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Stripe-like orbital order resulting from pure orientational orbital motion

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Abstract

We introduce an elementary model based upon the orientational nature of orbitals, which may arise from the influence of a cubic-symmetric crystal field. We focus on orbital ordering induced by correlated charge motion: a phenomenon often ignored. Motivated by the Nagaoka ferromagnetism, we seek the analogue single-hole result for our model in the strong-coupling regime. For two-fold degenerate orbitals on the square lattice, we show that the system promotes stripe phases as energetically favourable. In such phases, the system breaks the symmetry, with lines of one species of fermion being periodically separated and the other species filling in the gaps. For the simplest form of stripe, all periodicities are exactly degenerate, but we can show rigorously that such states are actually higher in energy than a small number of more exotic states which show the same long-range behaviour but are locally disrupted from the simplest case. Such states have a preferred periodicity of three.

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1. Introduction

The orbital degree of freedom present in many transition metal compounds, such as those containing the ions Mn^{3+}, Cu^{2+}, must be carefully described in order to produce an accurate model of such compounds. Notably, the point-symmetry of orbitals requires that they behave fundamentally rather differently to spins, in two main ways. Firstly, due to crystal symmetry, each orbital takes on an innate shape and, crucially, *orientation* in space. The consequence of this is that the hopping matrix elements of each orbital become spatially anisotropic. Secondly, while electron spin is conserved upon hopping, electron orbital is not required to be. For cubic *d*-electron systems, the so-called e_g orbitals exhibit both of these properties, whereas the symmetry of the t_{2g} orbitals requires that, under conventional 180° exchange, they show only

the former effect. As well as exchange of orbitals through super-exchange processes, there are also metallization processes where species with different charge move around, such as double-exchange [1]. It is this style of charge motion which is studied in this paper. Specifically, we focus upon a simplified orbital model with a clear susceptibility to *stripe ordering*.

Stripes are not a new phenomenon. High temperature superconductors exhibit a weak form [2], and the analogue nickelates, $La_{1-x}Sr_xNiO_4$ [3], exhibit much more pronounced effects. The heavily studied manganites, $La_{1-x}Ca_xMnO_3$ reveal a plethora of striped phases [4, 5] (although these ordered phases are *not* of paramount interest). Such stripes are often explained as styles of orbital ordering which is another well-documented phenomenon in the literature [6–8]. Indeed, such conundra as V_2O_3 [9, 10], $LiVO_2$ [11, 12] and $RNiO_3$ [13] have all been studied and are not easy to predict. Theoretically, investigation has pursued two main paths. Firstly, in insulating compounds a classical pseudo-spin ordering or a combined spin and pseudo-spin ordering has been looked for [14, 15], using effective Hamiltonians coming from second-order perturbation theory. Secondly, in metals, band-structure calculations (which are glorified mean-field calculations) have been used to investigate the orbital occupancy and charge–density-wave like symmetry breaking [16]. Our model and investigation is not well represented by either of these approaches. Although it is strong coupling, the system is metallic and a classical solution is inappropriate because the hole permutes the spins and requires a proper description. The more aggressive problem is the uselessness of mean-field theory: as the hole changes direction, a site fluctuates between two states and in strongly correlated systems, mean-field theory necessitates a *fixed* state on each site. One needs approaches which go beyond the standard techniques in order to unravel our model.

Although the ultimate target of our studies is the phase diagram of the model, in this paper we demonstrate only one simple limit: an occupancy of one particle per site plus a single hole in the infinite-coupling limit, analogous to the Nagaoka problem for the Hubbard model [17]. While the Hubbard model chooses ferromagnetism as the solution to this problem on bipartite lattices, we shall show that our model has a rather large number of competitive states, all of a similar stripe-like form; detailed investigation picks out one particular style of stripe as the ground state. It will become apparent that this issue is equivalent to selecting a style of *geometry* for the hole, from which the orbital order may be inferred.

This paper is organized in the following way: firstly we introduce the model and describe its behaviour in an elementary way, culminating in the behaviour in the extreme strong-coupling limit. Then we proceed to an investigation of the Nagaoka problem, selecting and discarding potential ground states according to both basic physical intuition and also to some numerical simulation. Having selected a number of competitive states, we exactly solve such geometries. Finally, we discuss these results and also hint at further work performed on this model.

2. Introducing the model

The simplest example of a pure orientational system is provided by the physics of p-orbitals. In a cubic environment a p-orbital may be oriented in the x-, y- or z-direction, and the symmetry of these orbitals immediately posits that there be no inter-orbital hopping. However, there is a strong spatial anisotropy as a consequence of the shape of the orbitals, which is reflected in the hopping matrix elements

$$\begin{aligned} t^{\boldsymbol{x}}_{x\to x} &= t^{\boldsymbol{y}}_{y\to y} = t^{\boldsymbol{z}}_{z\to z} = t_+ \\ t^{\boldsymbol{y},\boldsymbol{z}}_{x\to x} &= t^{\boldsymbol{z},\boldsymbol{x}}_{y\to y} = t^{\boldsymbol{x},\boldsymbol{y}}_{z\to z} = t_- \\ t_{x\to y} &= t_{x\to z} = t_{y\to z} = 0 \end{aligned}$$

where the superscript provides the direction of hopping and the subscripts describe the orbital before and after hopping. It is quite apparent that $t_+ \gg t_-$ and when t_- is neglected, the result is pure directional motion

$$H = -t_+ \sum_{\langle ii' \rangle_x} c^\dagger_{ix} c_{i'x} - t_+ \sum_{\langle ii' \rangle_y} c^\dagger_{iy} c_{i'y} - t_+ \sum_{\langle ii' \rangle_z} c^\dagger_{iz} c_{i'z}.$$

This style of hopping is the essence of the model studied in this paper. Although we have only outlined the case of p-orbitals, we may consider a more general case. For a lattice Λ of coordination number Z, a $(Z/2)$-fold orbital degeneracy is required to provide an analogous model. Inclusive of an on-site Coulomb interaction, the generalized model is

$$H_0 = -t \sum_\alpha \sum_{\langle ii' \rangle_\alpha \in \Lambda} c^\dagger_{i\alpha} c_{i'\alpha} + \frac{U}{2} \sum_i \left(\sum_\alpha c^\dagger_{i\alpha} c_{i\alpha} \right) \left(\sum_{\alpha'} c^\dagger_{i\alpha'} c_{i\alpha'} - 1 \right) \tag{1}$$

where $\alpha(')$ labels the bond direction, $\langle ii' \rangle_\alpha$ denotes the nearest neighbours in the α-direction and the operator $c^{(\dagger)}_\alpha$ annihilates (creates) a fermion in an orbital oriented in the α-direction. We have neglected the spin label of our fermions for the simple reason that we intend to take the strong-coupling limit; we shall comment further on this issue shortly.

In this model, the pseudo-spin is conserved upon each hop. The orbital-type nature comes in via the independent *one-dimensional* hopping of each fermion. Despite this feature, the coupling of the various pseudo-spins via the Coulomb interaction imposes the true lattice dimensionality upon the system. At strong coupling, $t/U \to 0$, the fermion–fermion interaction amounts simply to blocking, where one species of fermions must wait for the other to move in order to occupy a neighbouring site. At half-filling, where the number of fermions $N = |\Lambda|$, the pseudo-spin degeneracy is lifted at second order in degenerate perturbation theory, yielding an Ising-like interaction. For the extreme $U = \infty$ limit, the model maps onto an effective strong-correlation model, analogous to the Hubbard t-model:

$$H_1 = -t \sum_\alpha \sum_{\langle ii' \rangle_\alpha} \left(2 - \sum_{\alpha'} c^\dagger_{i\alpha'} c_{i\alpha'} \right) c^\dagger_{i\alpha} c_{i'\alpha} \left(2 - \sum_{\alpha''} c^\dagger_{i'\alpha''} c_{i'\alpha''} \right). \tag{2}$$

One major reason for studying our chosen model in the ultra-strong-coupling limit, is that the spin degree of freedom becomes *irrelevant*. Since our particles are constrained to move on one-dimensional chains, and the strong-correlations eliminate exchange, statistics become irrelevent and the spin of the particle becomes a degeneracy label. This *huge* simplification makes the model more tractable, but how robust is it and can it invalidate our eventual picture? To understand this issue, we need to think about how the spin degeneracy is lifted as the correlations are reduced and processes at order t^2/U become permitted. The strongest interaction is the kinetic 'exchange' (i.e. any second-order process involving more than one species of particle) of neighbours in different orbitals, essentially irrespective of the spin configuration. Consequently, where this interaction is dominant there will be an inclination towards a staggered orbitally ordered state—the standard Jahn–Teller orbital ordering. The spin degeneracy of this interaction is lifted on a weaker energy scale and is likely to be ferromagnetic; this effect would be ascribed to a Hund's coupling in the intermediate state. The next largest interaction is kinetic exchange of neighbours in the same orbital and this would be expected to control the spin physics and correlate the spins along any chain into an antiferromagnetic Heisenberg-like state (for the particles in the same orbital). As a result, the spins of *different* species are largely uncorrelated, and the antiferromagnetic correlations between the same species would be expected to have little effect on the charge motion, suggesting that the neglect of spin is reasonable.

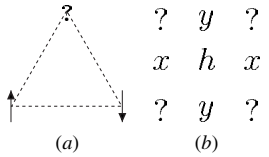

Figure 1. Geometric frustration of (*a*) Heisenberg spins compared to (*b*) 'frustration' of pseudo-spins in the orientational model.

At $U = \infty$, the model has some intriguing features, substantially different to the Hubbard model. Firstly, due to hopping constraints, particles cannot exchange and hence closed loops are eliminated. Secondly, the fermions are strongly limited in their motion and are able to only access a small subset of the lattice Λ, a one-dimensional line on which they reside. This leads to a large number of conservation laws which scales up dramatically with the linear size of the system. Finally, and related to the second feature, the system exhibits a style of frustration similar to geometric frustration. This effect is best illustrated by analogy with the Heisenberg model on a triangle (figure 1(*a*)). There is no way of making all three spins form antiparallel pairs on a triangle, so one cannot naively say what spin state the site labelled with a question mark should take. Returning to the simple example of the directional motion of *p*-orbitals (figure 1(*b*)), the sites labelled with a question mark are also frustrated, as there is no possible choice of pseudo-spin which can enable the hole to access such sites from *both* the nearest neighbours. Much of the difficulty in solving these models arises from this frustration.

Henceforth we limit consideration to the simplest manifestation of this model: that of two-fold degenerate orbitals on the square lattice. Consequently $\alpha = x, y$, and we shall thence refer to our orbital species as x- and y-fermions.

3. A single hole

This paper is purely concerned with the situation of a single hole, where $N = |\Lambda| - 1$, and how the motion of the hole lifts the pseudo-spin degeneracy. The difficulty in solving this problem for the Hubbard model is that the spins may be permuted by the motion of the hole around loops. On bipartite lattices, this issue is resolved by choosing a pure ferromagnet, with a hole energy of $-Zt$. This choice is clearly *not* the ground state for our model due to the hopping constraints. In such an all-x or all-y-fermion state, the hole is confined to move in a one-dimensional subspace only and can achieve an energy of only $-2t$. By including *both* species of fermion, the hole may move in two dimensions and gain extra energy by potentially being able to gain from four hops rather than just two.

It is immediately apparent that the motion of the hole is strongly coupled to the overall pseudo-spin arrangement; in fact, one can consider the pseudo-spin arrangement as producing an effective 'lattice' Λ_{eff} on which the hole is constrained to move (figure 2). As a result, the problem reduces to that of selecting the appropriate lattice which maximizes the kinetic energy of the hole. To motivate our selection, we appeal to small systems in order to obtain intuition about the infinite system. The first task is to resolve the frustration issue of figure 1: one might expect the choice of the frustrated orbitals to be arbitrary, but this is *not* so. Making a choice *biases* the motion parallel to one of the two Cartesian directions and to leading order it is best to reinforce this and choose all four frustrated orbitals to be equivalent. If we choose that the hole should continue this bias (figure 2(*a*)), then we are drawn into considering a *stripe-like*

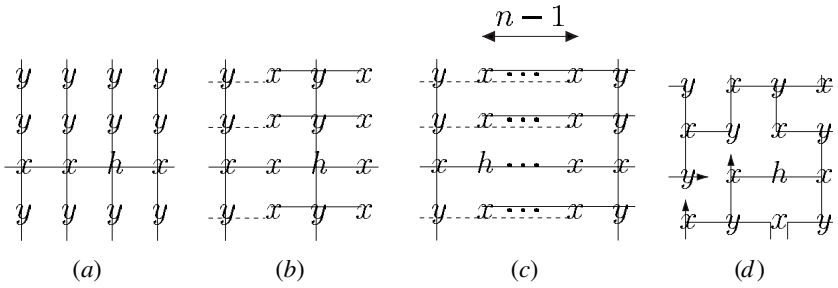

Figure 2. Motion of a hole, h, in pseudo-spin background, for various states; (a) period-one stripe (b) period-two stripe (c) period-n stripe and (d) orbital Néel state. Arrows in rightmost state indicate that many more unique states are generated by hole motion in the arrow direction.

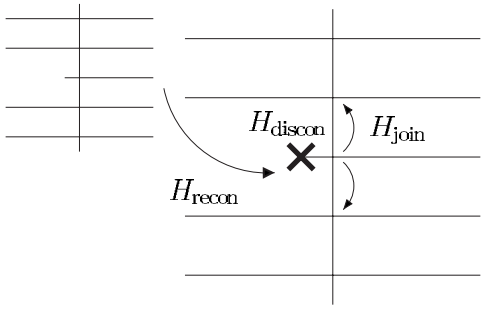

Figure 3. Action of local operators to generate the stripe geometries.

phase, where the hole moves along a central 'backbone' with some tunnelling into the bulk. This style of phase can be generalized into a stripe of arbitrary periodicity, as illustrated in the two central diagrams in figures 2(b) and (c); note that the motion of the hole in all such states leaves the pseudo-spin structure fairly intact. The other 'natural' choice, the orbital antiferromagnet (figure 2(d)), is quite different. The hole is now bounded to a maximum connectivity of three from *any* given site, and as it moves the order is strongly distorted from the pure Néel state. We conjecture that such states are energetically unfavourable, and shall comment further at a later juncture.

Hence, our initial task is to solve the situation of the motion of a single hole on the effective geometry produced by the stripe phases.

$$H_2 = t \sum_{\substack{\langle ii' \rangle \\ i,i' \in \Lambda_{\rm eff}}} h_i^\dagger h_{i'}. \tag{3}$$

We use impurity theory to perform such calculations, and in fact can solve *all* such periodicities simultaneously. This technique cannot be applied easily to nonperiodic stripe phases. The method is described pictorially in figure 3, and is roughly summarized as follows: a collection of finite linear chains are connected together at the origin ($i = j = 0$) with the appropriate tight-binding phase, using $H_{\rm join}$. Then the bond connecting the origin to one nearest neighbour is disconnected, using $H_{\rm discon}$. Finally, we periodically connect up this resulting subgeometry to itself with the phase of a single hop, using $H_{\rm recon}$. Each operator is purely *local* so the three nontrivial Green's functions can be calculated exactly; the poles of the final Green's function provide the hole energy.

We have carried out this analysis, and find that the ground-state energy is *independent of the stripe periodicity*. All stripes have energy

$$E = -2\sqrt{2}t. \tag{4}$$

This result conflicts with the previous idea of 'reinforcing the bias' and suggests that the problem is fundamentally a lot more subtle than the elementary physical ideas so far offered. To try to better understand this result, we have considered the elementary ways in which this degeneracy might be lifted. Probably the simplest mechanism which one might expect to effect this is that of scattering from a localized impurity, and investigation of this issue is straightforward. Curiously, this additional interaction does *not* lift the degeneracy; *all* of the states are reduced in energy by the same amount, governed by the attractive energy of the impurity.

It is important to realise that these states have been chosen purely using intuition, based upon small systems, and it is entirely possible that these states might *not* be favourable. We require a means of testing our conjectured ground states, and the natural way is to use numerics. Performing an effective numerical investigation of the orientational model is rather difficult, largely due to the fact that the number of x-fermions on each row and the number of y-fermions on each column is independently conserved, with the number of conservation laws scaling as the length of a finite system. To reach any large system size, it is imperative that one makes use of these conservation laws. However, for a large system, the number of calculations required grows as L^L, where L is the length of the system, and soon becomes uncontrollable. We concluded that it was more important to make use of the conservation laws than to be completely exhaustive on small systems, enabling us to exactly diagonalize some stripe phases up to a system size of 12×12, while the conventional Lanczos techniques permit *exhaustive* diagonalization of up to only around a 5×5 system. To investigate a representative proportion of the state-space, in addition we diagonalized several thousand random states for increasing size of system. In the cases where the state-space exceeded the computational storage space available to us, we elected to truncate the matrix, providing a variational estimate to the energy. The first style of state to investigate was, of course, the stripe phases which have been analysed analytically. This proved to be slightly more subtle than our simple result might purport, due to the effect of finite size upon any choice of state. We found that the system appears to choose as small a periodicity as possible which is an exact fraction of the system size. As a result, wherever possible, the system forms an alternating stripe phase or the closest it can get to alternating. There are some interesting aberrations, highlighted in table 1, for example for the 8×8 system, where some stripes with a nonuniform separation were found to be of lower energy than the period-four stripe; however, this actually agrees with the criterion above. In diagonalizing all similar stripe phases, no information was observed which contradicted our assertion that the degenerate stripes were indeed the best.

Unfortunately, the use of random states brought up an anomaly: the numerics found a number of exotic states which were of lower energy than even the best stripe phases (in fact, low energy states were *manually* distorted by a few judiciously chosen pseudospin flips to achieve the *very* low energy states). This led us to investigation of the kind of state visualized in figure 4, where the central 'backbone' of x-fermions is enclosed in a central strip of y-fermions, with periodic stripes, as before, at long range. This style of state can be generalized in two ways: by increasing the strip width w or changing the stripe periodicity p. In this scheme, the conventional stripes are interpreted as being of width $w = 1$. Table 1 indicates that almost without exception, these states are of lower energy than the appropriate $w = 1$ stripes; in this table, a Néel state (or variational estimate) is also included for comparison,

Table 1. Summary of numerical results up to a 10×10 system obtained using exact diagonalization, with only a single row of trial state shown. Starred states have $w = 3$, and AF denotes (orbital) antiferromagnetic state.

4×4	Energy	5×5	Energy	6×6	Energy	7×7	Energy
$yxxx*$	−2.903 21	$yxyxx$	−2.865 58	$yxyxyx$	−2.864 63	$yxyxyxx*$	−2.850 80
$yyyy$	−2.903 21	$yxyxx*$	−2.862 41	$yxyxyx*$	−2.860 25	$yxyxyxx$	−2.848 89
$yxyx$	−2.903 21	$yyyyy$	−2.860 81	$yxxyxx*$	−2.854 86	$yxxyxxx*$	−2.846 29
$yyyx*$	−2.888 92	$yyxyx*$	−2.860 51	$yxxyxx$	−2.852 94	$yxxyxxx$	−2.842 95
$yxyx*$	−2.887 94	$yyyyx*$	−2.856 20	$yyyxyx*$	−2.846 76	$yyyyxyx*$	−2.838 52
AF	−2.653 89	AF	−2.686 82	AF	−2.671 91		
8×8	Energy	9×9	Energy	10×10	Energy		
$yxyxyxyx*$	−2.848 35	$yxxyxxyxx*$	−2.846 83	$yxxyxxyxxx*$	−2.842 58		
$yxyxyxyx$	−2.847 10	$yxyxyxyxx*$	−2.843 69	$yxyxyxxyxx*$	−2.842 41		
$yxyxxyxx*$	−2.847 07	$yxxyxxyxx$	−2.842 22	$yxyxyxyxyx*$	−2.842 30		
$yxyxxyxx$	−2.842 63	$yxyxxyxxx*$	−2.840 74	$yxyxxyxyxx*$	−2.840 49		
$yxyxyxxx*$	−2.841 17	$yxyxyxyxx$	−2.832 96	$yxyxyxyxyx$	−2.838 19		

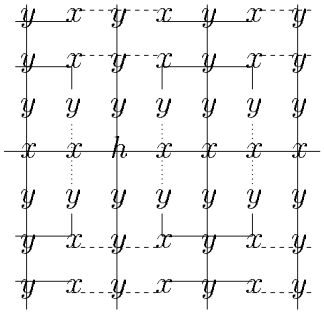

Figure 4. New style of stripe, with central strip width $w = 3$ and stripe periodicity $p = 2$.

highlighting simply how much lower in energy the stripe phases are compared to any other possible state.

These numerical results purport that one should analytically solve these new stripe phases to compare such states for the *infinite* system with our previous analytic results. This can be performed in the same way as for the degenerate stripes, by connecting and disconnecting linear-chain subgeometries, although this task is considerably more complicated for these more exotic geometries. We elected not to generalize these calculations and simply solve the simplest few of these new states directly. Indeed, we calculated the three smallest stripe periodicities for the width-three and width-five systems and all three proved to be lower in energy than the conventional stripes

$$E_{w=3,p=2} = -t2.836\,051\,8\cdots \qquad E_{w=5,p=2} = -t2.830\,253\,2\cdots$$
$$E_{w=3,p=3} = -t2.836\,360\,7\cdots \qquad E_{w=5,p=3} = -t2.830\,993\,8\cdots$$
$$E_{w=3,p=4} = -t2.832\,286\,7\cdots \qquad E_{w=5,p=4} = -t2.830\,090\,4\cdots .$$

The minimum energy is provided by the $w = 3$, $p = 3$ state, which is shown in figure 5.

$$
\begin{array}{cccccccc}
y & x & x & y & x & x & y & x \\
y & x & x & y & x & x & y & x \\
y & x & x & y & x & x & y & x \\
y & y & y & y & y & y & y & y \\
x & x & h & x & x & x & x & x \\
y & y & y & y & y & y & y & y \\
y & x & x & y & x & x & y & x \\
y & x & x & y & x & x & y & x \\
y & x & x & y & x & x & y & x
\end{array}
$$

Figure 5. Proposed ground state for orientational model.

4. Discussion

In this paper, we have introduced an elementary model reflecting one main feature of orbital physics—directional motion. Although such a model can be constructed for many different lattice geometries and orbital degeneracies, we have merely considered the simplest case of doubly degenerate orbitals on the square lattice and discussed the solution of such a model for the case of one electron per site plus one hole in the extreme strong-coupling limit. The solution of this problem for the Hubbard model is well known and proposes a ferromagnetic state for bipartite lattices, while the solution for geometrically frustrated lattices is not generally known. A striking feature of our model is that it exhibits a kind of 'frustration' on any lattice; this immediately leads us intuitively to a selection of stripe-like phases, where the hole moves coherently along a line in one dimension with some 'weak' tunnelling perpendicular to that line at periodic intervals. We proceeded to demonstrate rigorously that such phases, rather unexpectedly, are exactly degenerate. However, a thorough numerical investigation of the problem suggested that these stripes could be slightly modified to lower their energy, by introducing a domain of opposite pseudo-spin surrounding the line of one-dimensional motion. Unlike the previous calculations, a preferred periodicity is promoted. Hence, we predict that the ground state is as shown in figure 5. However, there still may remain states lower in energy, but we are confident that neither intuition nor numerics provide us with anything further to look for.

An interesting issue is how the system has chosen to deal with the frustration. In our best state, the hole can gain from approximately 2.836 hops per site. This state has some sites with connectivity of four, some with connectivity three, some doubly connected and some only singly connected. In *all* of the stripe phases, the system has elected to form many sites with a connectivity of four, even though this implies that there are a number of sites of low connectivity, so biasing the hole towards regions of high connectivity might provide a gain in energy. However, this line of argument is clearly insufficient, as highlighted by the degenerate ($w = 1$) states, which have a wide variety of connectivities. Consequently, we have no real explanation for the choice of the period-three, $w = 3$ stripe as the ground-state, although all states with $w > 1$ necessarily have high connectivity along the *whole* backbone which undoubtedly contributes towards the favourability of these states.

Usually, one considers the single-hole behaviour of a system as being representative of the behaviour at finite U of a *finite fraction* of holes rather than a single hole, as the energetics of the single-hole system are necessarily dominated by the intensive kinetic exchange processes

(which scale with the volume of system) rather than the energy gained by motion in the vicinity of the hole. As a result, our suggestion is that these stripe-like phases will be the natural choice for the system at arbitrary doping, with the stripe periodicity depending on the doping level. However, this reasoning may be fallacious as interactions between holes may drive the system into an entirely different state. We require a significantly more powerful technique to approach the general problem; such a technique shall be discussed elsewhere [18]. However, we believe that the stripe phases remain stable between half and one electron per site, while a ferromagnetic state forms the low density half of the phase diagram.

Acknowledgments

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References

[1] Zener C 1951 *Phys. Rev.* **82** 403
Anderson P W and Hasegawa H 1955 *Phys. Rev.* **100** 675
[2] Cheong S-W *et al* 1991 *Phys. Rev. Lett.* **67** 1791
[3] Yoshizawa H *et al* 2000 *Phys. Rev.* B **61** R854
[4] Goodenough J B 1955 *Phys. Rev.* **100** 564
[5] Mori S, Chen C H and Cheong S-W 1998 *Nature* **392** 473
[6] Kugel K I and Khomskii D I 1982 *Sov. Phys. Usp.* **25** 231
[7] Stojković B P *et al* 2000 *Phys. Rev.* B **62** 4353
[8] Tokura Y and Nagaosa N 2000 *Science* **288** 462
[9] Castellani C, Natoli C R and Ranninger J 1978 *Phys. Rev.* B **18** 4945
[10] Mila F *et al* 2000 *Phys. Rev. Lett.* **85** 1714
[11] Goodenough J B, Dutta G and Manthiram A 1991 *Phys. Rev.* B **43** 10170
[12] Pen H F *et al* 1997 *Phys. Rev.* B **55** 15500
[13] García-Muñoz J L, Rodríguez-Carvajal J and Lacorre P 1994 *Phys. Rev.* B **50** 987
[14] Kugel K I and Khomskii D I 1972 *JETP Lett.* **15** 446
Kugel K I and Khomskii D I 1973 *Sov. Phys.-JETP* **37** 725
[15] Long M W 1998 *Phil. Trans. R. Soc.* A **356** 1493
[16] Popovic Z and Satpathy S 2002 *Phys. Rev. Lett.* **88** 197201
[17] Nagaoka Y 1966 *Phys. Rev.* **147** 392
[18] Guest P M and Long M W 2003 in preparation