Statistical Models of the Polaronic Phase Transition in Manganites

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We propose two statistical models for description the metal-insulator phase transition coupled with paramagnetic-ferromagnetic phase transition in manganites of the type La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3}. The first one based on the competition of small polarons and delocalized carriers. In the second one the conductivity appears as a result of overlapping of large polarons. We compare our models with the experimental data.

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The interplay of the metal-insulator (M-I) and ferromagnetic-paramagnetic (FM-PM) transitions in mixed metal oxides is one of the most important and least understood topics in material physics. The early explanation of the combined metal-insulator (M-I) and ferromagnetic-paramagnetic (FM-PM) transitions was based on the Double-Exchange (DE) mechanism\textsuperscript{[1]}. In this mechanism the exchange interaction between spins is provided by conduction electrons. The electron tunneling amplitude from one site to another depends strongly on orientation of spins on these sites. Therefore, magnetic phase transition causes simultaneous drop in resistivity.

Recently, Millis \textit{et al}.\textsuperscript{[2], [3]} have shown that the Double Exchange itself does not explain the transition from the conducting to insulating phase. They argued that Jahn-Teller distortions are strong enough and lead to formation of polarons. The high temperature phase in their picture contains presumably polaronic carriers and is insulating\textsuperscript{[4]}. In the low temperature phase delocalized carriers appear together with the magnetization. This idea is supported by experimental observations of large Jahn-Teller distortions\textsuperscript{[5, 6]}. It was confirmed experimentally that small polarons are responsible for transport at high temperature\textsuperscript{[7]}. For reviews on the experimental state of art see\textsuperscript{[8, 9, 10]}. Quantitative description of the phenomenon was based on a phenomenological Hamiltonian proposed by Millis, Schraiman and Mueller (MSM)\textsuperscript{[3]} which describes electrons coupled via elastic deformations and interacting with localized spins

\begin{equation}
\mathcal{H} = \sum_{r,a} t_{r,r+a} \psi^\dagger(r) \psi(r + a) - \sum_{r} J_H S_{\sigma} \cdot \psi^\dagger(r) \sigma \psi(r) + \sum_{r} \left( \frac{\kappa}{2} Q_{\tau}^2 - g Q_{\tau} \cdot \psi^\dagger(r) \tau \psi(r) - \mu \psi^\dagger(r) \psi(r) \right)
\end{equation}

Here $t_{r,r+a}$ is the nearest neighbor tunneling amplitude, $\psi(r), \psi^\dagger(r)$ are fermion operators, $Q_{\tau}$ are local Jahn-Teller-displacements, $\sigma$ and $\tau$ are spin and pseudospin Pauli matrices, $J_H$ is the Hund energy, $g$ is the electron-phonon coupling constant and $\kappa$ is the elastic coefficient. $J_H$ is assumed to be the largest energy scale in the problem. In this approximation electron spins follow adiabatically the direction of localized spins on a site. The authors\textsuperscript{[3]} treated their model Hamiltonian in the mean field approximation. For the number of carriers per site $n = 1$ they have found an insulator phase with strong Jahn-Teller distortion. For $n > 1$ the high temperature phase in the framework of this approximation remains conducting, though the conductivity can decrease rapidly above transition temperature. In particular, no remarkable magneto-resistance have been found at experimentally optimal value $n = 0.3$. These results allow a following interpretation. The fermion variables can be eliminated explicitly from the partition function based on the Hamiltonian\textsuperscript{[11]}. After elimination we arrive at an effective free energy for variables $Q$ and $S$: \begin{equation} \frac{F}{T} = -Tr \ln \left( 1 + \exp \left( \hat{t} - \hat{J} - \hat{Q} + \hat{\mu} \right) \right) - \frac{\kappa}{2} \sum_{r} Q_{\tau}^2 \end{equation} where operator $\hat{\mu}$ is diagonal $4N \times 4N$ matrix in variables $r, \sigma, \tau$, whereas operator $\hat{t}$ is off-diagonal only with respect to variable $r$ with non-zero matrix elements \begin{equation} t \sum_{a} \delta_{r, r + a}; \text{other two operators } \hat{J} \text{ and } \hat{Q} \text{ are off-diagonal with respect to variables } \sigma \text{ and } \tau \text{ with matrix elements } J_H S_{\tau} \cdot \sigma_{\sigma'} \text{ and } g Q_{\tau} \cdot \tau_{\tau'} \text{, respectively. The mean-field (Landau) counterpart of the free energy (2) reads: } \end{equation} \begin{equation} F_L = aS^2 + b(S^2)^2 + AQ^2 + B(Q^2)^2 + cS^2Q^2. \end{equation} This is well-known problem of two interacting order parameters (see, e.g.\textsuperscript{[12]}). Its typical phase diagram contains 4 phases with $S$ and $Q$ either equal to zero or non-zero. It is tempting to identify phases with $Q = 0$ as insulating and those with $Q = 0$ as metallic. Then mentioned phases would be paramagnetic metal (PM), paramagnetic insulator (PI), ferromagnetic metal (FM) and ferromagnetic insulator (FI). However, this model being applied for description of manganites with CMR has...
two substantial failures: i) its high-temperature phase is metallic, whereas in real manganites it is insulating; ii) the transition from the PI to the FM phase proceeds at one point only, whereas in real systems it proceeds along a line. Therefore, the mean-field approximation applied by MSM from our point of view is insufficient to explain the real phase diagram in manganites. It happens because any solution with the homogeneous displacement field \( Q \) does not describe formation of a localized objects - polarons. The fact that MSM obtained large magneto-resistance at \( n \approx 1 \) is readily explained as a result of splitting of the double-degenerate upper level by strong Jahn-Teller effect. But this effect does not work properly at smaller values of \( n \), since the lower band is not fully occupied.

In this article we propose simple statistical models in which polaron states are incorporated phenomenologically. These models have the two most important phases found in the experiment: paramagnetic insulator (PI) and ferromagnetic metal (FM). In the first model which we call Small Polaron (SP) Model we start with the free energy written in the form:

\[
\mathcal{F} = (-1 + m^2) + \frac{\beta}{2} m^4 / T m^2 + \mathcal{F}_{LG}
\]

where \( \mathcal{F}_{LG} = -n_p \varepsilon + T(n_c \ln n_c + n_p \ln n_p) \) is the small polaron lattice gas free energy. \( n_c \) is the density of conductance electrons, \( n_p = n - n_c \) is the density of localized electrons (small polarons), \( n \) is the total electron density; \( t \) is the bandwidth, \( -\varepsilon \) is the small polaron energy, \( m \) is the magnetization; the constant \( \beta \) allows to vary the saturation magnetization. In the insulating (polaron) phase \( m = 0 \). Minimizing free energy Eq. \( 4 \) with respect to \( m \) one finds equation for \( x = n_c/n \):

\[
x \Delta + \frac{m^2}{x^2} + T \ln \frac{x}{m} = 0.
\]

Depending on parameters, this equation has one, two or no roots. For \( \Delta > 0 \) and \( T = 0 \) this equation has no roots. It means that the polaronic phase is stable. For \( \Delta < 0 \) the FM phase is stable at \( T = 0 \). Since the polaronic phase always wins at large temperature, it implies that for \( \Delta < 0 \) the PI-FM phase transition takes place at any value of \( n \). The phase diagram was calculated numerically. For \( \beta < 1/(n \ln 2) \) the transition temperature grows monotonously with \( n \). If \( \beta > 1/(n \ln 2) \) the ferromagnetic phase exists not at any \( n \), but only at the carrier density exceeding a critical value \( n_c < n \). An interesting feature of this model is the possibility of re-entrant polaronic phase at low temperature. This peculiarity may be related to the reentrant behavior of resistivity found in the experiment \( 6 \).

The energy parameters of the model \( \varepsilon \) and \( t \) are in the range \( 1 eV \), but numerical values of the transition temperature are relatively small: \( a t < T_c < b n t \), where \( a \approx 0.01, b \approx 0.3 \).

Though the SP model discussed above displays PI and FM phases and the colossal magneto-resistance, some its features seem unrealistic. It implies the first order phase transition with rather large discontinuities of the values \( m, n_c \) and entropy for a reasonable set of parameters, whereas there is no experimental indication of remarkable hysteresis near the transition line. These discontinuities may be smeared out by a small number of impurities or other defects. We simulated the action of defects by averaging of the resulting values \( m(T/t, \varepsilon), n_c(T/t, \varepsilon) \) over a small range \( (3 \div 4\%) \) of the parameter \( \varepsilon \). The results are shown in Fig. \( 1 \) for zero and small finite magnetic field. In this calculation we identified \( n_c^{-1} \) with the resistance. In reality they differ by a factor (mobility) which varies slowly, at least near the transition line. Another unrealistic feature of the SP model is too large scale of magnetic fields (this feature is shared with the MFA calculations of the MSM work). If one accepts the intersite tunneling constant equal to \( 0.6 eV \) \( [3] \), the essential magnetic field at room temperature is about 10-100 times more than experimental values (field \( h_0 \) in Fig. \( 1 \) corresponds to \( \sim 50 T \) for \( t = 0.6 eV \)).

Our second model was inspired by the neutron scattering experiments \( [6], [10] \) which showed the occurrence of large magnetic polarons (LP) coexisting with the small polarons (SP). This phenomenon lies beyond the scope of the simple SP model. Below we discuss an alternative mechanism of the PI-FM phase transition based on the LP.

We employ Varma theory \( [5] \) modified to incorporate the Jahn-Teller effect. The free energy of an individual carrier localized in a sphere of radius \( R \) reads:

\[
F(R) = -W + \frac{t}{R^2} - CTR^3 - \frac{\varepsilon_0}{R^3}
\]

Here \( W \propto t \) is the half-width of the conductivity band, \( R \) is measured in the lattice constants, \( t \) and \( \varepsilon_0 \sim \varepsilon \) have the same meaning as before; \( C \) is a numerical constant which can be roughly estimated as \( (4/3) \pi \ln 4 = 5.8 \). The latter figure is probably overestimated since it is found for the case of full saturation of magnetization in large polaron.
which is scarcely realized. Further we assume $C$ to be of the order of one. The first three terms in the r.-h. s. of eqn. 3 were discussed in [11]. The last term describes the polaronic effect. It contributes a term proportional to $|\Psi(R)|^4$ to the energy density where $\Psi(R)$ is the electron wave-function (see, for example [14]). The contribution to the total energy is inverse proportional to the volume of the localized state. Exactly as in the work [11], the localization on large scale of $R$ originates from the entropy term $TR^3$. The Jahn-Teller term can be neglected if $t$ and $\varepsilon_0$ have the same order of magnitude and $T$ is small. Minimizing $F(R)$, we find the radius of the stable or metastable polaron $R_p \approx (2t/3T)^{1/5}$. This result shows that the linear size of the LP changes very slowly with temperature. At reasonable values of $t \sim 0.6eV$ [14] and $T \sim 0.01 \div 0.03eV$ it does not exceed 2.5. Thus, the large polaron is not so large. Still it contains between 30 and 60 sites and its magnetic moment is large.

The ratio of numbers of the LP and SP is given by the Boltzmann factor $\exp[-(\varepsilon - F(R_p))/t]$ where $\varepsilon$ is, as above, the energy of the small polaron. We introduce the value $\Delta_p = \varepsilon + W$. If $\Delta_p$ is positive, this ratio tends to a small number $\exp(-R_p^2)$ at high temperature. At some low enough temperature $T_p$ the LP density becomes equal to the inverse volume of the LP. This temperature can be found from equation: $\frac{\Delta_p}{t} = 1.96 \left(\frac{R_p}{\pi}\right)^{3/5} + \ln (nV_p) = 0$

where $V_p = (4/3)\pi R_p^3$ is the volume of the LP. At this (or slightly higher) temperature large polarons overlap forming an infinite cluster. The percolation leads to a rapid decrease of resistivity. Indeed, the magnetization inside the cluster is homogeneous. The condition at which the spontaneous magnetization appears was shown to be $tn_c > T$. The concentration of delocalized carriers $n_c$ in the cluster is equal to $V_p^{-1}$. Thus, $tn_c/T_p \approx (t/T_p)^{2/5} > 1$.

Normally the percolation transition proceeds continuously. The Coulomb repulsion prevents formation of macroscopic magnetic droplets before percolation. The Coulomb energy $e^2/\epsilon R$ must be compared with the kinetic energy $t/R^2$. Even for static dielectric constant $\epsilon = 25$ the Coulomb energy prevails. We expect that the screening is even weaker at small distances.

It is important to note that the existence of magnetization inside the cluster does not guarantee the total non-zero magnetization. The percolation and the spontaneous magnetization appearance proceed simultaneously in 2 dimensions. The reason is that two infinite clusters for different spin orientations would unavoidably intersect. In 3 dimensions they can interpenetrate without intersection as long as their branches are thin enough. The spontaneous magnetization appears when the cross section of each infinite cluster increases. This fact was established for Ising model [14], but its geometrical origin is quite general. In the frameworks of the LP model the Mott transition proceeds, generally speaking, at a temperature higher than the Curie point.

An approximate solution of equation for $T_p$ is: $T_p \approx t(\Delta_p/2t)^{5/2}$. At $\Delta_p \approx 0.5t$ we find $T_p \approx 0.03t \approx 200K$. This estimate looks reasonable. The logarithmic term in equation for $T_p$ provides a weak dependence of $T_p$ on the dopant concentration $n$.

Statistics of LP can be constructed via a kind of the lattice model with the sites either occupied by a LP or empty (the elementary cell of this auxiliary lattice has the volume $V_p$). Introducing occupation numbers $\tau_r = 0, 1$ and polaron spins $\bf{S}_r = S\bf{n}_r$ on sites, the proposed lattice Hamiltonian reads:

$$\mathcal{H}_{lp} = - \sum_{r,a} Jn_r \cdot n_{r+a}\tau_r\tau_{r+a} + \sum_{r,a} K\tau_r\tau_{r+a} - \sum_r (h \cdot n_r\tau_r + \mu\tau_r),$$

(6)

where $J$ is the effective exchange constant, $h = g\mu_B H$ is an effective magnetic field for polarons, $K$ stays for the Coulomb interaction between neighboring polarons and $\mu = W - CW^3/5T^{2/5}$ is the polaron free energy. The mean-field counterpart of the Hamiltonian [10] reads:

$$F_{lp} = -Jm^2x^2 - TS_H(m) - hmx - F_I(x)$$

(7)

where $m = \langle n_r \rangle$ and $x = \langle \tau_r \rangle$, $J = zJ$, $K = zK$, $z$ is coordination number. $F_I(x) = Kx^2 - T[x\ln x + (1-x)\ln(1-x)] - \mu x$. $S_H(m)$ is the spin entropy per site for the Heisenberg system. For large $S$ we are interested in, $S_H(m)$ is determined by a following equations:

$$S_H(m) = \ln 2S - \ln(1 - (1-m)\zeta(m)) - (m + 1)\zeta(m),$$

where $\zeta(m)$ is determined by equation: $\coth\zeta - 1/\zeta = m$.

We calculated magnetization by minimization of free energy [4] and resistance employing the effective medium approximation [16]. The results for magnetization and large polaron density are shown in Fig. 2.

FIG. 2. Magnetization (line) and large polaron concentration (+) vs $T/W$ for the set of parameters $J = 2W$ $K = 0.6W$.
Despite of visible similarity of the LP mean-field model to corresponding SP model, the former displays the second order transition in a broad range of parameters. The resistivity show magnetic field dependence qualitatively similar to that in Fig. 4. However, due to large value of $S$ for a polaron, the scale of magnetic field displaying the CMR is about 100 times lower than for the SP model and, thus, it fits satisfactory the experimental data. Transition temperature in Fig. 2 is in qualitative agreement with estimation from the simple large polaron model of Eq. 5. The phase diagram of the model Eq. 6 displays region of second order phase transitions for $0.5W \leq \bar{K} \leq 1.5W$ and for $\bar{J} \leq 0.2/0.3W$ with $T_p \propto \bar{J}$. The Mean Field Approximation (MFA) is insensitive to percolation threshold near which the phase transition occur. However, one can estimate correction to the MFA phase diagram by using results known from dilute magnetic models [16]. Corresponding corrections decrease the transition temperature in the region with LP concentration larger than percolation threshold by $\approx 10\% \div 20\%$. More detailed description of the phase diagram will be given elsewhere.

In conclusion, we proposed statistical models explicitly incorporating polaron formation in manganites. One of them (the SP model) displays first order phase transition from paramagnetic state with localized electrons to the ferromagnetic state with metallic conductivity in perovskites, the colossal magneto-resistance and the re-entrant resistivity in a range of variables. The second LP model is based on percolation of large polarons. It predicts a continuous isolator-conductor transition at a temperature higher than the magnetic transition. Experimental data on neutron scattering, the magnetic transition from paramagnetic state with localized electrons to the ferromagnetic state with metallic conductivity in perovskites, the colossal magneto-resistance and the re-entrant resistivity in a range of variables. The second LP model is based on percolation of large polarons. It predicts a continuous isolator-conductor transition at a temperature higher than the magnetic transition. Experimental data on neutron scattering, the magnetic transition from paramagnetic state with localized electrons to the ferromagnetic state with metallic conductivity in perovskites, the colossal magneto-resistance and the re-entrant resistivity in a range of variables.

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