# Magnetotransport properties of $LaMnO_3$

Ibha Chatterjee
*Saha Institute of Nuclear Physics, Block "1/AF" Bidhannagar, Kolkata 700064, India*
(Received 13 November 2003; published 12 March 2004)

The magnetotransport properties of $LaMnO_3$ have been studied using the crystal-field theory and the correlated effective-field theory. The crystal-field theory is used to treat the many-body problem of an atom or ion in the crystal and the correlated effective-field theory is used to treat the many-body effect of the magnetic part of the Hamiltonian. The crystal-field theory exploits the symmetry of the electrostatic field generated by the ligands around the magnetic ion in the transition-metal compounds. The parent compound of colossal magnets, e.g., $LaMnO_3$ is a Mott-Hubbard and charge-transfer antiferromagnetic insulator. The magnetotransport properties of this compound have been studied using a theory which goes beyond the mean-field theory. This theory includes fluctuations and explains the experimental results better than the mean-field theory.

DOI: 10.1103/PhysRevB.69.094406 PACS number(s): 75.10.Jm, 75.10.Dg, 75.40.Cx, 75.47.Lx

## I. INTRODUCTION

The discoveries of colossal magnetoresistance and high-temperature superconductivity have led to a renewed interest in transition-metal oxides which are Mott insulators and become metals or superconductors when doped with a critical concentration. $LaMnO_3$ is a Mott-Hubbard and charge-transfer antiferromagnetic insulator and it is the parent compound of Colossal magnetoresistive materials. These materials are obtained by doping divalent alkaline-earth metals (Ca, Mg, Ba, Sr), and a critical doping leads to a drastic change in transport properties near the magnetic transition temperature. At a temperature close to the phase transition, the fluctuation becomes important and the magnetotransport properties get enhanced by the application of magnetic field. These materials show insulator-to-metal transition around 250 K and it gets enhanced by the magnetic field. These properties have been reviewed by Salamon and Jaime,[1] Dagotto *et al.*,[2] and Imada *et al.*[3] in great detail. In the parent compound of high-temperature superconductors, the magnetic ions lie in a plane whereas in colossal magnetoresistive materials they are arranged in three-dimensional (3D) perovskite structure. As the Mott insulators are transition-metal oxides, the magnetic ions have orbital degrees of freedom. The orbital degeneracy plays an important role in these materials. Therefore, not only the spin fluctuations but also the orbital fluctuations are important. In the present calculation the orbital degeneracy of *d* electron and the multiplet structure of transition-metal ion are treated in a crystal-field theory.

In the magnetically ordered phase, there is an internal magnetic field which is added to the applied external field and gives rise to an effective field. In the mean-field approximation, the exchange interaction is the source of this internal magnetic field. As in the presence of magnetic field there is a magnetoresistance effect in the magnetically disordered phase, so it is in the magnetically ordered phase. In the case of an antiferromagnetic material it happens within a sublattice. Hence, without an external magnetic field, there is a possibility of magnetoresistance effect in the magnetic insulator as long as the material is magnetically ordered and disappears in the magnetically disordered phase. The metallic character present in the magnetically ordered phase might be due to ferro-orbital ordering. This is inherent in the compound, and a metal-insulator transition takes place near the magnetic transition temperature due to correlation effect. As discussed by Searle and Wang,[4] the magnetoresistance is calculated in the ordered phase by using the double exchange interaction and the mean-field theory. Here we use the same double exchange interaction in correlated effective-field theory to study the magnetotransport properties. Due to spin-orbit interaction, spin ordering gets affected by the orbital ordering. In the present theory, both the orbital ordering and spin ordering are considered in the ground state. Usually, the transition temperature gets shifted by doping, and with a critical doping the localization completely vanishes. There is a metal-insulator transition near the magnetic transition. Here correlation or fluctuation is the driving force and the transport is caused not only by the charge carriers but by the spin part as well. Hence the magnetic polaron is the right choice to explain the transport properties of magnetoresistive materials. The small polaron theory[5] in the double exchange model[6] can explain qualitatively the transport properties of colossal magnetoresistive materials but the satisfactory explanations are still lacking, particularly a sudden drop in the resistivity below the critical temperature. This suggests that a strong Jahn-Teller distortion should be responsible for the transport properties.[7] In the present calculation, the effect of strong Jahn-Teller distortion has been presented in the study of magnetotransport properties in the localized model, which is true for magnetic insulators.

The compound $LaMnO_3$ is a ferromagnetic insulator and $CaMnO_3$ is an antiferromagnetic insulator. Both the low doping and high doping regions of $LaMnO_3$ are antiferromagnetic insulators, and the magnetic transition from ferromagnetic insulator to paramagnetic insulator or antiferromagnetic insulator to paramagnetic insulator takes place. It is shown in the phase diagram[8] where a gradual change of critical temperature with concentration of $Ca^{2+}$ leads to a maximum at around 250 K with a critical concentration $\sim(0.3–0.4)$. In the localized model one can study the ferromagnetic to paramagnetic transition and the transport properties using double exchange model for low doped $\sim(0.1–0.3)$ $LaMnO_3$ compounds.[4] Due to doping there is a disorder due to inequivalent sites occupied by $Mn^{4+}$ ions in the sample and

 

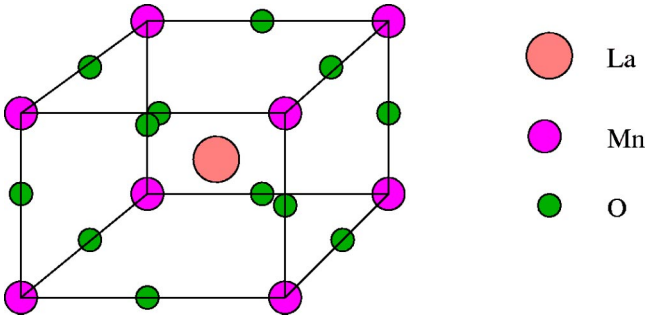


FIG. 1. (Color online) Perovskite structure of $LaMnO_3$.

the coexistence of insulating and conducting regions occurs. As the doping concentration increases the antiferromagnetic coupling between $Mn^{4+}$ ions sets in. In the perovskite structure, $Mn^{4+}$ has $t_{2g}^3$ electronic configuration and the ground multiplet is ${}^4A_{2g}$. This ground state is orbitally nondegenerate and there is no orbital ordering. The magnetic coupling between two $Mn^{4+}$ ions is antiferromagnetic. Hence as a result of doping a competition between ferromagnetic and antiferromagnetic coupling starts, and for a critical concentration $\sim(0.3–0.5)$ the metallic regime survives and it disappears beyond it.

## II. THEORY

The theory known as the correlated effective-field (CEF) theory initiated by Lines[9,10] has been extended[11,12] to study the magnetic properties in the ordered phase as well. In $LaMnO_3$, $Mn^{3+}$ has the electronic configuration $(3d)^4$ and the ground configuration is $(t_{2g})^3e_g$ as the fivefold $d$ level splits into a triplet $t_{2g}$ and a doublet $e_g$ in presence of octahedral crystal field. Due to strong Hund's coupling $(t_{2g})^3e_g$ gives rise to a high spin ground state ${}^5E_g$. This is a doubly degenerate state with spin $S=2$. As the spin-orbit interaction is small compared to Hund's coupling, this multiplet is perturbed by the spin-orbit interaction and it is treated on equal footing with the exchange interaction. In the transition-metal compound $LaMnO_3$ having perovskite structure shown in Fig. 1, there is no direct exchange interaction between the $Mn^{3+}$ ions, but there is a superexchange interaction via the intermediate $O^{2-}$ ion.

Due to this superexchange interaction and the covalency effect, electron is not strictly localized on the magnetic ion but can spend sometime on the nearest magnetic ion. Thus a partial delocalization can take place. This virtual hopping gives rise to conductivity at low temperatures and becomes insignificant at higher temperatures. Due to spin-orbit interaction and Jahn-Teller effect, this hopping is not negligible and shows metallic character at higher temperatures $\sim$300 K. These metallic properties appear as a result of spin-spin correlation in magnetic materials and show transport-magnetism correlations observed in ferromagnetic oxides. The ground state of Mn ion in $LaMnO_3$ corresponds to a real spin $S=2$ and pseudospin 1/2 having twofold orbital degeneracy and fivefold spin degeneracy. In our calculations we consider these ten states. There is no first-order spin-orbit splitting of the ground state but there is second-order splitting of this state which gets enhanced by an axial distortion.[13,14]. The ground state is Jahn-Teller sensitive, and the orbital degeneracy cannot be lifted by the first-order static Jahn-Teller distortion but can be lifted in the second order by dynamic Jahn-Teller effect. This effect introduces an axial distortion of the cluster. It is introduced in the Hamiltonian as a single-ion anisotropy and causes a zero-field splitting of the ground state ${}^5E_g$. This splitting is small in cubic field and becomes large in presence of an axial distortion.

The many-body Hamiltonian for $LaMnO_3$ is given by

$$H=\sum_i D(S_i^z)^2-2\sum_{ij>i} J_{ij}\vec{S}_i\cdot\vec{S}_j. \tag{1}$$

In this many-body Hamiltonian, there is a two-body interaction which can be reduced to a one-body Hamiltonian by the mean-field (MF) approximation. In the MF theory $\vec{S}_j$ is replaced by $\langle\vec{S}_j\rangle$. Here we will consider a theory which goes beyond the MF theory and is known as the CEF theory.[10] In this theory fluctuation has been incorporated semiempirically by introducing a phenomenological parameter to be determined self-consistently via the fluctuation-dissipation theorem. As a result, $\vec{S}_j$ is replaced by $\langle\vec{S}_j\rangle+A_{ij}(\vec{S}_i-\langle\vec{S}_i\rangle)$ and the anisotropic Heisenberg Hamiltonian is written as

$$H=-\sum_{ij\gamma} J_{ij}^{\gamma}S_i^{\gamma}S_j^{\gamma}. \tag{2}$$

The correlated effective-field Hamiltonian at the ith site is given by

$$H_i^{CEF}=-2\sum_{j>i\gamma} J_{ij}^{\gamma}S_i^{\gamma}[\langle S_j^{\gamma}\rangle+A_{ij}^{\gamma}(S_i^{\gamma}-\langle S_i^{\gamma}\rangle)], \tag{3}$$

where $A_{ij}^{\gamma}$ is the temperature-dependent static correlation parameter. If all the lattice sites are equivalent, we can write

$$\sum_j A_{ij}^{\gamma}J_{ij}^{\gamma}=\alpha^{\gamma}\sum_j J_{ij}^{\gamma}, \tag{4}$$

where $\alpha$ is the correlation parameter and $\gamma=x,y,z$ directions.

In absence of magnetic ordering, i.e., in the paramagnetic phase, the effective Hamiltonian is

$$H_i^{(0)}=H_i-\sum_{j\gamma} J_{ij}^{\gamma}\alpha^{\gamma}(S_i^{\gamma})^2, \tag{5}$$

where $H_i$ is the free-ion Hamiltonian. In the ordered phase CEF Hamiltonian is

$$H=D\sum_i (S_i^z)^2-\sum_{ij\gamma} J_{ij}^{\gamma}[\alpha^{\gamma}(S_i^{\gamma})^2-2S_i^{\gamma}(\langle S_j^{\gamma}\rangle-\alpha^{\gamma}\langle S_i^{\gamma}\rangle)]. \tag{6}$$

In the magnetic structure of perovskite $LaMnO_3$ shown in Fig. 2, there are six nearest neighbors out of which four are aligned in the same direction in a plane and two are in opposite directions perpendicular to the plane. Therefore, there

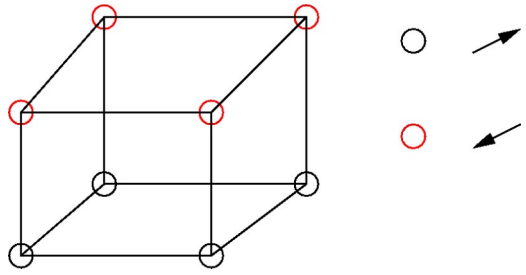

FIG. 2. (Color online) Spin alignment of $LaMnO_3$.

is ferromagnetic coupling for four nearest neighbors and antiferromagnetic coupling for two nearest neighbors. Assuming $J$ to be of same magnitude for all nearest neighbors, the one-body Hamiltonian is

$$H_i = D(S_i^z)^2 - 6J(\alpha^{\parallel} - \alpha^{\perp})(S_i^z)^2 - 12J(1-\alpha^{\parallel})\langle S_i^z\rangle S_i^z . \tag{7}$$

Here $z$ is the direction in which the spins are aligned and $D$ is the single-ion anisotropy parameter. Using this Hamiltonian and the ten wave functions of the form $|M_\tau M_S\rangle$ for the ground state ${}^5E_g$, the static magnetic susceptibility and the magnetic order parameter are calculated. $\tau$ is the pseudospin for $E_g$ orbital. The correlation parameters $\alpha$ are determined self-consistently using fluctuation-dissipation theorem.[10] Using this Hamiltonian, the static magnetic susceptibility is given by[11]

$$\chi^{\gamma}(\vec{q}) = \frac{1}{kT}\Bigg[\langle\langle \mu_i^{\gamma} : \mu_i^{\gamma}\rangle\rangle - \frac{[J(\vec{q}) - \alpha^{\gamma}J(0)]\langle\langle \mu_i^{\gamma} : S_i^{\gamma}\rangle\rangle^2}{kT - [J(\vec{q}) - \alpha^{\gamma}J(0)]\langle\langle S_i^{\gamma} : S_i^{\gamma}\rangle\rangle}\Bigg], \tag{8}$$

where $J(\vec{q}) = \Sigma_{nn} J e^{i\vec{q}\vec{\delta}}$ and $\vec{\mu}_i = \vec{\tau} + 2\vec{S}_i$, $\tau = 1/2$ in the present calculation. $\delta$ is the nearest-neighbor spacing. The correlation parameters are determined self-consistently[11] from the equation

$$\alpha^{\gamma} = \sum_{\vec{q}} \frac{J^{\gamma}(\vec{q})kT}{kT - 2[J^{\gamma}(\vec{q}) - \alpha^{\gamma}J^{\gamma}(0)]\ll S_i^{\gamma} : S_i^{\gamma}\gg} \Big/ \sum_{\vec{q}} J^{\gamma}(0). \tag{9}$$

For any operators $\vec{A}, \vec{B}$ the following meanings hold good:

$$\langle\langle \vec{A} : \vec{B}\rangle\rangle = \langle \vec{A} : \vec{B}\rangle - \langle \vec{A}\rangle\langle \vec{B}\rangle, \tag{10}$$

$$\langle \vec{A} : \vec{B}\rangle = \sum_n \rho_n \Bigg[A_{nn}B_{nn} + kT\sum_{m\neq n}(A_{mn}B_{nm} + A_{nm}B_{mn})/(E_m - E_n)\Bigg], \tag{11}$$

$$\langle \vec{A}\rangle = \sum_n \rho_n A_{nn}, \tag{12}$$

where $\rho_n$ denotes the probability of occupation of the eigenstate $|n\rangle$ of the Hamiltonian.

The magnetic order parameter is defined as the ratio of $\langle s_i^z\rangle_T$ and $\langle s_i^z\rangle_0$ and the magnetoresistivity $R_M$ is defined as[4]

$$R_M = \frac{1 - [M_s(T)/M_s(0)]^2}{1 + [M_s(T)/M_s(0)]^2}, \tag{13}$$

where $M_s$ is the spontaneous magnetization which is the saturation magnetization in presence of internal field in the magnetically ordered phase. In the magnetically disordered phase there is no temperature dependence of magnetoresistivity, it remains constant in the localized CEF or the MF theory.[4] The temperature dependence of the observed resistivity in the vicinity of transition temperature ($T_c \sim 250$ K) can be explained by the small polaron and the double exchange model.[5] In the transition-metal compounds there is a transport-magnetism correlation, and near the transition temperature the magnetoresistivity can be explained by thermoactivation model rather than the adiabatic polaron model or variable range hopping model. Using this model, the magnetoresistivity in the double exchange model in Eq. (13) is modified as

$$R_M(obs) = R_M \exp(T_c/T). \tag{14}$$

This formula has been applied at all temperatures and the magnetoresistivity is calculated below and above the transition temperature using the same formula. In order to study the effect of external magnetic field on magnetoresistivity, the Hamiltonian in Eq. (1) is modified as

$$H = \sum_i D(S_i^z)^2 - 2\sum_{ij>i} J_{ij}\vec{S}_i\cdot\vec{S}_j - B\sum_i \mu_i^z, \tag{15}$$

where $\mu_i^z$ is the $z$ component of the magnetic moment of $Mn^{3+}$ ion and $B$ is a measure of external magnetic field applied in $z$ direction. All the parameters $(D, J, B)$ in this Hamiltonian are in units of temperature.

## III. RESULTS AND DISCUSSION

In the perovskite structure of $LaMnO_3$ the atoms are arranged as shown in Fig. 1 and according to the magnetic structure the spin alignment of Mn ions is as evident from Fig. 2. A neutron-scattering study of $LaMnO_3$ compound indicates an antiferromagnetic phase transition[15] at temperature $T_N = 139.5$ K. Using our theoretical model and without the single-ion anisotropy the transition temperature has been found[16] to be $T_N = 140$ K with $J = 5.59$ K. The temperature dependence of sublattice magnetization in the ordered phase has been calculated and shown in Fig. 3 where the experimental results[15] are also shown for comparison. The critical exponent $\beta$ of the order parameter has been calculated from the slope of the straight-line curve obtained by plotting the squared order parameter vs $(T_N - T)/T_N$ in log scale as shown in Fig. 4. $\beta$ has been estimated to be 0.308 which is very close to the experimental value[15] and the 3D Ising exponent.[17] The mean-field exponent is, however, 0.5, and the present calculation shows a major improvement of this

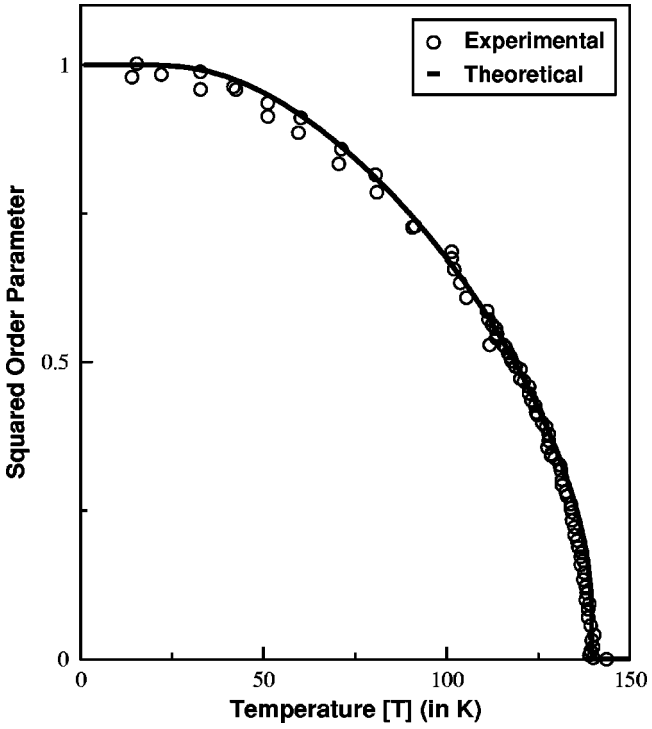


FIG. 3. Magnetic order parameter as a function of temperature.

exponent as fluctuation is included in the calculation. If the single-ion anisotropy due to spin-orbit interaction is taken into consideration, the same transition temperature can be found with the parameters $J=5.39$ K and $D=-2$ K.

The susceptibility behavior in Fig. 5 shows a spike in the susceptibility in the $z$ direction which is also observed experimentally.[18] The susceptibilities in other directions as shown in this figure gradually diminish as the distortion in the cluster increases and disappears when the distortion is large ($-100$ K). From our calculations, it is evident that the orbital degeneracy plays an important role in the microscopic level, and due to this degeneracy the many-body effect of an ion is important. This effect is treated in the crystal-field theory by taking into account the crystal field generated by the ligands which are $O^{2-}$ ions in the compound under investigation. Very close to the transition temperature, fluctuations are equally important and they have been considered in the present calculation.

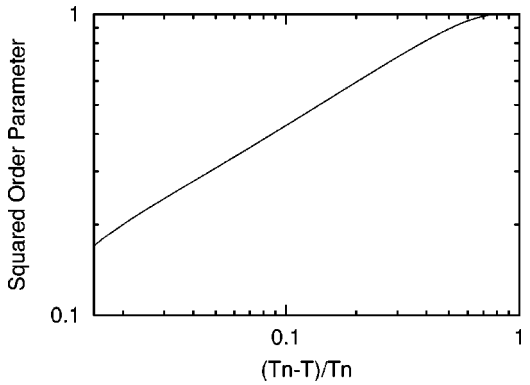


FIG. 4. Magnetic order parameter near the critical temperature in log scale.

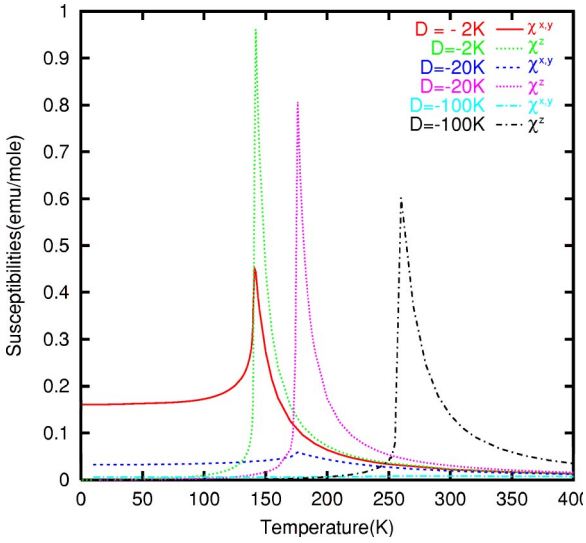


FIG. 5. (Color online) Susceptibility as a function of temperature.

The ground state[5] $E_g$ is Jahn-Teller sensitive and it undergoes a Jahn-Teller splitting due to distortion in the octahedral crystal field. There is no first-order splitting of the ground multiplet due to either spin-orbit interaction or the axial distortion but it suffers a splitting in higher order as a result of both these effects.[13,14] This gives rise to a single-ion anisotropy in the Hamiltonian as shown in Eq. (6). If the ligand field is purely octahedral, the single-ion anisotropy arises due to spin-orbit interaction only and it is very small[18] ($\sim 2$ K) as in the case of $LaMnO_3$. Doping with a low concentration causes a shift in the transition temperature and the magnetoresistivity of the ferromagnetic insulator appears below this temperature as shown in Fig. 6. This resistivity is caused by the internal magnetic field originated from the exchange in-

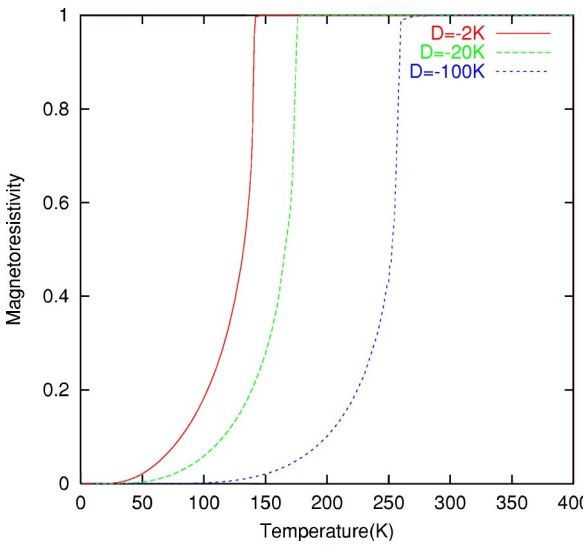


FIG. 6. (Color online) Magnetoresistivity as a function of temperature.

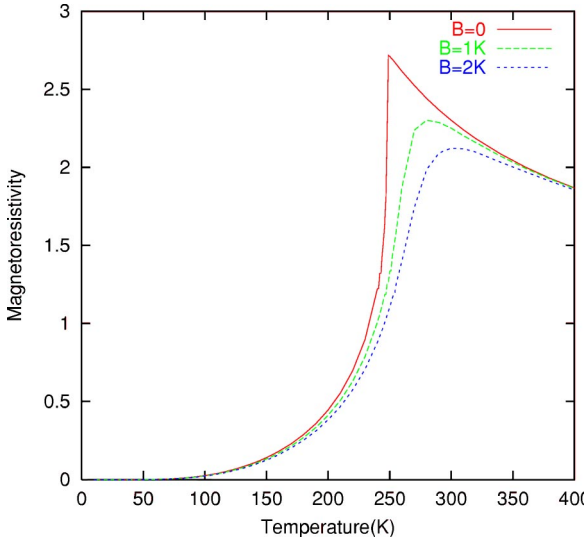


FIG. 7. (Color online) Magnetoresistivity as a function of temperature.

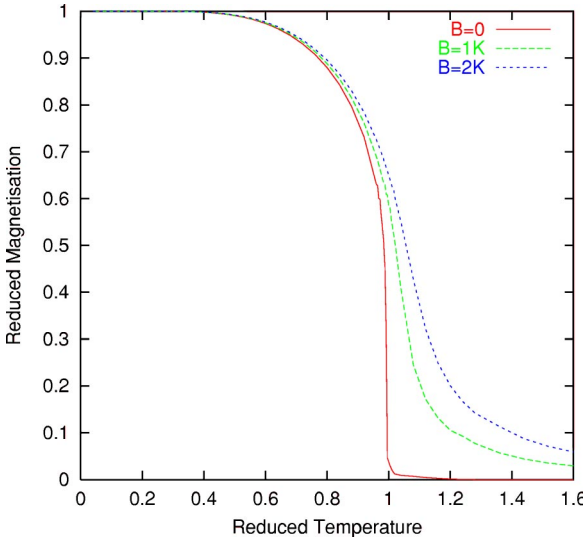


FIG. 8. (Color online) Reduced magnetization as a function of reduced temperature.

teraction between magnetic ions. This behavior has been observed earlier[4] in case of ionic ferromagnet. The magnetoresistivity is related to the susceptibility as mentioned by Sheng *et al.*,[7] and from the susceptibility behavior shown in Fig. 5 one can conclude that sharp change in resistivity near the magnetic transition might appear due to fluctuation and a strong Jahn-Teller distortion may be responsible for the observed transport properties in colossal magnetoresistive materials. Using the formula given in Eq. (14), the magnetoresistivities are calculated at various magnetic fields and the results are shown in Fig. 7. The corresponding reduced magnetizations are shown in Fig. 8. The behavior of magnetoresistivity shown in Fig. 7 explains the experimental results[19,20] qualitatively, and the variation of reduced magnetizations shown in Fig. 8 is very similar to the results obtained earlier[5] using mean-field theory in the small polaron picture.

## IV. CONCLUSION

The magnetotransport properties of $LaMnO_3$ in presence of Jahn-Teller distortion and external magnetic field have been studied using a theory which goes beyond the mean-field theory. This theory takes into account the spin fluctuations which are important near the magnetic transition and explains the critical behavior of this compound better than the mean-field theory. The calculation clearly indicates a transport-magnetism correlation and this may lead to a drastic change in transport properties near the magnetic phase transition. The present model and the calculations presented here might help in understanding the colossal magnetoresistance phenomena and recent experiments on doped manganites.[21–25]

## ACKNOWLEDGMENTS

The author wishes to acknowledge the help and cooperation of S. Mukhopadhyay and K. Das.

[1] M.B. Salamon and M. Jaime, Rev. Mod. Phys. **73**, 583 (2001).
[2] E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. **344**, 1 (2001).
[3] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).
[4] C.W. Searle and S.T. Wang, Can. J. Phys. **48**, 2023 (1970).
[5] Sudhakar Yarlagadda, Phys. Rev. B **62**, 14 828 (2000).
[6] P.G. de Gennes, Phys. Rev. **118**, 141 (1960).
[7] L. Sheng, D.Y. Xing, D.N. Sheng, and C.S. Ting, Phys. Rev. Lett. **79**, 1710 (1997).
[8] P. Schiffer, A.P. Ramirez, W. Bao, and S.W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).
[9] M.E. Lines, Phys. Rev. B **5**, 3690 (1972).
[10] M.E. Lines, Phys. Rev. B **9**, 3927 (1974).
[11] Ibha Chatterjee, Phys. Rev. B **19**, 3827 (1979).
[12] Ibha Chatterjee and V.P. Desai, Phys. Rev. B **24**, 5133 (1981).
[13] J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, Cambridge, 1961).
[14] S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic Press, New York, 1970).
[15] F. Moussa, M. Hennion, J. Rodriguez-Carvajal, H. Moudden, L. Pinsard, and A. Revcolevschi, Phys. Rev. B **54**, 15 149 (1996).
[16] I. Chatterjee, Phys. Status Solidi A **196**, 267 (2003).
[17] C. Domb and M. S. Green, *Phase Transitions and Critical Phenomena* (Academic Press, New York, 1976), Vol. 5a.
[18] V. Skumryev, F. Ott, J.M.D. Coey, A. Anane, J.P. Renard, L. Pinsard-Gaudart, and A. Revcolevschi, Eur. Phys. J. B **11**, 401 (1999).
[19] M.F. Hundley, M. Hawley, R.H. Heffner, Q.X. Jia, J.J. Neumeier, J. Tesmer, J.D. Thompson, and X.D. Wu, Appl. Phys. Lett. **67**, 860 (1996).

[20] S.H. Chun, M.B. Salamon, Y. Lyanda-Geller, P.M. Goldbart, and P.D. Han, Phys. Rev. Lett. **84**, 757 (2000).
[21] Fei Gong, Wei Tong, Shun Tan, and Yuheng Zhang, Phys. Rev. B **68**, 174410 (2003).
[22] X.J. Chen, H.U. Habermeier, and C.C. Almasan, Phys. Rev. B **68**, 132407 (2003).
[23] J. Hejtmanek, E. Pollert, Z. Jirak, D. Sedmidubsky, A. Strejc, A. Maignan, Ch. Martin, V. Hardy, R. Kuzel, and Y. Tomioka, Phys. Rev. B **66**, 014426 (2002).
[24] T. Hayashi, N. Miura, Y. Tomioka, and Y. Tokura, J. Phys. Chem. Solids **63**, 925 (2002).
[25] K.N. Clausen, W. Hayes, D.A. Keen, R.M. Kusters, R.L. McGreevy, and J. Singleton, J. Phys.: Condens. Matter **1**, 2721 (1989).