Pressure-Induced Insulator-Metal Transition in $LaMnO_3$: A Slave-Boson Approach

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The recent observation of a pressure-induced insulator to metal (*I-M*) transition in pure $LaMnO_3$ [I. Loa *et al.*, Phys. Rev. Lett. **87**, 125501 (2001).], opens the way to a study of the role of the orbital degrees of freedom on the electronic structure in a stoichiometric material and its interaction with lattice distortion. To obtain the energy of the system, we resort to a slave boson description for the electronic part and add an elastic term associated to the Jahn-Teller distortion. We obtain the evolution of the electronic structure and the Jahn-Teller distortion with pressure. We find that the Jahn-Teller distortion does not vanish before entering the metallic phase, that the gap closes with pressure in a way similar to that indicated by the temperature dependence of the conductivity, and that both Coulomb and Jahn-Teller interactions are necessary to describe appropriately the phase transition in $LaMnO_3$.

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Introduction.—The discovery of colossal magnetoresistance in half metallic perovskites, 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 $La_{1-x}Sr_xMnO_3$ or in the two dimensional ones as $La_{2-2x}Sr_{2+2x}Mn_2O_7$ the interplay of several degrees of freedom, charge, spin, orbit and lattice displacements determine the physical properties of the system. The interactions between the different degrees of freedom cannot be reduced to 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. Loa *et al.* [1] observed an *I-M* transition in pure $LaMnO_3$ at 32 GPa and room temperature, well above the Neel temperature (145 K) and below the Jahn-Teller (JT) transition temperature (780 K). By extrapolation from their experimental results of the evolution of the JT distortion with pressure they inferred that the distortion disappears well before the *I-M* transition, concluding therefore that the transition should be of the Mott type. However, recent experimental results obtained by Ramos *et al.* [2] lead them to infer that the *I-M* transition and the local JT distortion disappearance should be closely related.

The question of the relative importance of the electron-electron (*e-e*) against electron-lattice (*e-l*) JT interactions in producing the insulating character of $LaMnO_3$ at normal pressure has been the matter of a long discussion. The experimental results under pressure of Loa *et al.* [1] reactivated this debate and several theoretical papers [3–6] have appeared since then. Two of them [3,4] are concerned with the orbital ordering (OO) in the normal pressure ground state (*A*-type antiferromagnetic structure), indicating that this question is still controversial and requires further clarification. Tyer *et al.* [3], used the self-interaction correction (SIC) to local density approximation (LDA) to estimate the energy scales involved in the orbital ordering and claimed that the JT interaction is the dominant source, more than the *e-e* interactions, strong enough to account for the observed OO. Within LDA + Hubbard U (LDA + U) Wei-Guo Yin *et al.* [4], concluded that the JT interaction by itself is not sufficient to stabilize the OO and emphasizes the importance of the *e-e* interaction to facilitate the JT distortion. On the other hand, using also LDA + U, Trimarchi and Binggeli [5] focus mainly on the structural properties under pressure. The relative changes of the Mn-O distances obtained are in good agreement with the experimental results [1] below 11 GPa, but indicate a nonvanishing JT distortion up to the transition pressure. Finally, Yamasaki *et al.* [6] analyze the *I-M* transition with LDA + U and LDA+ dynamical mean-field theory. They calculate the evolution of the electronic structure with pressure for fixed values of the distortion using the experimental values of the volume. They identify the *I-M* transition at the finite value of the distortion for which the gap vanishes at the appropriate experimental pressure, concluding that the distortion does not vanish before the transition.

In this Letter we focus our attention on the orbital aspects of the insulator to metal transition, with a special attention on the combined effect of electron correlation and lattice distortions. To go beyond the mean-field approximation of methods such as LDA + U, we use a slave-boson approach to obtain the total electronic plus elastic energy.

Model.—In $LaMnO_3$, the Mn^{3+} ions form a nearly simple cubic lattice with oxygen ions located between each pair of Mn neighbors, and La ions at the body center of the cube. The octahedral symmetry around each Mn splits the $3d$ levels into a lower energy t_{2g} triplet and a higher energy e_g doublet. Moreover, a JT deformation of the O octahedron lifts the degeneracy of these groups. Because of Hund's rule, the three t_{2g} orbitals are all singly occupied with their spins coupled to form a total spin $S = 3/2$. The additional electron on the Mn^{3+} ion occupy the e_g

orbitals and it is considered, due again to Hund's rule, with its spin parallel to t_{2g} electrons.

We model then the e_g electrons by a spinless Hamiltonian on a cubic lattice

$$H = \sum_{\langle ij\rangle\alpha\beta} t_{ij}^{\alpha\beta} c_{i\alpha}^{\dagger} c_{j\beta} + U\sum_i n_{i1} n_{i2} + \sum_i \Delta\varepsilon_i (n_{i2} - n_{i1}) + \frac{1}{2} K \sum_i \Delta\varepsilon_i^2 \quad (1)$$

where the first term is the kinetic energy with $t_{ij}^{\alpha\beta}$ the hopping integrals that depend both on the type of orbitals α, β and on the direction between neighboring sites i, j. The second term is the on-site Coulomb repulsion for electrons occupying both e_g orbitals on the same site. The last two terms are the electron-lattice interaction, given in terms of the JT splitting $\Delta\varepsilon_i$, and the elastic energy represented by the lowest order in the JT distortion. We have written the Hamiltonian (1) in terms of the JT splitting $\Delta\varepsilon_i$ instead of the JT distortion Q_i. Therefore, the constant K can be expressed, in terms of the electron-lattice coupling λ and the elastic constant for the JT mode K_Q, as $K = K_Q/\lambda^2$.

In $LaMnO_3$, there is a staggered orbital order in the x-y plane and the orbitals are stacked ferromagnetically along the $\hat{z}$ 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 $|x^2 - z^2\rangle$. Moreover, this orbital order corresponds to an homogeneous JT splitting $\Delta\varepsilon_i = \Delta\varepsilon$.

The effect of the magnetic order on the electronic structure is introduced in the hopping integrals by the factor $\exp(iA_{ij})\cos(\theta_{ij}/2)$ [7], with θ_{ij} being the angle between the t_{2g} localized spins in the neighboring sites i, j and A_{ij} a hopping phase. To address the insulator-metal transition occurring at room temperature, well above the Neél temperature ($T_N = 153$ K), we consider that the localized spins are completely random. In a mean-field approximation, the factor is averaged giving a value $\langle \exp(iA_{it}) \times \cos(\theta_{ij}/2)\rangle = 2/3$. The $t_{ij}^{\alpha\beta}$ are the same than for a ferromagnetic phase with a factor $2/3$. In the following we take the renormalized hopping between $|3z^2 - r^2\rangle$ orbitals in the z direction as the reference t.

In order to include in an appropriate way the strong correlations induced by the dominant e-e interactions we introduce auxiliary fields to the description of the low energy states, a method already used by Feiner and Oleś [8] and by Schlottmann [9] in the study of manganites. We use the slave-boson theory of Kotliar and Ruckenstein [10] adapted to our case of two orbitals instead of two spin states. Therefore, we introduce new boson (e_i, d_i, $b_{i\alpha}$) and pseudofermion ($f_{i\alpha}$) operators, where as before the index i corresponds to the Mn site and $\alpha = 1, 2$ corresponds to the two orbitals base in each site. The boson numbers $e_i^{\dagger} e_i$, $b_{i\alpha}^{\dagger} b_{i\alpha}$ and $d_i^{\dagger} d_i$ 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 $e_i^{\dagger} e_i + b_{i1}^{\dagger} b_{i1} + b_{i2}^{\dagger} b_{i2} + d_i^{\dagger} d_i = 1$ and $b_{i\alpha}^{\dagger} b_{i\alpha} + d_i^{\dagger} d_i = c_{i\alpha}^{\dagger} c_{i\alpha}$. The original fermion operators are replaced by $c_{i1(2)}^{\dagger} = (b_{i1(2)}^{\dagger} e_i + d_i^{\dagger} b_{i2(1)}) f_{i1(2)}^{\dagger}$ which correspond to a representation of the empty ($|0_i\rangle = e_i^{\dagger}|\text{vac}\rangle$), singly occupied ($|\alpha_i\rangle = b_{i\alpha}^{\dagger} f_{i\alpha}^{\dagger}|\text{vac}\rangle$) and doubly occupied ($|d_i\rangle = d_i^{\dagger} f_{i2}^{\dagger} f_{i1}^{\dagger}|\text{vac}\rangle$) local states, $|\text{vac}\rangle$ being the vacuum state.

The anticommutation rules for the original fermions are guaranteed provided the constraints ($b_{i\alpha}^{\dagger} b_{i\alpha} + d_i^{\dagger} d_i = f_{i\alpha}^{\dagger} f_{i\alpha}$) are satisfied, which are implemented by means of the corresponding Lagrange multipliers $\{\lambda_i, \mu_{i\alpha}\}$. To recover the correct result in the uncorrelated ($U = 0$) limit, a renormalization of the bosonic factor is necessary. In analogy with the spin case, the renormalized bosons factors take the form

$$z_{i1(2)}^{\dagger} = \frac{b_{i1(2)}^{\dagger} e_i + d_i^{\dagger} b_{i2(1)}}{\sqrt{(1 - e_i^{\dagger} e_i - b_{i2(1)}^{\dagger} b_{i2(1)})(1 - d_i^{\dagger} d_i - b_{i1(2)}^{\dagger} b_{i1(2)})}}. \quad (2)$$

Within this slave-boson representation, the Hamiltonian (1) is written as

$$H = \sum_{\langle ij\rangle\alpha\beta} t_{ij}^{\alpha\beta} z_{i\alpha}^{\dagger} z_{j\beta} f_{i\alpha}^{\dagger} f_{j\beta} + U\sum_i d_i^{\dagger} d_i + \Delta\varepsilon \sum_i (n_{i2} - n_{i1}) + \frac{1}{2} K \sum_i \Delta\varepsilon_i^2 + \sum_{i\alpha} \mu_{i\alpha} (f_{i\alpha}^{\dagger} f_{i\alpha} - b_{i\alpha}^{\dagger} b_{i\alpha} - d_i^{\dagger} d_i) + \sum_i \lambda_i (e_i^{\dagger} e_i + b_{i1}^{\dagger} b_{i1} + b_{i2}^{\dagger} b_{i2} + d_i^{\dagger} d_i - 1), \quad (3)$$

where the pseudofermions number operators are $n_{i\alpha} = f_{i\alpha}^{\dagger} f_{i\alpha} = c_{i\alpha}^{\dagger} c_{i\alpha}$. 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 $n = 1$. In the absence of charge ordering $n_{i1} + n_{i2} = n_i = 1$, and the band renormalization factor $q = z_{i\alpha}^{\dagger} z_{j\beta}$ becomes independent of the type of orbitals involved.

Results.—The electronic part of the Hamiltonian (3) depends on two parameters: U/t and $\Delta\varepsilon/t$. We calculate both the band gap E_g and the orbital polarization, characterized by the occupancy n_1 of the low energy lying orbital, as functions of these two parameters.

To analyze the relative importance of the JT distortion and the e-e interaction on the electronic structure, we show in Fig. 1 the U-$\Delta\varepsilon$ phase diagram, where the JT splitting $\Delta\varepsilon$ of Eq. (3) is imposed and not minimized taking into account the elastic term. The gray tone represents the orbital polarization given by the value of n_1 ($0.5 \leq n_1 \leq 1$). The solid line correspond to the critical value U_c that separates the metallic and insulating regions. For $\Delta\varepsilon = 0$ we obtain a metallic phase with no orbital order for low U, and an insulating phase with orbital polarization for

$U \gtrsim 6.85t$. This means that for high values of U, the orbital liquid in no longer a stable solution and there is a spontaneous symmetry breaking. This result differs from the work of Feiner and Oleś [8], where in the $U \to \infty$ limit they concluded that the orbital liquid is the stable phase. As expected, U_c shifts to lower values as the JT splitting is increased, attaining a low value $U_c \simeq 2.3t$ for $\Delta\varepsilon = t$. We find three possible scenarios: (i) for $\Delta\varepsilon < \Delta\varepsilon_c \simeq 0.2t$, the transition from the low U metallic phase to the high U insulating phase is a discontinuous transition, with an abrupt appearance of a gap; (ii) for $\Delta\varepsilon > \Delta\varepsilon_c$ we find that the gap opens gradually in the metallic to insulator transition; (iii) for $\Delta\varepsilon \gtrsim 1.86t$ there is no metallic phase even for $U = 0$. In the inset in Fig. 1 we show the magnitude of the band gap in the insulating phase just after the transition. Regarding the orbital polarization, we can see a jump in the n_1 occupancy across the transition line when $\Delta\varepsilon < \Delta\varepsilon_c$. The evolution of orbital polarization becomes continuous when at larger JT splitting ($\Delta\varepsilon > \Delta\varepsilon_c$). We note that here we are only considering the same staggered orbital order as in $LaMnO_3$ at $P = 0$. For the case with $\Delta\varepsilon = 0$, the actual ground state solution should be obtained minimizing with respect to the character of the low energy orbital in each site.

To continue with the analysis of the competition between e-e and e-l interactions we take into account the elastic term in the Hamiltonian (3). The JT splitting $\Delta\varepsilon$ is now obtained minimizing the energy. In this way, we obtain the U-K phase diagram shown in Fig. 2. As before, the solid line correspond to the value of U_c separating metallic and insulating regions. One relevant results we find is that, except in an extremely narrow region close the transition line for $U/t \lesssim 3.5$, both the JT distortion and the orbital polarization disappear in the metallic phase. This means that in the process of minimization of the total energy, electronic plus elastic, the orbital polarization dissapear practically over almost all the metallic region. In the insulating phase the JT splitting depends on the value of K: the bigger K, the lower the corresponding $\Delta\varepsilon$. On the other hand, for high values of U the JT splitting is almost independent of U.

In an attempt to connect to the experimental results [1,2], we model the effect of pressure by introducing a P dependence on t and K, while considering U constant. For the hopping t we take into account: (i) the effective Mn-Mn hopping is proportional to the square of the Mn-O hopping $t_{\text{Mn-O}}$, (ii) the dependence of $t_{\text{Mn-O}}$ with the Mn-O distance $d_{\text{Mn-O}}$ is given by [11] $t_{\text{Mn-O}} \propto d_{\text{Mn-O}}^{-7/2}$, (iii) the mean distance $d_{\text{Mn-O}}$ dependence with unit cell volume as $d_{\text{Mn-O}} \propto V^{1/3}$, and finally (iv) the volume-pressure relation $V(P)$ taken from the experimental data. We obtain then

$$t(P) = t_0\left(\frac{V_0}{V(P)}\right)^{7/3}. \tag{4}$$

On the other hand, we take the simplest form for the dependence K with pressure: $K(P) = K_0 + \alpha P$

We choose the parameters of the model in the following way: $K_0 t_0 = 1.08$ is taken in order to have a $\Delta\varepsilon/t_0 \simeq 0.9$ according to Yin *et al.* [4]; $\alpha = 0.08$ is chosen such that K varies with pressure approximately as the bulk modulus B_0; finally, $U/t_0 = 8.15$ is chosen such that the insulator to metal transition occurs around the experimental pressure $P \simeq 32$ GPa. This value of U/t_0 turns out to be very similar to the one used in Ref. [6]. Using this model, the evolution of the parameters (U/t, Kt) with pressure, from 0 to

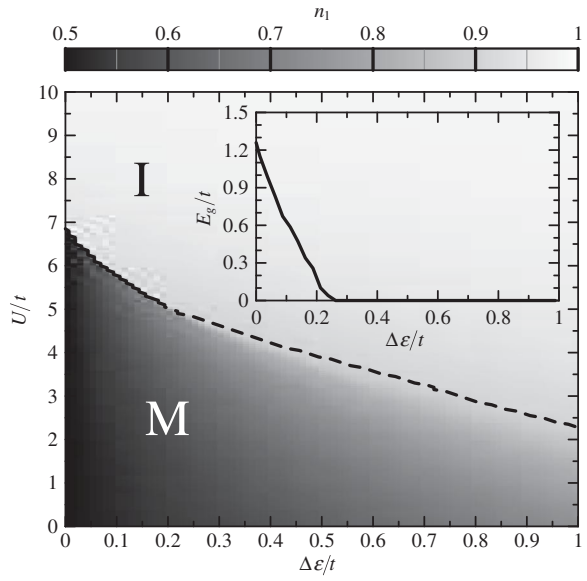

FIG. 1. Phase diagram U-$\Delta\varepsilon$. Solid line: metal-insulator transition. Gray tone: occupancy of the low energy orbital n_1. Inset: magnitude of the band gap in the insulating phase along the transition line.

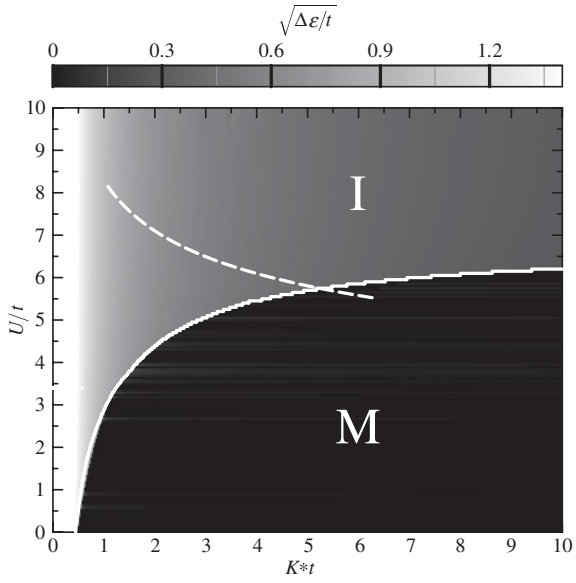

FIG. 2. Phase diagram U-K. Solid line: metal-insulator transition. Gray tone: Jahn-Teller splitting of e_g orbitals. Dashed line: variation of parameters with pressure from 0 GPa (left) to 40 GPa (right).

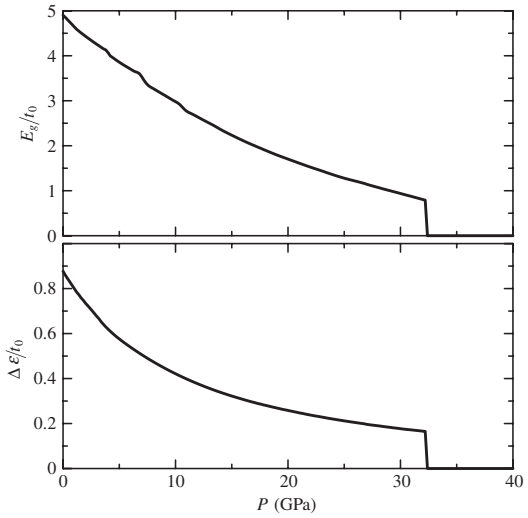

FIG. 3. Dependence with pressure of the pseudofermion band gap E_g and the JT splitting $\Delta\varepsilon$.

40 GPa, is shown by a dashed line in Fig. 2. The I-M transition occurs where there is no JT splitting in the metallic phase. We show in Fig. 3 the evolution with pressure of the pseudofermion band gap E_g and the JT splitting $\Delta\varepsilon$. Even though they are not directly comparable, the pressure dependence of the gap and the pressure dependence of the logarithm of the resistivity [1] show a similar behavior indicating compatibility and qualitative agreement between the model results and experiment. Both parameters (E_g and $\Delta\varepsilon$) decreases monotonically with pressure up to the critical pressure where they show a discontinuous jump to zero.

In summary, we have used a minimum parameters model Hamiltonian to study the evolution of orbital polarization in $LaMnO_3$. In order to include appropriately the effects of correlation, we resort to the slave bosons technique. From the electronic energy calculated with this model, we obtain phase diagrams U-$\Delta\varepsilon$ and U-K. We characterize each phase by the magnitude of the pseudofermions gap (which defines the line separating the metallic and insulating phases), and by the magnitude of the orbital polarization. To make contact with experiment we introduce the effect of pressure by proposing a dependence of the parameters with the pressure. The precise values of the parameters do not affect the main conclusions of this paper, i.e., the evolution of the system with the pressure as shown in Fig. 3 do not change substantially with another reasonable choice of parameters.

In conclusion, the simplified model presented here is sufficient to describe the evolution of the relevant structural and electronic characteristics with pressure, as well as the metal-insulator transition found by Loa *et al.* [1] at 32 GPa. The transition occurs between a distorted and orbitally polarized insulating phase and a undistorted and orbitally unpolarized metallic phase. The jump of the band gap magnitude is in agreement with the experimental results of Loa *et al.* [1], contrary to the assertion of Yamasaki *et al.* [6] that the I-M transition takes place when the bands start to overlap. From the JT distortion point of view, the experimental results about the nature of the transition are contradictory. While Loa *et al.* [1] conclude that the JT distortion disappears well below the I-M transition, Ramos *et al.* [2] propose that the I-M transition and the local JT distortion disappearance should be closely related. We find that the insulating phase remains distorted up to the transition pressure, where the distortion disappears discontinuously in the metallic phase. This differs from the assertion of Yamasaki *et al.* [6] that the transition occurs within the orbitally symmetry-broken phase. This difference comes from the fact that elastic energy is not explicitly included in Ref. [6]. This is what we would get from our Fig. 1 with a fixed value of $\Delta\varepsilon/t$.

More experimental results are necessary to determine how appropriate is the model presented here for reproducing the evolution with pressure of the system properties and to elucidate the nature of the transition.

Finally, we have shown here that the inclusion of the orbital degeneracy and the coupling with the lattice can modify substantially the character of U-induced metal-insulator transitions.

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[1] I. Loa, P. Adler, A. Grzechnik, K. Syassen, U. Schwarz, M. Hanfland, G. K. Rozenberg, P. Gorodetsky, and M. P. Pasternak, Phys. Rev. Lett. **87**, 125501 (2001).
[2] Aline Y. Ramos, Hélio C. N. Tolentino, Narcizo M. Souza-Neto, Jean-Paul Itié, Liliana Morales, and Alberto Caneiro, Phys. Rev. B **75**, 052103 (2007).
[3] R. Tyer, W. M. Temmerman, Z. Szotek, G. Banach, A. Svane, L. Petit, and G. A. Gehring, Europhys. Lett. **65**, 519 (2004).
[4] Wei-Guo Yin, Dmitri Volja, and Wei Ku, Phys. Rev. Lett. **96**, 116405 (2006).
[5] G. Trimarchi and N. Binggeli, Phys. Rev. B **71**, 035101 (2005).
[6] A. Yamasaki, M. Feldbacher, Y.-F. Yang, O. K. Andersen, and K. Held, Phys. Rev. Lett. **96**, 166401 (2006).
[7] E. Müller-Hartmann and E. Dagotto, Phys. Rev. B **54**, R6819 (1996).
[8] Louis Felix Feiner and Andrzej M. Oleś, Phys. Rev. B **71**, 144422 (2005).
[9] P. Schlottmann, Phys. Rev. B **62**, 439 (2000); P. Schlottmann, *ibid.* **73**, 214428 (2006).
[10] G. Kotliar and A. E. Ruckenstein, Phys. Rev. Lett. **57**, 1362 (1986).
[11] W. A. Harrison, *Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond* (W. H. Freeman, San Francisco, 1980).