ground state phases with inhomogeneous charge, spin and orbital order at the dopings \( x = 1/3 \) and \( 1/2 \) are reproduced very well by the model. Although the Jahn–Teller distortions are weak, we show that they play a crucial role and stabilize the observed cooperative charge, magnetic and orbital order in the form of a diagonal stripe phase at \( x = 1/3 \) doping and a chequerboard phase at \( x = 1/2 \) doping.

1. Introduction

The nature and origin of stripe phases in transition metal oxides continuously attracts considerable attention in the theory of strongly correlated electrons. The phenomenon of stripes occurs in doped materials and, as one of the few developments in the physics of superconducting cuprates, was discovered first in theory [1] before its existence was confirmed by experimental observations [2]. In a system with dominant electron–electron interactions novel phases with charge order in the form of a Wigner crystal or stripe phases with nonuniform charge distribution are expected. In the well known example of the cuprates, charge order coexists with the modulation of antiferromagnetic (AF) order between alternating domains [3, 4]. The stripe phases in realistic models for cuprates were obtained, \textit{inter alia}, by calculations using the Hartree–Fock (HF) approximation [1], correlated wavefunctions [5], dynamical mean-field theory [6] and slave bosons [7]. These studies have shown that correlation effects play an important role in the physical properties of stripes.

The physical origin of stripes becomes more complex in systems with active orbital degrees of freedom, as in the doped manganites with \( e_g \) orbital degrees of freedom [8–10], and it was soon recognized that the mechanism of stripes has to explain charge and magnetic order coexisting with a certain type of orbital order [11, 12]. The mechanism of stripe formation in such systems is subtle and involves directional hopping between the orbital wavefunctions, in particular for \( t_{2g} \) orbital states [13], that could play a role in the properties of doped iron pnictides [14].

In contrast to the stripes in cuprates [3], the stripes in nickelates are along the diagonal direction in the square lattice [15]. This by itself is puzzling and suggests that other degrees of freedom may contribute. The properties of doped perovskite nickelates are still not completely understood in spite of considerable effort put forward both in theory [12, 16–21] and in experiment [22, 23]. The main difficulty in the theoretical description of this class of compounds is related to the simultaneous importance of numerous degrees of freedom. Unfortunately, all of them contribute and one cannot argue that only some types of interactions are essential and could be considered in a simplified approach, while the others are of secondary importance and would be responsible for quantitative corrections only. We argue that attempts to consider only some interactions, for instance either including only strong on-site
Coulomb and Hund’s exchange interactions and neglecting the coupling to the lattice via the Jahn–Teller (JT) distortions, or studying the coupling to the lattice distortions in the absence of strong local Coulomb interactions, is insufficient to account for the experimental situation. The phase situation in this class of compounds is a result of a subtle balance between numerous factors.

On the theoretical side, the multiband models and/or approaches based on the \textit{ab initio} local density approximation (LDA) computations extended by static corrections due to the local Coulomb interaction \( U \) (within the LDA + \( U \) scheme) [19, 21], seem to be the most realistic and complete approaches to theoretical description of the nickel oxides with a perovskite structure. The drawback of such approaches, however, is the considerable technical difficulty in working with doped systems especially for arbitrary doping levels \( x \) because in such a case very large unit cells (or clusters) need to be considered.

Therefore it is quite helpful (and complementary to LDA + \( U \) approaches) to identify first all physical mechanisms which are essential in doped nickelates and then develop a simplified but still well motivated effective model to describe them. In the present paper we use such an effective model (featuring only Ni sites renormalized by the presence of surrounding oxygens) for the description of itinerant \( e_g \) electrons which includes all essential interactions present in layered nickelates. We do not develop new concepts here but use the model well tested before in the manganese perovskites, including also monolayer and bilayer systems [24]. Further justification of this model follows from similar microscopic approaches developed earlier to describe doped nickelates [11, 12, 16, 18]. With this microscopic model we investigate the nature and type of coexisting magnetic, orbital and charge order in the ground state when local electron correlations and the coupling to JT distortions are both included. In this paper we focus on the quasi-two-dimensional (2D) monolayer nickelates \( \text{La}_2-x\text{Sr}_x\text{NiO}_4 \).

The paper is organized as follows. First, we introduce in section 2 a realistic model for \( e_g \) electrons in a 2D monolayer nickelate which includes the electron interactions and the local potentials due to static JT distortions. In this section we also introduce the method to treat electron correlation effects beyond the HF approximation, and discuss realistic values of the model parameters. The results obtained for various doping levels are presented and analysed in section 3. Next we concentrate on the role played by the JT distortions (in section 4) and show that they are crucial for the stability of the stripe phase at \( x = 1/3 \) doping. Finally we present a short summary in section 5 as well as some general conclusions.

### 2. The microscopic model and methods

#### 2.1. The effective model Hamiltonian

We investigate strongly correlated electrons in doped monolayer nickelates \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_4 \) (with doping \( 0 < x < 0.5 \)), using an effective model describing only Ni sites, where the state of the surrounding oxygens is included by an effective potential at each site. (A realistic effective Hamiltonian which acts in the subspace of low energy \( e_g \) states and the precise values of the Hamiltonian parameters can be derived by a procedure of mapping the results of HF, or LDA + \( U \), or all-electron \textit{ab initio} calculations obtained within a more complete approach.) A local basis at each nickel site is given by two Wannier orbitals of \( e_g \) symmetry, i.e., \( x^2 - y^2 \) and \( 3z^2 - r^2 \) orbitals.

In the present study we use a Hubbard-type Hamiltonian \( \mathcal{H} \) for two \( e_g \) orbital states defined on a finite cluster:

\[
\mathcal{H} = \mathcal{H}_{\text{kin}} + \mathcal{H}_{\text{cr}} + \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{spin}} + \mathcal{H}_{\text{JT}},
\]

which consists of kinetic (\( \mathcal{H}_{\text{kin}} \)), crystal field (\( \mathcal{H}_{\text{cr}} \)), on-site Coulomb (\( \mathcal{H}_{\text{int}} \)), spin (\( \mathcal{H}_{\text{spin}} \)), and JT (\( \mathcal{H}_{\text{JT}} \)) terms. 

The kinetic part \( \mathcal{H}_{\text{kin}} \) is expressed using two \( e_g \) orbitals,

\[
|z\rangle = |3z^2 - r^2\rangle/\sqrt{6}, \quad |x\rangle = |x^2 - y^2\rangle/\sqrt{2},
\]

per site, with anisotropic phase dependent hopping which depends on the orbital phases on neighbouring sites,

\[
\mathcal{H}_{\text{kin}} = -\frac{1}{2}t_{0} \sum_{\langle ij \rangle \mid a, \sigma} \left( (3d_{i \sigma}^\dagger d_{j \sigma} + d_{i \sigma}^\dagger d_{j \sigma}) \right) \pm \sqrt{3}(d_{i \sigma}^\dagger d_{j \sigma} + d_{i \sigma}^\dagger d_{j \sigma}) \right) \quad \text{(3)}
\]

Here \( d_{i \mu} \) are creation operators for an electron in orbital \( \mu = x, z \) with spin \( \sigma = \uparrow, \downarrow \) at site \( i \). The \( \langle ij \rangle \) runs over pairs of nearest-neighbours (bonds); \( \pm \) is interpreted as a plus sign for \( \langle ij \rangle \) being parallel to the crystal axis \( a \) and minus for \( \langle ij \rangle \) being parallel to the axis \( b \).

The kinetic energy is supplemented by the crystal field term which describes orbital splitting

\[
\mathcal{H}_{\text{cr}} = \frac{1}{2}E_z \sum_{i \in \text{int}} (n_{i \sigma} - n_{i \bar{\sigma}}),
\]

For the present convention and for negative values of the crystal field parameter \( E_z < 0 \) the \( z \) orbital is being favoured over the \( x \) orbital.

\( \mathcal{H}_{\text{int}} \) and \( \mathcal{H}_{\text{spin}} \) stand for approximate forms of the local Coulomb and exchange interactions for electrons within degenerate \( e_g \) orbitals used before for monolayer, bilayer and cubic perovskite manganites [24]:

\[
\mathcal{H}_{\text{int}} = U \sum_{\langle ij \rangle} n_{i \uparrow} n_{j \uparrow} + \left( U_0 - \frac{2}{3}J_0 \right) \sum_{i} n_{i \uparrow} n_{i \downarrow},
\]

\[
\mathcal{H}_{\text{spin}} = -\frac{1}{2}J_{\text{R}} \sum_{i} (n_{i \uparrow} - n_{i \downarrow})(n_{i \uparrow} - n_{i \downarrow}).
\]

The on-site Coulomb interaction is denoted as \( U \), the Hund’s exchange interaction constant is \( J_0 \). Here the spin symmetry is explicitly broken: the quantization axis is fixed in spin space and the full Hund’s exchange interactions with \( SU(2) \) symmetry are replaced by the Ising term. However, the above form suffices as it gives the same Hamiltonian in the HF approximation as an exact expression for two \( e_g \) orbitals [25].
The simplified JT part \( H_{JT} \) is
\[
H_{JT} = g_{JT} \sum_i \left(Q_i (2 - n_{ix} - n_{ix}) + Q_{ij} \tau_i^j + Q_{ij} \tau_i^j \right)
\]
\[
+ \frac{1}{2} k \sum_i \left(2 Q_{ii}^2 + Q_{ii}^2 + Q_{ii}^2 \right),
\]
where the pseudospin operators, i.e., \( \{ \tau_i^j, \tau_i^j \} \) operators, are defined as follows:
\[
\tau_i^j = \sum_a (d_{iota}^j d_{iota}^j + d_{iota}^j d_{iota}^j),
\]
\[
\tau_i^j = \sum_a (d_{iota}^j d_{iota}^j - d_{iota}^j d_{iota}^j).
\]

The Hamiltonian equation (7) includes three different static JT modes, where \( \{ Q_1, Q_2, Q_3 \} \) denote the JT static deformation modes of the \( i \)th octahedron. (For simplicity, the harmonic constant of the isotropic JT (breathing) mode \( Q_1 \) is assumed to be double with respect to those corresponding to the \( Q_2 \) and \( Q_3 \) unsymmetric modes, as discussed in [8, 12].) Note that \( H_{JT} \) taking the above form is a simplification: (i) first, some anharmonic terms were omitted (compare, for example, the corresponding terms in [26]), and (ii) second, all JT distortions are treated here as independent from each other. Contrary to this, in reality two neighbouring Ni atoms share one oxygen ion in between them, and thus neighbouring JT distortions are not really independent. The present approximation is the simplest one to describe the coupling to the local JT modes in a model where oxygen ions are not explicitly included (for a more detailed discussion see [12]).

2.2. Calculations within the Hartree–Fock approximation

We performed extensive calculations for clusters with periodic boundary conditions. A systematic study of increasing doping from \( x = 0 \), through \( x = 1/8, 2/8, 3/8, \) up to \( x = 4/8 \) was performed for \( 8 \times 8 \) clusters, and was supplemented by the doping \( x = 1/3 \) for the \( 6 \times 6 \) cluster. We investigate the ground state at zero temperature \( (T = 0) \).

First, the calculations within the single-determinant HF approximation were performed to determine the ground state wavefunction. Also the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the HOMO–LUMO gap,
\[
\Delta \equiv E_{LUMO} - E_{HOMO},
\]
was extracted at this step. In the next step the HF wavefunction was modified to include the electron correlations by employing a local ansatz [27], see below.

The calculations were performed as follows. In the first step HF computations were run starting from one of several different initial conditions (on average a few thousand for each set of Hamiltonian parameters are necessary as the identification of a true energy minimum is difficult), i.e. from predefined (some symmetry fixed, but mostly random) charge, spin and orbital configurations and several predefined sets of classical variables \( \{ Q_1, Q_2, Q_3 \} \). For each fixed set of starting parameters and starting initial conditions we obtain on convergence a new HF wavefunction \( | \Psi_{HF} \rangle \) which is a candidate for a ground state wavefunction. This self-consistent procedure is assumed to also provide the energy minimum with respect to the classical \( \{ Q_1, Q_2, Q_3 \} \) variables [24].

2.3. Electron correlations

After completing the HF computations for a given wavefunction \( | \Psi \rangle \), we performed correlation computations (second step) which provide the total energy. (For details see [5, 24].) Following the local ansatz [27], the HF wavefunction \( | \Phi_0 \rangle \) was modified to include the electron correlation effects. Here we used an exponential local ansatz for the correlated ground state,
\[
| \Psi \rangle = \exp \left( -\sum \eta_m O_m \right) | \Phi_0 \rangle,
\]
where \( \{ O_m \} \) are local correlation operators. The variational parameters \( \eta_m \) (four singlet and two triplet ones) are found by minimizing the total energy,
\[
E_{tot} = \langle \Psi | H | \Psi \rangle - \langle \Psi | \Psi \rangle.
\]

Here for the correlation operators we use
\[
O_m = \sum_i \delta n_{i\mu\sigma} \delta n_{i\nu\sigma'}.
\]

The sum in the above equation ensures a smaller number of variational parameters; on the other hand the non-homogeneous correlations are treated in an averaged way (this procedure is somewhat similar to calculations performed within mean-field approaches). The symbol \( \delta \) in \( \delta n_{i\mu\sigma} \) indicates that only that part of the \( n_{i\mu\sigma} \) operator which follows from a strongly correlated regime. However, as yet there is no easy way to include them for large systems (in the thermodynamic limit), thus one is able to include within theory only the leading part of the correlation energy (i.e., the one which follows from two-particle excitations).

After obtaining the total energy for a given configuration, we repeat the procedure from the beginning, i.e. we take the second set of HF initial conditions and repeat all computations to obtain the second candidate for a ground state wavefunction. Other configurations for the third, fourth, etc. set of initial conditions are investigated in a similar way. Finally, the resulting set of total energies was inspected and the lowest one was identified as the best candidate for the true ground state. In general, the correlation energies are found to be large, in fact much larger than those found in the perovskite manganites [24].

2.4. Parameters of the model

The values of the Hamiltonian parameters used below follow closely the sets commonly employed in the literature to study doped nickelates. For the effective d–d hopping (ddr) we assume \( t_0 = 0.6 \) eV, following [18]. The local Coulomb
interactions are strong, and we assume $8 < U/t_0 < 12$
(the lowering of the considerably larger atomic value in nickel
is due to an appropriate screening of the $e_g$ electrons). The
Hund’s exchange coupling was taken as $J_H = 0.9$ eV [18, 19].
The crystal field values we considered were either $E_z = 0$
or $-0.3$ eV, with the latter value inducing a higher electron
density in the $z$ orbitals, as expected for a single NiO$_2$ plane
(compare with [12, 18]).

Unfortunately, very little is known about JT interactions
in nickelates, therefore the JT constant $K$ was fixed as $K = 13$
eV Å$^{-2}$ (like in manganite perovskites [24]), and the
coupling constant with the lattice distortions $g_{JT}$ was assumed
 to be in the range $2$ eV Å$^{-1} < g_{JT} < 3.8$ eV Å$^{-1}$,
following [8].

The best set of Hamiltonian parameters which allows
one to reproduce the experimental phase situation is given in
table 1. In some cases, other parameter values were used as
discussed below. However, the parameters one should use are
constrained by the experimental observations. It is fortunate
that the obtained types of spin, orbital and charge order turn
out to be rather sensitive to the parameter values. In fact, many
sets of Hamiltonian parameters (different than those in table 1)
were also considered in test computations but they do not
generate physically reasonable results (i.e., ground states with
ordering close to that reported in experiments). Although
the full phase diagram is of much interest and would be very
appropriate here, it is unfortunately too expensive to compute
it by the present method.

### 3. Results

The computations were repeated for many sets of Hamiltonian
parameters and for many (up to several thousand) charge, spin,
orbital and JT distortions (i.e., for local configurations required
to start HF iterations). Extensive calculations were required
to establish the parameter values which are realistic for doped
nickelates and allow one to reproduce basic experimental
observations. Below we present the results obtained for the
realistic parameter set as given in table 1.

#### 3.1. Low doping regime

The results obtained in the low doping regime are presented
in figures 1 and 2. First we consider $x = 1/8$ doping. At
this doping level in La$_{2-x}$Sr$_{1+x}$CuO$_4$ cuprates one finds stable
stripe phases [3, 5–7]. In the present case we observed isolated
Ni ions with holes doped in $x$ orbitals, as shown in figure 1. For
these ions the magnetic moments are due to $S = 1/2$ spins and
are therefore lower than the magnetic moments at $S = 1$ sites,
thus appearing as spin defects in the $G$-AF phase. While both
$x$ and $z$ orbitals are occupied at undoped sites, one finds that

only $z$ orbitals are occupied at doped sites. Of course, some
delocalization of electrons between the two sublattices takes
place as well in the doped antiferromagnet investigated here,
but the above ionic picture applies to a good approximation.
In fact, the obtained phase is insulating with a HOMO–LUMO
gap of 1.86 eV.
Local charge defects consist of $z$ electrons occupying doped Ni$^{3+}$ sites which couple to lattice distortions $\{Q_{i}\}$, as shown in the lower panel of figure 1. These distortions act as self-trapping on the doped charges and suppress the kinetic energy of doped holes. Therefore, this regime of doping is manifestly different from the observations in cuprates, where JT distortions are inactive and self-organization of doped holes in the form of horizontal stripes takes place [1–3].

At a higher doping, $x = 1/4$, the magnetic order changes to the C-AF phase shown in figure 2, with relatively large magnetic cells. This phase is weakly insulating, with the HOMO–LUMO gap $\Delta = 0.28$ eV. Horizontal ferromagnetic (FM) lines are characterized by charge modulations between almost undoped Ni$^{2+}$ ions and doped Ni$^{3+}$ ions. The latter doped sites are distributed far from one another both within FM chains and between consecutive AF horizontal lines. This may be seen as a physical reason which prevents the occurrence of stripes at this doping level. Furthermore, the doped sites couple actively to local distortions, and can be identified by looking at the pattern of JT distortions, see the lower panel in figure 2. It helps to identify imperfect long-range order of doped holes which avoid each other, similarly to the $x = 1/8$ doping considered above.

3.2. Diagonal stripes at doping $x = 1/3$

The case of $x = 1/3$ doping was investigated with a $6 \times 6$ cluster, see figure 3. Here the number of doped sites is the same as the doping, i.e. $x = 1/3$, meaning that some of the doped sites have to be located at next-nearest-neighbour positions. This follows the observed trend of doping by one hole at doped Ni sites. The resulting stripe phase with diagonal
lines of reduced charges (doped sites) may be therefore seen as a modification of the C-AF phase obtained at \( x = 1/4 \) doping by adding more doped holes (Ni\(^{3+}\) ions). Indeed, one finds that every third site in an AF row (FM column) contains the reduced charge close to one added hole, and these sites form a (11) stripe phase. Note that the horizontal and vertical lines are here interchanged as compared with figure 2, but this configuration is of course equivalent to the one with FM horizontal lines, and AF order between them.

Large JT distortions accompany the sites with minority charges, so the stripe pattern can be also recognized by analysing them. It reproduces the experimental results in [22, 23], with the long-range order, i.e. with charge, spin and orbital order in the form of diagonal stripes, present at the doping \( x = 1/3 \). This phase is also insulating, with a HOMO–LUMO gap \( \Delta = 0.57 \) eV.

We emphasize that the JT distortions play a crucial role in the observed stripe phase at \( x = 1/3 \) doping. We have verified that when one switches off the JT coupling, i.e. when one takes \( g_{JT} = 0 \) with the other parameters unchanged, the stripes vanish and the ground state becomes conducting (HOMO–LUMO gap \( \Delta = 0.03 \) eV), see below. In this case one finds the same magnetic phase with horizontally arranged FM lines coupled in the vertical direction in the C-AF order, with slightly nonuniform charge distribution and slightly nonuniform orbital order (the \( z \) orbital occupancy is then larger than the \( x \) one on most sites in the cluster).

### 3.3. Large doping regime \( 1/3 < x \leq 1/2 \)

Coming to the large doping regime, \( x > 1/3 \), we have found further modifications of the C-AF spin order. First of all, the next doping level considered by us, \( x = 3/8 \), is incompatible with the stripes shown in figure 3. As shown in figure 4, in this case the ionic picture does not apply anymore and the electron charge is distributed uniformly. Therefore the values of the magnetic moments are close to 1.6 \( \mu_\text{B} \) per site, and the \( e_g \) orbitals are occupied in a similar way at all cluster sites. Hole doping reduces the electron density in \( x \) orbitals, therefore at the present doping level of \( x = 3/8 \) the ratio of electron density in \( x \) and \( z \) orbitals is close to 1:2. Unlike for the lower doping levels considered above, this electron distribution does not favour JT distortions at particular cluster sites with minority charge, and one finds uniform and rather small JT distortions at all the sites. Nevertheless, the electronic structure predicts that this ground state is insulating, having a HOMO–LUMO gap \( \Delta = 0.72 \) eV.

The next physically interesting and experimentally much studied doping is half filling, i.e. \( x = 1/2 \). One finds that the C-AF spin order remains unchanged, but charge modulation develops. This doping level is compatible with a two-sublattice structure in the charge ordered state shown in figure 5. The alternating electron charges are close to \( n = 2 \) and 1 on the majority and minority charge sites. Therefore, the ionic picture applies again to this doping level, and the system may be viewed as alternating charge order, with Ni\(^{2+}\) and Ni\(^{3+}\) ions on the two sublattices. This result reproduces the experimental results [22, 23], with long-range chequerboard-like charge order found at half-doping. Similarly to all the other cases, this configuration is also insulating, with a HOMO–LUMO gap \( \Delta = 0.91 \) eV.

The charge order found for \( x = 1/2 \) doping is closely followed by JT distortions, as shown in figure 5. Large JT distortions at charge minority sites stabilize the chequerboard charge order in this case. Large \( \{Q_{12}\} \) distortions stabilize the charge order, and the nonuniform electron distribution over \( e_g \) orbitals is stabilized by large \( \{Q_{13}\} \) distortions. As a result, the \( x \) orbitals are almost empty at charge minority sites, and the occupancy of \( z \) orbitals is close to one electron at each site.

### 3.4. Maximal doping \( x = 1 \) for LaSrNiO\(_4\)

Experimental studies have established that for the examined class of La\(_{2-x}\)Sr\(_x\)NiO\(_4\) compounds with large doping \( x \approx 1 \), the ground state is paramagnetic and conducting [28], with a semiconductor-like conductivity (at low temperature close
Figure 5. Perfect chequerboard crystal-like order with two sublattices, as obtained for \( x = 1/2 \) doping in the \( 8 \times 8 \) cluster.

C-AF spin order with alternating spin values between \( S = 1 \) and \( S = 1/2 \) spins for charge majority/minority sites, and holes doped into \( x \) orbitals at charge minority sites. Uniform electron distribution between \( x \) and \( z \) orbitals results in no JT distortions at charge majority sites, while considerable JT distortions at charge minority sites stabilize the orbital order with (almost) empty \( x \) orbitals. The meanings of symbols and the values of parameters are as in figure 1.

to zero Kelvin) [29]. We investigated this case using the present model by numerical computations, either using the parameter set of table 1 or somewhat modified parameters. Extensive calculations have shown that reasonable values of the parameters do not give results in agreement with the experimental observations. In all the considered cases one obtains perfect AF order, with homogeneous charge distribution (one electron per site) and with purely \( z \)-orbital occupation. In addition, the HOMO–LUMO gap is quite large \( \Delta = 4.5 \) eV (for the parameters given in table 1).

While this theoretical result is very reasonable and may be expected taking the broken symmetry between two \( e_g \) orbitals in a monolayer LaSrNiO\(_4\) system, it stimulates the question as to whether this result could invalidate all the previous results reported above. In our opinion the disagreement found between theory and experiment for such a large doping level is only an indication that the effective model presented in this paper (without extra modifications) is too limited to perform satisfactorily. Our reasoning, based entirely upon experimental data, is twofold.

First of all, the conductivity at \( x \approx 1 \) could be likely due to a completely different mechanism [29], namely to sample quality and the near impossibility of growing perfect LaSrNiO\(_4\) crystals. In reality what one grows are samples with oxygen vacancies (at vertices of NiO\(_6\) octahedra). The level of oxygen vacancies is estimated to be at best 0.01–0.04 which seems to be enough to form a narrow donor band and therefore p-type conduction could set in. How this p-band destroys the AF order is another and difficult question. Still, it is clear that the two-band model is not appropriate for the description of LaSrNiO\(_4\).

Second, the model computations are based on a formal scheme: the doping level is equal to the fraction \( x \) in the actual chemical formula \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_4 \). It is commonly accepted that this is possibly not true, similarly to the case in YBa\(_2\)Cu\(_3\)O\(_{6+y}\) superconductors [30], and most probably this simple assumption works here reasonably well only for small values of \( x \). (Note that the same fault can be attributed to modelling carried out in doped cuprates and manganites.) Clearly, for larger doping one can expect sizeable deviations between the electron doping level and the \( x \) fraction in the chemical formula. These deviations depend on the type of crystal lattice, on the atom–atom distances, and on the constituent atoms, and no simple formula exists to compute them.

We suggest that the question as to whether the first or second explanation is more appropriate cannot be answered at present. It could be that both are partly valid at the same time.

There are, however, some indications which can signal when and where the above proportionality between the doping level and the chemical concentration \( x \) could not be obeyed. In our particular case such indications can be read from [31] where true quantum-chemistry ab initio computations (HF, BLYP and PBE) for LaNiO\(_3\) were performed (using the CRYSTAL06 computer code) and where Mulliken population analysis was carried out. This is a different (three-dimensional) conducting substance, not the one studied in this paper, but still the problem is more or less the same. The Mulliken charges found on Ni atoms are \( \approx 1.7 \) instead of the formal +3 and on oxygen atoms the Mulliken charges are \( \approx -1.2 \) instead of the formal –2. It is true that the Mulliken charges are only a rather crude estimate but still from the above ab initio data it follows that the effective model with formal occupation number of one d-electron-type Wannier function (per site) is not correct for LaNiO\(_3\).

One can envisage the modification of our model which could possibly work properly for the description of LaSrNiO\(_4\). It seems necessary to supplement the model with at least one extra Wannier orbital per site. For the first trial, in the spirit of the Anderson lattice model, this could be a simple s-type Wannier orbital of the oxygen type (assuming spherically symmetric distribution of the oxygen p electrons around the central nickel). The new extra Hamiltonian terms would be simple kinetic s-type nearest-neighbour hopping supplemented...
4. The crucial role played by Jahn–Teller distortions

4.1. Finite Jahn–Teller coupling \(g_{JT}\)

We have already remarked several times on the importance of JT coupling. Here we try to draw some more general conclusions and provide extra information.

Test computations for the undoped \(\text{La}_2\text{NiO}_4\) substance \((x = 0)\) invariably (independently of the initial conditions) give the insulating \(G\text{-AF}\) ground state (for \(S = 1\) spins) with uniform charge distribution and equal occupation of \(x\) and \(z\) orbitals, in perfect agreement with experiment \([32, 33]\). In this state no JT distortions can arise. This result was obtained for almost any set of the Hamiltonian parameters with one notable exception. For too large JT coupling, in particular for \(g_{JT}\) the simplified form of the JT Hamiltonian which we use is not appropriate for a correct description of the JT effects i.e. equation (4), and in particular the simple form of the coupling to the lattice given in equation (4) requires substantial corrections.

Further extensive tests for the \(x = 1/3\) doped substance revealed that only in a narrow range of \(2.8 < g_{JT} < 3.2\) (in eV \(\AA\) units) do diagonal stripes form. Hence, the role of the JT distortions is crucial for stripe formation. Furthermore, it was also interesting to establish that for zero crystal field, \(E_z = 0\), the diagonal stripes disappear, though the charge, orbital and magnetic order remains almost the same as that for the standard parameters listed in table 1 (see figure 6, compare with figure 3). The resulting phase is insulating, with the HOMO–LUMO gap \(\Delta = 0.58\) eV. (This is a somewhat similar scenario to the one reported for \(\text{Nd}_{1.6}\text{Sr}_{0.3}\text{NiO}_4\) \([34]\).)

However, when one switches to smaller values of the on-site Coulomb repulsion, for example taking \(U = 5\) eV and \(E_z = 0\), diagonal stripes reappear again (i.e. when all the other parameters \([t, J_{JJ}, g_{JT}, K]\) have the values given in table 1). The value \(U = 5\) eV corresponds to the suggestion that the screening of \(U\) by hybridization with oxygen orbitals is larger than usually assumed. It follows that the diagonal stripes do not appear for any set (or even in a broad range) of the Hamiltonian parameters, but result from a subtle balance between several competing mechanisms. Furthermore, it is difficult to conclude which is more appropriate for our nickelate model, either \(U/t \simeq 8\) or rather a higher value \(U/t \simeq 12\) (\(U/t \simeq 12\) was our preference for the bulk of the computations).

Figure 6. Insulating ground state obtained for the \(6 \times 6\) cluster with \(x = 1/3\) doping and zero crystal field \((E_z = 0)\). The \(C\text{-AF}\) order develops, with spins \(3 = 1\) and uniform charge distribution (the same electron density in \(x\) and \(z\) orbitals) on undoped sites and lower spins on charge minority sites. The charge minority sites do not form diagonal stripe boundaries here (as in figure 3) but a superlattice with long-range order develops, which is more visible in the lower panel. The meanings of symbols and the values of other parameters are as in figure 1.

4.2. Setting the Jahn–Teller coupling to zero \(g_{JT} = 0\)

For zero JT coupling \(g_{JT} = 0\) and small doping \(x = 1/8\) we detected no change in the ground state—it looks just like the one shown in figure 1 (resulting from the computations performed for the standard parameter set of table 1) and is insulating.

The situation changes somewhat for higher doping. While for two doping levels, \(x = 1/4\) and \(3/8\), the ground states remain very similar to the ones obtained before, i.e. the \(C\text{-AF}\) order is accompanied by a small charge modulation, when the JT distortions are absent the \(x = 1/4\) state is metallic, and the opposite for the state for doping \(x = 3/8\), where a relatively large gap \(\Delta \simeq 0.7\) eV separates the HOMO and LUMO states in the \(8 \times 8\) cluster. For other larger dopings (up to \(x = 1/2\)) the ground states are conducting.
This result, i.e. the exception obtained for \( x = 3/8 \), is puzzling and could be either a finite size effect and/or an indication of quite different electron correlation energies in systems with different electron numbers. Here it seems that a full explanation and a few digressions are appropriate. To be precise we performed control computations for the \( 8 \times 8 \) cluster doped with 26 holes (quite close to the 24 holes which correspond to \( x = 3/8 \)). The true ground state was conducting.

Then we performed another set of control computations for the \( 6 \times 6 \) cluster doped with 14 holes. (This is as close as possible to \( 3/8 \) doping in the case of the \( 8 \times 8 \) cluster.) This time the situation turns out to be a little bit more complex. The best HF ground state (charge homogeneous with well-developed C-AF order) was found to be insulating. The corresponding correlation energy correction was rather small. However, for a group of higher HF energy levels (with a similar but non-perfect ordering and with the HOMO–LUMO gap being about 0.1 eV, i.e. possibly conducting) much stronger correlation corrections develop and when included the total energy turned out to be lower than that obtained for the first HF ground state including its correlation energy. In other words for \( 6 \times 6 \) and for doping \( x \approx \frac{1}{8} \) the true ground state is conducting and strong correlations are responsible for that. Why the same situation was not found for the \( 8 \times 8 \) cluster can, possibly, be due to poor selection of the local operators (within the local ansatz), see equation (12), which could thus be responsible for not catching some sizeable part of the total correlation energy. In other words the mean-field-type treatment of correlations (which we employ) could not be enough, and the true physical picture is that various contributions to the correlation energy are highly non-homogeneous and strong in the doped, charge and spin non-homogeneous, nickelates.

In the closing remarks to this lengthy discussion of the case of having no coupling to the lattice, let us mention that similar control computations were performed in \( 6 \times 6 \) clusters for different dopings—the results corroborated the results obtained in \( 8 \times 8 \) clusters (the \( x = \frac{3}{8} \) doping was the only exception).

Now, let us return to the main subject and other doping levels. For \( x = 1/2 \) the ground state is again an experimental chequerboard: one finds a two-sublattice arrangement, exactly like the one displayed in the top panel of figure 5. The long-range charge and orbital order are both close to being perfect here. This demonstrates that the chequerboard phase can form by a purely electronic mechanism, and the JT distortions only make this state more robust. (For zero JT coupling this state is also conducting.)

As mentioned before, for the doping \( x = 1/3 \), one obtains a conducting ground state with \( g_{JT} = 0 \), i.e. the HOMO–LUMO gap is \( \Delta = 0.03 \) eV. The obtained phase shows a slightly non-homogeneous C-AF order which looks very similar to the upper panel in figure 2. The true long-range order is, however, not present and diagonal stripes do not form.

5. Summary and conclusions

Let us address the correlated wavefunctions first. As expected, the correlation effects turned out to be much stronger here than in the manganites [24]. This could be recognized by investigating the nonmagnetic states, where the energy is dramatically reduced by the correlation effects (not shown). In the states with either G-AF (for \( x = 0 \)) or C-AF order (for \( 0 < x \leq 0.5 \)) the correlation energy is rather small as the magnetic states are well developed. This demonstrates that the HF approximation provides a realistic energy estimate for the states with broken symmetry when the Coulomb interactions are strong. A similar situation was also found in the two-band model for superconducting cuprates [35].

Coming to detailed analysis, the obtained energies of the ground state found in the HF approximation and using the local ansatz are shown in table 2. In each case the correlation energy, \( E_{\text{corr}} = E_{\text{HF}} - E_{\text{tot}} \), is rather small. The insulating gap exhibits a non-monotonic behaviour. It is large for the undoped \( \text{La}_2\text{NiO}_4 \) compound \( (x = 0) \), with a HOMO–LUMO gap of 7.42 eV (see table 2). It drops to 1.86 eV for \( x = 0.125 \), and becomes rather small for \( x = 0.25 \), where we found a local minimum of 0.28 eV. In the case of the stripe phase at \( x = 1/3 \) it is again larger (note that the size of the cluster \( 6 \times 6 \) is different here, but this should not significantly influence the estimated gap \( \Delta \)), and next increases steadily up to \( \Delta = 0.91 \) eV at \( x = 0.5 \). This confirms the experimental observation that the \( \text{La}_{2−x}\text{Sr}_x\text{NiO}_4 \) nickelates are insulators [32] in the entire doping regime up to half-doping \( x = 1/2 \).

The role of JT distortions for the phase situation in \( \text{La}_{2−x}\text{Sr}_x\text{NiO}_4 \) has been discussed in the literature [12, 19], but the results are controversial to some extent. In [19] the stripes were attributed to JT distortions but in [12] it was argued (for the model explicitly featuring oxygens in between nickel atoms) that JT distortions are not consistent with the local symmetry and with the experimental results. Our simple effective model is not able to resolve this controversy and to answer the question concerning the origin of the stripe phase found at \( x = 1/3 \) doping as it considers distortions as being independent from one another (i.e., not cooperative). Still, within the framework of the present model we support the claim by Hotta and Dagotto [19] that JT distortions are essential for the development of the stripe order for the doping \( x = 1/3 \). On the other hand, other results of our computations show that the short-range order (on average) does not change
due to the lattice distortions, and it is only the global population of $3z^2 - r^2$ orbitals at defect sites and long-range order which are stabilized by the JT effect.

The results of the present study uncover the fundamental difference between the stripes in cuprates and in nickelates. While a competition between the magnetic energy (superexchange) and the kinetic energy of doped holes drives the stripe structures in doped cuprates [3] with site-centred structures [36, 37], or could also be responsible for stripes in certain $t_{2g}$ systems [13], this mechanism is absent in layered nickelates for two reasons: (i) when hole doping occurs in the $d^0$ (instead of the $d^9$) configuration, the ions occupied by holes carry a spin 1/2 of the remaining $e_g$ electron and participate in the magnetic order, and (ii) the doped ions are active for the JT effect and local distortions form around them. Both these effects suppress the kinetic energy of the doped holes and the competition between the magnetic and kinetic energy is absent. Therefore, the stripes cannot form at low doping (up to $x = 0.25$ considered here) but this regime is dominated by isolated charge defects stabilized by local lattice distortions. The doping $x = 1/3$ is the first one where the doped sites have to appear as next-nearest-neighbours, and they order in the form of a stripe phase. We suggest that the electronic structure has a local minimum for this phase rather than for a random distribution of doped sites. This pattern does not hold at higher doping $x = 0.375$, but decides the stability of the chequerboard phase at the doping $x = 0.5$, where again the configurations with doped ions being next-nearest-neighbours to one another occur along both diagonal directions. Altogether, the diagonal stripe pattern for $x = 1/3$ is thus favoured by the characteristic properties of doped holes in layered nickelates which avoid one another.

Summarizing, the main virtue (in our opinion) of this paper is a demonstration that the same model which worked very well for doped perovskite manganites [24] performs equally well for the layered nickelates. It helped to identify the leading mechanism, being the JT effect in the presence of strong local correlations, responsible for the stripe phase which occurs only at $x = 1/3$ doping and for the chequerboard phase found at $x = 1/2$ doping. At the same time some open questions still remain which could be resolved by future studies. In particular, it would be interesting to perform a theoretical study with cooperative JT distortions including oxygen ions explicitly. Furthermore, it would be very helpful in future theoretical modelling of doped nickelates if a more precise relation between the electron doping level (used in computations) and the chemical electron doping level (used in computations) and the chemical formula could be established.

Acknowledgments

We acknowledge financial support by the Polish Ministry of Science and Higher Education under Project No. N202 104138, A M Oleś was also supported by the Foundation for Polish Science (FNP).

References

[1] Zaenen J and Gunnarsson O 1989 Phys. Rev. B 40 7391
[2] Poliblanc D and Rice T M 1989 Phys. Rev. B 39 9749
[3] Kato M, Machida K, Nakamishi H and Fujita M 1990 J. Phys. Soc. Japan 59 1047
[4] Zaenen J and Oleś A M 1996 Ann. Phys., Lpz. 5 224
[5] Tranquada J M, Sternlib B J, Axe J D, Nakamura Y and Uchida S 1995 Nature 375 561
[6] Kivelson S A, Bindloss I P, Fradkin E, Oganesyan V, Tranquada J E, Kapitulnik A and Howald C 2003 Rev. Mod. Phys. 75 1201
[7] Raczkowski M, Fréraud R and Oleś A M 2006 Low Temp. Phys. 32 305
[8] Vojta M 2009 Adv. Phys. 58 699
[9] Oleś A M 2010 Acta Phys. Pol. A 118 212
[10] Góra D, Rościszewski K and Oleś A M 1999 Phys. Rev. B 60 7429
[11] Rościszewski K and Oleś A M 2003 J. Phys.: Condens. Matter 15 8363
[12] Fleck M, Lichtenstein A I, Pavarini E and Oleś A M 2000 Phys. Rev. Lett. 84 4962
[13] Fleck M, Lichtenstein A I and Oleś A M 2001 Phys. Rev. B 64 134528
[14] Raczkowski M, Fréraud R and Oleś A M 2006 Phys. Rev. B 73 174525
[15] Raczkowski M, Fréraud R and Oleś A M 2006 Europhys. Lett. 76 128
[16] Dagotto E, Hotta T and Moreo A 2001 Phys. Rep. 344 1
[17] Dagotto E 2005 New J. Phys. 7 67
[18] Weisse A and Fehske H 2004 New J. Phys. 6 158
[19] Tokura Y 2006 Rep. Prog. Phys. 69 797
[20] Hotta T, Feiguin A and Dagotto E 2001 Phys. Rev. Lett. 86 4922
[21] Hotta T and Dagotto E 2004 Phys. Rev. Lett. 92 227201
[22] Wöbel P and Oleś A M 2010 Phys. Rev. Lett. 104 206401
[23] Krüger F, Kumar S, Zaenen J and van den Brink J 2009 Phys. Rev. B 79 054504
[24] Tranquada J M, Buttrey D J, Sachan V and Lorenzo J E 1994 Phys. Rev. Lett. 73 1003
[25] Sachan V, Buttrey D J, Tranquada J M, Lorenzo J E and Shirane G 1995 Phys. Rev. B 51 R12742
[26] McQueeney R J, Bishop A R, Yi Y-S and Yu Z G 2000 J. Phys.: Condens. Matter 12 L317
[27] Zaenen J and Littlewood P B 1994 Phys. Rev. B 50 7222
[28] Raczkowski M, Fréraud R and Oleś A M 2006 Phys. Rev. B 73 094429
[29] Yamamoto S, Fujiwara T and Hatsugai Y 2007 Phys. Rev. B 76 165114
[30] Mazin I I, Khomskii D I, Lengsdorf R, Alonso J A, Marshall W G, Ihberson R M, Podlesnyak A, Martinez-Lope M J and Abd-Elmeguid M M 2007 Phys. Rev. Lett. 98 176406
[31] Schwingenschlögl U, Schuster C and Fréraud R 2008 Europhys. Lett. 81 27002
[32] Schwingenschlögl U, Schuster C and Fréraud R 2009 Europhys. Lett. 88 67008
[33] Chen C H, Cheong S-W and Cooper A S 1993 Phys. Rev. Lett. 71 2461
[34] Tranquada J M, Buttrey D J and Sachan V 1996 Phys. Rev. B 54 12318
[35] Kajimoto T, Kakeshita T, Yoshizawa H, Tanabe T, Katsufuji T and Tokura Y 2002 Appl. Phys. A 74 (Suppl.) S1765
[36] Yoshizawa H, Kakeshita T, Kajimoto R, Tanabe T, Katsufuji T and Tokura Y 2000 Phys. Rev. B 61 R854
[37] Freeman P G, Boozhoyd A T, Prabhakaran D, Gonzalez D and Enderle M 2002 Phys. Rev. B 66 212405
[38] Kaimoto R, Ishizaka K, Yoshizawa H and Tokura Y 2003 Phys. Rev. B 67 014511
Vigliante A, von Zimmermann M, Schneider J R, Frello T, Andersen N H, Madsen J, Buttery D J, Gibbs D and Tranquada J M 1997 Phys. Rev. B 56 8248
Du C H, Hhazi M E, Su Y, Hatton P D, Brown S D, Stirling W G, Cooper M J and Cheong S-W 2000 Phys. Rev. Lett. 84 3911
Hatton P D, Ghazi M E, Wilkins S B, Spencer P D, Mannix D, d’Almeida T, Prabhakaran P, Boothroyd A T and Cheong S-W 2002 Physica B 318 289
Ghazi M E, Spencer P D, Wilkins S B, Hatton P D, Mannix D, Prabhakaran D, Boothroyd A T and Cheong S-W 2004 Phys. Rev. B 70 144507
Spencer P D, Ghazi M E, Wilkins S B, Hatton P D, Brown S D, Prabhakaran D and Boothroyd A T 2005 Eur. Phys. J. B 46 27
Rościszewski K and Oleś A M 2007 J. Phys.: Condens. Matter 19 186223
Rościszewski K and Oleś A M 2008 J. Phys.: Condens. Matter 20 365212
Rościszewski K and Oleś A M 2010 J. Phys.: Condens. Matter 22 425601
Oleś A M 1983 Phys. Rev. B 28 327
Popovic Z and Satpathy S 2000 Phys. Rev. Lett. 84 1603
Stollhoff G and Fulde P 1980 J. Chem. Phys. 73 4548
Stollhoff G 1996 J. Chem. Phys. 105 227
Fulde P 1991 Electron Correlations in Molecules and Solids (Springer Series in Solid State Sciences vol 100) (Berlin: Springer)
Cava R J, Batlogg B, Palstra T T, Krajewski J J, Peck W F Jr, Ramirez A P and Rupp L W Jr 1991 Phys. Rev. B 43 1229
Ivanova T A, Jacyna-Onyszkiewicz I and Yablokov Yu V 2002 Phys. Solid State 44 1622
Zaanen J, Paxton A T, Jepsen O and Andersen O K 1988 Phys. Rev. B 60 2685
Masys S, Mickievicius S, Greboinskij S and Jonauskas V 2010 Phys. Rev. B 82 165120
Thanh T D and Hong L V 2008 J. Korean Phys. Soc. 52 1456
Buttrey D J, Honig J M and Rao C N R 1986 J. Solid State Chem. 64 287
Hücker M, Gu G D, Tranquada J M, von Zimmermann M, Klaus H-H, Curro N J, Braden M and Büchner B 2007 Physica C 460–462 170
Oleś A M and Zaanen J 1988 Phys. Rev. B 39 9175
Tranquada T M et al 2008 Phys. Rev. B 78 174529
Greiter M and Schmidt H 2010 Phys. Rev. B 82 144512