Jahn-Teller, Charge and Magnetic Ordering in half-doped Manganese Oxides

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Abstract. The phase diagram of half-doped manganese systems of formula A₀.5A₀.5MnO₃ is investigated within a single-orbital model incorporating magnetic double-exchange and superexchange, together with intersite Coulomb and electron-lattice interactions. Strong Jahn-Teller and breathing mode deformations compete together and result in shear lattice deformations. The latter stabilize the charge-ordered CE-type phase, which undergo first-order transitions with temperature or magnetic field to either Ferromagnetic metallic or Paramagnetic insulating phases. An essential feature is the self-consistent screening of Coulomb and electron-phonon interactions in the ferromagnetic phase.

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Manganese perovskite oxides are currently the object of intense activity. Motivated initially by the colossal magnetoresistance phenomena, more recent studies have revealed an extremely rich phase diagram originating from the interplay of charge, lattice, orbital and magnetic degrees of freedom. The general formula is A₁₋ₓAₓMnO₃ where A is in general a trivalent rare earth element (La, Pr, Nd) and A' a divalent alkaline element (Sr, Ca). Substitutional doping allows to explore the full phase diagram, from x = 0 to x = 1. At the extremes, LaMnO₃ and CaMnO₃ are antiferromagnetic insulators. The former is a layered antiferromagnet, which can be explained thanks to the large Jahn-Teller couplings of the e_g electrons of Mn³⁺ ions. The latter shows a Néel ordering due to antiferromagnetic exchange of t₂g electrons. With doping, the double-exchange phenomena originating from Hund’s coupling between e_g and t₂g electron spins can stabilize a metallic ferromagnetic phase: Coherent band motion occurs for ferromagnetic ordering, while strong inelastic scattering takes place in the high temperature paramagnetic phase. Very large magnetoresistance is obtained when the applied magnetic field is able to align t₂g spins, thereby favouring the metallic phase. Nevertheless, it has been pointed out that spin scattering alone is not sufficient to quantitatively explain the phenomenon. Millis et al. suggested that a large electron-lattice coupling is involved, with the formation of Jahn-Teller polarons in the insulating phase. Such large couplings are quite expected from the very large cooperative Jahn-Teller distortions existing in LaMnO₃. Those deformations indeed involve more than ten per cent variations of the Mn – O bond lengths around all Mn³⁺ ions. Local deformations have been indeed revealed in charge-disordered phases by X-ray and neutron spectroscopy, as well as optical measurements. They consist of Jahn-Teller deformations around Mn³⁺ ions, and ”breathing mode” deformations with shorter Mn – O bonds around Mn⁴⁺ ions. The role of these deformations becomes more stringent in the charge-ordered phases (CO) of doped manganites. These phases strongly compete with the ferromagnetic metallic (FM) one at sufficient doping. Besides the Coulomb interaction between electrons on Mn ions, electron-phonon interaction should play a prominent role in this phenomenon. This is exemplified by the nature of charge ordering at half-doping, for instance in La₀.₅Ca₀.₅MnO₃: While Mn³⁺ and Mn⁴⁺ ions alternate in two directions (say, a and b), in the other direction (which we here define as the c-axis), one finds rows of Mn³⁺ or Mn⁴⁺ ions. If CO were exclusively due to intersite Coulomb interaction, one would on the contrary expect a Wigner crystal ordering, alternated in all directions. This shows that cooperative lattice distortions are an essential ingredient to understand charge ordering.

Charge ordering at x = 0.5 is accompanied by CE-type antiferromagnetic order: In the ab directions, it involves ferromagnetic and antiferromagnetic zigzag chains crossing each other. A qualitative explanation was given a
long time ago by Goodenough [4], following the pioneering structural analysis of Wollan and Koehler [4]: The cooperative Jahn-Teller distortions are accompanied by orbital ordering, and induce the magnetic structure. Moreover, away from half-doping, this CE structure appears as an elementary "brick" to build more complicated charge ordering patterns such as "stripes" [5]. It is thus especially robust and calls for a detailed explanation.

A few models have been proposed to explain CE ordering, putting the emphasis either on intersite Coulomb interactions [1], magnetism and orbital ordering [12,13], Mizokawa et al. [4], and Yunoki and coworkers [8] have underlined the prominent role of Jahn-Teller deformations.

Let us first list and grossly estimate the various energy scales in the system. The on-site Hubbard repulsion \( U \) and the atomic level difference between the \( e_g \) orbitals of manganese and the 2\( p \) orbitals of the oxygen are of the order of several \( eV \)’s, and are larger than the total conduction bandwidth (\( W \sim 3eV \)). The Hund coupling \( J_H \) is of order 1eV, while the intersite Coulomb repulsion seems not to be larger than 0.5eV. The Jahn-Teller splitting in the insulating LaMnO\(_3\) phase is comparable, as shown by spectroscopy and optical absorption measurements [8,10]. In terms of a local electron-phonon coupling, it is reasonable to think of energies of the order of 0.2 – 0.3eV, comparable to the intersite \( e_g \) hopping integrals \( t_0 \sim 0.1 – 0.4eV \) depending on the \( d \)-orbitals involved. On the other hand, the magnetic couplings (which in a cubic lattice give rise to critical temperatures \( T_c \) between 100K and 400K) are in the range of a few \( meV \). This holds as well for the superexchange (antiferromagnetic) couplings as, more surprisingly, for the (ferromagnetic) double-exchange ones. It has been shown by Zener [4] that \( T_{DE}^{J} \sim \alpha t_0 \), \( e.g. \) is proportional to the total kinetic energy of the carriers. As will be shown below, \( \alpha \) is quite small and the actual values of \( T_{DE}^{J} \) can be easily explained with a realistic \( t_0 \), for instance within De Gennes’s mean-field picture [8]. This hierarchy of energy scales is completed by the one set by the external magnetic field needed to turn the FM phase into the CE (AFCO) phase: It ranges from a few Teslas to 20 Teslas or more. In terms of energy scale per atom, this is very small, of the order of 0.4 – 4meV. It is thus consistent with the values of the magnetic exchange constants, but much smaller than all the other scales. This points towards an important conclusion: The stringent competition between the above phases require that their free energies be very close, in the range of a few \( meV \) per atom. Owing to the much larger electron-phonon and Coulomb interactions, it is reasonable to suppose that they play a dominant role in stabilizing the low-temperature CE phase. The necessary conclusion is that CE and FM phases are (meta)stable minima of the free energy, separated by rather high barriers. This is consistent with the fact that the phase transitions (with temperature or magnetic field) between charge ordered and charge disordered phases are first-order, with strong hysteresis under magnetic field. Tendencies to phase separation between FM and CO phases have been demonstrated in La\(_{0.5}\)Ca\(_{0.5}\)MnO\(_3\), Pr\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) and other compositions. One should also notice that charge ordering is always strong when it exists. Fine tuning of the chemical composition between CO and FM low temperature phases [7] does not allow to stabilize "weak" charge ordering. This points towards strong interactions (electron-phonon or Coulomb) in the insulating phase, while they are screened in the metallic phase. This feature is overlooked by mean-field treatments, but can be recovered by taking into account exchange-correlation corrections to the intersite Coulomb repulsion, as shown by Sheng and Ting [4]. Since the lattice distortions here also come from Coulomb interactions (between \( Mn \) and \( O \) ions), we propose here to generalize the screening idea to electron-phonon interactions and use for this purpose a phenomenological approach.

Given the complexity of the overall Hamiltonian, here we restrict ourselves to a single-orbital model in two dimensions, which quantitatively reproduces the various phase diagrams and their tuning by subtle variations of the bandwidth. Our goals are i) obtaining, for realistic values of the parameters, FM, CE and paramagnetic phases; ii) exploring by small variations of those parameters the different kinds of phase diagrams, with temperature and magnetic field: Of the type of La\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) (no charge ordering, FM-PM transition with increasing \( T \)); of the type of Nd\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) (CE-FM-PM transitions with \( T \), CE-FM with \( H \)); of the type of Pr\(_{0.5}\)Ca\(_{0.5}\)MnO\(_3\) (CE-PMCO-PM transitions with \( T \), CE-FM with \( H \)). iii) obtaining first-order transitions between CE and FM phases.

Taking into account explicitly orbital ordering should not change qualitatively the results since it works in the same direction [8,10] but may lead to quantitative improvement.

1 Model and approximations

1.1 Hamiltonian

According to the arguments given in the introduction, we assume an infinite repulsion \( (U = \infty) \) between electrons on the same lattice site, and an infinite Hund coupling \( (J_H = \infty) \) between the localized \( t_{2g} \) spins and the itinerant \( e_g \) spins. One can therefore consider spinless electrons, their spin degree of freedom being unequivocally defined by the direction of the local \( t_{2g} \) spins \( S \). Furthermore, we consider in this work a two-dimensional plane of the structure, with a half-filled band made of a single \( e_g \) orbital. The effective model Hamiltonian is then:

\[
H = H_{DE} + H_{Coul} + H_{ph} + H_{SE} + H_H
\]  

(1)

with

\[
H_{DE} = - \sum_{<ij>} \tilde{t}_{ij} c_i^\dagger c_j
\]

\[
H_{Coul} = \sum_{<ij>} V(n_i - n_j)(n_j - n_i)
\]

\[
H_{ph} = \frac{1}{2} \sum_i [K_b Q_{bi}^2 + K_2 Q_{2i}^2 + K_s Q_{si}^2]
\]
\[-\sum_i g_2 Q_{2i}(n_i - n) + \sum_i g_6 Q_{6i}(n_i - n) - L_s \sum_{<ij>} Q_{s_i} Q_{s_j}\]

\[H_{SE} = \sum_{<ij>} [J_1 - J_2 Q_s] \mathbf{S}_i \cdot \mathbf{S}_j\]

\[H_H = -g_\mu B \sum_i \mathbf{S}_i\]

The first term \(H_{DE}\) represents the double exchange hopping of electrons on a square lattice. Here \(c_i^\dagger, c_i\) are respectively the creation and annihilation operators for spinless electrons from a single band, and \(t_{ij} = t \cos(\theta_{ij}/2)\) is the transfer integral between neighboring Mn sites whose ionic spins \(\mathbf{S}_i\) and \(\mathbf{S}_j\) make an angle \(\theta_{ij}\).

The second term \(H_{Coul}\) describes the Coulomb repulsion between nearest neighbors \((n_i = c_i^\dagger c_i\text{ and } n\text{ is the average electron density, which is equal to }1/2\text{ in the present case})\).

The third term \(H_{ph}\) is the elastic part, which includes the coupling of electrons to a Jahn-Teller (JT) mode \(Q_s\) and of holes to a “breathing” mode \(Q_b\). \((g_2\text{ and }g_6\text{ are the coupling strengths, }K_2\text{ and }K_6\text{ the spring constants})\). In the planar geometry considered here, the other Jahn-Teller mode \(Q_l\) is not relevant. We have also introduced a shear mode \(Q_s\), which is driven by \(Q_2\). Such a shear deformation, which is experimentally observed at low temperatures, is essential to reconcile the alternating Mn\(^{3+}\) breathing and Mn\(^{4+}\) JT distortions which develop in the ordered phases. A substantial shear deformation is indeed observed in \(La_{0.5}Ca_{0.5}MnO_3\) \([19]\). It results in some Mn–O–Mn bonds being shorter and other larger (“zig-zag” chains, see Fig. 1). The term \(H_{SE}\) represents the antiferromagnetic (AF) superexchange interaction \(J_1\) between the ionic spins on neighboring sites, which are treated as classical. The additional term \(J_2 Q_s\) is a phenomenological implementation of the Goodenough rule: It can either enhance or reduce the AF coupling depending on the sign of the shear deformation, which accounts for the fact that longer (shorter) Mn–Mn bonds have a more (less) antiferromagnetic character \([8]\). The last term \(H_H\) takes into account the external magnetic field.

We shall study the Hamiltonian \([8]\) in the mean-field approximation, describing the charge ordered (CO) phase as a charge density wave (CDW) with momentum \((\pi, \pi)\). Let us call \(\bar{n}_A\) and \(\bar{n}_B\) the average electron densities in the two resulting sublattices, which correspond respectively to the Mn\(^{3+}\) and Mn\(^{4+}\) ions. We shall further assume that the JT coupling is only active on A sites, while the breathing deformations arise on B sites. With these approximations, the terms in the Hamiltonian which depend explicitly on \((n_i - n)\) reduce to

\[H_{MF} = -\Delta \sum_{i \in \text{AorB}} (\bar{n}_A - \bar{n}_B) + \text{const}\]

where the order parameter \(\Delta\) is defined as

\[\Delta = 2V(\bar{n}_A - \bar{n}_B) + (g_6 Q_b + g_2 Q_2)/2\]

and the chemical potential has been set to zero by adding a term \(\Delta \mu = -(g_2 Q_2 - g_6 Q_b)/2\) to recover particle-hole symmetry (with these notations, the choice \(\bar{n}_A \geq \bar{n}_B\) corresponds to the \(Q_s\)’s being all positive).

The magnetic part is also treated in mean-field, according to de Gennes’ procedure \([6]\), using a gaussian distribution for the angle of the classical spins with respect to the mean field direction. We consider the following magnetic phases: Ferromagnetic (F), paramagnetic (P), Néel anti-ferromagnetic (NAF), and CE-type ordering, with ferromagnetic zig-zag chains, coupled anti-ferromagnetically (CE). The most general unit cell which allows to describe all these phases is made of 8 nonequivalent Mn sites in a plane (Fig. 1). In each of these magnetic configurations, the total free energy is minimized with respect to the following parameters: i) the magnetization on nonequivalent magnetic sites, ii) the average electron density \(\bar{n}_A\) on sublattice A (\(\bar{n}_B\) being just \(1 - \bar{n}_A\)) and iii) the lattice displacements.

1.2 Phenomenological treatment of screening effects

As mentioned in the Introduction, to have a realistic description of the phase diagram which includes both the metallic and charge ordered phases at half-filling, it is necessary to go beyond the simple mean-field approach described in the preceding section by including the effects of exchange and correlation. Such effects on the intersite Coulomb repulsion in the half-doping manganites have recently been analyzed within an RPA-like calculation \([8]\), which is known to be appropriate for interacting electron systems at metallic densities. Since a detailed study goes...
beyond the scope of this paper, we propose here a semi-
phenomenological treatment of screening which allows a
qualitative description of the transition between CO and
metallic states, and which correctly reproduces the results
of reference [8]. The method is further generalized to
describe the screening of the electron-lattice interactions.
Actually, the latter are due to the Coulomb repulsion be-
 tween M$n$ and O ions and are therefore also screened in
the metallic phase. This screening should be weaker than
that of M$n$ − M$n$ interactions, since it involves M$n$ − O
rather than M$n$ − M$n$ charge fluctuations, but it should
be sizeable.

The procedure will be carried out in two successive
steps. The first step consists in writing a reasonable es-
 timate for the exchange-correlation energy $E_{xc}$, which
is defined as the correction to the ground-state energy be-
yond the Hartree mean-field result. In the second step, we
shall define an effective hamiltonian $\hat{H}_{xc}$ to be treated in
the mean-field approximation, such that

$$\langle \hat{H}_{xc} \rangle = E_{xc}$$

This results in a modification of the atomic energy levels
±$\Delta$ (i.e. in a reduction of the CDW gap), and it yields a
correction to the free energy which is precisely of the form
$E_{xc}$.

1.2.1 Exchange-correlation energy

Let us start by analyzing the simple ferromagnetic case at
$T = 0$, where the electron hopping is not renormalized by
the mechanism of double exchange. In the metallic phase,
which corresponds to a vanishing order parameter $\Delta$, the
leading correction comes from the exchange (Fock) terms.
These terms are responsible for an increase of the carrier
itinerancy, which can be viewed as a renormalization of the
hopping parameter $t \to t + V(c_{i \uparrow}^\dagger c_{i+\delta \uparrow})$. Hence the kinetic
energy is lowered by a quantity proportional to the in-
 teraction potential $V$, and one can write $E_{xc} = -aV$ (the
parameter $a$ is related to the dielectric constant of the
 system). On the other hand, in the CO phase, i.e. at strong
$\Delta$, the correlation energy corresponds to the interaction
between density fluctuations on neighboring sites, each of
them being proportional to $\delta n \sim t/\Delta$. Therefore, in this
case the appropriate limiting formula is $E_{xc} \sim -V(t/\Delta)^2$.
These results can be generalized to the screening of the
electron-lattice interactions, by replacing $V \to g^2/K$ and
by introducing the corresponding parameter $\Delta$ as given by eq. (6).

A smooth interpolation between the weak and strong
coupling behaviors can be obtained by writing the following
expression for the exchange-correlation energy:

$$E_{xc} = -\frac{aV + b(g_b^2/K_b + g_z^2/K_z)}{1 + c(\frac{\Delta}{t})^2}$$

where $a, b$ and $c$ are phenomenological parameters (the
ratio $a/c = 1.44$ can be deduced from ref. [8] and $b/a =
1/10$ is chosen according to the ionic distances).

As was stated at the beginning of this section, this
formula is only appropriate in the ferromagnetic case. It
does not account for the fact that the mobility of the car-
riers taking part in the screening process is affected by the
magnetic structure through the DE mechanism. We shall
give here the arguments which allow a generalization of eq.
(3) to the different kinds of magnetic orderings.

In the free-electron limit ($\Delta \to 0$), where screening is
due to coherent band motion, one expects the correlation
energy to be reduced by a factor $i/t$, where

$$i = t(\cos(\theta_{ij}/2))$$

is the effective DE hopping parameter averaged in all space
directions (this gives respectively 1, 8/9, 1/2 in the $F, P, CE$
phases). The situation is slightly more complicated in
the charge ordered phases, because $E_{xc}$ comes from incoherent hopping of the carriers to neighboring sites.
According to Hund’s rule, such processes will be allowed
only between sites with parallel spins, which defines an
effective number of neighbors $\tilde{Z} \leq z$.

In the CE phase, for instance, the lattice can be divided
into U (up) and D (down) sites, according to the spin di-
rection. Since each site has 2 U and 2 D neighbors, a given
electron can only hop to the 2 neighbors with the same
spin direction, and consequently $\tilde{Z}/z = 1/2$. At finite tem-
peratures, however, thermal fluctuations will reduce the
absolute value of the local magnetization $m$. Accordingly,
there will be a finite probability that a given U site has a
$\downarrow$ spin, which is given by $n_i^+ = (1 - m_U)/2$ (an equiv-
alent expression holds for D sites). The total probability
for hopping away from a U site is therefore

$$2n_i^+ n_U^+ + 2n_i^+ n_D^+ + 2n_i^+ n_D^+ + 2n_i^+ n_U^+$$

where obviously $n_i^+ = 1 - n_i^-$. By adding the contribu-
tions for hopping processes starting from both U and D sites
and dividing by 2, we obtain

$$\tilde{Z} = \frac{1}{2} \left[ 4 + (m_U + m_D)^2 \right]$$

which correctly gives $\tilde{Z}/z = 1, 1/2, 1/2$ for the $F, P, CE$
phases at $T = 0$. Here the factors (6) and (7) introduce a
feedback on the itinerancy of the electrons in the case of
an applied magnetic field, which tends to align the spins
ferromagnetically. This effect is essential in reducing the
critical $H$ for the CE-FM transition at low temperatures, as
we shall see below.

For each given magnetic configuration, instead of eq.
(6), we shall use the following formula for the exchange-
correlation energy:

$$\tilde{E}_{xc} = -\frac{\tilde{a}V + \tilde{b}(g_b^2/K_b + g_z^2/K_z)}{1 + \tilde{c}(\frac{\Delta}{t})^2}$$

where the screening parameters $\tilde{a}, \tilde{b}, \tilde{c}$ have been modified
according to

$$\tilde{a} = \frac{a}{t}, \quad \tilde{b} = \frac{b}{t}, \quad \tilde{c} = \frac{c}{z}$$
We emphasize here that the terms in the numerator of Eq. (3) are rescaled by the $t/t$ factor since they arise from the coherent screening processes (mostly active when $\Delta \rightarrow 0$). On the other hand the local (incoherent) screening processes related to the term in the denominator of Eq. (3) are also rescaled by the effective number of accessible nearest neighbor sites.

1.2.2 Mean-field potential from exchange and correlation

We wish to define an effective hamiltonian $H_{xc}$ to be treated in the mean-field approximation such that the correction to the free energy is equal to $E_{xc}$. To this purpose, we replace $\Delta$ by an operator $\tilde{\Delta}$ (e.g. the mean-field parameter $n^A$ is replaced by $\sum_{i \in A} n^A_i$), and linearize the resulting expression. This gives

$$H_{xc} = B \tilde{c} \frac{V}{t} \Delta \sum_{i \in A \lor B} (n_i^A - n_i^B) + \text{const} \quad (10)$$

where we have defined

$$B = \left[ \tilde{a}V + \tilde{b}(g_0^2/K_b + g_2^2/K_2) \right] / \left[ 1 + \tilde{c}\left(\frac{\Delta}{t}\right)^2 \right]^2 \quad (11)$$

The constant part in eq. (11) is

$$-B \left\{ 1 + \tilde{c}\frac{\Delta}{t^2} \left[ 6V(\tilde{n}^A - \tilde{n}^B) + (g_bQ_b + g_2Q_2)/2 \right] \right\} \quad (12)$$

It is easy to verify that eq. (11) holds when $\tilde{n}^A = \langle n^A \rangle$ and $\tilde{n}^B = \langle n^B \rangle$.

One notices that a dielectric constant can be deduced from the screening of the gap, by writing

$$\Delta \rightarrow \Delta_{eff} = \Delta - B \tilde{c} \frac{V\Delta}{t^2}$$

which gives

$$\varepsilon = \frac{\Delta}{\Delta_{eff}} = \frac{1}{1 - c \tilde{a} \frac{V}{t} \frac{\tilde{b}(g_0^2/K_b + g_2^2/K_2)}{1 + \tilde{c}(\frac{\Delta}{t})^2}}$$

2 Results

2.1 The phase diagram: Existence of a CE phase

The Hamiltonian in Eq. (1) is formed by several competing terms, and the corresponding phase diagram contains several phases, each one dominating in some region of the parameter space. To make the analysis simpler, we choose to vary together those parameters having similar physical effects. In particular, the electron-phonon couplings generically reduce the electron mobility and, at mean-field level, tend to give rise to a staggered charge ordering, acting similarly to the n.n. electron-electron repulsion $V$. Therefore in varying $V$ we keep constant the ratio $V/(g^2/K)$. For the sake of simplicity, we also keep a fixed $J_2/J_1$ ratio, although it is not the only possible choice.

Figure 2 reports typical phase diagrams at various temperatures as a function of the magnetic coupling $J = J_1S^2/t$ with $J_1 = J_2 \left( S = 3/2 \right)$ and of the repulsive e-e interaction $V = 0.5(g^2/K)$. At low temperature (left panel) there is a metallic (i.e. without charge-ordering) ferromagnetic phase (FM) when the charge-ordering (CO) terms $V$ and $g^2/K$ are not too large. This FM phase is naturally suppressed by the increase of the antiferromagnetic (AF) superexchange coupling $J_1$. When the charge mobility is suppressed by the CO terms, one finds two distinct possible phases. At low values of the AF coupling the pure CO effects dominate and a ferromagnetic (F) CO phase occurs at sufficiently large values of $V$ (F-CO). The transition is first order, as found in Ref. [3], due to the exchange-correlation terms. On the other hand, by increasing the AF coupling, the CO ferromagnetism is destabilized and a CE phase takes place. This latter phase naturally realizes the best compromise between the electron mobility, favored by the ferromagnetic bonds, the CO, and the AF interactions increasing with $J_1$. The CE ordering arises due to competing lattice displacements. In particular a substantial shear mode is induced in the lattice to reconcile the (asymmetrical) JT deformations occurring in the Mn$^{3+}$ ions with the (centrosymmetric) breathing deformations around the Mn$^{4+}$ ions. The resulting lattice structure displays zig-zag chains formed by long bonds interleaved with zig-zag chains of short bonds. Then the peculiar CE magnetic structure naturally appears. In particular, according to Goodenough [3], orbital ordering makes the sign of the magnetic couplings to be correlated to the length of the bonds, with AF (F) magnetic couplings corresponding to short (long) bonds. Therefore, the lattice-driven chains with short bonds and with long bonds naturally translate into a lattice-driven CE magnetic structure.

The temperature evolution is represented in the three panels of figure 2. By increasing $T$ the weak ferromagnetism surviving in the CO phase at small $J$ is rapidly suppressed in favor of a CO paramagnetic phase. Also the CE region, being due to a delicate balance between CO, FM, and AF interactions, is reduced rather rapidly. The FM phase at small values of $J_1$ is instead based on the double-exchange mechanism, which is more robust and, upon increasing $T$, is only weakly “invaded” by the CO paramagnetic phase. One also observes that compounds with a low-temperature CE magnetic structure, but laying near the CE-FM phase boundary, can undergo a first-order CE-to-FM transition upon increasing the temperature.

It is worth pointing out that, within our formal scheme, the CO paramagnetic phase is the only possible mean-field description of an insulating non-magnetic phase at moderate temperature values. The explored temperature range is indeed much too low to allow for a thermal disruption of the CO, which instead occurs at temperatures of the order of $V$. However, in strong coupling, one may speculate that a more refined description would allow for the disordering of the charge (possibly without spoiling the local lattice deformations around the charges) thus producing...
the disordered paramagnetic (and polaronic) phase which is observed in all manganites above a few hundreds of kelvins.

### 2.2 Sensitive role of the electronic bandwidth

A key issue is the role of the kinetic energy in the competition between the different phases. An extended experimental analysis of the phase diagrams of the various manganites [20,17] suggests that the electronic bandwidth, among other parameters such as lattice disorder, plays a primary role in determining the stability and the competition between the FM and the insulating phases. In our model we investigated this relevant point by varying the bare hopping amplitude in front of the double-exchange term in the Hamiltonian (1). We also assume that the same hopping amplitude in front of the double-exchange term between the FM and the insulating phases.

The more insulating (i.e., with smaller $J$) system having $J = 0.037$ (so that $(V/t) = 1.081$) never becomes metallic at zero field, but only undergoes a first-order transition from a low-temperature CE phase to a paramagnetic insulating phase at $T \simeq 0.032t$ (left panel, see also Figs.4,5). In the more metallic system (center panel) having $J = 0.038$ (and $V/t = 1.053$), the CE phase disappears at a lower temperature $T \simeq 0.02t$ and it is replaced by an intermediate FM phase. The ferromagnetic order and the metallic phase is then destroyed at a higher temperature $T \simeq 0.032t$.

The relevant role of the kinetic energy in stabilizing the uniform metallic FM phase at the expenses of the CO phases and particularly of the one with CE magnetic order is made even more apparent in the presence of a magnetic field. This is particularly clear in the first panel of Fig. 3, where the FM phase, which would be absent at zero field becomes the most stable solution at large enough $H$. 

![Fig. 2. Phase diagrams as function of the AF coupling $J_1$ and the electron-phonon or Coulomb parameter $V$, for different temperatures (see text).](image-url)
It is also worth mentioning that, due to the presence of screening, the metallic uniform solution is always a (local) minimum of the free energy. Therefore an (at least metastable) metallic solution is present even at zero field. The existence of a (local) minimum is a necessary condition for the occurrence of an hysteretic behavior at the transition. Of course the region of the hysteresis also depends on the height of the free energy barrier between the maxima, of domain walls and of other non-equilibrium properties. Nevertheless the region in T and H where two minima exist provides an (excess) estimate for the hysteresis region experimentally observed in half-doped Pr_{0.5}Sr_{0.5}MnO_3, Nd_{0.5}Sr_{0.5}MnO_3, (Nd_{1-y}Sm_y)_{0.5}Sr_{0.5}MnO_3 and Pr_{0.5}Ca_{0.5}MnO_3 [20,17].

2.3 Discussion

The previous subsection illustrated the main results of the present work:

i) The CE phase does arise in the present one-orbital model and is crucially related to competition between the JT and breathing distortions involved in the charge-ordered state on Mn^{3+} and Mn^{4+} sites respectively. The shear lattice deformation results from this competition and couples to the magnetic degree of freedom, merely through orbital ordering.

ii) Exchange-correlation corrections are essential to stabilize a metallic ferromagnetic phase, due to substantial screening of both Coulomb and electron-lattice interactions.

iii) The kinetic energy is a most effective parameter in determining the relative stability of the various phases upon varying the temperature and the magnetic field.

As far as point i) is concerned, in the present work we show that the CE phase not only arises from electronic mechanisms based on the presence of (at least) two orbitals per Mn site. The existence of a CE phase in a model without orbital degrees of freedom is quite remarkable. It is indeed repeatedly stated in the literature [12,13,21] that the CE phase is stabilized by the kinetic energy gain arising from the orbital ordering forming ferromagnetic chains. Our results are not in contrast with this viewpoint, but underline that the above purely electronic mechanism is not the only possible one, and that the coupling with lattice degrees of freedom can be of primary importance. In this regard our results are related to...
The most metallic system in the right panel is a good qualitative description of La_{0.5}Sr_{0.5}MnO_3. Nevertheless, it has been pointed out [23] that a rapid change in lattice constant $K$, rather than necessarily small changes of $t$, could be the clue for the very different behaviours of the systems $(A,A')_{0.5}$MnO_3. In our case this would correspond to an abrupt change along a vertical line in Figs. 2, and would enhance the first-order character of the transitions.

A semi-quantitative agreement can even be reached. In fact, the pure double-exchange ferromagnetic critical temperature ($J/t = 0$) is, from our 2D mean-field calculation, $T_c \approx 0.085t$. A 3D estimate enhances this value by a factor 3/2 owing to the number of nearest neighbours, yielding $T_{DE}^{3D} \approx 0.13t$. For an average value $t = 0.3eV$ one gets a transition temperature $\approx 450K$. It is reduced by the presence of the antiferromagnetic coupling, for instance in panel c of Figure 3, in zero field $T_c \approx 0.05t$ thus $\approx 270K$ in 3D, thus supporting De Gennes’ simple mean-field picture. Then one obtains in the center panel the value $T_{CE}^{3D} \approx 180K$, and in the left panel $T_{CE}^{3D} \approx 170K$. These values are reasonable, as compared with experimental ones, in particular one notices that $T_{CE}^{3D}$ is strongly reduced compared to $T_{DE}^{3D}$. This is due to the competition between the two order parameters (ferro and antiferro). Another way to understand it is to notice that in the CE phase the effective dimensionality is reduced by chain formation, together with charge localization this reduces the effective strength of double-exchange. On the other hand the effective antiferromagnetic exchange is close to that of stoechiometric CaMnO_3 with a $T_c$ of 120K.

We have also systematically investigated the role of the magnetic field in stabilizing the uniform FM phase. The typical energy differences involved in the first-order transitions are so small that accessible magnetic fields are sufficient to drive the transition from the insulating to the FM phases. Specifically, by taking a typical value of $t \approx 0.3eV$, one can see that $H/t = 0.015$ (where $H = g\mu_B SH$) roughly corresponds to ten Teslas. This value agrees well with the typical values experimentally used to investigate the (T,H) dependence of the low-temperature CE insulating phase and the intermediate-temperature uniform FM phase [21][17].

Fig. 5. Energy, order parameter (density) and magnetization vs magnetic field at $T = 0.01$. Full line: FM, dashed line: PI, dotted line: CE. The parameters correspond to the case PrCaMnO of figure 3. In the CE phase, the magnetization is staggered.
In both cases, however, the AF coupling $J \sim 0.1t$ necessary to achieve the CE state is one order of magnitude higher than what is estimated from experiments, signaling that there must be some additional effect contributing to the CE ordering. Finally, we reiterate that self-consistent screening is necessary to explain that phases with marked charge order come in very close competition with metallic phases. We believe that this is a crucial feature of doped manganites, that further models addressing coexistence and texturing of those phases at small scales must take into account.

References

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