PROPERTIES OF MANGANITES: PHASE DIAGRAM, JAHN-TELLER EFFECT

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Abstract

Properties of manganites are greatly affected by cooperative Jahn-Teller effect and Hund's interaction. The insulating (undoped) as well as metallic ferromagnetic states can be described from a unified point of view based on two-band picture. The system is intrinsically inhomogeneous and the metal-insulator transition is treated by means of percolation theory.

Introduction

The paper is concerned with the properties of magnetic oxides (manganites) , such as $La_{1-x}D_xMnO_3$ (D is a divalent ion). The recent discovery of colossal magnetic resistance (CMR) has resulted in the revival of an intense interest in these oxides (see e.g. review [1]). In this paper we focus mainly on the low temperature region, that is on the ground state of the system. Our approach was described in [2-6]. Below we present key points of our treatment and introduce some new aspects. The compounds are characterized by a rich phase diagram and our goal is to study its evolution with doping. The Jahn-Teller effect appears to be a key factor which determines the properties of the materials.

Total Hamiltonian

The $LaMnO_3$ crystal has the following structure.

The Mn^{3+} ions are located at the corners, and the La ion at the center of the unit cell . This cubic structure represents our starting point. In addition, the Mn^{3+} is caged by the O^{-2} octahedron ; locally this forms an MnO_6 complex with the Mn ion in the central position surrounded by light O ions.

The d-shell of the Mn ion in the cubic environment is splitted into a doublet and triplet. It is important that the three -fold manifold (t_{2g}) is occupied by three d-electrons , whereas the upper double-degenerate term e_{2g} is occupied by one electron only.

The key ingredients (interactions) are the following:

1. The strong Hund's rule coupling (this is the largest energy scale in our theory, see below) aligns all spins in the same direction ;
2. Hopping, and
3. Cooperative Jahn- Teller effect. As a result , the total Hamiltonian is a sum:

$$H_{JT} = H_H + H_t + H_{JT} \qquad (1)$$

Here

$$H_H = - J_H \sum_i \boldsymbol{\sigma}\, \mathbf{S_i} \qquad (2)$$

$$H_t = \sum_i t_{i,i+\delta} \qquad (3)$$

$$H_{JT} = \sum_i g\,(\tau_i\, Q_i) + \sum_{i,j} J_{el.}\, Q_i\, Q_j \qquad (4)$$

The Hund's coupling between the local spin **S** (**S**=3/2) formed by the t_{2g} electrons and the e_{2g} electron is described by the term

(2) ; $\boldsymbol{\sigma}$ (Pauli matrices) correspond to the spin of the e_{2g} electron ;

$J_H \approx 1$ eV. Note ,that the unit cell contains one e_{2g} electron and its motion through the lattice is described (in the tight-binding picture) by the term (3).

The third term in Eq. (1) descibes another important ingredient which also affects the behavior of the system , namely the Jahn-Teller (JT) instability. Indeed, the e_{2g} electron is in the double-degenerate state ,and it follows from the JT theorem (see, e.g. [7]

) , that the electron-lattice couplng will lead to a static distortion and consequently, to a change in the crystal symmetry. In Eq.(4) g is the coupling constant, Q_i are the local active JT modes, τ is the "pseudospin" matrix (see e.g. [8]).

Let us make several comments. Hamiltonian (1) does not contain correlation effects (Hubbard term) used in many papers. We've challenged such approach for several reasons. First of all, there is no doubt about the importance of hopping and the Hund's and JT terms. It is essential, and this is demonstrated in our papers [2-4, 6] that this is sufficient to explain the major properties of manganites. It will be proven (see below) that the undoped compounds can be treated as band insulators. The analysis of the metallic phase shows that the band picture provides an excellent description of various data and, therefore insulating and metallic phases can be described from an unified point of view. The next, but not a least reason, stressed by one of the authors in [3] is that the JT effect which is also due to Coulomb interaction, corresponds to the fact that there is only one electron on

the degenerate level, and this already reflects the correlation effect. Finally, it is of course clear that dealing with the strictly atomic

d-orbitals would be a strong oversimplification. If a Mn ion is placed into the oxygen octahedron environment, the e_{2g^-} terms are formed by the whole ligand, so that the "pure"

d-functions become considerably

hybridized with the surrounding oxygen states (e.g. see the discussion in [9,10]). Hence the electronic polarization would undoubtly reduce the magnitude of the "Hubbard"- like(on-site) interactions.

Speaking of term (3),we restrict the analysis to nearest-neighbor hoping. In a simple band picture with one electron per unit cell, the system should be metallic. Nevertheless, a more careful analysis which includes not only the hopping term, but also a strong Hund's

interaction along with the cooperative Jahn-Teller effect, leads one to the picture of a peculiar band insulator (see below).

Another essential point that we are dealing with a collective JT effect (see e.g. [11]). Indeed, the key element of the picture is that the oxygen ion along the Mn-O-Mn bond is shared between two neighboring octahedra. As a result, the distortions are not independent. If a static distortion is fixed for a given site (in practice, this distortion is an elongation along one of the axis), it induces a contraction of the octahedra on the neighboring site. In other words,

such collective JT effect would result in the so-called "antiferroelastic" distortion of the lattice , characterized by a structural vector, Q_0. The

Hamiltonian (4) describes the collective JT effect. The last term in (4) describes the elastic energy. We are dealing (see [12], [8]) with two normal modes Q_2 and Q_3, where:

$$\begin{aligned} Q_2 &= \frac{1}{\sqrt{2}}(x_1 - x_4 - y_5 - y_2), \\ Q_3 &= \frac{1}{\sqrt{6}}(2z_2 - 2z_6 - x_1 - x_4 - y_2 + y_5). \end{aligned} \tag{5}$$

Note also that we start with, a somewhat oversimplified (the so-called “pseudocubic”) crystalline structure for manganites. As it is

well-known [1], in that approximation the unit cell, say, for $LaMnO_3$, may be taken as a cube, with the lattice constant $a_0 \cong 3.9^{\circ}A$. Rare-

earth or alkaline ions are placed at the center, while the manganese ions occupy the corner sites. Mn^{3+} sites are caged into the oxygen octahedra, which share the O^{2-} ions along the Mn-O-Mn bond (another view would be that each La^{3+} ion is cooped up in the midst of twelve O^{2-} ions). The ideal structure is then modified for real materials, $AMnO_3$, due to a mismatch in the ionic radii. The latter is commonly characterized by the tolerance factor, t_f (see e.g. in [1]):

$$t_f = \frac{1}{\sqrt{2}} \bullet \frac{R_A + R_O}{R_{Mn} + R_O} \qquad (6)$$

The effect of $t_f \neq 1$ is that the oxygen octahedra become periodically tilted, and the unit cell may then be comprised of a few "pseudocubic" cells. It is shown below that deviations from the "pseudocubic" structure, i.e. deviations in the angle, α, of the Mn-O-Mn bond from 180° are not of much importance for the "average" electronic structure. However, *local* fluctuations in the tolerance factor (6) may play rather significant role for the conducting properties of the "doped" manganites $A_{1-x}B_xMnO_3$.

As noted above, Hund,s coupling corresponds to the largest energy scale, so that

$$J_H >> t,\ gQ_0\ ;\quad J_H \approx 1eV\ ;\ t \approx gQ_0 \approx 0.1\ eV. \qquad (7)$$

Band insulator

The undoped compound contains terromagnetic layers along with the antiferromagnetic ordering along the z-axis (A-structure). The presence of the A-structure leads to the 2D transport which occurs along ferromagnetic layers. This is a consequence of the transport being provided by spin-polarized carriers; then the charge transfer between two neighboring sites with opposite spins (AF ordering in the z-direction) is frustrated.

To calculate the one-electron spectrum it is convenient to use the normalized basic functions of the form:

$$\Psi_1 \propto z^2 + \varepsilon x^2 + \varepsilon^2 y^2\ ;\ \Psi_2 = \Psi_1^* \qquad (8)$$

where $\varepsilon = \exp(2\pi i/3)$. This choice allows us to account for the cubic symmetry of the initial lattice. We are using the tight binding approximation. One can use also the real basis set: $\phi_1 \propto d_{z^2}$ and

$\phi_2 \propto d_{x^2-y^2}$ The functions (8) can be expressed in terms of real basis: $\Psi_1 = (1/\sqrt{2})(\phi_1 + i\phi_2)$; $\Psi_2 = (1/\sqrt{2})(\phi_1 - i\phi_2)$.

Let us consider first the band spectrum of the Hamiltonian (3) (the Hund's term and JT term being temporary omitted). The matrix $\hat{t}$ in (3) on the basis (8) has the form:

$$\begin{pmatrix} \Sigma_{11} & \Sigma_{12} \\ \Sigma_{21} & \Sigma_{22} \end{pmatrix}, \tag{9}$$

where

$$\begin{aligned} \Sigma_{11} = \Sigma_{22} = \Sigma_0 = (A+B)[\cos(k_y a) + \cos(k_y a)], \\ \Sigma_{12} = \Sigma_{21}^* = \Sigma_0 = (A-B)[\cos(k_x a) + \cos(k_y a)]. \end{aligned} \tag{10}$$

A and B in (10) are two overlap integrals:

$$\begin{aligned} A \propto \overline{\varphi_1(z;x,y)\varphi_1(z+a;x,y)}, \\ B \propto \overline{\varphi_2(z;x,y)\varphi_2(z+a;x,y)}. \end{aligned} \tag{11}$$

where the bar $\overline{(...)}$ means the matrix elements for the interaction potential on the two Wannier functions, $\varphi_{1,2}$, of the neighboring atoms (in the tight binding approximation A= -| A| < 0). Simple geometric considerations for the d-shell show that $|B| < |A|$ ($|B| \cong \frac{1}{16}|A|$, according to [10,13]). The cubic spectrum consists of the two branches:

$$\varepsilon_{1,2}(\mathbf{p}) = (|A|+|B|)(c_x + c_y) \pm (|A|+|B|)\sqrt{c_x^2 + c_y^2 - c_x c_y} \tag{12}$$

(we introduced the notations $c_i = \cos(k_i a), i = x,y,z$).

We can see from Eq.(12) that in this case we are dealing with two degenerate bands . All electrons are spin-polarized, so that we have a peculiar filling of the band (one electron per level) .If the energy band is partly occupied, the system is in the half-metallic state. In our case the bands are half-occupied. However, the presence of the JT distortion leads to an

additional splitting. The JT deformations lead to the Brillouin zone being reduced by a factor of two. As a result of filling the reduced zone, we obtain a band insulator.

The cooperative JT effect has an "antiferrodistorsive" nature. In order to obtain an energy spectrum in the presence of the JT
distortion, one should solve a general secular equation which reflects the competition between hoping and the JT terms. Let us calsulate the electronic spectrum of our model in the presence of the "antiferrodistorsive" JT collective deformations. Experimentally, the arrangment close to the one in which octahedrs are elongated along each x- or y- axis preserves the tetragonal symmetry in the perpendicular plane. That will lead to the band's secular equation which can not be solved in the analytic form. However, one can consider the contribution, which comes from the Q_2 mode only; this deformation just changes the sign on the adjacent sites of two sublattices. The we obtain:

$$\begin{vmatrix} [\varepsilon^2 - (gQ_0/2)^2 - \frac{5}{4}f_+^2 + \frac{3}{4}f^2] + i\frac{\sqrt{3}}{2}f_+f & f_+^2 - i\varepsilon\sqrt{3}f \\ f_+^2 + i\varepsilon\sqrt{3}f & [\varepsilon^2 - (gQ_0/2)^2 - \frac{5}{4}f_+^2 + \frac{3}{4}f^2] - i\frac{\sqrt{3}}{2}f_+f \end{vmatrix} = 0$$

where

$f_+(\mathbf{p}) = |A|(c_x + c_y), f_-(\mathbf{p}) = |A|(c_x - c_y)$

The resulting bi-quadratic equation produces the following four branches, $\varepsilon_i(\mathbf{p})(i = 1, \ldots 4)$. Each of these four branches is determined in the reduced Brillouin zone:

$$\begin{aligned} \varepsilon_{1,2}(\mathbf{p}) &= \left\{(gQ_0/2)^2 + \frac{5}{4}f_+^2 + \frac{3}{4}f^2 \pm \sqrt{3f^2[(gQ_0/2)^2 + f_+^2] + f_+^4}\right\}^{\frac{1}{2}} \\ \varepsilon_{3,4}(\mathbf{p}) &= -\left\{(gQ_0/2)^2 + \frac{5}{4}f_+^2 + \frac{3}{4}f^2 \pm \sqrt{3f^2[(gQ_0/2)^2 + f_+^2] + f_+^4}\right\}^{\frac{1}{2}} \end{aligned} \qquad (13)$$

At large enough $|gQ_0/2|$ the branches $\varepsilon_{1,2}(\mathbf{p})$ are not crossing two other branches, $\varepsilon_{3,4}(\mathbf{p})$. Filling them up by two polarized electrons per

doubled unit cell, completes the proof that, indeed, insulating $LaMnO_3$ may be considered as *band* insulator.

For example, two sets of the spectrum branches (13), $\varepsilon_{1,2}(\mathbf{p})$ and $\varepsilon_{3,4}(\mathbf{p})$ begin to overlap for $\varepsilon_{j=1}(\mathbf{p})$ and $\varepsilon_{j=3}(\mathbf{p})$ at $p_x = p_y = \pi / 2$. The overlap is direct which imposes some limit on the value of the JT mode which makes $LaMnO_3$ to be an insulator:

$$|gQ_0| > 0.1|A| \qquad (14)$$

Ferromagnetic metallic state

In this section we focus on the ferromagnetic metallic state (FMS) of the manganites. This phase corresponds to the doping level $0.5 \geq x \geq 0.17$ and undergoes the most intensive study, because the CMR phenomenon has been observed in this region. We treat the ferromagnetic metallic compound as a 3D Fermi liquid with a two-band spectrum. The transport data show that in many manganites the mean free path greatly exceeds the lattice period.

The evaluation of the Fermi surface for FMS and analysis of the optical properties and the spin-wave spectrum has been describe in detail in [6]. The analysis is interesting for its own sake, but, in addition, allows one to evaluate the major parameters of our model. As was mentioned above, the ferromagnetic phase ($0.17 \leq x \leq 0.5$) is a 3D system. According to the data [14], the JT distortion is not essential in

the low temperature region, and the energy spectrum is determined by the first two terms in the Hamiltonian (1), that is, by the hopping and by the Hund's interactions. The treatment can be easily generalized for the 3D case and in the approximation A>>B (see above), the carriers occupy two energy bands determined by the relation (in units A):

$$\varepsilon_{\pm} = \tilde{f}^{+} \pm r \qquad (15)$$

where $\tilde{f}^{+}$ and r are defined by Eq. ( ) and

$$\tilde{f}^{+} = c_x + c_y + c_z \tag{15'}$$

$$r = [c_x^2 + c_y^2 + c_z^2 - c_x c_y - c_y c_z - c_z c_x]^{\frac{1}{2}} \tag{15''}$$

The topology of the Fermi surface strongly depends on the carrier concentration, that is, on the doping level. Hund's interaction leads to the carrier system being spin-polarized. As a result, each level is occupied by single e_{2g} electron ("half-metallic state").

Note also that the transport data (see e.g. [15]) allow us to calculate the mean free path l. The calculation is based on the relation $\rho=m(ne^2\tau)^{-1}$ and consequently, on the expression $l = (3\pi^2)^{1/3} h(e^2\rho)^{-1} n^{2/3}$. For example we obtain, with use of values: $n\cong10^{21}$ and $\rho\cong10^{-4}$ $\Omega\bullet$cm, the value $l\cong10^2$Å. This value greatly exceeds the interatomic distance and corresponds to the clean metal. Then the band picture is justified.

Making use of the spectrum (15), we calculate the concentration dependence of the Fermi-level, $E_F(x)$, the density of states (DOS), $\nu(x)$, the spin stiffness, D(x), and the whole magnon spectrum, $\omega(\mathbf{k},x)$, and the conductivity, $\sigma(\omega,x)$, both on the single hopping integral, $|A|$, see [6].

Let us write down also the wave functions which corresponds to the terms $\varepsilon_{\pm}$. These wave functions are linear combinations of the wave functions formed the basic set. For the case of real basics $\phi_1 \propto d_{z^2}$ and $\phi_2 \propto d_{x^2-y^2}$ we obtain

$$\begin{aligned} \psi_1 &= \frac{1}{\sqrt{2}} \sum e^{i\bar{k}\bar{n}} \left\{ s^{+}\varphi_1(\bar{r}-\bar{n}) + s^{-}\varphi_2(\bar{r}-\bar{n}) \right\} \\ \psi_2 &= \frac{1}{\sqrt{2}} \sum e^{i\bar{k}\bar{n}} \left\{ s^{-}\varphi_1(\bar{r}-\bar{n}) - s^{+}\varphi_2(\bar{r}-\bar{n}) \right\} \end{aligned} \tag{16}$$

$$s^{\pm} = (1 \pm (\gamma/r))^{1/2} \tag{16'}$$

where r is defined by Eq. (15') and $\gamma = 2\cos\kappa_z + f^+, f^+$ is defined by (15').

The analysis of the spin-wave excitations and optical properties (see below) of manganites is of particular interest because it provides an unique information about the carrier's system. In this section we describe the calculation of the spin-wave spectrum for various doping levels in the metallic phase.

Our goal is to evaluate the spin-wave dispersion law for the ferromagnetic metal described by the Hamiltonian

$$H = A\sum a^+_{i\sigma} a_{i+\delta,\sigma} + J_H \sum a^+_{i\sigma} \hat{\mathbf{S}}_{\sigma\sigma'} a_{i\sigma'} \mathbf{S}_i \qquad (17)$$

Here A is the hopping parameter (see Eqs. (11), (15)) which determines the bands widths. The spectrum has been evaluated in [16] for the one-band model. Below we describe a rigorous, self-consistent calculation of the spin wave dispersion law in the framework of the two-band picture. Indeed, the e_{2g}-degeneracy leads to the two band picture, it is essential that the presence of such picture is explicitly taken into account. In addition, our approach allows to determine with good accuracy the values of the key parameters, A and J_H, along with their dependence on the doping level.

Let us write the deviations from the average spin, $\langle S_z \rangle$, for localized t_{2g} - spins ($\mathbf{s}=\mathbf{S}-\langle S_z \rangle$) as:

$$s^+(\mathbf{q}) = (2\langle S_z \rangle)^{1/2} \hat{b}(\mathbf{q}), \qquad s(\mathbf{q}) = (2\langle S_z \rangle)^{1/2} b^+(\mathbf{q}) \qquad (18)$$

$$s_z(\mathbf{q}) = (\hat{b}^+ \hat{b})_{\mathbf{q}}$$

($\hat{b}^+, \hat{b}$ -the magnon's operators). The first (δE_1) and second (δE_2) order corrections to the ground state are calculated as perturbations in:

$$\hat{V} = J_H \sum_i \mathbf{s}_i (\hat{a}^+_i \sigma \hat{a}_i) = \quad J_H \sum_i \mathbf{s}_i \mathbf{n}_i \qquad (19)$$

For δE_2, the matrix elements in (19) are of the form:

$$V^{l,l'}_{\mathbf{p}k,\uparrow;\mathbf{p}\downarrow} = J_H \langle \uparrow | s^{\pm}(k) | \downarrow \rangle \times (\alpha^{l}_{\mathbf{p}-k}\, \alpha^{*l'}_{P} + \beta^{l}_{\mathbf{p}-k} \beta^{*l'}_{P}) \qquad (19')$$

The coefficients $(\alpha^{l}_{\mathbf{p}}, \beta^{l}_{\mathbf{p}})$ are from the Bloch's states on the basis (8):

$$\alpha^{l,l'}_{\mathbf{p}} = (\Sigma_{12} / 2|\Sigma_{12}|)^{1/2}, \;\; \beta^{l,l'}_{\mathbf{p}} = \pm(\Sigma_{21} / 2|\Sigma_{12}|)^{1/2} \qquad (20)$$

(here Σ_{12}, Σ_{21} are the off-diagonal elements of the hopping matrix $\hat{t}(\mathbf{p})$ on this basis). As a result, we obtain a series of the Heisenberg spin

Hamiltonians accounting for interaction with the increasing number of neighbors. (For a single band it was first noticed in [16]; in this paper we are using the realistic two bands picture). After straightforward calculations (see [6]) we obtain

$$h\omega(\mathbf{k}) = |A|(3 - c_x - c_y - c_z)D(x) / 3 \qquad (21)$$

and D(x)≡D(E(x)) is given by the integral:

$$\int \frac{d^3p}{(2\pi)^3} \left[\sum_{(+,)} \theta(E - \varepsilon_i(p)) \left\{ 1 \pm \frac{2c_x - c_y - c_z}{2R(\mathbf{p})} \right\} \right]$$

(here E is in units of $|A|$, $p_i \equiv ap_i$)>

Let us calculate the conductivity $\sigma_{ij}(\omega)$ which is described by the general Kubo-Grinwood equation:

$$\sigma_{ij} = -\frac{\pi e^2 h^2}{V} \frac{1}{\omega} \sum_{\bar{\kappa},\bar{\kappa}'} f_0(\varepsilon_\kappa)[1 - f_0(\varepsilon_{\kappa'})] \langle \psi_\kappa | \hat{v}_i | \psi_{\kappa'} \rangle \langle \psi_{\kappa'} | \hat{v}_j | \psi_\kappa \rangle \times$$
$$\times [\delta(\varepsilon_{\kappa'} - \varepsilon_\kappa - \omega) - \delta(\varepsilon_{\kappa'} - \varepsilon_\kappa + \omega)] \qquad (22)$$

Here f is the distribution function, κ is a quasi-momentum, $\hat{v}$ is the velocity operator. For the cubic crystal $\sigma_{ij} \equiv \sigma_{ii}\delta_{ij}$. In our case of the two overlapping energy bands the major contribution comes from the interband transitions. Then

$\langle \psi_{\kappa'} | \hat{v} | \psi_{\vec{\kappa}'} \rangle \cong (i/h)\left[\varepsilon_s(\vec{\kappa}) - \varepsilon_{s'}(\vec{\kappa})\right]\left\langle s\vec{\kappa}|\Omega|s'\vec{\kappa}\right\rangle$ (see [17]), where s,s'≡{1,2} is the band index, and

$$\left\langle s\vec{\kappa}|\Omega|s'\vec{\kappa}\right\rangle = -i\int d\mathbf{r}\left(\partial u_{s\vec{\kappa}}/\partial\vec{\kappa}\right)u^*_{s'\vec{\kappa}} \tag{23}$$

As usual, the Bloch function is $\psi_{s\vec{\kappa}}(\vec{r}) = u_{s\vec{\kappa}}(\vec{r})e^{i\vec{\kappa}\vec{r}}$. As a result, we obtain the following expression for the components σ_{ii} (i=x,y,z) of the conductivity:

$$\sigma_{ii}(\omega_x) = (\beta/\tilde{\omega}^3)\sum_{\vec{\kappa}}\sin^2\tilde{\kappa}_z(\cos\tilde{\kappa}_x - \cos\tilde{\kappa}_y)^2\delta(\varepsilon_1 - \varepsilon_2 - \omega) \tag{24}$$

Here $\beta = 3\pi e^2/hav$; $\tilde{\omega} = h\omega/|A|$;

One can calculate also the intraband (Drude) contribution. Then $\left\langle s\vec{\kappa}|\hat{v}|s\vec{\kappa}\right\rangle = h\nabla\varepsilon_s(\vec{\kappa})$, and we obtain:

$$\sigma_{Dr}(\omega, x) = \frac{e^2|A|}{24a\pi^2h^2}\delta(\omega)\sum_{l=1,2}\int dS^l_{\vec{\kappa}}\left|\nabla\varepsilon(\vec{\kappa})\right| \tag{25}$$

Expression (25) contains as integration over the Fermi surface.

Major parameters. Experimental data.

Properties of manganites in the ferromagnetic metallic region (x~0.3) at low temperatures are described by single hopping parameter A. This quantity can be treated as a single adjustable parameter which enters our theory and allows one to describe various properties of the ferromagnetic manganites. Its value can be determined from the spin-wave spectrum in the long-wave region ($\omega=Dq^2$, D is the stiffness coefficient). Indeed, it is better to use the

data for small q because the long-wave region is less sensitive to an intrinsic disorder. Using values a≅3.86Å [18], $\tilde{D}$ (x=0.3)≅0.45 [6], and

the measurements of D [19], we obtain from the relation $D = a^2\tilde{D}(x)|A|/6$ the value |A|≅0.12-0.17eV, so that the bandwidth, W=6|A| does not vary for various materials (W≅0.7-1eV). For example |A|=0.17eV for $La_{0.7}Sr_{0.3}MnO_3$, |A|=0.15eV for $Nd_{0.7}Sr_{0.3}MnO_3$, |A|=0.12eV for $La_{0.7}Pb_{0.3}MnO_3$.

The Fermi surface for x=0.3 is plotted in [6], Fig. 3. It is interesting that the Fermi surface contains a "neck" section near the zone boundary; this leads to "2.5"-Lifshitz transition.

We can determine also the value of the Fermi energy which is equal (see above) $E_F(x)=|A|E(x)$. For example, for $La_{0.7}Sr_{0.3}MnO_3$ the value of the Fermi energy is E_F≅0.2eV. One can see that this value is small relative to that in conventional metals.

Metal-Insulator Transition at Low Temperatures: Percolative Approach.

Let us focus now on the transition from insulating to metallic state in manganites occurring at x_c≅0.16. The initial doping leads to formation of polaronic states. The hole is localized by Coulomb force inside of the unit cell. When concentration is small, average distances between B atoms are large, which makes holes remain isolated.

Increase in doping leads eventually to transition to the metallic state at some threshold value x_c which is equal to 0.16. The question arises about the nature of such transition. It is essential that the position of the dopant is completely random. The origin of the

threshold x_c and its value have been first understood in [2-6] in terms of percolation theory . The latter considers any process which, roughly speaking, corresponds to some exchange between two adjacent local sites. In the theory of percolation one may look for the concentration at which the nearest neighbor atoms start to form infinite clusters piercing the whole crystal. For the dopant atoms on the cubic sites it is known as the ``site'' problem: on the simple cubic lattice it gives the critical concentration value at ~ 0.31. However, this is not exactly our case. For the doped holes, gathering on few manganese sites around the dopant, charge transfer takes place only along Mn-O-Mn bonds. Therefore the picture of a critical cluster, constructed from the dopant -ions must be corrected: such cluster would already have a finite "thickness" due to the holes spread over surrounding Mn - sites. Numerical studies on the percolative models [20], see also [21], have shown that this circumstance (i.e. the presence of the scale of a few lattice constants) strongly decreases the value for the critical concentration, rapidly converging to its value for the homogeneous problem, x_{cr} ~0.16. It is remarkable that the experimentally observed

value of the critical concentration $x_c \cong 0.16$ corresponds to the value of the invariant of the percolation theory.

The percolative nature of the metal-insulator transition implies the inhomogeneity of the system, that is, we are dealing with a coexistence of two phases: metallic and insulating. The mixture of

"two" phases, depending on the concentration, x, may look as intervened tiny "islands" and "layers" of different "phases". Well below and well above the threshold concentration x_{cr} one may imagine each corresponding phase as a bulk formation into which the second phase is sparsely embedded. If there is a spill-over of charge carriers between two phases, it is the electro-neutrality condition which regulates the tiny domain sizes.

The percolative description of the metal-insulator transition implies coexistence of two percolative phases. This concept has a substantial experimental support. For example, let us mention the pulsed neutron experiments [14]. According to [14] in $La_{1-x}Sr_xMnO_3$ the presence of such insulating inclusions is seen up to x=0.35. It is essential that in the 3D percolative regime, the percolative paths (infinitely connected clusters) may coexist for both phases simultaneously. The analysis of low temperature metallic properties performed in the previous Section, seems to indicate that at least for concentrations x ~ 0.3, the ferromagnetic phase component, in the first

approximation, occupies most of the bulk with other phase embedded into it and also seen as reasonably small scattering centers.

According to the percolation approach, the metallic ferromagnetic "islands" exist at $x<x_{cr}$; they form an infinite cluster at $x=x_{cr}$. Below the threshold these "islands" are finite clusters containing delocalize holes, and their presence should lead to possibility to observe such phenomena as electronic contribution to heat capacity at $x<x_c$, finite a.c. conducting, etc. To our knowledge, such systematic study has not been carried out. Nevertheless, according to the data [], one can observe the finite value of the Sommerfeld's constant at x<0.16 in $La_{1-x}Sr_xMnO_3$.

Note also that in the band picture the magnetization M(x) is $(4-x)\mu_B$ as it is known [1] that M(x) actually increases at x>0.1. Interesting thing is that M(x) has dependence, close to $(4-x)\mu_B$ (B, even at x ~ 0.3-0.4, indicating that admixture of "insulating phase" still persists at these concentrations.

References

1. J. M. D. Coey, M.Viret, and S. vonMolnar, Adv.Phys.48, 167 (1999).

2. L. Gor'kov and V. Kresin, JETP Lett. 67, 985 (1998).

3. L. Gor'kov, Soviet Phys. - Uspekhi 41, 589 (1998).

4. M. Dzero, L. Gor'kov and V. Kresin, Solid State Comm.

5. L. Gor'kov and V. Kresin, J of Supercond. & Novel Magnetism, _____,_____(2000)

6. M. Dzero, L. Gor'kov, and V. Kresin, Europhys. Journal B14, 459 (2000)

7. L. Landau and E. Lifshits, Quantum Mechanics, Pergamon, Oxford (1977)

8. K. Kugel and D. Khomskii, Sov. Phys. - Usp. 25, 231 (1982).

9. W. Pickett and S. Singh, Phys. Rev. B53, 1146 (1996).

10. P. W. Anderson, Phys. Rev. 115, 2 (1959).

11. M. Kaplan and B. Vekhter, Cooperative Phenomena in Jahn - Teller Crystals (Plenum Press, New York, 1995).

12. J. Kanamori, J. Appl. Phys. (Suppl.) 31, 145 (1961).

13. J. B. Goodenough, Magnetism and the Chemical Bond (N.Y. - London, 1963).

14. D. Louca and T. Egami, Phys. Rev. B 59, 6193 (1999); J. Supercond. 12, 23 (1999).

15. M. Quijada, J. Cerne, J. R. Simpson, H. D. Drew, K. H. Ahn, A. J. Millis, R. Shreekala, R. Ramesh, M. Rajeswari and T. Venkatesan, Phys. Rev. B58, 16093 (1998).

16. N. Furukawa, J. Phys. Soc. Jpn. 65, 1174 (1996).

17. E. M. Lifshitz and L. P. Pitaevskii, Statistical Physics, Part 2 (Pergamon Press, Oxford1989) p. 227.

18. J. A. Fernandez-Baca, P. Dai, H. Y. Hwang, C. Kloc and S.-W. Cheong, Phys. Rev. Lett. 80, 4012 (1998).

19. A. H. Moudden, L. Vasiliu-Doloc, L. Pinsard and A. Revcolevschi, Physica B 241-243,276 (1998); Y. Endoh and K. Hirota, J. Phys. Soc. Jpn. 66, 2264 (1997).

20. H. Scher and R. Zallen, J. Chem. Phys. 53, 3759 (1970); for review see G. Deutcher, in Chance and Matter, p. 1, edited by J. Souletie, J. Vannimenus and R. Stora (Elsevier Amsterdam, 1987).

21. B. Shklovskii and A. Efros, Electronic properties of Doped Semiconductors (Springer- Verlag, Berlin 1984).