

Theory of Colossal Magnetoresistance in $R_{1-x}A_x\text{MnO}_3$

L. Sheng,¹ D. Y. Xing,^{1,2} D. N. Sheng,¹ and C. S. Ting¹

¹*Department of Physics and Texas Center for Superconductivity, University of Houston, Houston, Texas 77204*

²*National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China*

(Received 22 April 1997)

A localization model comprising spin disorder and nonmagnetic randomness is presented to account for novel magnetotransport properties in Mn oxides $R_{1-x}A_x\text{MnO}_3$. Localization length of electrons as a function of magnetization is determined by means of the transfer matrix method. Including the Coulomb interaction between electrons, the variable-range hopping resistivity is calculated as a function of temperature and magnetic field. The resulting sharp resistivity peak near the Curie temperature and, in particular, the magnitude of the colossal negative magnetoresistance are in good agreement with experimental measurements. [S0031-9007(97)03932-X]

PACS numbers: 72.10.Bg, 71.30.+h, 72.15.Gd

In recent years, there has been much interest in the magnetic compounds $R_{1-x}A_x\text{MnO}_3$ ($R = \text{La, Nd, Pr}$ and $A = \text{Ca, Sr, Ba, Pb}$) with a $\text{Mn}^{3+}/\text{Mn}^{4+}$ mixed valence. In the doping range $0.2 < x < 0.5$, these manganites undergo a paramagnetic (PM) insulator to ferromagnetic (FM) metal phase transition upon cooling, leading to a sharp resistivity peak near the Curie temperature T_C . An applied magnetic field can drive the transition point and the accompanied resistivity peak to higher temperatures, thereby producing a negative magnetoresistance. The magnetoresistance in the Mn oxides is usually termed as the colossal magnetoresistance or CMR, because the magnitude of the relative magnetoresistance can be extraordinarily large (99% or more) [1–16].

The basis for the theoretical understanding of the Mn oxides is usually the notion of double exchange (DE) [17], which considers the exchange of electrons between neighboring Mn^{3+} and Mn^{4+} sites with strong on-site Hund's coupling. Attempts based on mean-field treatments of a Kondo lattice model for DE [18] and a Hubbard-Kondo lattice model [19] have been made to account for the transport properties in the Mn oxides. However, the sharp change in the resistivity near T_C and the CMR were not reproduced successfully in these works. Perturbative calculation carried out by the authors of Ref. [20] showed that DE alone could not explain the experimental data of the Mn oxides, and suggested that a strong Jahn-Teller distortion should be responsible for the transport properties. Despite some efforts [21–23] that have included the strong Jahn-Teller type interaction between electrons and lattice, this theory still needs to be refined to account for the large magnetoresistance observed in experiments. Contrary to the above approaches, it was suggested [24,25] later that the localization effect in the DE model based upon nonperturbative treatments might be able to account for the novel properties of the Mn oxides. However, recent numerical studies [26,27] on this problem using the one-parameter scaling theory [28] indicate that the DE model alone would not be able to explain the experiments. Further investigation on the underlying mechanism of the metal-insulator (M-I)

transition and the associated CMR effect in the Mn oxides is thus urgently needed.

In this Letter, we make an effort to investigate the magnetotransport properties of the Mn oxides by considering the electronic localization effect. The Mn oxides are modeled as systems with both DE off-diagonal disorder [24,25] and nonmagnetic diagonal disorder. By using the scaling theory and assuming a mean-field distribution for the spin orientation, the localization length of electrons can be evaluated as a function of the magnetization. The resistivity in the variable-range hopping regime is then calculated as a function of temperature for different values of applied magnetic field. Suitable strength of nonmagnetic disorder is found to be a prerequisite for the occurrence of a sharp resistivity peak and a large magnetoresistance. We show that our theoretical results reproduce the main features of the experimental observations. In particular, the magnitude of relative magnetoresistance obtained is quantitatively comparable with experimental data.

In the Mn oxides, two features aside from the known spin disorder might be important for electronic localization. Substitution of R^{3+} with A^{2+} may lead to a local potential fluctuation. A rough estimation [9] shows that this potential fluctuation may be comparable with the width of the conduction (e_{2g}) band. The other is the lattice distortion around A^{2+} and R^{3+} due to their different ionic sizes. These two effects can give rise to a rather strong nonmagnetic electron-impurity scattering potential. Based on these considerations, we propose the following Hamiltonian to describe the transport behavior of the e_g electrons in the Mn oxides:

$$H_{e_g} = - \sum_{ij} \tilde{t}_{ij} d_i^\dagger d_j + \sum_i \varepsilon_i d_i^\dagger d_i. \quad (1)$$

Here the first term is the effective DE Hamiltonian [24] in which $\tilde{t}_{ij} = t\{\cos(\theta_i/2)\cos(\theta_j/2) + \sin(\theta_i/2) \times \sin(\theta_j/2)\exp[i(\varphi_i - \varphi_j)]\}$ with t the hopping integral in the absence of Hund's coupling and the polar angles (θ_i, φ_i) characterizing the orientation of local spin \mathbf{S}_i .

For simplicity, we assume all the nonmagnetic scattering or randomness to be included effectively in the diagonal-disorder term in Hamiltonian (1), where ε_i stand for random on-site energies distributed within the range $[-W/2, W/2]$. The localization problem in Hamiltonian (1) for the FM state with saturated magnetization M_s and the PM state with $M = 0$ has been solved [27] by using the one-parameter scaling theory [28]. From the phase diagram obtained in the W - E plane with E the single-electron energy, it is found [27] that, in the presence of a suitable diagonal disorder, the system will undergo a M-I transition as the magnetization is decreased from $M = M_s$ to $M = 0$ on warming. The necessary strength of diagonal disorder measured by W for the occurrence of such a transition is estimated [27] to fall into the range $12t < W < 16.5t$ for $0.2 < x < 0.5$, which also yields the observed dirty-metal-like residual resistivities in the Mn oxides. In this Letter, we focus our attention on the close correlation between the M-I transition and the magnetotransport properties.

To investigate the M -dependent localization effect in the range of $0 \leq M \leq M_s$, the distribution of the orientations of the localized spins is assumed to be Boltzmann-Maxwell-like [18]

$$f(\theta) = C \exp\left(-\frac{2\mu_B S_{\text{eff}} \mathcal{H} \cos \theta}{k_B T}\right), \quad (2)$$

where μ_B is the Bohr magneton, $S_{\text{eff}} = 3/2 + (1 - x)/2$ is the effective spin on a Mn site, and \mathcal{H} is the sum of the applied magnetic field and the molecular field. Using the scaling approach [28] together with Eqs. (1) and (2), we evaluate the scaling parameter ξ at the Fermi level E_F as a function of \mathcal{H}/T for $x = 0.3$ and $W = 13t$. For a given value of \mathcal{H}/T , the normalized magnetization is easily calculated by $M/M_s = \langle \cos \theta \rangle$. As a result, we obtain the ξ vs M/M_s curve as shown in Fig. 1. It can be seen that ξ divergences around $M = M_0 \approx 0.4M_s$, indicating that the system undergoes a M-I transition at $M = M_0$. It is interesting to note that such a M-I transition occurs at $M = M_0$ rather than $M = 0$. In the small magnetization

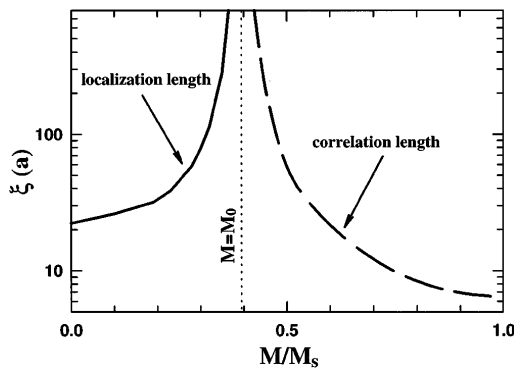


FIG. 1. Scaling parameter ξ in the unit of lattice constant a as a function of M/M_s at the Fermi surface for $x = 0.3$ and $W = 13t$.

region $M < M_0$, electrons at E_F are localized and ξ is the localization length. In the large magnetization region $M > M_0$, electrons at E_F are delocalized and ξ stands for the correlation length of electrons, which can be related to the residual resistivity of the system at low temperature [28].

In order to study the temperature behavior of the resistivity, we determine M and ξ as functions of temperature by using the mean-field approximation

$$\mathcal{H} = H + \gamma M/M_s, \quad (3)$$

where γ is a parameter independent of the temperature T and applied magnetic field H . From T_C formula in the mean-field theory, the value of γ can be determined by $\gamma = 3k_B T_C / (2\mu_B S_{\text{eff}})$ if T_C is assumed to be known. Let us first consider the case of $H = 0$. $M/M_s = \langle \cos \theta \rangle$ is readily determined as a function of T from Eqs. (2) and (3), which is plotted in Fig. 2 with T_C taken to be 200 K. The ξ vs M/M_s relation obtained above is then transformed into a ξ vs T relation as given in Fig. 2. The critical temperature T_{MI} , at which $M = M_0$, corresponds to the M-I transition point. Usually, T_{MI} is not identical to T_C . For $T > T_{\text{MI}}$, the electrons at the Fermi surface are localized, and the variable-range hopping dominates the transport.

It is believed [29] that when electrons at the Fermi level E_F become localized, a depression or Coulomb gap should appear in the density of states at E_F as a result of electron-electron interactions. Varma [25] recently pointed out that this feature might have an important effect on the hopping conduction of electrons in the Mn oxides. Indeed, if the Coulomb interactions among electrons are neglected, the variable-range hopping resistivity obeys the $\exp[(T_0/T)^{1/4}]$ Mott's law, as observed in most of the semiconductors where the electron densities are very low. In the present Mn oxides with high electron density, the localization length ($\xi \approx 20a$) is comparably long as shown in Fig. 1, but the localization length needed to fit experiments by using the Mott's law has been found to be unrealistically short ($\xi \approx 1 \text{ \AA}$) [9,13]. Under this

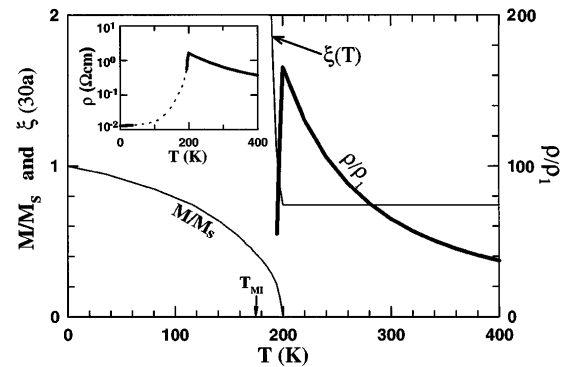


FIG. 2. Normalized magnetization M/M_s , localization length ξ in the unit of $30a$, and hopping resistivity ρ/ρ_1 as functions of temperature T in the absence of magnetic field for $x = 0.3$ and $W = 13t$. Inset illustrates the full resistivity curve where ρ_1 is taken to be $\rho_1 = 10^{-2} \Omega \text{ cm}$.

situation, we have to take the electron-electron interaction into consideration. So far there exists no self-consistent transport theory for interacting electrons in the localized regime. In the following we shall adopt the approximate method of Shklovskii and Efros [29] to treat this problem. In the presence of the Coulomb interactions, the resistivity due to variable-range hopping in the localization regime takes the following form [25,29]:

$$\rho(T) = \rho_1 \exp\left[\left(\frac{T_1}{T}\right)^{1/2}\right], \quad (4)$$

with $T_1 = 2.8e^2/(4\pi k_B \epsilon_0 \xi)$. Here, ξ is [29] the localization length in the absence of Coulomb interactions, and ρ_1 has negligible weak dependence on T and ξ . The background dielectric constant κ has been taken to be $\kappa = 1$, similar to that in the jellium model for simple metals, by considering the high-density nature of electrons in the Mn oxides.

Using the localization length $\xi(T)$ obtained above, the resistivity $\rho(T)$ is calculated and also shown in Fig. 2, in which the lattice constant is taken to be $a = 4 \text{ \AA}$, a typical value for the Mn oxides. Noting that $T_1 \propto 1/\xi$, we see from Eq. (4) that the resistivity exhibits a peak when the product of ξ and T reaches minimum. In Fig. 2 the resistivity peak is found at T_C , since just below T_C the localization length ξ increases rapidly and $\xi(T)T$ has its minimum at T_C . The resistivity drops sharply as the temperature decreases below T_C , which can be attributed to the rapid decrease of spin disorder. The full resistivity curve between 0 and 400 K is plotted in the inset, where the solid parts are our calculated results and the resistivity in the low-temperature metallic phase is calculated from the Landauer formula [28] $\rho = (2h/e^2)\xi$ by neglecting the inelastic scattering. The dotted part is difficult to be determined since the full information of the inelastic scattering is lacking.

Next we turn to study the magnetoresistance effect. Using a similar calculation, we obtain $M(T)$ and $\rho(T)$ in the presence of applied magnetic field. The M vs T curves for different values of magnetic field are shown as dotted lines in Fig. 3(a), and the corresponding resistivities in the localization region are given by solid lines. We see that the applied magnetic field lowers the resistivity peak and drives it to higher temperatures, which is consistent with most experimental measurements [1,2,8,12]. Define the magnitude of relative magnetoresistance as

$$\frac{\Delta\rho}{\rho} = \frac{\rho(T, 0) - \rho(T, H)}{\rho(T, 0)}. \quad (5)$$

In the present definition, $\Delta\rho/\rho$ cannot exceed 100%. $\Delta\rho/\rho$ as a function of temperature for several values of applied magnetic field is given in Fig. 3(b). With decreasing temperature, the CMR increases to a maximum near T_C and then decreases. This behavior is in good agreement with most experimental results, e.g., Fig. 2 in Ref. [8]. Moreover, the maximum magnetoresistance

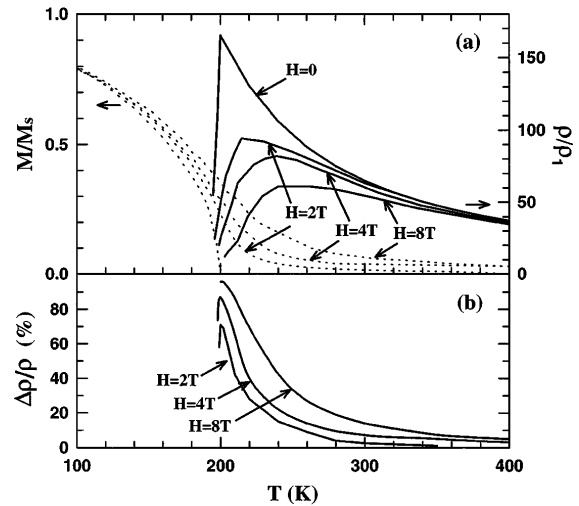


FIG. 3. (a) Magnetization, hopping resistivity, and (b) magnitude of magnetoresistance as functions of temperature for several values of applied magnetic fields.

obtained here, $\Delta\rho/\rho \approx 70\%$, 90% , and 97% for $H = 2, 4,$ and 8 T, respectively, is quantitatively comparable to the experimental data (see Ref. [12], for example).

We now turn to consider the effect of the nonmagnetic randomness on the CMR. The normalized resistivity $\rho(H)/\rho(0) = 1 - \Delta\rho/\rho$ as a function of the applied magnetic field at $T = T_C (= 200 \text{ K})$ is shown in Fig. 4 for several values of diagonal-disorder strength. The curves for $W = 13t$ and $15t$ are calculated by using Eq. (4) (the critical magnetization for the latter case being found to be $M_0 \approx 0.7M_s$). These theoretical results resemble the resistivity vs magnetic field behavior observed in the Mn oxides, e.g., Fig. 1 in Ref. [16]. In the weak disorder limit ($W \rightarrow 0$), where the localization effect is found to be negligible [26,27] and a perturbative theory is adequate, we have $\rho \propto [1 - A(M/M_s)^2]$ with A being of the order of unity [18,19], which yields much smaller magnetoresistance ($\Delta\rho/\rho \approx 10\%$ for $H = 6$ T) as shown in Fig. 4. Among the three values of W considered here, $W = 13t$ gives the largest relative magnetoresistance $\Delta\rho/\rho$, indicating that a suitable nonmagnetic disorder is necessary for the occurrence of a large $\Delta\rho/\rho$, but too strong or too weak nonmagnetic disorder disfavors CMR.

We wish to stress the importance of the FM-PM and M-I transitions to the CMR effect. An applied magnetic field changes the magnetization and hence the spin disorder, leading to a CMR. The changing rate of the resistivity due to an applied magnetic field is given by

$$\left(\frac{\delta\rho}{\delta H}\right)_T = \chi(T) \left(\frac{\delta\rho}{\delta M}\right)_T, \quad (6)$$

whose integral over H yields the total magnetoresistance response $\rho(H) - \rho(0)$ to a finite magnetic field. It is well known that the magnetic susceptibility $\chi(T) = (\delta M/\delta H)_T$ has its maximum at $T = T_C$. The other factor $(\delta\rho/\delta M)_T$ on the right-hand side of Eq. (6) is

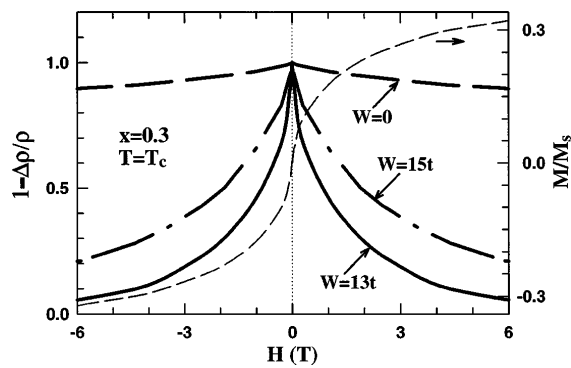


FIG. 4. Normalized resistivity and magnetization as functions of magnetic field for several values of nonmagnetic disorder strength.

always negative and, as a function of M , has its maximum absolute value near $M = M_0$ where the M-I transition occurs. For $M < M_0$, the system is in the insulator phase with high resistivity, while for $M > M_0$ the system is in the metallic state with low resistivity, so it is expected that the resistivity has a rapid change with changing M near $M = M_0$. If the two transition temperatures T_{MI} and T_C are close enough, Eq. (6) can be largely enhanced and one will observe a large magnetoresistance in the vicinities of these transition points. In essence, the CMR effect is closely correlated to the critical behavior of the two phase transitions, from which it follows that extremely strong or weak nonmagnetic randomness disfavors the CMR effect. Therefore, a possible way for enhancing the CMR is to tune the strength of nonmagnetic disorder in the system so that the M-I transition could occur and be close to T_C ; the residual resistivity corresponding to the optimum strength of nonmagnetic randomness ($W \approx 12t$) is estimated to be of several mΩ cm.

In summary, we have shown that the novel magneto-transport phenomena in the Mn oxides can be understood systematically by considering the electronic localization effect due to DE spin disorder and nonmagnetic randomness. An important effect of the nonmagnetic disorder on the CMR, which was omitted previously, has been studied. The theoretical results including the sharp peak in the ρ vs T curve and the CMR effect are well consistent with experimental data.

This work is supported by the Texas Center for superconductivity at the University of Houston, and by the Robert A. Welch foundation. D. Y. X. is also supported by the National Natural Science Foundation of China.

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