Domain Formation and Orbital Ordering Transition in a Doped Jahn-Teller Insulator

Sanjeev Kumar, Arno P. Kampf, and Pinaki Majumdar

1Institute of Physics, Theoretical Physics III, Center for Electronic Correlations and Magnetism, University of Augsburg, D-86135 Augsburg, Germany
2Institut Laue-Langevin, Boîte Postale 156, 38042 Grenoble Cedex 9, France
3Harish-Chandra Research Institute, Chhatnag Road, Jhusi, Allahabad 211 019, India

(Received 25 July 2006; published 24 October 2006)

The ground state of a double-exchange model for orbitally degenerate $e_g$ electrons with Jahn-Teller lattice coupling and weak disorder is found to be spatially inhomogeneous near half filling. Using a real-space Monte Carlo method we show that doping the half-filled orbitally ordered insulator leads to the appearance of hole-rich disordered regions in an orbitally ordered environment. The doping driven orbital order to disorder transition is accompanied by the emergence of metallic behavior. We present results on transport and optical properties along with spatial patterns for lattice distortions and charge densities, providing a basis for an overall understanding of the low-doping phase diagram of La$_{1-x}$Ca$_x$MnO$_3$.

DOI: 10.1103/PhysRevLett.97.176403

PACS numbers: 71.10.−w, 72.10.−d, 75.47.Lx, 81.16.Rf

Hole-doped perovskite manganites, for example La$_{1-x}$Ca$_x$MnO$_3$ (LCMO), are well known for their colossal magnetoresistance (CMR) effect [1,2]. The “optimally doped” CMR compounds with $x \sim 0.3$ have been the focus of numerous theoretical studies and are qualitatively understood in terms of the interplay of the double-exchange mechanism, electron-phonon interactions, and disorder in a single electronic band [3–6]. Less attention has been given to the low-doping regime, where the two-band character of manganites is crucial and in addition to charge, spin, and lattice variables, the orbital degrees of freedom and their ordering become important. The undoped compounds are orbitally ordered (OO), A-type antiferromagnetic insulators [7] with large Jahn-Teller (JT) distortions of the MnO$_6$ octahedra [8], which lift the degeneracy of the two Mn-$e_g$ levels. Electronic and cooperative lattice effects lead to simultaneous staggered ordering in both, the JT lattice distortions and the local orbital occupancies. Upon doping, the antiferromagnetic insulator evolves into a ferromagnetic insulator, with weakened orbital order, and eventually undergoes a transition to an orbitally disordered ferromagnetic metal (OD-FM-M) [9]. Despite the achieved progress towards an understanding of magnetic and orbital ordering in the undoped compounds [10], efforts for analyzing the doping driven transition from the orbitally ordered insulating to the orbitally disordered metallic phase have remained limited. A simple view of this transition rests on an entirely classical picture in terms of random fields introduced by the doped holes [11].

The critical hole doping $x_{OD}$ for the loss of orbital order is close to the doping $x_{IMT}$ for the insulator-metal transition (IMT) in LCMO, where $x_{IMT} \sim 0.22$ [12]. In lower bandwidth materials like Pr$_{1-x}$Ca$_x$MnO$_3$ (PCMO) the insulating phase persists to even larger hole concentrations [13]. NMR and neutron scattering experiments suggest, that the doping regime $x \leq x_{IMT}$ is spatially inhomogeneous in LCMO with coexisting “hole poor” orbitally ordered and “hole-rich” orbitally disordered regions [14], and the observation of confined “spin waves” confirms the existence of magnetic clusters on the nanoscale [15]. It has remained unclear how the JT insulator evolves from the homogeneous OO state at $x = 0$ to the homogeneous OD metal at optimal doping through an intermediate inhomogeneous state.

In this Letter we present results on a two-band double-exchange model with electron-lattice coupling and disorder in two dimensions (2D) using a real-space technique. We provide a description for the doping driven loss of orbital order and the detailed doping vs temperature phase diagram at intermediate electron-lattice coupling, appropriate to LCMO. Results for charge transport and spectral properties are presented, which characterize the metal-insulator transitions. Real-space structures for the inhomogeneous state of the hole-doped insulator allow us to follow the emergence of orbitally disordered domain walls and their evolution with doping.

Specifically, we consider a two-band model for itinerant $e_g$ electrons coupled to JT lattice distortions and to localized $S = 3/2$ $t_{2g}$ spins in the presence of substitutional disorder, described by the Hamiltonian:

$$H = \sum_{\langle ij \rangle \sigma} \epsilon_{ij} c_{i \sigma}^\dagger c_{j \sigma}^\dagger + \sum_i (\epsilon_i - \mu)n_i - J_H \sum_i S_i \cdot \sigma_i + J_S \sum_{\langle ij \rangle} S_i \cdot S_j + \lambda \sum_i Q_i \cdot \tau_i + \frac{K}{2} \sum_i |Q_i|^2.$$ (1)

The magnetic properties arise from the competition between the Hund’s rule coupling $J_H$ driven double exchange and the antiferromagnetic superexchange $J_S$ between the $t_{2g}$ core spins $S_i$.

In Eq. (1), $c$ and $c^\dagger$ are annihilation and creation operators for $e_g$ electrons and $\alpha, \beta$ are summed over the two Mn-$e_g$ orbitals $d_{x^2-y^2}$ and $d_{3z^2-r^2}$, which are labeled (a) and (b) in what follows. $t_{ij}^\alpha$ are the hopping matrix elements between $e_g$ orbitals on nearest-neighbor sites and $\epsilon_{ij}$ are the on-site energies.

Hole-doped perovskite manganites, for example La$_{1-x}$Ca$_x$MnO$_3$ (LCMO), are well known for their colossal magnetoresistance (CMR) effect [1,2]. The “optimally doped” CMR compounds with $x \sim 0.3$ have been the focus of numerous theoretical studies and are qualitatively understood in terms of the interplay of the double-exchange mechanism, electron-phonon interactions, and disorder in a single electronic band [3–6]. Less attention has been given to the low-doping regime, where the two-band character of manganites is crucial and in addition to charge, spin, and lattice variables, the orbital degrees of freedom and their ordering become important. The undoped compounds are orbitally ordered (OO), A-type antiferromagnetic insulators [7] with large Jahn-Teller (JT) distortions of the MnO$_6$ octahedra [8], which lift the degeneracy of the two Mn-$e_g$ levels. Electronic and cooperative lattice effects lead to simultaneous staggered ordering in both, the JT lattice distortions and the local orbital occupancies. Upon doping, the antiferromagnetic insulator evolves into a ferromagnetic insulator, with weakened orbital order, and eventually undergoes a transition to an orbitally disordered ferromagnetic metal (OD-FM-M) [9]. Despite the achieved progress towards an understanding of magnetic and orbital ordering in the undoped compounds [10], efforts for analyzing the doping driven transition from the orbitally ordered insulating to the orbitally disordered metallic phase have remained limited. A simple view of this transition rests on an entirely classical picture in terms of random fields introduced by the doped holes [11].

The critical hole doping $x_{OD}$ for the loss of orbital order is close to the doping $x_{IMT}$ for the insulator-metal transition (IMT) in LCMO, where $x_{IMT} \sim 0.22$ [12]. In lower bandwidth materials like Pr$_{1-x}$Ca$_x$MnO$_3$ (PCMO) the insulating phase persists to even larger hole concentrations [13]. NMR and neutron scattering experiments suggest, that the doping regime $x \leq x_{IMT}$ is spatially inhomogeneous in LCMO with coexisting “hole poor” orbitally ordered and “hole-rich” orbitally disordered regions [14], and the observation of confined “spin waves” confirms the existence of magnetic clusters on the nanoscale [15]. It has remained unclear how the JT insulator evolves from the homogeneous OO state at $x = 0$ to the homogeneous OD metal at optimal doping through an intermediate inhomogeneous state.

In this Letter we present results on a two-band double-exchange model with electron-lattice coupling and disorder in two dimensions (2D) using a real-space technique. We provide a description for the doping driven loss of orbital order and the detailed doping vs temperature phase diagram at intermediate electron-lattice coupling, appropriate to LCMO. Results for charge transport and spectral properties are presented, which characterize the metal-insulator transitions. Real-space structures for the inhomogeneous state of the hole-doped insulator allow us to follow the emergence of orbitally disordered domain walls and their evolution with doping.

Specifically, we consider a two-band model for itinerant $e_g$ electrons coupled to JT lattice distortions and to localized $S = 3/2$ $t_{2g}$ spins in the presence of substitutional disorder, described by the Hamiltonian:

$$H = \sum_{\langle ij \rangle \sigma} \epsilon_{ij} c_{i \sigma}^\dagger c_{j \sigma}^\dagger + \sum_i (\epsilon_i - \mu)n_i - J_H \sum_i S_i \cdot \sigma_i + J_S \sum_{\langle ij \rangle} S_i \cdot S_j + \lambda \sum_i Q_i \cdot \tau_i + \frac{K}{2} \sum_i |Q_i|^2.$$ (1)

The magnetic properties arise from the competition between the Hund’s rule coupling $J_H$ driven double exchange and the antiferromagnetic superexchange $J_S$ between the $t_{2g}$ core spins $S_i$.

In Eq. (1), $c$ and $c^\dagger$ are annihilation and creation operators for $e_g$ electrons and $\alpha, \beta$ are summed over the two Mn-$e_g$ orbitals $d_{x^2-y^2}$ and $d_{3z^2-r^2}$, which are labeled (a) and (b) in what follows. $t_{ij}^\alpha$ are the hopping matrix elements between $e_g$ orbitals on nearest-neighbor sites and $\epsilon_{ij}$ are the on-site energies.
have the cubic perovskite specific form: $t^{aa}_s = t^{aa}_y = t$, $t^{bb}_s = t^{bb}_y = t/3$, $t^{ab}_s = t^{ab}_y = -t/\sqrt{3}$, $t^{ba}_y = t^{ba}_y = t/\sqrt{3}$ \cite{1}, where $x$ and $y$ denote the spatial directions on a square lattice. The disorder is modeled by random on-site potentials $e_i$, with equally probable values $\pm \Delta$. The $e_g$-electron spin is $\sigma^i_g = \sum_\alpha c^{\dagger}_{i\alpha} \Gamma^\alpha_{\mu} c^\mu_{i\alpha}$, where $\Gamma^\mu$ are the Pauli matrices. $\lambda$ denotes the strength of the JT coupling between the distortion $Q_i = (Q_{ix}, Q_{iy})$ and the orbital pseudospin $\tau^i_\mu = \sum_\sigma \Gamma^\mu_{\sigma\alpha} c^\dagger_{i\alpha} c^\sigma_{i\alpha}$ \cite{1}. $K$ controls the lattice stiffness, and $\mu$ is the chemical potential.

We set $\lambda = 1$ as the reference energy scale. In the manganites $J_H \gg 1$, and we adopt the frequently used limit $J_H \to \infty$, which retains the essential physics \cite{1}. We use $J_s = 0.05$ throughout, which is estimated from the Néel temperature for CaMnO$_3$, where antiferromagnetism is purely superexchange driven. The parameters $\lambda$ and $\Delta$ will be selectively explored. The spins are assumed to be classical unit vectors, $|S| = 1$; quantum effects in the lattice variables are not considered, and the stiffness is set to $K = 1$. In the limit $J_H \to \infty$ the spin of the $e_g$ electrons is tied to the orientation of the local core spin leading to a two-orbital “spinless” fermion model with core spin configuration dependent hopping amplitudes \cite{1}.

Replacing a fraction $x$ of rare earth ions with $2^+$ cations in the parent manganites affects the mean A-site ionic radius $r_A(x)$ as well as its variance $\sigma_A(x)$. The varying $r_A$ modifies the electronic hopping amplitude, and hence the $\lambda/t$ ratio, while $\sigma_A$ controls the disorder strength $\Delta$. In most of what follows we set $\lambda = 1.6$, which reproduces the transport gap ~0.4 eV (if we assume $t \sim 0.2$ eV) in LaMnO$_3$ estimated from the activated resistivity behavior \cite{16}. We set $\Delta = 0.4$ as a typical value for weak disorder, and explore the doping and temperature dependence. Naturally the amount of disorder depends on the doping level, but this variation is not addressed here.

The model defined in Eq. (1) has been studied earlier using mean-field methods, as well as exact diagonalization (ED) based Monte Carlo (MC) simulations \cite{17}. While the mean-field approximation excludes by construction the possible existence of inhomogeneous phases, the accessible system sizes within ED-MC simulations are too small (~100 sites) to explore spatial clustering effects, the orbital order to disorder transition, or the IMT itself. Here we use the traveling cluster approximation (TCA), which readily allows access to systems of ~1000 sites to anneal the classical spin and lattice variables. ED of the full fermionic Hamiltonian is used only for computing the electronic quantities in the TCA-generated classical configurations. This method has been benchmarked before \cite{18} and applied to a one-band version of Eq. (1) \cite{5}.

Figure 1 summarizes our results for the OO-OD transition, magnetism, and the doping and temperature driven IMT. Panel (a) shows the $x - T$ phase diagram for $\lambda = 1.6$ and $\Delta = 0.4$. Squares mark the ferromagnetic (FM) to paramagnetic (PM) crossover and circles denote the orbital ordering transition temperatures $T_{OO}$ as inferred from the $T$ dependence of the $q = (\pi, \pi) \equiv q_0$ component of the lattice structure factor, $D_Q(q) = N^{-2}\sum_i (Q_i \cdot Q_i)_{av} \times e^{-i q \cdot (\sigma_r - \sigma_i)}$ shown in panel (c). Here and below $\langle \cdot \rangle_{av}$ denotes the combined average over thermal equilibrium configurations and over the realizations of quenched disorder. The I-M boundary is obtained from the sign of the slope of the resistivity $\rho(T)$ [see Fig. 2(a)]. At $T = 0$ the system is ferromagnetic at all doping levels, despite the presence of the antiferromagnetic superexchange coupling $J_S$; the doping driven OO-OD transition at $x_{OD} \sim 0.22$ occurs close below the IMT. For $x < x_{OD}$ the system loses either ferromagnetic order (for $x \to 0$) or orbital order first (for $x$ near $x_{OD}$) with increasing $T$, and for $T \approx 0.1$ the system becomes an orbitally disordered paramagnetic insulator (OD-PM-I).

A broader perspective for the OO-OD transition is obtained from the low temperature $\lambda - x$ phase diagram for $\Delta = 0.4$, shown in Fig. 1(b). For our choice of $J_S$ the system is FM over the entire selected parameter range. In the clean limit, $\Delta = 0$, the major feature is phase separation (PS), as indicated by the gray shaded area, between the OO-IM at $x = 0$ and the OD-PM for $x > 0$. PS is identified from the existence of a jump in the average hole density upon varying the chemical potential. In the pres-
experiments on PCMO [13,19]. We remark that some xists to much larger The lower bandwidth materials would correspond to larger from an 2D calculation; e.g., we cannot address the crossoverpling regime where single electrons can be “self-trapped” and orbital ordering is not a prerequisite for the insulating behavior. This is consistent with our observation in the disordered one-band model [5] and appears as a generic feature of the interplay of disorder and electron-lattice coupling. Figure 2(d) shows how the DOS evolves from the “clean gap” at $x = 0$ through the low $x$ pseudogap to the high $T_c$ “metallic” regime. The clean gap at $x = 0$, which originates from the nesting instabilities at weak coupling [22] and effective repulsions between self-trapped electrons at strong coupling, is stable in the presence of weak disorder [23]. From the combination of $N(\mu)$, $\rho(T)$, and $\sigma(\omega)$ we conclude that the electron system at $T = 0$ has an “IMT” near $x = 0.25$.
For a more microscopic understanding of these results, we have examined the doping evolution of the real-space patterns for the local charge density $n_i$ and the local spatial correlations of the lattice distortions $C_Q = \frac{1}{4} \sum_{i} \mathbf{Q}_i \cdot \mathbf{Q}_{i+\delta}$ for a representative disorder realization, where $\delta$ is summed over the nearest neighbors of site $i$. The $n_i$ in the upper row in Fig. 3 show (with white marking the hole-poor and black the hole-rich regions) that the doped holes at low $x$ lead to a strong density variation, although the holes are not "site localized". The hole positions are spatially correlated with a short range charge order pattern. The spatial pattern is filamentary, rather than "puddle-like", with the linear structures connecting up for $x \sim x_{OD}$. The $C_Q$ pattern is understood from the hole locations, and the above discussed supression of $D_Q(q_0)$ arises from the loss of OO in the vicinity of the holes as well as from the presence of antiphase domains separated by the hole-rich domain walls.

Although local Coulomb interactions were not explicitly included in our model analysis their effects are nevertheless partially captured. For example, the large $J_H$ avoids double occupancy of a single orbital and therefore acts like an intraorbital Hubbard repulsion. The JT polaron binding energy, $\sim \lambda^2/2K$, has effects similar to an interorbital Hubbard repulsion since it prefers one $e_g$ electron per site [10]. Therefore we do not expect qualitative changes in our phase diagrams if explicit electron-electron interactions were included. The $T_{OO}$ scale however will be affected. The cooperative nature of the lattice distortion will also enhance $T_{OO}$ as we have checked. The critical doping for the OO-OD transition, however, does not seem to be significantly affected by cooperative effects, and neither are the spatial patterns for $x \sim x_{OD}$ [23].

Naturally the IMT that we observe in our 2D model with disorder is to be understood as a crossover from an insulating phase to a weakly localized (WL) phase with a finite density of states at the Fermi level. In three dimensions the gapped insulator to WL crossover is expected to become a genuine IMT.

In summary, our results on the 2D Jahn-Teller double-exchange model reveal a doping driven transition from an orbitally ordered insulator to an orbitally disordered ferromagnetic metal in agreement with the experiments on LCMO. In the orbitally disordered regime, the system undergoes a thermally driven transition from a ferromagnetic metal to a paramagnetic insulator, characteristic of the CMR materials. The intermediate inhomogeneous phase, with coexisting orbitally ordered and orbitally disordered regions, allows a natural interpretation of the neutron scattering and NMR data in LCMO [14].

S. K. and A. P. K. gratefully acknowledge support by the Deutsche Forschungsgemeinschaft through No. SFB 484. P.M. was supported by Trinity College, the EPSRC, and the Royal Society, UK. Simulations were performed on the Beowulf Cluster at HRI.

[1] For overviews see, Nanoscale Phase Separation and Colossal Magnetoresistance, edited by E. Dagotto (Springer-Verlag, Berlin, 2002) and [2].

[2] Colossal Magnetoresistive Oxides, edited by T. Chatterji (Kluwer, Dordrecht, 2004).

[3] H. Röder et al., Phys. Rev. Lett. 76, 1356 (1996).

[4] J. A. Vergés et al., Phys. Rev. Lett. 88, 136401 (2002).

[5] S. Kumar and P. Majumdar, Phys. Rev. Lett. 96, 016602 (2006).

[6] C. Sen et al., Phys. Rev. B 73, 224441 (2006).

[7] A-type magnetic order refers to the antiferromagnetic stacking of ferromagnetic planes.

[8] Y. Murakami et al., Phys. Rev. Lett. 81, 582 (1998).

[9] G. Biotteau et al., Phys. Rev. B 59, 1364 (1999).

[10] T. Hotta et al., Phys. Rev. B 53, 8434 (1996).

[11] A. J. Millis, Phys. Rev. B 60, R15009 (1999).

[12] B. B. Van Aken et al., Phys. Rev. Lett. 90, 066403 (2003).

[13] Y. Tomioka et al., Phys. Rev. B 53, R1689 (1996).

[14] G. Papavassiliou et al., Phys. Rev. Lett. 91, 147205 (2003); M. Hennion et al., ibid. 81, 1957 (1998).

[15] M. Hennion et al., Phys. Rev. Lett. 94, 057006 (2005).

[16] T. T. M. Palstra et al., Phys. Rev. B 56, 5104 (1997).

[17] R. Kilian and G. Khaliullin, Phys. Rev. B 60, 13458 (1999); S. Yunoki et al., Phys. Rev. B 81, 5612 (1998).

[18] S. Kumar and P. Majumdar, Eur. Phys. J. B 50, 571 (2006).

[19] For a comparison with larger bandwidth materials, see, e.g., A. Pimenov et al., Phys. Rev. B 59, 12419 (1999).

[20] S. Kumar and P. Majumdar, Eur. Phys. J. B 46, 237 (2005).

[21] M. J. Calderón and L. Brey, Phys. Rev. B 58, 3286 (1998).

[22] D. V. Efremov and D. I. Khomskii, Phys. Rev. B 72, 012402 (2005).

[23] S. Kumar et al. (unpublished).