Charge Localization in Disordered Colossal-Magnetoresistance Manganites

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The metallic or insulating nature of the paramagnetic phase of the colossal-magnetoresistance manganites is investigated via a double exchange (DE) mechanism. Mobility edge trajectory is determined with the transfer matrix method. Density of states calculations indicate that random hopping alone is not sufficient to induce Anderson localization at the Fermi level with 20-30% doping. We argue that the metal-insulator transition is likely due to the formation of localized polarons from nonuniform extended states as the effective band width is reduced by random hoppings and electron-electron interactions.

\[ H = \sum_{\langle ij \rangle} \left( t_{ij} \gamma_j \gamma_i + \text{h.c.} \right) + \sum_i \left( \epsilon_i - \mu \right) n_i, \]

where \( \epsilon_i \) is the electronic spin operator and \( \vec{S}_i \) is the local spin \( S = 3/2 \) of three Mn \( t_{2g} \) d-electrons. The operators \( c_{\gamma i}^\dagger \) annihilate (create) a mobile \( \sigma \) electron with spin \( \sigma \) at orbital-\( \gamma \) \( (\gamma \in \{a, b\}) \), \( n_i = c_{\gamma i}^\dagger c_{\gamma i} \).

The random diagonal energy \( \epsilon_i \) is included to account for substitutional disorder [13]. The \( J_H \)-term describes the Hund’s rule coupling between the local spin of \( t_{2g} \) electrons and the \( \sigma \) electrons; the \( V \)-term describes the on-site inter-orbital electron-electron (\( e-e \)) interactions. In the Mn-oxides, \( J_H \gg t/S \). Here we neglect the on-site intra-orbital \( e-e \) interactions and exchange interactions, which is reasonable in the large \( J_H \) limit.

We consider only the limit \( SJ_H/t \rightarrow \infty \). As a consequence, the electronic spin at each site is parallel to the local spin, for the low energy states of interest. To study these low energy states, we can use a projection operator \( \mathcal{P} \) to project out the high energy states. Then the Hund’s rule coupling interaction can be dropped and the hopping term is renormalized to

\[ t_{ij} = t \cos(\theta_i/2) \cos(\theta_j/2) + \sin(\theta_i/2) \sin(\theta_j/2) e^{i(\phi_i - \phi_j)}, \]

in the classical spin limit \( S = \infty \), where \( (\theta_i, \phi_i) \) is the polar angles of the classical spin at site-\( i \). Both finite \( J_H \) and \( S \) will decrease the localization effect, while the inter-orbital \( e-e \) interaction \( V \) will probably increase it.

To simplify the problem further, we will neglect the \( e-e \) interaction here and assume that its only important contribution is to renormalize Hamiltonian parameters. The Hamiltonian [13] is then transformed to an effective one-electron Hamiltonian of the form

\[ H = \sum_i (\epsilon_i - \mu) n_i + \sum_{\langle ij \rangle} (t_{ij} \epsilon_i \epsilon_j + H.c.). \]
The Hamiltonian \( H \) describes the dynamics of electrons in a static background of classical spins, with the hopping matrix elements dependent on the spin configuration via Eq. (2). This approximation of dynamic disorder by static disorder is valid in the large \( S \) limit. Note that we also replace the two-orbitals by one effective orbital. If there is no Jahn-Teller coupling, the carrier density of each orbital would be approximately half of the doping \( x \). However, static or dynamic JT effects will complicate this issue and the exact correspondence is not well understood at the metallic region at present.

In the simplified Hamiltonian \( H \), electron localization is due to both off-diagonal and diagonal disorder. The off-diagonal disorder is intrinsic to the DE model in the paramagnetic phase, and the resistivity due to this spin-disordered scattering was calculated in Born-approximation \( 14 \) or memory function approach \( 14 \). Localization via off-diagonal disorder has not been studied extensively. A few calculations \( 15 \) have been done for uniform distributions of real hopping integrals \( t \) in one and two-dimensional systems. Also there are studies on 2D random flux systems with uniform \( |t| \) \( 14 \). The most relevant work for the present model was a study by Economou and Antoniou \( 17 \) for systems with a semi-circle distribution of hopping integrals. Their work was based on the localization criteria of Economou and Licciardello \( 18 \). A recent calculation \( 19 \) based on the Ziman criterion \( 20 \) was also reported. None of these calculations produce the precise mobility edge. Moreover, the random Berry’s phases (the phase of \( t_{ij} \) in Eq. (2)) are not included, and their importance is difficult to assess.

Here we investigate the localization properties of Hamiltonian \( H \) with the transfer matrix method \( 22 \). This technique, coupled with finite size scaling analysis, produces the most reliable information about the extended or localized nature of the eigenstates. In this technique, one considers a bar of length \( N \) and cross section \( M \times M \). One determines the largest localization length \( \lambda_M \) as \( N \to \infty \) from the smallest Lyapunov coefficient of the product of the random transfer matrix relevant to Eq. (3). The nature of the eigenstate can be determined by studying the scaling property of the localization length of finite systems. For extended (localized) states, \( \lambda_M/M \) increases (decreases) with increasing \( M \). At the mobility edge, which separates the extended from the localized states, \( \lambda_M/M \) is independent of \( M \) and this behavior defines the Anderson transition.

In the paramagnetic phase, the direction of the local spin \( \vec{S}_i \) is chosen to be uniformly distributed on a sphere: \( P(\phi_i) = 1/(2\pi); P(\cos(\theta_i)) = 1/2 \). Once the spin configuration \( \{ \vec{S}_i \} \) is specified, the nearest neighbor hopping integrals can be obtained via Eq. (3). The random diagonal site-energy \( \epsilon_i \) is assumed to be distributed uniformly between \([-W/2, W/2]\). In our calculation, we have used systems with widths \( M = 4 - 14 \) and the length \( N \) on the order of \( N = 30,000 \) to minimize errors.

We first investigate the localization effects in the absence of any diagonal disorder, \( W = 0 \), to see whether random hoppings with Berry phases in the paramagnetic phase is alone sufficient to lead to localization of a large fraction of electrons, as has been argued in \( 14 \). Our results are presented in Fig. 1, in which we plot the ratio of the calculated finite size localization length \( \lambda_M \) with \( M \), as a function of \( M \) for different energies. It is clear that the mobility edge \( E_c \), where \( \lambda_M/M \) should be a constant independent of \( M \), is located between \( 3.55 < |E_c|/t < 3.6 \). To determine whether the Fermi level is below or above \( E_c \) at certain doping levels, we need to know the density of states (DOS) of the system, which we obtain by directly diagonalizing the Hamiltonian matrix for a finite size (10x10x10) cluster. The integrated DOS and the DOS, averaged over many (100) configurations, are shown in Fig. 2. This indicates that less than 0.5% of states are below \( E_c = -3.56t \) (Fig. 2), far less than the required 20-30% for the CMR system. Therefore, the present calculation confirms the suggestion \( 14 \) that purely off-diagonal disorder in the DE model is far from sufficient to localize electrons in the CMR materials at the 20-30% doping level. The inefficiency of the off-diagonal disorder can be understood by looking at the distributions of the amplitude of the hopping integral \( t_{ij} \), \( P(|t_{ij}|) = 2|t_{ij}|/t^2 \). This distribution has small weight for small \( |t_{ij}| \) which are most important for localization. The presence of the Berry phase, on the other hand, weakens further the localization effect by breaking the time-reversal symmetry \( 22 \). In fact the mobility edge without the Berry phase is located at \( |E_c| \approx 3.3t \). The inefficiency of the pure DE model to localize electrons clearly points towards the necessity to include other effects, such as JT electron-phonon coupling, electron-electron interaction effects, and diagonal substitutional disorders.

To investigate the effect of diagonal disorders, we have calculated \( \lambda_M \) for different values of \( W \) and \( E \), similar to the \( W=0 \) case, to determine the location of the mobility edge at fixed \( W \). The mobility edge trajectories in the \( W-E \) plane is shown as in Fig. 3. The shape of the mobility edge bears remarkable resemblance to the mobility edge trajectory in the Anderson model with diagonal disorder alone \( 22 \). The main difference is in the energy scale which is smaller in the present system due to the smaller average value of the hopping integrals. For the DE model, we obtain \( \langle |t_{ij}| \rangle = 0.6t \), leading to an effective band edge \( 22 \) at \( E_b = -4.0t \) at \( W=0 \). This reduction of band width also accounts for the smaller critical disorder \( W_c \) at the band center. The outward shift of the mobility edge for small \( W \) is due to the increase of the effective band width with \( W \). If \( E \) is normalized with the effective band width instead of \( t \), the region of extended states will always shrink with increasing disorder \( W \). In the same figure, we have also plotted the equal-integrated-DOS lines. Figure 3 shows that to achieve localization of 20-30% of
the electrons, the presence of a substantial amount of di-
gonal disorders \( W \), in the range of 10-12 in units of \( t \), is required.

The true mobility edge is controlled by the formation of localized polarons in systems with strong electron-
phonon couplings. The presence of disorder changes the character of the polaron formation in three dimensions. In
ordered systems, an abrupt change of the polaron state from nearly free type (large polaron) to self-trapped
type (small polaron) occurs as the electron-phonon coupling
reaches a critical value \[24\]. In disordered systems, however, localized polaron of intermediate sizes can form
from the nonuniform extended electronic states above the
mobility edge even with moderate coupling \[24\]. This
transition occurs at \( \xi \approx 10\lambda^{-2/3} \), where \( \lambda \) is the dimen-
sionless electron-phonon coupling constant. The true mo-
bility edge, obtained by using the coherent length \( \xi \) from
the finite size scaling analysis to be discussed below, is
indicated in Fig. 3, for \( \lambda = 0.03 \) and 1. For large val-
ues of coupling constant, \( \lambda >> 1 \), small polaron picture
prevails. Figure 2 and 3 are the principal results of this
work.

The presence of the Berry phase breaks time-reversal
symmetry, and hence the present model belongs to the
unitary universality class. The critical property around
the MIT is investigated using the one-parameter-scaling
procedure \[12\]. We have been successful (Fig. 4) in plac-
ing all our data on the same universal scaling curve,
\( \lambda_c / M = f(\xi / M) \), where \( \xi(W, E) \) is the scaling param-
eter corresponding to the infinite size localization and
correlation length in the localized and metallic regimes
respectively. Moreover, our scaling data fail on the scal-
ing function (shown as solid line in fig. 4) of the stan-
ard Anderson model with diagonal disorder alone. The
critical exponent \( \nu \) for the localization and correlation
lengths, \( \xi \sim |E - E_c|^{-\nu} \), is found to be \( \nu = 1.0 \pm 0.2 \), con-
sistent with the value for the standard Anderson model
\[12,27\]. Our result further supports previous conclusions
\[26,27\] that the critical property of the disorder-induced
MIT is not modified by broken time-reversal symmetry
in three dimensional systems.

In the Mn-oxides La\(_{1-x}\)A\(_{x}\)MnO\(_3\), the potential fluctuation
experienced by the \( e_g \) electrons due to the La\(^{3+}\) and
A\(^{2+}\) ion cores, if unscreened, would amount to \( U \sim 0.6 \)
eV. This is equivalent to \( W \approx 0.6[12x(1-x)]^{1/2} \) eV =
0.95 eV at \( x=0.3 \). Using Gutzwiller approximation \[3\] the
band narrowing from e-e interactions at \( V = 20t \) is esti-
mated to be around 0.5 for \( x = 0.2 \) and 0.6 for \( x = 0.3 \), if
the two orbitals are degenerate. Hence \( W / t_{\text{eff}} \) can be as
large as 13, if we assume \( t=0.15 \) eV. Screening certainly
will reduce this value, so our estimate is only meant to
stress the importance of disorder in MIT in Mn-oxides.

We feel that disorder in CMR materials is not strong
eough to induce localization by itself, but its sizable
presence can certainly modify small polaron formation
picture \[14\] for systems with strong but less than criti-
cal value of electron-phonon coupling. This mechanism
also has the advantage of not restricting to any particular
form of electron-phonon coupling, and thus may apply to
a wide range of CMR materials described by the double
exchange mechanism.

In summary, we have investigated the charge local-
ization properties in the Mn-oxides in the classical spin
limit. We find that a substantial amount of diagonal dis-
order is required to localize 20-30% of electronic states.
This suggests that large electron-phonon coupling and
polaronic effect are necessary to explain the MIT close
to \( T_c \).

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FIG. 1. The ratio of the finite size localization length to the width, \( \lambda_M/M \), as a function of M, for the double exchange model in the absence of any diagonal disorders. The mobility edge is located around \( E_c = -3.56t \). All states with \( E < E_c \) are localized.

FIG. 2. The integrated density of states of the double exchange model in the absence of any diagonal disorder, \( W = 0 \). The density of states (in units of \( t^{-1} \)) is shown in the inset. The results are obtained from exact diagonalization of \( 10 \times 10 \times 10 \) clusters averaged over 100 random spin configurations.

FIG. 3. The mobility edge trajectory of the double exchange model with diagonal disorder W for electron-phonon coupling constant \( \lambda = 0, 0.03, \) and 1. The dashed lines show equal integrated density of states lines at 10%, 20%, 30%, and 40% fractions. The density of states and the mobility edge trajectory are symmetric around \( E = 0 \) axis.
