# Resistivity of Mixed-Phase Manganites

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The resistivity $\rho_{dc}$ of manganites is studied using a random resistor-network, based on phase separation between metallic and insulating domains. When percolation occurs, both as chemical composition or temperature vary, results in good agreement with experiments are obtained. Similar conclusions are reached using quantum calculations and microscopic considerations. Above the Curie temperature, it is argued that ferromagnetic clusters should exist in Mn oxides. Small magnetic fields induce large $\rho_{dc}$ changes and a bad-metal state with (disconnected) insulating domains.

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The study of manganites is one of the main areas of research in strongly correlated electrons [1]. Three main reasons have triggered this wide interest: (1) The low-bandwidth materials have unexplained transport properties. They are insulators at room temperature, changing into bad metals at low temperatures. A sharp peak in the resistivity $\rho_{dc}$ appears at the ferromagnetic (FM) transition. Small magnetic fields turn the insulator into a metal, with a "colossal" magnetoresistance (CMR). (2) The phase diagram $T$-$x$ ($T$ = temperature, $x$ = hole density) is rich, with complex spin, charge, and orbital order. (3) Mn oxides have intrinsic inhomogeneities in most of the $T$-$x$ plane even in single crystals [2,3].

This challenging behavior has been addressed by previous theoretical studies. Regarding item (2), the various FM, antiferromagnetic (AF), orbital-ordered, and charge-ordered (CO) phases have already emerged from simulations and mean-field approximations [4]. Regarding item (3), phase separation (PS) has been proposed to explain the inhomogeneities. PS can be (a) electronic, with nanometer-size clusters [3] or (b) structural, where disorder can induce up to micrometer-size clusters and percolation, when influencing on first-order transitions [5]. However, the explanation of transport, item (1), is more complicated since theoretical estimations of $\rho_{dc}$ are notoriously difficult. In addition, the prominent inhomogeneities of Mn oxides [2] have not been incorporated into $\rho_{dc}$ calculations [6]. The behavior of $\rho_{dc}$ remains unexplained, although it is central to manganite physics.

Our goal in this paper is to present a rationalization of the $\rho_{dc}$ vs $T$ curves of Mn oxides based on the currently prevailing phase-separated/percolative framework for these compounds. In this context, items (1) and (3) above are closely related. The analysis necessarily involves phenomenological considerations, since percolation cannot be addressed on sufficiently large lattices using accurate microscopic models. However, the $\mu$-meter clusters in experiments [2] strongly suggest that a coarse-grain approach should be sufficient. In addition, results of microscopic calculations presented below are consistent with those of the macroscopic approach.

The main concept introduced here is summarized in Figs. 1a and 1b. The manganite state in the CMR regime is assumed to be percolative, with metallic filaments across the sample (Fig. 1a). Percolation indeed occurs in models [5] and in many experiments [2]. The insulating and metallic (percolative) regions are assumed to have resistances $R_I(T)$ and $R_M^{per}(T)$, respectively, as sketched in Fig. 1b. $R_M^{per}$ is large at $T = 0$ due to the complex shape of the conducting paths and grows with $T$ as in any metal, eventually diverging when the percolative path melts with increasing $T$. Note that at room temperature $R_I < R_M^{per}$ and, thus, most of the conduction in this regime occurs *through the insulator*. On the other hand, $R_I$ is so large at low $T$

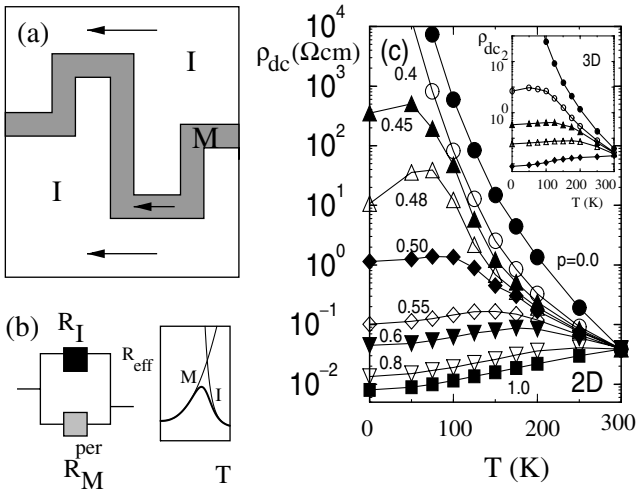


FIG. 1. (a) Mixed-phase state near percolation. Arrows indicate conduction through insulating or metallic regions depending on $T$ (see text). (b) Two-resistances model for Mn oxides. Effective resistance $R_{eff}$ vs $T$ (schematic) arising from the parallel connection of metallic (percolative) $R_M^{per}$ and insulating $R_I$ resistances. (c) Net resistivity $\rho_{dc}$ of a $100 \times 100$ cluster vs $T$, at the indicated metallic fractions $p$. Inset: Results for a $20^3$ cluster with (from top) $p = 0.0$, 0.25, 0.30, 0.40, and 0.50. In both cases, averages over 40 resistance configurations were made (errors the size of the points). The $p = 1$ and 0 limits are from Ref. [2]. Results on $200 \times 200$ clusters (not shown) indicate that size effects are negligible.

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that current can flow only through the percolative paths. This suggests a simple two parallel resistances description (Fig. 1b), where a peak in the effective resistance at intermediate $T$ is natural.

To substantiate this idea, first consider results obtained using a *random-resistor network* that mimics the prominent FM-CO mixtures [2] in Mn oxides in the CMR regime. Two-dimensional (2D) and three-dimensional (3D) square and cubic clusters are used, with link resistivities randomly selected as metallic ($\rho_M$) or insulating ($\rho_I$), with a fixed metallic fraction $p$ [which in, e.g., $(La_{5/8-y}Pr_y)Ca_{3/8}MnO_3$ (LPCMO) it is proportional to the amount of La [2]]. The lattice spacing of this effective network is comparable to the FM or CO domain size, much larger than the Mn-Mn distance. The actual values of $\rho_M$ and $\rho_I$ vs $T$ were directly taken from LPCMO data [2] ($y = 0.00$ and 0.42, respectively), and for simplicity they are used in both 3D and 2D clusters. Other materials were tried and the analysis below does not depend qualitatively on the reference compounds.

The Kirchoff equations for the network were solved iteratively using well-known techniques [7], and the net resistivity was found [8]. Typical results are shown in Fig. 1c. Only the limiting cases $p = 0$ (all insulator) and 1 (all metal) are taken from experiments. As expected, a percolative regime exists between $p = 0.4$ and 0.5, where $\rho_{dc}(T = 0)$ is as large as in LPCMO and other materials [9]. $\rho_{dc}$ has insulating behavior at room $T$, even for $p$ as high as 0.65, while at low $T$ a (bad) metallic behavior is observed. A broad peak appears at intermediate $T$'s and $p$'s. Similar results exist in 3D (Fig. 1c inset).

It is remarkable that Fig. 1c is already in good qualitative agreement with some Mn-oxide experiments, such as for $La_{0.96-y}Nd_yK_{0.04}MnO_3$ [10], or even non-manganite materials, such as $CaFe_{1-x}Co_xO_3$, where an AF-FM competition occurs [11]. However, many manganites present a more pronounced $\rho_{dc}$ peak at intermediate $T$'s. To reproduce this feature, it is necessary to introduce a percolative process not only as $p$ (or $x$) varies, but also as $T$ changes. This is reasonable since the metallic component triggered by ferromagnetism is sensitive to $T$, and the FM clusters shrink in size as $T$ increases. This proposal was tested qualitatively using two models: (i) the random field ising model (RFIM), which describes the disorder-induced PS [5], with spin up and down crudely representing the competing metal and insulator, and (ii) the well-known one-orbital model [3] (with parameters $t$, $J_H$, and $J'$ representing the $e_g$ hopping, Hund coupling, and Heisenberg exchange among $t_{2g}$ spins, respectively). The latter is supplemented by a term $\sum_i \phi_i n_i$, with $\phi_i$ randomly taken from $[-W, W]$, and $n_i$ the on-site density at site $i$. This disorder generates coexisting clusters near first-order FM-AF transitions, as explained in Ref. [5].

In Fig. 2a, a portion of a typical Monte Carlo (MC) simulation of the RFIM on a $500 \times 500$ cluster is shown, with fixed random fields taken from $[-1.0, 1.0]$ ($J = 1$ is the FM Ising coupling). These parameters are the same as in Ref. [5]. Three main domains were found: spin up (black), spin down (white), and regions with a small spin expectation value (gray). The generation with increasing $T$ of paramagnetic (PM) areas in the surface of the up and down domains weakens the percolative tendencies of the RFIM: e.g., in Fig. 2a domains weakly connected at $T = 0$ become disconnected at finite $T$. Similar behavior occurs in the microscopic one-orbital case, as shown in Fig. 2b for a disordered configuration with percolative features [12]. Increasing $T$ from $\sim$0.0 to $0.05t$ decouples the two FM regions. FM, AF, and PM regimes dominate at finite $T$, as in the RFIM. The $T = 0.05t$ Drude weight (not shown) is much smaller than at $T \sim 0.0$.

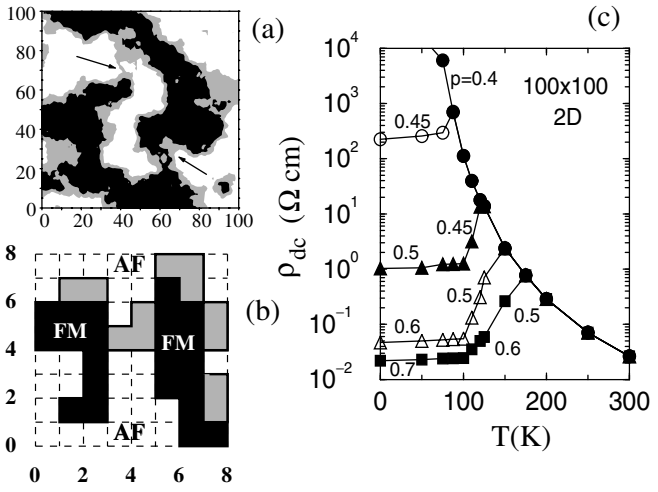


FIG. 2. (a) MC results for the random field Ising model at $T = 1.6$ ($J = 1$), and a fixed set of random fields taken from $[-1.0, 1.0]$. Shown is a $100 \times 100$ subset of a $500 \times 500$ cluster with periodic boundary conditions (PBC). Black, white, and gray denote regions with Ising spin mean value $\langle\sigma\rangle$ in the intervals $(0.66, 1.0)$, $(-1.0, -0.66)$, and $(-0.66, 0.66)$, respectively. The arrows indicate regions where percolation occurs as $T$ decreases. (b) MC results for the one-orbital model on a PBC $8 \times 8$ cluster, $J_H = 8$, $J' = 0.0$, $t = 1$, density $\langle n\rangle = 0.875$, and a (fixed) realization of disorder ($W = 0.5$) with percolative characteristics at $T \sim 0$. Black and white denote FM and AF regions, respectively. Gray domains are FM at $T \sim 0$, but the nearest-neighbor (NN) spin correlations become much smaller (PM) at $T = 0.05$. (c) Net $\rho_{dc}$ of a $100 \times 100$ cluster as in Fig. 1c, but with $p$ changing with $T$ (representative values indicated). Averages over 40 resistance configurations are shown.

To incorporate the indications of $T$-induced percolation (Figs. 2a and 2b) in the phenomenological approach, a $T$-dependent metallic fraction $p(T)$ is needed. $p$ must decrease as $T$ grows, should vary rapidly near the Curie temperature $T_C$ as the magnetization does, but otherwise its $T$ dependence is unknown. Fortunately, the qualitative results using several functions are similar, and a typi cal case is shown in Fig. 2c. The $\rho_{dc}$'s obtained by this simple procedure now clearly resemble those found in experiments, with a robust peak at intermediate $T$'s, moving toward lower $T$'s as the system becomes more insulating. This agreement with experiments is unlikely to be accidental and justifies *a posteriori* our assumptions. Note

that if our approach is correct, consistency requires that in Mn oxides above $T_C$ there should exist (disconnected) FM clusters on an insulating matrix, since $p$ does not drop abruptly to 0 at $T_C$. A new temperature scale $T^*$ is predicted, with those FM clusters existing in the range $T_C \leq T \leq T^*$. The density of states in this regime likely has a *pseudogap,* according to previous investigations of mixed-phase states [3,5].

Consider now nanometer-scale clusters. Here quantum effects cannot be neglected. However, the problem is still too difficult to be treated microscopically, and an effective description is needed. For this purpose, instead of a resistor network, a 3D lattice model with NN electron hopping (and zero chemical potential) is here used, with link hopping amplitudes randomly selected to be either "metallic" ($t_M$) or "insulating" ($t_I$), representing effective hoppings through the nanoclusters with 1 (0) corresponding to the FM (AF) regions of the microscopic model at large $J_H$. Such "lattice of quantum wires" has been used before to study quantum percolation [13]. The cluster conductance $C$ (in $e^2/h$ units) is calculated using the Kubo formula within a Landauer setup [14,15]. The hoppings $t_M$ and $t_I$ are not available from experiments. However, $t_M$ should decrease with increasing $T$ following the FM-phase magnetization, while $t_I$ increases with $T$ (since, e.g., the zero conductivity $T = 0$ AF configuration disorders as $T$ grows). $C$ was obtained on up to $20^3$ clusters using the $t_M(T)$ and $t_I(T)$ in the inset of Fig. 3a, but the results do not depend qualitatively on the particular functions used, as long as $t_I$ changes rapidly with $T$ near room $T$, as $\rho_I$ does in experiments. $p$ in Fig. 3a was made $T$ dependent as in Fig. 2c, and the critical percolation at $T = 0$ is expected to be located near $p_c \sim 0.45$ [13]. Results are shown in Fig. 3a [16]. Once again good qualitative agreement with experiments is obtained; nanometer and micrometer clusters lead to similar results.

For completeness, $C$ was also calculated using microscopic models on small lattices. A MC simulation of the one-orbital model on an $8 \times 8$ PBC cluster and density $x = 0.5$ was performed. From previous work [5], it is known that a metal-insulator first-order transition occurs at $J_c' \sim 0.07$ (if $J_H = \infty$). Disorder is introduced such that in the NN-sites link $\langle ij \rangle$ the hopping is $t_{ij} = 1 + \delta_{ij}$ and Heisenberg coupling is $J_{ij}' = J'(1 + \delta_{ij})$, where $\delta_{ij}$ is randomly taken from $[-\Delta, \Delta]$, and $J'$ is uniform. This disorder makes the transition continuous [5]. The MC procedure generates $t_{2g}$-spin configurations from which NN sites effective hoppings can be calculated (as in double exchange models). These hoppings are used to evaluate $C$ (Fig. 3b). Because of the disorder, $C$ interpolates smoothly from metal to insulator varying $J'$ (otherwise a discontinuous transition occurs). $C^{-1}(T \sim 0)$ can be very large, but finite, if the appropriate value of $J'$ is selected [17]. In this respect the result has clear similarities with those of the macroscopic approach. However, the full shape of the experimental $\rho_{\rm dc}$ curves is difficult to reproduce with microscopic models on small clusters where percolation cannot be studied. Nevertheless, for the (few) disorder configurations with percolativelike characteristics found on small systems (as in Fig. 2b), the associated $C$ vs $T$ has a broad maximum at a finite $T$.

Consider now nonzero magnetic fields ($H$). In the random-network model mimicking coexisting FM-AF regions, a small $H$ will increase the FM fraction $p$ by a concomitant small amount. However, near percolation tiny

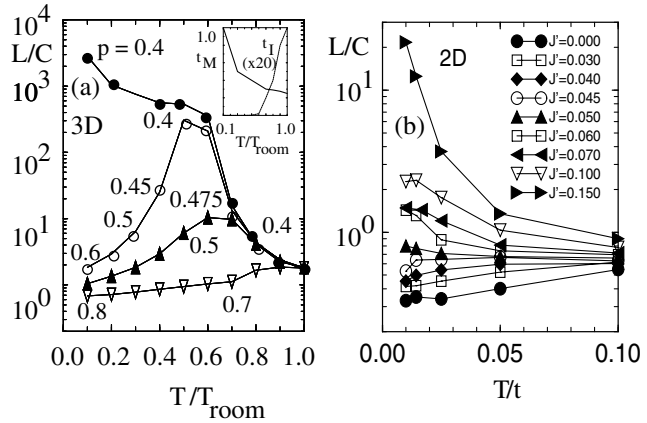


FIG. 3. (a) Inverse conductance of a tight-binding (NN sites) $20^3$ ($L = 20$) cluster with hoppings $t_M$ and $t_I$. Temperature is considered through changes in those hoppings, shown in the inset. $p$ is the fraction of metallic links, and representative values are indicated. The chemical potential was set to 0. (b) Inverse conductance of the half-doped one-orbital model on a PBC $8 \times 8$ ($L = 8$) cluster, and $J_H = \infty$ ($t = 1$), varying $J'$. Disorder strength is $\Delta = 0.1$. Averages over 15 disorder configurations are shown. Error bars in (b) and Fig. 4a are of the order of the oscillations of each curve.

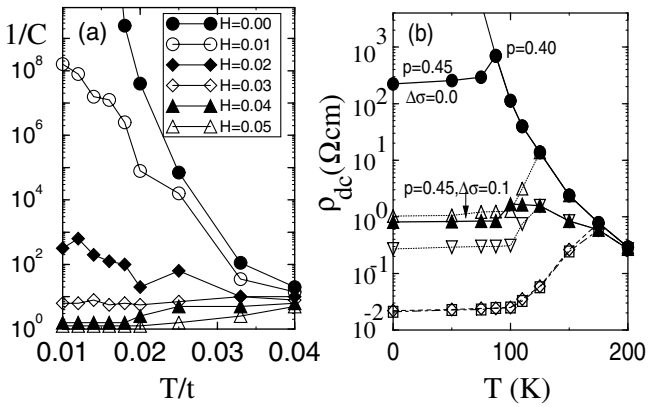


FIG. 4. (a) Inverse conductivity of the half-doped one-orbital model on a 64-site chain, with $J_H = \infty$, $J' = 0.14$, $t = 1$, and $\Delta = 0.03$, varying a magnetic field $H$ as indicated. The data shown corresponds to one disorder configuration, but results with other configurations are similar. (b) Effective resistivity of a $100 \times 100$ network of resistances. Results at $\Delta\sigma = 0.0$ (full circles, open triangles, and open squares starting at $T = 0$ with $p = 0.45$, 0.50, and 0.70, respectively) are the same as found in Fig. 2c. Full triangles, inverse open triangles, and diamonds correspond to the same metallic fractions, but with a small addition to the insulating conductivity [$\Delta\sigma = 0.1\ (\Omega\ \mathrm{cm})^{-1}$], to simulate the effect of magnetic fields (see text).

modifications in $p$ can induce large $\rho_{dc}$ changes, as shown in Fig. 2b where a 5% modification in $p$ at low $T$ can alter $\rho_{dc}$ by 2 orders of magnitude. In the percolative regime, "small" perturbations can drastically change the conductivity. This analysis predicts that the metallic state reached from the insulator with magnetic fields is *not* homogeneous but must still have a substantial fraction of insulating clusters. This is consistent with the experimental large $\rho_{dc}(T = 0)$ of such a state.

Another effect contributes to this phenomenon. It exists even on chains where percolation does not occur, and it is illustrated in Fig. 4a where $C^{-1}$ is shown using the microscopic half-doped one-orbital model at $J' = 0.14$ where the system is at a FM(metal)-AF(insulator) transition, the latter with the periodic spin structure $\uparrow\uparrow\downarrow\downarrow$, as shown in Ref. [5]. The field is introduced as $H \sum_i M_i^z$, where $M_i^z = s_i^z + (3/2)S_i^z$, with $S_i^z$ the $z$ component of the classical $t_{2g}$ spin at site $i$ with norm 1, and $s_i^z$ the spin of the mobile electron at the same site. Disorder in the hopping and $J'$ (as in Fig. 3b) of strength $\Delta = 0.03$ produces coexisting FM-AF clusters [5]. The nearly perfect AF links at low $T$ induce a huge $C^{-1}$ at $H = 0$. However, field modifications of just $0.01t$ ($\sim$17 T, if $t = 0.2$ eV) produce dramatic changes in $C^{-1}$ at low $T$ (Fig. 4a). The resulting $C^{-1}$ at $H \neq 0.0$ is still large, but compared with $C^{-1}(H = 0)$ the effect is notorious. An analysis of the spin correlations vs $H$ shows that these large resistance changes mainly originate in the AF regions, since small fields produce a small spin canting and concomitant small conductivity, creating a *valve* effect between metallic domains. In real manganites, a relatively modest $\rho_{dc}$ change in the insulating regions could contribute appreciably to the large MR. To simulate this effect, $\rho_I$ of the 2D network of Fig. 2c was slightly modified [$\Delta\sigma_{dc} = 0.1(\Omega\,\mathrm{cm})^{-1}$], with $\rho_M$ untouched. The resulting $\rho_{dc}$ changes (Fig. 4b) are indeed large at low $T$, comparable to those obtained changing $p$ by a few percent.

Summarizing, $\rho_{dc}$ of manganites was studied within the PS framework using a semiphenomenological approach. At room $T$, conduction predominantly through the insulating regions leads to $d\rho_{dc}/dT < 0$, while at low $T$ the metallic filaments carry the current. The magnetic-field-induced large MR is caused by small changes in the metallic fraction $p$ and/or in the insulator's conductivity, effects which severely affect transport near percolation. Our approach provides a simple explanation of the CMR effect, without invoking polaronic or Anderson localization concepts, and independently of the origin (Coulomb vs Jahn-Teller) of the competing metal and insulator [18]. The mixed-phase character of manganites is the key ingredient to understand their surprising CMR properties.

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[1] Y. Tokura and N. Nagaosa, Science **288**, 462 (2000); E. Dagotto *et al.,* Phys. Rep. (to be published).
[2] M. Uehara *et al.,* Nature (London) **399**, 560 (1999); see also M. Ibarra and J. De Teresa, J. Magn. Magn. Mater. **177–181**, 846 (1998); D. Louca and T. Egami, Phys. Rev. B **59**, 6193 (1999).
[3] A. Moreo *et al.,* Science **283**, 2034 (1999); S. Yunoki *et al.,* Phys. Rev. Lett. **80**, 845 (1998). For analogous ideas in doped AF semiconductors, see E. L. Nagaev, JETP Lett. **16**, 558 (1972); V. A. Kashin and E. L. Nagaev, Sov. Phys. JETP **39**, 1036 (1974).
[4] S. Yunoki *et al.,* Phys. Rev. Lett. **81**, 5612 (1998); **84**, 3714 (2000); T. Hotta *et al., ibid.* **84**, 2477 (2000); J. van den Brink *et al., ibid.* **83**, 5118 (1999).
[5] A. Moreo *et al.,* Phys. Rev. Lett. **84**, 5568 (2000).
[6] Localization to understand the insulator above $T_C$ was studied in L. Sheng *et al.,* Phys. Rev. Lett. **79**, 1710 (1997). However, V. Smolyaninova *et al.,* cond-mat/9903238, showed that the metal-insulator transition of $La_{0.66}Ca_{0.33}MnO_3$ is not due to Anderson localization.
[7] S. Kirkpatrick, Rev. Mod. Phys. **45**, 574 (1973).
[8] For a similar approach, see K. H. Kim *et al.,* Phys. Rev. Lett. **84**, 2961 (2000). For studies of impurity conduction, see A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).
[9] Since $\rho_I(T \sim 0)$ of $y = 0.42$ LPCMO is finite, the net $\rho_{dc}(T = 0)$ does not diverge below the naively expected critical point $p_c = 0.50$ of a simple 2D network with $\rho_I = \infty$.
[10] R. Mathieu *et al.,* cond-mat/0007154.
[11] S. Kawasaki *et al.,* J. Phys. Soc. Jpn. **67**, 1529 (1998).
[12] "Percolative" configurations are rare in small clusters.
[13] Y. Avishai and J. M. Luck, Phys. Rev. B **45**, 1074 (1992).
[14] J. A. Vergés, cond-mat/9905235; M. Calderon, J. Vergés, and L. Brey, Phys. Rev. B **59**, 4170 (1999).
[15] The finite clusters are connected to semi-infinite leads using an infinitesimal voltage drop. The self-energy of these leads is known, and $C$ is evaluated using known formulas [14]. Since this is *quantum* percolation, the study is only in 3D (2D localization leads to zero conductivity).
[16] It was verified by a finite-size-scaling analysis that the conductances shown in Fig. 3a are in the Ohmic regime.
[17] Similar results were obtained using the two-orbital model [4] in one dimension, near a FM-AF transition [5].
[18] Our approach also applies to large MR nonmanganite materials, such as the Eu-based compounds [S. Yoon *et al.,* Phys. Rev. B **58**, 2795 (1998); E. L. Nagaev, *Physics of Magnetic Semiconductors* [Mir, Moscow, 1983]; A. Mauger and D. L. Mills, Phys. Rev. Lett. **53**, 1594 (1984)].