Unveiling New Magnetic Phases of Undoped and Doped Manganites

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Novel ground-state spin structures in undoped and lightly-doped manganites are here investigated based on the orbital-degenerate double-exchange (DE) model, by using mean-field and numerical techniques. In undoped manganites, a new antiferromagnetic (AFM) state, called the E-type phase, is found adjacent in parameter space to the A-type AFM phase. Its structure is in agreement with recent experimental results. This insulating E-AFM state is also competing with a ferromagnetic metallic phase as well, suggesting that large magneto-resistant effects could exist even in undoped Mn oxides. For doped layered manganites, the phase diagram includes another new AFM phase of the $\mathrm{C}_x\mathrm{E}_{1-x}$-type. Experimental signatures of the new phases are discussed.

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In the recent decade, the study of manganites – materials that show a remarkable Colossal Magneto-Resistance (CMR) – has been one of the most important areas of research in condensed matter. This CMR effect occurs when the manganite ground-state changes from insulating to ferromagnetic (FM) metallic after a small magnetic field is applied. Based on the concept of two-phase competition, the CMR behavior has been successfully qualitatively reproduced in computational simulations employing resistor-network models. However, more work remains to be done to fully understand Mn oxides, both regarding their unusual magneto-transport properties and the nature of the many competing phases.

The appearance of the FM metallic phase in manganites is usually rationalized by the so-called Hund coupling between mobile $e_g$ electrons and localized $t_{2g}$ spins. On the other hand, the insulating phase in manganites occurs due to the coupling between degenerate $e_g$ electrons and Jahn-Teller (JT) distortions of the MnO$_6$ octahedra, leading to the various types of charge and/or orbital orderings observed experimentally.

The parent compound of CMR manganites is undoped RMnO$_3$, where R denotes rare earth ions. For R=La, as is well-known, the A-type antiferromagnetic (AFM) phase appears, with the C-type ordering of $(3x^2-r^2)$- and $(3y^2-r^2)$-orbitals. By substituting La by alkaline earth ions such as Sr and Ca, holes are doped into the $e_g$-electron band and due to the DE mechanism, the FM metallic phase occurs, with its concomitant CMR effect. Most of the discussion in manganites has centered on the many phases induced by doping with holes the A-type AFM state, at different values of their bandwidths. In this framework, it is implicitly assumed that the undoped material is always in an A-type state. However, quite recently, a new AFM phase has been reported as the ground-state in the undoped limit for R=Ho, suggesting that CMR effects could be found even at $x=0$. Light-hole doping of the E-type phase is also discussed and another novel magnetic phase, defined as the “$\mathrm{C}_x\mathrm{E}_{1-x}$” phase, is found. The ubiquitous phase-separation tendencies observed when insulating and metallic phases compete is also expected near the FM–$\mathrm{C}_x\mathrm{E}_{1-x}$ boundary.

The Hamiltonian studied in this paper is

$$H = - \sum_{i\alpha\gamma\sigma} t^{\alpha}_{i\sigma} d^\dagger_{i\gamma\sigma} d_{i\alpha\gamma\sigma} - J_H \sum_i s_i \cdot s_j$$

$$+ J_{AF} \sum_{(i,j)} s_i \cdot s_j + \lambda \sum_i (Q_{1i} \tau_i + Q_{2i} \tau_{3i} + Q_{3i} \tau_{x})$$

$$+ \left(1/2\right) \sum_i (\beta Q_{1i}^2 + Q_{2i}^2 + Q_{3i}^2),$$

(1)
where \( d_{i\sigma \sigma'} \) (\( d_{i\sigma \sigma'} \)) annihilates an \( e_g \)-electron with spin \( \sigma \) in the \( d_{i2 \gamma \sigma', \gamma'} \) (\( d_{i2 \gamma \sigma', \gamma'} \)) orbital at site \( i \), and \( a \) is the vector connecting nearest-neighbor (NN) sites. The first term is the NN hopping of \( e_g \) electrons with amplitude \( t_{\gamma \gamma'} \) between \( \gamma \)- and \( \gamma' \)-orbitals along the \( a \)-direction: 

\[
t_{\gamma \gamma'} = -\sqrt{3} t_{\gamma \gamma'} - \sqrt{3} t_{\gamma \gamma'} = t \\
\]

for \( a = x \), \( t_{\gamma \gamma'} = \sqrt{3} t_{\gamma \gamma'} = 3t_{\gamma \gamma'} = t \\
\]

for \( a = y \), and \( t_{\gamma \gamma'} = 4t/3 \) with \( t_{\gamma \gamma'} = t_{\gamma \gamma'} = t_{\gamma \gamma'} = 0 \) for \( a = z \). Hereafter, \( t \) is taken as the energy unit. In the second term, the Hund coupling \( J_H (> 0) \) links \( e_g \) electrons with spin \( S_i = \sum_{\gamma} d_{\gamma \sigma}^{\dagger} \sigma_{\gamma} \sigma_{\gamma} \) with the localized \( t_{2g} \) spin \( S_i \) assumed classical with \( |S_i| = 1 \). \( J_H \) is here considered as infinite or very large. The third term is the AFM coupling \( J_{AF} \) between NN \( t_{2g} \) spins. The fourth term couples \( e_g \) electrons and MnO\( 6 \) octahedra distortions \( [11] \). \( \lambda \) is a dimensionless coupling constant, \( Q_{11} \) is the breathing-mode distortion, \( Q_{22} \) and \( Q_{33} \) are, respectively, \( (x^2−y^2) \)- and \( (3z^2−r^2) \)-type JT-mode distortions, \( p_1 = \sum_{\alpha} d_{\alpha \sigma}^{\dagger} d_{\alpha \sigma} \), \( p_2 = \sum_{\alpha, \sigma} d_{\alpha \sigma}^{\dagger} \sigma_{\alpha} \sigma_{\alpha} + d_{\alpha \sigma} \sigma_{\alpha} \sigma_{\alpha} \), and \( p_3 = \sum_{\alpha, \sigma} (d_{\alpha \sigma}^{\dagger} d_{\alpha \sigma} − d_{\alpha \sigma}^{\dagger} d_{\alpha \sigma}) \). The fifth term is the usual quadratic potential for adiabatic distortions and \( \beta \) is the spring-constants ratio for breathing- and JT-modes. In actual manganites, \( \beta = 2 \). In undoped manganites, all oxygens are shared by adjacent MnO\( 6 \) octahedra and the distortions are not independent, suggesting that the cooperative effect is even more important than for the doped case \( x > 0 \). To consider this cooperation, here oxygen ion displacements are directly optimized \([12]\).

Let us first describe our two-dimensional (2D) results, which essentially the physics behind the stabilization of the E-type phase can be grasped by using MC simulations with relatively short CPU times. The phase diagram on a \( 4 \times 4 \) lattice is shown in Fig. 1(a). The continuous curves are obtained by comparing the energies of the competing phases in the MF calculations, while the circles are obtained by monitoring the nature of the dominant spin correlation \( S(\mathbf{q}) \) in MC simulations. A typical result for \( S(\mathbf{q}) \) is shown in Fig. 1(b). A new regime characterized by \( q = (\pi/2, \pi/2) \) is clearly observed between the FM and G-AFM phases. The good agreement between MF and MC results in the region of interest shows the high accuracy of the present MF calculations for manganites \([14]\).

In Fig. 1(c), the spin and orbital structure of the novel intermediate phase (E-phase) is shown. Along the zigzag chains, \( t_{2g} \) spins order ferromagnetically, but they are antiparallel perpendicular to the zigzag direction. In the three-dimensional (3D) case, the MF study shows that the pattern Fig. 1(c) just stacks along the \( z \)-axis, while the spin directions are reversed from plane to plane. Note that the orbital structure is the same as that of the AFM phase, namely, the staggered pattern of \( (3x^2−r^2) \)- and \( (3y^2−r^2) \)-like orbitals. Our investigations show that the E-phase is robust at weak- and intermediate-\( \lambda \), but for \( \lambda > 1.5 \), the E-type regime narrows.

A surprising aspect of our results is that the E-type spin arrangement is the ground-state for a wide range of \( J_{AF} \), even at \( \lambda = 0 \), indicating that the coupling with JT phonons is not a necessary condition for its stabilization. This is in sharp contrast to the case of the A-AFM phase. To understand this point, it is instructive to study the \( e_g \)-electronic structure of the zigzag FM chains that appear in the E-phase spin arrangement. Taking \( J_H \) as infinity for simplicity, the \( e_g \) electrons move only along the zigzag FM chain, and cannot hop to the adjacent FM chains. The dispersion energy for \( e_g \) electrons in this zigzag FM chain is given by \( \varepsilon_{e_g} = (2/3)(\cos \delta \pm \sqrt{\cos^2 \delta + 3}) \) and \( (2/3)(−\cos \delta \pm \sqrt{\cos^2 \delta + 3}) \), indicating that there appears a large band gap equal to \( 4t/3 \) at half-filling. In fact, even on the \( 4 \times 4 \) cluster, there is a clear gap of the order of \( t \) for the E-phase in the density of states (DOS) (Fig. 1(d)). Since \( t_{\mu \nu} = −t_{\mu \nu} \) for \( \mu \neq \nu \), the sign in the hopping amplitude changes periodically in the zigzag situa-
tion, leading to a periodic potential for $e_g$ electrons and its concomitant band-insulator nature. In other words, the E-type phase is stable due to the zigzag geometry of the FM chains that induce a band-insulator 16.

Another related interesting point is the orbital structure of the FM phase. In the strong-coupling region, an orbitally ordered (OO) state appears, essentially with the same pattern as that observed in the E-AFM phase for large $\lambda$. The OO pattern for large $\lambda$ may change in larger systems 16.

Fermi level in the DOS (Fig. 1(e)). The transition observed using a 4x4 bi-layer lattice. All solid lines emerge from MF calculations.

FIG. 2: (a) Energies of the FM, A-AFM, E-AFM, C-AFM, and G-AFM phases on 4x4x2 bi-layer lattices ($\lambda=1.5$). Solid circles indicate the results of optimizations, while lines denote the MF results. (b) Phase diagram for the 4x4x4 cubic lattice. The transition between E-AFM and FM phases is at the heart of the CMR phenomena, by tuning experimentally the lattice parameters in RMnO$_3$, which is intuitively reasonable. Note that near $\lambda\approx 1.6$, a realistic value for manganites, the A-AFM phase is adjacent to the E-type state. This region could correspond to the actual situation observed in experiments for RMnO$_3$. When the ionic radius of the R-site decreases, $T_N$ of the A-AFM phase decreases as well, and eventually the E-AFM phase is stabilized for R=Ho 6. In the weak-coupling region, the E-type phase is stable in a wide range of $J_{AF}$, as in the 2D calculation.

Consider now the very interesting effect of light hole doping on the E-phase. Hole doping will be here studied in the weak coupling limit, since the E-type phase is well understood at $\lambda=0$. Figure 3(a) shows the ground-state phase diagram in the $(x, J_{AF})$ plane, obtained using analytic calculations on 2D lattices at $\lambda=0$. A remarkable feature of this phase diagram is the appearance of the novel C$_x$E$_{1-x}$ phase, composed of long-period zigzag FM chains, antiferromagnetically coupled to each other (see Fig. 3(b) for $x=1/6$). As the doping fraction grows, it is expected that the previously reported

FIG. 3: (a) Phase diagram in the $(x, J_{AF})$ plane for layered manganites at $\lambda=0$ obtained by analytic calculations. (b) Schematic view for spin structure of the C$_{1/6}$E$_{5/6}$-type phase at $x=1/6$. Hatched squares denote hole-rich C-type regions. (c) $S(q)$ and (d) the DOS in the C$_{1/6}$E$_{5/6}$-type phase.
In practice, considering sites $i$ and $i+a$, the oxygen in between is allowed to move along the $a$-axis, i.e., buckling and rotations are neglected. In the 2D case apical oxygens are assumed to be fixed, consistent with previous treatments to produce stripe-like charge ordering in the 2D FM-phase.

Note that the curvature of the boundary between FM and $C_xE_{1-x}$ phases is found to be negative for $0 \leq x < 0.5$, indicating that phase separation occurs between those two phases. Here it is again stressed that the FM phase is metallic, while $C_xE_{1-x}$ is insulating. The latter can be considered as a microscopic phase separated state, since the C- and E-type structure are mixed at the length scale of a lattice constant. This phase is expected to be made unstable easily near the phase boundary region, and to turn into a phase-separated state with a mixture of metallic FM and insulating $C_xE_{1-x}$ clusters, which may induce CMR effects.

In the $C_xE_{1-x}$ phase, $e_g$ holes tend to localize in the C-type region (hatched squares in Fig. 3(b)), i.e., in the straight segment portion of the zigzag FM chain, and as a consequence charge-ordering of the stripe form is induced even in the $\lambda=0$ limit [20]. This causes incommensurate peaks in the charge correlation at $q=(2\pi,2\pi)$. The spin sector is also nontrivial (Fig. 3(c)) and the state is an insulator according to the DOS (Fig. 3(d)) [21].

In summary, the extended phase diagrams of manganites for $x=0$ and $x>0$ have been discussed. A novel E-AFM phase, stabilized at $x=0$ in the region of weak- and intermediate-couplings, is adjacent to both FM metallic and A-AFM states. The competition between E-AFM insulating and FM metallic phases suggests the possibility of CMR effects even in undoped manganites. Several features of the E- to A-AFM transition, at least at the qualitative level, agrees with currently available experimental results. For the doped case, a microscopically inhomogeneous $C_xE_{1-x}$-AFM state is predicted. This state may contribute to the phase separation tendencies widely observed experimentally in Mn-oxides for $0 \leq x < 0.5$. The discovery of these many “hidden” interesting phases in real manganites – undoped and doped – should be actively pursued experimentally. This will open a new sub-branch of investigations in the already much interesting context of Mn oxides.

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[10] Although $x=0$ corresponds to one $e_g$ electron per site which naively may suggest insulating behavior, there are two active orbitals and the mean density per state is 1/2. Note also that previous work [2] has shown that a large Hund coupling is equivalent to a large Hubbard repulsion.
[11] Since JT distortions suppress double occupancy as short-range Coulomb interaction does, a large $\lambda$ is quite fine to mimic the physics of manganites, as shown in [2].
[12] In practice, considering sites $i$ and $i+a$, the oxygen in between is allowed to move along the $a$-axis, i.e., buckling and rotations are neglected. In the 2D case apical oxygens are assumed to be fixed, consistent with previous treatments to produce stripe-like charge ordering in the 2D FM-phase.
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[16] By analytic calculations it has been confirmed that the metal-insulator transition driven by JT phonons occurs at a finite value of $\lambda$ in the infinite lattice. (see T. Hotta, cond-mat/0212575).
[17] While finite clusters do not show true thermodynamic singularities, a rapid increase in the strength of correlations is observed at fairly well defined temperatures, here referred to as $T_H$ and $T_C$ for simplicity. Previous computational experience shows that these estimations are fairly accurate upon increasing lattice sizes [2].
[18] Both spin directions and oxygen positions are optimized.
[19] Note that the FM/OO state of Fig. 2(b) is another phase not previously observed experimentally, here predicted to exist for low-JAF manganites at $x=0$.
[20] As in any striped state, further work should be carried out to check the stability of the structure against long-range Coulomb interactions. [21] For $x>0.5$ in the strong-coupling case, the $C_xE_{1-x}$-phase is compatible with the so-called Wigner-crystal CO/OO structure suggested for $x=2/3$ and 3/4 in La$_{1-x}$Ca$_x$MnO$_3$ (P. G. Radaili et al., Phys. Rev. B59, 14440 (1999); M. T. Fernández-Díaz et al., Phys. Rev. B59, 1277 (1999)). However, the bi-stripe CO/OO phase suggested by Mori et al. (S. Mori et al., Nature 392, 473 (1998)) is consistent with the $C_xE_{1-x}$-AFM state, which emerges from the competition with the Wigner-crystal structure [5]. Experimentally, the $C_xE_{1-x}$-AFM phase has been reported for $x>0.5$ in Nd$_{1-x}$Sr$_{1+x}$MnO$_4$ (T. Kimura et al., Phys. Rev. B65, 020407(R) (2001)).