

## Metal-insulator transition in colossal magnetoresistance materials

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We report on resistivity measurements in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  thin films in order to elucidate the underlying mechanism for the colossal magnetoresistance behavior. The experimental results are analyzed in terms of quantum phase-transition ideas to study the nature of the metal-insulator transition in manganese oxides. Resistivity curves as functions of magnetization for various temperatures show the absence of scaling behavior expected in a continuous quantum phase transition, which leads us to conclude that the observed metal-insulator transition is most likely a finite temperature crossover phenomenon.

The mixed-valence perovskite manganese oxides  $R_{1-x}A_x\text{MnO}_3$  (where  $R = \text{La, Nd, Pr}$ , and  $A = \text{Ca, Sr, Ba, Pb}$ ) have been the materials of intense experimental and theoretical studies over the past few years.<sup>1,2</sup> These materials show colossal magnetoresistance (CMR) in samples with  $0.2 < x < 0.5$ . In such a doping region, the resistivity exhibits a peak at a temperature  $T = T_p$ . The system is metallic ( $d\rho/dT > 0$ ) below  $T_p$  and is insulating ( $d\rho/dT < 0$ ) above  $T_p$ . Under an external magnetic field  $B$ ,  $\rho$  is strongly suppressed and the peak position  $T_p$  shifts to a higher temperature. Thus, a huge magnetoresistance may be produced around  $T_p$  to give rise to the CMR phenomenon. It is widely believed that the CMR behavior in these mixed-valence oxides is closely related to their magnetic properties. This is supported by the fact that  $T_p$  is very close to the Curie temperature  $T_c$ , the transition temperature from the ferromagnetic to the paramagnetic phase.

Despite intensive investigations of the CMR phenomenon, the nature of the metal-insulator ( $M-I$ ) transition remains an open question. The manganese oxides are usually modeled by the double-exchange Hamiltonian,<sup>3-5</sup> which describes the exchange of electrons between neighboring  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions with strong on-site Hund's coupling. As pointed out by Millis *et al.*,<sup>6</sup> however, the double-exchange model alone does not explain the sharp change in the resistivity near  $T_c$  and the associated CMR phenomenon. Based on the strong electron-phonon coupling in these materials, Millis *et al.*<sup>6</sup> proposed that the  $M-I$  transition involves a crossover from a high- $T$  polaron dominated magnetically disordered regime to a low- $T$  metallic magnetically ordered regime. On the other hand, some authors have argued the possible importance of the quantum localization effect (caused presumably by the strong magnetic disorder fluctuations in the system around and above the magnetic transition), and proposed that the  $M-I$  transition in the CMR materials is the Anderson localization transition—a quantum phase transition<sup>7-9</sup> driven by magnetic disorder. It will be interesting to examine the consequences of these Anderson localization theories against experimental results.

In this paper, we report resistivity measurements in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  thin films, and analyze the results to compare with the scaling behavior expected from an Anderson localization transition. Assuming the  $M-I$  transition in manganese oxides is of Anderson lo-

calization type, the resistivity curves as functions of magnetization (or more precisely the magnetic moment correlation of the neighboring Mn ions) for different temperatures should cross at a single point and show scaling behavior associated with quantum criticality. Our experimental results, however, clearly demonstrate the absence of this scaling behavior. We conclude that the Anderson localization is not the cause of the  $M-I$  transition in the CMR materials.

We start with a brief review of a well-known case, which exhibits the scaling properties of the Anderson localization transition, namely, the  $M-I$  transition in thin Bi films.<sup>10</sup> In this case the disorder effect is solely controlled by the thickness of the thin films,  $d$ . One of the most basic scaling properties is the existence of a critical value of the film thickness  $d_c$ , and a critical value of the resistivity  $\rho_c$ . The resistivity is metallic for  $d > d_c$ , and insulating for  $d < d_c$ . Scaling laws are established for physical quantities with parameters near these critical values. Absence of these critical values would imply the absence of scaling behavior, incompatible with the theory of the Anderson transition, which is a continuous quantum phase transition manifesting scaling behavior.

If we assume the  $M-I$  transition in manganese oxides to be an Anderson localization, the question then naturally arises about what would be the physical quantity or the tuning parameter that corresponds to the layer thickness in the Bi thin films describing the disorder strength. We believe that the tuning parameter in the CMR  $M-I$  transition should be the magnetization of the system. To make the discussion more concrete, let us consider a model discussed in Ref. 9 to describe the possible Anderson transition in Mn oxides,

$$H_{eff} = - \sum_{ij} t'_{ij} d_i^+ d_j + \sum_i \epsilon_i d_i^+ d_i + \text{c.c.} \quad (1)$$

Here, the first term is the effective double-exchange Hamiltonian in which  $t'_{ij} = t \{ \cos(\theta_i/2) \cos(\theta_j/2) + \sin(\theta_i/2) \sin(\theta_j/2) \exp[i(\phi_i - \phi_j)] \}$ , with  $t$  the hopping integral in the absence of the Hund's coupling and the polar angles  $(\theta_i, \phi_i)$  characterizing the orientation of local spin  $\vec{S}_i$ . The second term in Eq. (1) represents an effective on-site disorder Hamiltonian (which should lead to the  $M-I$  Anderson transition in this model), which includes all possible diagonal disorder terms in the system, such as the local potential fluctuations due to the substitution of  $R^{3+}$  with  $A^{2+}$ . Here  $\epsilon_i$

stands for random on-site energies distributed within the range  $[-W/2, W/2]$ . For a given sample, the diagonal disorder, namely,  $\{\epsilon_{ij}\}$ , or  $W$ , is fixed, but the bandwidth is controlled by the double-exchange hopping integral. Therefore, the effective strength of the disorder is determined by  $t'$ . Experimentally the disorder strength may be tuned by introducing an external magnetic field  $B$  and/or by changing the temperature  $T$ . For instance, as  $B$  increases, the magnetic ions tend to align along the same direction so that the magnitude of  $t'$ , hence, the bandwidth, increases. As  $T$  is lowered below  $T_c$ , there is spontaneous magnetization, which can also increase the bandwidth to reduce the disorder strength. Note that the role of temperature in this localization model is somewhat indirect in the sense that it only controls the disorder strength—the usual role of finite temperature in quantum phase transition is the introduction of a dynamical exponent  $z$  that would not play an explicit role in the discussion and analysis of the experimental data presented in this paper.

The hopping integral  $\langle t'_{ij} \rangle$  in the double-exchange model depends on the magnetic-moment correlation between the neighboring Mn ions,  $\chi = \langle \vec{M}_i \cdot \vec{M}_j \rangle$ , where  $\langle \dots \rangle$  denotes the thermal average.  $\chi$  can be divided into a static part and a fluctuation part,  $\chi = M^2 - \Delta M^2$ , where  $M$  is the magnetization, which can be measured directly, and  $\Delta M^2 = \chi - M^2 \geq 0$  for ferromagnetic interacting systems including the present case. Sufficiently away from the magnetic transition point ( $T = T_c$  and magnetic field  $B = 0$ ), the fluctuation part can be dropped, and the bandwidth is controlled by the magnetization. In what follows, we first neglect the fluctuation effect, and focus on the static part to discuss the scaling behavior. This approximation is equivalent to the mean-field approximation made in Ref. 9. The fluctuation effect does not alter our qualitative conclusion.

The effect of off-diagonal disorder (arising, for example, from a random  $t'$ ) was previously discussed by Varma for the paramagnetic phase.<sup>7</sup> In that work, the core-spin fluctuation was treated in the adiabatic approximation and the primary effect of the magnetic field was argued to alter the localization length. A more detailed calculation by Li *et al.*,<sup>11</sup> including both random hopping and on-site disorder, showed that random hopping alone is not sufficient to induce Anderson localization at the Fermi level relevant to the observed CMR phenomenon. We believe the main effect of the magnetic field in the high field limit is to partially polarize the electron spins, thus to increase the electron bandwidth. Our analyses should apply to the experimental situation reported in this paper, where the magnetization is as high as a fraction of the saturated value.

Similar to the layer thickness in the Bi thin films, we would thus expect a critical value in magnetization  $M_c$  in the CMR materials, i.e.,  $M$  is the control or the tuning parameter for the quantum phase transition. For  $M < M_c$ , the system is an insulator and  $\rho$  decreases with increasing temperature. For  $M > M_c$ , the system is a metal and  $\rho$  increases with increasing temperature. In Fig. 1, we schematically illustrate the expected resistivity as functions of  $M$  for three temperatures  $T_1$ ,  $T_2$ , and  $T_3$  with  $T_1 < T_2 < T_3$ . All  $T_i$  ( $i = 1, 2, 3$ ) are above the Curie temperature  $T_c$  and the peak temperature  $T_p$ . These different temperature curves should cross at a single value  $M_c$  if the transition is of Anderson type. The reason for

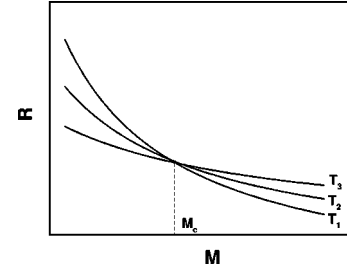


FIG. 1. The behavior of resistance  $R$  shown schematically as a function of magnetization  $M$  for three different temperatures under the assumption that  $M$  can induce the Anderson delocalization transition. The quantum critical point is indicated by  $M_c$ .

the crossing is as follows. A given temperature gives an effective cutoff length scale. The resistivity depends on the ratio of this length scale to the localization length. At the critical point, the localization length diverges, thus the resistivity is independent of temperature. Below we first present our resistivity and magnetization measurements at various external field  $B$  for different  $T$ . We then analyze our results and discuss the magnetization dependence of the resistivity for various  $T$ . These data will be shown to be incompatible with the critical scaling requirement of an Anderson localization transition.

The samples used in this study are epitaxial thin films of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  grown by pulsed laser deposition on  $\text{LaAlO}_3$  substrate. The film thickness is 1200 Å for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and 2100 Å for  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  samples. X-ray studies were used to ensure good structural quality of the samples.

Resistivity was measured by a standard four-probe technique. Magnetization was measured with a commercial superconducting quantum interference device magnetometer. The magnetic field was applied parallel to the film plane in order to minimize the demagnetization factor. The diamagnetic contribution of the substrate was measured separately and subtracted.

The Curie temperature of the samples was determined from the temperature dependence of magnetization at low magnetic field, and is found to be 270 K ( $T_c$ ) for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and 205 K for  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ . At zero field the resistance has a peak around  $T_p \sim 275$  K for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  (Fig. 2, inset) and  $T_p \sim 217$  K for  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ , which is close to the corresponding Curie temperatures. The peak values of resistivity are  $\sim 10$  mΩ cm for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and  $\sim 145$  mΩ cm for  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  and the residual low-temperature resistivity values are 170 μΩ cm for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and 550 μΩ cm for  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ , which are typical values for good quality epitaxial films of these compositions.

We now discuss our experimental results. All the results are from  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  films except those in Fig. 4(b). In Fig. 2, we show resistance  $R$  as a function of magnetic field for  $B = 0$  to 5 T for the temperatures just above  $T_p$ . At zero field,  $R$  has a peak around  $T_p \sim 275$  K, above which the sample is an insulator. At  $B = 5$  T, the insulating phase has been eliminated by the applied field, and  $\partial R(B, T) / \partial T > 0$  within the measured temperature region  $275 \text{ K} < T < 300 \text{ K}$ .

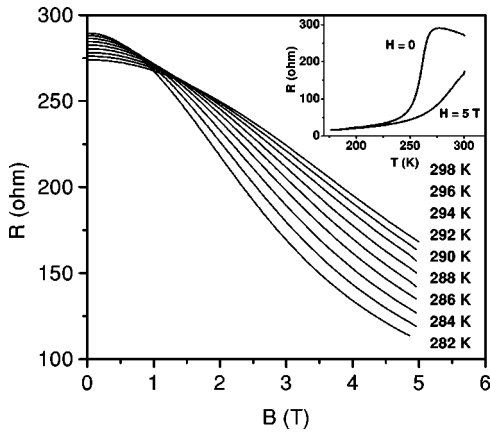


FIG. 2. Measured resistance vs magnetic field for different temperatures. Temperature dependence of the resistance at  $B=0$  and 5 T is shown in the inset.

In Fig. 3, we show the measured magnetization  $M$  as a function of magnetic field for a temperature range between  $T=282$  K and  $T=298$  K.

The main result of this paper is shown in Fig. 4. In Fig. 4(a) the resistance  $R$  is plotted as a function of magnetization  $M$  for several temperatures ranging between  $T=282$  and 298 K. These curves were obtained by combining the data from Figs. 2 and 3. The  $R(M)$  curves appear to be approximately crossing with each other at the magnetization value about  $3 \times 10^{-4}$  emu. This crossing might appear to indicate localization due to the reduction of the bandwidth, represented by  $M$  here. However, there is no single crossing point for all these curves, as shown in the inset to Fig. 4(a). Intersections of the curves occur from  $M=2.6 \times 10^{-4}$  emu to  $M=3.6 \times 10^{-4}$  emu. This interval is about 15% of the studied magnetization range, which could hardly be defined as a single point. Besides, at higher magnetization values  $R(M)$  curves converge again. This result is manifestly incompatible with the Anderson  $M-I$  transition behavior in Fig. 1 or equivalently, with the general behavior of a continuous quantum phase transition. Therefore, we conclude that Anderson localization is not the mechanism for the  $M-I$  transition in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  thin films. In addition, we have explicitly verified that our  $R(M, T)$  data do not exhibit quantum scaling behavior and cannot be collapsed into one effective curve by choosing suitable localization and dynamical exponents.

To determine whether our results from the  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  samples are generic, we have carried out

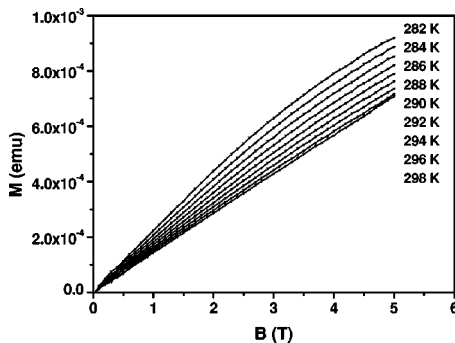


FIG. 3. Measured magnetization  $M$  vs magnetic field  $B$  for temperature range  $T=282$  to 298 K.

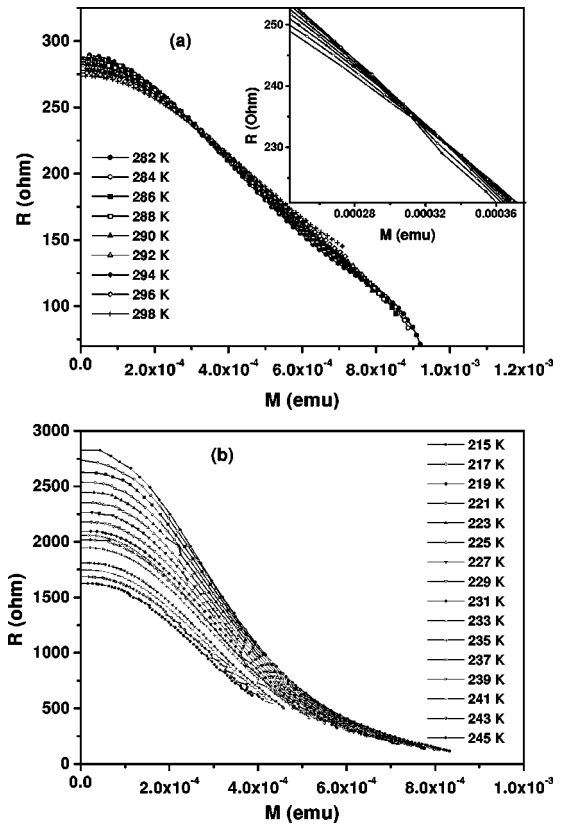


FIG. 4. (a) Resistance vs magnetization for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  for temperature range  $T=282$  to 298 K. Portion of the graph near the intersections is shown enlarged in the inset. (b) Resistance vs magnetization for  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  for temperature range  $T=217$  to  $T=245$  K.

measurements on  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  films. In Fig. 4(b) the resistance  $R$  is plotted as a function of magnetization  $M$  for several temperatures ranging between 217 and 245 K. Different curves from different temperatures do not even cross for the  $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  film, which is inconsistent with the behavior of Fig. 1, expected for a quantum phase transition.

Our main experimental conclusion, as shown in Figs. 2–4, is that the measured thin-film resistivity  $R(M, T)$  of CMR manganite materials plotted as a function of the measured magnetization ( $M$ ) at different temperatures ( $T$ ) does not exhibit any simple quantum criticality around the measured  $M-I$  transition temperature  $T_p$ . This is manifestly obvious from in Fig. 4 since  $R(M)$  for different temperatures around  $T_p$  do not cross through a single critical magnetization value ( $M_c$ ) as they should if the underlying cause is a continuous quantum phase transition as in Anderson localization. Our analysis has been based on the assumption that the magnetization is the appropriate tuning parameter for the localization quantum phase transition in manganites (i.e., the transition is driven by magnetic fluctuations). Magnetization as the tuning parameter is entirely reasonable for a quenched disorder that we have implicitly assumed in our analysis. If the disorder is arising entirely from temperature-dependent (intrinsic) magnetic fluctuations, then the relevant disorder is annealed, and recent detailed numerical work<sup>11</sup> shows that such intrinsic annealed disorder is unlikely to lead to localization without additional strong quenched magnetic disorder arising from, for example, structural disorder. Our experimental results indicate that a continuous quantum phase tran-

sition is unlikely to be the underlying cause for the CMR  $M$ - $I$  transition, and the observed phenomenon is most likely a rapid crossover behavior at  $T_p$ . We cannot, however, comment on the nature of this crossover behavior based only on our experimental results.

One issue requiring some elaboration in the context of metal-insulator transitions in CMR materials is the fact that phenomenologically this  $M$ - $I$  transition is thought to occur at a transition temperature  $T_p$  with the system being “metallic:”  $\frac{d\rho}{dT} > 0$  (also ferromagnetic) for  $T < T_p$  and “insulating:”  $\frac{d\rho}{dT} < 0$  (paramagnetic) for  $T > T_p$ . The true  $M$ - $I$  localization transition is a  $T=0$  quantum phase transition with the insulating phase having zero conductivity and the metallic phase having finite conductivity. The sign of  $d\rho/dT$  is not always a good indicator for a  $M$ - $I$  transition. In our analyses of the data (as well as in the current discussion on  $M$ - $I$  transitions in CMR materials) one assumes the temperature to be a parameter affecting the magnitudes of the physical quantities (e.g., magnetic behavior) defining the  $M$ - $I$  transition. It may actually be more natural to think of the CMR  $M$ - $I$  transition as a temperature-induced crossover behavior, and any critical discussion of a true  $M$ - $I$  transition in CMR materials should await an experimental observation of a  $M$ - $I$  transition at a fixed low temperature as a function of a system parameter (e.g., disorder, magnetic impurities, sample thickness, composition). All of the current activity on the nature of the  $M$ - $I$  transition in CMR materials may thus be premature unless one can experimentally induce a low-temperature transition by varying a system parameter. In that context the most important experimental result produced by our investigation is the finding that the resistivity  $R(M, T)$  in CMR materials around the  $M$ - $I$  “transition” temperature  $T_p$  cannot be written simply as  $R(M(T))$  as has been almost universally assumed in prior work<sup>12</sup> on the subject. We find, as is obvious from Figs. 2–4, that the measured resistance  $R$  is not just a function of the system magnetization  $M(T)$  at that particular temperature, but is also a function of temperature  $T$  directly (i.e.,  $R$  at a fixed  $M$ , but different  $T$  values, takes on different values as can be seen in Fig. 4). Thus  $R$  is a two-parameter function  $R(M, T)$  with  $M(T)$  depending also on  $T$ . While the direct temperature dependence of  $R$  is not extremely strong, it is clear that  $R$  cannot be expressed as a simple one-parameter function  $R(M(T))$ . We believe that this finding should have important implications for the CMR phenomena that far transcends the specific issue of whether the observed CMR  $M$ - $I$  transition is a continuous quantum phase transition or a crossover behavior. We also note that our measured resistance can be approximately fitted by an

exponential function in  $M/M_{sat}$ , but such fits are manifestly approximate since the measured resistance always depends on both  $M$  and  $T$  independently.

One may question our choice of the magnetization as the control parameter in driving the  $M$ - $I$  transition in contrast to, for example, the applied magnetic field, which superficially may appear to be the tuning parameter for the Anderson localization. We believe the appropriate tuning parameter to be the magnetization [at least with the double-exchange Hamiltonian defined in Eq. (1)], since it determines the effective hopping integral  $t'$ , and hence the disorder strength in the Hamiltonian. We have, of course, studied the resistivity as a function of the magnetic field in the temperature range  $T=282$  to  $298$  K, as shown in Fig. 2. No single transition point and/or quantum scaling can be defined from the magnetic field study in Fig. 2, leading to the same conclusion about the nonexistence of a continuous  $M$ - $I$  transition. A more appropriate quantity to characterize the disorder strength in the manganese oxides would perhaps be the magnetic moment correlation  $\chi$  of the neighboring Mn ions, which is difficult to measure directly. A quantitative experimental study of resistivity as a function of  $\chi$  for various  $T$  would be very difficult. We can, however, make a general statement that a measurement of  $R(\chi, T)$  is unlikely to exhibit quantum critical scaling because our  $R(M, T)$  data manifest nonscaling behavior in Figs. 2–4. We believe that our measured  $R(T, M)$  behavior is exhibiting the intrinsic metal-insulator crossover in the system, and there is no continuous metal-insulator phase transition in the problem.

In conclusion, we have carried out resistivity measurements in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  and  $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$  thin films to study the possible Anderson metal-insulator transition. An external magnetic field is applied to induce the paramagnetic to ferromagnetic transition. As a function of magnetization, the resistivity curves for different temperatures are found not to cross at a single point, establishing the nonexistence of a quantum critical point. This result is incompatible with theoretical expectations from Anderson metal-insulator transition. Thus, we conclude that the Anderson localization is not the cause of the metal-insulator transition in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  thin films. The precise nature of the metal-insulator transition in CMR materials requires further experimental and theoretical investigations. The present experiments seem to be consistent with the picture that the transition is a crossover from a metal to a magnetically disordered polaronic insulator.<sup>6</sup>

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