Orbital Order, Stripe Phases and Mott Transition in a Planar Model for Manganites

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(Dated: February 1, 2008)

Understanding orbital ordered (OO) Mott insulating states lies at the heart of a consistent resolution of the colossal magneto-resistance (CMR) observed in manganites, where its melting induces a low-$T$ insulator-metal transition for $0.25 \leq x \leq 0.45$. Motivated thereby, we study the OO states in a planar model for bilayer manganites using DMFT and finite-size diagonalisation methods. We derive the correct OO ground states observed in manganites for $x=0, \frac{1}{2}, \frac{3}{4}$ in exact agreement with observations, including the charge-orbital-magnetic ordered stripe phases for $x>\frac{1}{2}$. These OO states are exactly shown to be associated with an “alloy” ordering of the $d_{\alpha x^2-r^2}/d_{\beta y^2-r^2}$ orbitals on each Mn$^{3+}\_\text{C}$ site.

PACS numbers: 71.28+d,71.30+h,72.10-d

Colossal magnetoresistance (CMR) materials have received much attention\textsuperscript{[1, 2]}, due to their extreme sensitivity to small perturbations\textsuperscript{[3]}. The parent (cubic perovskite) materials are Mott-Hubbard insulators with $G$-type (AF) orbital order of $d_{\alpha x^2-r^2}/d_{\beta y^2-r^2}$ orbitals and $A$-type AF spin order\textsuperscript{[3]}. Upon hole doping, $x$ (divalent ion substitution) in La$_{1-x}$Ca$_x$MnO$_3$, for example, they evolve through ferromagnetic, orbital ordered (OO) Mott insulators with unusual properties\textsuperscript{[4]}, to a ferromagnetic metal (FM) at low-$T$. A transition to a paramagnetic insulator (PI), dependent upon cation-dopant type, is seen for $T > T_c$\textsuperscript{[3]}. A small magnetic field suppresses this I-M transition, leading to CMR. These phenomena are also seen in bilayer manganites. Further, more “strange” OO states are found in “overdoped” (with Ca) manganites. The half-doped manganites show a charge (C), orbital and AF order that is very sensitive to small perturbations\textsuperscript{[3]} ($H_{\text{ext}} = 5 - 7$ T gives a ferromagnetic metal with no CO/OO). The “overdoped” manganites with $x = \frac{1}{2}, \frac{3}{4}$ show extremely stable pairs of Mn$^{3+}\_\text{O}_6$ Jahn-Teller distorted stripes having periods between 2 - 5$a$ (a=unit cell length); for other values of $x$, a mixture of the two adjacent commensurate configurations is found\textsuperscript{[5]}. For $x = 1$, CaMnO$_3$ is again an AF ($S = \frac{3}{2}, t_{2g}$) Mott insulator. Finally, the correlated nature of manganites is shown by dynamical spectral weight transfer (SWT) over large energy scales $O(4.0 \text{eV})$ in various\textsuperscript{[7, 8, 9]} studies as a function of $x, T, B_{\text{ext}}$ - this can only result from strong electronic correlations. The importance of the Jahn-Teller (JT) coupling is evidenced by the large isotope effects\textsuperscript{[10]} and by I-M transitions driven by $O^{18} \rightarrow O^{16}$ isotope substitution\textsuperscript{[11]} (see, however, Ref.\textsuperscript{[12]}, where the JT coupling is argued to be much weaker than in\textsuperscript{[10, 11]}). Thus, understanding CMR is inextricably linked to understanding how these strongly coupled orbital-spin-charge correlations are modified by small perturbations as a function of $x$. A unified description of these unusual observations in one picture is a formidable challenge for theory.

The CMR problem has been extensively tackled in literature\textsuperscript{[13, 14]} using a variety of numerical and analytic (QMC and $D = \infty$) methods, for double exchange (DE) models, with/without Jahn-Teller phonons, as well as with strong multi-orbital Coulomb interactions with static/dynamic JT phonons\textsuperscript{[14]}. For OO states, the full multi-orbital Hubbard model has been studied by mapping it to a Kugel-Khomskii (KK) model\textsuperscript{[15]}. However, a controlled treatment (semiclassical analysis\textsuperscript{[16]} indicates an order-by-disorder mechanism) is hard: even the type of order is unclear there, and the results sensitively depend on the approximations used\textsuperscript{[17]}

Here, we take the first step to study the OO, Mott insulating phases observed in CMR manganites within a 2D, multi-orbital Hubbard model incorporating the above-mentioned strongly coupled correlations. Our conclusions apply, with small additional modifications (to be treated separately) to bilayer manganites. We show that a 2D model suffices to capture the correct OO states observed as a function of doping, $x$, and leave the full 3D problem for a separate work. Going beyond previous studies\textsuperscript{[14, 17]}, we show how incorporation of the realistic structure of a single MnO$_4$ layer explicitly in the one-electron hopping integrals introduces new, unanticipated features, making a qualitative difference to the physical results for all $x$. Further, we show how the “strange” stripe-ordered phases in the global phase diagram are naturally rationalised from our effective model.

We start with a model that explicitly includes orbital degeneracy of the $e_g$ orbitals in manganites\textsuperscript{[2]},

\begin{equation}
H = - \sum_{i<j>\alpha,\beta} t_{ij}^{\alpha\beta} (a^{\dagger}_{i\alpha} b_{j\beta} + h.c) + U \sum_{i,\beta=a,b} n_{i\beta} n_{i\beta\dagger} + U' \sum_{i,\sigma,\sigma'} n_{i\sigma} n_{i\sigma'} - J_H \sum_{i,\sigma,\sigma'} S_{i\sigma}^{\dagger} \cdot \sigma (a_{i\sigma} a_{i\sigma'} + b_{i\sigma}^{\dagger} b_{i\sigma'}) + H_{JT},
\end{equation}

where the $a$ and $b$ are fermion annihilation operators in the doubly degenerate $e_g$ orbitals, $t_{ij}^{\alpha\beta} (a, b =$
$d_{3z^2-r^2}, d_{3p^2-r^2}$) is a 2x2 matrix in orbital space incorporating realistic features of the basic Mn-O perovskite structure [18]. $U, U'$ are the on-site, intra- and inter-orbital Hubbard interactions, and $J_H$ is the (strong) Hund’s rule coupling giving rise to the FM state as in the usual DE model. Polaronic effects are described by $H_{JT}$ (see below).

At strong coupling, setting $U, J_H >> t$ gives the following effective Hamiltonian, $H_0 = -\sum_{ij\alpha,\beta,\mu} t_{ij}^{\alpha\beta}(\gamma_{ij}(S)(a_i^{\dagger}\beta_{j} + h.c)$ with $\mu = x, y$. Here, $t_x = \frac{t}{\sqrt{3}[\sqrt{3}, \sqrt{3}, 1]$ and $t_y = \frac{t}{\sqrt{3}[-\sqrt{3}, \sqrt{3}, 1]$ define the one-electron hopping matrix for a single manganite layer. We now turn on $U'$. One is effectively dealing with spinless fermions, but now with an orbital index. Clearly, this model ($U' = 0$) cannot access the interplay between magnetism and OO in manganites. With $U'$ and the JT coupling terms, $H$ becomes

$$H_{eff} = H_0 + U' \sum_{i,\alpha,\beta} n_{i\alpha}n_{i\beta} + H_{JT},$$

where $\gamma_{ij}(S)$ is the usual DE projection factor [3].

Transform to new variables, $c_{\alpha \uparrow} = (a + (-1)^n\sqrt{3}b)/\sqrt{2}$, $c_{\alpha \downarrow} = (-1)^n\sqrt{3}a - b)/\sqrt{2}$ with $(-1)^n \equiv \pm 1$ ($\alpha | x \rangle$ and $\equiv -1$ ($\alpha | y \rangle$. The $c_{\alpha \alpha}$ transform exactly like $d_{3z^2-r^2}(\uparrow), d_{3p^2-r^2}(\downarrow)$. This exactly yields a Falicov-Kimball model (FKM) where only the $c_{\alpha \uparrow}$ hop; the $c_{\alpha \downarrow}$ are strictly immobile as long as no JT distortions are included. Thus,

$$H_{eff} = \sum_{i,j>\alpha} t_{ij}(S)(c_{i\alpha \uparrow}c_{j\alpha \downarrow} + h.c) + U' \sum_{i,\alpha} n_{i\alpha}n_{i\alpha} + H_{JT} \equiv H_{FKM} + H_{JT},$$

reflecting the correlation between the magnetic and orbital degrees of freedom described above.

In orbital space, the JT coupling corresponds to addition of external fields [18], $H_{JT} = Q_2 \sum_{\alpha}(n_{i\alpha} - n_{i\beta}) + Q_3 \sum_{\alpha}(a_i^{\dagger}b_{i} + h.c)$. In the rotated basis, this is,

$$H_{JT} = Q_{++} \sum_{i,\alpha}(n_{i\alpha \uparrow} - n_{i\alpha \downarrow}) + Q_{+-} \sum_{i,\alpha}(c_{i\alpha \uparrow}c_{i\alpha \downarrow} + h.c),$$

where $Q_{++} = ((-1)^n\sqrt{3}Q_2 - Q_3)/2$ and $Q_{+-} = (Q_2 + (-1)^n\sqrt{3}Q_3)/2$ are staggered JT distortions which follow the orbital (electronic) variables. So $H_{eff} = H_{FKM} + H_{JT}$ is a FKM with a local, staggered hybridisation between the $c_{\alpha \uparrow}, c_{\alpha \downarrow}$ at each site. Inclusion of finite phonon frequency ($M\Omega^2(Q_2^2 + Q_3^2)/2$) and intersite phonon coupling terms is required in a full analysis: we have not done this here.

For a half-filled band of spinless fermions, the exact solution of $H$ in $D = 2$ implies an anti-ferro orbital order of $d_{3z^2-r^2}, d_{3p^2-r^2}$, exactly as required [19]. Such a FKM has been employed earlier [14, 17] for manganites, but $c_{\alpha \uparrow} = d_{3z^2-y^2}, c_{\alpha \downarrow} = d_{3z^2-r^2}$. This would lead to an AFOO of $d_{3z^2-y^2}/d_{3z^2-r^2}$, at variance with observations. Here, such a FKM follows exactly from the realistic hopping structure. Moreover, the AF-OO (Mott insulating, see below) state is driven by large $U'$, in contrast with band-based scenarios. We note that Yamasaki et al. [20] have derived an AF-OO Mott insulator for cubic LaMnO$_3$ (with $x = 0$) using LDA+DMFT. Our work is thus complementary to theirs for $x = 0$, but goes much further, permitting us to study the “exotic” OO states for $x > \frac{1}{2}$ as well (see below). Moreover, given our effective FK mapping [21], the OO state(s) are readily understood in terms of an “alloy” ordering of $d_{3z^2-r^2}, d_{3p^2-r^2}$ orbitals at each $Mn$ site.

We now solve $H_{eff} = H_{FKM} + H_{JT}$ in $d = \infty$. As shown earlier [19], DMFT works surprisingly well for the 2D FKM. The FKM with/without $Q_{+-}$ has an almost exact solution in $D = \infty$ [22]. The formalism is essentially the same as that used previously, and gives very good agreement with QMC results for the same model [23]. Keeping $U'/t$ fixed and large, phase transitions from the Mott insulator with AF-OO to correlated (incoherent) metal with no OO, to a correlation-assisted band insulator, again with AF-OO, occur: this is indeed borne out in the $D = \infty$ solution, as shown in Fig. 1. Given that $U'$ is much larger than $Q_{++}, Q_{+-}$ in $H$ above, we conclude that manganites fall into the CMI class with AF-OO, and that the JT terms lead to additional stabilization of both. Finally, DMFT gives the full, correlated spectral functions of the model for arbitrary parameter values and band-fillings, at a very modest numerical cost. This allows us to study the filling driven Mott transition.
Away from an AFOO Mott insulator to an incoherent metal (see below).

The relevant DMFT equations were derived earlier [22], so we do not repeat them here. Since the JT terms are staggered, but bilinear in the $e_g$ basis, they are easily incorporated into the earlier DMFT structure. The Green function is now a $(2 \times 2)$ matrix in orbital space. The staggered, JT “external field” terms imply an averaging over their orientations, which is carried out within the DMFT equations to yield the DOS. We choose $U' = 2.6$ eV, $Q_{++} = 0.3$ eV, $Q_{+-} = 0.4$ eV as model parameters along with a non-interacting DOS for the 2D square lattice with bandwidth, $W = 2.0$ eV and variable band-filling, $n = (1 - x)$, in the DMFT solution. For $n = 1$, (see Fig. 2) we obtain an AFOO Mott insulator. This is obtained from the computed value of $D_{1\alpha} = (-1)^{\alpha}(\langle i\alpha^\dagger c_{i\alpha\uparrow} + h.c. \rangle) = C(\nu_r, Q_{++}+, -) = 0.07$ and $D_{2\alpha} = (-1)^{\alpha}(\langle n_{i\alpha\uparrow} - n_{i\alpha\downarrow} \rangle) = C(\nu_r, Q_{++}+, -) = 0.05$ (not shown), obtained directly from $D_{2\alpha} = -\frac{1}{2} \int \sigma \text{Im} G_{\alpha\sigma}(\omega) d\omega$ and $D_{1\alpha} = -\frac{1}{2} \int \text{Im} G_{\alpha\uparrow\downarrow}(\omega) d\omega$ from the DMFT equations. From away from $n = 1$, the DMFT equations have to be supplemented with the Friedel-Luttinger sum rule, $\langle n \rangle = -\frac{1}{2} \int_{-\infty}^{\infty} \sum_{\alpha, \sigma} \text{Im} G_{\alpha\sigma}(\omega) d\omega$. This is computed self-consistently within the DMFT.

For $\langle n \rangle = 0.9, 0.8$, we obtain an incoherent, pseudogapped, metallic state (see Fig. 2) with a sharp reduction of local anti-ferro orbital (AFO) correlations ($D_{1\alpha} = 0.009$). Thus, appearance of the doping-driven (FM) metallic state is intimately linked to the “melting” of local anti-ferro orbital correlations of the Mott insulator with $x$. The non-FL character of the FM contrasts with what is expected in the FKM with uniform hybridisation ($V = Q_{++}$ in the usual FKM with hybridization), where a correlated FL metal is obtained whenever $V$ is relevant [24]. In our model, the staggered “fields” $Q_{++}$, $Q_{+-}$ produce a low-energy pseudogap, suppressing FL coherence. Chemical disorder will further reinforce incoherence [26]. Given the $d$-wave character of the staggered JT terms (note that both $Q_{++}$, $Q_{+-}$ have components that change sign under a $\pi/2$ rotation in $xy$ plane), as well as the (more important) fact that $d$-wave ground states are obtained near half-filling in a Hubbard-like (FKM) model [27], we predict that this incoherent FM-metal phase will exhibit a $d$-wave pseudogap.

In contrast to earlier FKM work [14, 17], however, the ordered, insulating phases in un(doped) manganites arise naturally from our model. The checkerboard order of $d_{3x^2-r^2}, d_{3y^2-r^2}$ corresponds to an AFOO insulator. The exotic bi-stripe states too are naturally predicted from the analysis of our FKM. In the insulating phases, the “hybridisation” ($Q_{++}$) is irrelevant, and the resulting FKM rigorously undergoes phase separation into hole-rich (orbital disordered) and hole-poor (orbitally ordered) phases, as shown by Freericks et al. [21] by minimizing the total energy for various $x$. We have repeated their analysis for various $x \geq 0.5$. For $x = \frac{1}{2}, \frac{3}{4}, \frac{7}{8}$, we obtain stripe phases with periods $2, 3, 4, 5$, as observed by Mori et al. [8] using electron diffraction. In Fig. 3 we show only the OO ground states for $x = \frac{1}{2}, \frac{3}{4}$, these exactly correspond to those observed in manganites for
these hole dopings.

Given that $Mn^{3+,4+}$ correspond to one/zero $e_g$ electron on each $Mn$ site, the 2D model automatically has charge order (CO) of the correct types for these values of $x$. Also, the stripe OO of pairs of $Mn^{3+}O_6$ (distorted) octahedra automatically corresponds to a bi-stripe charge-order (CO) of $e_g$ electrons with the periodicity determined by $x$ [2]. Given the bi-stripe OO states, Goodenough-Kanamori-Anderson rules directly imply that intersite interactions between the “core” $t_{2g}$ spins ($S = 3/2$) will lead to AF-coupled ladders ($Mn^{3+}$) separated by strips of JT-distorted ($Mn^{4+}$) regions. Given suppression of $e_g$ hopping in an AF “background”, these stripe states will be insulators, as observed [1, 2]. These states will be further stabilised upon inclusion of JT terms and longer range elastic interactions.

To conclude, we have shown how consideration of the actual multi-orbital structure of the hopping matrix in the $e_g$ sector within a multi-orbital correlated model results in an understanding of the various OO insulating phases observed in CMR manganites, especially in bilayer cases, as a function of $x$. These are now understood simply as an “alloy” ordering of $d_{3z^2-r^2}, d_{3g^2-r^2}$ orbitals, driven predominantly by the inter-orbital correlations ($U'$). Our study shows that OO in overdoped ($x > 0.5$) manganites need not imply very strong JT coupling, in agreement with [12]: by itself, $U'$ leads directly to such phases as a function of $x$. A moderate JT distortion will further stabilise these ordered phases. Within multi-orbital DMFT, we have shown how an AFOO/F Mott insulator turns into a correlated, incoherent, ferromagnetic “bad metal” upon hole doping. This goes hand-in-hand with a drop in local AFO correlations. These results are fully consistent with indications from a host of experiments probing various phases of doped bilayer manganites. Interestingly, planar nickelates are also modelled by a similar Hamiltonian, and our work also naturally explains the OO/stripe phases observed there [24]. We expect our analysis to be broadly applicable to a variety of TMO systems showing a variety of OO/magnetic ground states as a function of a suitable “tuning parameter”.

M.S.L thanks Prof. P. Fulde for advice and support at the MPIPKS, Dresden. L.C. thanks the Emmy Noether-Programm of the DFG for financial support.

[1] see “Colossal Magnetoresistance Manganites”, ed. Y. Tokura (Gordon and Breach, New York, 2000).
[2] see “Nanoscale Phase Separation in Manganites”, by E. Dagotto (Springer Verlag, NY and Heidelberg, 2002), and references therein.
[3] S. Ishihara, J. Inoue, and S. Maekawa, Phys. Rev. B 55, 8280 (1997).
[4] S. Uhlenbruck et al., Phys. Rev. Lett. 82, 185 (1999).
[5] Y. Tomioka et al., Phys. Rev. Lett. 74, 5108 (1995).
[6] S. Mori, C. H. Chen and S.-W. Cheong, Nature 392, 473 (1998).
[7] Y. Okimoto et al., Phys. Rev. Lett. 75, 109 (1995).
[8] D. Dessau et al., Phys. Rev. Lett. 81, 192 (1998).
[9] J. Simpson et al., Phys. Rev. B 60, R16263 (1999).
[10] G.-M. Zhao et al., Nature, (London) 381, 676 (1996).
[11] N. A. Babushshina et al., Nature 391, 159 (1998).
[12] J. C. Loudon et al., Phys. Rev. Lett. 94, 097202 (2005).
[13] N. Furukawa, J. Phys. Soc. Jpn. 64, 2734 (1995); see also Ref. [2].
[14] M. S. Laad, L. Craco, and E. Müller-Hartmann, Phys. Rev. B 63, 214419 (2001); T. V. Ramakrishnan et al., in “Colossal Magnetoresistance Manganites”, ed T. Chat-terji, Kluwer Acad. Publ, Netherlands (2003).
[15] K. Kugel and D. I. Khomskii, Sov. Phys.-JETP 37, 725 (1973).
[16] G. Khaliullin and V. Oudovenko, Phys. Rev. B 56, R14243 (1997); L. F. Feiner, A. M. Oles, and J. Zas-zen, J. Phys. Cond. Matter. 10, L555 (1998). These reach opposite conclusions, which sensitively depend on the decouplings used.
[17] V. Ferrari, M.J. Rozenberg, and R. Weht, Mod. Phys. Lett. B 15, 1031 (2001); also see Ref. [14].
[18] T. Kennedy and E. H. Lieb, Physica 138A, 320 (1986); ibid E. H. Lieb, Physica 140A, 240 (1986).
[19] J. Freericks and V. Zlatić, Rev. Mod. Phys. 75, 1333 (2003).
[20] A. Yamasaki et al., Phys. Rev. Lett. 96, 166401 (2006).
[21] R. Lemsanski, J. K. Freericks, and G. Banach, J. Stat. Phys. 116, 699 (2004).
[22] L. Craco, Phys. Rev. B 59, 14837 (1999).
[23] Q. Si et al., Phys. Rev. Lett. 72, 2761 (1994).
[24] E. Müller-Hartmann, T. V. Ramakrishnan, and G. Touloise, Phys. Rev. B 3, 1102 (1971).
[25] T. Stanescu and G. Kotliar, Phys. Rev. B 74, 125110 (2006).
[26] M. S. Laad, L. Craco, and E. Müller-Hartmann, Phys. Rev. B 64, 195114 (2001).
[27] D. de Fontaine, in “Solid State Physics”, eds. H. Ehrenreich et al., Vol 34, pg. 73 (Academic Press, NY, 1979).
[28] A. Taraphder, J. Phys. Condens. Matt. 19, 125218 (2007).
[29] T. Hotta and E. Dagotto, Phys. Rev. Lett. 92, 227201 (2004).