

MANGANITES AT LOW TEMPERATURES AND LIGHT DOPING: BAND APPROACH AND PERCOLATION

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A tight-band model is employed for the e_{2g} -orbitals in manganites. It is shown that a large intraatomic Hund's coupling, J_H and the resulting double-exchange mechanism lead to antiferromagnetic ordering along one of the cubic axis stabilized by the cooperative JT effect which further decreases the band energy of electrons. As a result, LaMnO_3 is a band insulator built of 2D ferromagnetic layers. The critical concentration $x_c \simeq 0.16$, for onset of ferromagnetic and metallic behavior at low temperatures in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and the phase transition are treated in the percolation approach.

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Current efforts in studies of the "colossal magnetoresistance" (CMR) in the manganites, $\text{R}_{1-x}\text{B}_x\text{MnO}_3$ (usually, $\text{R}=\text{La}$, $\text{B}=\text{Ca}$, Sr ; see e.g. [1-3] for a review and references) are, naturally, focused on phenomena occurring in the vicinity of the metal-insulator transition temperature, T^* , which for $x = 0.2 - 0.3$, reaches the room temperature range. There are no doubts that both the Jahn - Teller (JT) distortions and Zener's double exchange (DE) mechanism [4,5] are two key ingredients of CMR.

The transition between the paramagnetic and conducting ferromagnetic phases is treated in [6] as a localization-delocalization "crossover" driven by thermal fluctuations of the local JT-modes. In this paper we focus on the analysis of phenomena occurring at low T . In this region the approach should be different. Indeed, the two end members of the series, LaMnO_3 and CaMnO_3 , are both antiferromagnetic (AF) insulators. "Doping" of LaMnO_3 by divalent atoms results in metallic conductivity only above some critical concentration, $x_c \simeq 0.16$.

Low temperature phases of manganites are habitually interpreted in terms of localized orbitals [7, 8], more often that not in the modified Hubbard model (see. e.g. [9]). Although it is widely accepted that electron-electron correlations play the key role in low temperature behavior of manganites, we show that their major properties can be understood within the framework of the band approach, as well, or in percolation terms.

The following facts have to be explained: 1) the insulating state of the parent LaMnO_3 ; 2) the A -type of antiferromagnetic ordering (alternating ferromagnetic planes); 3) the small value of the Néel temperature, $T_N \sim 150$ K in the low x -range, while the structural changes occur at about 900 K; 4) the localization of "holes" introduced into the Mn^{3+} -subsystem at $x < x_c$; 5) the threshold concentration, $x_c \simeq 0.16$, above which metallic conductivity sets in at low T .

In the band model the properties from 1) to 4) are brought about by the DE- and JT-mechanisms. We interpret the value $x_c \simeq 0.16$ in terms of percolation theory: both the cluster approach and the phase separation picture, as suggested first for the cuprates [10], seem to give the same criterion [11].

Let us start from the *A*-type of the ground state of LaMnO_3 . According to our picture, appearance of such a magnetic state is *not* caused by any exchange interaction between localized spins on different sites. The mutual arrangement of the distorted octahedra and of the core ${}^3t_{2g}$ -spins, \mathbf{S}_i ($S=3/2$), is stabilized only by gains in the kinetic *band* energy of the “conduction” e_{2g} -electrons.

The single electron Hamiltonian is then of the form [6]

$$\hat{H} = \sum_{i,\delta} (\hat{t}_{i,i+\delta} - J_H \mathbf{S}_i \cdot \hat{\sigma} + g \hat{\tau}_i \cdot \mathbf{Q}_i + J_{el} \mathbf{Q}_i^2). \quad (1)$$

Here $\hat{t}_{i,i+\delta}$ is the nearest neighbor tunneling matrix, defined on some basis of the two-dimensional cubic representation, e_{2g} ; \mathbf{Q}_i are the active local JT-modes with the matrix elements on that electronic basis in terms of a “pseudospin” matrix, $\hat{\tau}$ (see e.g., in [7]; \mathbf{Q}_i are defined as dimensionless parameters). The static JT deformations and the staggered magnetization, $\langle \mathbf{S}_i \rangle = (-1)^i \langle S \rangle$ of the *A*-type phase are treated below in the mean field approximation.

To avoid cumbersome expressions, we first discuss the competition between ferro- and antiferromagnetic order for the *one* band model:

$$\varepsilon(\mathbf{p}) = t \cos(ap_z) + \bar{t}(\mathbf{p}_\perp). \quad (2)$$

Assume first that the local (${}^3t_{2g}$) spins are ordered ferromagnetically. At large $J_H \gg t$ the low energy band is shifted down, by $-J_H \langle S \rangle$. The main contribution to the total energy is $E_H = -J_H \langle S \rangle n$ (n is the number of electrons per unit cell), while the kinetic energy contribution due to the polarized electrons is linear in t, \bar{t} .

Consider the same problem for AF-ordering along the z -axis (with the period $2a$). It is convenient to discuss a more general case:

$$\mathbf{S}_i = (\pm \langle S_z \rangle, M_x) \quad (S_z^2 + M_x^2 = S^2), \quad (3)$$

i.e. the canted AF-structure [8] for the ${}^3t_{2g}$ -spins. Solving the periodic electron spectrum problem in a manner similar to the solution for the two local sites [5], one obtains the following four branches:

$$\varepsilon_l(\mathbf{p}) - \bar{t}(\mathbf{p}_\perp) = \pm \sqrt{J_H^2 S^2 + t^2(p_z) \pm 2J_H |t(p_z)| |M_x|}. \quad (4)$$

At $J_H \gg t, \bar{t}$, the low energy spectrum reduces to:

$$\varepsilon(\mathbf{p})_{1,2} - \bar{t}(\mathbf{p}_\perp) \simeq -J_H S \pm |t(\mathbf{p}_z)| (|M_x|/S). \quad (5)$$

The second term restores the familiar expression for transport [5]: $M_x = 2S |\cos \theta/2|$ (θ is the angle between the adjacent local spins).

For the AF-case ($M_x \equiv 0$), the Brillouin zone is reduced by half, but there are now two branches in (5). As the result, the main term, $-J_H S$, does not change. For a single band,

the antiferromagnetic order may even be energetically favorable, although the energy gain would be small, of the order of (see (4)):

$$t^2/J_H \ll t. \quad (6)$$

For two bands there are terms linear in t . The JT-band splitting is necessary if we wish to decrease the ground state energy below that one for the ferromagnetic state.

We obtained the "bare" band spectrum of the cubic material with the e_{2g} -electrons. For calculating \hat{t}_{ik} , and hence, the electronic spectrum, $\epsilon(\mathbf{p})$, use of the normalized basis functions of the form:

$$\psi_1 \propto z^2 + \epsilon x^2 + \epsilon^2 y^2, \quad \psi_2 \equiv \psi_1^* \quad (7)$$

($\epsilon = \exp(2\pi i/3)$), proves to be more convenient to account for the cubic symmetry of the initial lattice. The functions (7) are connected with the real basis, $\varphi_1 \propto d_{z^2}$ and $\varphi_2 \propto d_{x^2-y^2}$:

$$\psi_1 = (\varphi_1 + i\varphi_2)/\sqrt{2}, \quad \psi_2 = (\varphi_1 - i\varphi_2)/\sqrt{2}. \quad (8)$$

The tight-binding spectrum of the e_{2g} -electrons consists of two branches, which are discussed below.

Before proceeding further, we write down explicitly the local, JT-part of the Hamiltonian (1) in the basis (7):

$$-\frac{g}{2}Q_0 \begin{pmatrix} 0 & \exp(i\theta) \\ \exp(-i\theta) & 0 \end{pmatrix}. \quad (9)$$

In the standard notations [7]: $Q_2 = Q_0 \sin \theta$; $Q_3 = Q_0 \cos \theta$. Here Q_0 is the magnitude of the JT distortions, while the "angles", $\theta = 0, 2\pi/3, -2\pi/3$ correspond to elongations of the octahedron along the z , x , and y -axes, respectively.

With the above in mind, consider the options for possible ground states in manganites. In the case of stoichiometric LaMnO_3 there is exactly one e_{2g} -electron (Mn^{3+}) per unit cell. The ferromagnetic filling-up for two bands will produce a metallic spectrum. AF-ordering along one axis results in the same main contribution, $-J_H S$ (at large J_H), while the corresponding kinetic energy contribution becomes of the order of $t^2/J_H \ll t$. Second order terms in t in Eq. (4) imply that the spectrum is much less dispersive along the z -axis ($M_x \equiv 0$). Planes with the antiparallel core spins become almost isolated.

AF-ordering along any other direction would lack electronic transport along this direction, again shrinking bands. Thus, it is enough to have the AF-order along one axis to access the major energy gain, $-J_H S$. However, to stabilize the AF-order along *one* axis, one needs to further reduce the total energy by the antiferroelastic JT-distortions along the remaining directions.

Note again that after the AF-ordering sets in, say, along the z -axis, the communication between adjacent layers in real space becomes very weak. Therefore, at large J_H it is possible to reduce the problem, to main approximation, to the one of two-dimensional (2D) electrons. For decoupled layers, electrons inside the layer are ferromagnetically polarized along the $^3t_{2g}$ -core spins. Again, in this 2D problem there is one electron per (2D) cell. The metallic spectrum simplifies to the form:

$$\begin{aligned} \epsilon_{1,2}^{2D}(\mathbf{p}) &= (A + B)(\cos ap_x + \cos ap_y) \pm \\ &\pm (A - B) \{(\cos ap_x + \cos ap_y)^2 + 3(\cos ap_x - \cos ap_y)^2\}^{1/2}, \end{aligned} \quad (10)$$

where $i, k = (x, y, z)$;

$$A \propto \overline{\varphi_1(z; x, y)\varphi_1(z + a; x, y)}, \quad B \propto \overline{\varphi_2(z; x, y)\varphi_2(z + a; x, y)}$$

are the two overlap integrals between the two sites separated by the lattice constant, a . Introduce now JT-distortions in the layer with the structure vector (π, π) in a plane. If the JT-splitting is strong enough, then instead of (9), the new spectrum will consist of two pairs of bands separated by energy gaps over the entire (new) Brillouin zone, with the low-energy bands fully occupied. This completes the band picture for the insulating A -type ground state in LaMnO_3 .

For this interpretation one needs:

$$J_H \gg t, \quad gQ_0; \quad gQ_0 \gtrsim t. \quad (11)$$

Eq.(10) does not impose any severe limitations on the model parameters. The above physics should be present in any realistic band structure. Usually the band calculations use the experimental lattice parameters, and it is not straightforward to single out (e.g. in [3]) the competition of the effects considered above.

Finding the single electron spectrum in presence of the JT-distortions from (8), (9), writing down the total energy of the filled-up bands and subsequent minimization of the total energy, is a straightforward but rather tedious task. In the general case, there is no small parameter. We will consider numerical aspects elsewhere.

Below we take advantage of the transparent physics of the independent 2D-layer approximation. First of all, the 2D ferromagnetic ground state in each layer which was obtained in the mean field approximation, will be smeared out by fluctuations: ferromagnetism does not exist as a stable thermodynamical phase in 2D, unless there is a weak interlayer coupling, t^2/J_H , of eq. (6). This results in a rather low Néel temperature, $T_N \simeq 150 \text{ K}$, in LaMnO_3 , at $t \sim 0.1 \text{ eV}$, $J_H \sim 1 \text{ eV}$.

To illustrate the above, consider the "symmetric" model [9], $A = B = t/2$ in (9):

$$\varepsilon(\mathbf{p}) = t(\cos ap_x + \cos ap_y) \equiv \tilde{t}(\mathbf{p}). \quad (12)$$

Eq. (11) gives the two degenerate bands. For one polarized 2D electron per unit cell, the two Fermi surfaces run along the lines $p_x \pm p_y = (\pm\pi/a)$. In the presence of the JT-distortion (8) the new spectrum (in the reduced Brillouin zone, with the structural vector $(\pi/a, \pi/a)$) consists of the four branches: $\varepsilon_l(\mathbf{p}) = \pm|t(\mathbf{p})| \pm \Delta$, where $\Delta = |gQ_0/2|$. At $\Delta > 2t$ there are two pairs of energy bands, and the insulating gap sets in at $p_x = p_y = 0$, equal to $\Delta - 2t$. The distortion $gQ_0 = g^2/J_{el}$ is defined from the on-site problem.

Turning back to the parameters (J_H, J_{el}, g, A, B) of our general model, connections between gQ_0, J_{el} and A and B are established by minimization of the total (electronic and elastic) energies with respect to Q and M_x (see eq. (5)). The deformations of octahedra (Q_0) are known from the structural data (see e.g., in [3]). One may also expect that $B \ll A$: tunneling between Mn-sites takes places through the shared oxygen ions, and the notion that the d -shell size, d , is small compared to the lattice constant, $a(d \ll a)$, is quite helpful, as oxides of transition metals are concerned [7, 12, 13]. Currently the spin wave spectrum in LaMnO_3 is available [14]. Although we postpone the study of the spin wave spectrum for the future, it is worth mentioning that coexistence of the localized $^3t_{2g}$ -spins and itinerant e_{2g} -electronic states (which in the AF-environment are

not characterized by the spin-projection quantum number), may result in deviations from an anisotropic Heisenberg model.

Finally, we briefly discuss the concentration dependence. At small x the two mechanisms lead to localization of a doped hole. The first one is directly related to the 2D physics. According to (1), interaction of a hole with the JT-modes may decrease the hole's energy by an amount of order of g^2/J_{et} . If its energy is now below the band's bottom, the hole becomes self-trapped. Two-dimensionality plays the crucial role in that there are no energy barriers for the process [15]. If a dimensionless parameter $C \sim g^2/J_{et}W$ (W is a band-width) exceeds a critical value of order of unity, no itinerant states are possible in the 2D system. The second mechanism is the Coulomb binding of holes near dopants [8].

At larger x the band approach becomes useless. Instead, we adopt the point of view of the percolation theory. Let us start first with the *cluster* description [11]. In the so-called site problem, consider formation of an infinite cluster of the neighboring divalent ions. For the simple cubic lattice the critical $x_{cr}(s) = 0.31$. This value is not universal.

It is well known [11] that correlations between sites rapidly reduce $x_c(s)$ to the value $x_c \simeq 0.16$, which is also a threshold concentration for a continuous percolation problem. Although holes are located near divalent ions (forming the cluster's skeleton), the hole's hopping takes place along the adjacent Mn-sites correlated by the fact that the wave function of a single hole is spread over a few interatomic distances tending to suppress JT-distortions and align spins ferromagnetically in its vicinity. The cluster's structure is complicated, however, at $x > x_c$ one may expect that locally its properties are close to the ones of the homogeneous metallic ferromagnetic state. The rest of the sample does not conduct.

Another plausible view is that the material may separate into coexisting insulator and metallic phases [10]. In the cluster approach the Coulomb energy is playing the crucial role confining holes in the skeleton's vicinity. In the continuous description the Coulomb energy would limit sizes of the phases' domains. In both approaches the Coulomb energy may be strongly reduced by sufficiently large dielectric constant of the insulating phase and due to metallic screening in the ferromagnetic phase.

With the temperature increase, concentration of the metallic phase decreases: temperature-induced JT-distortions [6] provide stronger localization of "doped" holes. From such a point of view the metal-insulator transition temperature, T^* , may also be treated as a percolation point (at fixed x), and this agrees well with the extreme sensitivity of CMR to applied magnetic field.

To summarize, the view of LaMnO₃ as a band insulator, is consistent with the main experimental facts. Large intraatomic Hunds' exchange, J_H , forces the cubic system to order antiferromagnetically along one direction because the band energy of electrons can then be effectively reduced by the JT-instability resulting in the new (tetragonal) lattice ($\sqrt{2}a \times \sqrt{2}a \times 2a$). At $J_H \gg t, gQ_0$, the e_{2g} -electrons form almost disconnected 2D layers. This manifests itself in the low Néel temperature. The percolation analysis can explain the value of the critical concentration, $x_c \simeq 0.16$ and CMR itself suggesting new interesting physics.

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