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Lattice and magnetic effects in doped manganites

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<u>Abstract.</u> The 'double exchange' mechanism and Jahn – Teller instabilities are shown to account for the low-temperature properties of slightly doped LaMnO₃ in the framework of the band insulator model. Analysis of the doping of La_{1-x}A_xMnO₃ with divalent *A* atoms suggests that Coulomb forces cause holes to be localized near dopants, which makes the formation of conducting clusters along these charged centers a major factor in the physics of such compounds. A percolation theory analysis of experimental data is given. The two-phase coexistence regime and the large-volume Fermi surface at high concentrations are discussed. The relevance of some of the results to doping physics in cuprates is suggested.

Among phenomena attracting strong attention both on the experimental and theoretical sides, the so-called 'colossal' magnetoresistance (CMR) in manganites, $La_{1-x}A_xMnO_3$ (A — a divalent atom, usually, Ca, Ba, or Sr) has recently become the subject of numerous intense studies. The presentation below is an attempt to shed some light on the rather controversial theoretical situation in the field[†].

The recent activity relating to manganites is stimulated, of course, by the enormous potential of CMR for practical applications. Doped manganites in the concentration range 0.16 < x < 0.4 undergo a phase transition from the high temperature paramagnetic state with a huge (insulating) resistivity into the ferromagnetic phase with the Curie point, T_c , around room temperature, moreover, the resistivity drops by an order of magnitude in the close vicinity of the transition temperature. A reasonably weak magnetic field (on the scale of 5 Tesla) moves the temperature of transition upwards, resulting , thus, in the colossal negative magnetoresistance. (For a review see, e.g., Ref. [2].)

On the theoretical side, the phenomenon presents many challenges. There is a consensus that some basic features are due to the so-called 'double-exchange mechanism' (DE), first suggested in Ref. [3] and elaborated in more detail in Ref. [4]. The recent discovery [5] of the isotope effect in CMR proves that the lattice also plays an important role. Another side of

[†] Most of the results and qualitative conclusions were obtained together with V Kresin.

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Received 25 February 1998 Uspekhi Fizicheskikh Nauk **168** (6) 665–671 (1998) Translated by L P Gor'kov; edited by A Yaremchuk the story is that these perovskite systems bear a remarkable resemblance to high-temperature superconducting oxides (HTS). The major problem which brings manganites closer to cuprates is the mechanism of doping, i.e., the mechanism by which the system acquires metallic properties when divalent atoms substitute La-sites.

As a starting point, we have chosen the ideal 'cubic' structure for LaMnO₃: each La³⁺ resides at the center of a cubic cell with the Mn³⁺ ions at the cube's corners. In turn, each Mn³⁺ is caged by the oxygen octahedron locally forming the complex MnO_6 with the Mn^{3+} ion in the cubic symmetry position. In real materials, due to the difference in the ionic radii between La and a substituted divalent atom, the lattice may experience considerable local distortions. It is not clear yet whether such distortions (characterized by the so-called 'tolerance factor') constitute a factor crucial for the physics of the doping process which takes place in CMR-materials most likely, they do not. Nevertheless, in some details, say for the resistivity behavior, Ca-doped or Sr-doped materials may display considerable differences [6]. Below we disregard these complications which, however, may essentially affect the tunneling integral's values through deviations of the angle in the Mn - O - Mn bond from 180° .

A very important fact regarding the manganese d-shell is that in the cubic environment it would be split into a doublet and a triplet. In manganites the three-fold manifold of the t_{2g} levels is fully occupied by three (t_{2g}^3) electrons, while the double-degenerate e_{2g} -term contains only one electron (Mn³⁺). This arrangement comes about through the strong Hund's rule coupling which orients all the spins in one direction. The strongly coupled (and localized) three electrons of the t_{2g}^3 -term form the local spin, S_i (S = 3/2). One may then write down the Hund's interaction between these spins and those of the e_{2g} -electrons in the form

$$\hat{H}_{\rm H} = -J_{\rm H} \sum_{i} \hat{\boldsymbol{\sigma}} \cdot \mathbf{S}_{i}, \qquad (1)$$

where $\hat{\sigma}$ stands for the Pauli matrices.

The Hund's coupling, $J_{\rm H} > 0$, being estimated on the scale of ~ 1 eV, considerably exceeds the other energy scales, as evaluated from the phase diagram for manganites.

The above ionic picture for a single manganese ion, Mn^{3+} immediately poses the question about the role of the Jahn-Teller (JT) instability (see in Ref. [7]). The idea of an instability in the high symmetry molecular configuration in the presence of one electron occupying a degenerate level was first formulated by L D Landau in 1934. The theorem was proven by Jahn and Teller in 1937 by the method of enumerating and investigating the possible symmetry cases for all the finite point groups. (The reader can find the whole story, as told by E Teller, in Ref. [8]; for the modern formulation of the Jahn–Teller theorem see, e.g., Ref. [9]).

$$\hat{H}_{\rm JT} = \sum_{i} g(\hat{\mathbf{r}}_i \, \mathbf{Q}_i) + \sum_{i,j} J_{\rm el} \mathbf{Q}_i \cdot \mathbf{Q}_j \,, \tag{2}$$

where \mathbf{Q}_i characterizes the local lattice distortions coupled to the e_{2g} -electron (the two-fold degenerate representation). Its specific form is of no immediate importance. In addition, the specific form of Eqn (2) also depends on the choice of the electronic basis (φ_1, φ_2) for the 2D-representation e_{2g} ; the matrix, $\hat{\tau}$, describes the lifting of the degeneracy and mixing of the wave functions in the presence of the local modes. As in Eqn (1), the indices (*i*, *j*) run over the manganese sites.

The second term in Eqn (2) corresponds to the respective elastic energy arising from the coupling of the JT-distortions at the neighboring sites. Such a coupling, more often than not, is ascribed to elastic interactions which involve phonon degrees of motion [10]. For the LaMnO₃-structure shown in Fig. 1, the key element in the interaction is the geometrical factor: namely, neighboring octahedra share the oxygen atom along the Mn-Mn-bond. If a static JT-distortion is fixed at a given site, *i* (in practice, this is an elongation of the octahedron along one of the three cubic axes), it induces a corresponding contraction of the octahedra on neighboring sites. In other words, the collective JT-effect would result in 'antiferroelastic' distortion of the lattice characterized by a structure vector, \mathbf{Q}_0 . In what follows, the elastic energy is omitted. The low temperature lattice structure in our model is exclusively due to the gains in the electronic kinetic energy, i.e., due to the band structure which depends on the mutual orientations of distorted octahedra.

As for the latter, here we adopt a simple tight binding model in which the e_{2g} -electron may tunnel between two manganese sites via a virtual exchange with the electrons on oxygen orbitals. Here lies the main distinction in how we view manganites and cuprates. In cuprates (at least, at a low doping level) it is commonly accepted that the added hole resides on some oxygen site, while in manganites we assume below that doping with divalent elements, such as Ca or Sr, results locally in the removal of the e_{2g} -electron from a given Mn-ion (Mn⁴⁺). In other words, the 'charge transfer' gap between Mn and O has a sign opposite to that between Cu and O in cuprates. Nevertheless, the view that, as in cuprates, holes go onto oxygen sites (see in Ref. [2]) is another option. Experimentally there is no answer to this dilemma yet.

In the single electron picture (the band model) we add to the Hamiltonians (1) and (2) a phenomenological tunneling term:

$$\hat{H}_{\rm T} = \sum_{i,\delta} \hat{t}_{i,i+\delta} \,. \tag{3}$$



Figure 1. LaMnO₃-an ideal cubic structure (\bullet — La, x — Mn, \circ — O).

Although we restrict ourselves to hopping between nearestneighbors, $\hat{t}_{i,i+\delta}$ in Eqn (3) is a two-by-two matrix due to the two-fold degeneracy of the e_{2g} -level on each site.

Before proceeding further with the model (1)-(3), it is worth mentioning that a more common approach to the interpretation of magnetic properties of manganites is usually based on the localized spin picture, i.e., both the t2gand e_{2g} - states are localized, forming the total spin S_i , S = 2, of the Mn-site. The magnetic order in this approach is due to the indirect anisotropic exchange via oxygen orbitals [11]. The local spin model can account for the observed magnetic order by choosing specific values for the anisotropic exchange constants. On the other hand, the localization of the e_{2g} electrons would be equivalent to assumptions of strong electron-electron interactions. On the microscopic level, such physics is often described in terms of the modified Hubbard model [7]. We do not expect, of course, that interactions between electrons are absent. However, we do believe that electron-electron interactions do not play the dominant role, and that lattice effects have more relevance to the physics of manganites.

Exactly the same Hamiltonian as the sum of Eqns (1)-(3) has been studied in Ref. [12]. The paramagnetic-to-ferromagnetic transition was treated as a 'crossover' from the high temperature regime, where electrons are effectively localized by thermally excited random distortions in Eqn (2), to the regime where the coherent transport (3) starts to prevail. Although Ref. [12] is probably qualitatively correct in emphasizing the importance of lattice (polaronic) effects on the resistivity at elevated temperatures, the approach [12] is not applicable at lower temperatures.

Among the main facts that our band model is to explain, are the insulating behavior of the parent LaMnO₃, the localization of an added hole (at small concentrations), and the very peculiar antiferromagnetic order called the A-phase [13] with its characteristic ferromagnetic alignment of spins in alternating planes. Also, the Neel temperature being of order of 140K (at x < 0.08) is surprisingly low, if compared with the temperature scale for structural transitions in stoichiometric LaMnO₃ (~ 900K).

It has been suggested [1] to depict the ground state of LaMnO₃ as a band insulator. The key ingredient of the theory which makes it possible, is the DE-mechanism [3, 4] together with the JT-distortions. The underlying physics may be explained without entering into more detailed calculations [1]. For the two-center problem, $Mn^{3+} - Mn^{4+}$ and local spins, S_1 , and S_2 , the low energy electronic term has the form [4]

$$E = -J_{\rm H}|S| \pm t \left| \cos\left(\frac{\theta}{2}\right) \right| - O\left(\frac{t^2}{J_{\rm H}}\right),\tag{4}$$

where θ is the angle between S_1 and S_2 (if treated as classical spins). Therefore, at $J_H \gg t$, the major gain in the electronic energy, $-J_H|S|$, is the same for ferro- and antiferromagnetic arrangements of the two spins. The term linear in *t* in Eqn (4) favors the ferromagnetic spin alignment due to the band formation for the e_{2g} -electrons. There is one e_{2g} -electron per unit cell in the system, which would fill-up the band in a 'half-metallic' way, i.e., because spins of both itinerant e_{2g} - and local t_{2g} -electrons are parallel Eqn (1), each site in the momentum space can be occupied by a single electron only. Since there are two bands (the band spectrum is calculated in Ref. [1]) due to the double degeneracy of the e_{2g} -level, such a state would be ferromagnetic and metallic.

Such a state as just described may be a reality at finite doping (see the discussion below), but experimentally this is not the ground state of the nominally pure LaMnO₃. In fact, the possibility of lowering the electronic energy by JT-effects has not been explored yet. In principle, one would need to calculate and compare the ground state's energies for all possible symmetries. Fortunately, the true ground state structure of LaMnO₃ is well known: in addition to the Atype antiferromagnetism, the structure is characterized by the in-plane staggered distortions of the oxygen octahedra, as shown in Fig. 2. [Solid segments represent the elongated octahedra, and the new unit cell is also shown (dashed)].



Figure 2. In-plane staggered distortions inside the ferromagnetic layer. Solid segments represent the elongations of octahedra. The new unit cell is shown as a dashed square.

We show here in simple terms that the structure is, in fact, compatible with the band insulator state. Indeed, for the antiferromagnetic spin arrangements along the one of three cubic axes, according to Eqn (4), we already obtain the giant gain in energy due to the $-J_{\rm H}S$ term. Although there are no terms linear in *t*, a smaller gain, of the order of $t^2/J_{\rm H}$, is achieved. One may notice, however, that an antiferromagnetic arrangement in any other direction would not considerably change that estimate. To obtain any further decrease in the ground state energy, capable of competing with the energy of the ferromagnetic state above, one must turn in the Jahn–Teller instability.

The initial assumption that $J_{\rm H}$ exceeds all other energy scales involved $(J_{\rm H} \ge t)$ considerably simplifies the further analysis. In fact, with accuracy $t^2/J_{\rm H} \ll t$, there is no communication between adjacent layers, and the problem turns out to be a two-dimensional one. In a *single* layer, electrons again may be treated as being ferromagnetically polarized. There are two electrons per new 2D unit cell shown in Fig. 2. The two branches of the electronic spectrum in the absence of the JT-distortions are of the general form [1]:

$$\epsilon(\mathbf{p}) = (A + B)(\cos p_x + \cos p_y) \pm (A - B) \\ \times \left[(\cos p_x + \cos p_y)^2 + 3(\cos p_x - \cos p_y)^2 \right]^{1/2}.$$
 (5)

This spectrum becomes split into four branches (in the new Brillouin zone), when the lattice superstructure, shown in Fig. 2, is imposed. If the JT-gaps are large enough, the new spectrum consists of two pairs of bands. The lower energy pair is fully occupied by electrons with only one spin direction, as shown in Fig. 3, implying that the ground state of LaMnO₃ would be that of the band insulator.



Figure 3. JT-split bands in ferromagnetic layers. Two low energy bands are fully occupied by polarized electrons resulting in the band insulator for LaMnO₃.

Consider, as an illustrating example, A = B in Eqn (6). The new spectrum in the presence of the JT-deformation, gQ, is of the form [1]

$$\varepsilon_l(\mathbf{p}) = \pm ||t(\mathbf{p})| \pm \Delta|, \quad l = 1, \dots, 4,$$
(6)

where $(A + B)(\cos p_x + \cos p_y) \equiv t(\mathbf{p}), \quad \Delta = |gQ/2|.$ At $\Delta > 2t(0)$, the spectrum is of the form shown in Fig. 3. The direct insulating gap, $\Delta - 2t(0)$, appears at $\mathbf{p} = 0$.

The concept of two-dimensional ferromagnetic layers emerging from the DE-mechanism $(J_H \ge t, gQ)$, is also helpful in understanding the two remaining questions regarding low temperature properties of lightly doped manganites. Thus, we have seen from Eqn (4) that the coupling between layers is rather weak ($\sim t^2/J_H$). It is also well known, on the other hand, that fluctuations make a phase transition into the ferromagnetic state impossible in two dimensions, unless there is a coupling between layers. Therefore, the weakness of the interlayer interaction is in good correspondence, at least, on a qualitative level, with the surprisingly low value for the Neel temperature, $T_N \simeq 140$ K. (The estimates for t give a few tenths of an eV.)

Another interesting problem concerns the fact that at low concentrations doped materials preserve their insulating behavior. This is rightly treated as the trapping of the doped hole, but self-trapping is easier to achieve in a two-dimensional situation: the difference is that in the 3D-case, a carrier, before getting self-trapped, must pass across a large energy barrier, while in the 2D-case carriers may be *either* itinerant, *or* localized depending on the numerical value of some combination, *C*, characterizing the relative role of the gain in elastic energy (2) due to the JT distortion, $\sim g^2/J_{el}$, to the band width, *t*. If the value

$$C \sim \frac{g^2}{J_{\rm el}t} \tag{7}$$

exceeds a threshold, usually of order unity, the doped hole would go into a trapped state [14]. In a simple minded interpretation, Eqn (7) tells us whether, due to lattice deformations, the hole energy level goes below the bottom of the band and thus becomes localized. In 2D there is no energy barrier to overcome.

The criterion imposed by Eqn (7) makes sense only in the limit of low concentrations. If the concentration of induced holes increases, while the problem is still considered in the framework of a spatially homogeneous (averaged) underlying ionic structure, a phase transition into the ferromagnetic state would take place at some concentration. The superstructure $(\sqrt{2}a \times \sqrt{2}a \times 2a)$ imposed on the 'cubic' lattice by the JTdistortions of octahedra and the AF spin order, would not be energetically favored anymore. It seems rather obvious that such a transition is of I-order resulting, hence, in a separation of the sample into coexisting 'carrier-rich' and 'carrier-poor' regions. Such an idea of two coexisting phases was proposed in Refs [15, 16] for HTS-cuprates where it is now the topic of countless numerical studies (see, e.g., Ref. [17] and references therein). To do justice to the pioneering work [13], an intrinsic heterogeneous structure has already been suggested to interpret the neutron data [13] on doped manganites.

The main theoretical difficulties in sorting out whether a phase separation may occur in cuprates or manganites, arise due to the need to balance the Coulomb forces: even though lattice effects favor phase segregation (we do not mean the role of the 'tolerance factor' here), separation into regions with different electronic concentrations breaks the electroneutrality condition. It was argued [15] that such phases may coexist only as a 'foggy' state, with the sizes of 'droplets' regulated by the Coulomb energy. Whether the individual sizes may be large enough to be resolved, say, in neutron diffraction experiments, is not clear. (In brief below we discuss some experiments pertinent to the problem.)

Now we return to the phenomena of CMR and metallicity in manganites. In Figure 4 a schematic phase diagram characterizes the magnetic and conducting properties of $La_{1-x}Sr_xMnO_3$ depending on the Sr-content (the data from Ref. [18]; PI — paramagnetic insulator; PM — paramagnetic metal; CNI — canted AF, insulator (Ref. [19]); FI ferromagnetic insulator; FM — ferromagnetic metal; the meaning of the dot-dashed line will be discussed later). In Figure 5, data from the same paper [18] show the temperature dependencies of the resistivity for samples with different Srconcentrations. A glance at data in Fig. 5 convinces us of the



Figure 4. Schematic phase diagram of $La_{1-x}Sr_xMnO_3$ (from Ref. [18]; the notation is explained in the text). The dot-dashed lines show the expected behavior of the Curie temperature near the threshold concentration, $x_{cr} \simeq 0.16$, for a model with nearest-neighbor interactions.



Figure 5. Resistivity for samples of $La_{1-x}Sr_xMnO_3$ with different *x* as a function of temperature (data from Ref. [18]; the triangles mark positions of structural transitions). Two distinct phenomena are seen: a drop in resistivity at the CMR point, T_0 , and a sharp onset of metallic behavior at low *T* for samples with $x \ge 0.16$.

existence of two *different* phenomena depending on the concentration. The high temperature CMR corresponds to a sharp drop in the resistivity accompanying the onset of the ferromagnetic moment at some T_0 . 'Metallicity', on the other hand, means a metal-like behavior down to the lowest temperatures. The latter takes place only for concentrations above a threshold concentration, $x_c \simeq 0.16$. Details of the phase diagram in the concentration range below x_c still remain to be better clarified experimentally. Therefore, we will first concentrate on the possible origin of an apparently sharp onset of metallic behavior at some $x = x_c$.

The concentrations $x \sim x_c$ are quite high to treat our materials in terms of an average homogeneous solution. Let us turn our attention first to a better understanding of the processes taking place in the vicinity of the substituted divalent ion (Sr^{2+}) . The change in the charge, (-1), on the La-site introduces a hole positioned on surrounding Mn-ions. A characteristic energy of the order of a few eV is responsible for such hole localization. One may ask about the concentration at which divalent ions sitting on adjacent sites first start forming an infinite path, or cluster. In terms of the theory of percolation, this is a familiar site problem, which for a simple cubic lattice gives $x_c \simeq 0.31$ (for reviews on the theory of percolation see Ref. [20]). It is well known that this threshold value is not universal and depends on the specific lattice. More important is this: if there is a correlation between sites, the threshold value rapidly decreases and tends to the value of 0.16 when the effective correlation radius exceeds the interatomic distances, i.e., to the value for a continuous percolation problem. To see implications of this result for our problem, note that one hole produced by one Sr-ion may go to at least eight manganese sites. Hence, one cannot say that the hole resides on a single Mn-site and then apply the site-percolation results just counting Mn⁴⁺ in the same manner as for Sr^{2+} -sites. Each of the eight Mn-sites provides equivalent positions for occupation by one hole. One may go further and say that the hole's wave function is probably spread beyond the unit cell size. The Coulomb forces over these distances prevail over all energies involved in the Hamiltonian (1)–(3) except the Hund exchange, $J_{\rm H}$, which also results in the ferromagnetic magnetization of the spins of Mn-ions surrounding Sr^{2+} -ion.

In the simple percolation approach, which, in essence, is classical, there are no specific details regarding the microscopic mechanism for conductivity. One merely assumes a possibility of charge transfer along a bond on the cluster. When the infinite (critical) cluster is formed at x_c , a current may flow across the sample, and the conductivity rapidly increases as $(x - x_c)^{-t}$ for the 3D-random resistor network [20]. There are not enough reliable data yet to verify whether the residual resistivity as a function of concentration behaves in accordance with this prediction.

With $x > x_c$ the conducting path acquires a 'finite thickness', so that one can treat this part of the sample as a 'conducting phase', in terms of which a question about the sort of 'band' mechanism seems possible to formulate. Recall that although the conducting paths are localized in some vicinity of the Sr²⁺-clusters, the role of the Coulomb forces is rapidly diminished by effective charge screening. If the latter statement is correct, such a conducting phase would be locally close in properties to the ferromagnetic state for the homogeneous sample except that it is not clear how to determine the 'density of carriers'. (The structure of the critical cluster, around which this new 'phase' grows, is known [20] to be extremely irregular. Some of the doped holes may go into localized states.) In Ref. [21], samples with x = 0.2 (La_{1-x}Sr_xMnO₃) have shown excellent metallic behavior up to 200 K:

$$\rho = \rho_0 + AT^2 \,. \tag{8}$$

Taking the standard expression for conductivity,

$$\sigma = \frac{ne^2\tau}{m^*} \equiv \frac{ne^2l}{p_{\rm F}} \,, \tag{9}$$

and expressing $p_{\rm F}$ in terms of *n*, the carrier concentration in the isotropic model, we get from Eqns (8), (9) for the mean free path, *l*,

$$l \sim 100 \,\mathrm{A}; \quad E_{\mathrm{F}} \sim t \sim 10^3 \,\mathrm{K}$$
 (10)

(we assumed $n \sim 10^{21} \text{ cm}^{-3}$, $m^* \sim 3 - 5m_0$).

In addition to the 'conducting' (and ferromagnetic) phase in the above picture, the rest of the sample would be occupied by an 'insulating' phase. Its meaning is understood for low x: according to the mechanism of Eqn (7), lightly doped LaMnO₃ is an insulator with 'canted' AF order [19]. For the three-dimensional percolation problem one may have percolation along both phases simultaneously. In other words, two phases may simultaneously display their properties on macroscopic scales. Thus, the canted phase is clearly seen at low temperatures by neutrons† in La_{2-x}Sr_xMnO₃ at x = 0.12. Below x = 0.16, we believe, the 'conducting' phase exists in the form of insulated ferromagnetic islands (clusters). Above $x_c = 0.16$, both AF and F-phases may coexist, while with a further increase of x the AF and JT-structural order, in

† J Lynn (private communication).

turn, may be present only locally. There has been no systematic work yet done to prove or disprove this view, although, there are many indications that intrinsic inhomogeneities [13] are, indeed, present in the concentration range up to $x \sim 0.3-0.4$. Most experiments confirming this point of view use one or other local probe technique: NMR [22], ion channeling [23], or the so-called pair-distribution function analysis of neutron scattering data [24]. This short presentation is intended to briefly expose some basic theoretical ideas, and we will not consider any longer other experimental means of detecting the existence of the phase separation phenomena or evaluating the current experimental situation.

An alternative picture to that described above, is a phase transition to a metallic (and ferromagnetic) ground state at $x > x_{c}$. Thermodynamically, such a transition should be a first order phase transition between insulating and metallic states tuned by the increase of dopant concentration. Even though disorder is always present, screening may make the new phase similar to a metallic state possessing a large Fermi surface. The first order nature of the transition is obscured by the fact that the tuning mechanism, namely, doping by divalent elements, is not a thermodynamical way of addressing the phase transition. One again sees a clear similarity in problems regarding the doping mechanisms between manganites and HTS-cuprates. In both cases doping is a 'forced' way to cross some 'miscibility' gap, separating the insulator from a metallic ground state. In cuprates it is often assumed the existence of small Fermi pockets (with x for the number of carriers) which evolve somehow with doping in a large Fermi surface [number of carriers $\sim (1-x)$]. The percolation interpretation above, if correct, would eliminate the notion of small pockets in cubic manganites as well as in cuprates.

We now turn our attention to finite temperatures. One necessary comment is that the Curie temperature for transition into ferromagnetic state, $T_c(x)$, is , in fact, finite at $x = x_c$. For site-problems on the lattice the Heisenberg spin Hamiltonian with the exchange interaction between *nearest neighbors only* would require $T_c(x) \rightarrow 0$ at $x = x_c$ (see in Ref. [25]). Such behavior was shown in Fig. 4 by the dotdashed line. There is no such theorem proven for the nonlocal DE-mechanism. In Ref. [19] arguments are given in favor of a long-range character for spin-spin interactions between holes localized near substituted defects.

Finally, we consider whether the concept of the two phases' coexistence may be of some use in explaining the phenomenon of CMR. For that we assume that although the 'insulator' phase acquires a finite resistivity at elevated temperatures, it is still much higher than the resistivity of the 'metallic' phase. Ferromagnetic order (and, hence, conductivity due to DE-mechanism) would be naturally oppressed with the temperature increase. This qualitative behavior may also be interpreted as a reduction in the amount of the wellconducting phase, and the percolation approach will immediately come into effect again. Indeed, above some temperature, T_0 , the concentration of the 'metallic' phase is not enough to ensure current flow across the whole sample, so that the conductivity is zero (we neglect a contribution from the insulating phase). Below T_0 percolation is restored, and the conductivity $\sigma(T)$ dramatically increases. CMR is then well understood as due to an increase in the amount of the conducting phase in the presence of a magnetic field which drives the system above the percolation threshold.

The alternative view that the Curie point (or T_0) is due to a sudden change in the conduction mechanism (localization-

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delocalization crossover) has already been emphasized in Ref. [12]. It is in no apparent contradiction with the above picture, except it is assumed in Ref. [12] that the new state below T_0 is homogeneous along the whole sample. There is a consensus now that the conductivity above T_0 is related to a polaronic mechanism. However, it is also established that JTdistortions are also present in the conducting (ferromagnetic) phase below T_0 (see, e.g., in Ref. [24]). Whether these findings should be considered as proof of the phase-coexistence, or there are strong fluctuations below T_0 not only in the magnetic moment [26] orientations, but also in the structural order, remains to be better understood.

The drop in resistivity below onset of ferromagnetic order is often related [27] to scattering on short-range spin correlations in the ordered phase [28]:

$$\frac{\tau(T_0)}{\tau(T)} = 1 - \frac{|M|^2}{S(S+1)},$$
(11)

where $\tau(T)$ is the mean free time for an electron spin to scatter on the moment fluctuations. It has been noted [27] that results on the resistivity behavior follow the $|M|^2$ -term in (11) rather closely. On the other hand, there are some theoretical difficulties with the derivation of Eqn (11). Equation (11) was obtained in Ref. [28] by treating the electronic scattering as an elastic process, a provision which seems to us selfcontradictory, because short-range correlations are due to short-wave magnons the spectrum of which experience no sharp changes at the transition and their typical frequencies are of the order of T_0 itself.

The agreement between the experimental data on resistivity with the temperature dependence of the magnetization, in accordance with Eqn (11), is, indeed, a remarkable fact, since this behavior is exactly that which follows from the predictions of the percolation approach. Namely, it has been shown (see in Ref. [29]) that there exists a proportionality between the conductivity, $\sigma(x, T)$, magnetization, M(x, T), and the stiffness coefficient, which determines the low frequency magnon spectrum:

$$\omega = D(x, T)k^2$$

(if all characteristics are averaged over the same random ensemble). This relation,

$$\sigma(x,T) \propto M(x,T)D(x,T), \qquad (12)$$

leads to the same singular behavior in resistivity near T_0 as Eqn (4), since, in turn, D is proportional to M. The critical behavior for $M \propto (T_0 - T)^{\beta}$ is well described by $\beta \sim 0.3$ in La_{1.8}Sr_{0.2}MnO₃ [21]. The same exponent was obtained for D in Ref. [30]. Finally, for conductivity below T_0 , plotting σ in the form

$$\sigma \propto (T - T_0)^{\mu},$$

with μ about 0.6 results in a good fit to the experimental data[†] (note that the samples of Refs [21, 30] are from the same batch).

This fact, at least, does not contradict the two-phase interpretation.

To summarize, the band-approach properly describes the low temperature properties of pure and lightly doped LaMnO₃. The band structure is determined by the superstructure imposed onto an initially cubic lattice due to involvement of the DE-mechanism and the JT-instability. A new interpretation is suggested for process of doping: from the extreme of low concentration the doped holes are kept bound to the vicinity of substituted ions by Coulomb forces. The finite conductivity and ferromagnetic phase arise along the percolation clusters growing with increasing concentration. There are theoretical reasons and experimental evidence in favor of phase separation in doped manganites.

The author belongs to the last generation of Landau's pupils, whose scientific style was formed under the direct influence of his unique personality. The author gladly acknowledges this fact in the presentation to be published in the special Uspekhi's issue devoted to the memory of Lev Davidovich Landau.

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