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Pressure induced insulator-metal transition in LaMnO$_3$

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The recent observation of an insulator to metal transition (IMT) [1] in pure LaMnO$_3$ at 32 GPa and at room temperature, well above the Neel temperature (145 K) and below the Jahn-Teller transition temperature (780 K), opens the way to a study of the role of the orbital degrees of freedom in the electronic structure of a stoichiometric material. In this paper we focus our attention on the orbital aspects of the insulator to metal transition. We use a Hamiltonian model for the $e_g$ orbitals of Mn that includes the on site Coulomb repulsion $U$, the hopping $t$, and its pressure dependence. In order to include in an appropriate way the strong correlations induced by the dominant electron-electron interactions, we introduce auxiliary fields (Slave Bosons,SB) to the description of the low energy states. We use the O-Mn distance ($d$) and the pressure dependence from the experimental data to describe the evolution of the electronic structure with pressure. Our results confirm and make transparent the conclusion reached in previous ab-initio calculations: the inclusion of the Coulomb energy is necessary and constitutes an important factor enhancing the orbital polarization in these compounds.

Keywords: Manganites; Jahn-Teller effect; orbital order; strongly correlated electrons; insulator-metal transition.

La observación de la transición metal aislante (IMT) [1] del LaMnO$_3$ a 32 GPa y temperatura ambiente, por encima de la temperatura de Neel (145 K) y por debajo de la temperatura de transición Jahn-Teller (780 K), da lugar al estudio del rol de los grados de libertad orbitales en la estructura electrónica de un cristal puro. En este artículo nos focalizamos en los aspectos orbitales de la transición aislante metal. Para lo cual usamos un Hamiltoniano modelo para los orbitales $e_g$ del Mn que incluye la repulsión coulombiana $U$, el elemento de matriz de salto $t$ y su dependencia con la presión. Para describir de forma apropiada la correlación inducida por la fuerte interacción electrón-electrón, introducimos campos auxiliares (bosones esclavos) para la descripción de los estados de baja energía. Usamos la dependencia de $t$ con la distancia O-Mn ($d$) y la relación presión-$d$ de los datos experimentales para describir la evolución de la estructura electrónica con la presión. Nuestros resultados confirman y hacen transparentes las conclusiones obtenidas en cálculos ab-initio anteriores: la inclusión de la energía coulombiana es necesaria y constituye un factor importante en incrementar la polarización orbital en estos compuestos.

Descripores: Manganitas; efecto Jahn-Teller; orden orbital, electrones fuertemente correlacionados; transición aislante-metal.

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1. Introduction

The discovery of colossal magneto-resistance in manganites, of relevance to spintronics and other technological applications, has opened a new field to the study of highly correlated systems (HCS). In the three dimensional compounds like La$_{1-x}$Sr$_x$MnO$_3$, or in the two dimensional ones, such as La$_{2−2x}$Sr$_{2+2x}$Mn$_2$O$_7$, the interplay of several degrees of freedom, charge, spin, orbit and lattice displacements determines the physical properties of the system. The interactions between the different degrees of freedom cannot be reduced to a perturbation theory, as in other materials, and the disorder produced by alloying to obtain the metallic state does not contribute to the clarification of theory nor to the interpretation of experiments.

The recent observation of an insulator to metal transition (IMT) [1] in pure LaMnO$_3$ at 32 GPa and at room temperature, well above the Neel temperature (145 K) and below the Jahn-Teller transition temperature (780K), opens the way to a study of the role of the orbital degrees of freedom on the electronic structure in a stoichiometric material.

Two theoretical studies relevant to this matter have appeared in the literature almost simultaneously after the publication of the experimental result: both papers are based on local density approximation+Hubbard U (LDA+U) approximation.

In the first one by Wei-go Yin et al. [3], the electronic structure of the ground state of LaMnO$_3$ (antiferromagnetic A phase) is analysed to determine the relative importance of the electron-electron (e-e) against electron-lattice (e-l) Jahn-Teller interactions. It concludes that the e-l interaction by itself is not sufficient to stabilize the orbital ordered state and emphasizes the importance of the e-e interaction to facilitate the Jahn-Teller distortion.

In the second paper by Yamasaki et al. [4], LDA+U and LDA+ dynamical mean field theories are used to analyze the metal insulator transition taking place at 32 GPa in the paramagnetic phase of the same material. The authors conclude that the transition at 32 GPa is caused by the orbital splitting of the $e_g$ bands and that both e-e and e-l interactions are needed to explain the insulating character of the substance at lower pressures.
In this paper we focus our attention on the orbital aspects of the insulator to metal transition. In order to include in an appropriate way the strong correlations induced by the dominant e-e interactions, we follow Feiner and Oleš in introducing auxiliary fields (Slave Bosons,SB) to the description of the low energy states. [5]

We start by defining a simplified Hamiltonian, two parameters: \( U \) on site Coulomb repulsion, and \( \Delta \varepsilon \) a measure of the Jahn Teller splitting, to describe the \( e_g \) states of the system and use SB to calculate the lowest energy varying the parameters to obtain a phase diagram. This procedure allows us to identify the values of the parameters that are appropriate to describe the transition, as well as the thermodynamics and transport properties of \( \text{LaMnO}_3 \) in the paramagnetic phase.

2. Methods

2.1. Hamiltonian

To describe the active electrons in \( \text{LaMnO}_3 \), we use the double-exchange model that contains the essential physics of manganites [6]. The four 3\( d \) electrons in each Mn\(^{3+} \) site are polarized in the same direction due to the large Hund coupling. Three of them occupy the \( t_{2g} \) orbitals and are considered localized forming a spin \( S = 3/2 \), while the fourth occupying the \( e_g \) state is itinerant. We treat the localized spin classically, and since the fourth has to be parallel to the local spin, we can consider the \( e_g \) electron as spinless with Hamiltonian

\[
H = H_t + H_U + H_{JT}
\]  

(1)

where the first term, \( H_t \), is the kinetic energy given by

\[
H_t = \sum_{(ij)\alpha\beta} t_{ij}^{\alpha\beta} c_{i\alpha}^\dagger c_{j\beta}
\]  

(2)

with \( \alpha, \beta = 1, 2 \) corresponding to the (possibly site dependent) orthogonal basis for the two \( e_g \) orbitals. The values of the hopping integrals \( t_{ij}^{\alpha\beta} \) depend both on the type of orbitals involved and on the direction between sites \( i, j \). In \( \text{LaMnO}_3 \), there is a staggered order in the \( x-y \) plane, and the orbitals are stacked ferromagnetically along the \( z \) axis. The dominantly occupied orbitals alternating in the \( x-y \) plane are \( |x\rangle = |3x^2 - r^2\rangle \) and \( |y\rangle = |3y^2 - r^2\rangle \), which define then the low energy orbitals \( |1\rangle \) in each of the sublattices, respectively \( A \) and \( B \). The corresponding higher energy orbitals \( |2\rangle \) are therefore, respectively \( |y^2 - z^2\rangle \) and \( |x^2 - z^2\rangle \). The hopping parameters between these orbitals are the following:

\[
\begin{align*}
\tilde{t}_{x}^{AB} & = t \begin{pmatrix} 1/2 & 0 \\ -\sqrt{3}/2 & 0 \end{pmatrix} \\
\tilde{t}_{y}^{AB} & = t \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ 0 & 0 \end{pmatrix} \\
\tilde{t}_{z}^{AA} & = \tilde{t}_{z}^{BB} = t \begin{pmatrix} -1/4 & -\sqrt{3}/4 \\ -\sqrt{3}/4 & -3/4 \end{pmatrix}
\end{align*}
\]  

(3)

\( t \) being the hopping between \(|x\rangle \) (\(|y\rangle \)) orbitals along the \( x \) (\( y \)) direction.

The magnetic order is introduced by modulating the hopping integrals by the factor \( \exp(iA_{ij}\cos(\theta_{ij}/2)) \), [7], with \( \theta_{ij} \) being the angle between the \( t_{2g} \) localized spins in the neighboring sites \( i, j \) and \( A_{ij} \) a hopping phase. As we are interested in the paramagnetic phase that appears at room temperature \( T \gg T_N \), we assume that the localized spins are completely random and consider a mean field approximation in which this factor is averaged, giving a value \( \langle \exp(iA_{ij}\cos(\theta_{ij}/2)) \rangle = 2/3 \). These \( t_{ij}^{\alpha\beta} \) are the same as for a ferromagnetic phase with a factor 2/3. Henceforth, we take this renormalized hopping as the reference \( t \).

The on-site Coulomb interaction between \( e_g \) electrons occupying both orbitals on the same site is given by

\[
H_U = U \sum_i n_{i1} n_{i2}
\]  

(4)

with \( n_{i\alpha} = c_{i\alpha}^\dagger c_{i\alpha} \) the number operators.

Finally, to model the effect of the Jahn-Teller (JT) deformation, we add a term that shifts the on-site energies of the \( e_g \) orbitals 1, 2 in opposite directions

\[
H_{JT} = \Delta \varepsilon \sum_i (n_{i2} - n_{i1})
\]  

(5)

which corresponds to a JT splitting of \( 2\Delta \varepsilon \).

2.2. Slave bosons method

In order to treat the Hamiltonian Eq. (1), we used the slave boson theory of Kotliar and Ruckenstein [8] adapted to our case of two orbitals instead of the two spin projection. Therefore, we introduce new boson \( (e_i, d_i, b_{i\alpha}) \) and pseudofermion \( (f_{i\alpha}) \) operators. The boson numbers \( c_{i\alpha}^\dagger c_{i\alpha}, b_{i\alpha}^\dagger b_{i\alpha} \) and \( d_{i\alpha}^\dagger d_{i\alpha} \) represent the projectors onto the possible states \(|0_i\rangle\langle 0_i|\), \(|\alpha_i\rangle\langle \alpha_i|\) and \(|d_i\rangle\langle d_i|\) so that

\[
e_{i\alpha}^1 e_i + b_{i\alpha}^d b_{i\alpha} + d_{i\alpha}^d d_{i\alpha} + c_{i\alpha}^\dagger c_{i\alpha} = 1
\]  

(6)

and

\[
b_{i\alpha}^d b_{i\alpha} + d_{i\alpha}^d d_{i\alpha} = c_{i\alpha}^\dagger c_{i\alpha}
\]

The original fermion operators are replaced by

\[
c_{i1}^1 = (b_{i1}^1 e_i + d_{i1}^1 b_{i1}) f_{i1}^1 \\
c_{i2}^1 = (b_{i2}^1 e_i + d_{i2}^1 b_{i2}) f_{i2}^1
\]  

(7)

which correspond to a representation of the empty \(|0_i\rangle\), single occupied \(|1_i\rangle, |2_i\rangle\) and doubled occupied \(|d_i\rangle\) local states by

\[
|0_i\rangle = e_{i1}^1 |\text{vac}\rangle \\
|1_i\rangle = b_{i1}^1 f_{i1}^1 |\text{vac}\rangle \\
|2_i\rangle = b_{i2}^1 f_{i2}^1 |\text{vac}\rangle \\
|d_i\rangle = d_{i1}^d f_{i1}^d f_{i1}^1 |\text{vac}\rangle
\]  

(8)
with $|\text{vac}\rangle$ corresponding to the vacuum state.

The anticommutation rules for the original fermions are guaranteed, provided the following constraints are satisfied

$$b_{i\alpha}^\dagger b_{i\alpha} + d_i^\dagger d_i = f_{i\alpha}^\dagger f_{i\alpha} \quad \alpha = 1, 2$$

(9)

which are implemented by means of the corresponding Lagrange multipliers $\{\lambda_1, \mu_{i1}, \mu_{i2}\}$. To recover the correct result in the uncorrelated ($U = 0$) limit, a renormalization of the bosonic factor in Eq. (7) is necessary. In analogy with the spin case, the renormalized bosons factors take the form

$$z_{i1}^\dagger = \frac{b_{i1}^\dagger e_i + d_i^\dagger b_{i2}}{\sqrt{(1 - e_i^\dagger e_i - b_{i2}^* b_{i2}) (1 - d_i^\dagger d_i - b_{i1}^* b_{i1})}}$$

$$z_{i2}^\dagger = \frac{b_{i2}^\dagger e_i + d_i^\dagger b_{i1}}{\sqrt{(1 - e_i^\dagger e_i - b_{i1}^* b_{i1}) (1 - d_i^\dagger d_i - b_{i2}^* b_{i2})}}$$

With this slave boson representation, the Hamiltonian (1) reduces to

$$H = \sum_{(ij)\alpha\beta} t_{ij}^\beta z_{i\alpha}^\dagger z_{j\beta} f_{i\alpha}^\dagger f_{j\beta}$$

$$+ U \sum_i (d_i^\dagger d_i + \Delta \varepsilon \sum_i (n_{i2} - n_{i1}))$$

$$+ \sum_{i\alpha} \mu_{i\alpha} (f_{i\alpha}^\dagger f_{i\alpha} - b_{i\alpha}^* b_{i\alpha} - d_i^\dagger d_i)$$

$$+ \sum_{i\alpha} \lambda_1 (e_i^\dagger e_i + b_{i1}^\dagger b_{i1} + b_{i2}^\dagger b_{i2} + d_i^\dagger d_i - 1)$$

(11)

where the pseudo-fermions number operators are $n_{i\alpha} = f_{i\alpha}^\dagger f_{i\alpha} = e_i^\dagger e_i$. We have studied the solutions of this Hamiltonian in the mean-field approximation, in which we replace the boson operators by their averages obtained from the minimization of the band energy. In pure LaMnO$_3$, the number of conduction electrons is $n = 1$, and in the absence of charge ordering $n_{i1} + n_{i2} = n_i = 1$. In this case, the band renormalization factor is independent of the type of orbitals involved $q = z_{i\alpha}^\dagger z_{j\beta}$.

### 3. Results

To characterize the solutions of Eq. (11) for different values of the two parameters $U$ and $\Delta \varepsilon$, we considered both the magnitude of the pseudofermion band gap and the orbital polarization. In Fig. 1 we show the dependence of the band gap with the value of $U$. We can see that for $\Delta \varepsilon = 0$ there is a jump in the band gap at a critical value $U_c$, corresponding to a first order metal-insulating transition (in the parameter $U$). When we begin to increase the value of the JT splitting, $U_c$ shifts to lower values and also the initial band gap in the insulating phase also diminishes. Beyond a certain value of $\Delta \varepsilon$ (between 0.225$U$ and 0.250$U$), the metal-insulating transition is no longer of first order, and the band gap opens smoothly.

![Figure 1](image1.png)

**Figure 1.** Dependence of the band gap as a function of $U$.

![Figure 2](image2.png)

**Figure 2.** Dependence of the orbital polarization as a function of $U$.

![Figure 3](image3.png)

**Figure 3.** Phase diagram $U$-$\Delta \varepsilon$. Solid line: metal-insulating transition. Gray tone: occupancy of the low energy orbital $n_1$. 

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Similar features can be observed in the orbital polarization shown in Fig. 2, where for small values of $\Delta \varepsilon$ there is a jump in the polarization at the same critical value $U_c$. From these results, we can see that an insulating phase with orbital polarization is possible even without a JT deformation. However, an orbital polarization will induce a JT deformation due to the electron-lattice interaction. We also note that for $\Delta \varepsilon = 0$, the orbital polarization is symmetric, i.e. the low energy orbital can be any combination of $\varepsilon_g$ orbitals, and the actual one will depend on the electron-lattice interaction.

In Fig. 3 we show the phase diagram $U - \Delta \varepsilon$ where the line corresponds to the value of $U_c$ at the metal-insulating transition, and the gray tone represents the orbital polarization given by the occupancy of the low energy orbital $n_1$. While in the insulating phase there is always a high orbital polarization, in the metallic phase the amount of orbital polarization depends on $\Delta \varepsilon$: the higher the value of $\Delta \varepsilon$, the higher the polarization. The critical value is close to $U_c = 7t$ for the case without JT splitting, and descends to almost $2t$ for a splitting $\Delta \varepsilon = t$.

To better characterize the different phases, we have calculated the pseudofermion density of states (DOS). In Fig. 4 we show this DOS for three different representative parameters in the phase diagram:

- $(U = 3.5t, \Delta \varepsilon = 0.0t)$: metallic phase with very small orbital polarization, which we have named orbital liquid (MOL). In this case, there is almost no orbital polarization ($n_1 = 0.502$) and the renormalization factor is $q = 0.917$.

- $(U = 3.5t, \Delta \varepsilon = 0.4t)$: metallic phase with orbital order (MOO). The orbital polarization is now higher ($n_1 = 0.764$), and the renormalization factor is closer to one ($q = 0.941$).

- $(U = 3.5t, \Delta \varepsilon = 0.8t)$: insulating phase, also with orbital order (IOO). In this case, the system is almost fully polarized with $n_1 = 0.920$, and as a consequence, $q = 0.986$ is also close to one.

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To simulate the effect of pressure on the electronic properties, we take the experimental data on the IM transition and model the dependence of the parameters with the pressure. All magnitudes are given in terms of the effective hopping at $P = 0$, which is of the order of $t_0 \approx 0.4 \text{ eV}$ [3]. The JT splitting is taken to vary linearly from a value of $\Delta \varepsilon = 1.85t_0$ [4] at $P = 0$ to $\Delta \varepsilon = 0$ at the experimental JT suppression pressure $P = 18 \text{ GPa}$. The $e-e$ interaction constant is considered constant. Finally, the effective hopping has a dependence of the form [2]

$$t(P) = t_0 \left( \frac{d_0}{d(P)} \right)^7$$  \hspace{1cm} (12)

where $d(P)$ is the mean Mn-O distance as a function of the pressure, taken from the experimental data, and $d_0 = d(0)$.

From this dependence of the parameters with the pressure, in Fig. 5 we show the phase diagram $U-P$ where the solid line corresponds to the value of $U_c$ at the metal-insulating transition, the gray tone represents the orbital polarization given by the occupancy of the low energy orbital $n_1$. Note that the values of $U$ in the vertical axis are in units of $t_0$, and we have added a dot line showing that for the estimated value of $U = 11.5t_0$, we obtain an insulator to metal transition pressure close to the experimental one of $P \approx 32 \text{ GPa}$.

4. Conclusions

We use a minimum parameter Hamiltonian model to study the evolution of orbital polarization in LaMnO$_3$. In order to appropriately include the effects of correlation, we resort to the Slave Bosons technique, which was previously used by Feiner and Oles in the context of manganites.

We calculate the electronic structure and from it, the electronic energy to obtain a phase diagram in terms of two independent parameters $U/t$ and $\Delta \varepsilon/t$. The results can be translated to the effect of pressure on the material by modelling the variation of the parameters with volume and connecting to pressure through the compressibility.

The same Hamiltonian could be used to represent the orbital state of other compounds where trivalent Rare Earths partially or totally substitute La, again though modelling of the variation of the hopping, $U/\Delta \varepsilon$ as an effect of substitution and pressure, as for example in equation 12.

Our results confirm and make transparent the conclusion reached in previous ab-initio calculations: The inclusion of the Coulomb energy is necessary and constitute an important factor enhancing the orbital polarization in these compounds.

From the density of the states, it is possible to calculate the gap in the insulating phases and the number of carriers as a function of temperature and pressure in order to compare it with the results of Loa et al. [1]

A natural continuation of these results is the evaluation of the elastic energy involved in the Jahn-Teller distortion that will appear at the polarized phases; these results will be published elsewhere.

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