# A universal relation between resistivity and magnetization in paramagnetic state of manganites

J. Z. Wang, J. R. Sun,[a] G. J. Liu, F. X. Hu, T. Y. Zhao, and B. G. Shen
*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*

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A systematic study on the resistivity-magnetization relation above the Curie temperature ($T_C$) has been performed for the manganites with different properties, such as the epitaxial $La_{0.67}Ca_{0.33}MnO_3$ film on a $SrTiO_3$ substrate, which has the weakest magnetic correlation above $T_C$, the $La_{0.27}Nd_{0.4}Ca_{0.33}MnO_3$ polycrystalline, which exhibits a charge ordering in the paramagnetic state, and the ceramics $Eu_{0.55}Sr_{0.45}MnO_3$ and $La_{0.474}Bi_{0.193}Ca_{0.33}Mn_{0.994}Cr_{0.006}O_3$, which show strong short-range magnetic orders above $T_C$. A quantitative, yet universal, relation of the form $\rho = AT\exp[(\varepsilon - \alpha m^2)/T]$ is observed in all of the manganites, with an essentially constant coefficient of $\alpha \approx 800 \pm 60$ K, where $m$ is the normalized magnetization and $\varepsilon$ is the activation energy for polarons. The underlying physics for this relation has been analyzed based on the double exchange model. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2825473]

Perovskite manganites have received wide attention in the past decade due to their colossal magnetoresistance (CMR) and related effects. It has been found that the resistivity ($\rho$) undergoes a great reduction around the temperature of the metal-to-insulator transition (MIT) under magnetic field.[1] According to the double exchange theory,[2] conduction electrons hop between Mn ions, under the help of intermediate oxygen, with a transfer integral proportional to $\cos(\psi/2)$, where $\psi$ is the angle between the core spins of Mn ions. In this picture, conduction will be enhanced by improving spin alignment. This actually implies the presence of a strong magnetic-resistive interplay in manganites and stimulated the attempt searching for the quantitative relation between resistivity and magnetization. For the typical CMR manganite $La_{0.7}Ca_{0.3}MnO_3$, Hundley *et al.*[3] established a simple relation $\rho \propto \exp(-\beta m)$, and all the $(\rho, m)$ pairs obtained under different temperatures and magnetic fields collapse into the same master curve, where $m$ is the normalized magnetization and $\beta$ is a constant independent of temperature and magnetic field. This relation has been regarded as the evidence of polaron conduction. As an alternative, Kim *et al.* studied transport behavior of phase-separated $La_{5/8-x}Pr_xCa_{3/8}MnO_3$, and reproduced the $\rho$-$m$ dependence based on the effective medium theory.[4] There are also studies on the $\rho$-$m$ relations in other phase-separated manganites such as $Pr_{0.63}Ca_{0.37}MnO_3$, $La_{0.5}Ca_{0.5}MnO_3$, etc., to clarify the effects of phase percolation.[5,6] In contrast, work on the $\rho$-$m$ relation of the paramagnetic (PM) phase has been very limited, and even the only two reports by Urushibara *et al.*[7] and Chen *et al.*,[8] respectively, are inconsistent with each other. The former found that $\rho \propto (1 - Cm^2)$ for $La_{1-x}Sr_xMnO_3$ when $T > T_C$ ($C$ is a constant depending on Sr content), while the latter declared that $\rho \propto \exp(-\alpha M^2/T)$ for $La_{0.67}Ca_{0.33}MnO_3$ (Boltzmann's constant $k_B$ has been set to unity).

There is evidence for the occurrence of lattice polarons well above the Curie temperature, and the presence of short-range charge-ordered regions due to the strong correlation between polarons.[9] A characteristic temperature that separates static and dynamic polaron correlations has also been observed,[10] which is in good agreement with theoretical prediction.[11] It was further revealed that the correlated and uncorrelated distortions play different roles in affecting the magnetic and resistive properties of the PM phase.[12] All these demonstrate the rich physics underlying the PM phase. Therefore, a thorough study on the magnetic-resistive correlation in the PM state, which could be completely different from the ferromagnetic (FM) state, is expected to provide valuable information about the electronic process undergoing in the manganites.

In this letter, we will present a systematic study on the $\rho$-$m$ relation of the PM state in the manganites with different properties, such as the epitaxial $La_{0.67}Ca_{0.33}MnO_3$ film on a $SrTiO_3$ substrate, which has the weakest magnetic correlation above $T_C$, the $La_{0.27}Nd_{0.4}Ca_{0.33}MnO_3$ (LNCMO) polycrystalline, which exhibits a charge ordering in the PM state, and the $Eu_{0.55}Sr_{0.45}MnO_3$ and $La_{0.474}Bi_{0.193}Ca_{0.33}Mn_{0.994}Cr_{0.006}O_3$ ceramics, which show strong short-range magnetic orders above $T_C$.

The polycrystalline sample LNCMO was prepared by using the conventional solid-state reaction technique.[13] For a comparison study, another two polycrystalline samples $La_{0.474}Bi_{0.193}Ca_{0.33}Mn_{0.994}Cr_{0.006}O_3$ and $Eu_{0.55}Sr_{0.45}MnO_3$ and an epitaxial $La_{0.67}Ca_{0.33}MnO_3$ film (~200 nm in thickness) on $SrTiO_3$ substrate were also prepared following the procedures described in Refs. 14, 13, and 15, respectively. As revealed by the powder x-ray diffraction analyses, all the samples are of single phase with the orthorhombic structure (polycrystalline samples) or pseudocubic structure (film). The lattice parameters are $a = 0.5434$ nm, $b = 0.5456$ nm, and $c = 0.7671$ nm for LNCMO. The structure parameters of other samples can be found in Refs. 14, 13, and 16.

The magnetic and resistive measurements were conducted by a Quantum Design superconducting quantum interference device magnetometer (MPMS-7) equipped with an electric measurement unit. To eliminate spurious effects, exactly the same sample was used for all of the measurements. Figure 1 shows the temperature-dependent magneti-

[a]Author to whom correspondence should be addressed. Electronic mail: jrsun@g203.iphy.ac.cn

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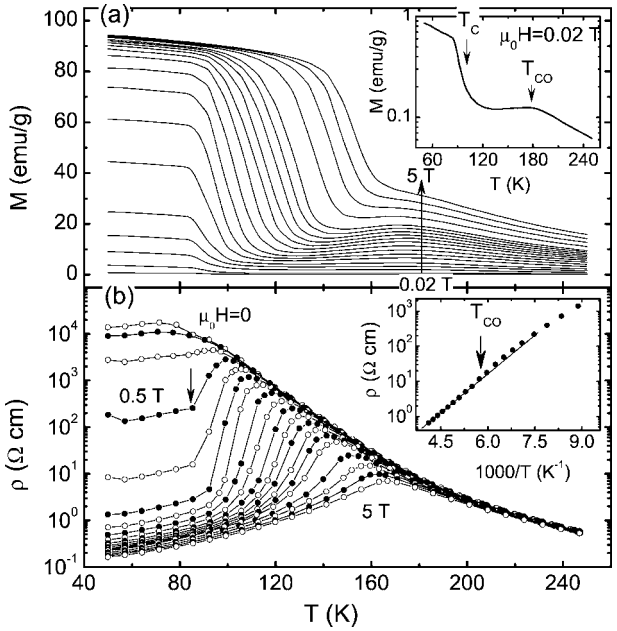


FIG. 1. (a) Temperature-dependent magnetization measured under selective fields between 0.02 and 5 T. (b) Temperature-dependent resistivity of LNCMO measured under various magnetic fields. The inset plot shows the resistive anomaly associated with the CO transition.

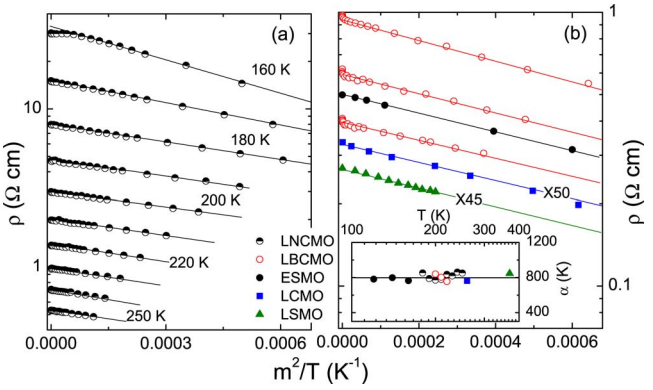


FIG. 2. (Color online) Semilog plot of resistivity as a function of $m^2/T$ obtained at different temperatures for (a) LNCMO and (b) LCMO films, LSMO single crystal, LBCMO, and ESMO ceramics. The inset plot shows the $\ln \rho$-$m^2/T$ slopes for different manganites at various temperatures. LCMO=$La_{0.67}Ca_{0.33}MnO_3$; LSMO=$La_{0.7}Sr_{0.3}MnO_3$; LBCMO =$La_{0.474}Bi_{0.193}Ca_{0.33}Mn_{0.994}Cr_{0.006}O_3$; ESMO=$Eu_{0.55}Sr_{0.45}MnO_3$. Solid lines are guides for the eyes.

zation and resistivity measured under the fields up to 5 T. Two obvious magnetic anomalies, occurring at $T_C \approx 90$ K and $T_{CO} \approx 172$ K, respectively, can be identified from the $M$-$T$ curve obtained under the field of 0.02 T. The former is a signature for the occurrence of parasitical FM phase, and the latter is a typical feature of charge ordering transition. It should be noted that the charge ordering occurs in the PM background, and remains under the field of 5 T as evidenced by the visible hump in the $M$-$T$ curve, though $T_{CO}$ decreases slightly with applied field (~1.54 K/T). The magnetization of the PM phase exhibits a significant variation, increasing, for example, from ~0.13 emu/g for $\mu_0 H=0.02$ T to ~30 emu/g ($m \approx 1/3$) for $\mu_0 H=5$ T at the temperature of 170 K. The Curie temperature is ~150 K under the field of 5 T, and the saturation magnetization is $\sim 3.63 \mu_B$/Mn, obtained by extrapolating the $M$-$T$ curve under 5 T to 0 K, which is in good agreement with the theoretical value $3.67 \mu_B$/Mn if only the magnetic moment of Mn ions is considered. As shown in Fig. 1(b), the sample exhibits an insulating behavior without magnetic field, with an unobvious anomaly at ~170 K due to the CO transition [inset in Fig. 1(b)]. Accompanying the PM-FM transition, a MIT occurs as usually happened to the manganites, and a resistivity drop over three orders of magnitude can be resulted. Although it is not as large as that occurred in the low temperature range, the resistivity decrease with applied field is also significant in the temperature range above the MIT. For example, $\rho$ reduces from ~15.9 Ω cm for $\mu_0 H=0$ to ~6.7 Ω cm for $\mu_0 H=5$ T at the temperature of 170 K.

Based on the data in Fig. 1, a quantitative $\rho$-$m$ relation can be established for the PM state of LNCMO. It is interesting that excellent liner variations of $\ln \rho$ with $m^2/T$ occur for all of the temperatures near or well above $T_C$ [Fig. 2(a)], and the increase in temperature causes only a downward shift of the $\ln \rho$-$m^2/T$ curve, without affecting the $\ln \rho$-$m^2/T$ slope $\alpha$. A direct calculation shows $\alpha=800\pm60$ K for the temperatures between 180 and 250 K, where 250 K is the highest temperature for the present measurements. In Fig. 2(b), we show the $\rho$-$m^2/T$ relations of the $La_{0.67}Ca_{0.33}MnO_3$ film, and ceramics $La_{0.474}Bi_{0.193}Ca_{0.33}Mn_{0.994}Cr_{0.006}O_3$ and $Eu_{0.55}Sr_{0.45}MnO_3$, obtained from the magnetic and resistive data presented in Refs. 15, 14, and 13. The data obtained by Urushibara *et al.*[7] for single crystal $La_{0.7}Sr_{0.3}MnO_3$ are also presented for comparison. It is surprising that not only a similar exponential relation but also essentially the same $\ln \rho$-$m^2/T$ slope as that of LNCMO are observed [inset plot in Fig. 2(b)], though these samples exhibit very different magnetic behaviors above $T_C$. These analyses actually indicate a relation of $\rho(m,T)=\rho_0(T)\exp(-\alpha m^2/T)$, the same result as that obtained by Chen *et al.*[8] for $La_{0.67}Ca_{0.33}MnO_3$ except for a considerably smaller coefficient $\alpha$ (~800 vs ~1600 K). It means that any variations in magnetization will considerably affect resistivity, even in the PM state. Effects thus produced could be strong. A direct calculation gives, for example $[\rho(0,T)-\rho(m=0.3,T)]/\rho(0,T) \approx 36\%$ for $T=160$ K.

As a supplement, we would like to point out that the relation $\rho \propto (1-Cm^2)$, proposed by Urushibara *et al.*[7] for $La_{1-x}Sr_xMnO_3$, is a natural inference of $\rho(m,T)=\rho_0(T)\exp(-\alpha m^2/T)$ with $\alpha=CT$ when $m$ is small. Figure 3 illustrates the experimental data plotted in a semilog or a linear scale of the $\rho$-$m$ curve for the $La_{0.67}Ca_{0.33}MnO_3$ film. It shows that a satisfactory description can only be obtained by the former when $m$ is large. Using the parameters $C \approx 2.2$ and $T=1.01T_C \approx 373$ K given by Ref. 7, we can obtain $\alpha \approx 820$ K for $La_{0.7}Sr_{0.3}MnO_3$. This is a value in reasonably agreement with those of other samples studied here. These results reveal the universality of the $\rho$-$m$ relation obtained, which could capture the essence of the magnetic-resistive interplay in manganites.

To get a deep understanding of the underlying physics behind the $\rho$-$m$ relation, it would be instructive to perform a further analysis of the electronic transport process in the manganites. It is obvious that the downward shift of the $\ln \rho$-$m^2/T$ curve, with the increase of temperature, origins from $\rho_0(T)$, which has the form of $\rho_0(T)=AT\exp(\varepsilon/T)$ in the scenario of polaronic transport. This, in turn, leads to the general expression of $\rho=AT\exp[(\varepsilon-\alpha m^2)/T]$ for the electronic transport of the PM phase. Compared with the stan-

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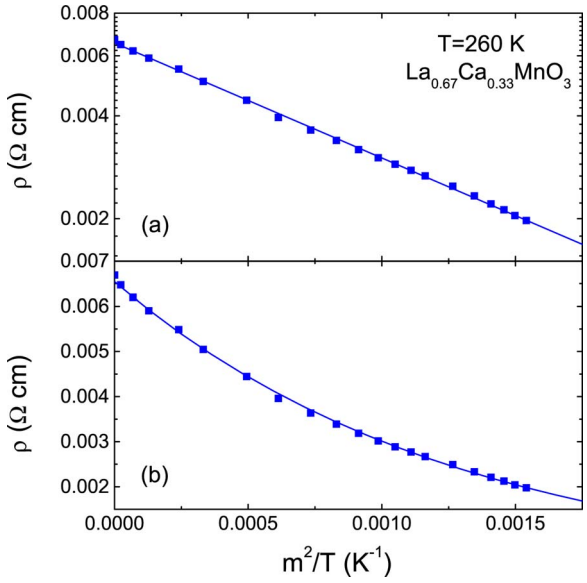


FIG. 3. (Color online) A comparison of (a) the ln $\rho$-$m^2/T$ and (b) the $\rho$-$m^2/T$ relations for the $La_{0.67}Ca_{0.33}MnO_3$ film obtained at the temperature of 260 K. Solid lines are guides for the eyes.

dard equation $\rho=AT\exp[(\varepsilon'-\eta)/T]$,[17] it is easy to see $\eta=\alpha m^2$, i.e., $\alpha m^2$ has the meaning of transfer integral. In general, $\eta$ is nearly temperature independent and, therefore, is not explicitly expressed in the formula. For the manganites, however, thermal spin fluctuation will certainly affect the charge transferring, making $\eta$ temperature/magnetization dependent. According to the double exchange theory,[2] the conduction proceeds via the migration of $e_g$ electrons between $Mn^{3+}$ and $Mn^{4+}$ ions with a transfer integral of $\eta'=\eta_0\cos(\psi/2)$, where $\psi$ is the angle between two adjacent core spins of Mn ions. Approximating $\eta$ by $\eta'$, after a direct calculation based on the mean field approximation, we have

$$\eta=\eta_0\sqrt{\frac{1+\langle\cos\psi\rangle}{2}}\approx\eta_0\left(\frac{1+m^2/2}{\sqrt{2}}\right), \tag{1}$$

where the statistical average $\langle\cos\psi\rangle=m^2$ has been used in the derivation. The expansion in Eq. (1) requires that $m$ is small, which is a condition that can be well satisfied in the PM state. Replacing $\eta$ in $\rho=AT\exp[(\varepsilon'-\eta)/T]$ with Eq. (1), we obtain

$$\rho=AT\exp\left(\frac{\varepsilon'-\eta_0/\sqrt{2}-\eta_0 m^2/2\sqrt{2}}{T}\right). \tag{2}$$

Equation (2) is the same as $\rho=AT\exp[(\varepsilon-\alpha m^2)/T]$ in form after setting $\alpha=\eta_0/2\sqrt{2}$ and $\varepsilon=\varepsilon'-\eta_0/\sqrt{2}$. It has been experimentally proved that $\eta_0$ varies between 0.1 and 0.2 eV for the optimally hole-doped manganites ($Mn^{4+}$: Mn $\approx 0.33:1$),[18] which implies $\alpha\approx 400-810$ K. This result is in reasonable agreement with the observed $\alpha\approx 800\pm 60$ K.

Based on the above analysis, the increase of $m$ enhances the probability of polaron transferring, and the activation energy derived from the $\rho$-$T$ relation includes the effect of magnetization. This explains the decrease of activation energy under magnetic field considering the increase of $m$ under applied field. We have analyzed the $\rho$-$T$ curves obtained under the constrictions of $m=0$ and 0.32, respectively, and found that the activation energy is ~1746 K for the former and ~1664 K for the latter. The reduction in activation energy is ~82 K, in good agreement with the result $\Delta\varepsilon=\alpha m^2 \approx 83$ K adopting $\alpha\approx 810$ K.

According to the previous work, strong correlations exist between polarons, and the correlated and uncorrelated distortions play different roles in affecting the physical properties of the PM phase.[9–12] The present work gives an identical $\rho$-$m$ relation above $T_C$. The reason may be that the temperature range concerned here is completely in the correlated region [static polaron correlation does not vanish until $T>1.5T_C$ (Ref. 10)]. It would be instructive to extend the temperature range above $1.5T_C$ to examine the effect of static to dynamic crossover. In this case, however, data collected under much higher magnetic fields may be required to get reliable $\rho$-$m$ relation because of the rapid decrease of magnetization with temperature.

The phase separation picture proposed by Moreo *et al.*[19] is compatible with the experimental data below $T_C$, where the percolation feature can be identified from the $\rho(T)$ and $\rho(H)$ relations (not shown). However, the similarity of the $\rho$-$m$ relation for $T>T_C$ in different manganites suggests the unimportance of the details of phase separation for the magnetic and resistive correlation at high temperatures. It is possible that the collected magnetization and resistivity are relatively long time averaged values compared with the rapid thermal fluctuation of phase-separated domains.

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