Continuous Charge Modulated Diagonal Phase in Manganites.

Luis Brey
Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, 28049 Madrid, Spain.

We present a novel ground state that explain the continuous modulated charge diagonal order recently observed in manganese oxides, at hole densities \( x \) larger than one half. In this diagonal phase the charge is modulated with a predominant Fourier component inversely proportional to \( 1-x \). Magnetically this state consist of antiferromagnetic coupled zig-zag chains. For a wide range of relevant physical parameters as electron-phonon coupling, antiferromagnetic interaction between Mn ions and on-site Coulomb repulsion, the diagonal phase is the ground state of the system. The diagonal phase is favored by the modulation of the hopping amplitude along the zig-zag chains, and it is stabilized with respect to the one dimensional straight chain by the electron phonon coupling. For realistic estimation of the physical parameters, the diagonal modulation of the electron density is only a small fraction of the average charge, a modulation much smaller than the obtained by distributing Mn\(^{+3}\) and Mn\(^{+4}\) ions. We discuss also the spin and orbital structure properties of this new diagonal phase.

PACS numbers: 75.47.Gk, 75.10.-b, 75.30Kz, 75.50.Ee.

Oxides of type \((R_{1-x}A_x)\text{MnO}_3\) where \( R \) denotes rare earth ions and \( A \) is a divalent alkaline ion, are called generically manganites. In these compounds \( x \) coincides with the concentration of holes moving in the \( e_g \) orbital band of the Mn ions that ideally form a cubic structure of lattice parameter \( a \). The ground state (GS) properties of manganites are determined by the competition between at least four independent energy scales: the anti-ferromagnetic (AF) interaction between the Mn spins, the electron phonon coupling, the electronic repulsion and the kinetic energy of the carrier.

In manganites the energy magnitude of these effects is the same and very different states can have very similar energies. Consequentially by varying slightly parameters as carrier concentration, strain, disorder, temperature etc, different GS as ferromagnetic metallic phases\([1]\), AF Mott insulator\([2]\), charge and orbital ordered stripe phases\([3, 4, 5, 6]\), or ferromagnetic charge ordered phases\([7]\) can be experimentally observed.

Studies based in pure double-exchange (DE) model\([8, 9]\), electron-phonon coupling\([10]\), orbital ordering\([11]\), strain interactions\([12]\), or ab initio calculations\([13]\) have been successfully applied for explaining the existence of ferromagnetic metallic phases at \( x \sim 0.2-0.4 \) and the existence of the CE phase at half doping. Also for large enough AF coupling between the Mn spins orbital ordering could induce stripes at \( x=1/m \) being \( m \) an integer\([14, 15]\). In the CE phase the \( x-y \) layers are AF coupled and into the plains the magnetic structure is formed by AF coupled zig-zag chains. The horizontal \((x)\) and vertical \((y)\) steps of the zig-zag chains contain three Mn ions. In the CE phase the charge is stacked in the \( z \)-direction whereas in the \( x-y \) planes it is ordered in a checkerboard form.

For \( x >1/2 \) microscopic models\([11, 16]\) predict the existence of a C phase formed by vertical one dimensional chains coupled AF. However experiments reveal the existence of a diagonal charge modulation, that was interpreted\([13, 14]\) as a mixture of two commensurate adjacent integer period sub-units. On the other hand, by similitude with ferroelectric it has been argue that for \( x >1/2 \) the GS could be formed by commensurate regions of density \( x=(1-\frac{m}{n}) \) separated by solitons where the extra charge is localised\([17]\). In this picture the stripes are formed by an array of solitons. However recently, for doping \( x \geq 0.5 \), low temperature electron microscopy experiments\([18]\) shown an uniform periodicity proportional to \( 1-x \), ruling out the existence of a mixture of integer period units joined by discommensurations or solitons. Also at \( x=2/3 \) a diagonal supercell structure has been proposed for modelling neutron scattering data\([19]\).

In this work we propose a new GS for the manganites at doping \( x=(1-\frac{m}{n}) >0.5 \). In this phase the charge is stacked in layers and at each plane it is modulated diagonally with only a predominant Fourier component \((\frac{2\pi}{a}, \frac{2\pi}{a}, \frac{m}{n})\). Magnetically this diagonal phase consists of AF coupled \( x-y \) layers formed of zigzag chains also coupled AF. The horizontal and vertical steps of the chain are formed by \((m+1)\) Mn ions. By varying the values of \( n \) and \( m \) this phase describe a GS where the periodicity of the charge changes continuously with \( x \).

**Model.** In ideal manganites the Mn ions form a cubic lattice. The crystal field split the Mn \( d \) levels into an occupied strongly localised \( t_{2g} \) triplet and a doublet of \( e_g \) symmetry. Coulomb repulsion prevents double occupancy and aligns the spins of the \( d \) orbitals. At \( x=1 \) the \( e_g \) orbitals are empty and the superexchange coupling between the Mn spins produces an AF GS. At \( x \neq 1 \) the hopping of electrons between empty \( e_g \) states is possible. The Hund’s coupling between the spins of the carriers and each core spin is much larger than the kinetic energy, and each electron is forced to
align with the core spin texture. Then the carriers can be treated as spinless particles and the hopping amplitude between two Mn ions is modulated by the factor $f_{1,2} = \cos \frac{\alpha_i}{2} \cos \frac{\phi_i}{2} e^{i(\phi_i - \phi_j)} \sin \frac{\alpha_i}{2} \sin \frac{\phi_j}{2}$ where $\{\alpha_i, \phi_i\}$ are the Euler angles of the, assumed classical, Mn core spins $\{S_i\}$. This is the so called DE model.

For obtaining the GS of the system we study a three dimensional DE model coupled to Jahn-Teller (JT) phonons. We also include the AF coupling between the Mn core spins $J_{AF}$ and a Hubbard term $U$ for describing the strong inter-orbital Coulomb interaction.

$$H = - \sum_{i,j,a,a'} f_{i,j} t^a_{i,a} C^+_{i,a} C_{j,a'} + U \sum_{i,a,n,a'} n_{i,a} n_{i+a,a'}$$

$$+ J_{AF} \sum_{<i,j>} S_i S_j + \frac{1}{2} \sum_i (\beta Q^2_{1i} + Q^2_{2i} + Q^2_{3i})$$

$$+ \lambda \sum_i (Q_{1i} \rho_i + Q_{2i} \tau_{zi} + Q_{3i} \tau_{zi}) \quad (1)$$

Here $C^+_{i,a}$ creates an electron in the Mn ions located at site $i$ in the $e_g$ orbital $a$ ($a=1,2$ with $1=|x^2-y^2\rangle$ and $2=|3z^2-r^2\rangle$). The hopping amplitude is finite for next neighbors Mn and depends both on the type of orbital involved and on the direction $u$ between sites $i$ and $j$ ($(x^2+y^2) = \pm \sqrt{3} t^2_{0,1,2} = \pm \sqrt{3} t^2_{0,2,1}$). The on-site Coulomb term $t^2_{0,2,1} = 4/3t$ and $t^2_{0,1,2} = 3t^2_{0,2,1} = 3t^2_{0,1,2} = 0$.

In the rest of the paper $t$ is taken as the energy unit.

In the second term of Eq. (1) $n_{i,a} = C^+_{i,a} C_{i,a}$. The fifth term couples the $e_g$ electrons with the three active MnO$_6$ octahedra distortions: the breathing mode $Q_{1i}$, and the JT modes $Q_{2i}$ and $Q_{3i}$ that have symmetry $x^2-y^2$ and $3z^2-r^2$ respectively. $Q_{1i}$ couples with the charge at site $i$, $\rho_i = \sum_a C^+_{i,a} C_{i,a}$ whereas $Q_{2i}$ and $Q_{3i}$ couple with the $x$ and $z$ orbital pseudospin densities $\tau_{zi} = C^+_{i,a} C_{i,a} + C^+_{i,a} C_{i,a}$ and $\tau_{zi} = C^+_{i,a} C_{i,a} - C^+_{i,a} C_{i,a}$, respectively. $\lambda$ is the electron-phonon coupling constant. The forth term is the elastic energy of the octahedra distortions, being $\beta$ the spring constant ratio for breathing and JT-modes $Q^{\pm}_{1i}$. In the perovskite structures the oxygen atoms are shared by neighbors MnO$_6$ octahedra and the $Q^\pm$ distortions are not independent, being cooperative effects very important.

In order to consider this collective effect we consider the position of the oxygen atoms as the independent variables of the JT distortions.

For a particular electron density, a given set of values $\lambda$, $J_{AF}$ and $U$, and a texture of core spins $\{S_i\}$, we solve self-consistently the mean field version of Hamiltonian (1) and obtain the energy, the local charges $\{\rho_i\}$ and orbital pseudospin orientation $\{\tau_{zi}\}$. We have solved the Hamiltonian for $x \leq 0.5$ and with the appropriated parameters we have recovered the GS obtained previously by different groups of $\{21, 22\}$. Therefore we are in conditions for studying the different phases that can appear for $x > 0.5$.

Results. We have studied different magnetic texture states, as the three dimensional (3D) ferromagnetic (FM) phase, the A phase formed by FM two dimensional (2D) planes coupled AF, the C and the CE phases, the island phases of the form ($\pi/3, \pi, \pi$), the $C_g E_{1g}$ phases, the Skyrmion phases and the 3D AF phases. Neither of the GS’s obtained by comparing the energy of these magnetic phases present a diagonal modulation of the charge, in any range of the parameters $\{\lambda, J_{AF}, U\}$. Neither of them present a continuous variation of the period of the charge modulation when the hole concentration varies.

In this work we propose, for $x=(1-\frac{n}{m})$, a new magnetic phase consisting of AF ordered layers composed of AF coupled zig-zag chains, with vertical and horizontal steps formed by $n+1$ Mn ions. As the tunnelling amplitude depends on the direction between sites $(t^2_{0,2,1} = -t^2_{0,1,2})$ in this phase the hopping amplitude is modulated with period $2m$ along the zig-zag chains, and this make possible the existence of fourier components of the charge of the form $\{2\frac{m}{a}, 2\frac{m}{a}, m\}$. Even in absence of interactions, the modulation of the hopping along the chain produces the appearance of gaps in the energy spectra at hole concentrations $1-\frac{n}{m}$ and the system behaves as a band insulator. In the case of $m=2$ this phase coincides with the CE phase. When the Hubbard term or the electron-phonon coupling is included, the gap at the hole density $1-\frac{n}{m}$ is enlarged and the charge density modulation with period $2\frac{m}{a}$ is privileged, being the charge modulated diagonally basically with a single Fourier component.

The unit cell of this phase contains $4m \times 4m$ Mn ions and this impose a computational restriction to the studied hole densities. We have calculated, for $x=2/3$ and $x=3/5$, the energy of the diagonal and other established phases for different values of $\lambda$, $U$ and $J_{AF}$. By comparing energies we build the corresponding phase diagrams. In Fig.1 we plot the $\lambda - J_{AF}$ phase diagram for $x = 2/3$. 
and $U = 0$. At small values of $J_{AF}$ and $\lambda$ the GS is the uniform charge 3D FM phase, this state is the standard FM metallic phase that appear in the canonical DE model. At small values of $J_{AF}$ and large values of $\lambda$ the GS is an insulating 3D FM phase where the electric charge and the orbital are ordered. This charged ordered FM phase is the 3D analog to the 2D charge ordered phase reported in reference [25]. At moderate values of $J_{AF}$ and in a wide range of values of $\lambda$ there is a large window in the phase diagram where the GS is the diagonal phase. At small $\lambda$ the 3D-FM state is separated from the diagonal phase by the A phase. For large values of $J_{AF}$ island phases of the form $(\pi/3, \pi)$ appear [20] and for much larger values of $J_{AF}$ (not shown in Fig.1) the pure AF phase wins in energy. Topologically equivalent phase diagram is obtained for $x = 3/5$. The important point to note is that the window of $\lambda$-$J_{AF}$ values, where the diagonal phase is stable includes the values for which the CE phase is the GS at $x=1/2$. Therefore we expect the diagonal phase to be the GS for $x > 1/2$.

In Fig.2 we plot schematically the spin-orbital ordering in the unit cell of the diagonal phase at $x=2/3$. Open and solid symbols represent up and down Mn core spins. The lobes indicates that the electron occupy $3x^2 - r^2$ or $3y^2 - r^2$ orbitals whereas small circles represent the occupation of the $x^2 - y^2$ orbital. The charge density is constant along diagonal directions marked in Fig.2 and periodic along the perpendicular direction. At $x=2/3$ the electric charge on the Mn ions have only two values $n_1$ or $n_2$, and the charge disproportionation of the electron charge depends on $\lambda$ and $U$. For realist values of $\lambda=0.6t$ and $U=4t$ the difference of charge is $n_1-n_2=0.15$. This value is very different from the extreme value of 1 obtained by distributing periodically Mn$^{3+}$ and Mn$^{4+}$ ions.

The phase diagram above presented correspond to $U=0$. It is known [20] that at $x=1/2$ the $U$ interaction destabilizes the CE phase against the C phase. For analyzing the estability of the diagonal phase we plot in Fig.3 the $\lambda$-$U$ phase diagram for $x=2/3$ and $x=3/5$. In the C phase only an orbital $3y^2 - r^2$ is occupied and the energy of this phase is independent of $U$. Therefore the on site Coulomb interaction favors the C phase against the diagonal phase and it is necessary a finite electron phonon coupling to stabilize the diagonal phase. However the require values of $\lambda$ are moderate and the diagonal phase has lower energy than the C phase for realistic estimation of this parameter [20].

The results shown until here indicate the existence of a diagonal phase at $x=2/3$ and $x=3/5$. As commented above the Hubbard term and the electron phonon interaction favor the existence of a predominant Fourier component, $\hat{m}_l(\frac{2\pi}{a}, \frac{2\pi}{a}, 0)$ of the charge density. In Fig.4(a) we plot the Fourier transform of the electrical charge for $x=1/2, x=2/3$ and $x=3/5$ and $\lambda=0.6t$ and $U=4t$. Only the Fourier components $\pm(\frac{2\pi}{a}, \frac{2\pi}{a}, 0)$ have values considerably different from zero.

There is experimental evidence [18] that the period of the charge modulation varies continuously with the hole density. The study of a system with a hole concentration close to half filling, as $x=0.52$ or $x=0.58$, requires the use of very large unit cell and it is computationally unaccessable. However for zero electron phonon coupling the properties of the diagonal phase can be obtained by solving one dimensional system with $2m$ Mn ions per unit cell. In this form we study systems with $x$ close to 1/2. In Fig.4(b) we plot the Fourier transform of the electron charge for $U=4t$, $\lambda=0$ and hole densities $x=1/2,$

FIG. 2: (Color online) Schematic view of the diagonal phase in the $x$-$y$ plane. Open and solid symbols indicates up and down $t_{2g}$ spins respectively.

FIG. 3: Phase diagram ($\lambda$-$U$), for the three-dimensional DE two orbital model with cooperative Jahn Teller phonons, at hole concentrations $x=2/3$ and $x=3/5$. 

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FIG. 4: Diagonal, \((q, q)\) Fourier component of the electric charge in the diagonal phase. (a) corresponds to \(\lambda=0.6t\) and \(U=4t\) and (b) to \(\lambda=0\) and \(U=4t\).

**Recognizing** 4.1/2 and 4.1/3. It is noticeable that even in absence of electron phonon coupling the charge density is diagonally periodic with a prevailing Fourier component \(\frac{m}{n} \left( \frac{2\pi}{a}, \frac{2\pi}{a} \right)\). We expect that the inclusion of electron phonon coupling will make more predominant this Fourier component. These results indicate that the diagonal phase describes an state where the electric charge is ordered diagonally and the periodicity of the charge modulation changes continuously as \(a/(1 - x)\).

**Summarizing**, we propose a diagonal phase for manganites at doping \(x=(1 - \frac{n}{m})\). In this phase the charge is modulated diagonally with a prevalent Fourier component \(\frac{m}{n} \left( \frac{2\pi}{a}, \frac{2\pi}{a} \right)\). Magnetically this phase consists of zig-zag chains with horizontal and vertical steps formed by \(m+1\) Mn ions. We obtain that this phase has lower energy than the previous suggested phases and is the ground state for a wide range of the relevant physical parameters. In agreement with recent experimental results this phase describes a state where the periodicity of the charge changes continuously with the hole doping.

**Acknowledgments** I am grateful to F.Guinea, Mar Garcia, M.P.López Sancho and N.Mathur for helpful discussions. Also I thank H.Aliaga for calling my attention on the island phases. Financial support is acknowledged from Grants No MAT2002-04429-C03-01 (MCyT, Spain) and Fundación Ramón Areces.

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