Charge localization in disordered colossal-magnetoresistance manganites

Qiming Li
Ames Laboratory–U.S. Department of Energy and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011

Jun Zang and A. R. Bishop
Theoretical Division and Center for Nonlinear Studies, Los Alamos National Laboratory, MS B262, Los Alamos, New Mexico 87545

C. M. Soukoulis
Ames Laboratory–U.S. Department of Energy and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011

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The metallic or insulating nature of the paramagnetic phase of the colossal-magnetoresistance manganites is investigated via a double-exchange Hamiltonian with diagonal disorder. The 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 bandwidth is reduced by random hoppings and electron-electron interactions. [S0163-1829(97)04832-7]

The recent discovery of colossal magnetoresistance[1] (CMR) in Mn oxides $La_{1-x}A_xMnO_3$ (where A can be Ca, Sr, or Ba) has generated extensive interest in these perovskites. The essential correlation between the magnetization and resistivity[2] in these compounds was well explained by the double-exchange (DE) mechanism.[3] However, the precise nature of the ferromagnetic metal to the paramagnetic insulator transition is still not well understood. Recently, Millis *et al.*[4] argued that Jahn-Teller (JT) effects[5] have to be included to explain the observed resistivity behavior and the magnetic transition temperature. It was then proposed[6,7] that the metal-insulator transition (MIT) is a consequence of the large to small polaron transition, induced by the reduction of effective hopping integrals at temperatures near T_c. However, there are competing proposals[8,9] that advocate that the DE mechanism alone can explain the magnetic properties and MIT in Mn oxides. Notably, Varma[9] argued that random hopping in the paramagnetic phase due to the DE mechanism is sufficient to localize electrons and induce a MIT at T_c. Although there is mounting experimental evidence of lattice effects[10] and small polaron dynamics above T_c,[11] it is still not clear at present whether the small polaron formation for temperatures close to T_c is the driving force of the MIT or merely a consequence of the MIT from the DE mechanism itself. To investigate the origin of the MIT, a precise calculation of the localization effects in the DE model is needed. In this paper we study the localization properties in the DE model using the well-developed transfer-matrix method.[12]

The DE mechanism can be described by the Hamiltonian

$$H=\sum_{\langle ij\rangle}(t_{ij}^{\gamma\gamma'}c_{i\gamma\sigma}^{\dagger}c_{j\gamma'\sigma}+\text{H.c.})+\sum_i(\epsilon_{i\gamma}-\mu)n_{i\gamma}$$
$$-J_H\sum_i\vec{\sigma}_{i\gamma}\cdot\vec{S}_i+V\sum_i n_{ia}n_{ib}, \tag{1}$$

where $\vec{\sigma}_{i\gamma}$ 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 $c_{i\gamma\sigma}$ ($c_{i\gamma\sigma}^{\dagger}$) annihilate (create) a mobile e_g electron with spin σ at orbital γ ($\gamma\in\{a,b\}$). $n_{i\gamma}=c_{i\gamma\sigma}^{\dagger}c_{i\gamma\sigma}$. The random diagonal energy $\epsilon_{i\gamma}$ is included to account for substitutional disorders.[13] The J_H term describes the Hund rule coupling between the local spin of t_{2g} electrons and the e_g 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 intraorbital e-e interactions and exchange interactions, which is reasonable in the large-J_H limit.

We consider only the limit $SJ_H/t\to\infty$. 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 rule coupling interaction can be dropped and the hopping term is renormalized to

$$t_{ij}^{\gamma\gamma'}=t^{\gamma\gamma'}\left[\cos\left(\frac{\theta_i}{2}\right)\cos\left(\frac{\theta_j}{2}\right)+\sin\left(\frac{\theta_i}{2}\right)\sin\left(\frac{\theta_j}{2}\right)e^{i(\phi_i-\phi_j)}\right] \tag{2}$$

in the classical spin limit $S=\infty$, where (θ_i,ϕ_i) are the polar angles of the classical spin at site i. Both finite J_H and S will decrease the localization effect, while the interorbital 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 (1) is then ''transformed'' to an effective (two-orbital) single-electron Hamiltonian. The localization properties of the simplified two-orbital Hamiltonian can be investigated via the transfer-matrix method. Without e-e interaction, the localization properties in a two-orbital model are similar to those in a one-orbital model. Thus we will investigate the Hamiltonian with only *one* effective orbital:

$$H=\sum_i (\epsilon_i-\mu)n_i+\sum_{<ij>}(t_{ij}c_i^\dagger c_j+\text{H.c.}). \qquad (3)$$

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 e_g-degeneracy splitting is not well understood in the metallic region at present. The Hamiltonian (3) 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.

In the simplified Hamiltonian (3), 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 approximation.[4] Localization via off-diagonal disorder has not been studied extensively. A few calculations[15] have been made for uniform distributions of real hopping integrals t in one- and two-dimensional (2D) systems. Also there are studies on 2D random flux systems with uniform $|t|$.[16] The most relevant work for the present model was a study by Economou and Antoniou[17] for systems with a semicircular distribution of hopping integrals. Their work was based on the localization criteria of Licciardello and Economou.[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 phases[9,21] [the phases of t_{ij} in Eq. (2)] are not included and their importance is difficult to assess.

Here we investigate the localization properties of the Hamiltonian (3) with the transfer-matrix method.[12] This technique, coupled with a 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 λ_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, λ_M/M increases (decreases) with increasing M. At the mobility edge, which separates the extended from the localized states, λ_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. (2). The random diagonal site energy ϵ_i is assumed to be distributed uniformly between $-W/2$ and $W/2$. 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 Ref. 9. Our results are presented

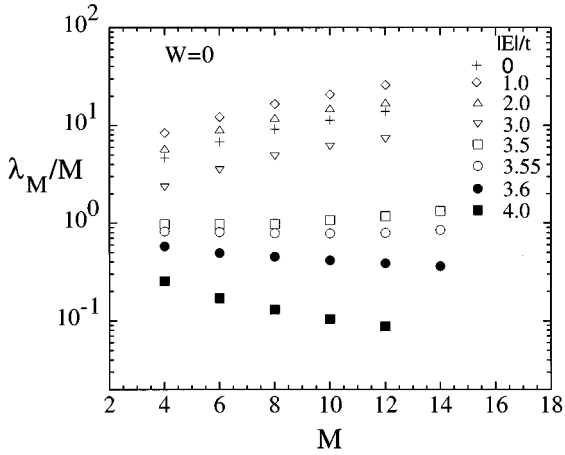

FIG. 1. Ratio of the finite-size localization length to the width λ_M/M as a function of M for the double-exchange model in the absence of any diagonal disorder. The mobility edge is located around $E_c=-3.56t$. All states with $E<E_c$ are localized.

in Fig. 1, in which we plot the ratio of the calculated finite-size localization length λ_M with M, as a function of M for different energies. It is clear that the mobility edge E_c, where λ_M/M should be a constant independent of M, is located in the region $3.55<|E_c|/t<3.6$. 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 $(10\times10\times10)$ 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 the 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[6] 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}, $P(|t_{ij}|)=$

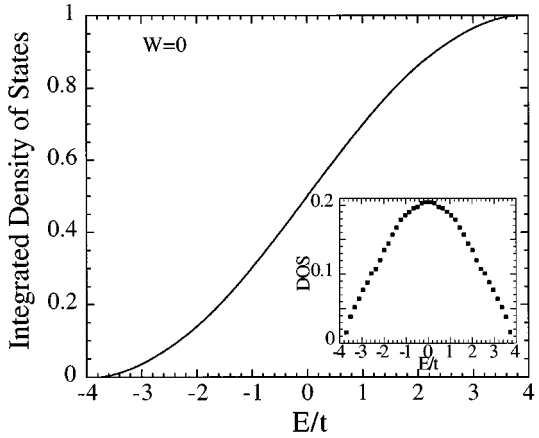

FIG. 2. Integrated density of states of the double-exchange model in the absence of any diagonal disorder $W=0$. The density of states (in units of t^{-1}) is shown in the inset. The results are obtained from exact diagonalization of $10\times10\times10$ clusters averaged over 100 random spin configurations.

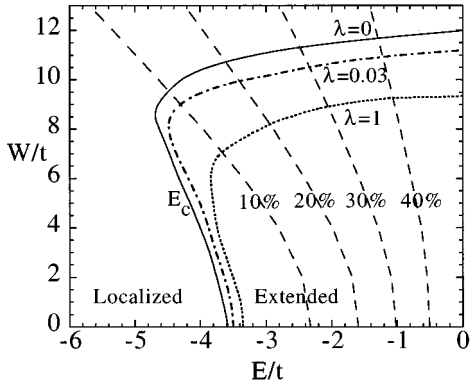

FIG. 3. Mobility edge trajectory of the double-exchange model with diagonal disorder W for electron-phonon coupling constant $\lambda=0$, 0.03, and 1. The dashed lines show equal integrated density of states lines at 10%, 20%, 30%, and 40% fractions. The density of states and the mobility edge trajectory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

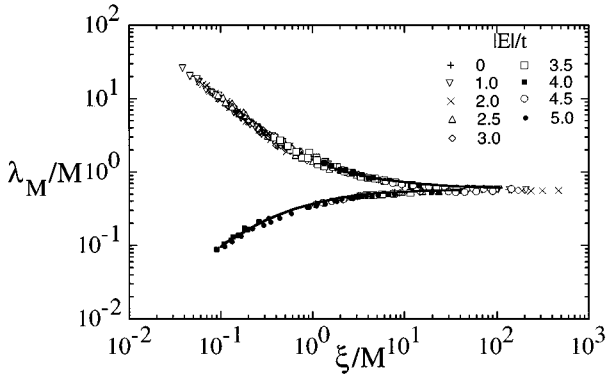

FIG. 4. Universal scaling function of the double-exchange model for different W, E, and M. At the critical point, $\lambda_M/M\approx 0.6$. The solid line is the universal scaling curve for the standard Anderson model with diagonal disorder alone.

$2|t_{ij}|/t^2$. 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, further weakens 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 disorder.

To investigate the effect of diagonal disorder, we have calculated λ_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 are shown in Fig. 3. The shape of the mobility edge bears a remarkable resemblance to the mobility edge trajectory in the Anderson model with diagonal disorder alone.[23] 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 $\langle|t_{ij}|\rangle=\frac{2}{3}t$, leading to an effective band edge[24] at $E_b=-4.0t$ at $W=0$. This reduction of bandwidth 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 bandwidth with W. If E is normalized with the effective bandwidth 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 diagonal disorders W, in the range 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 coupling. 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 the nearly free type (large polaron) to the self-trapped type (small polaron) occurs as the electron-phonon coupling reaches a critical value.[25] In disordered systems, however, localized polarons of intermediate sizes can form from the nonuniform extended electronic states above the mobility edge even with moderate coupling.[26] This transition occurs at $\xi\approx 10\lambda^{-2/3}$, where λ is the dimensionless electron-phonon coupling constant. The true mobility edge, obtained by using the coherent length ξ from the finite-size scaling analysis to be discussed below, is indicated in Fig. 3 for $\lambda=0.03$ and 1. For large values of coupling constant $\lambda\gg 1$ the small polaron picture prevails. Figures 2 and 3 are the principal results of our 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 placing all our data on the same universal scaling curve $\lambda_m/M=f(\xi/M)$, where $\xi(W,E)$ is the scaling parameter corresponding to the infinite-size localization and correlation length in the localized and metallic regimes, respectively. Moreover, our scaling data fall on the scaling function (shown as a solid line in Fig. 4) of the standard Anderson model with diagonal disorder alone. The critical exponent ν for the localization and correlation lengths $\xi\sim|E-E_c|^{-\nu}$ is found to be $\nu=1.0\pm 0.2$, consistent with the value for the standard Anderson model.[12] Our results indicate that the differences in the scaling functions, as well as critical exponents between systems with and without time-reversal symmetry in three dimensions, is much more difficult to find than in two dimensions, as noted[27,28] previously. The critical behavior of model (3) is interesting on its own merit and will be investigated in the future.

In Mn oxides $La_{1-x}A_xMnO_3$ 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 the Gutzwiller approximation[7] the band narrowing from e-e interactions at $V=20t$ is estimated 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_{eff} can be as large as 13 if we assume that $t=0.15$ eV. Screening certainly will reduce this value, so our estimate is only meant to stress the importance of disorder on the MIT in Mn oxides. We feel that disorder in CMR materials is not strong enough to induce localization by itself, but its sizable presence can certainly modify the small polaron formation picture[6,7] for systems with a strong but less than

critical value of electron-phonon coupling. This mechanism also has the advantage of not being restricted 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 localization properties in Mn oxides in the classical spin limit using the simplified Hamiltonian (3). In our numerical calculations, we have neglected the effects of the electron-electron interaction, electron-phonon couplings, quantum fluctuation of spins ($S=3/2$), and finite Hund rule coupling. The first two will substantially enhance the electron localization, while the last two will delocalize electrons. Even taking into account the band narrowing effect due to e-e interactions in the Gutzwiller approximation, we find that a substantial amount of diagonal disorder is required to localize 20–30 % of electronic states. This suggests that a large electron-phonon coupling and polaronic effects are necessary to explain the MIT close to T_c.

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