Theory of Ferromagnetic Metal to Paramagnetic Insulator Transition in $R_{1-x}A_x\text{MnO}_3$

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Abstract

The double-exchange model for the Mn oxides with orbital degeneracy is studied with including on-site Coulomb repulsion, Jahn-Teller (J-T) coupling and doping-induced disorder. In the strong interaction limit, it is mapped onto a single-band Anderson model, in which all scattering mechanisms can be treated on an equal footing. A sharp rise in the mean square fluctuation of lattice distortions is found near the Curie temperature $T_c$, in agreement with experiments. We show that the spin and J-T disorders lead to a metal-insulator transition (MIT) only at low carrier density. The MIT observed in samples with $0.2 \leq x < 0.5$ can be explained by further including the disorder effect of cation size mismatch.

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The importance of electron-lattice coupling to the transport properties of the Mn oxides $R_{1-x}A_x\text{MnO}_3$, which exhibit colossal magnetoresistance (CMR) effect \cite{1, 2} in the hole-doping range $0.2 \leq x < 0.5$, was pointed out in early theoretical works \cite{3, 4}. Experimental measurements \cite{5} \cite{6} have repeatedly given evidences for the existence of Jahn-Teller (J-T) effect in the Mn oxides. In those works, the novel ferromagnetic metal (where $d\rho/dT > 0$ with $\rho$ as the resistivity) to paramagnetic insulator ($d\rho/dT < 0$) transition was understood as a crossover from large to self-trapped small polarons caused by the band narrowing accompanying with local spin disordering during the transition. Such a description does make sense if the carrier density is low enough so that the small polarons are well separated in space. In the high density regime, e.g., for the Mn oxides with intermediate doping, there should be large overlaps among the polaron wave functions, and the validity of small polaron picture becomes questionable. On the other side, recent experiments \cite{7} showed that large and small polarons actually coexist in the insulating paramagnetic phase, an indication that even large polarons can also be localized and do not contribute to metallic conductivity. These issues suggest that a more accurate criterion for the metal-insulator transition (MIT) is urgently needed.

A valid theory for the MIT at intermediate doping has to be based upon a unified non-perturbative treatment of these equally important scattering mechanisms: (i) strong double-exchange (DE) interaction between conduction $e_g$ electrons and localized spins \cite{11} \cite{12}, (ii) J-T coupling and on-site Coulomb repulsion associated with doubly degenerate $e_g$ bands, and (iii) doping-induced nonmagnetic disorder. Factor (iii) playing an important role in the transport properties of the Mn oxides has been well demonstrated in experiments \cite{3} \cite{4}. It was proposed there that the size mismatch between $R$ and $A$ atoms leads to bending of local Mn-O-Mn bonds, and hence strongly reduces the electron hoping integral. With the basic structure of the MnO$_6$ octahedra being similar, the compounds $R_{1-x}A_x\text{MnO}_3$ with different $R$ and $A$ should have about the same J-T coupling strength. Therefore, tuning the cation size mismatch has become a practical way to control their transport properties \cite{4}. Previous theoretical works on the MIT focused on only one or two of these features. For example, in Refs. \cite{5} and \cite{6} the lattice effect has been emphasized but the on-site Coulomb interaction and doping-induced disorder were neglected. These theories failed to account correctly for the doping dependence of the MIT. On the other hand, nonmagnetic disorder effect was considered within the single-band DE model in Refs. \cite{15} and \cite{16} with the J-T distortions being omitted. The works \cite{15} and \cite{16} overestimated the strength of nonmagnetic disorder necessary for the occurrence of MIT. A complete theory, which is able to describe the essential physics of the MIT in the Mn oxides, is still lacking.

In the present work, the MIT in the Mn oxides will be investigated by incorporating all scattering mechanisms outlined above. Employing the path-integral approach, we map our Hamiltonian onto a single-band Anderson model in the strong interaction limit. From this model, the MIT can be numerically studied using the transfer matrix method without further approximation \cite{17}. The J-T coupling strength is estimated by comparing our calculated resistivity with the experimental data of La$_{1-x}$Sr$_x$MnO$_3$. For the first time, the role of the J-T distortion on the MIT has been determined very precisely. The phase diagram obtained describes consistently the behavior of the MIT observed in samples with CMR as a function of doping concentration and cation size mismatch.

In the Mn oxides, each Mn atom has five outer-shell 3$d$ orbitals, three half-filled $t_{2g}$ states
giving rise to an $S = 3/2$ localized spin, and two $e_g$ states $|+\rangle = |x^2 - y^2\rangle$ and $|-\rangle = |3z^2 - r^2\rangle$ forming two-fold degenerate conduction bands. Strong Hund’s rule coupling forces electron spins on a site to polarize completely, so we can write down a Hamiltonian, in which the conduction electrons are effectively spinless,

$$H = -\sum_{ij} f_{ij}(d_i^\dagger t_{ij} d_j) + \sum_i U' n_i n_i - g \sum_i (d_i^\dagger \tau d_i) \cdot Q_i + \frac{k}{2} \sum_i Q_i^2.$$  

The first term represents the two-band DE model \[13\]-\[16\], where $d_i^\dagger = (d_{i+}^\dagger, d_{i-}^\dagger)$ and $f_{ij} = \cos(\theta_i/2) \cos(\theta_j/2) + \sin(\theta_i/2) \sin(\theta_j/2) e^{-i(\varphi_i - \varphi_j)}$. The second term stands for the on-site inter-orbital Coulomb repulsion. The third and fourth terms describe the coupling between electrons and two J-T distortion modes $Q_i = Q_x \hat{i} + Q_y \hat{k}$, and the harmonic lattice deformation energy, respectively \[3\], where $\tau$ are the Pauli matrices. The hopping integral matrix $t_{ij}$ can be written as \[18\]

$$t_{ij} = (t - r_{ij} \Delta t)(1 + \tau \cdot n_{ij}),$$  

where $t$ is the bare hopping integral, $r_{ij} \Delta t$ is used to model the disorder originated from cation size mismatch with $\Delta t$ as its amplitude and $r_{ij}$ random numbers between 0 and 1. Since $R$ and $A$ atoms are randomly distributed, their size mismatch not only decreases the average electron band width but also leads to off-diagonal disorder. Here, $n_{ij} = n_\alpha$ with $\alpha = x, y$ and $z$ for hopping along the $x, y$ and $z$ directions, and $n_x = -(\sqrt{3} \hat{i} + \hat{k})/2$, $n_y = (\sqrt{3} \hat{i} - \hat{k})/2$, $n_z = \hat{k}$.

Since both the J-T coupling and on-site Coulomb interaction disfavor double occupancy, they have the common tendency to split the degenerate $e_g$ bands. From Eq. (1), it is easy to derive a mean-field Stoner criterion for the occurrence of band splitting at half-filling ($x = 0$)

$$(U' + 2E_J)D(0) > 1,$$  

where $E_J = g^2/k$, and $D(0)$ is the single-band density of states at the band center before the band splitting. Equation (3) is also the criterion at which static J-T distortions ($\langle Q_i \rangle \neq 0$) occurs. In the absence of Coulomb repulsion, it needs relatively strong J-T coupling to split the $e_g$ bands and induce static J-T distortions. In the opposite limit where $U'$ is larger than the band width, any small J-T coupling will lead to static J-T distortions. The on-site Coulomb repulsion enhances substantially the J-T effect. This is consistent with the argument of Varma that the Mn oxides at half-filling ($x = 0$) are Mott insulators, while the J-T effect occurs parasitically \[14\].

According to experiments, the condition in Eq. (3) should be well satisfied in the Mn oxides. In order to ensure the system being insulator at $x = 0$ and to reduce the number of involved parameters, we shall project out double occupancy by setting $(U' + 2E_J) \to \infty$. In the path-integral representation, the isospin-charge separation transformation $d_i = c_i y_i$ can be introduced, where $y_i$ is the $CP^1$ field for the isospin and $c_i$ is the charge operator \[19\]. The effective Lagrange corresponding to Hamiltonian Eq. (1) is then derived to be

$$L(\tau) = \sum_i \left[ c_i^\dagger c_i y_i^\dagger \partial_\tau y_i + c_i^\dagger (\partial_\tau - \mu) c_i \right. \right.$$  

$$- \left. \sum_j f_{ij} (y_j^\dagger t_{ij} y_j) c_i^\dagger c_j - g \Omega_i \cdot Q_i c_i^\dagger c_i + \frac{k}{2} Q_i^2 \right],$$  

(4)
where $\mathbf{o}_i(\tau) = \mathbf{y}_i^\dagger(\tau)\mathbf{r}\mathbf{y}_i(\tau)$ is a unit vector characterizing the instantaneous isospin orientation. The third term in Eq. (4) indicates that the isospin kinetic motion is characterized by the energy scale $K_0 = t\langle c_i^\dagger c_j \rangle$, which for $0.2 \leq x < 0.5$ is numerically obtained as $K_0 \simeq 0.10t \sim 0.16t$ at $\Delta t = 0$. Disorder will further decrease this value. On the other hand, the J-T coupling given by the fourth term in Eq. (4) is estimated to be $-E_J$. Therefore, as long as $E_J > t$, the J-T coupling dominates and parallel configuration between $\mathbf{Q}_i$ and $\mathbf{o}_i$ is energetically favorable; namely, $\mathbf{o}_i = \mathbf{Q}_i/Q_i$ being confined to the $x - z$ plane. A permitted parametrization \cite{19} of $\mathbf{y}_i^\dagger$ is $\mathbf{y}_i^\dagger = [\cos(\phi_i/2), \sin(\phi_i/2)]$ with $-\pi < \phi_i \leq \pi$, where $\phi_i$ is the angle between the isospin and the $z$-axis.

To study the statistics of the J-T distortions, we can carry out the Gaussian integral of the charge variables $c_i(\tau)$ in Eq. (4). The saddle point equation of the resulting Lagrange yields $\langle Q_i \rangle = g(1 - x)/k$. Then expanding the Lagrange around $\langle Q_i \rangle$ up to quadratic order in $\delta Q_i = Q_i - \langle Q_i \rangle$, we obtain a Gaussian distribution $P(\varepsilon_i) = \exp(-\varepsilon_i^2/2\Delta_j^2)/\sqrt{2\pi}\Delta_j$ for the dynamical fluctuations of J-T distortions with $\varepsilon_i = -g\delta Q_i$.

$$\Delta_j^2 = (k_BT)/[1 - E_JD(\mu)]$$

is equal to $\langle \varepsilon_i^2 \rangle = g^2\langle (\delta Q_i)^2 \rangle$. For fixed $E_J$, the amplitude $\Delta_j/g$ of lattice fluctuations depends on temperature $k_BT$ and electron density of states $D(\mu)$ at the chemical potential $\mu$ for $\delta Q_i \equiv 0$. The denominator of Eq. (5) represents the dynamical aspect of the lattice distortions due to electron density fluctuations within the random phase approximation (RPA). According to Eq. (4), we obtain an effective single-band Hamiltonian

$$H_{\text{eff}} = -\sum_{ij} \tilde{t}_{ij} c_i^\dagger c_j + \sum_i \varepsilon_i c_i^\dagger c_i,$$  

where $\tilde{t}_{ij} = f_{ij}(y_i^\dagger t_{ij} y_j)$, and a constant energy $-(1 - x)^2 E_J/2$ per site has been omitted. With explicit parametrization, $\tilde{t}_{ij}$ can be written as

$$\tilde{t}_{ij} = f_{ij}(t - r_{ij}\Delta t)\{\cos[(\phi_i - \phi_j)/2] + \cos[(\phi_i + \phi_j)/2 - \gamma_{\alpha}]\},$$

with $\gamma_{\alpha} = 2\pi/3, -2\pi/3$ and 0 for electron hopping in the $x$, $y$ and $z$ directions. Equation (7) is the effective electron hopping integral renormalized by spin disorder, ionic size mismatch and orbital disorder.

To investigate the magnetic and orbital ordering transitions, we replace $c_i^\dagger c_j$ in Eq. (6) by its average $K_0/t$. The resulting Hamiltonian for the spins and isospins is studied by Monte Carlo simulation on a $20 \times 20 \times 20$ site lattice. We find the spin and isospin ordering transition temperatures $T_c$ and $T^*$, respectively, to be

$$T_c \simeq 1.3K_0, \quad T^* \simeq 0.5T_c.$$

If the bare band width $W = 12t$ is taken to be $2eV$, then $T_c$ is about $250K$ to $400K$ for $0.2 \leq x < 0.5$ in the absence of disorder. The disorder effect may still lower $T_c$ by a finite amount \cite{16}. The value of $T_c$ evaluated here is comparable to experimental data for the Mn oxides. Our finite-size calculation seems to indicate that the isospins are ordered below $T^*$, while the result based on a mean-field approximation implies only strong short-range ordering \cite{18}.
The Hamiltonian Eq. (6) represents an Anderson model with temperature-dependent diagonal and off-diagonal disorders. Well below $T_c$, the spins are ordered and the fluctuations of the on-site J-T energy $\varepsilon_i$ are relatively weak, so we expect a metallic phase there. As the temperature is increased to above $T_c$, the local spins rapidly become disordered, leading to DE off-diagonal disorder. Besides, along with the local spin disordering, the electron band narrows and $D(\mu)$ increases. From Eq. (5), it follows that the fluctuation amplitude $\Delta f$ of $\varepsilon_i$ also increases near $T_c$. For simplicity, we assume the local spins $(\theta_i, \varphi_i)$ to be completely ordered and disordered below and above $T_c$, respectively. The isospins $(\hat{\phi}_i)$ are disordered above $T^* = 0.5T_c$ according to Eq. (8). If $E_J^\prime$ is taken to be $E_J^\prime = 3.7t$ (see later discussion), by exact diagonalization of Eq. (6) with $\varepsilon_i \equiv 0$ on a lattice with $10 \times 10 \times 10$ sites to calculate $D(\mu)$, it is found that $\Delta f$ increases by $30\%$ at $\Delta t = 0$ during the magnetic transition. This result is consistent with the extensive experimental observations \cite{7,8} of rapidly enhanced lattice fluctuations near $T_c$. The increased spin and lattice disorders may possibly lead to an Anderson MIT. The picture of Anderson localization is applicable to finite temperatures, as long as the electron localization lengths are smaller than the dephasing length $\ell_{in}$ due to inelastic scattering. This condition could be expected in the Mn oxides in the experimental temperature range; otherwise their insulator transport behavior could not be observed.

Before determining the localization effect due to Eq. (6), we need to estimate the J-T coupling $E_J^\prime (= k^2/g)$ by comparing our calculated resistivity with experimental data. Since the effect of DE spin disorder and J-T distortions is most prominent in the cleanest systems, we consider La$_{1-x}$Sr$_x$MnO$_3$ \cite{9}, where the ionic mismatch can be assumed negligible ($\Delta t \simeq 0$). According to the sign of $d\rho/dT$, one finds the paramagnetic phase of La$_{1-x}$Sr$_x$MnO$_3$ becomes obviously metallic in the doping range $x = 0.3 \sim 0.4$ with resistivity of the order of $10^{-3}\Omega \cdot cm$ at $T = 400 K$ \cite{10}. On the other hand, we can calculate the resistivity from Eq. (6) numerically. By using the well-known transfer matrix method developed by Mackinnon and Krammer \cite{11} to calculate the mobility edge, we first determine the phase diagram in the $n_e (= 1 - x)$ vs $\Delta_J$ plane at $\Delta t = 0$ in the paramagnetic phase, as given in Fig. 1(a). Here, the disorder coming from both the randomly oriented localized spins and J-T distortions has been considered. In the corresponding metallic region, we then apply the Landauer formula \cite{20} to calculate the conductivity at $T > T_c$ as a function of $x$ for different values of $\Delta_J$, as plotted in Fig. 1(b), where the experimental data at $T = 400 K$ of Ref. [9] are shown by squares. For $0.2 \leq x < 0.5$, it is found that $D(\mu)$ changes very slowly with electron density $n_e$, so for a given temperature $\Delta_J$ is approximately constant. By comparison of the calculated and experimental data in Fig. 2(b), we find $\Delta_J \simeq 1.5t$ at $T = 400 K$ for the Mn oxides, which means $E_J \simeq 3.7t$. This value of $E_J$ corresponds to $\lambda = 1.1$ in the theory of Millis et al. \cite{12}. According to Fig. 1(a), for such strength of J-T coupling, the DE spin disorder and J-T distortions lead to an insulator paramagnetic phase only for $n_e \geq 0.88$ or $x \leq 0.12$. It is important to notice that since no additional scattering mechanisms besides spin disorder and J-T distortions are considered here, the estimated J-T coupling strength $E_J = 3.7t$ should be regarded as an upper bound.

In order to study the MIT for samples with $x > 0.12$, the effect of the cation size mismatch or nonzero $\Delta t$ must be included. The electron density of states and mobility edge are calculated numerically by finite-size diagonalization and scaling calculation \cite{21}. From the calculated results, we obtain the phase diagram Fig. 2 in $n_e$ vs $\Delta t$ plane for the MIT. In the limit of large $\Delta t$, the denominator of Eq. (5) may possibly go to zero or negative, giving
rise to the RPA instability. Within mean-field approximation, it is easy to see that the RPA instability simply means $\delta\mu/\delta n_e \leq 0$, an indication of phase separation into hole-rich regions with relatively weak lattice distortions and hole-poor regions with strong lattice distortions. Such unstable region is also shown in Fig. 2. It is clear that the MIT occurs in broad ranges of values of $n_e$ and $\Delta t$. With increasing $\Delta t$, localized hole number increases and Anderson transition always precedes phase separation. The phase diagram Fig. 2 is in agreement with the experimental observation that the transport properties of the Mn oxides could be drastically altered by tuning the ionic size mismatch. To further determine the system properties in the phase-separation regime, one needs to consider anharmonic deformation energy of the lattice and take nonuniform states into account. The residue resistivity coming from the cation size mismatch in the low-temperature metallic state can also be calculated. The critical residual resistivity as shown by the open circles in Fig. 2 for occurrence of a MIT is found to be the order of $10^{-4}\Omega\text{cm}$ or less, being smaller than that estimated in the absence of J-T effect. The present result seems to be more reasonable, and is comparable to data from epitaxial films or single crystal systems.

In summary, employing the path-integral approach and numerical scaling calculations, we have shown that the essential physics of the MIT in the Mn oxides with $0.2 \leq x < 0.5$ can be understood as an Anderson transition driven by DE spin disorder, J-T distortions and cation size mismatch. The phase separation predicted in Fig. 2 for strong cation size mismatch is also consistent with the inhomogeneous electron states observed recently near and above $T_c$ in the certain Mn oxides.

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FIGURES

FIG. 1. (a) Phase diagram in $n_e$ vs $\Delta J/t$ plane in the paramagnetic phase where $n_e = 1 - x$ is the electron density, and (b) the resistivity in the metallic paramagnetic phase as a function of $n_e$ for several values of $\Delta J/t$ at $T = 400K$.

FIG. 2. Phase diagram for the metal-insulator transition in $\Delta t/t$ vs $n_e$ plane for $E_J = 3.7t$. In the region labeled “Metal” the system is metallic in both the ferromagnetic and paramagnetic phases, while in the regions labeled “M-I(AL)” and “M-I(PS)” the system undergoes a metal-insulator transition near $T_c$, where AL or PS indicates Anderson localization or phase separation as the origin of the insulator paramagnetic phase. The corresponding critical residual resistivity at some points indicated by small circles is shown in unit $10^{-4}\Omega\text{cm}$.
Fig. 1

(a) Insulator

(b) La$_{1-x}$Sr$_x$MnO$_3$

$\Delta J/t = 2.0$

$\Delta J/t = 1.5$

$\Delta J/t = 1.0$

$\Delta J/t = 0.5$
Fig. 2